Universität Rostock

Traditio et Innovatio

Synthesis and characterization of a masked *N*-heterocyclic phosphinidene (NHP)

Dissertation

to obtain the academic degree

Doctor rerum naturalium (Dr. rer. nat.)

of the Faculty of Mathematics and Natural Sciences

at the University of Rostock

submitted by Tim Suhrbier, born on October 21 1992 in Ribnitz-Damgarten, Germany

Rostock, [Veröffentlichungsdatum]

The work presented in this thesis was carried out between October, 2018 and April, 2021 in the research group of Prof. Dr. Axel Schulz, holder of the chair for Inorganic Chemistry at the Institute of Chemistry of the University of Rostock.

Primary Reviewer: Prof. Dr. Axel Schulz
Secondary Reviewer:

Statement of authorship

I hereby declare that this thesis and the work presented in it are my own and that this thesis is the result of my own original research. I confirm that I have acknowledged all main sources of help and that I have clearly indicated the presence of all material I have quoted from other sources. This thesis has not been submitted for any other qualification or at any other institution.

Rostock, [Veröffentlichungsdatum]

Tim Suhrbier

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Summary

This thesis summarizes the synthesis and characterization of an unprecedented heterocyclobutane derivative, based on carbon, nitrogen and phosphorus. To further assess the biradical character and facilitate the naming of this structural motif, complementary quantum mechanical computations were carried out. The second part of this thesis elaborates on the reactivity of this heterocyclic compound. Therefore, a set of reagents representative of compound classes was employed and the reactivity compared to the extensively investigated biradical [Ter–NP]$_2$. Similar outcomes were found to occur for LEWIS acids/bases, as well as an isonitrile and carbon monoxide. By contrast, oxidations by chalcogens and the addition of alkenes/alkynes gave, in part, different results. Notably, the addition of alkenes/alkynes to form phosphiranes/phosphirenes highlights the phosphinidene-type reactivity of the novel compound. In the last part, the preparation of heavier congeners (As, Sb, Bi) of chlorinated open-chain precursors and theoretical investigations of their corresponding reduced heterocycles is discussed.

Zusammenfassung

Die folgende Arbeit behandelt die Synthese und Charakterisierung eines neuartigen, auf Kohlenstoff, Stickstoff und Phosphor basierenden Heterocyclobutanderivats. Hierbei wurden unterstützende quantenmechanische Berechnungen durchgeführt, um den Biradikalcharakter des Systems abzuschätzen und eine adäquate Benennung des Strukturmotivs zu ermöglichen. Im zweiten Teil der Arbeit wurde der Heterocyclus mit verschiedenen Testreagenzien umgesetzt, um eine Einordnung der Reaktivität gegenüber dem ausführlich untersuchten Biradikal $[Ter–NP]_2$ vorzunehmen. Hierbei zeigten sich vergleichbare Reaktionen beim Einsatz von LEWIS-Säuren und –Basen, sowie Insertionen eines Isonitrils und Kohlenstoffmonoxids. Oxidationen durch Chalcogene, sowie Additionsreaktionen mit Alkenen und Alkinen führten jedoch teilweise zu neuartigen Reaktionsmustern. Insbesondere die Addition von Alkenen/Alkinen unter Ausbildung von Phosphiranen/Phosphirenen verdeutlicht die Phosphiniden-Reaktivität der neuen Verbindung. Der letzte Teil der Arbeit behandelt die Synthese schwerer Homologa (As, Sb, Bi) von offenkettigen chlorierten Vorläuferverbindungen und theoretische Untersuchungen zu entsprechenden cyclisierten reduzierten Spezies.

To Kobe

Content

Index of abbreviations

APCI	Atmospheric pressure chemical ionization
ATR	Attenuated total reflection
BTMSA	Bis(trimethylsilyl)acetylene
calcd.	Calculated
CASSCF	Complete active space self-consistent field
cov	Covalent
Cp*	Pentamethylcyclopentadienyl
Cy	Cyclohexyl
d	Doublet (NMR)
DABCO	1,4-Diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM	Dichloromethane
dec	decet (NMR)
decomp.	Decomposition
DFT	Density functional theory
Dipp	2,6-Di(*iso*-propyl)phenyl
DMAP	4-Dimethylaminopyridine
DME	1,2-Dimethoxyethane
Dmp	2,6-Dimethylphenyl
EA	Elemental analysis
eq.	Equivalent(s)
Et	Ethyl
et al.	*Et alii/aliae* (and others)
FLP	Frustrated LEWIS pair
HOMO	Highest occupied MO
HONO	Highest occupied NO
*i*Pr	*iso*-Propyl
IR	Infrared
LA	LEWIS acid
LB	LEWIS base
LUMO	Lowest unoccupied MO
LUNO	Lowest unoccupied NO
m, m	Meta, multiplet (NMR), medium (IR)
Me	Methyl
^{Me}Bhp	2,6-Bis(benzhydryl)-4-methyl-phenyl
^{Me}Bhp*	2,6-Bis(4-*tert*-butyl-benzhydryl)-4-methyl-phenyl
^{Me}IMe	1,3-Dihydro-1,3,4,5-tetramethyl-2*H*-imidazol-2-ylidene
Mes	2,4,6-Trimethylphenyl
Mes*	2,4,6-Tris(*tert*-butyl)phenyl
MO	Molecular orbital
Mp.	Melting point
MS	Mass spectrometry
NAO	Natural atomic orbital
NBO	Natural bond orbital
*n*Bu	*n*-Butyl
NHC	*N*-heterocyclic carbene
NHO	*N*-heterocyclic olefin
NHP	*N*-heterocyclic phosphinidene
NMR	Nuclear magnetic resonance
NO	Natural orbital

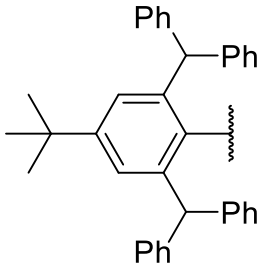
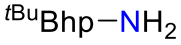
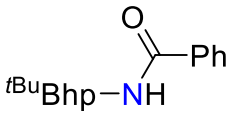
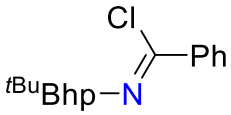
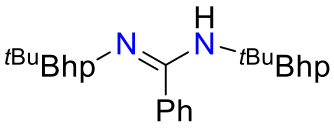
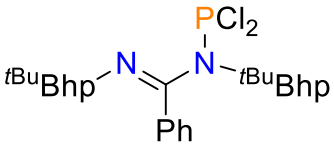
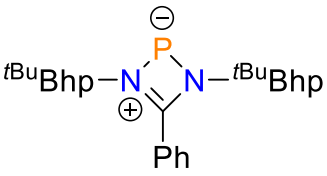
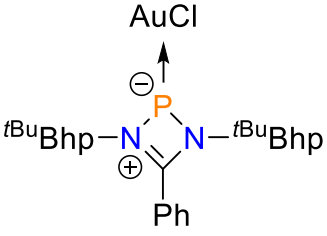
NRT	Natural resonance theory
o	Ortho
p	Para
Ph	Phenyl
quat.	Quaternary
Ref.	Reference
rt	Room temperature
s	Singlet (NMR), strong (IR)
t	Triplet (NMR)
*t*Bu	*tert*-Butyl
$^{t\text{Bu}}$Bhp	2,6-Bis(benzhydryl)-4-*tert*-butyl-phenyl
Ter	2,6-Bis(2,4,6-trimethylphenyl)phenyl
THF	Tetrahydrofuran
TMS	Trimethylsilyl
TMSA	Trimethylsilylacetylene
UV/Vis	Ultraviolet/visible light
vs	Very strong (IR)
vw	Very weak (IR)
w	Weak (IR)
XRD	X-ray diffraction

Units of measurement

The International System of Units (SI) is generally used for physical quantities. Deviating units are displayed in the following table, including their unit names and their conversions:

Physical quantity	**Unit symbol**	**Unit name**	**Conversion**
Amount of substance	mmol	millimole	1 mmol = 1 × 10^{-3} mol
Energy	kJ eV	kilojoule electronvolt	1 kJ = 1 × 10^{3} m^2 kg s^{-2} 1 eV = 1.60 × 10^{-19} m^2 kg s^{-2}
Frequency	MHz	megahertz	1 MHz = 1 × 10^{6} s^{-1}
	Hz	hertz	1 Hz = 1 s^{-1}
Length	Å	ångström	1 Å = 1 × 10^{-10} m
Mass	g	gram	1 g = 1 × 10^{-3} kg
Power	mW	milliwatt	1 mW = 1 × 10^{-3} kg m^2 s^{-1}
Temperature	°C	degree celsius	ϑ/°C = T/K − 273.15
Time	d	day	1 d = 8.64 × 10^{4} s
	h	hour	1 h = 3.6 × 10^{3} s
Volume	mL	milliliter	1 mL = 1 cm^3 = 1 × 10^{-6} m^3
Wavenumber	cm^{-1}	reciprocal centimeter	1 cm^{-1} = 100 m^{-1}

Index of synthesized compounds

Compound	Structural formula
$^{t\mathrm{Bu}}$Bhp	
1	
2	
3	
4	
5	
6	
7	

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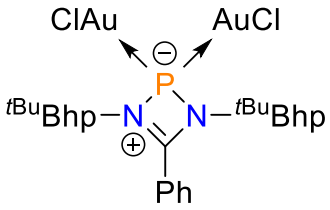
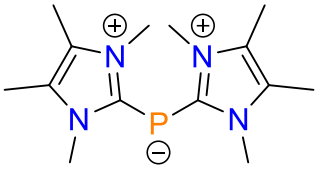
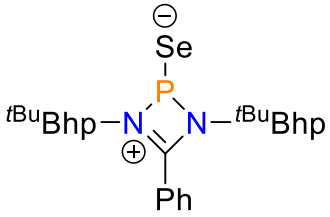
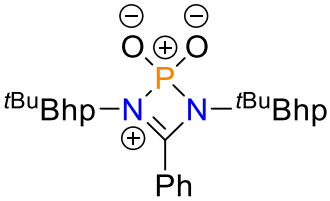
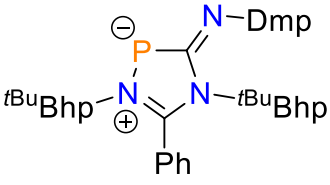
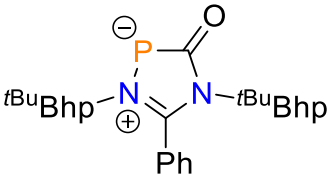
8	
9	
11a	
12	
13	
14	

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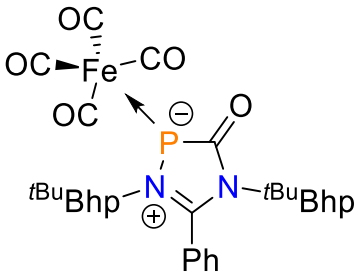
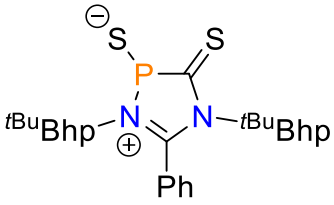
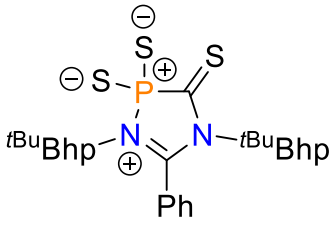
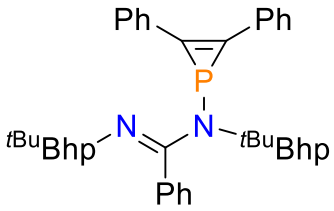
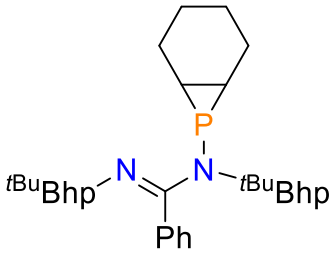
15	
16	
17	
18	
19	

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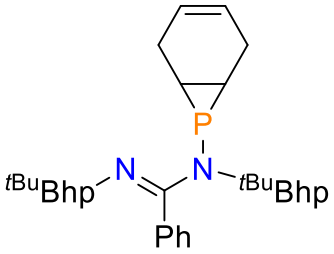
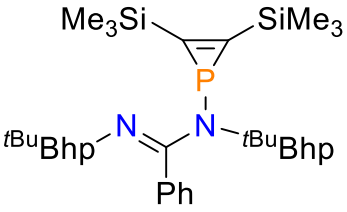
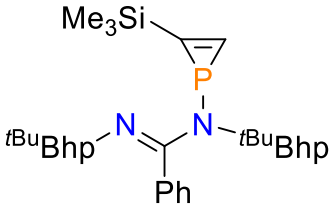
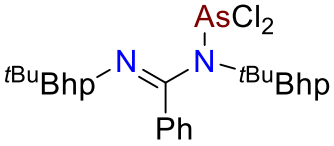
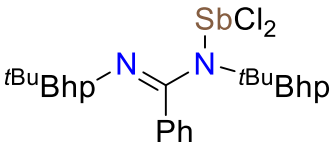
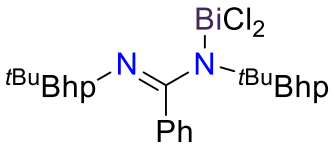
20	
21	
22	
23	
24	
25	

1 Aim

The aim of the presented work was the synthesis and characterization of a hitherto unprecedented cyclic structural motif (Figure 1), continuing the systematic development of previously reported low-valent phosphorus-based heterocyclobutane-1,3-diyls. Such compounds are known for their reactive behavior towards a wide array of substances, including, but not limited to, the activation of small molecules.[1–4] This type of main-group chemistry was initially reserved for rather expensive and rare transition metals and thus opened a new field in inorganic chemistry in recent history.[5–8]

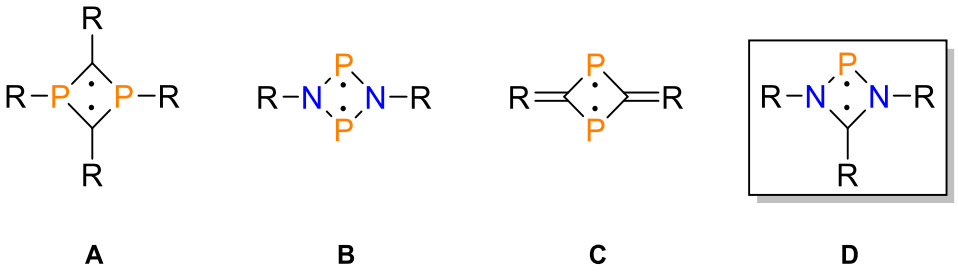


Figure 1. Representation of established heterocyclobutane-1,3-diyl derivatives (**A**: NIECKE, 1995; YOSHIFUJI/ITO, 2003; **B**: SCHULZ, 2011; **C**: GRÜTZMACHER/GHADWAL, 2017; **D**: this work) (R = organic substituent).[9–13]

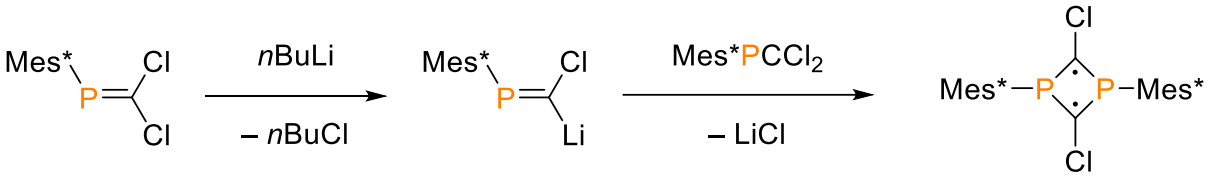
Because of the novelty of compounds of class **D**, additional computational analyses were to be carried out, in order to assess biradical properties and gain further insight into the bonding situation. In the second part, the novel compound was to be reacted with a variety of different reagents in a set of test reactions, including LEWIS acids and bases, oxidants and multiple-bond systems, with the reactivity to be compared in particular to the extensively studied compound class **B**. In the last part, the applicability of the established synthetic and theoretical concepts was to be investigated on the heavier congeners (As, Sb, Bi).

2 Introduction

2.1 Heterocyclobutane-1,3-diyls

The term biradical refers to even-electron species with two radical centers that exhibit significant interaction, namely antiferromagnetic coupling (open-shell singlet biradical) or ferromagnetic coupling (triplet biradical).[1,14–16] While some simple biradicals and their reactivity, like molecular oxygen, are generally well understood among chemists, more complex structures remain a fruitful area of fundamental research.[17–19] In particular, one of the most diverse classes are heterocyclobutane-1,3-diyls.[20–27] Since open-shell singlet species have no unique experimental characteristic that allows for distinction from common closed-shell molecules (S = 0), some structural features (planarity of the ring system, elongated atom distances), as well as several theoretical aspects (LUNO occupancy, HOMO-LUMO gap, singlet-triplet gap) can be used for the identification and comparison of biradicals. For planar compounds that do not satisfy all theoretical requirements, a zwitterionic resonance structure should be preferably used.

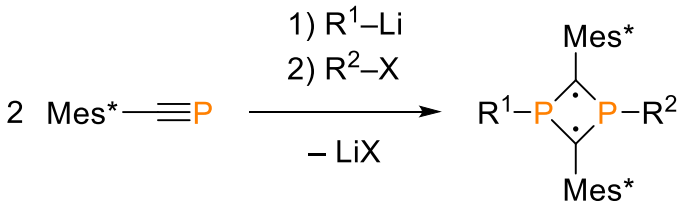
The first undisputed heterocylobutane-1,3-diyl belongs to the compound class **A** and was reported by NIECKE et al. in 1995.[9] Synthesis of the cyclic structure was achieved via base-induced dimerization of a phosphaalkene (Scheme 1).



Scheme 1. Synthesis of NIECKE's carbon- and phosphorus-based biradical (Mes* = 2,4,6-tris(*tert*-butyl)phenyl.[9]

In consecutive experiments, the chlorine atoms could be successfully exchanged for trimethylsilyl groups or hydrogen. The groups of YOSHIFUJI and ITO introduced a more generalized approach to this structural motif.[10] Using an isolable phosphaalkyne as the starting

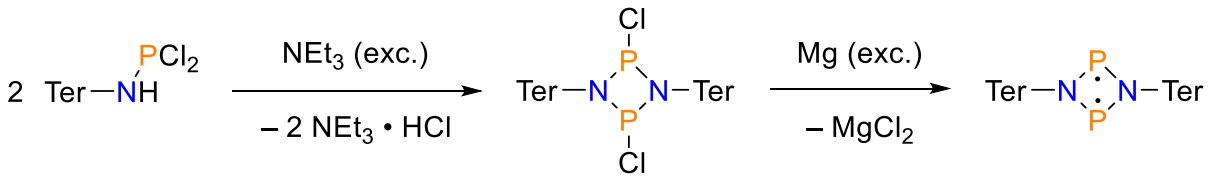
point, the stepwise addition of organolithium and halocarbon reagents afforded a variety of different diyls (Scheme 2). Substituents at the phosphorus atoms included a wide range of alkyl, aromatic and even heterocyclic compounds.



Scheme 2. Generalized preparation of 1,3-diphospha-cyclobutane-2,4-diyls by YOSHIFUJI and ITO (R^1 = Me, Et, *n*Bu…; R^2 = Me, Et, CH_2Ph…).[10]

To prevent dimerization of the initial phosphaalkyne, the sterically demanding Mes* substituent is required and thus, all derivatives feature this group attached to the central carbon atoms. This is in contrast to NIECKES biradical, where only the carbon substituents could be exchanged.

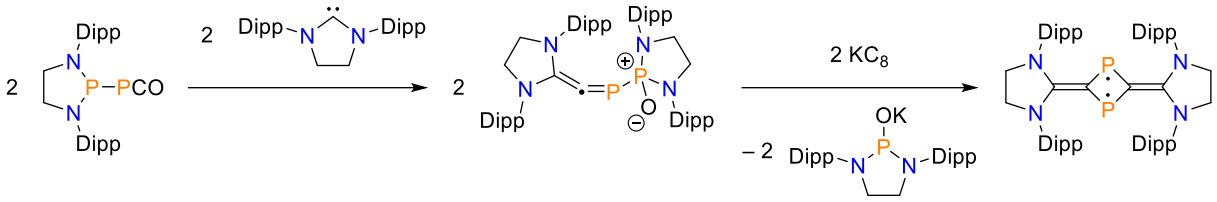
The first example of an 1,3-diaza-2,4-diphospha-cyclobutane-2,4-diyl (**B**) was introduced by the group of SCHULZ in 2011.[11] While the original synthesis involved titanocene-based reducing agents, an updated protocol relies on comparably inexpensive and robust magnesium chips (Scheme 3).[28]



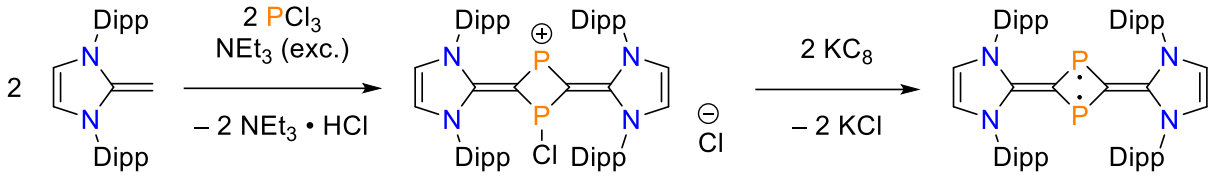
Scheme 3. Preparation of 1,3-diaza-2,4-diphospha-cyclobutane-2,4-diyl by SCHULZ (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl).[11]

With regard to the configuration of the chlorine substituents, the base-induced dimerization of the monomer precursors affords cyclic *cis* and *trans* isomers in different ratios. However, the subsequent reduction results in quantitative formation of only one species. Contrary to the Mes* substituent, the Ter substituent exhibits less steric protection, which is a prerequisite for the initial dimerization. The biradical was found to be quite reactive towards a high number of molecules (cf. Chapter 2.3) and enabled the isolation of several unprecedented compound classes.[4]

Examples of the compound class **C** were first reported independently by the groups of GRÜTZMACHER and GHADWAL in 2017. While the synthesis by GRÜTZMACHER et al. involves the reaction of a phosphanyl phosphaketene with an NHC (Scheme 4),[12,29,30] the synthesis by GHADWAL et al. relies on a base-induced reaction between an NHO and PCl_3 (Scheme 5).[13] Nevertheless, both pathways feature similar concluding reductions with KC_8.



Scheme 4. Preparation of NHC-stabilized C_2P_2 biradicals by GRÜTZMACHER (Dipp = 2,6-di(*iso*-propyl)phenyl).[12,29,30]



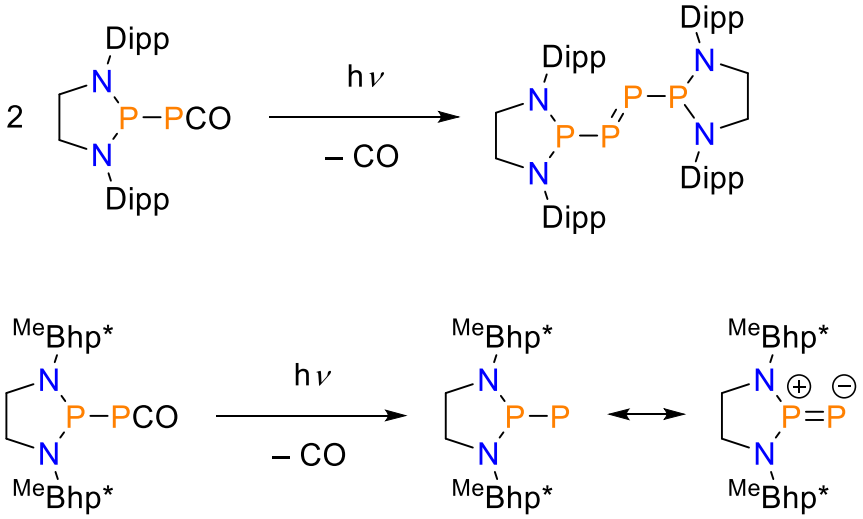
Scheme 5. Preparation of NHC-stabilized C_2P_2 biradicals by GHADWAL.[13]

Further investigations of the C_2P_2 biradicals by GRÜTZMACHER et al. and LI et al. showed reactivity towards a variety of substrates, among them hydrogen, ferrocenium salts, molecules with N–H and O–H bonds and transition metals.[31,32]

2.2 The concept of masked phosphinidenes

Phosphinidenes R–P, which are phosphorus analogs of carbenes with an electron sextet including two lone pairs at the phosphorus atom, are generally elusive and inherently reactive species (prone to dimerization or C–H activation within the substituents), and have thus been studied for more than 40 years.[33–40] Owing to similar energies of singlet and triplet ground states of these compounds, the electronic nature of the substituents has a significant influence on the stabilization of either state.[41] Due to the aforementioned reactivity, most phosphinidenes are not stable in their free state and are therefore generated in situ from transition metal complexes[42,43] or thermal activation of main-group stabilized derivatives.[44,45] In this regard, the successful isolation and characterization of a stable singlet phosphinidene by BERTRAND et

al. in 2016 underlined the importance of a sterically demanding substituent to prevent side reactions.[46,47] UV-induced elimination of CO led to (phosphino)phosphinidenes, which dimerized when no trapping reagent was present and a monomer could only be isolated for an even bulkier modification of the ^{Me}Bhp substituent (Scheme 6).



Scheme 6. Phosphinidene generation via CO elimination of (phosphino)phosphaketene (^{Me}Bhp* = 2,6-bis(4-*tert*-butyl-benzhydryl)-4-methyl-phenyl).[46]

A rather novel concept are so-called "masked phosphinidenes", which contain two-coordinate phosphorus atoms trapped in rigid environments and exhibit comparable reactivity to conventional phosphinidene sources.[48–53] While phosphinidene-type resonance structures (Figure 2) can be formulated for these molecules (demonstrative of donor-acceptor interactions), NRT calculations of model compounds often only yield vanishingly low relative weights. As a result, zwitterionic structures, consistent with experimental bond parameters, are more fitting representations of the actual electronic situation.

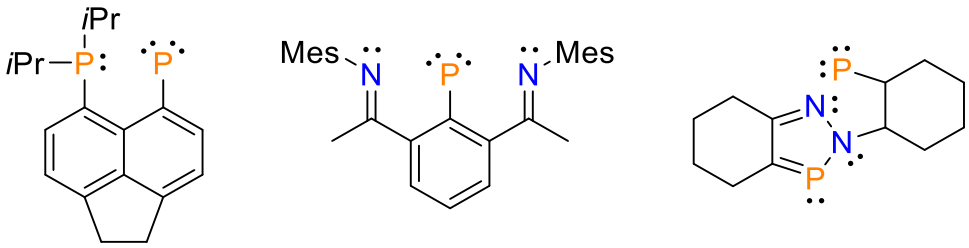
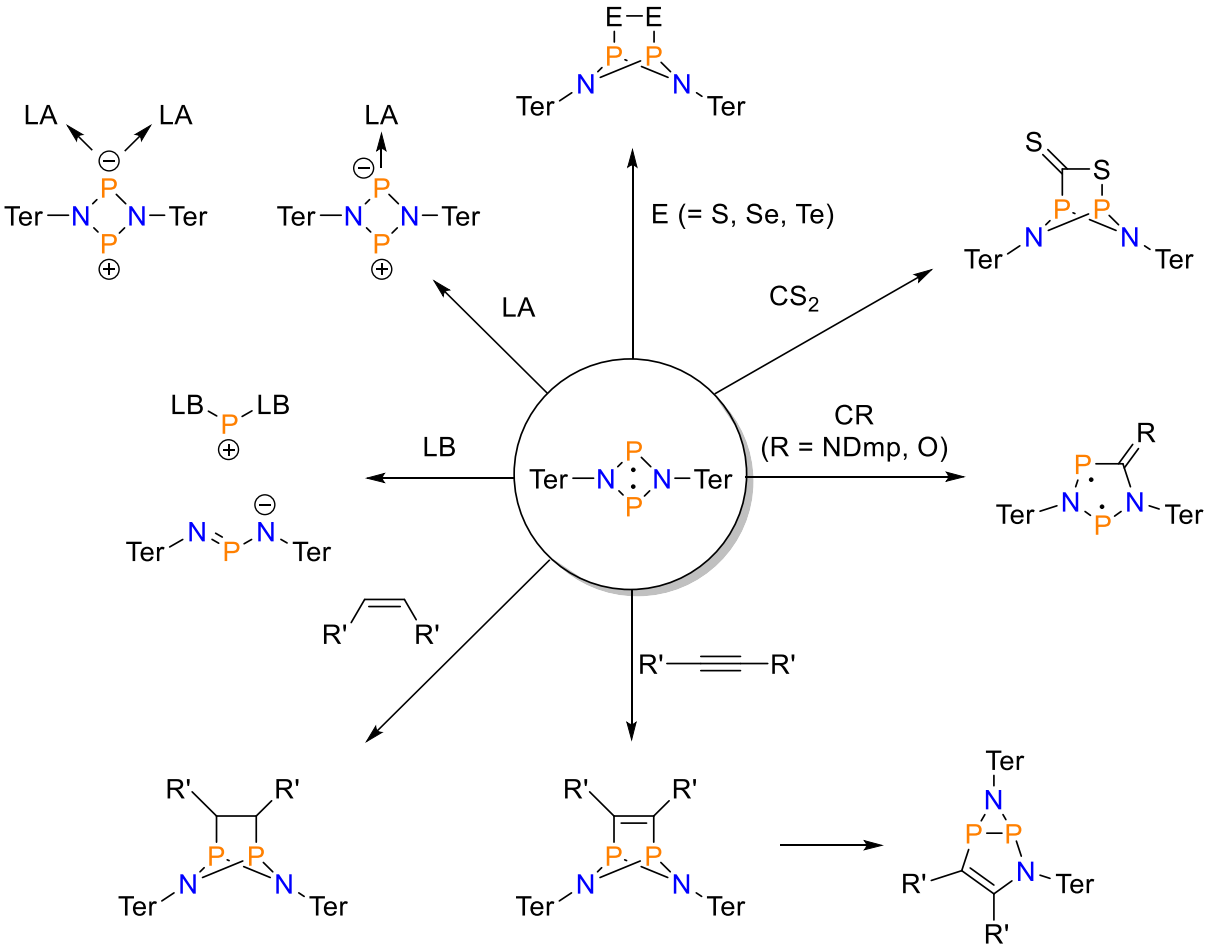


Figure 2. Phosphinidene-type resonance structures of masked phosphinidenes (Mes = 2,4,6-trimethylphenyl).[48,49,51]

However, the envisaged heterocyclic compound of this work may still be described as a masked *N*-heterocyclic phosphinidene (NHP, cf. Chapter 3.1, Figure 9), based on its subsequently discussed reactivity (cf. Chapter 3.2.5).

2.3 Reactivity studies of [Ter–NP]$_2$

The biradical [Ter–NP]$_2$, first introduced in 2011 by the group of SCHULZ,[11] was shown to react with a plethora of compounds (Scheme 7), as evidenced by roughly a dozen publications in the last ten years.[54,55,64,56–63] While LEWIS acids lead to mono- or double-coordination of a single phosphorus atom, strong LEWIS bases like NHCs can selectively cleave two N–P bonds, resulting in a weakly interacting ion pair.[62] Heavier chalcogens like sulfur, selenium and tellurium, as well as carbon disulfide, form bridged cage compounds.[56,65]

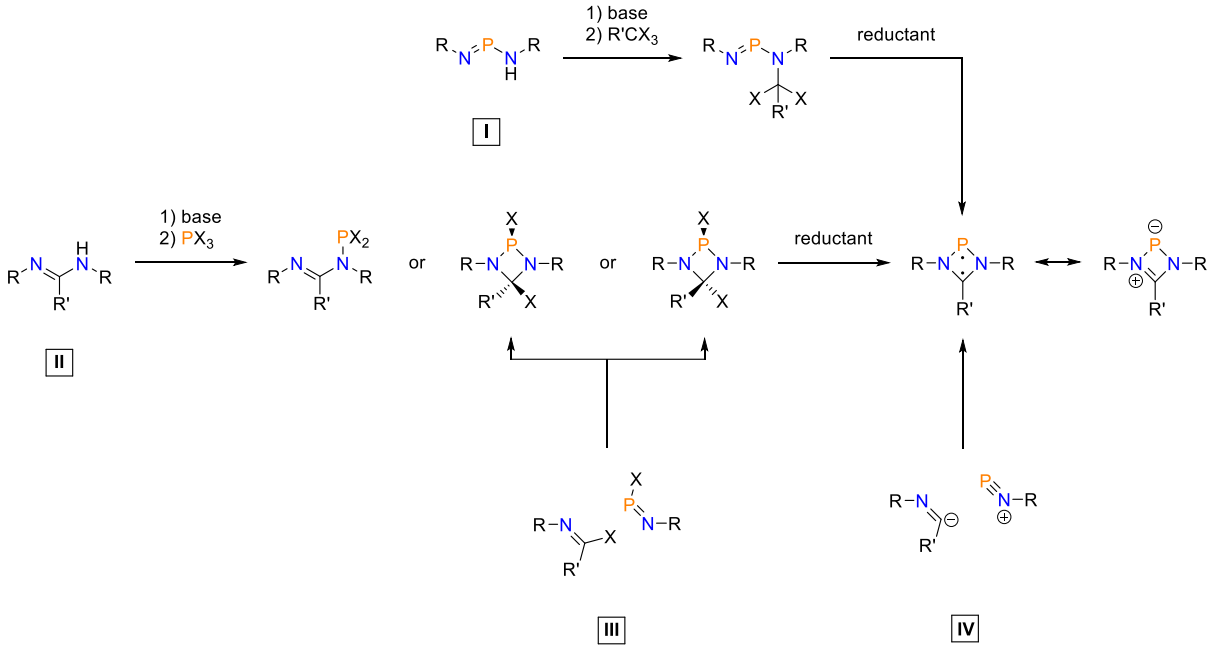


Scheme 7. Selection of coordinative, insertion and addition reactions of [Ter–NP]$_2$ (R = organic substituent, R' = H or organic substituent, Dmp = 2,6-dimethylphenyl).[4,55,56,62,65]

Meanwhile, isonitriles and carbon monoxide yield five-membered heterocycles via insertion into an N–P bond, which also exhibit significant biradical character.[4] These novel heterocyclopentane-1,3-diyls can be used as molecular switches, with a reversible photochemical housane formation and a thermal reverse reaction.[28] Furthermore, alkenes and alkynes react in [2+2]-cycloadditions, forming bicyclic structures with phosphorus acting as bridgehead atoms. In this regard, the reaction with alkynes stands out, due to quantitative rearrangement reactions in solution, yielding a variety of azadiphosphiridines.[55]

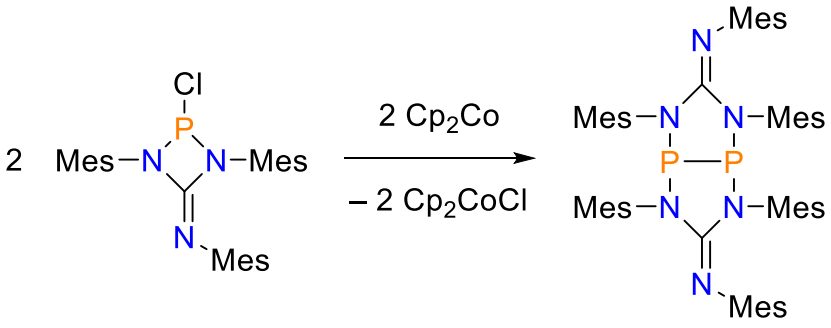
2.4 Retrosynthetic analysis of the titular compound

Synthesis of the novel compound class **D** (Figure 1) may be approached via different intermediates (Scheme 8). The final step towards the envisaged biradical/zwitterionic structure involves either a reductive cleavage of C–X or P–X bonds (route **I**, **II** or **III**) or a cycloaddition of charged unsaturated monomers (**IV**).[66] Route **I** starts out with an air-sensitive amino(imino)phosphane, compounds first described more than 100 years ago,[67] which can be readily deprotonated.[68] However, selective introduction of trihalomethane derivatives and concurrent reductive cleavage of C–X bonds may prove to be challenging, as no literature examples are known. Cycloadditions of monomer units (**III** and **IV**) rely on highly air-sensitive NP compounds that require steric protection to prevent initial dimerization.[69,70] This may also lead to inhibition problems when addition to the respective CN counterparts is tried.



Scheme 8. Retrosynthetic analysis via pathways **I**, **II**, **III** and **IV** (R and R' = organic substituent, X = halogen).

In contrast, air-stable amidines (**II**) are known for a range of substituents[71–73] and comparable structures with phosphorus could already be synthesized.[74,75] Nevertheless, reductive experiments (with R = Dmp, Mes) revealed insufficient kinetic protection of the formed species, resulting in dimers (Scheme 9). It was therefore necessary to employ more sterically demanding substituents.[76]

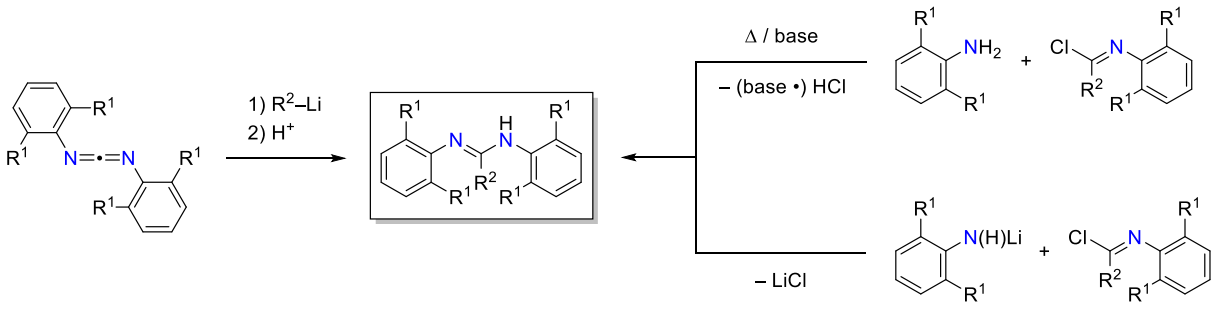


Scheme 9. Reductive dimerization of insufficiently bulky precursors.[75]

3 Results and discussion

3.1 Synthesis of the masked NHP

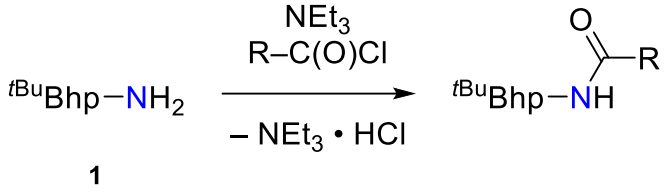
With an amidine as the designated starting point, two main syntheses can be found in literature. Results were limited to compounds with *meta*-substituted (alkyl or aryl groups) phenyl rings attached to the nitrogen atoms for steric protection (PAULI repulsion) of the central structural motif. The reaction can either proceed via addition of organolithium reagents to carbodiimides (Scheme 10, left side),[77] yielding the corresponding lithium amidinates, which can be used directly or protonated, to make them easy to handle in air. The other main approach involves the combination of imidoyl chlorides and amines (necessitating reflux conditions and/or addition of a base)[71,78–82] or imidoyl chlorides and alkali metal amides (as activated amines, Scheme 10, right side).[83,84]



Scheme 10. Principal pathways to amidines (R^1 = Me, *i*Pr; R^2 = Me, CF_3, *t*Bu, Ph, 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-NMe_2-C_6H_4, 4-NO_2-C_6H_4, 4-Br-C_6H_4).[71,77–84]

Starting from an amine, both pathways proceed via three reaction steps (amine → thiourea → carbodiimide → amidine; amine → amide → imidoyl chloride → amidine). However, the intended amidine should be rather bulky, while not being too sterically demanding, in order to still allow for reagents to approach the central core of the molecule. The Bhp substituent, which was already shown to satisfy these prerequisites,[85] has been recently employed in the synthesis of "superbulky" amidines for the kinetic stabilization of reactive alkali and alkaline earth metal compounds.[81,82] Therefore, the reaction of the respective amine and imidoyl chloride was

deemed to be more fitting. The first step is the transformation of the amine **1** to the respective amide by addition of a base and an acid chloride (SCHOTTEN-BAUMANN-like reaction, Scheme 11). Differently-sized acid chlorides were tried (acetyl chloride, pivaloyl chloride and benzoyl chloride), however only benzoyl chloride resulted in a clean, straightforward reaction with no byproducts.

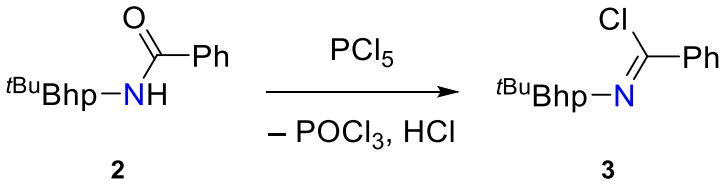


Scheme 11. Preparation of amides from **1** (R = Me, *t*Bu, Ph).

When adding together the reagents on larger scales (> 10 g), the mixture should be cooled with an ice bath. Appropriate amounts of solvent (at least 20 mL/g) and a big stir bar are essential, due to poor solubility of the product and precipitation of high amounts of triethylamine hydrochloride within minutes.

Due to aforementioned reasons, the phenyl derivative of the amide was used for further experiments, since the aromatic phenyl substituent in the amidine might also participate in electron delocalization via the NCN fragment.

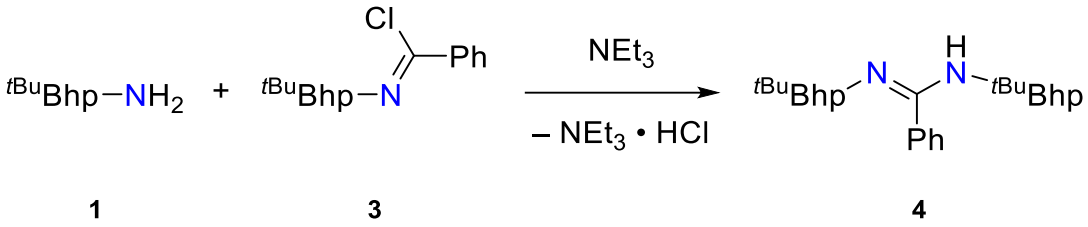
The next step is the conversion of the amide **2** to the respective imidoyl chloride **3**, which can be achieved by employing thionyl chloride or phosphorus pentachloride as chlorinating reagents. However, PCl_5 was found to yield the desired product in a more selective manner (Scheme 12). Contrary to previous protocols, no heating was required (in dichloromethane) and the reaction proceeded overnight.[81,82]



Scheme 12. Preparation of imidoyl chloride **3** from amide **2**.

An excess of PCl_5 was used, which might influence the kinetics of the reaction and lead to an acceleration, compared to literature protocols. Residual chlorinating reagents can be easily removed *in vacuuo* (10^{-3} mbar) at temperatures up to 130 °C.

The last step is the combination of the isolated imidoyl chloride **3** and the starting amine **1** to form the desired amidine **4** (Scheme 13). Several reaction conditions were tried (without base in refluxing toluene, with NEt_3 in dichloromethane at 60 °C, with NEt_3 in refluxing toluene), however, only the last one gave the product in adequate yield (60–65 %). Contrary to previous reports,[81,82] addition of a base and several days at reflux conditions were found to be crucial, as the reported conditions resulted in low conversion. After 10 d, only low amounts of starting material were still present, which could be removed by fractional crystallization in ethyl acetate. The amide **2**, which is formed from residual imidoyl chloride **3** after the aqueous workup, has the lowest solubility and usually precipitates as a fine powder upon concentrating the solution, which can be filtered off.



Scheme 13. Preparation of amidine **4** from amine **1** and imidoyl chloride **3**.

The amidine **4** displays a lower solubility than the amine **1** and can be isolated in sufficient purity via crystallization from ethyl acetate. Crystals suitable for single-crystal XRD measurements were obtained by slow evaporation of a saturated solution of **4** in 1,2-dimethoxyethane. The molecular structure in the single crystal (Figure 3) reveals an obtuse angle in the central NCN unit (118.6(3)°), close to the ideal 120° of an sp^2-hybridized carbon atom. While the distance between C1 and N1 (1.279(4) Å) matches the sum of covalent radii for a C–N double bond ($\sum r_{cov}$ (C=N) = 1.27 Å),[86] the distance between C1 and N2 (1.376(4) Å) is shortened compared to a C–N single bond ($\sum r_{cov}$ (C–N) = 1.46 Å), indicating electron delocalization within the NCN motif. WIBERG bond indices (BO (C1–N1) = 1.62, BO (C1–N2) = 1.17) from an NBO analysis of the energetically optimized structure (PBE-D3/def2-TZVP) and natural charges from a natural population analysis (N1 = –0.49 *e*, C1 = +0.42 *e*, N2 = –0.56 *e*) further support this assumption.

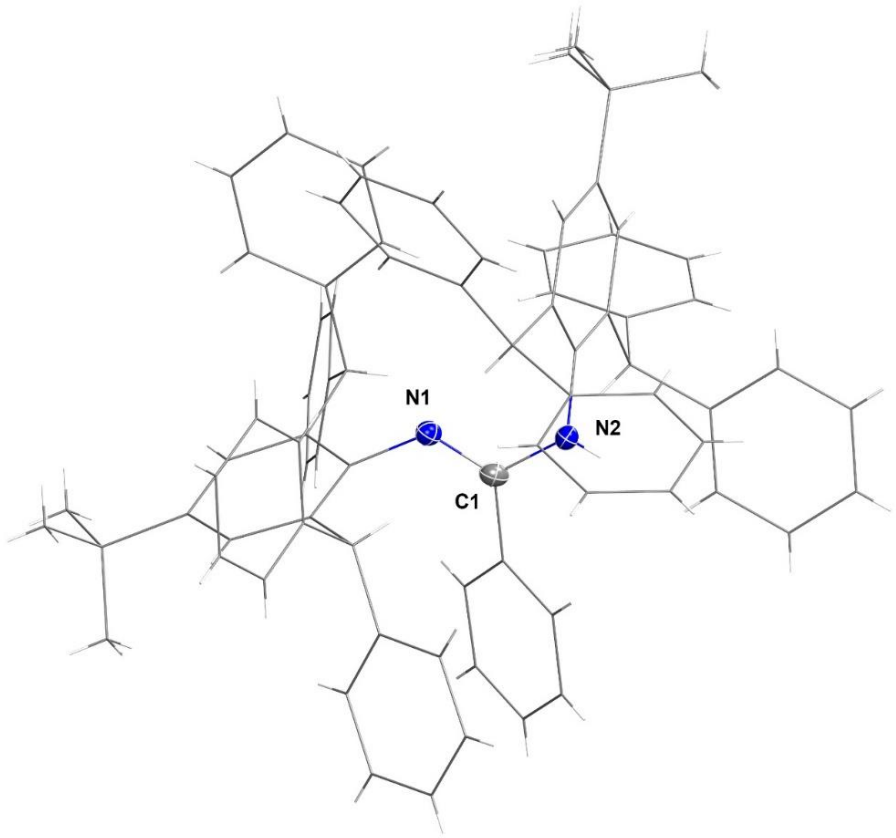
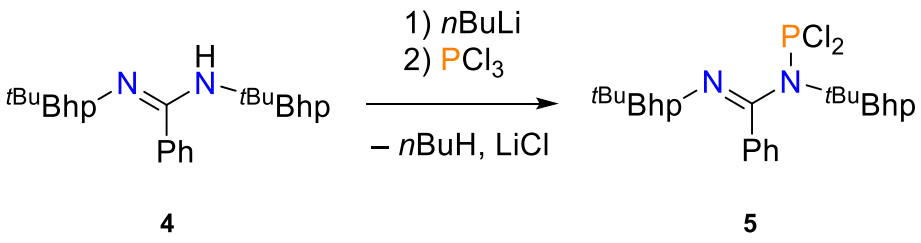


Figure 3. Molecular structure of **4** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The $^{t\text{Bu}}$Bhp and phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N1–C1 = 1.279(4), C1–N2 = 1.376(4), N1–C1–N2 = 118.6(3).

Deprotonation of comparable structures (amidines and guanidines) to introduce a phosphorus moiety was achieved with *n*BuLi or NEt_3.[74,75] For the herein presented bulky amidine **4**, *n*BuLi was chosen for its fast-acting and irreversible deprotonation (Scheme 14).



4 **5**

Scheme 14. Preparation of **5** from amidine **4**.

Upon addition of *n*BuLi, the colorless solution changes to orange-red and decolorizes to light yellow after the addition of PCl_3. Despite the assumed C_1 symmetry of **5** in the solid-state, only one singlet appears in the aliphatic region of the ^{1}H NMR spectrum. This observation was

already made by JONES et al., when they investigated reactions of guanidines and amidines with pnictogen halides ("The spectroscopic data for all complexes […] are more symmetrical than their solid-state structures would suggest.").[74] Temperature-dependent ^{1}H NMR spectra of **5** show signal broadening below –20 °C and coalescence somewhere between –40 °C and –60°C (Figure 4), with the proposed migration of the PCl_2 moiety via a cyclic transition state (Scheme 15) being significantly decelerated. Interestingly, no changes could be observed in temperature-dependent ^{31}P NMR spectra.

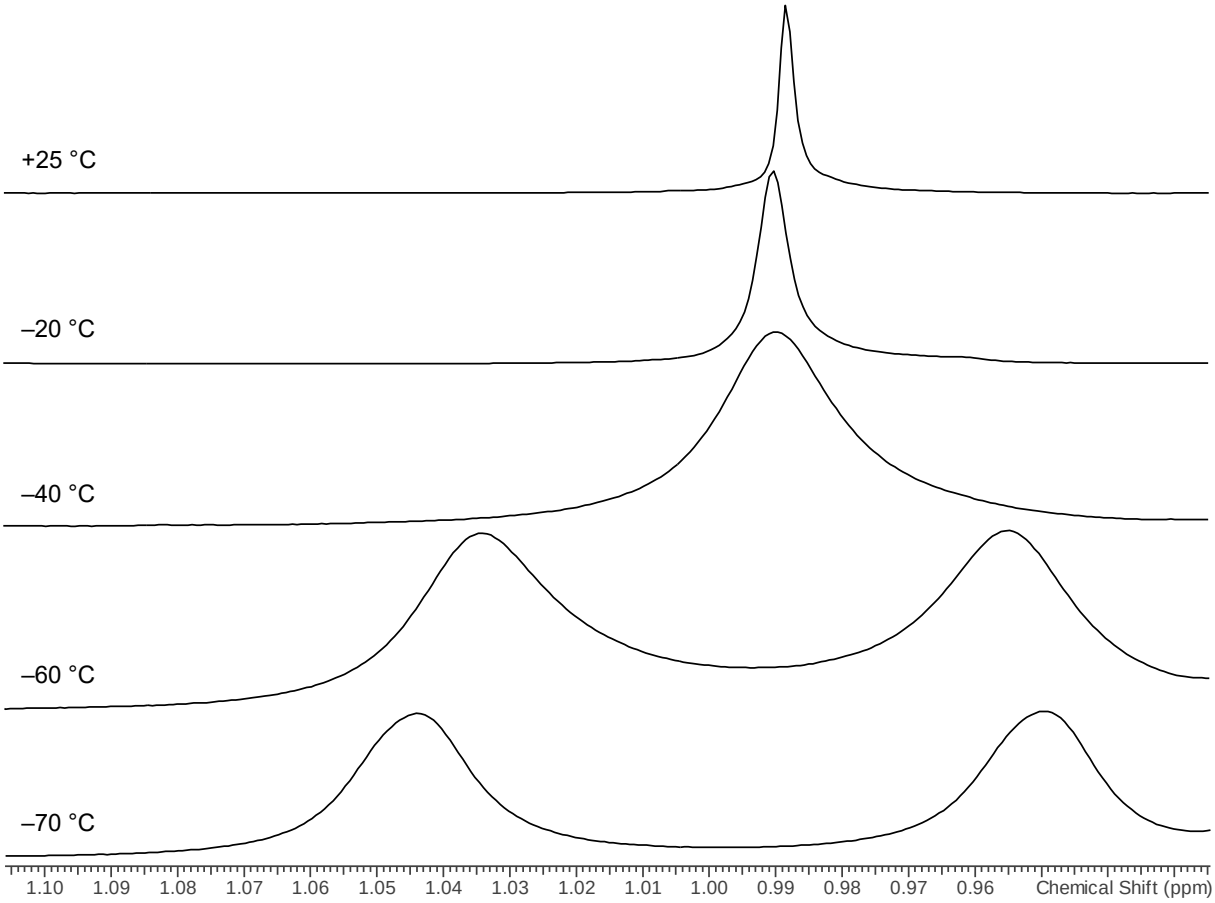
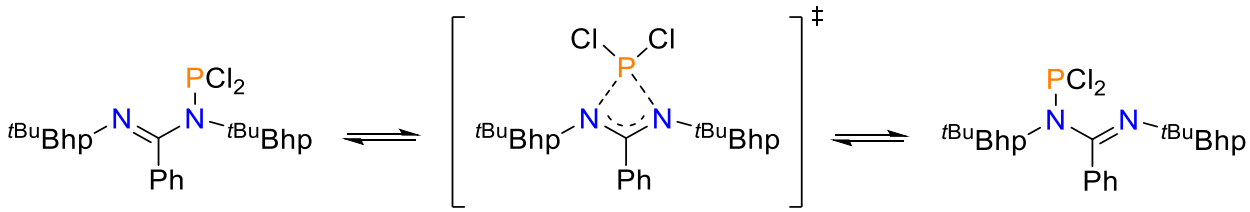


Figure 4. Temperature-dependent ^{1}H NMR spectra of **5** in toluene-d_8.



Scheme 15. Proposed intramolecular migration reaction of **5**.[68]

The chemical shift of **5** in the ^{31}P NMR spectrum (+112.9 ppm in CD_2Cl_2, +120.0 ppm in C_6D_6) corresponds to values between primary and secondary chlorophosphines,[87–89] as well as already reported guanidine derivatives, and indicates different conformers in polar and nonpolar solvents.[74,75] Single crystals grown via slow evaporation of a saturated solution of **5** in 1,2-dimethoxyethane reveal a near-planar N1–C1–N2–P1 structure with a dihedral angle of 10.4(2)° (Figure 5).

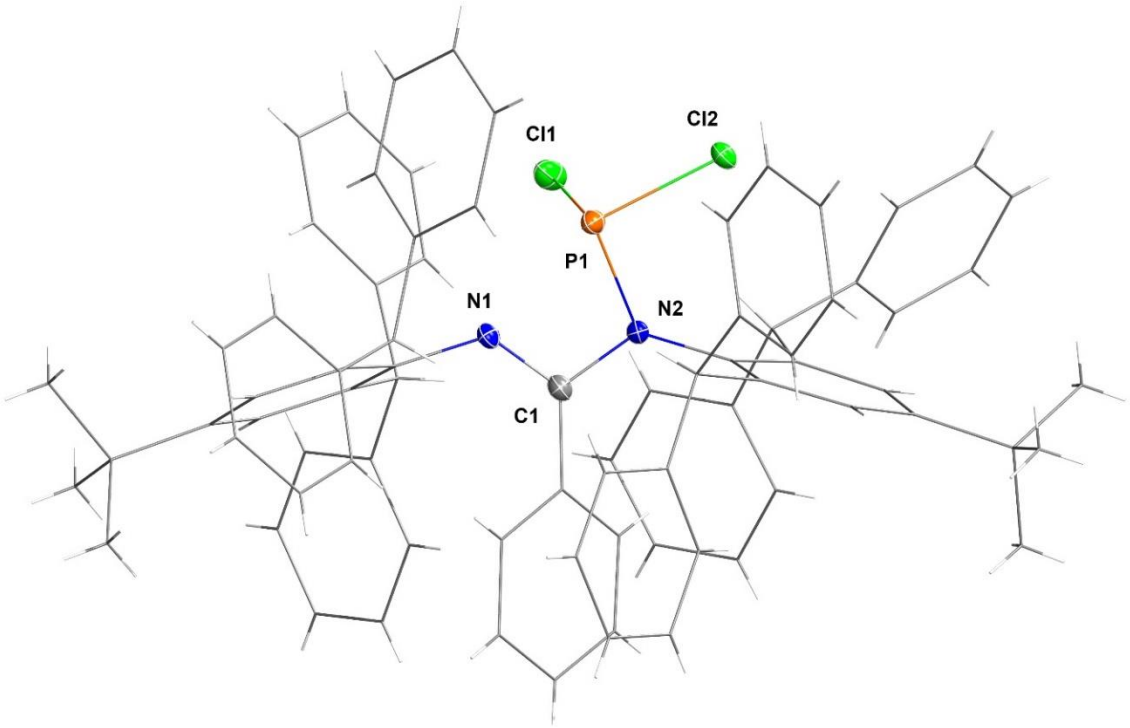
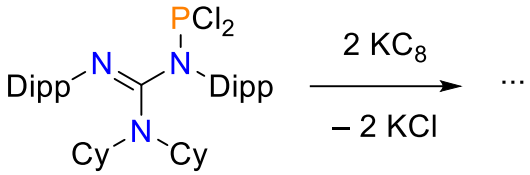


Figure 5. Molecular structure of **5** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The $^{t\text{Bu}}$Bhp and phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N1–C1 = 1.290(2), C1–N2 = 1.395(2), N2–P1 = 1.767(2), P1–Cl1 = 2.0691(7), P1–Cl2 = 2.1430(6), N1–C1–N2 = 108.9(2).

Both C–N bonds are slightly elongated compared to the amidine **4** and the $^{t\text{Bu}}$Bhp substituent at N2 is now twisted away from the core structure. This effect can be explained by significant interaction between N1 and P1, underlined by the close proximity of these atoms (2.254(2) Å), which is significantly shorter than the sum of the crystallographic VAN DER WAALS radii (3.55 Å)[90] and approaching the sum of covalent radii of an N–P single bond (1.82 Å).[86] Another aspect is the difference of the P–Cl bond lengths, where one bond is shortened (2.0691(7) Å) and the other elongated (2.1430(6) Å), compared to the sum of covalent radii for a single bond (2.10 Å).[86] NBO analyses of the energetically optimized structure (PBE-D3/def2-TZVP) also corroborate this with the respective WIBERG bond indices (BO (P1–Cl1) = 0.91,

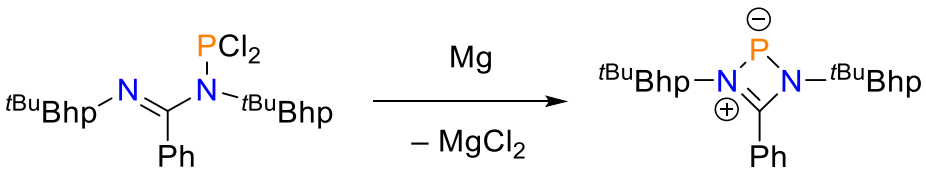
BO (P1–Cl2) = 0.79) and natural charges (P1 = +0.99 *e*, Cl1 = –0.28 *e*, Cl2 = –0.36 *e*). Additionally, second order perturbation analyses show considerable stabilization by lone pair donation of N1 into the antibonding σ* orbital (negative hyperconjugation) between P1 and Cl2 (LP (N1) → σ* (P1–Cl2) = 122.9 kJ/mol).

The last step in the synthesis of the target molecule is the reductive intramolecular cyclization. In their work, JONES et al. described the attempted reduction of a similar structure with KC_8, yielding a mixture of products (Scheme 16). They remarked that a "singlet at […] 446 ppm could […] indicate the presence of a diphosphene".[74]



Scheme 16. Attempted reduction by JONES et al. resulting in an unidentified product mixture.[74]

Within the framework of their extensive experimental and theoretical investigation of guanidate-based halophosphines, RAGOGNA et al. reacted their derivative with the reducing agent cobaltocene, isolating a bicyclic eight-membered ring system with a diphosphane unit as bridgehead atoms (cf. Scheme 9).[75] In the experience of our group, elemental magnesium (which was mechanically activated prior to use, by scrubbing off oxide layers with a glass-covered stir bar in an argon atmosphere) is a convenient reagent for P–Cl bond cleavage.[19,28,91] Therefore, **5** was reacted with Mg chips in THF (Scheme 17), in most cases leading to an almost immediate color change to orange, which turned slightly darker as the reaction progressed. The reaction was monitored via ^{31}P NMR spectroscopy, revealing a full selective conversion within 4 to 5 h, which gave rise to a singlet at +407.9 ppm.



5 **6**

Scheme 17. Preparation of **6** from the chlorinated precursor **5**. For reasons of clarity, only the most important LEWIS structure for **6** is subsequently used.

Orange single-crystals (λ_{max} = 430 nm), grown from a saturated solution in 1,2-dimethoxyethane, indeed matched the target molecule **6** (Figure 6), instead of a proposed diphosphene. The planar four-membered ring system adopts a slightly distorted kite-like structure, with all four bonds remaining under the sum of covalent radii for their respective single bond values (C–N = 1.46 Å, N–P = 1.82 Å).[86] This effect is more pronounced in the amidine backbone. Due to packing effects in the single crystal, bonds between the same atom types are not precisely equal within three times their standard deviation. WIBERG bond indices also correspond to higher bond orders within the NCN unit (BO (C–N) = 1.19), compared to the NPN unit (BO (N–P) = 0.78). The transannular P1–C73 distance (2.305(2) Å) is substantially longer than the sum of covalent radii for a single bond (1.86 Å), with the same situation also applying to the N1–N2 distance (2.087(2) Å), compared to the respective sum of covalent radii (1.42 Å).[86]

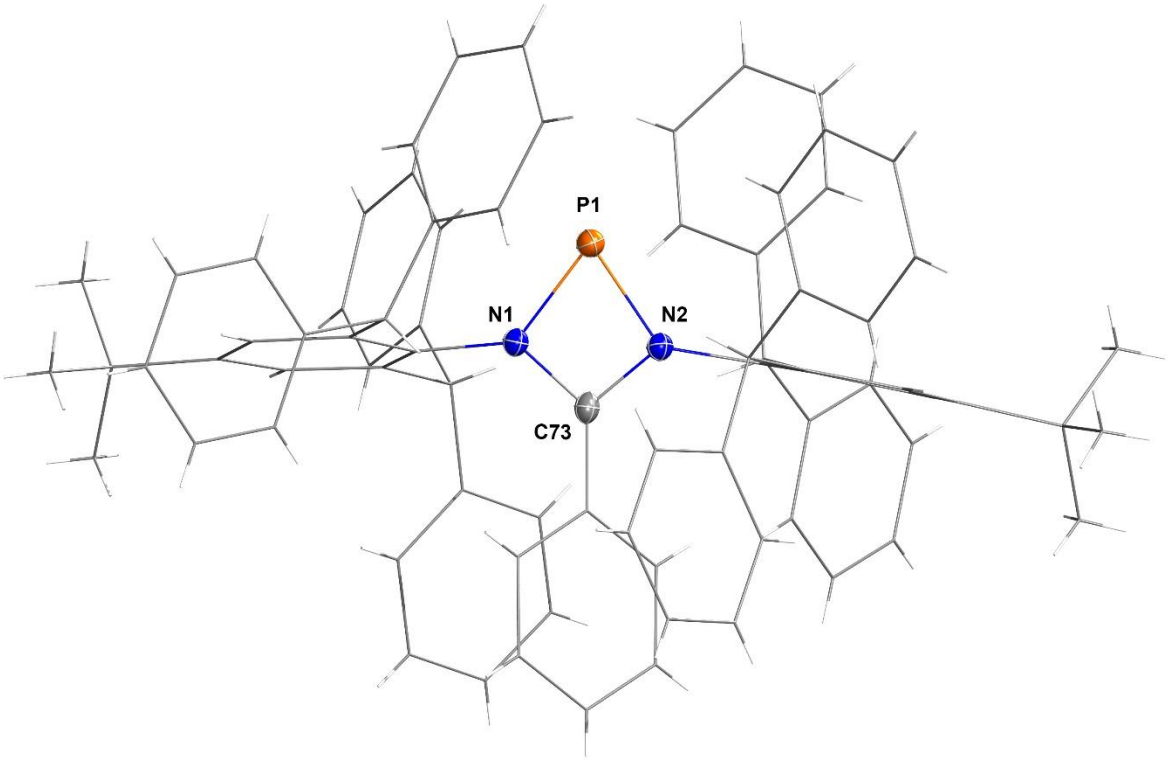


Figure 6. Molecular structure of **6** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The $^{t\text{Bu}}$Bhp and phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N1–P1 = 1.770(1), N1–C73 = 1.373(2), P1–N2 = 1.756(1), C73–N2 = 1.362(2), N1–P1–N2 = 72.58(6), P1–N2–C73 = 94.5(1), N2–C73–N1 = 99.4(1), C73–N1–P1 = 93.5(1), N1–P1–N2–C73 = 0.12(9).

A natural population analysis, taking the whole electron density of the respective NAOs into account, shows negative natural charges for N1 and N2 (–0.59 *e*) and positive values for C73 (+0.32 *e*) and P1 (+0.59 *e*).

6 is soluble in ethers (diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane), a variety of aromatic solvents (toluene, benzene, fluorobenzene, 1,2-dichlorobenzene) and even dichloromethane, without decomposition or reaction. With respect to potential applications of **6** as a ligand for transition metals, it should be noted that the polar solvent DMF reacts with **6** in a selective manner within minutes, as evidenced by a singlet in the ^{31}P NMR spectrum (+158.8 ppm).

In order to get a first idea of the charge localization within the π electron framework and to classify the biradical character of the novel compound class **D** next to symmetric N_2C_2, N_2P_2 and P_2C_2 systems, CASSCF(6,4)/def2-TZVP calculations of model systems (Figure 7) were carried out.

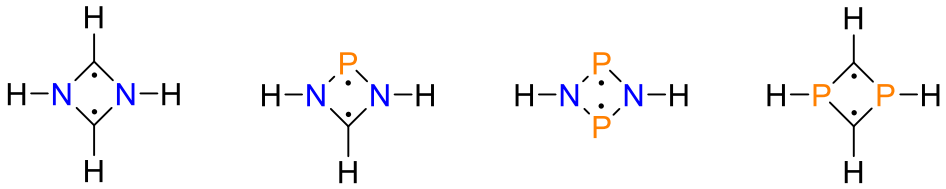


Figure 7. Biradical representations of symmetric model compounds and the titular model compound.

It should be noted that depicted biradical systems of the type N_2C_2 are not known yet, likely attributed to their instability with regard to a cycloreversion to imidoyl radicals. Nevertheless, all four LUNOs feature a similar transannular bonding situation (Figure 8). While the HONO in the N_2P_2 model compound shows electron localization exclusively at the phosphorus atoms, partial overlap among the central atoms is visible in the N_2C_2 and P_2C_2 model compounds. Electron delocalization is significantly more present in the NCNP model compound, with a clear distinction between the phosphorus atom and the NCN backbone. The LUNO occupancies for the P_2C_2 (0.19), N_2C_2 (0.20) and N_2P_2 (0.24) model compounds share comparable values and indicate significant biradical character (ideal occupancy of 1). On the other hand, the LUNO occupancy for the NCNP model compound exhibits a substantially smaller value of 0.08. Using NRT analyses, resonance structures for all four model compounds were calculated (Figure 9). Interestingly, a biradical-type resonance has the largest weight for the N_2P_2 model compound, while similar zwitterionic resonances are more prominent for the remaining three model

compounds. An open-chain, phosphinidene-type resonance for the NCNP model compound only contributes about 0.3 %. However, in the structure with the largest weight, two lone pairs are located at the phosphorus atom, akin to conventional phosphinidenes.

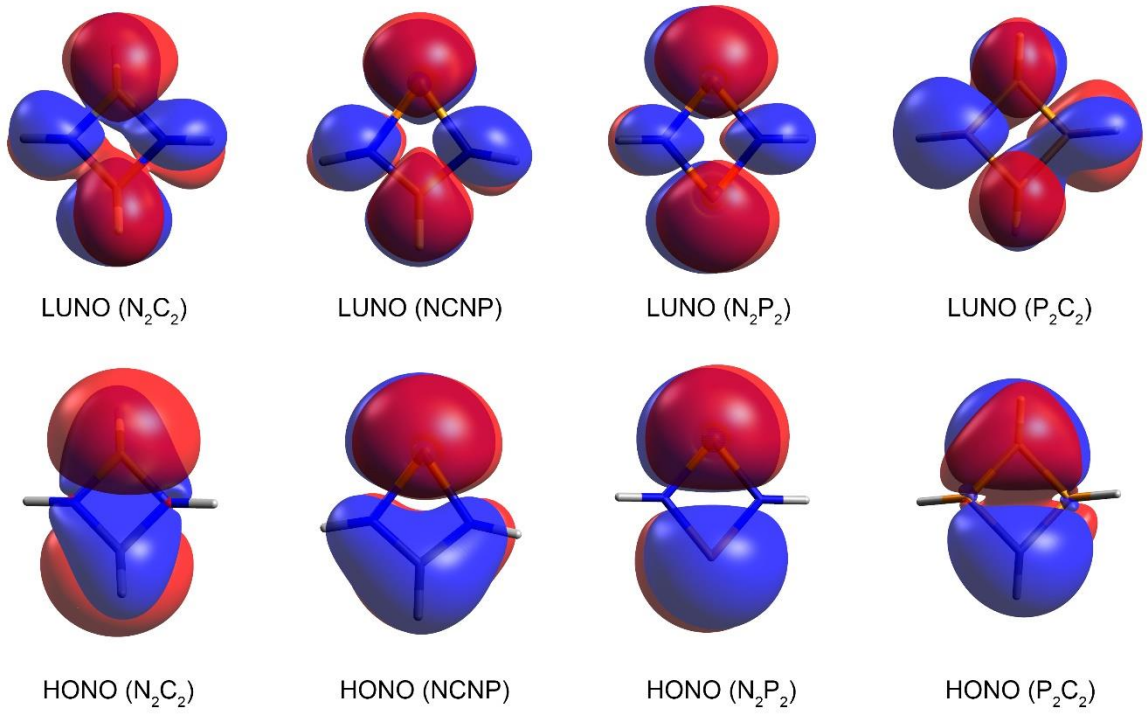


Figure 8. Depiction of LUNO and HONO of model compounds.

Additionally, NRT calculations also afforded bond orders for the four central bonds of the four model compounds (Table 1 to 4). While all values are higher than 1, due to the resonance structures featuring double bonds, the increase is most prominent in the NCN unit of the NCNP model compound. This is in agreement with the HONO representation, depicted in Figure 8.

Furthermore, the HOMO-LUMO gap can be used as a parameter to discuss biradical character. The energy difference increases from N_2P_2 (7.1 eV), to P_2C_2 (8.8 eV), to N_2C_2 (10.5 eV), to NCNP (10.9 eV), according to CASSCF(6,4)/def2-TZVP computations. A small gap, and thus nearly degenerate MOs, are a prerequisite to identify a molecule as a biradical. In this regard, the NCNP compound can be viewed as a closed-shell species, rather than a biradical.

Lastly, the singlet-triplet gaps decrease from N_2C_2 (178.6 kJ/mol), to NCNP (161.7 kJ/mol) to N_2P_2 (123.1 kJ/mol), to P_2C_2 (52.8 kJ/mol) (PBE-D3/def2-TZVP). The smallest gap correlates with the highest biradical character, which, thus far, is only partially corroborated by

experiments, as only the latter two compound classes were sufficiently investigated. Nevertheless, all four model compounds feature a singlet ground state.

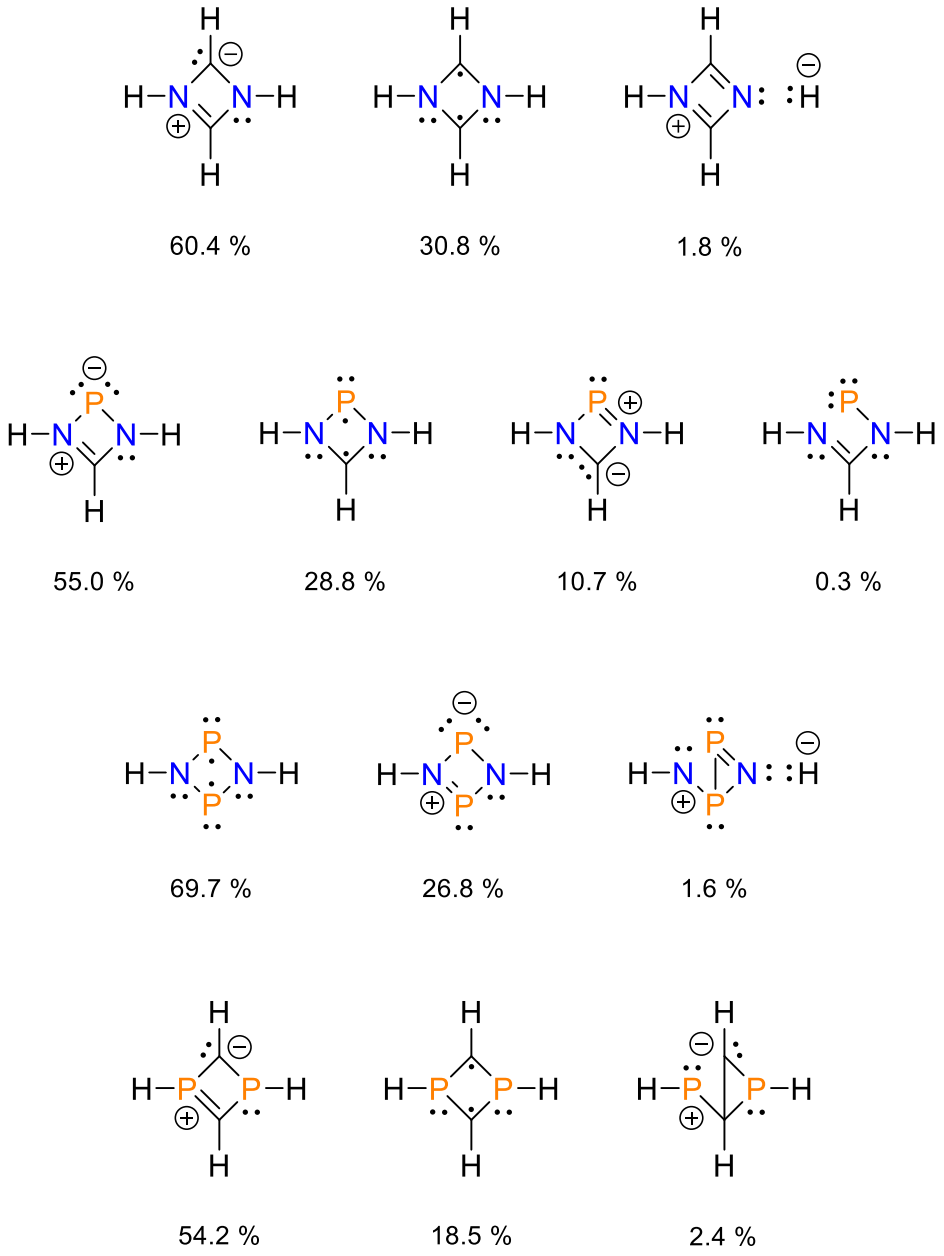


Figure 9. Resonance structures of model compounds and their relative weight, obtained by NRT calculations of optimized structures (PBE-D3/def2-TZVP). Displayed are the three most relevant structures, as well as a phosphinidene-type structure for NCNP.

Table 1. NRT bond orders and bond characters of N_2C_2 model compound.

	C–N
NRT bond order	1.17
Covalent character	69.7 %
Ionic character	30.3 %

Table 2. NRT bond orders and bond characters of NCNP model compound.

	C–N	N–P
NRT bond order	1.30	1.03
Covalent character	69.7 %	46.1 %
Ionic character	30.3 %	53.9 %

Table 3. NRT bond orders and bond characters of N_2P_2 model compound.

	N–P
NRT bond order	1.06
Covalent character	47.3 %
Ionic character	52.7 %

Table 4. NRT bond orders and bond characters of P_2C_2 model compound.

	C–P
NRT bond order	1.16
Covalent character	73.4 %
Ionic character	26.6 %

To gain further insight into the bonding situation of **6**, a CASSCF(2,2)/def2-TZVP calculation was run, which gave a LUNO occupancy of 0.09. This value is significantly lower than those for comparable NP-based cycles and indicates virtually no biradical character.[19] The LUNO and HONO (Figure 10) include contributions at the phenyl ring, attached to C73, and the HONO shows electron delocalization within the NCN unit. Akin to the model system, a transannular bonding interaction between P1 and C73 can be found in the LUNO and a transannular antibonding situation is present in the HONO. In total, the collective calculations justify the designation of **6** as a masked *N*-heterocyclic phosphinidene (Figure 11).

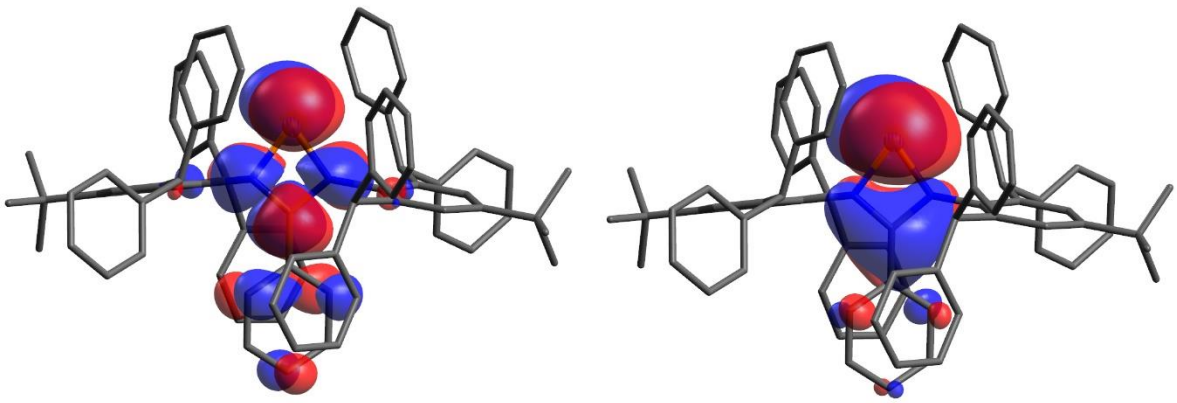


Figure 10. LUNO (left) and HONO (right) of **6** (hydrogens omitted for clarity).

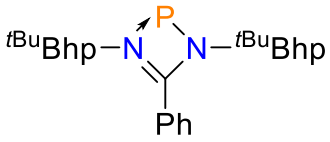
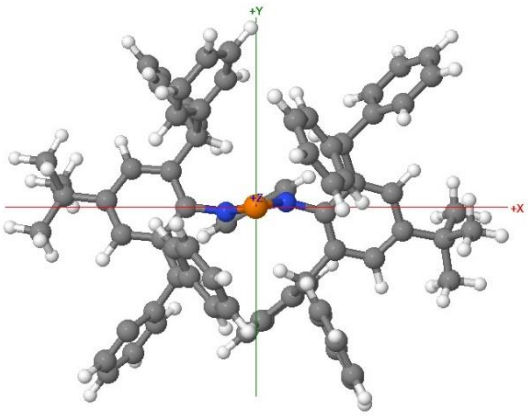


Figure 11. Depiction of **6** as a masked phosphinidene.

To further assess the influence of the surrounding $^{t\text{Bu}}$Bhp substituents on the phosphorus atom, the buried volume was calculated (Table 5).[92] The values represent considerable envelopment of the phosphorus center by the bulky $^{t\text{Bu}}$Bhp groups, even at larger distances, although this statement is only valid for a rigid structure and shielding most likely differs in solution.

Table 5. Buried volume for **6** at different distances. The phosphorus atom was placed at the center of a hypothetical sphere of varying radii (depicted on the right side).[92]

***r* / Å**	**%*V* buried**
1.0	61.7
2.0	58.9
3.0	88.3
3.5	79.1
4.0	87.5



In a few batches of **6**, trace amounts of two additional sets of triplets in the ^{31}P NMR spectrum with an integral ratio of 1:1 could be identified (Figure 12).

The chemical shift of the signals (–313.3 ppm and –72.4 ppm), as well as the *J* coupling constant (–218 Hz), are indicative of bicyclic tetraphosphanes.[93] Generally, three isomers for these butterfly-type structures are known, characterized by an A_2X_2 spin system (*exo-exo* and *endo-endo* isomer) or an AMX spin system (*endo-exo*). Due to the absence of a third signal and the steric bulk of the $^{t\text{Bu}}$Bhp substituents, the triplets can most likely be assigned to an *exo-exo* species (Scheme 18).

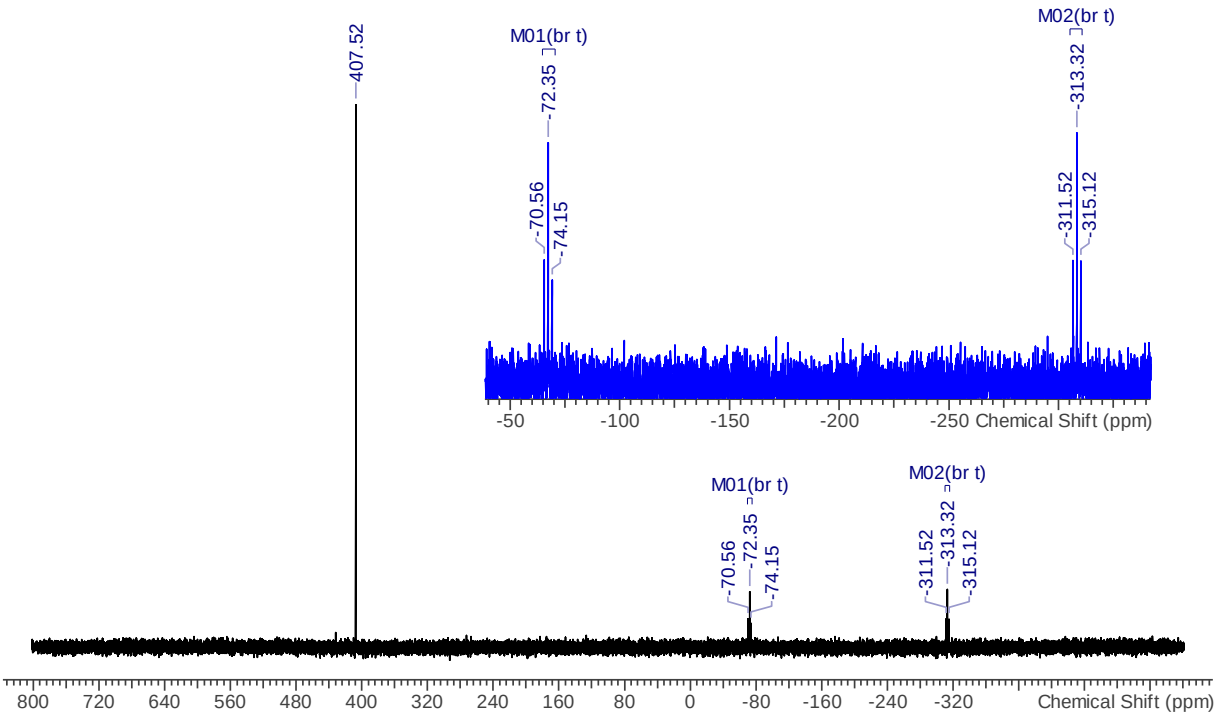
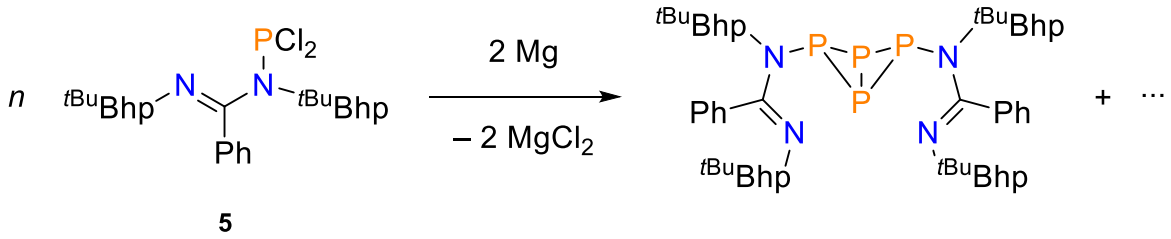


Figure 12. $^{31}P\{^{1}H\}$ NMR spectrum of **6** with an additional byproduct.



5

Scheme 18. Proposed *exo-exo* byproduct of the reduction of **5**.

The number of spectroscopically characterized bicyclotetraphosphanes is still small and to date only one example of a species with nitrogen attached directly to the core structure is known (Table 6). However, all values are quite similar and agree well with the observed experimental parameters.

Table 6. ^{31}P NMR data of selected *exo-exo*-bicyclotetraphosphanes (bh = bridgehead).

R =	δ (^{31}P), P_{bh} / ppm	δ (^{31}P), *P*–R / ppm	$^{1}J(^{31}P,^{31}P)$ / Hz	Ref.
$N(SiMe_3)_2$	–287.3	–79.1	–225	[94]
Cp*	–357.3	–133.6	–194	[95]
Mes*	–273.2	–128.3	–177	[93,96,97]
$C(SiMe_3)_3$	–333.9	–111.2	–203	[98]
$C(PPh_3)$–2,6-$Cl_2C_6H_3$	–354.5	–130.9	–197	[99]
2,6-$(Dipp)_2$–C_6H_3	–331.8	–163.0	–189	[100]
Ter	–322.3	–171.3	–182	[101]

While the exact mechanism for the byproduct formation remains unclear, bicyclotetraphosphanes were also observed in unrelated reduction experiments,[102] as they often represent thermodynamically favored species. Hence, the principally selective formation of **6** can be attributed to the sterically demanding $^{t\mathrm{Bu}}$Bhp substituents and their kinetically stabilizing effect. Leaving **6** in polar solvents for several days to weeks could lead to an increased concentration of the proposed bicyclotetraphosphane.

3.2 Reactivity of the masked NHP

3.2.1 Reactivity towards LEWIS acids

Due to the unprecedented nature of this particular structural motif, it was of interest to investigate the reactivity of **6** towards selected molecules, representative of whole compound classes. In a first step, **6** was reacted with the reagent Me_2SAuCl on NMR scale, which acts as a synthon for the LEWIS-acidic AuCl moiety. Due to a slight excess of Me_2SAuCl, two singlets were found in the $^{31}P\{^1H\}$ NMR spectrum (Figure 13), which were thought to represent a mono- and double-coordinated gold complex (**7** and **8**).[62]

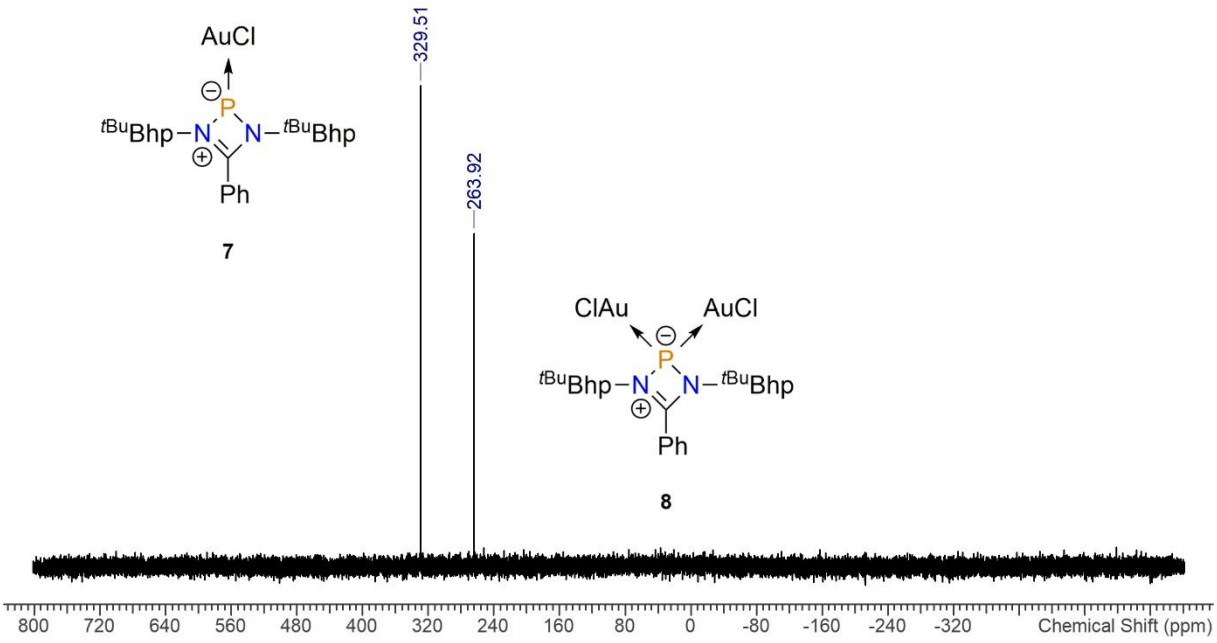
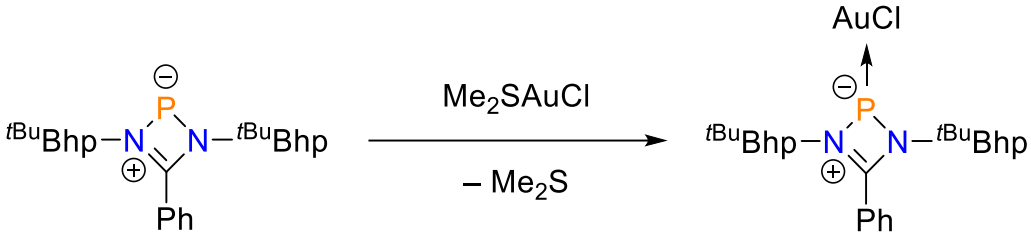


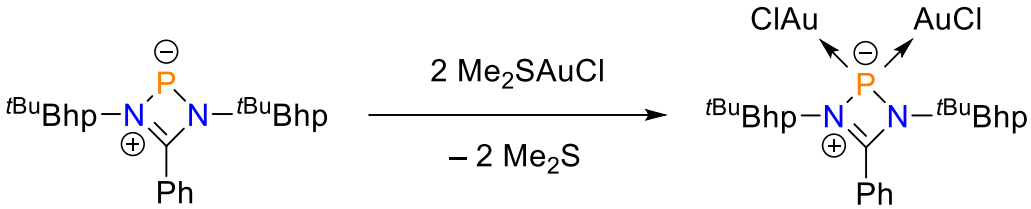
Figure 13. $^{31}P\{^1H\}$ NMR spectrum of a test reaction of **6** with a slight excess of Me_2SAuCl.

Thus, reactions were repeated on a larger scale with slower combination of the reagent solutions. Indeed, both species could be prepared individually. However, only the double-coordinated complex **8** (δ = +263.9 ppm) could also be isolated and fully characterized (Scheme 20).



6 **7**

Scheme 19. Reaction of **6** with 1 eq. of Me_2SAuCl.



6 **8**

Scheme 20. Reaction of **6** with 2 eq. of Me_2SAuCl.

Single crystals of **8** were grown from a saturated solution in fluorobenzene. The solution was filtered multiple times to remove excess gold, which precipitates over the course of several days. The molecular structure (Figure 14) shows a more symmetric core environment with a dihedral angle (–0.001(2)°) even closer to 0°, compared to **6**, while the P–Au–Cl units are slightly bent out of linearity (166.41(3)°). The NCN unit becomes more obtuse (102.0(3)°), while the benzhydryl groups are twisted away from the center to enable gold coordination to P1. Compared to **6** (2.305(2) Å), the transannular P1–C37 distance decreases (2.277(3) Å). WIBERG bond indices of **8** also decrease for N–P bonds (BO (N–P) = 0.64) and increase for C–N bonds (BO (C–N) = 1.30). Interestingly, the bond index for P–Au bonds (BO (P–Au) = 0.71) has a higher value than for Au–Cl bonds (BO (Au–Cl) = 0.46), which can be likely attributed to the larger ionic character of the latter bonds. For the monosubstituted complex **7**, the WIBERG bond index difference between the P–Au bond (BO (P–Au) = 0.76) and the Au–Cl bond (BO

(Au–Cl) = 0.40) is even more conspicuous. The observed experimental outcome agrees with both biradical[103] and phosphinidene[104] reactivity.

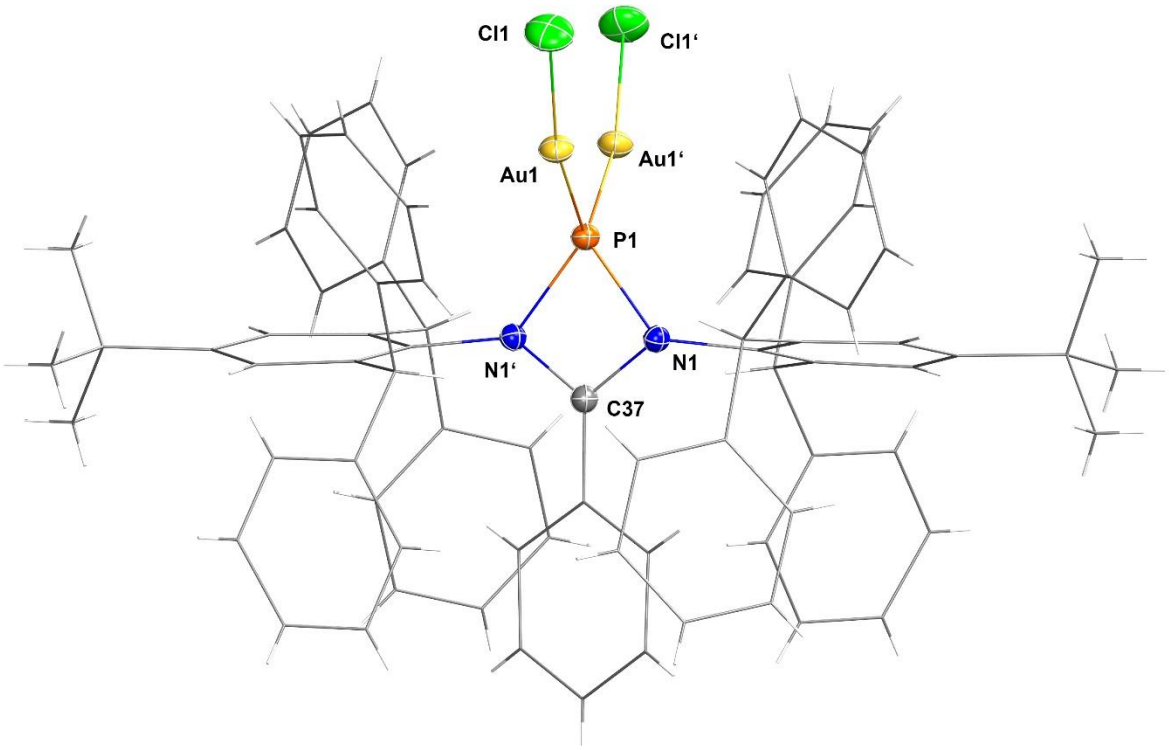
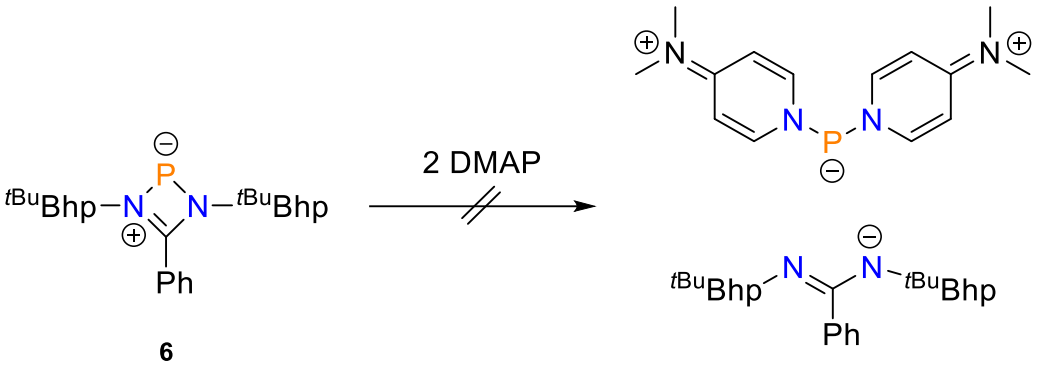


Figure 14. Molecular structure of **8** in the single crystal. Ellipsoids are set at 50 % probability (173(2) K). The Bhp and the phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N1–P1 = 1.772(2), N1–C37 = 1.355(3), P1–Au1 = 2.1972(5), Au1–Cl1 = 2.2741(6), N1–P1–N1’ = 72.9(1), P1–N1–C37 = 92.5(1), N1–C37–N1’ = 102.0(3), P1–Au1–Cl1 = 166.41(3), C37–N1–P1–N1’ = –0.001(2).

3.2.2 Reactivity towards LEWIS bases

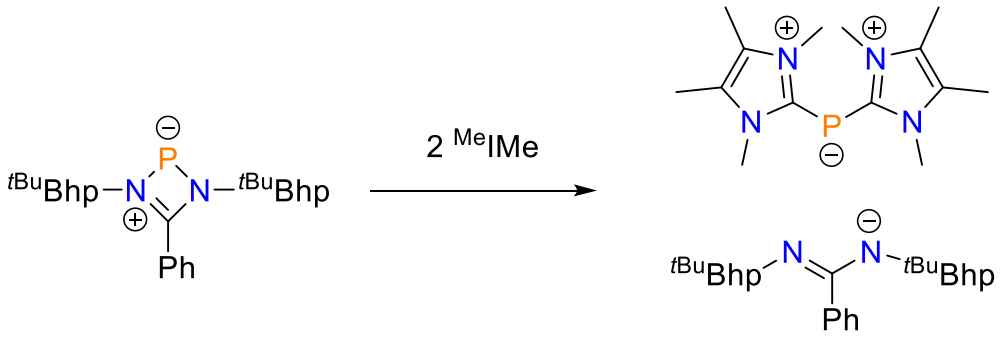
To test the properties of **6** in the presence of LEWIS bases, the compound was first reacted with 4-dimethylaminopyridine. Due to the basic nature of the amidinate backbone, substitution with DMAP and stabilization of a P^+ cation was expected (Scheme 21). However, no reaction was observed in THF or DCM, even at 60 °C and after several days of stirring.



6

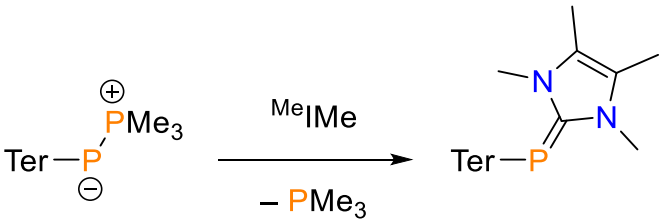
Scheme 21. Intended reaction of **6** with 2 eq. of DMAP.

Nevertheless, **6** was also reacted with 2 equivalents of ^{Me}IMe, one of the smallest stable and isolable NHCs.[105,106] In an analogous reaction to the biradical [Ter–NP]$_2$,[62] which features a four-membered central [NP]$_2$ unit, **6** reacted in quantitative manner to a phosphamethine cyanine cation (as evidenced by its distinctive ^{31}P NMR chemical shift of –112 ppm) and the amidinate anion (Scheme 22), with an observable color change from orange to yellow within minutes. Compared to other phosphinidene sources, **6** does not react with NHCs in an additive way to yield neutral products (Scheme 23), which can be attributed to the more fragile N–P bonds (as compared to the C–P bond).[107–109]



6 **9**

Scheme 22. Reaction of **6** with 2 eq. of the NHC ^{Me}IMe.



Scheme 23. Reaction of a phospha-WITTIG reagent with the NHC ^{Me}IMe.[107]

Crystallization of the ion pair proved to be challenging at first, as traces of Cl^- in the mixture always led to the isolation of [(^{Me}IMe)$_2$P]Cl. However, using benzene as a solvent, single crystals could eventually be obtained. The molecular structure of **9** (Figure 15) shows a comparable conformation of the amidinate anion to the amidine **4** (Figure 3). Nonetheless, bond lengths between N5/N6 and C15 are equalized, due to delocalization of the negative charge within the π electron framework.

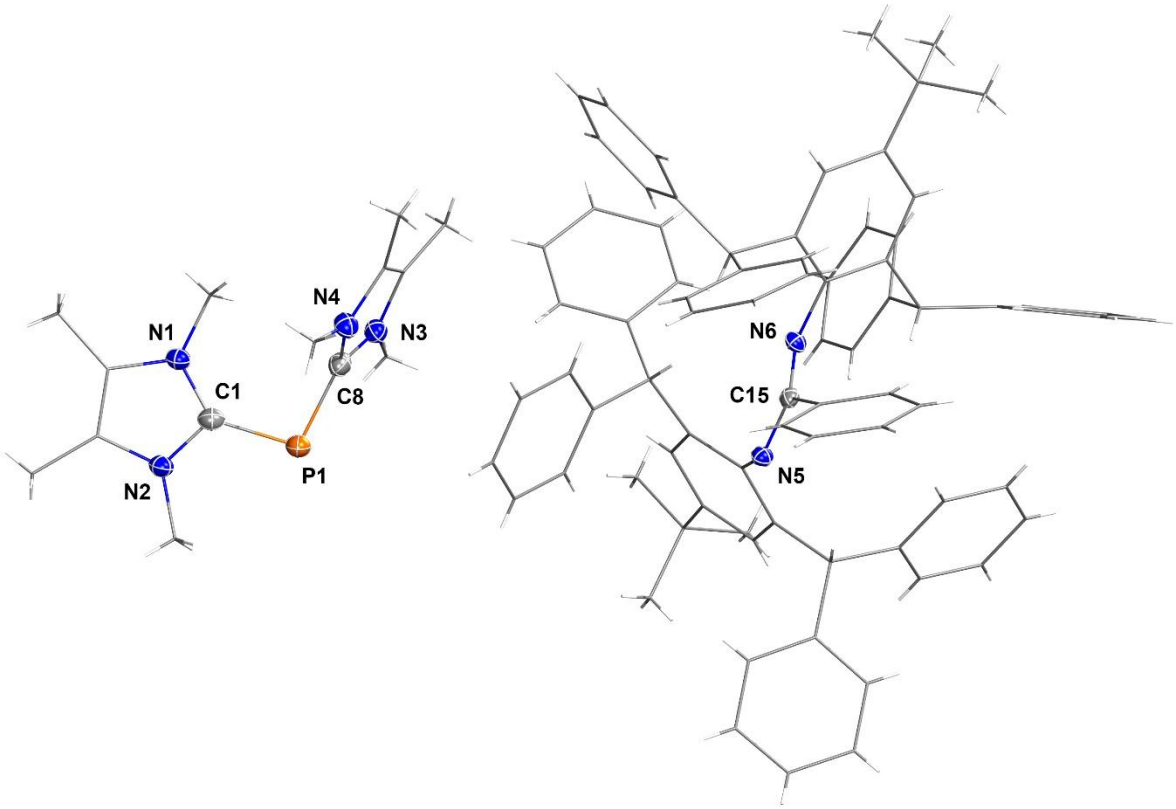


Figure 15. Molecular structure of **9** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Bhp and the phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N1–C1 = 1.361(3), N2–C1 = 1.358(3), C1–P1 = 1.794(2), P1–C8 = 1.813(2), C8–N3 = 1.349(3), C8–N4 = 1.359(3), N5–C15 = 1.330(2), C15–N6 = 1.319(2), C1–P1–C8 = 99.60(9), N5–C15–N6 = 126.5(2).

The shortest distance between P1 and N5 in the single-crystal corresponds to 7.124 Å, while the distance between P1 and N6 has a value of 8.747 Å. These values are even higher than for the comparable ion pair [(^{Me}IMe)$_2$P][Ter–NPN–Ter][62] (5.742 Å and 6.699 Å), suggesting an even weaker interaction between cation and anion and underlining the bulkiness of the ^{tBu}Bhp substituents. This is also evident by the high solubility of this salt in nonpolar solvents like benzene. However, utilization as an FLP-like compound is very likely limited by the low

electrophilicity of the cation, which can lead to the formation of dications, rather than neutral addition products.[110]

3.2.3 Reactivity towards oxidants

When **6** was treated with an excess of sulfur or selenium, a color change from orange to yellow was observed within minutes. The $^{31}P\{^{1}H\}$ NMR spectra (Figure 16) show similar signals, with high-field shifts compared to **6**, suggesting successful oxidation of the phosphorus atom. However, the reaction with sulfur was not as selective, as more species (+95.3 ppm, +101.4 ppm and +125.0 ppm) were present and the integral value of the main species at +293.4 ppm amounted to approximately 70 % of all phosphorus-containing compounds.

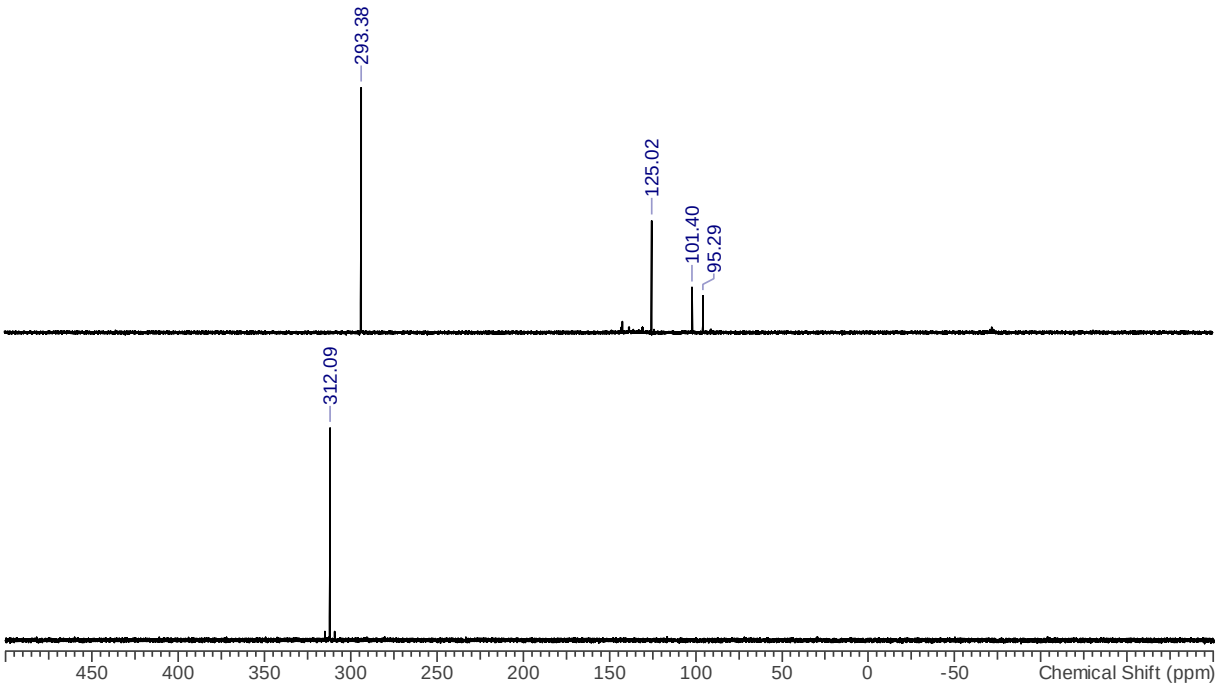


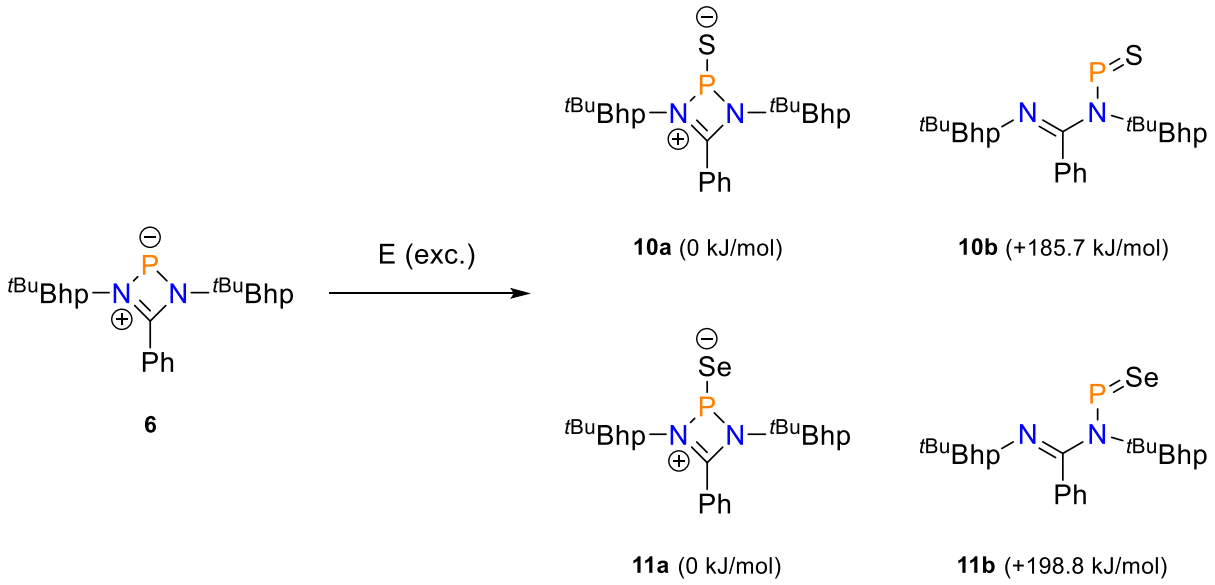
Figure 16. $^{31}P\{^{1}H\}$ NMR spectra of the reaction of **6** with sulfur (top) and selenium (bottom).

Since no single crystals could be isolated, a quantitative ^{31}P NMR spectrum of the selenium reaction was used to determine the number of attached chalcogen atoms. Due to the natural abundance (7.6(2) %)[111] of the only NMR-active selenium isotope ^{77}Se (nuclear spin = ½), small satellites are visible in the NMR spectrum. The integral ratio of the satellites and the main singlet gives a value of 7.4 %, suggesting only partial oxidation and addition of one selenium atom. Due to similarities in the chemical shifts, the same situation should apply, in part, to the sulfur reaction. The formation of an only partially oxidized, monosubstituted Se derivative is

furthermore supported by the ^{31}P NMR chemical shift of the species, which is only slightly high-field shifted (+312.1 ppm), compared to the starting material **6** (+407.9 ppm). A subsequent elemental analysis and the presence of a fitting molecular ion peak in the mass spectrum can be regarded as further evidence.

With one chalcogen atom attached to the phosphorus atom, formation of a cyclic or an open-chain structure seem most likely (Scheme 24). Analyses of the energetically optimized isomers (PBE-D3/def2-TZVP), affording the relative free GIBBS energies, show a clear preference for the cyclic structures.

This is also corroborated by only one alkyl signal in the ^{1}H NMR spectra, which indicates the presence of a cyclic C_2-symmetric molecule, rather than the C_1-symmetric open-chain isomers.



Scheme 24. Oxidation of **6** with chalcogens (E = S, Se) and possible isomers with their relative free GIBBS energies (PBE-D3/def2-TZVP) in parentheses.

Since ^{77}Se is an NMR-active nucleus, a $^{1}J(^{31}P,^{77}Se)$ coupling constant of 712 Hz could be determined. Commonly, these constants are used to discuss the σ-donor capabilities of tertiary phosphines.[112–114] In this regard, similar values with their respective structures are depicted in Figure 17.

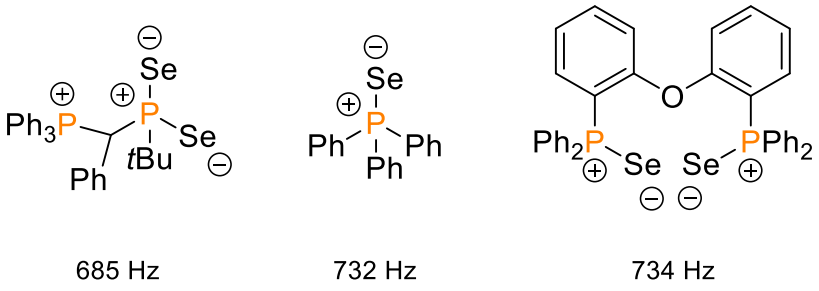
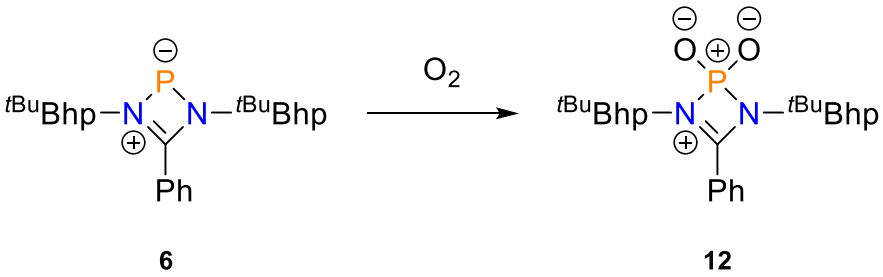


Figure 17. Selenium-substituted phosphines and their $^{1}J(^{31}P,^{77}Se)$ coupling constants.[112–115]

Due to the unprecedented structural nature of **6**, comparisons to literature-known selenides of the type R_3PSe are complicated. In general, an increase in the coupling constants is associated with electron-withdrawing substituents at the phosphorus atom and an increase of the s-type orbital character of the lone pair. However, since the largest-weighted resonance structure of **6** features two lone pairs, one s-type and one π-type, comparisons can hardly be drawn.

While no single crystals of the partially oxidized compound **11a** could be isolated, a fully oxidized product formed by accident. During a crystallization attempt of **6** in benzene, an apparent reaction with atmospheric oxygen took place (Scheme 25), resulting in the formation of **12**. It seems very plausible, that a controlled reaction of **6** with oxygen leads to the same product.



Scheme 25. Reaction of **6** with molecular oxygen.

The values of both P–O bonds (1.463(2) Å and 1.468(2) Å, Figure 18) are identical to the comparable structure $[Ter–NP]_2O_2$ (1.459(1) Å and 1.461(1) Å).[56] A similar reaction was also observed for in-situ generated phenylphosphinidene.[116] Despite being an accidental product, **12** could be fully characterized. The ^{31}P NMR chemical shift of **12** (+4.9 ppm) marks a significant difference to **6** and **11a** and is characteristic for pentavalent oxygen-bound phosphorus species. Albeit employing an excess of selenium (Scheme 24), only the partially oxidized derivative **11a** formed, while the reaction with oxygen to form **12** led to double

addition. This might be explained by the difference in the oxidation potentials between Se and O_2 and likely by vastly different reaction times. Mixing **6** with selenium for several days might eventually lead to an analogous double addition. This, however, was not tested anymore during the course of this work.

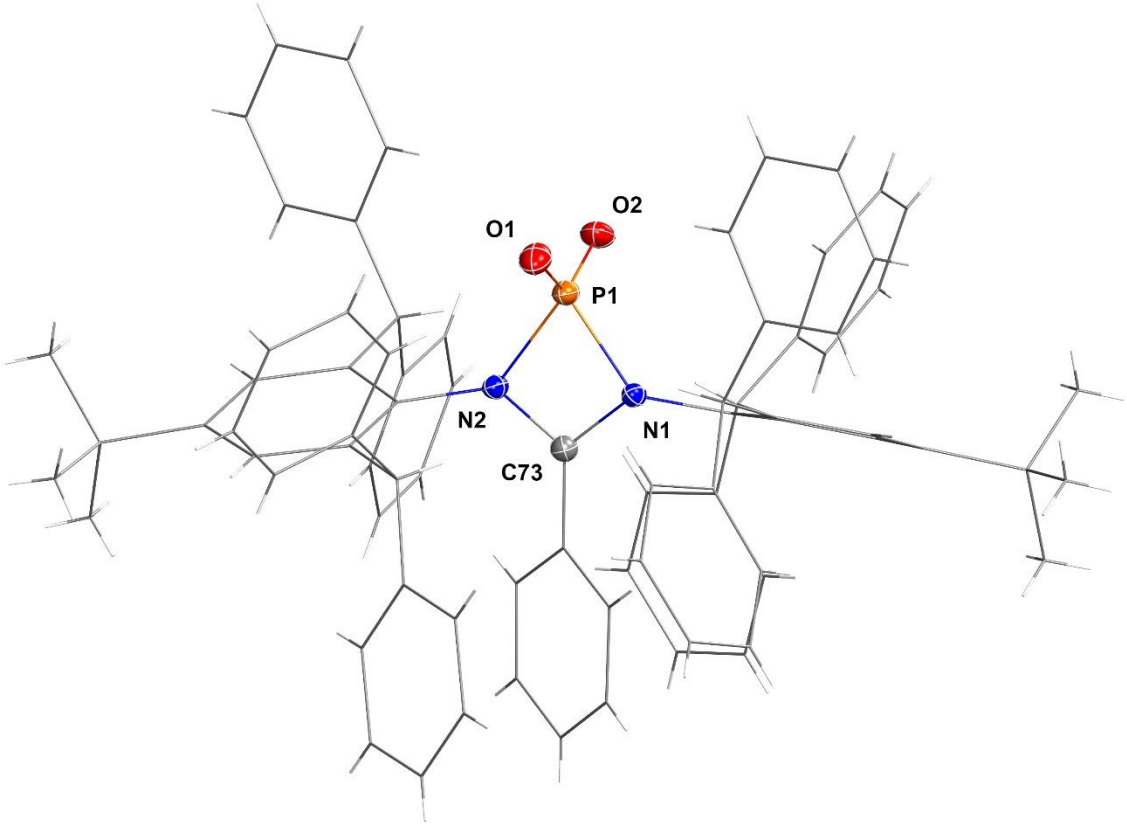
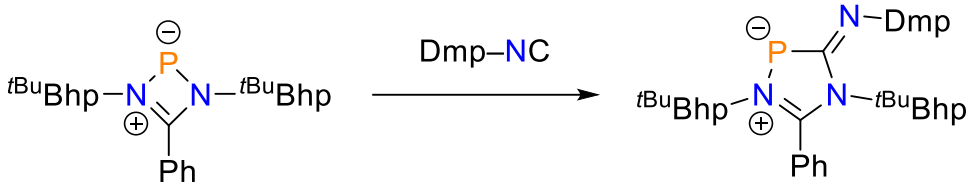


Figure 18. Molecular structure of **12** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Bhp and the phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N2–P1 = 1.784(2), P1–O1 = 1.463(2), P1–O2 = 1.468(2), P1–N1 = 1.777(1), N1–C73 = 1.345(2), C73–N2 = 1.345(2), N2–P1–O1 = 111.16(8), N2–P1–O2 = 112.07(8), N2–P1–N1 = 72.74(6), O1–P1–N1 = 112.25(8), O2–P1–N1 = 110.78(8), P1–N1–C73 = 92.1(1), N1–C73–N2 = 103.4(1), C73–N2–P1 = 91.8(1), N2–P1–N1–C73 = 0.5(1).

3.2.4 Insertion reactions

Reactions of the symmetric biradical [Ter–NP]$_2$ with a variety of small molecules like isonitriles[28,61,117–119] or CO[59] resulted in the insertion of the respective compounds into the four-membered ring system and their extension to five-membered cycles. Meanwhile, CS_2 reacted in a cycloaddition to form a bicyclic compound with a CS bridging unit between the two phosphorus atoms (cf. Chapter 2.3).[56] For the first experiment, the isonitrile

Dmp–NC was chosen, due to its relatively small bulkiness and concurrent volatility, which facilitates the workup (Scheme 26).



6 **13**

Scheme 26. Reaction of **6** with Dmp–NC.

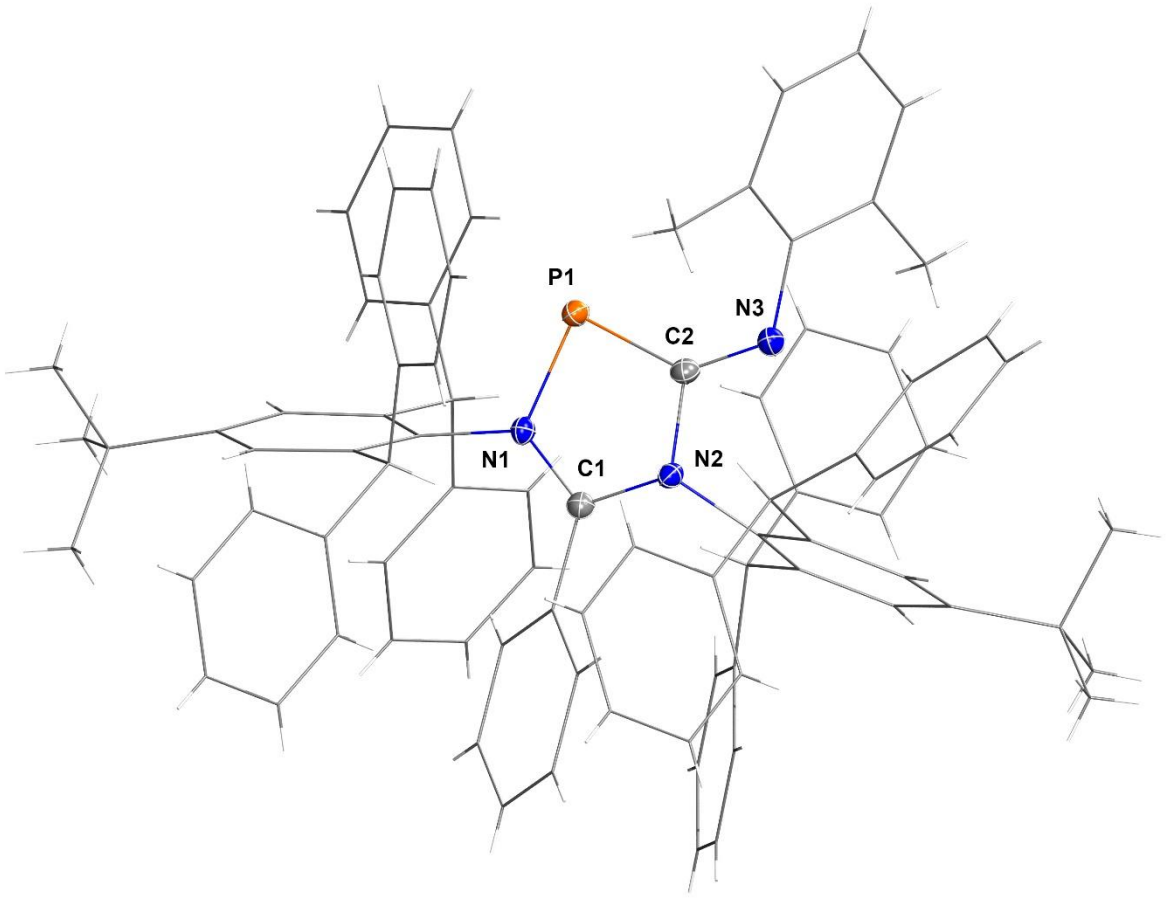


Figure 19. Molecular structure of **13** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Bhp and the phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N1–P1 = 1.770(2), P1–C2 = 1.773(2), C2–N3 = 1.287(2), C2–N2 = 1.443(2), N2–C1 = 1.359(2), C1–N1 = 1.330(2), N1–P1–C2 = 88.29(8), P1–C2–N3 = 134.9(1), P1–C2–N2 = 109.1(1), N3–C2–N2 = 116.0(2), C2–N2–C1 = 115.0(1), N2–C1–N1 = 112.0(2), C1–N1–P1 = 115.7(1), N1–P1–C2–N3 = 176.3(2), N1–P1–C2–N2 = –1.1(1), C1–N2–C2–P1 = 1.3(2), C1–N2–C2–N3 = –176.7(2), C2–N2–C1–N1 = –0.7(2), P1–N1–C1–N2 = –0.1(2).

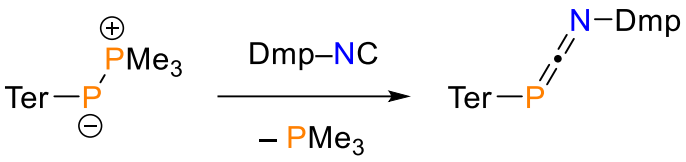
Upon combination of the reagents, the mixture instantly turned to an intense red color (λ_{max} = 508 nm) and the ^{31}P NMR spectrum indicated a selective reaction within 1 h, affording a new high-field shifted singlet at +152.9 (cf. +407.9 ppm for **6**).

Single crystals grown via slow evaporation of a saturated solution of **13** in diethyl ether reveal an analogous insertion of the isonitrile into an N–P bond, resulting in a novel planar five-membered ring system (Figure 19). The central motif can be described as a skewed pentagon with equal N1–P1 (1.770(2) Å) and P1–C2 (1.773(2) Å) bond lengths and an NCN unit, which is structurally similar to free **6**. WIBERG bond indices reveal double bond character in the isonitrile unit (BO (C2–N3) = 1.54), delocalization in the amidine NCN unit (BO (N1–C1) = 1.30, BO (C1–N2) = 1.20) and a minor double bond character between P1 and C2 (BO (P1–C2) = 1.13). Natural charges for all nitrogen atoms were found to be negative (N1 = –0.55 *e*, N2 = –0.36 *e*, N3 = –0.53 *e*), while the positive charge at P1 slightly decreases (+0.47 *e*), compared to **6**. The most important contributions from lone pair interactions with antibonding orbitals (negative hyperconjugation) can be found in Table 7.

Table 7. Summary of second order perturbation analysis for **13** (negative hyperconjugation).

Donor/acceptor	Energy / kJ/mol
LP (P1) → π* (N1–C1)	96.2
LP (P1) → π* (C2–N3)	165.1
LP (N2) → π* (N1–C1)	260.4
LP (N2) → π* (C2–N3)	119.7
LP (N3) → σ* (P1–C2)	67.9

At a first glance, the reactivity of **6** towards isonitriles differs from traditional phosphinidene sources, which yield phosphaazaallenes in a 1,1-addition (Scheme 27),[46,120–122] as the interaction of C2 with both P1 and N2 in **13** outweighs a single coordination to the phosphorus atom. Nevertheless, the P–C double bond character in **13** indicates similarity between these reactions.



Scheme 27. Reaction of a phospha-WITTIG reagent with an isonitrile.[122]

Due to the planarity of the heterocycle, it was of interest to investigate biradical properties of **13**. Therefore, a CASSCF(8,6)/def2-TZVP calculation was run on a model system, yielding a LUNO occupancy of 0.07 and a LUNO+1 occupancy of 0.06. Figure 20 shows the most important LEWIS structures incorporating π-type MOs in the localized depiction, with the largest-weighted resonance again including a negative charge and two lone pairs at the phosphorus atom, as well as a positive charge at the adjacent nitrogen atom. A heterocyclopentane-1,3-diyl-type resonance only contributes about 4 %.

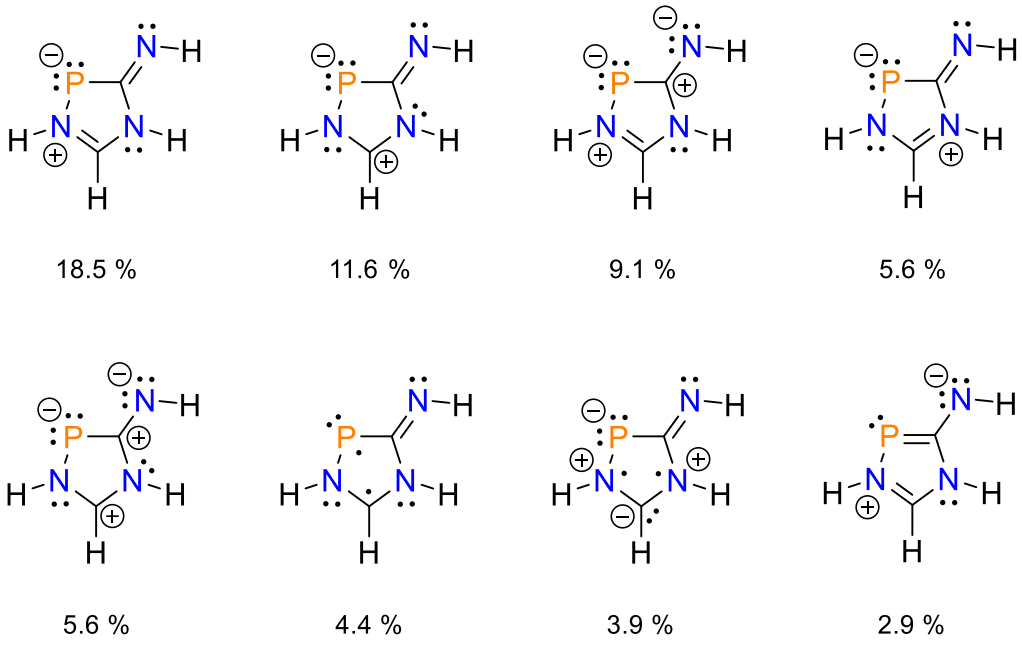


Figure 20. Most important Lewis structures (considering π-type MOs) for the model compound of **13**.

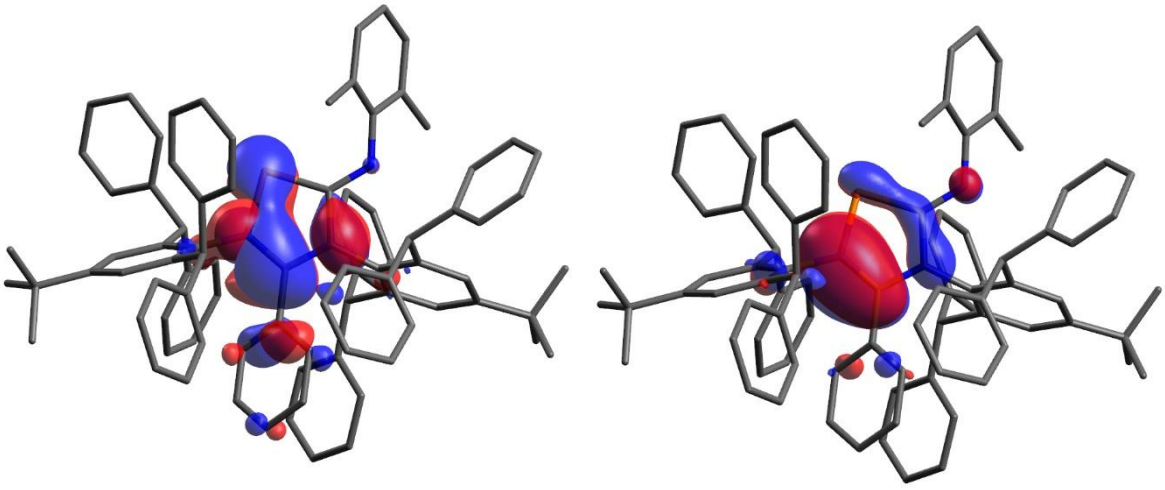
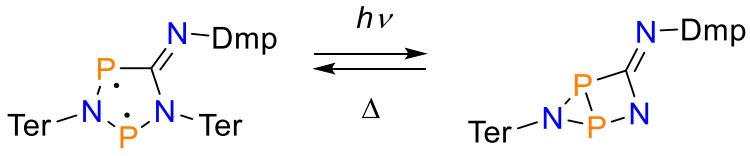


Figure 21. LUNO (left) and HONO (right) of **13** (hydrogens omitted for clarity).

A CASSCF(2,2)/def2-TZVP calculation of **13** afforded a LUNO occupancy of 0.05, while the LUNO depiction (Figure 21) shows a transannular bonding situation (between P1 and C1), as known from the [Ter–NP]$_2$ analog.

The HONO features delocalization among P1–C2–N2 and N1–C1. The combined theoretical investigations again show only negligible biradical character and no changes compared to **6**.

Upon irradiation with visible light, the similar insertion product of [Ter–NP]$_2$ undergoes a reversible bond formation to a housane species (Scheme 28), even in the solid-state.[28,119]



Scheme 28. Photochemical reaction between the heterocyclopentane-1,3-diyl derivative and the corresponding housane.

The formed housane isomerizes to the diyl starting material in a thermal reverse reaction, thus low temperatures are required for spectroscopic investigations. To test the applicability of this concept to **13**, a solution in THF-d$_8$ was cooled to the lowest achievable temperature of the NMR spectrometer and irradiated with diodes, emitting visible light of wavelengths that correspond to the absorption maximum.

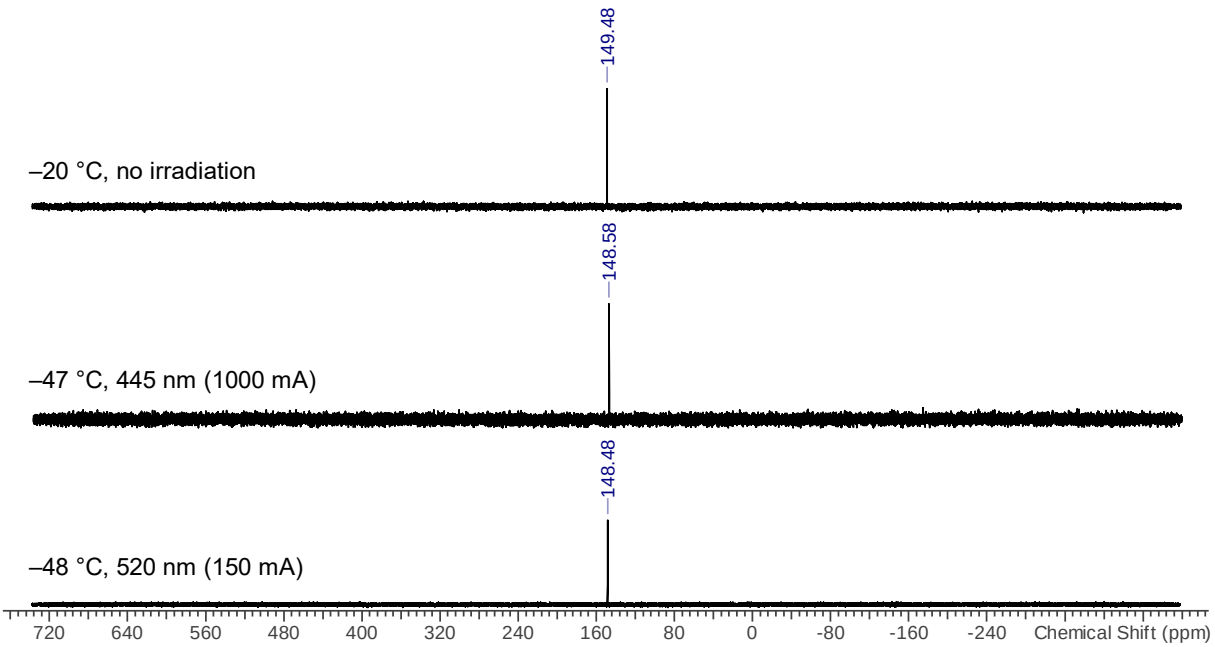
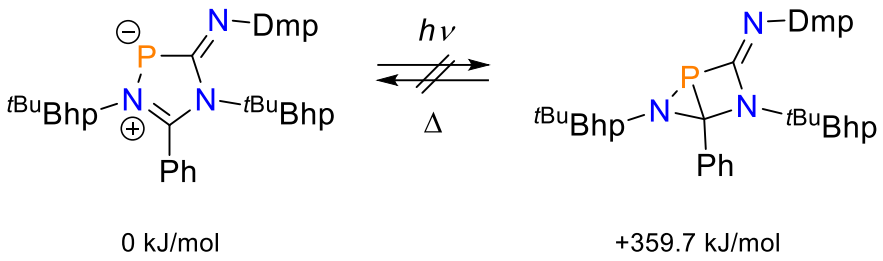


Figure 22. $^{31}P\{^1H\}$ NMR spectra of **13** at different temperatures and irradiation conditions.



Scheme 29. Proposed, but unobserved equilibrium between **13** and its housane isomer and relative free GIBBS energies (PBE-D3/def2-TZVP).

However, no changes were observed in the ^{1}H or ^{31}P NMR spectra (Figure 22). Additional calculations of the free GIBBS energies for the proposed bond formation (Scheme 29) indicate an insufficient excitation. Since a wavelength of 445 nm corresponds to a photon energy of approximately 268.8 kJ/mol, almost 100 kJ/mol less than necessary, the photochemical reaction will likely not be initiated. Other possible factors influencing an observable photochemical reaction are the kinetics of the thermal reverse reaction and the quantum yield.

The transannular bond formation would result in a highly strained bicyclic molecule with a hitherto unknown core motif (Figure 23). Literature examples for the three-membered azaphosphiridine subgroup are scarce, underlining the unlikelihood of this transformation.[123,124] To initiate a photochemical reaction, ultraviolet light (circa 333 nm) would be required. This high amount of energy could also lead to side reactions in some solvent systems or decomposition of **13**.

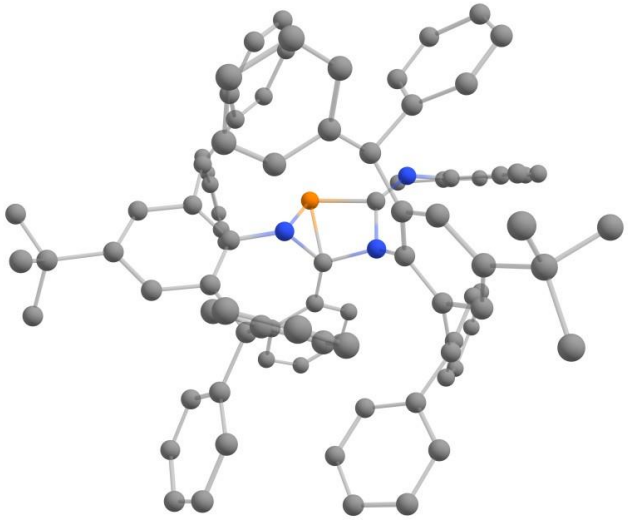
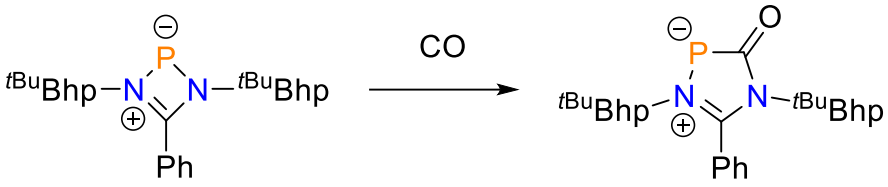


Figure 23. Energetically optimized structure (PBE-D3/def2-TZVP) of the housane isomer of **13** (hydrogens omitted for clarity).

Realizing the ability of **6** to insert a CN–R unit in an N–P bond, a reaction with the isolobal CO was carried out. Therefore, CO (1 bar) was bubbled through an orange solution of **6** in benzene and after 5 min, the color changed to (and remained) yellow (Scheme 30). To ensure full conversion, the mixture was left stirring overnight and analyzed the next day. A ^{31}P NMR spectrum revealed the selective formation of a single product (+132.7 ppm).



6 **14**

Scheme 30. Reaction of **6** with carbon monoxide.

While crystallization attempts in a variety of solvents (DME, Et_2O, PhF, THF) only resulted in thin, intergrown needles of **14**, a single block-shaped crystal could eventually be isolated from a slowly evaporating toluene solution.

Bond parameters of the molecular structure (Figure 24) are practically identical to **13** (Figure 19), with a C80A–O1A distance (1.225(8) Å) equal to the sum of covalent radii for a double bond (1.24 Å).[86]

Due to the near-planarity of the five-membered core, CASSCF(8,6)/def2-TZVP calculations of a model system were carried out, which gave a LUNO occupancy of 0.07 and a LUNO+1 occupancy of 0.05 and comparable LEWIS structures (cf. Figure 20) incorporating π-type MOs in the localized depiction (Figure 25).

A CASSCF(2,2)/def2-TZVP calculation of **14** gave a LUNO occupancy of 0.05, while the LUNO and HONO depictions (Figure 26) are basically identical to the isonitrile insertion product **13** (cf. Figure 21).

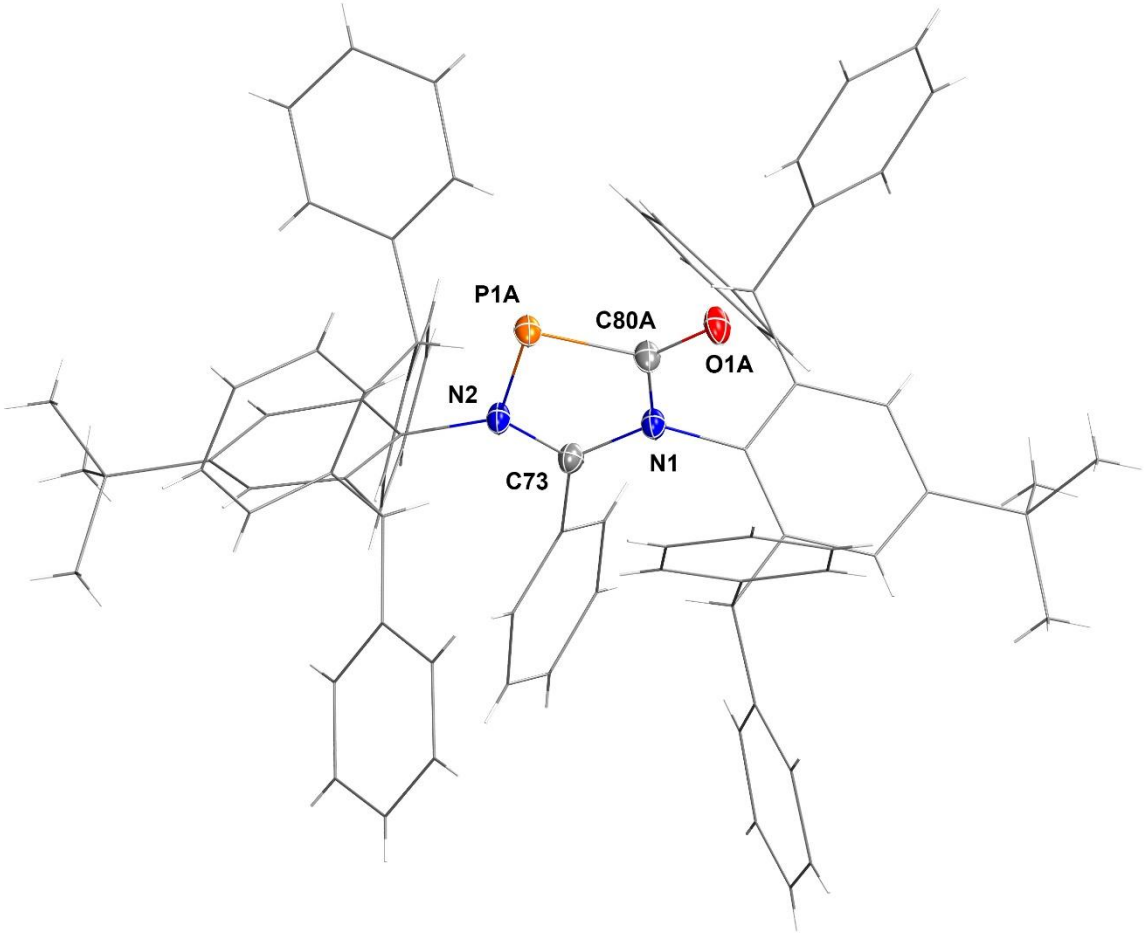


Figure 24. Molecular structure of **14** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Bhp and the phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): P1A–C80A = 1.78(1), C80A–O1A = 1.225(8), C80A–N1 = 1.441(4), N1–C73 = 1.348(2), C73–N2 = 1.345(2), N2–P1A = 1.763(2), N2–P1A–C80A = 88.0(2), P1A–C80A–O1A = 129.5(5), P1A–C80A–N1 = 109.0(4), O1A–C80A–N1 = 121.6(5), C80A–N1–C73 = 115.0(3), N1–C73–N2 = 111.7(1), C73–N2–P1A = 116.0(1), N2–P1A–C80A–O1A = –175.4(8), N2–P1A–C80A–N1 = 5.9(5), P1A–C80A–N1–C73 = –6.4(6), C80A–N1–C73–N2 = 3.0(4), O1A–C80A–N1–C73 = 174.8(5), P1A–N2–C73–N1 = 2.0(2), C80A–P1A–N2–C73 = –4.9(3).

Analogously to the isonitrile reaction (Scheme 28), a photochemical housane formation can be observed for the terphenyl-substituted heterocyclopentane-1,3-diyl (Scheme 31).

In the case of **14**, the absorption maximum of the yellow compound would be approximately 420 to 430 nm, close to the wavelength (445 nm) of the diode used for irradiation experiments. The relative free GIBBS energy for the corresponding housane isomer of **14** exhibits a smaller difference (+194.9 kJ/mol) than for the isonitrile derivative (Scheme 29).

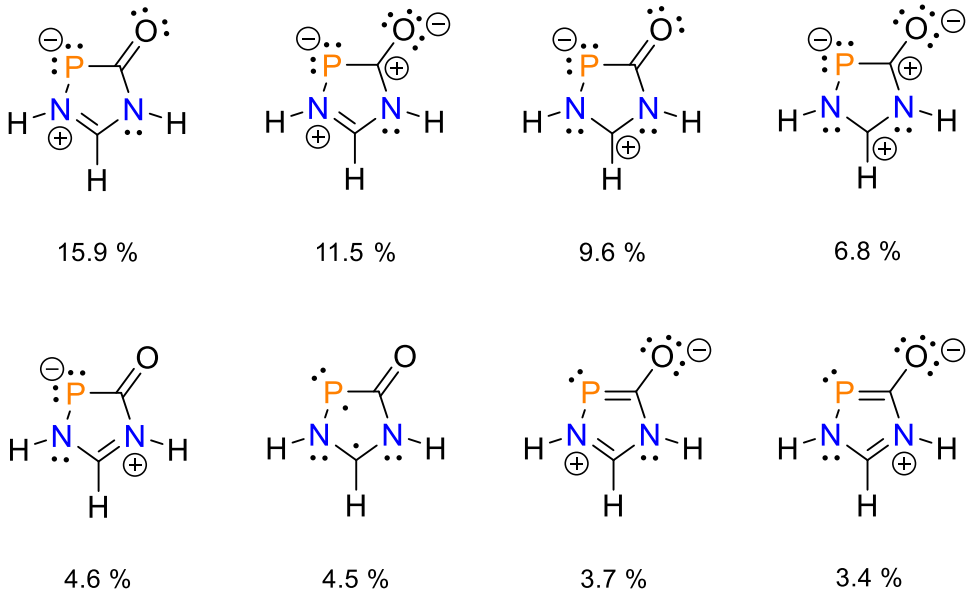


Figure 25. Most important Lewis structures (considering π-type MOs) for the model compound of **14**.

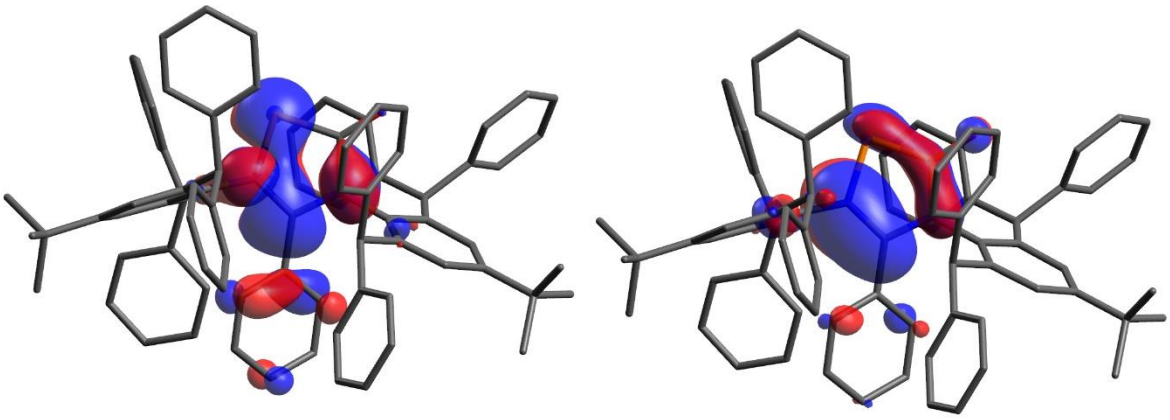
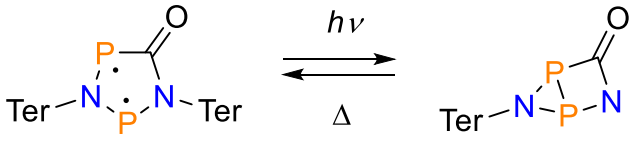


Figure 26. LUNO (left) and HONO (right) of **14** (hydrogens omitted for clarity).



Scheme 31. Photochemical reaction between the heterocyclopentane-1,3-diyl derivative and the corresponding housane and the relative free GIBBS energies.

Thus, formation of the strained isomer (Figure 27) seems possible, as the excitation energy (268.8 kJ/mol) is high enough. However, this was not tested during the course of this work anymore.

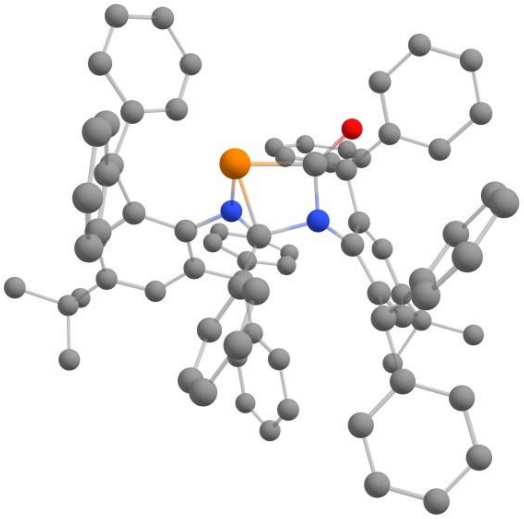
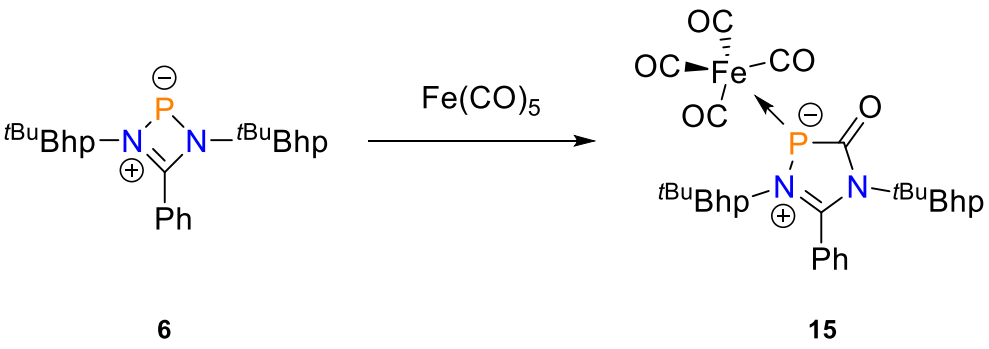


Figure 27. Energetically optimized structure (PBE-D3/def2-TZVP) of the housane isomer of **14** (hydrogens omitted for clarity).

In an effort to characterize the electron donating or accepting properties of **6**, the heterocycle was treated with iron pentacarbonyl. While this complex is known to also act as CO donor (under formation of diiron nonacarbonyl),[125] the primary goal was an iron complex with **6** acting as a ligand. Addition of a slight excess of $Fe(CO)_5$ to a solution of **6** in THF resulted in a color change to dark red and selective formation of a single species in the ^{31}P NMR spectrum (+171.7 ppm). This low-field chemical shift, compared to **14** (+132.7 ppm), can be explained by iron coordination and concomitant electronic deshielding of the phosphorus atom.

After workup, single crystals could be obtained from a saturated solution in diethyl ether. Interestingly, the molecular structure shows not only coordination to an iron center via the phosphorus atom, but also the previously observed CO insertion into an N–P bond (Scheme 32).



6 **15**

Scheme 32. Reaction of **6** with iron pentacarbonyl.

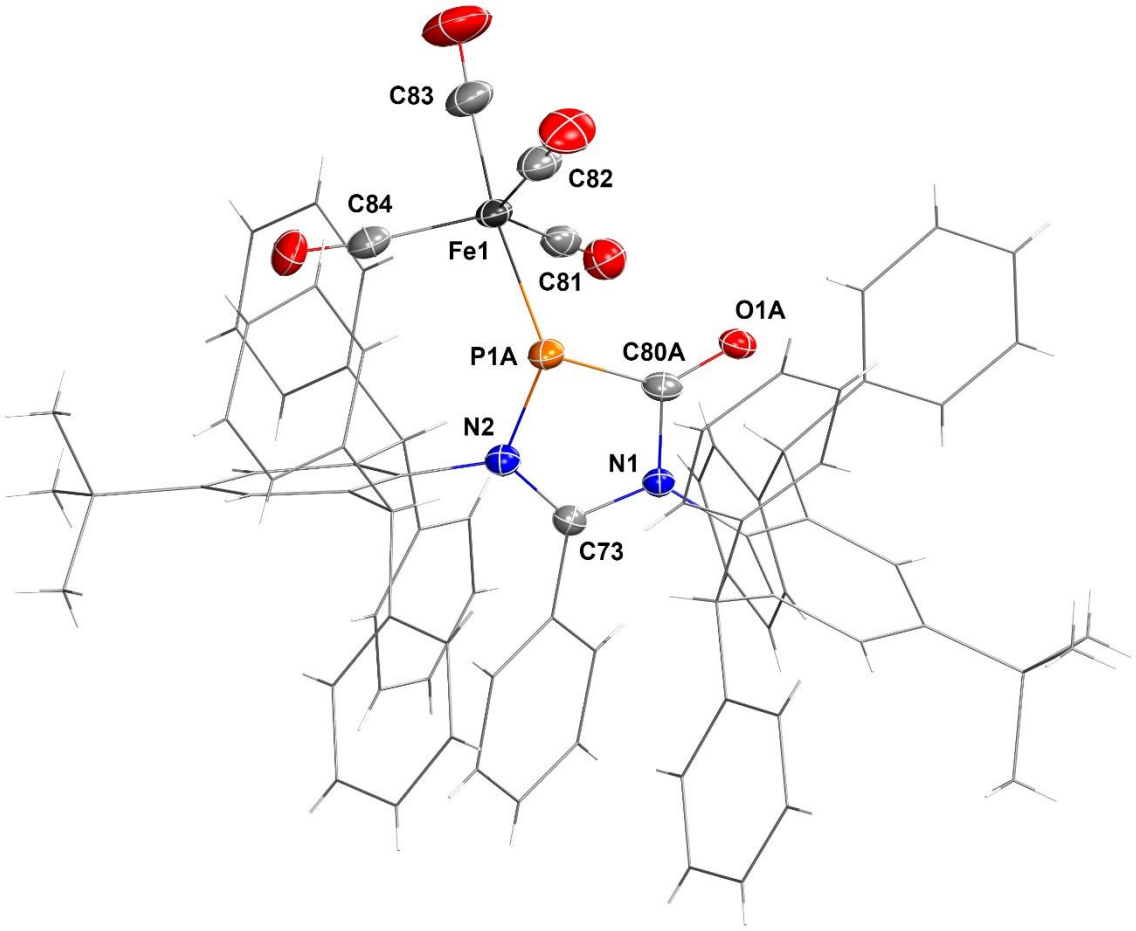


Figure 28. Molecular structure of **15** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Bhp and the phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): Fe1–C81 = 1.785(4), Fe1–C82 = 1.797(4), Fe1–C83 = 1.782(4), Fe1–C84 = 1.817(4), P1A–Fe1 = 2.2340(9), P1A–C80A = 1.796(4), C80A–O1A = 1.219(5), C80A–N1 = 1.441(4), N1–C73 = 1.358(3), C73–N2 = 1.331(3), N2–P1A = 1.775(2), N2–P1A–C80A = 87.7(2), P1A–C80A–O1A = 130.2(3), P1A–C80A–N1 = 108.8(3), O1A–C80A–N1 = 120.7(3), C80A–N1–C73 = 114.2(2), N1–C73–N2 = 113.1(2), C73–N2–P1A = 114.8(2), N2–P1A–C80A–O1A = 176.2(5), N2–P1A–C80A–N1 = –9.7(3), P1A–C80A–N1–C73 = 7.9(4), C80A–N1–C73–N2 = –0.3(3), O1A–C80A–N1–C73 = –177.3(3), P1A–N2–C73–N1 = –7.9(3), C80A–P1A–N2–C73 = 10.4(2).

The single crystal contained disordered layers, with circa 69 % of the novel five-membered cycle coordinated to iron (Figure 28) and 31 % being non-coordinating. Still, other analytical data matches solely the iron complex. The geometric parameters of the five-membered heterocycle are almost identical to the CO insertion product **14**, while the bond length between C80A and O1A is slightly shortened (1.219(5) Å), compared to the sum of covalent radii for a C–O double bond (1.24 Å).[86] Literature reports on comparable iron carbonyl complexes are limited and often discuss cluster-like structures.[126–130] While the Fe–C bond lengths of the three equatorial carbonyl ligands remain constant within three times the standard deviation,

compared to free $Fe(CO)_5$, the axial Fe1–C83 bond is shortened (1.811(2) Å → 1.782(4) Å).[131] The ATR IR spectrum of **15** showed several vibrations in the typical range of C–O stretching modes (around 2000 cm^{-1}), with the highest wavenumber assigned to the axial ligand (2042 cm^{-1}). This signifies a blue-shift, compared to $Fe(CO)_5$ (2009 cm^{-1}), concurrent with the observed reduced bond length.[132,133]

The last investigated reaction was the reaction of **6** with carbon disulfide. In a preceding test on NMR scale, two species could be identified in the $^{31}P\{^1H\}$ NMR spectrum (Figure 29).

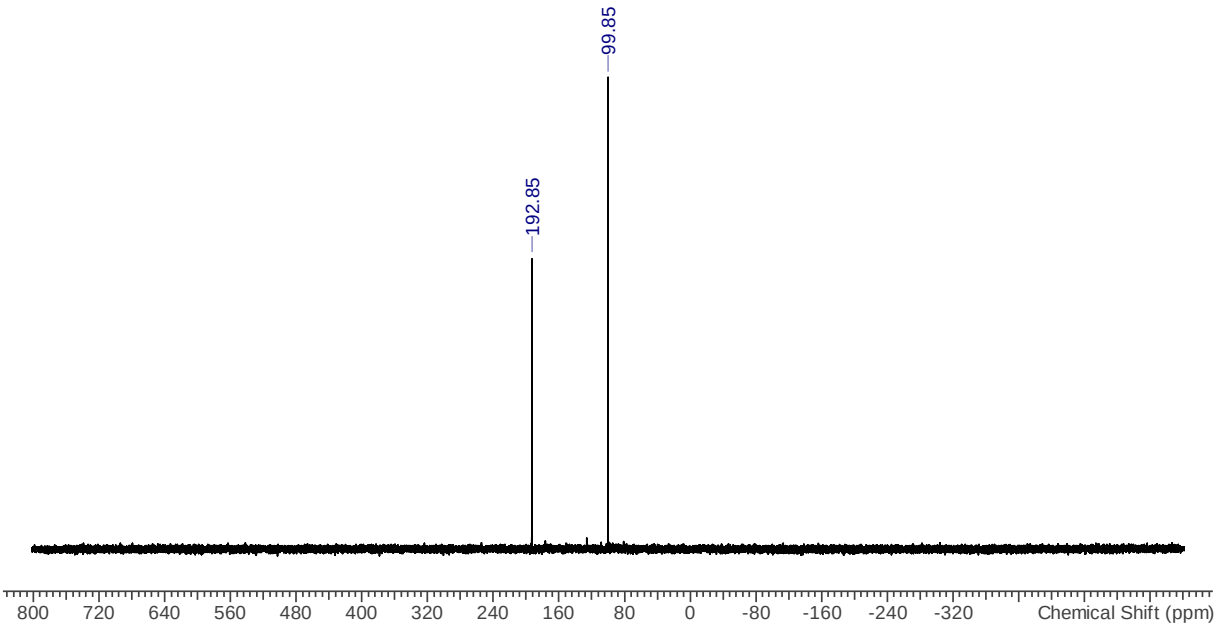


Figure 29. $^{31}P\{^1H\}$ NMR spectrum of the reaction of **6** with CS_2 (excess).

Dark red single crystals could be grown from a saturated solution in diethyl ether. Unfortunately, due to a moderately diffracting crystal and several disordered layers, the data was not sufficient enough for a full data refinement and thus, only a .res file was generated. With regard to the molecular structure (Figure 30), only the connectivity can be discussed. Data processing revealed a disorder at P1, with either one (**16**) or two sulfur atoms (**17**) attached. In both cases, a CS unit (isolobal to CN–R and CO) is inserted into the four-membered ring system and the adjacent phosphorus is oxidized by remaining sulfur. This is in contrast to the biradical $[Ter–NP]_2$,[56] which reacts in an additive manner, resulting in a cage compound (cf. Chapter 2.3).

Since addition of an excess of CS_2 still only yielded a product mixture (Scheme 33), it was of interest to generate the monosubstituted product **16** with one equivalent of CS_2. Therefore, the

reaction was retried with a stoichiometric amount of CS_2 in a dilute solution at –80 °C. At first, the solution remained at its intermediate dark green color, but eventually changed to dark red. Unfortunately, both species (**16**/**17**) were still present, with only minor differences in the product ratio.

An NRT analysis of a model compound of **16** afforded a wide range of resonance structures (Figure 31). Interestingly, there is no concise LEWIS structure, as the eight largest-weighted resonances only differ by a few percent. Additionally, several open-chain resonances contribute to a great extent, with the second most important resonance featuring a terminal P=S unit. Due to the elusiveness of the stoichiometric product **16**, a directed synthesis of the fully oxidized species **17** was retried.

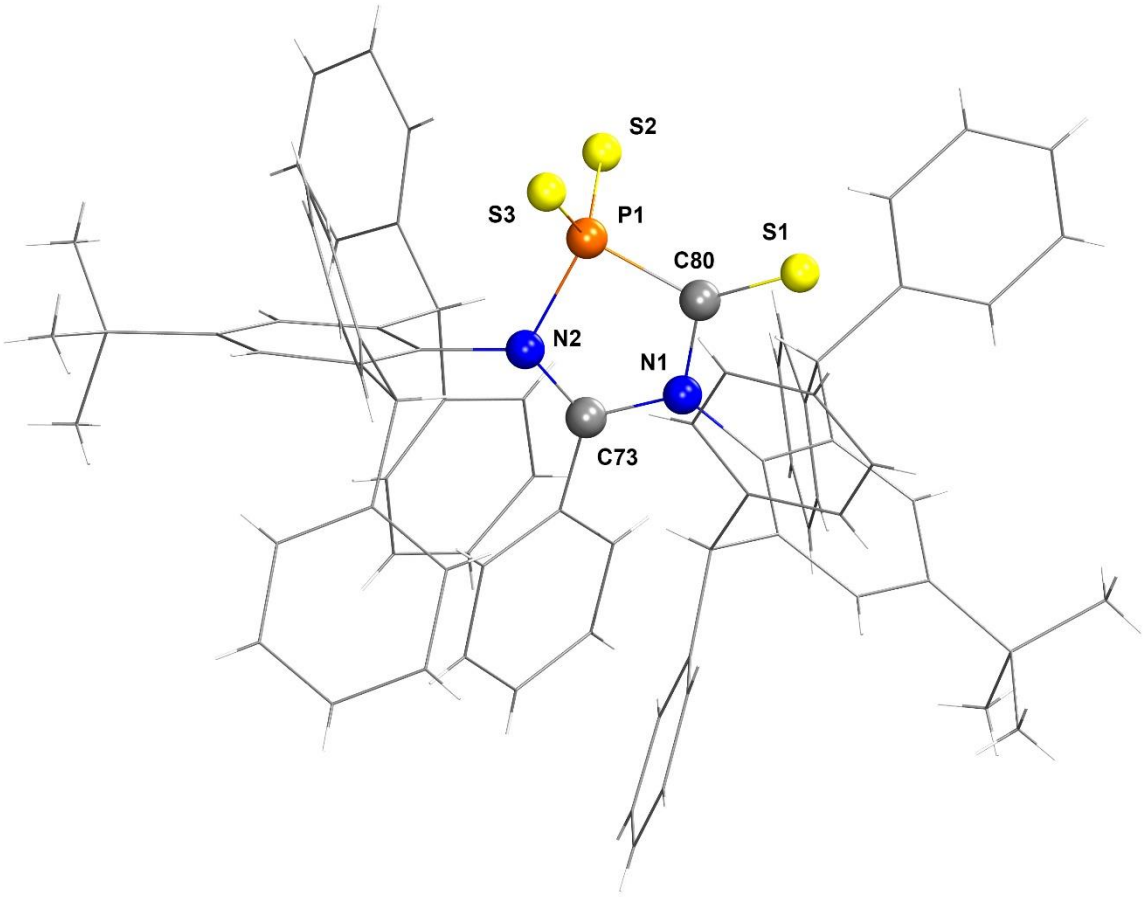
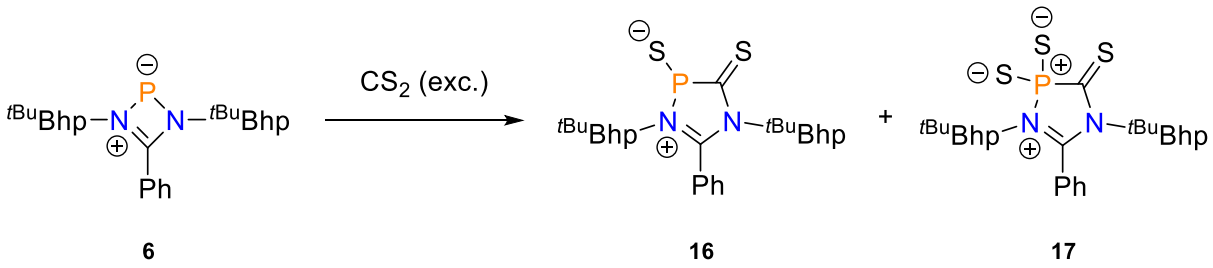


Figure 30. Molecular structure of **16**/**17** in the single crystal. Due to poor data, only a partially refined structure is presented and no bond parameters can be discussed.

Hence, **6** was again reacted with an excess of CS_2 and in a second reaction step, a slight excess of elemental sulfur was added (Scheme 34).



Scheme 33. Reaction of **6** with an excess of CS_2.

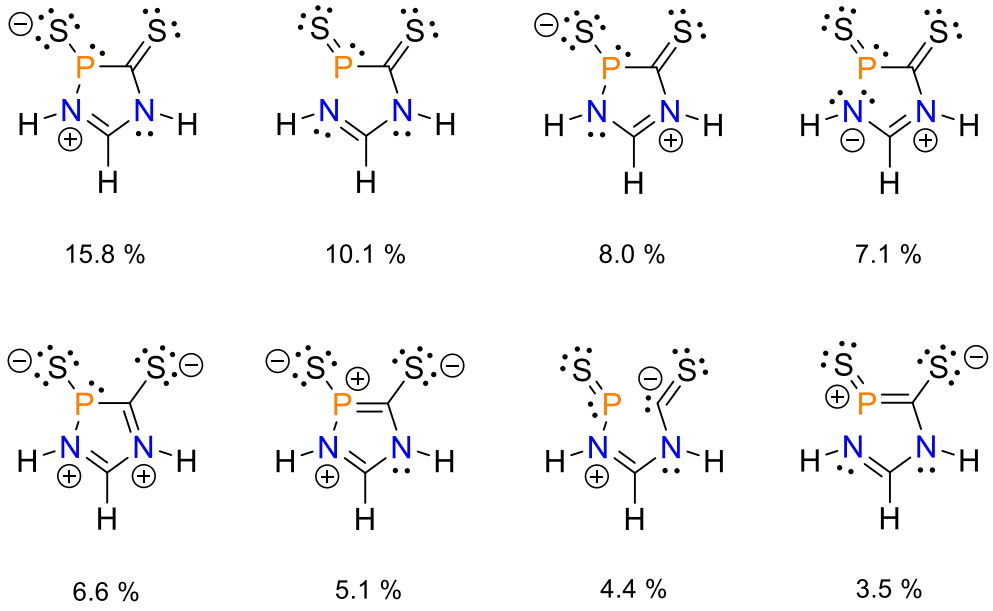
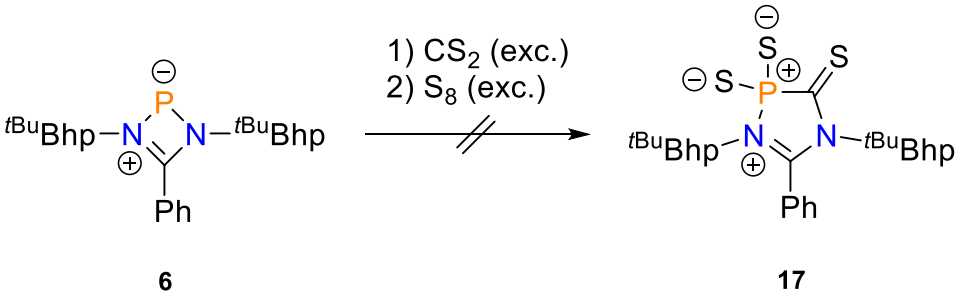


Figure 31. NRT largest-weighted resonance structures of **16**.



Scheme 34. Attempted sequential reaction of **6** with an excess of CS_2 and sulfur.

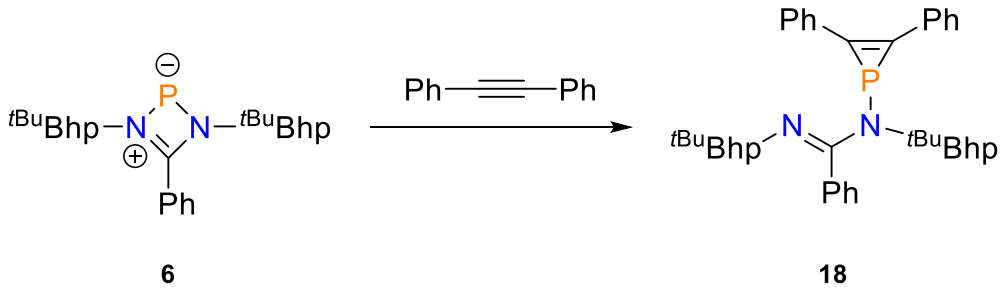
This, however, did not lead to exclusive formation of **17**, but instead two additional signals were present in the ^{31}P NMR spectrum (+125.2 ppm and +294.4 ppm), the latter being assigned to **10a**. Therefore, it seems likely that partial CS elimination occurs via reaction with additional sulfur.

3.2.5 Addition reactions

The symmetric biradical [Ter–NP]$_2$ reacts with alkenes and alkynes in cycloadditions, affording [2.1.1] cage products. In this regard, the reaction with alkynes stands out, due to slow isomerization in solution, yielding azadiphosphiridines (cf. Chapter 2.3).

Based on previous theoretical and experimental observations, a similar behavior was not expected for **6**, since reactions exclusively took place at the phosphorus atom and not within the amidine backbone.

In a first experiment, **6** was reacted with tolane (diphenylacetylene), resulting in selective formation of a single species (δ (^{31}P) = –96.4 ppm), a typical chemical shift for three-membered phosphorus heterocycles (Scheme 35).



6 **18**

Scheme 35. Reaction of **6** with tolane.

Single crystals grown from a saturated solution in diethyl ether verified this assumption (Figure 32). **18** shows similarities to the chlorinated compound **5**, although the P1–N2–C1–N1 dihedral angle diverges more from a planar core (–19.1(1)°) and the P1–N1 distance is significantly increased (2.6174(9) Å), possibly owed to PAULI repulsion. P–C bond lengths within the phosphirene subgroup are shortened (1.803(1) Å and 1.807(1) Å) compared to the sum of covalent radii (1.86 Å), while the C80–C87 bond (1.324(2) Å) is in the typical range of a double bond (1.34 Å).[86]

The formation of phosphirenes can be explained by the phosphinidene-type behavior (hence a masked *N*-heterocyclic phosphinidene) of **6** (cf. Chapter 2.2), resulting in the addition of unsaturated hydrocarbons. While the in-situ generation of highly reactive phosphinidenes often involved coordinating transition metals,[42,43,134] progress in recent years has focused on main-group transfer reagents, facilitating applications.[44–46] However, in most cases elevated reaction temperatures or prolonged reaction times are required to enable the transient formation of

phosphinidenes for subsequent additions to alkenes or alkynes. In this regard, the inherent reactivity of the heterocycle **6** allows for a selective and full conversion at room temperature within minutes.

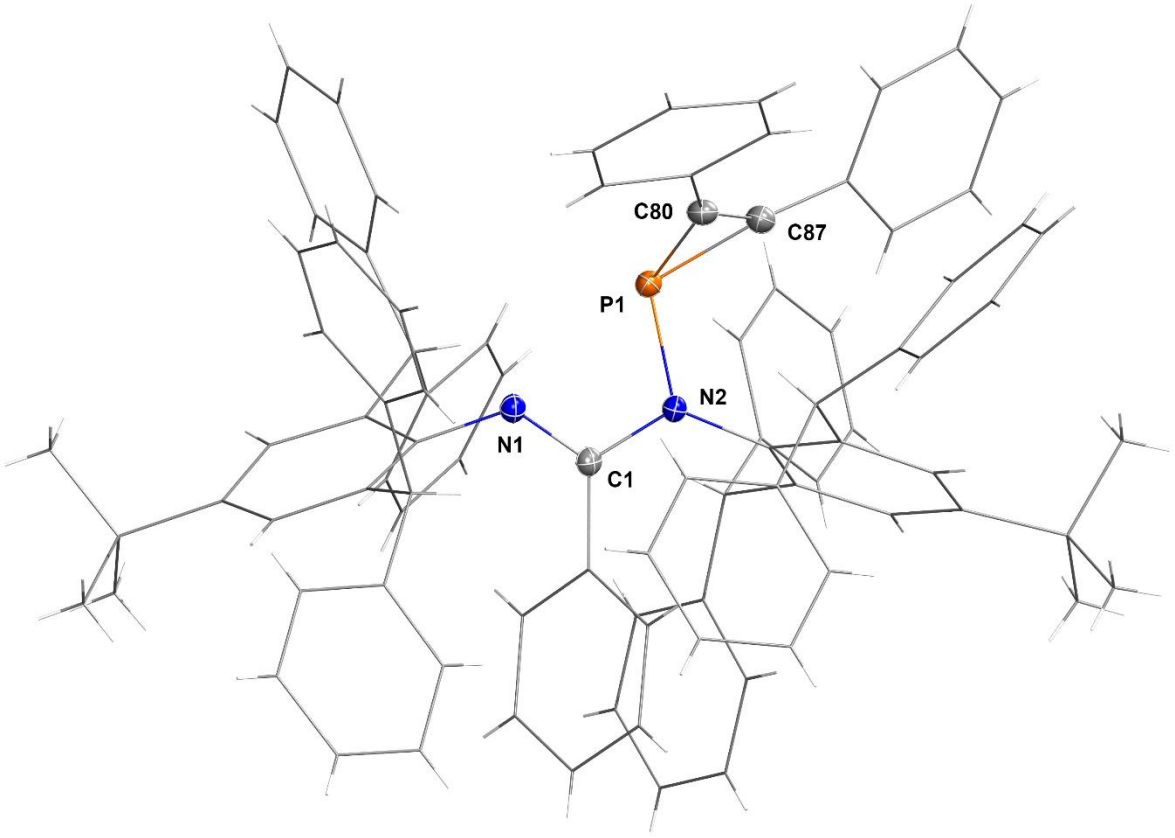
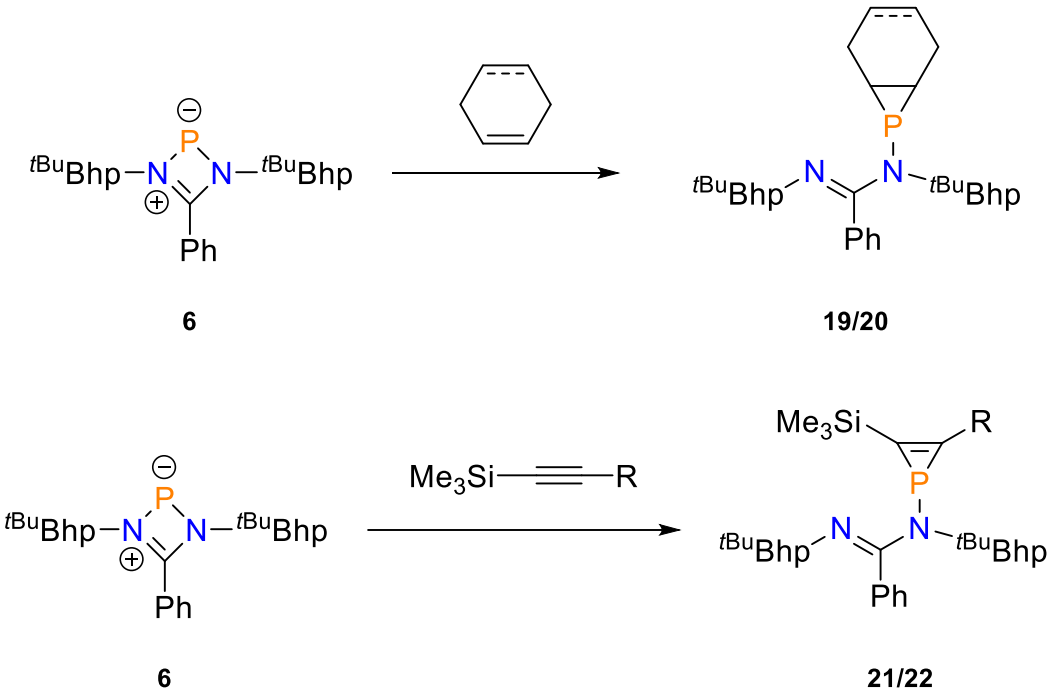


Figure 32. Molecular structure of **18** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Bhp and the phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N1–C1 = 1.292(1), C1–N2 = 1.392(1), N2–P1 = 1.8009(9), P1–C80 = 1.803(1), P1–C87 = 1.807(1), C80–C87 = 1.324(2), N1–C1–N2 = 113.63(9), C1–N2–P1 = 109.9(7), C80–P1–C87 = 43.03(5), C87–C80–P1 = 68.64(7), C80–C87–P1 = 68.33(7), P1–N2–C1–N1 = –19.1(1).

In order to test the versatility of the phosphinidene-type reactivity, further alkynes and also alkenes were reacted with **6** in a similar manner (Scheme 36). In all cases, the starting material was selectively converted to phosphirenes and phosphiranes, respectively, with chemical shifts (^{31}P NMR) varying between –90 and –120 ppm (Figure 33). While all unsaturated derivatives reacted within minutes (evident from immediate discoloration of the reaction mixture), the reaction with BTMSA changed its color significantly slower and was thus stirred overnight to ensure completion.



Scheme 36. Reaction of **6** with cyclohexene (**19**), 1,4-cyclohexadiene (**20**), BTMSA (R = $SiMe_3$, **21**) and TMSA (R = H, **22**).

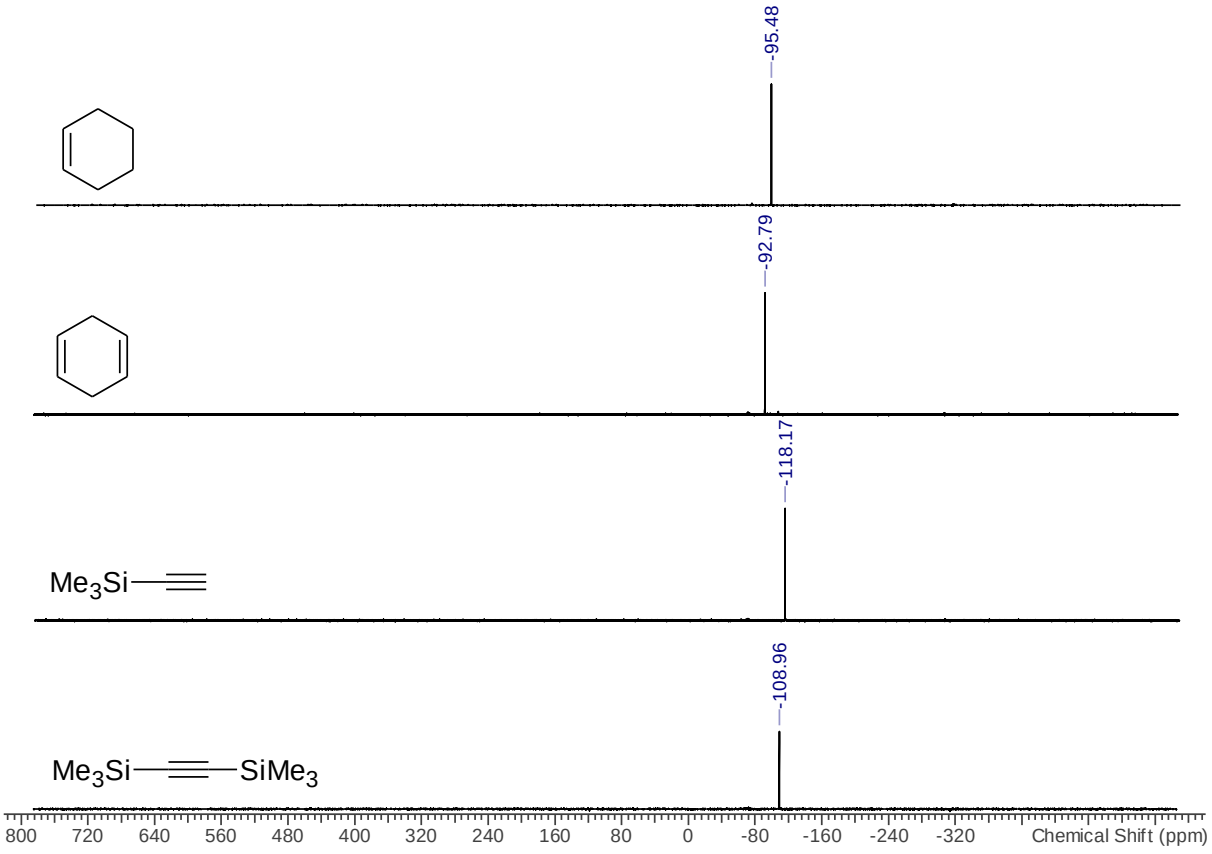
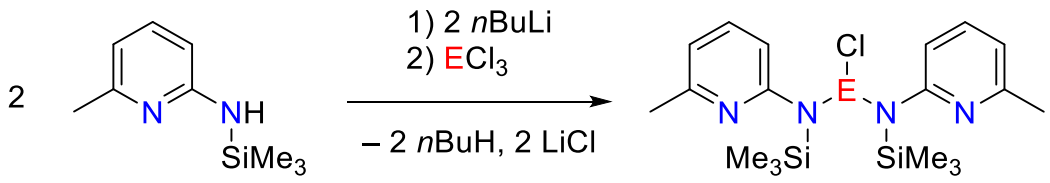


Figure 33. $^{31}P\{^{1}H\}$ NMR spectra of the reaction of **6** with different alkenes (**19**/**20**) and alkynes (**21**/**22**).

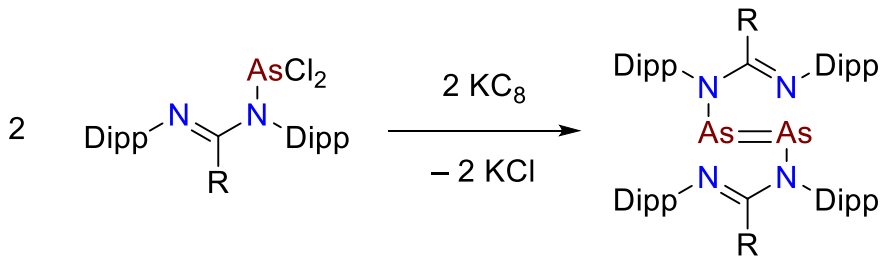
A reaction with (*E*)-stilbene, the *trans*-configured alkene analog of tolane, also led to no immediate conversion. This signifies the bulk of **6** and its impassivity towards sterically protected reaction centers. Furthermore, a reaction with 1,4-cyclohexadiene did not lead to a two-fold phosphirane formation, but instead only one double bond is attacked. A similar double substitution could neither be observed for the sterically less hindered biradical [Ter–NP]$_2$ and its reaction with conjugated dienes of various chain lengths.[135]

3.3 Synthesis of heavier dichloropnictogenamidinates

Literature-known reactions of amidines or guanidines with heavier pnictogen reagents to form compounds similar to the phosphorus derivative **5** (cf. Chapter 3.1) occasionally led to double or triple ligand complexes, especially for antimony and bismuth (Scheme 37).[136–139] In this regard, JONES et al. reported on the synthesis of P, As and Sb derivatives of Dipp-based amidines and guanidines and attempted reductions.[74] The successful isolation of a diarsene (Scheme 38) and the aforementioned steric influences created interest in the synthesis of heavier pnictogen congeners of **5**.



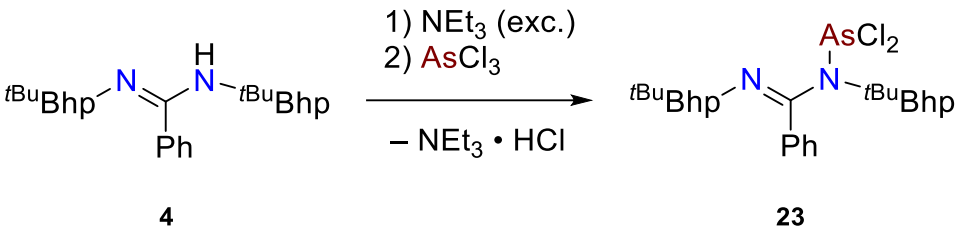
Scheme 37. Formation of monochloropnictogendiamidinates (E = Sb, Bi).[137]



Scheme 38. Formation of a diarsene (R = N(Cy)$_2$, N(*i*Pr)$_2$, *t*Bu).[74]

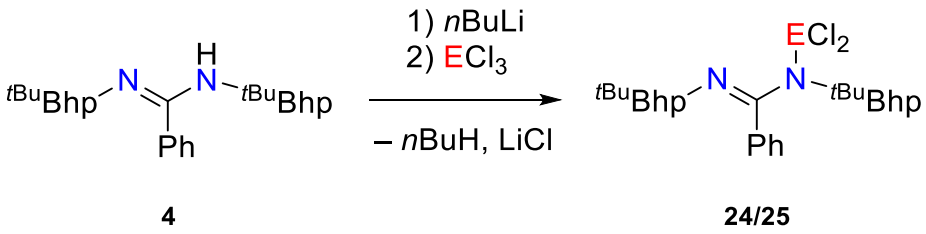
Reaction parameters for the three pnictogen trichlorides had to be adjusted in order to minimize the amount of byproducts and ensure almost quantitative conversion. While the Sb and Bi derivatives **24** and **25** were prepared in a stepwise reaction with *n*BuLi and THF solutions of

$SbCl_3$ and $BiCl_3$ (Scheme 40), the As derivative **23** was prepared via consecutive addition of an excess of NEt_3 and $AsCl_3$ (Scheme 39). This is owed to impurities in $AsCl_3$, which had to be synthesized (due to extremely limited commercial availability) and distilled twice to ensure only small amounts of acidic contaminants. For bismuth, the reaction time was extended to two days, concurrent with literature reports of comparable syntheses, and a gradual darkening of the reaction mixture indicated partial precipitation of elemental bismuth.[139]



4 **23**

Scheme 39. Reaction of **4** with arsenic trichloride.



4 **24/25**

Scheme 40. Reaction of **4** with pnictogen trichlorides to form the antimony (E = Sb, **24**) and bismuth (E = Bi, **25**) derivatives.

While the antimony derivative **24** was formed in sufficient purity, the arsenic and bismuth derivatives **23** and **25** had to be washed with small amounts of diethyl ether. Therefore, yields differ significantly and vary between 20 % (**25**) and 50–60 % (**23**/**24**).

Single crystals of **24** and **25** could be obtained from saturated diethyl ether solutions, while crystals of **23** were obtained from dichloromethane. While the arsenic and antimony derivatives are colorless solids (akin to the pale yellow phosphorus derivative **5**), the bismuth compound exhibits a canary-yellow color. Comparisons of the solid-state molecular structures (Figure 34 to 36) show very similar structural motifs and geometric parameters of the central core.

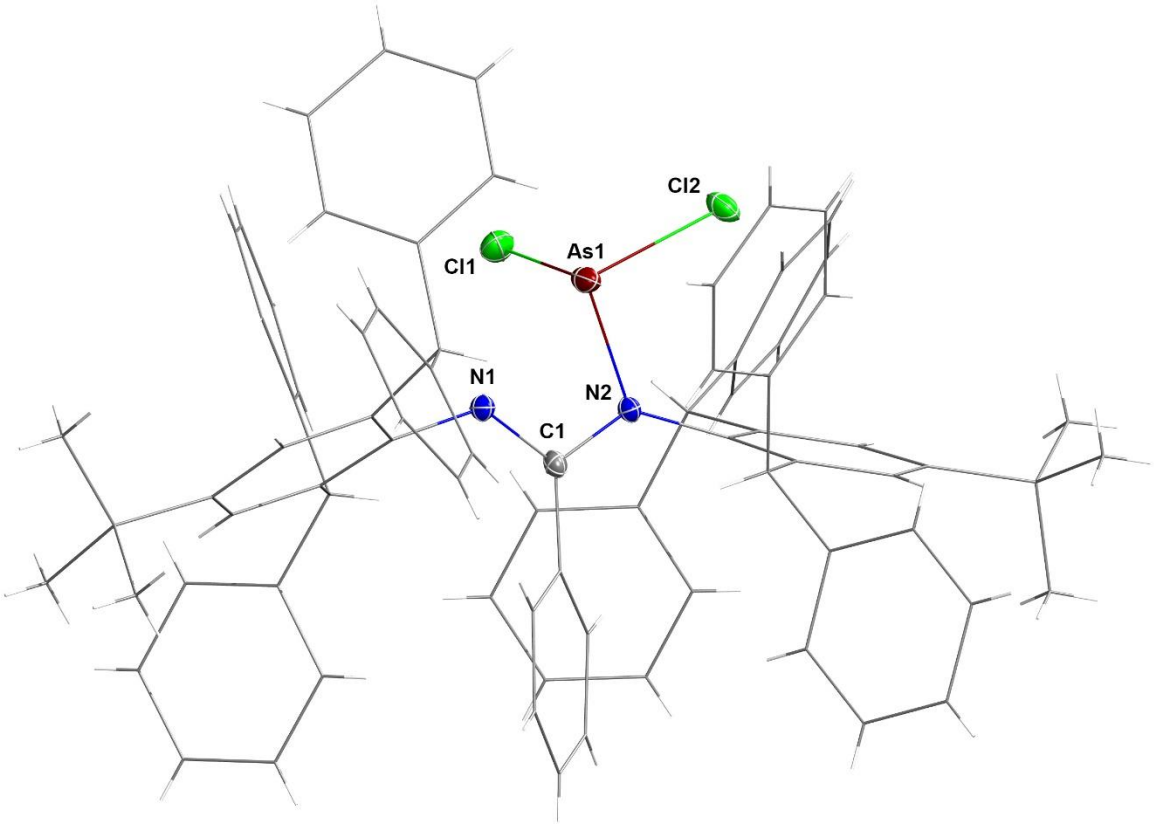


Figure 34. Molecular structure of **23** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Bhp and the phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N1–C1 = 1.302(2), C1–N2 = 1.377(2), N2–As1 = 1.918(1), As1–Cl1 = 2.1858(5), As1–Cl2 = 2.2761(4), N1–C1–N2 = 110.7(1).

An overview of the most important bond lengths and angles is listed in Table 8. While the bond length between N and P in **5** is slightly shorter than the sum of covalent radii, the experimental value matches the theoretical one for the arsenic derivative **23** and the N–E bonds of **24** and **25** are even elongated. This extension in the heavier congeners is accompanied by a more obtuse N–C–N angle. Meanwhile, the dihedral angle for the N–C–N–E core indicates near-planarity and comparable E–Cl bond elongation is present in all four derivatives, as one of the two bonds always exceeds the sum of covalent radii for a single bond.

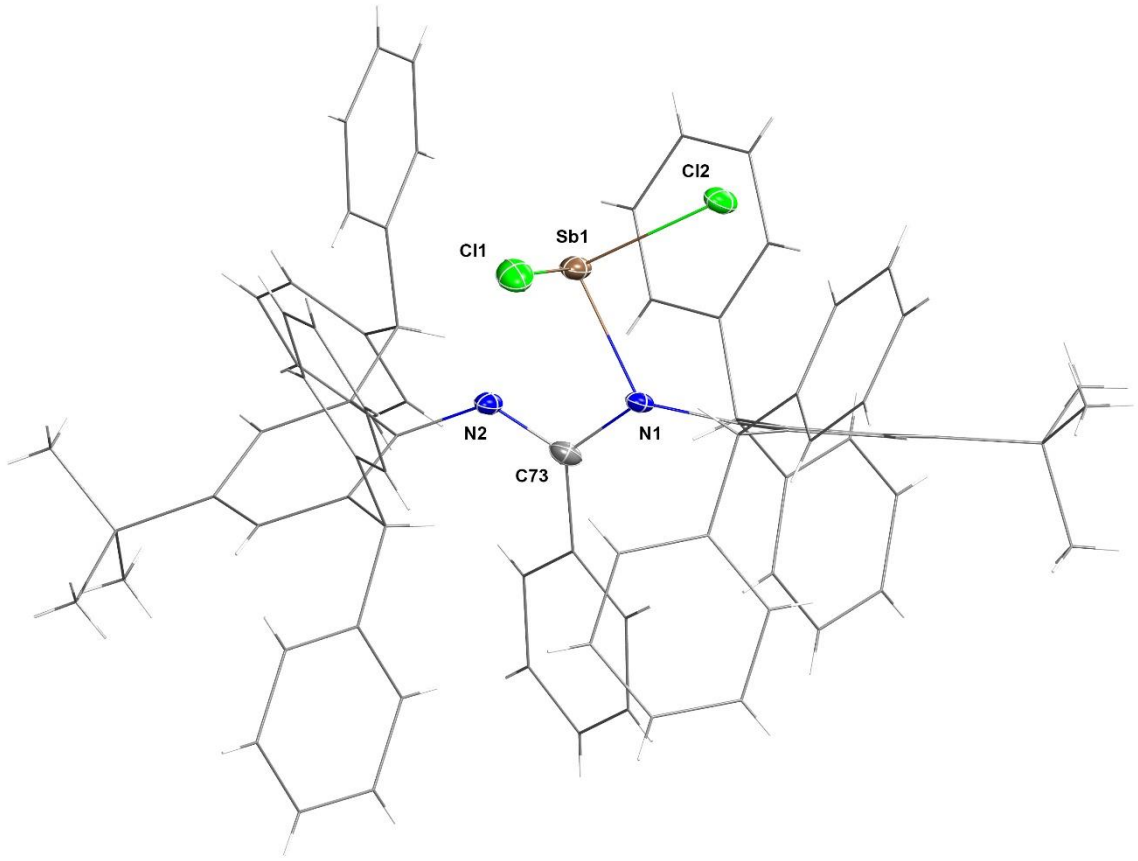


Figure 35. Molecular structure of **24** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Bhp and the phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N1–C73 = 1.364(5), C73–N2 = 1.313(5), N1–Sb1 = 2.125(3), Sb1–Cl1 = 2.349(1), Sb1–Cl2 = 2.442(1), N1–C73–N2 = 111.1(4).

The energetic contribution for negative hyperconjugation between the nitrogen lone pair at N1 and the antibonding σ* (As1–Cl2) orbital in **23** is almost 20 kJ/mol higher (141.3 kJ/mol) than for the phosphorus derivative **5**. It is interesting to note that no double substitution occurred, even for the bismuth compound **25**.

The ^{1}H NMR spectra of all congeners feature only one alkyl signal for the two $^{t\mathrm{Bu}}$Bhp substituents, indicating a similar symmetric transition state in solution (cf. Scheme 15).

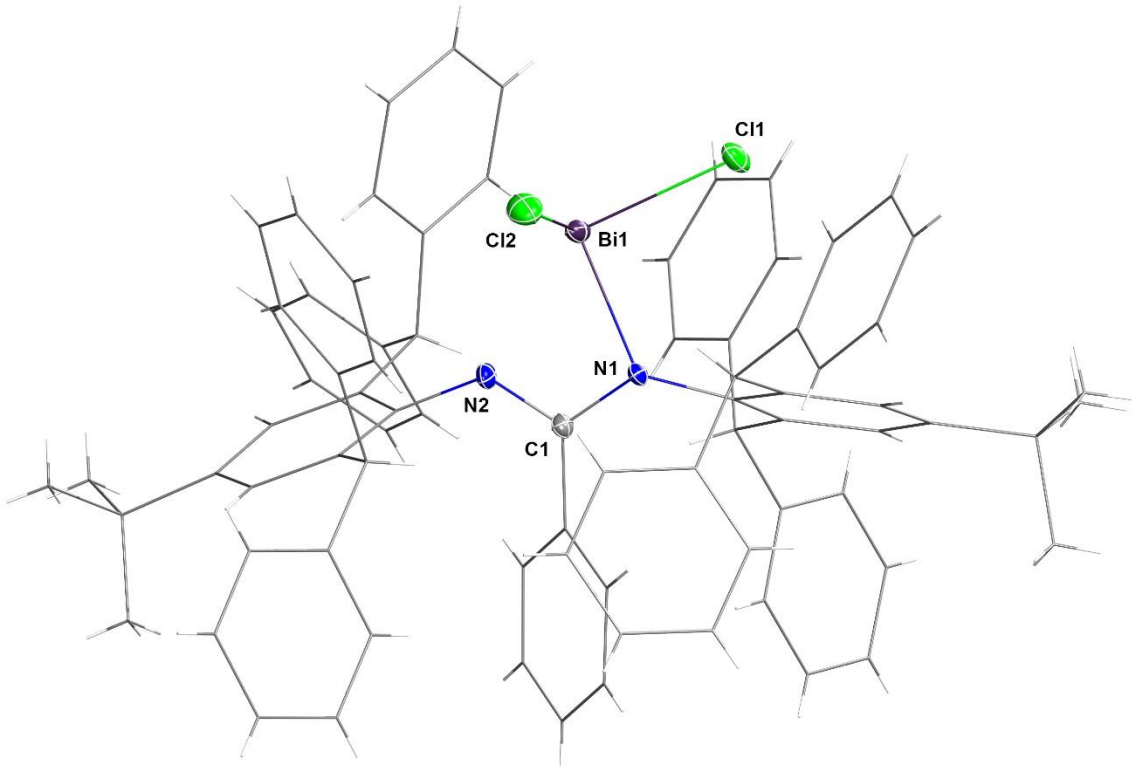


Figure 36. Molecular structure of **25** in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Bhp and the phenyl substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N2–C1 = 1.314(2), C1–N1 = 1.358(2), N1–Bi1 = 2.247(1), Bi1–Cl1 = 2.5528(4), Bi1–Cl2 = 2.4478(5), N2–C1–N1 = 113.2(1).

Table 8. Comparison of structural parameters for dichloropnictogenamidinates (asterisk denotes the non-bonding N–E distance).

	E =			
	P (5)	**As (23)**	**Sb (24)**	**Bi (25)**
N–E / Å	1.767(2)	1.918(1)	2.125(3)	2.247(1)
($\sum r_{cov.}$ (N–E) / Å)	1.82	1.92	2.11	2.22
E–Cl / Å	2.0691(7)	2.1858(5)	2.349(1)	2.4478(5)
E–Cl / Å	2.1430(6)	2.2761(4)	2.442(1)	2.5528(4)
($\sum r_{cov.}$ (E–Cl) / Å)	2.10	2.20	2.39	2.50
N–C–N / °	108.9(2)	110.7(1)	111.1(4)	113.2(1)
N–C–N–E / °	10.4(2)	11.3(1)	9.4(3)	10.4(2)
*** N–E / Å**	2.254(2)	2.299(1)	2.345(3)	2.465(1)
($\sum r_{vdW}$ (N–E) / Å)	3.55	3.65	3.80	3.90

A gradual high-field shift of these *tert*-butyl signals in CD_2Cl_2 can be observed from **5** (1.08 ppm), to **23** (1.03 ppm), to **24** (1.01 ppm), to **25** (0.98 ppm).

With respect to potential heavier congeners of the titular NHP **6**, computations of reduced model compounds were carried out. NRT analyses of the optimized structures (PBE-D3/def2-TZVP) reveal a decrease in the N–E bond orders and an increase in the ionic bond character

from P to Sb (Table 9), concomitant with a higher difference in the PAULING electronegativity values. An NRT analysis of the bismuth derivative was not successful, as no acceptable set of LEWIS orbitals for any of the proposed reference structures could be calculated, even with varying delocalization list threshold values. However, a continuation of the observed trend seems likely.

Table 9. Comparison of N–E bond parameters (NRT) in model compounds of reduced heterocyclic species.

Bond = N–E	**N–P**	**N–As**	**N–Sb**	**N–Bi**
NRT bond order	1.03	1.01	1.00	–
Covalent character	46.1 %	40.5 %	29.3 %	–
Ionic character	53.9 %	59.5 %	70.7 %	–

Meanwhile, the percentage of a pnictinidene resonance increases from P to Sb (Figure 37), although the values remain minuscule.

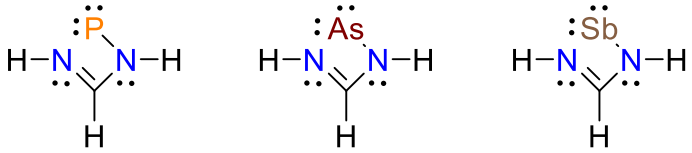


Figure 37. Percentage of pnictinidene resonances obtained from NRT calculations.

Additionally, CASSCF(6,4)/def2-TZVP calculations, taking all π-type MOs of the model compounds into account, gave LUNO occupancies of 0.05 for all three heavier congeners, which is a slight decrease, compared to the model compound of **6** (LUNO occupancy = 0.08).

Localization of the considered MOs allows for the formulation of the most important LEWIS structures (Figure 38), which are principally identical in all cases and feature similar values. Similar to the phosphorus derivative, the structure with the largest weight exhibits a formal negative charge at the pnictogen atom and a positive charge at the adjacent nitrogen atom. Compared to the model compound of **6**, the HOMO-LUMO gap further increases for the heavier congeners (Table 10).

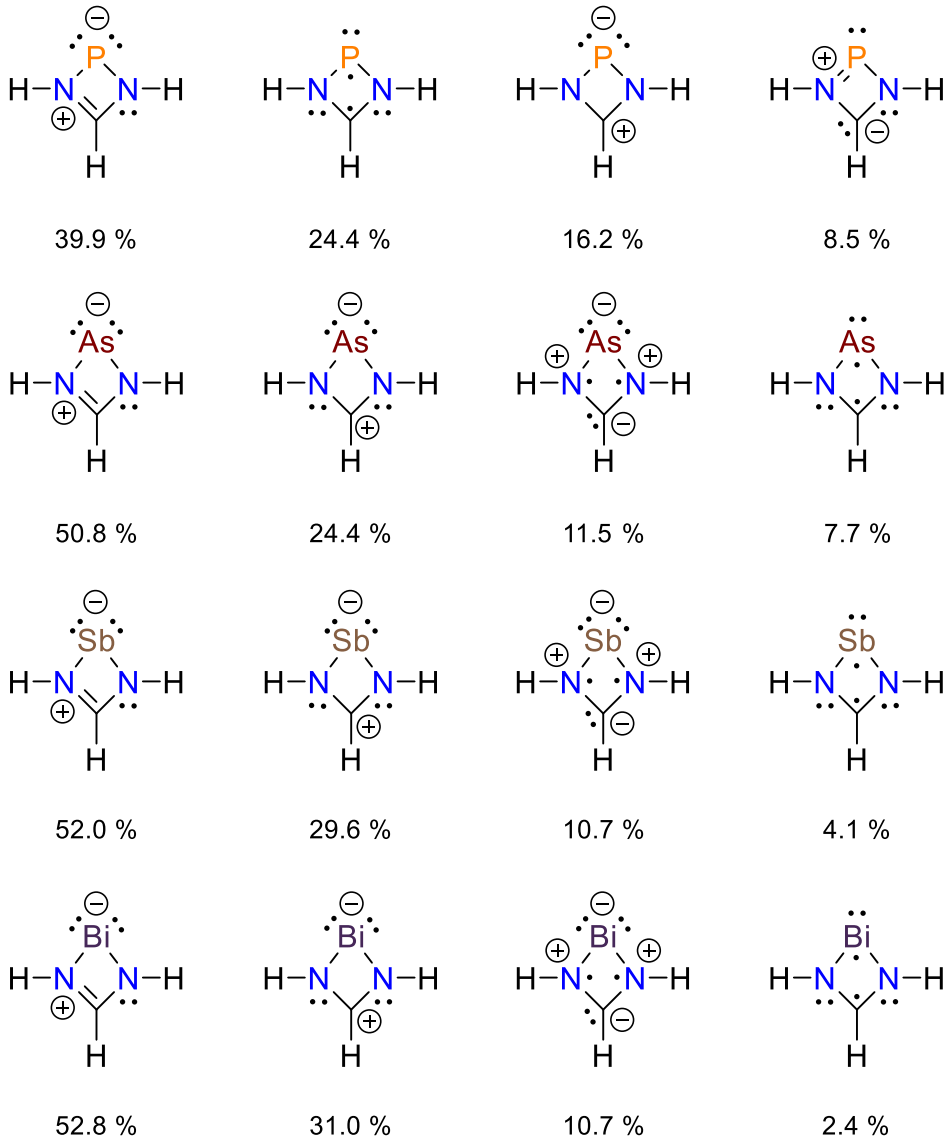


Figure 38. Depiction of LEWIS structures for reduced heterocycles, derived from CASSCF(6,4) calculations, and their relative weights (the largest-weighted resonances represent two equal mirror-imaged structures).

Table 10. HOMO-LUMO gap values of model compounds.

	P	As	Sb	Bi
HOMO-LUMO gap / eV	10.9	15.2	13.0	13.4

A preliminary reductive experiment for the Sb derivative **24** with KC_8 led to an auspicious color change to yellow and the corresponding ^{1}H NMR spectrum of the product indicates a successful conversion, as no starting material was left. The same experiment was repeated in the presence of tolane with the goal of a similar addition (Scheme 35) to the proposed heterocycle. However, both ^{1}H NMR spectra, with and without tolane, are identical (Figure 39).

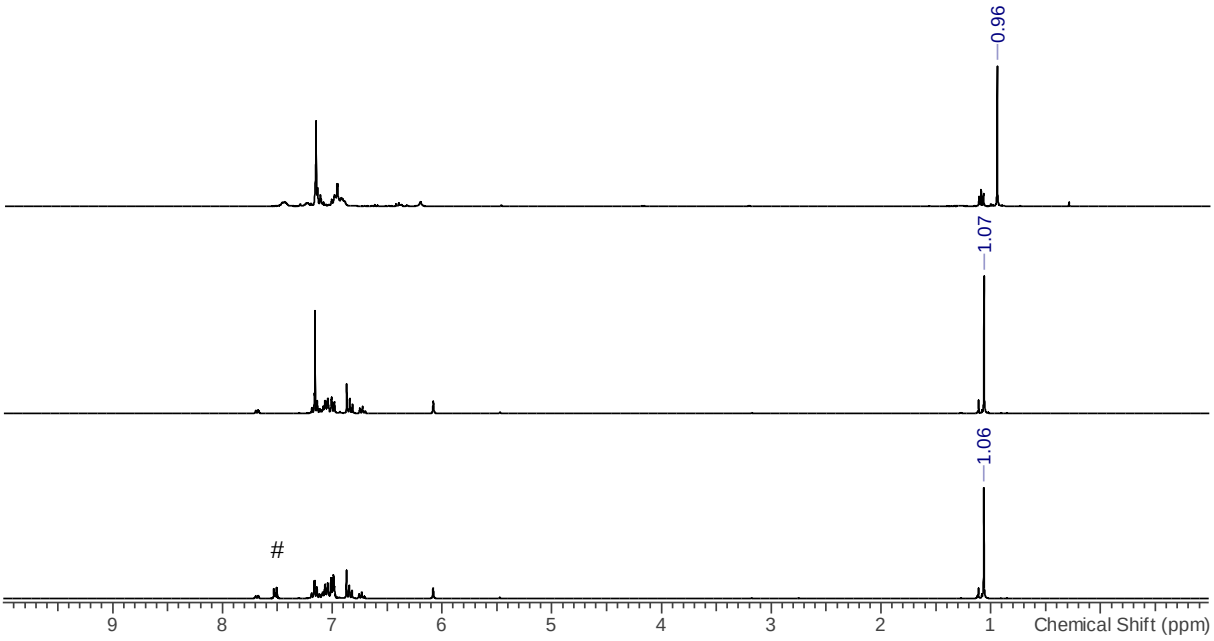
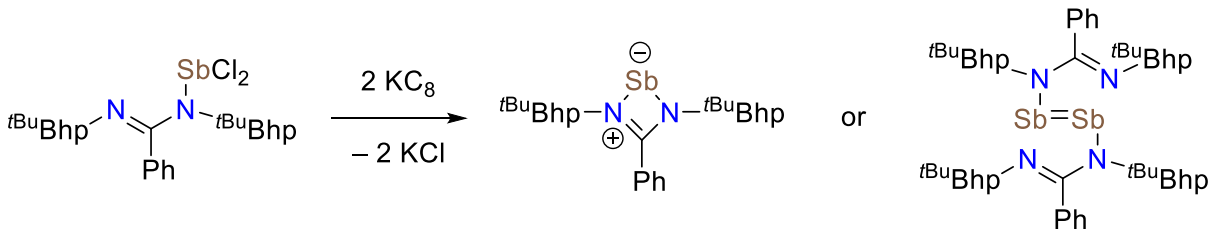


Figure 39. ^{1}H NMR spectra in C_6D_6 of **24** (top), a reaction with KC_8 (middle) and a reaction with KC_8 and tolane (bottom, tolane marked by hash).

Since a differentiation between a monomer and a dimer (distibene, Scheme 41) cannot be made based on NMR spectra (due to possible magnetic equivalence of all *tert*-butyl groups) and the isolated amount was too low for further analyses, a definite explanation for an absent reaction with tolane is not possible.



24 **26** **27**

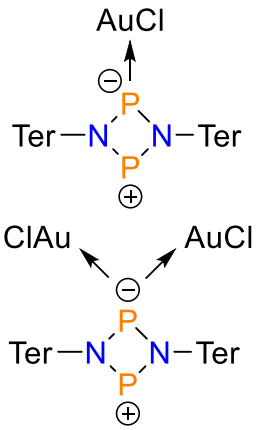
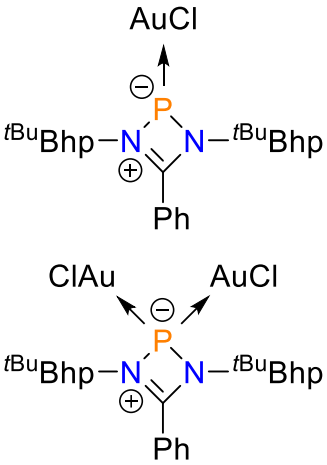
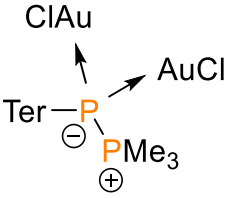
Scheme 41. Most probable products of **24** after reduction.

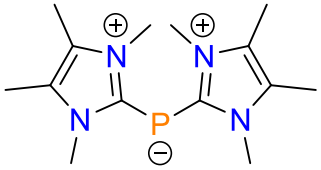
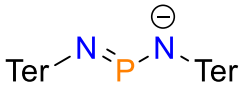
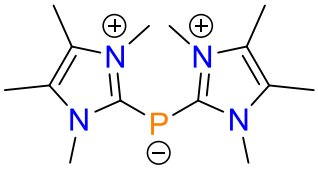
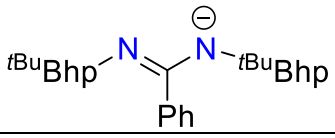
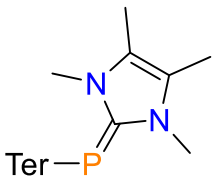
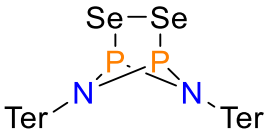
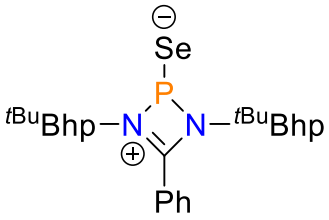
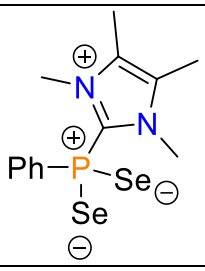
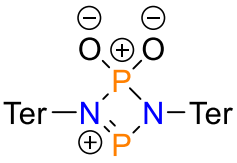
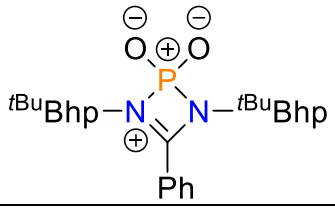
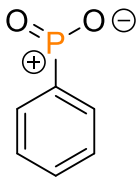
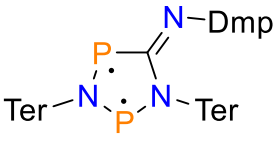
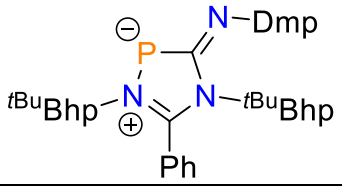
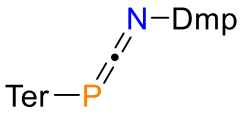
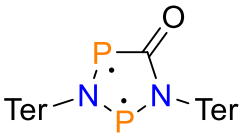
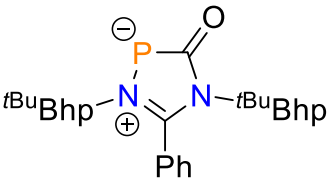
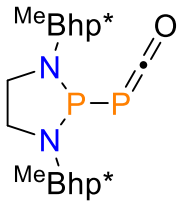
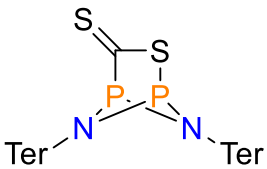
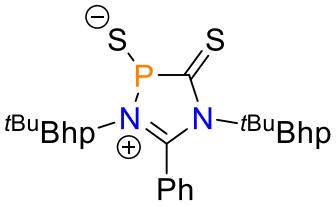
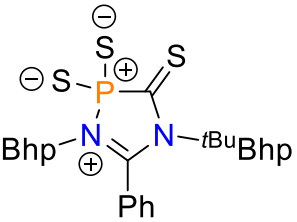
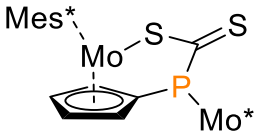
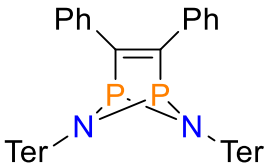
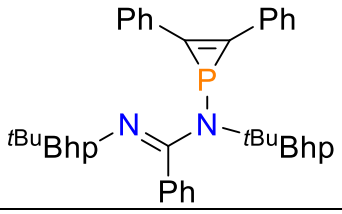
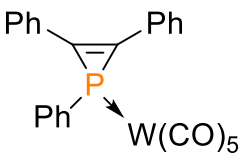
Nevertheless, a monomer seems more likely, due to the very bulky Bhp substituents, which should kinetically stabilize this species. The failed reaction with tolane might then be explained by the absence of significant stibinidene behavior.

4 Summary and outlook

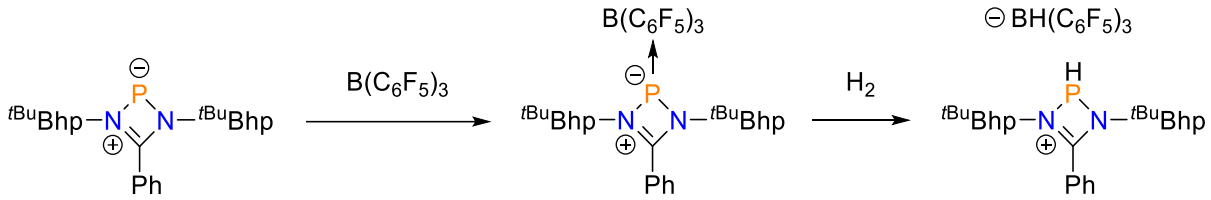
This work summarized the successful preparation and characterization of a novel four-membered heterocycle (**6**), which may be best described as a cyclic zwitterion and a masked *N*-heterocyclic phosphinidene (NHP), respectively. According to multiple computational analyses and experimental observations, the compound exhibits negligible biradical character. Nevertheless, the reactivity of **6** resembles that of the symmetric biradical [Ter–NP]$_2$ (LEWIS acid and NHC coordination, insertion reactions) in some cases, while other reactions (addition of alkenes/alkynes) are more in line with typical phosphinidene sources (Table 11). Furthermore, the unprecedented bulky amidine was successfully employed in the preparation of heavier dichloropnictogen congeners. The inherently reactive, yet kinetically stabilized, phosphorus center in **6** led to the clean formation of single products in most investigated reactions.

Table 11. Reactivity of **6** compared to the biradical [Ter–NP]$_2$ and conventional phosphinidene sources (Mo* = MoCp(CO)$_2$(PMe$_3$)).[4,104,107,116,122,140–143]

Reagent	[Ter–NP]$_2$	**6**	Phosphinidene source
AuCl			

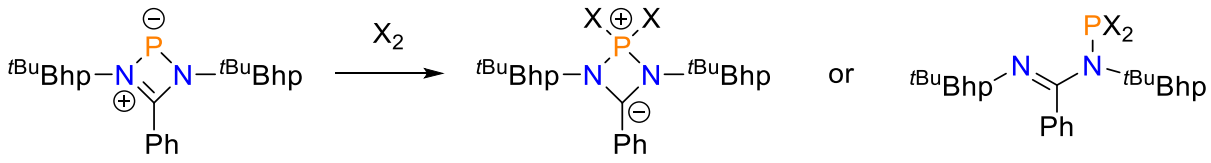
Reagent	[Ter–NP]$_2$	**6**	Phosphinidene source
^{Me}IMe	 	 	
Se			
O_2			
Dmp–NC			
CO			
CS_2		 	
Tolane			

In this regard, a variety of reagents are yet to be tested. Due to the observed coordination of LEWIS acids to the phosphorus atom, combination of **6** with a bulky borane like $B(C_6F_5)_3$ (perfluorinated for increased acidity and chemical inertness) might lead to a frustrated LEWIS pair (FLP) that could be employed in the activation of molecular hydrogen or other small molecules (Scheme 42).



Scheme 42. Possible formation of an FLP and reaction with H_2.

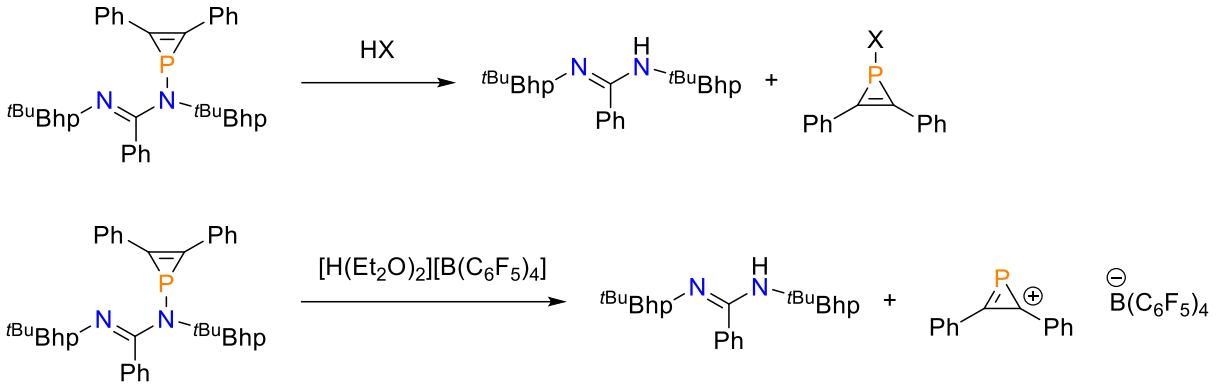
Furthermore, the stability of **6** towards halogens (acting as oxidants) can be tested with respect to cyclic products or comparable open-chain isomers (Scheme 43).



Scheme 43. Possible formation of cyclic or open-chain oxidized species (X = F, Cl, Br, I).

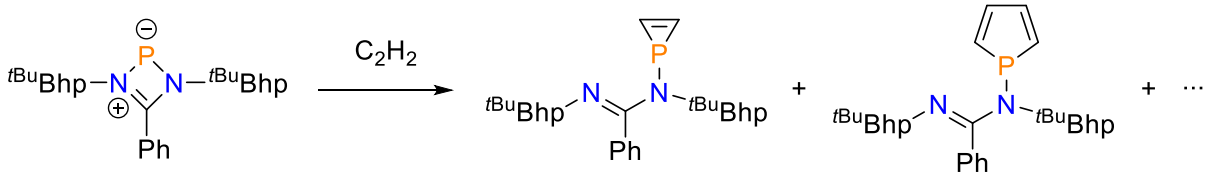
Akin to the CS_2 reaction (cf. Chapter 3.2.4), an analogous reaction with CO_2 could lead to a more defined product, instead of an inseparable mixture. Other gaseous reactants like N_2O, NO and NH_3 may result in a variety of different insertion or rearrangement products. Additionally, as gold and iron coordination to the phosphorus atom was observed, it would be interesting to study the reaction of **6** with other transition metal sources. While VCl_3, $RhCl_3$, $PdCl_2$ might result in catalytically active species, ligand properties could be further assessed by reaction with compounds like $RuCl_2(PPh_3)_3$ or cisplatin. It should be noted that DMF cannot be used as a solvent for these reactions, as it already reacts with **6** to an unidentified product in a quantitative manner.

Regarding the observed addition of alkenes and alkynes, a reaction with fullerene C_{60} might result in a comparable structural motif or even multiple additions. A reaction of phosphiranes/phosphirenes with hydrogen halides or other proton sources like JUTZI's acid could lead to halogenated derivatives or ion pairs, respectively (Scheme 44).



Scheme 44. Possible separation of the amidine backbone and phosphirenes by proton sources.

Lastly, employing acetylene as the smallest alkyne source might enable the formation of different unsaturated phosphorus-based heterocycles in a oligomerization-type reaction (Scheme 45).



Scheme 45. Possible formation of different phosphorus-based heterocycles.

Further reactions with unsaturated building blocks like covalently-bound pseudohalogens (cyanates, thiocyanates, azides), aldehydes, ketones, cumulenes and also pnictogen derivatives (dipnictenes, phosphaalkynes) could open new pathways to an abundance of heterocycles.

5 Appendix

5.1 Experimental methods

Unless stated otherwise, all experiments were carried out using standard SCHLENK techniques or in a GS Alpha glovebox under an inert argon atmosphere, using predried solvents. Glassware was dried under vacuum (10^{-3} mbar) at 250–300 °C, with three evacuate-heat-flush cycles. Compounds prone to hydrolysis or oxidation were handled in a glovebox. Solvents were distilled under argon atmosphere and handled with disposable syringes (flushed three times with argon prior to use). All solvents were purchased from distributors and, if necessary, purified and dried according to literature protocols. Starting materials were purchased from distributors or synthesized according to published protocols (Table 12).

Table 12. Employed compounds with their source and method of purification.

Compound	**Source**	**Method of purification**
CH_2Cl_2	local distributor	purified according to literature[144] dried over P_4O_{10}, stored over CaH_2 distilled prior to use and degassed (*freeze-pump-thaw*)
Et_2O, THF, DME	local distributor	dried over Na/benzophenone distilled prior to use
C_6H_6, C_7H_8	local distributor	dried over Na/benzophenone distilled prior to use
PhF	local distributor	dried over CaH_2 distilled prior to use
MeOH	local distributor	–
CD_2Cl_2	ARMAR	dried over P_4O_{10}, stored over CaH_2 distilled prior to use
C_6D_6, C_7D_8	ARMAR	dried over Na distilled prior to use
THF-d_8	ARMAR	dried over Na distilled prior to use, stored over molecular sieves (4 Å)
PCl_3	old stock	dried over P_4O_{10} distilled prior to use and degassed (*freeze-pump-thaw*)
NEt_3	old stock	dried over Na distilled prior to use

Compound	Source	Method of purification
$^{t\text{Bu}}$Bhp–NH_2	synthesized[19]	–
Benzoyl chloride	old stock	–
$NaHCO_3$	KMF Laborchemie	–
$MgSO_4$	Grüssing	–
PCl_5	Merck	–
Ethyl acetate	Local distributor	–
*n*BuLi	Sigma-Aldrich (2.5 M in hexane)	–
Mg turnings	old stock	stirred under argon for ≥ 1 week
Me_2SAuCl	abcr	–
4-DMAP	Sigma-Aldrich	–
$^{\text{Me}}$IMe	synthesized[106]	sublimation
S_8	old stock	sublimation
Se	Merck	–
Dmp-NC	synthesized[119]	sublimation
CS_2	old stock	dried over P_4O_{10} distilled prior to use and degassed (*freeze-pump-thaw*)
$Fe(CO)_5$	Sigma-Aldrich	–
CO	local distributor	–
Tolane	abcr	sublimation
Cyclohexene	old stock	dried over molecular sieves (4 Å)
1,4-cyclohexadiene	Sigma	dried over molecular sieves (4 Å)
BTMSA	old stock	dried over molecular sieves (4 Å)
TMSA	old stock	dried over molecular sieves (4 Å)
$AsCl_3$	synthesized[145]	distillation
$SbCl_3$	old stock	sublimation
$BiCl_3$	old stock	sublimation
KC_8	abcr	–

5.2 Analytical methods

NMR spectra were recorded on Bruker spectrometers (AVANCE 250, AVANCE 300 and AVANCE 500) and calibrated internally, based on the deuterated solvents (^{13}C: CD_2Cl_2 δ_{ref} = 54.0 ppm, C_6D_6 δ_{ref} = 128.4 ppm, THF-d_8 $\delta_{ref,1}$ = 25.4 ppm, $\delta_{ref,2}$ = 67.6 ppm) or residual protic species in the deuterated solvents (^{1}H: $CHDCl_2$ δ_{ref} = 5.32 ppm, C_6HD_5 δ_{ref} = 7.16 ppm, THF-d_7 $\delta_{ref,1}$ = 1.73 ppm, $\delta_{ref,2}$ = 3.58 ppm), or calibrated externally (^{31}P: 85% H_3PO_4 δ_{ref} = 0 ppm, ^{29}Si: $SiMe_4$ δ_{ref} = 0 ppm). All measurements were performed at room temperature, unless denoted otherwise. NMR signals were assigned based on experimental data (chemical shifts, coupling constants, integral values).

ATR IR spectra of solids were recorded on a Bruker Alpha II spectrometer, either in air or in a glovebox filled with argon (for air-sensitive compounds). Signal intensities are assigned based on the following relative values: *very weak* (vw, 0–10 %), *weak* (w, 10–30 %), *medium* (m, 30–60 %), *strong* (s, 60–90 %), *very strong* (vs, 90–100 %).

Raman spectra of crystalline samples were recorded on a LabRAM HR 800 Horiba Jobin YVON Raman spectrometer with an Olympus BX41 microscope with variable lenses. For excitations, either an IR laser (758 nm, 100 mW, air-cooled diode laser) or a red laser (633 nm, 17 mW, HeNe laser) was employed.

Elemental analyses were measured on a vario Micro cube CHNS analyzer.

Melting points (uncorrected) were measured on an EZ Melt by Stanford Research Systems at a heating rate of 10 °C/min. Clearing points are reported for all compounds.

Mass spectra were recorded on a Thermo Electron MAT 95-XP sector mass spectrometer or an Advion Expression CMS L.

UV-Vis spectra were recorded on a Perkin-Elmer Lambda 19 UV-Vis spectrometer.

5.3 Structure elucidation

Crystals suitable for single-crystal XRD were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at room temperature and cooled to 123(2) K during measurements, except for **8** (173(2) K). Data was collected on a Bruker D8 Quest diffractometer, using Mo K_α radiation (λ = 0.71073 Å). Structures were solved by iterative methods (SHELXT)[146] and refined by full matrix least squares procedures (SHELXL)[147]. Semi-empirical absorption corrections were

applied (SADABS).[148] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the refinement at calculated positions, using a riding model.

Table 13. Crystallographic data.

Compund	**4**	**4**	**4**
Formula	$C_{79}H_{72}N_2$•0.5($C_4H_{10}O_2$)	$C_{79}H_{72}N_2$•0.5(C_6H_5F)	$C_{80.68}H_{76.20}N_2O_{0.84}$
Formula weight [g/mol]	1094.44	1097.43	1087.26
Color	colorless	colorless	colorless
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*Pc*	*Pc*	*Pc*
a [Å]	14.2995(8)	14.3588(7)	14.352(3)
b [Å]	20.135(1)	20.098(1)	20.251(5)
c [Å]	22.187(1)	22.225(1)	22.206(4)
α [°]	90	90	90
β [°]	102.581(2)	102.697(2)	102.555(6)
γ [°]	90	90	90
V [Å^3]	6234.9(6)	6257.0(5)	6300(2)
Z	4	4	4
$P_{calcd.}$ [g/cm^3]	1.166	1.165	1.146
μ [mm^{-1}]	0.067	0.067	0.066
T [K]	123(2)	123(2)	123(2)
Measured reflections	92656	245924	245999
Independent reflections	28526	34934	31826
Reflections with $I > 2\sigma(I)$	20829	29360	26462
R_{int}	0.069	0.0583	0.0622
F(000)	2340	2340	2324
$R_1(R[F^2>2\sigma(F^2)])$	0.0540	0.0480	0.0453
w$R_2(F^2)$	0.1195	0.1169	0.1041
GooF	1.039	1.018	1.047
No. of parameters	1635	1577	1596
Labcode	is_ts329	is_ts379	ts_pb03
CCDC #			

Table 14. Crystallographic data.

Compund	**4•HCl**	**5**	**6**
Formula	$C_{79}H_{73}N_2^+ \bullet Cl^-$	$C_{79}H_{71}Cl_2N_2P \bullet C_4H_{10}O_2$	$C_{79}H_{71}N_2P \bullet C_4H_{10}O_2$
Formula weight [g/mol]	1085.84	1240.36	1169.46
Color	colorless	colorless	orange
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$Pna2_1$	$P\bar{1}$
a [Å]	15.4494(8)	24.975(1)	13.9436(8)
b [Å]	20.985(1)	25.595(1)	18.418(1)
c [Å]	19.138(1)	10.9085(6)	26.306(1)
α [°]	90	90	83.107(2)
β [°]	92.820(2)	90	84.786(2)
γ [°]	90	90	85.179(2)
V [Å^3]	6197.2(5)	6973.0(6)	6660.7(7)
Z	4	4	4
$P_{calcd.}$ [g/cm^3]	1.164	1.182	1.166
μ [mm^{-1}]	0.108	0.165	0.091
T [K]	123(2)	123(2)	123(2)
Measured reflections	129016	304902	327429
Independent reflections	18059	20346	32281
Reflections with $I > 2\sigma(I)$	11843	17846	24171
R_{int}	0.0793	0.058	0.0625
$F(000)$	2312	2632	2496
$R_1(R[F^2>2\sigma(F^2)])$	0.0535	0.0353	0.0536
$wR_2(F^2)$	0.1336	0.0842	0.1438
GooF	1.006	1.035	1.045
No. of parameters	753	820	1627
Labcode	is_ts385	is_ts331	ts_ts341
CCDC #			

Table 15. Crystallographic data.

Compund	**8**	**9**	**12**
Formula	$C_{79}H_{71}Au_2Cl_2N_2P$ •3(C_6H_5F)	$C_{91}H_{83}N_2^-$•$C_{14}H_{24}N_4P^+$	$C_{79}H_{71}N_2O_2P$•3(C_6H_6)
Formula weight [g/mol]	1832.48	1483.93	1345.67
Color	colorless	yellow	colorless
Crystal system	monoclinic	triclinic	monoclinic
Space group	*P*2/*n*	$P\bar{1}$	$P2_1$
a [Å]	16.8836(7)	12.7409(8)	10.5871(8)
b [Å]	11.1564(6)	14.3146(9)	27.355(2)
c [Å]	21.759(1)	23.696(1)	13.328(1)
α [°]	90	82.322(2)	90
β [°]	102.235(2)	82.047(2)	97.722(3)
γ [°]	90	80.948(2)	90
V [Å^3]	4005.3(3)	4199.1(4)	3824.9(5)
Z	2	2	2
$P_{calcd.}$ [g/cm^3]	1.519	1.174	1.168
μ [mm^{-1}]	3.801	0.086	0.088
T [K]	173(2)	123(2)	123(2)
Measured reflections	138761	16499	203561
Independent reflections	14495	16499	25472
Reflections with $I > 2\sigma(I)$	11311	13236	22247
R_{int}	0.0523	0.0892	0.0459
F(000)	1832	1588	1432
$R_1(R[F^2>2\sigma(F^2)])$	0.029	0.0659	0.0416
w$R_2(F^2)$	0.0635	0.1359	0.1037
GooF	1.028	1.108	1.023
No. of parameters	515	1023	926
Labcode	av_ts361c	is_ts422	ts451
CCDC #			

Table 16. Crystallographic data.

Compund	**13**	**14**	**15**
Formula	$C_{88}H_{80}N_3P$•1.5($C_4H_{10}O$)	0.919($C_{80}H_{71}N_2OP$)• 0.081($C_{79}H_{73}N_2^+$•Cl^-)	$C_{82.77}H_{71}Fe_{0.69}N_2O_{3.77}P$• 0.75($C_4H_{10}O_2$)
Formula weight [g/mol]	1321.69	1105.63	1291.28
Color	red	yellow	orange
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2	$P2_1/n$	$P2_1/c$
a [Å]	27.536(2)	15.7074(7)	28.108(1)
b [Å]	10.9918(5)	20.6488(9)	10.6114(4)
c [Å]	25.291(2)	19.2218(9)	24.6111(8)
α [°]	90	90	90
β [°]	100.435(2)	91.591(2)	97.098(1)
γ [°]	90	90	90
V [Å^3]	7528.4(7)	6232.0(5)	7284.4(5)
Z	4	4	4
$P_{calcd.}$ [g/cm^3]	1.166	1.178	1.177
μ [mm^{-1}]	0.088	0.094	0.224
T [K]	123(2)	123(2)	123(2)
Measured reflections	132410	134806	172086
Independent reflections	23933	16571	18538
Reflections with $I > 2\sigma(I)$	20485	12964	13468
R_{int}	0.0435	0.0471	0.0735
F(000)	2828	2349	2729
$R_1(R[F^2>2\sigma(F^2)])$	0.0445	0.0574	0.0794
w$R_2(F^2)$	0.1114	0.1589	0.1955
GooF	1.015	1.033	1.074
No. of parameters	1132	834	957
Labcode	is_ts399	ts427	is_ts410
CCDC #			

Table 17. Crystallographic data.

Compund	**18**	**24**	**25**
Formula	$C_{93}H_{81}N_2P$	$C_{79}H_{71}AsCl_2N_2$• 0.755(CH_2Cl_2)	$C_{79}H_{71}SbCl_2N_2$
Formula weight [g/mol]	1257.56	1258.13	1241.02
Color	colorless	yellow	colorless
Crystal system	monoclinic	triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	10.7510(5)	10.9665(7)	11.0267(6)
b [Å]	24.948(1)	13.1312(8)	13.1577(8)
c [Å]	26.443(1)	24.479(2)	24.443(2)
α [°]	90	88.601(3)	90.042(2)
β [°]	93.353(2)	87.693(3)	91.325(2)
γ [°]	90	70.089(3)	111.923(2)
V [Å^3]	7080.3(6)	3311.5(4)	3288.8(3)
Z	4	2	2
$P_{calcd.}$ [g/cm^3]	1.180	1.262	1.253
μ [mm^{-1}]	0.089	0.700	0.545
T [K]	123(2)	123(2)	123(2)
Measured reflections	224590	216107	63604
Independent reflections	19740	22052	11570
Reflections with $I > 2\sigma(I)$	16372	17373	8714
R_{int}	0.0372	0.0542	0.1084
F(000)	2672	1315	1288
$R_1(R[F^2>2\sigma(F^2)])$	0.0432	0.0459	0.0545
w$R_2(F^2)$	0.115	0.1179	0.1067
GooF	1.026	1.010	1.119
No. of parameters	871	884	797
Labcode	ts411	is_pb01	ts452
CCDC #			

Table 18. Crystallographic data.

Compund	**26**	**Ter–N(H)Si(Cl)$_2$Me**	**Ter–N(H)Si(Cl)$_2$Ph**
Formula	$C_{79}H_{71}BiCl_2N_2 \bullet C_4H_{10}O$	$C_{25}H_{29}Cl_2NSi$	$C_{30}H_{31}Cl_2NSi$
Formula weight [g/mol]	1402.37	442.48	504.55
Color	yellow	colorless	colorless
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [Å]	11.3420(7)	17.820(2)	11.709(1)
b [Å]	13.2090(9)	8.367(1)	8.6342(8)
c [Å]	24.840(2)	17.190(2)	27.596(3)
α [°]	95.014(2)	90	90
β [°]	92.330(2)	112.203(2)	99.291(2)
γ [°]	110.462(2)	90	90
V [Å^3]	3463.1(4)	2372.9(5)	2753.4(4)
Z	2	4	4
$P_{calcd.}$ [g/cm^3]	1.345	1.239	1.217
μ [mm^{-1}]	2.670	0.336	0.298
T [K]	123(2)	123(2)	173(2)
Measured reflections	228104	45295	50172
Independent reflections	23066	7549	8033
Reflections with $I > 2\sigma(I)$	21319	5777	5350
R_{int}	0.0371	0.0584	0.0507
F(000)	1436	936	1064
$R_1(R[F^2>2\sigma(F^2)])$	0.0258	0.0475	0.0452
w$R_2(F^2)$	0.0573	0.1283	0.1159
GooF	1.153	1.042	1.025
No. of parameters	855	273	362
Labcode	is_pb04	av_ts225	is_ts234
CCDC #			

5.4 Computational details

Computations were carried out using the software Gaussian09[149] or ORCA 4.2.1[150], as well as NBO 6.0.[151–154]

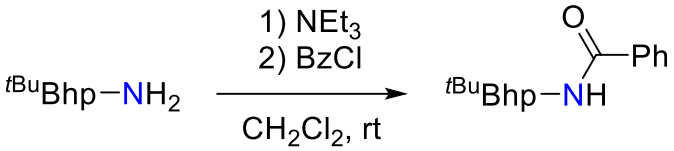
Structure optimizations were performed using the pure DFT functional PBE[155,156] in conjunction with Grimme‘s dispersion correction D3(BJ)[157,158] and the basis set def2-TZVP[159,160] (notation: PBE-D3/def2-TZVP). All structures were fully optimized and verified as local minima on the potential hypersurface via frequency analyses. Natural charges, Wiberg bond indices and second order perturbation interactions were derived from a natural population analysis, using the NBO software.

Potential biradicals were optimized using the PBE functional, Grimme’s dispersion correction and the def2-TZVP basis set. The resolution of identity (RI) approximation was employed, using the appropriate Coulomb fitting basis of the Weigend group.[161] The stability of all Kohn-Sham wavefunctions was checked to verify the validity of the single-determinantal, restricted Kohn-Sham DFT approach. In accordance with Complete Active Space SCF (CASSCF) computations, the restricted KS wavefunctions were stable in all instances with respect to symmetry breaking. All structures were fully optimized and confirmed as minima by frequency analyses.

It should be emphasized, that all computations were carried out for single, isolated molecules in the gas phase (ideal gas approximation) and there may be significant differences between gas phase and condensed phase.

5.5 Synthesis of compounds

5.5.1 $^{t\mathrm{Bu}}$Bhp–N(H)C(O)Ph (**2**)



The reaction protocol is based on previously published procedures.[81,82]

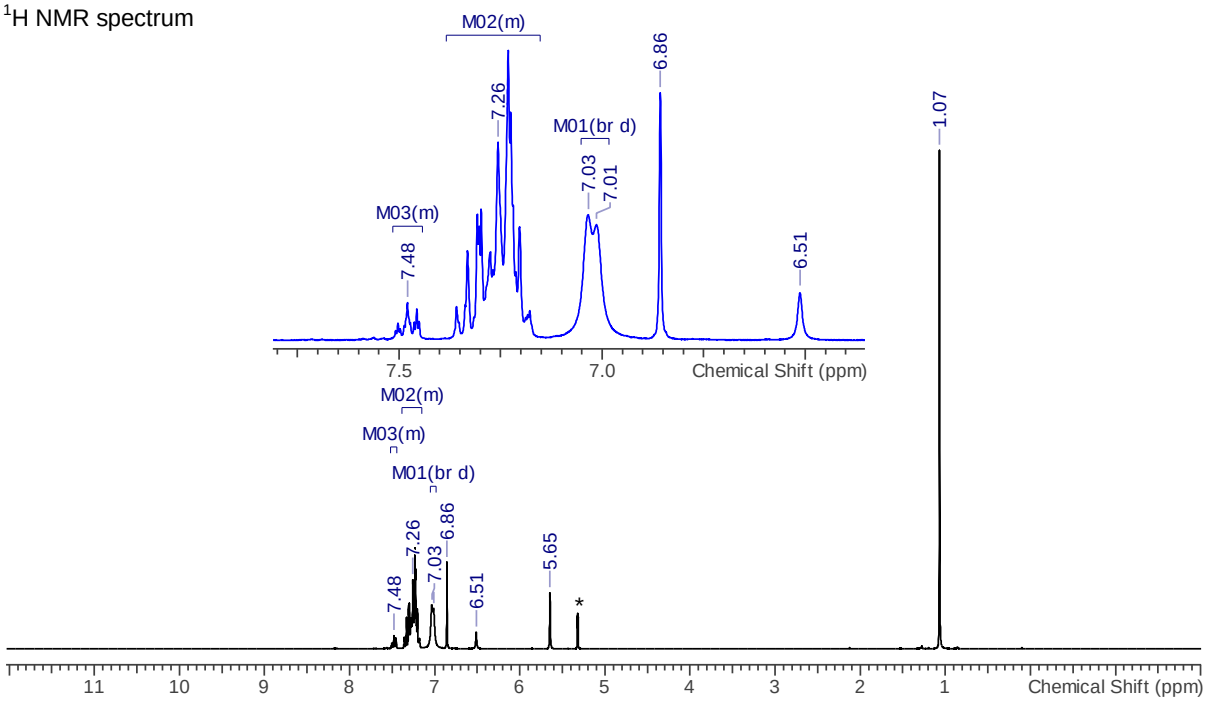
In a 500 mL Schlenk flask, the amine (19.21 g, 39.88 mmol) is dissolved in anhydrous dichloromethane (400 mL) and cooled to 0 °C (ice bath). Afterwards, triethylamine (7.05 g, 69.67 mmol) and benzoyl chloride (7.84 g, 55.74 mmol) are added via syringe and the mixture is left stirring at room temperature overnight. Then, a saturated aqueous solution of sodium bicarbonate (150 mL) and dichloromethane (250 mL) are added and layers are separated. The organic layer is washed with water (3 x 150 mL), dried over $MgSO_4$ and all volatiles are removed at the rotary evaporator. The crude product is washed repeatedly with MeOH (300 mL), resulting in a white solid, which is eventually dried at 130 °C (oil bath) and 10^{-3} mbar for 3 h. Yield: 19.04 g (32.51 mmol, 81.5 %).

Formula: $C_{43}H_{39}NO$. M = 585.79 g/mol. Mp. 274–277 °C. EA found (calcd.) in %: C 88.14 (88.17), H 6.41 (6.71), N 2.25 (2.39). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.07 (s, 9 H, *t*Bu), 5.65 (s, 2 H, C*H*Ph$_2$), 6.51 (s, 1 H, N*H*), 6.86 (s, 2 H, *m*-H (C$_6$*H*$_2$*t*Bu), 7.02 (d, $^3J(^1H,^1H)$ = 6.0 Hz, 8 H, *o-H*), 7.26 (m, 16 H, *m-H* + *p-H* (CH*Ph*$_2$), *o-H* + *m-H* (Ph)), 7.48 (m, 1 H, *p-H* (Ph)). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ = 31.3 (s, C(*C*H$_3$)$_3$), 35.1 (s, *C*(CH$_3$)$_3$), 53.5 (s, *C*HPh$_2$), 126.4 (s, *C*H), 127.0 (s, *C*H), 127.5 (s, *C*H), 129.0 (s, *C*H), 129.5 (s, *C*H), 129.8 (s, *C*H), 131.8 (s, $C_{quat.}$), 132.1 (s, *C*H), 134.5 (s, $C_{quat.}$), 142.4 (s, $C_{quat.}$), 143.7 (s, $C_{quat.}$), 150.6 (s, $C_{quat.}$), 166.2 (s, *C*O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3268 (w), 3056 (w), 3027 (w), 2961 (w), 2930 (w), 2866 (w), 1953 (vw), 1888 (vw), 1797 (vw), 1735 (vw), 1644 (m), 1599 (w), 1578 (w), 1517 (m), 1506 (m), 1494 (m), 1488 (m), 1447 (m), 1414 (w), 1393 (w), 1362 (w), 1341 (vw), 1298 (w), 1282 (m), 1265 (w), 1245 (w), 1216 (w), 1191 (w), 1156 (vw), 1129 (vw), 1078 (w), 1030 (w), 1001 (w), 973 (w), 952 (vw), 927 (vw), 911 (vw), 898 (vw), 863 (vw), 826 (vw), 797 (vw), 771 (w), 752 (m), 742 (m), 713 (m), 696 (vs), 653 (m), 622 (m), 604 (m), 581 (m), 565 (w), 542 (vw), 499 (w), 484 (vw), 470 (w). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3065 (3), 3040 (1), 3029 (1), 2972 (1), 2943 (1), 2922 (1), 2901 (1), 1647 (1), 1601 (3), 1583 (1), 1300 (1),

1283 (1), 1271 (1), 1191 (1), 1174 (2), 1157 (1), 1029 (2), 1001 (10), 927 (1), 917 (1), 911 (1), 866 (1), 836 (2), 826 (1), 634 (1), 619 (1), 298 (1), 276 (1), 252 (1), 235 (1), 213 (2), 190 (1), 183 (1), 170 (4), 144 (3). MS (APCI +, m/z): 587 ($[M+H]^+$).

Figure 40. ^{1}H NMR, ^{13}C{^{1}H} NMR, IR and Raman spectra of **2** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

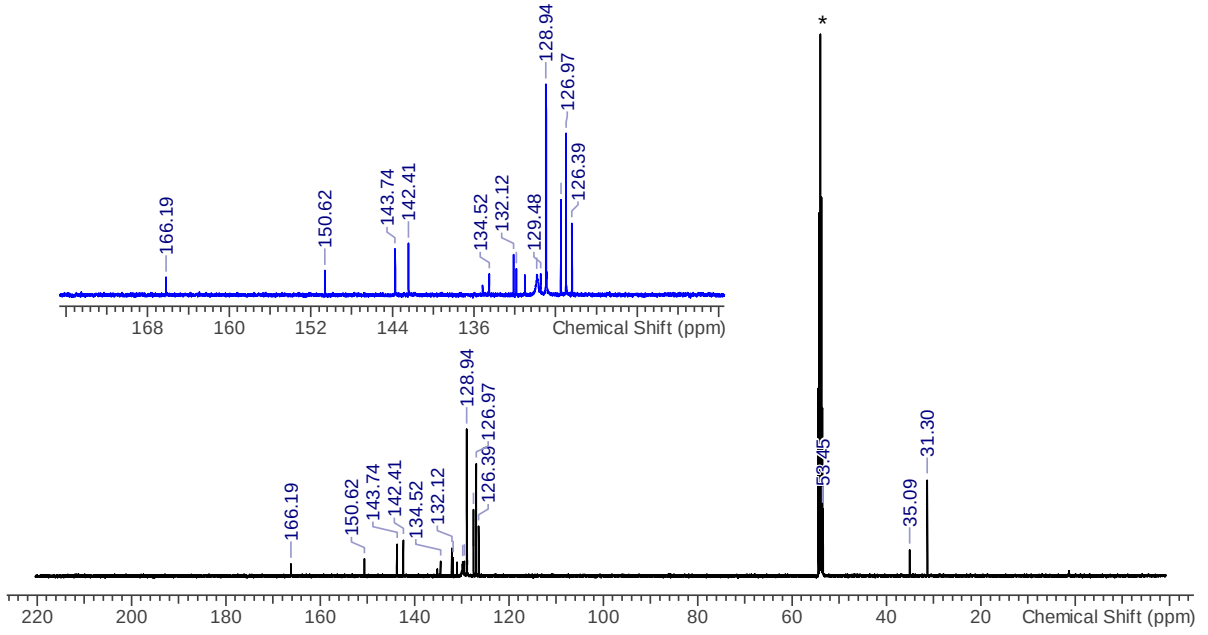
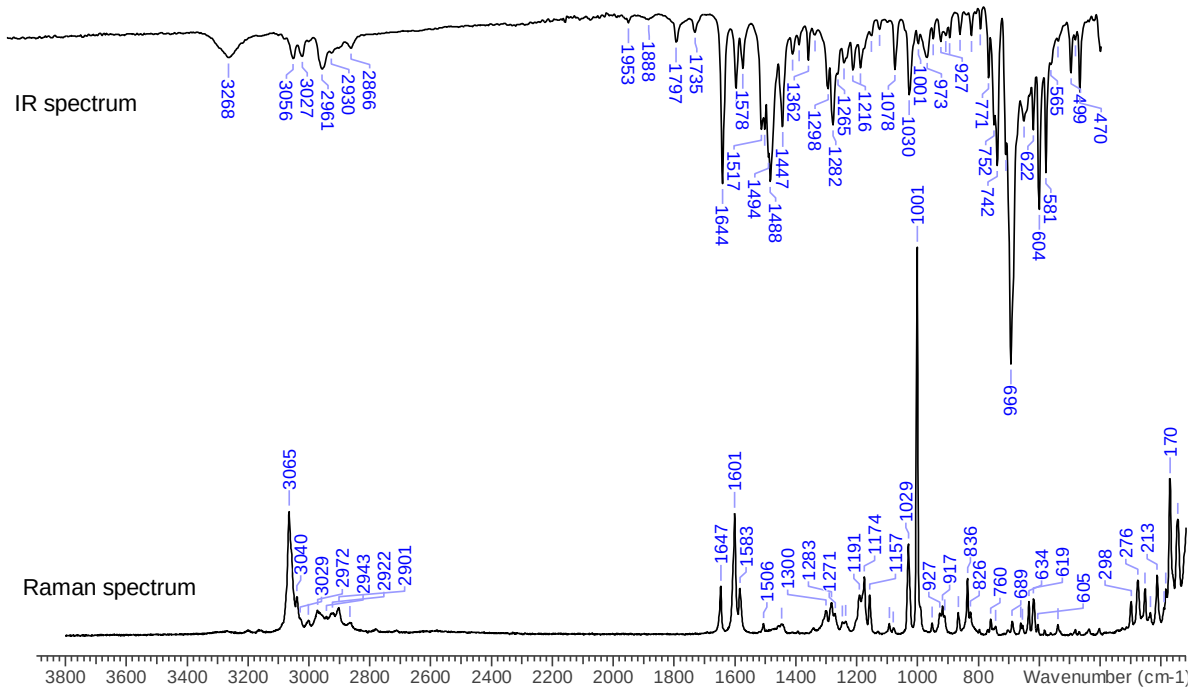
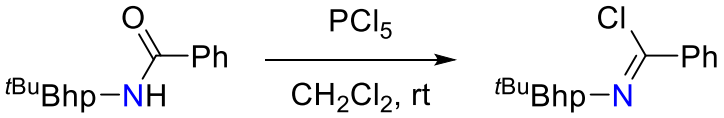


Figure 40. continued.



5.5.2 $^{t\mathrm{Bu}}$Bhp–NC(Cl)Ph (**3**)



The reaction protocol is based on previously published procedures.[81,82]

In a 500 mL Schlenk flask, the amide (18.90 g, 32.27 mmol) and phosphorus pentachloride (13.49 g, 64.79 mmol) are dissolved in anhydrous dichloromethane (200 mL) and the yellow mixture is left stirring at room temperature overnight, leading to a color change to dark green. The next day, all volatiles are removed *in vacuuo* (10^{-3} mbar) and the remaining solid is dried at 110 °C (oil bath) and 10^{-3} mbar for 2 h. The residue is pestled and dried again at 130 °C (oil bath) and 10^{-3} mbar for 5 h, leaving a greyish solid. Yield: 18.65 g (30.87 mmol, 95.7 %).

Formula: $C_{43}H_{38}ClN$. M = 604.23 g/mol. Mp. 165–167 °C. EA found (calcd.) in %: C 85.02 (85.48), H 6.35 (6.34), N 2.25 (2.32). ^{1}H NMR (CD_2Cl_2, 250.1 MHz): δ = 1.12 (s, 9 H, *t*Bu), 5.40 (s, 2 H, C*H*Ph$_2$), 6.94 (s, 2 H, *m*-H (C$_6$*H*$_2$*t*Bu), 7.06 (m, 8 H, *o*-*H*), 7.23 (m, 12 H, *m*-*H* + *p*-*H*), 7.40 (m, 2 H, Ph), 7.53 (tt, ^3J(^{1}H,^{1}H) = 7.3 Hz, ^4J(^{1}H,^{1}H) = 2.2 Hz, 1 H, *p*-*H* (Ph)), 7.73

(m, 2 H, Ph). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 62.9 MHz): δ = 31.5 (s, C(CH_3)$_3$), 34.9 (s, C(CH_3)$_3$), 53.1 (s, $CHPh_2$), 125.7 (s, CH), 126.8 (d, J = 2.3 Hz, CH), 128.7 (d, J = 2.3 Hz, CH), 128.8 (s, CH), 129.9 (d, J = 1.4 Hz, CH), 130.3 (s, CH), 132.6 (s, CH), 133.0 (s, $C_{quat.}$), 135.5 (s, $C_{quat.}$), 143.7 (d, J = 1.8 Hz, $C_{quat.}$), 143.7 (s, $C_{quat.}$), 145.6 (s, $C_{quat.}$), 147.0 (s, $C_{quat.}$). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3086 (vw), 3061 (w), 3026 (w), 3003 (vw), 2962 (w), 2869 (w), 1655 (m), 1599 (w), 1579 (w), 1560 (w), 1492 (m), 1472 (w), 1447 (m), 1412 (w), 1393 (w), 1362 (w), 1241 (w), 1206 (w), 1173 (m), 1101 (w), 1076 (w), 1033 (w), 1002 (w), 892 (m), 820 (w), 800 (w), 769 (m), 761 (m), 740 (m), 697 (vs), 688 (s), 647 (m), 618 (m), 606 (s), 569 (w), 497 (w), 468 (m). Raman (633 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3064 (3), 3004 (1), 2969 (1), 2929 (1), 2900 (1), 2863 (1), 1657 (4), 1641 (2), 1598 (4), 1585 (2), 1531 (1), 1489 (1), 1448 (1), 1306 (1), 1269 (1), 1251 (1), 1238 (1), 1206 (2), 1174 (3), 1157 (2), 1100 (2), 1077 (1), 1031 (3), 1003 (10), 947 (1), 923 (1), 895 (1), 862 (1), 834 (2), 820 (1), 807 (1), 750 (1), 686 (1), 648 (1), 630 (1), 620 (2), 609 (1), 531 (1), 422 (1), 374 (1), 355 (1), 333 (1), 269 (1), 249 (2), 231 (1), 214 (1), 165 (2), 140 (2). MS (CI +, m/z): 605 ($[M+H]^+$), 568 ($[M–Cl]^+$).

Figure 41. ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, IR and Raman spectra of **3** (solvent signals marked by asterisk).

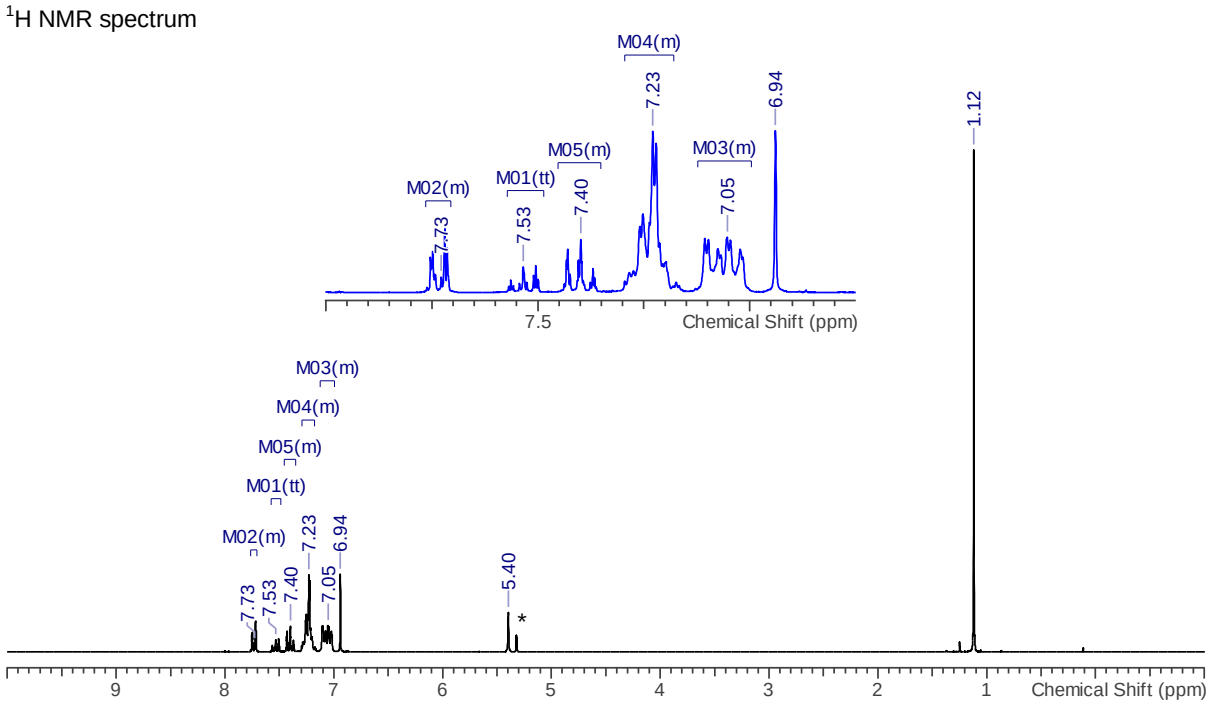
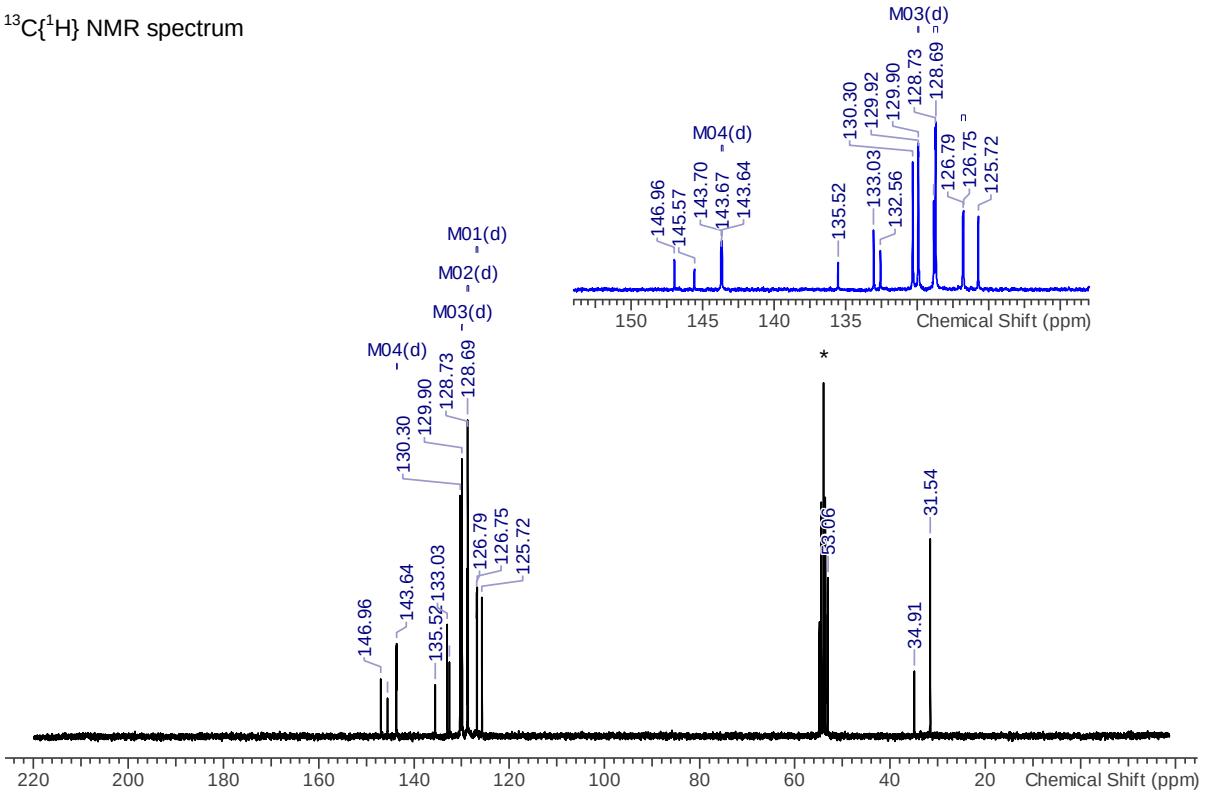
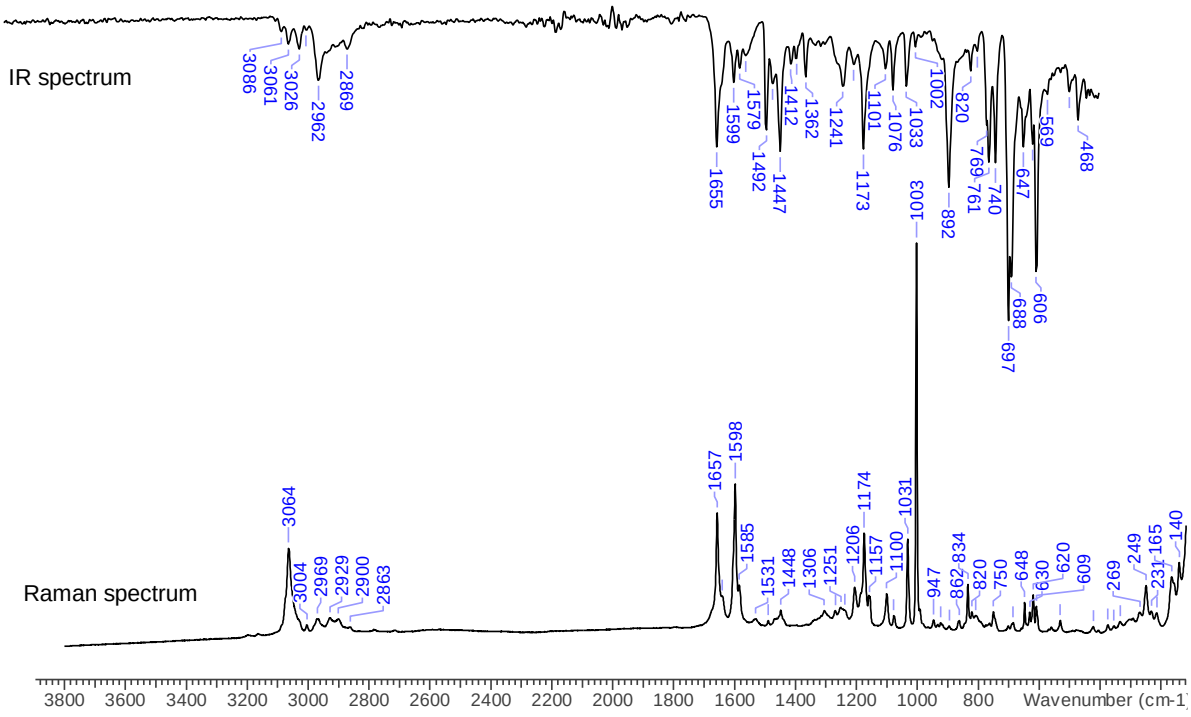


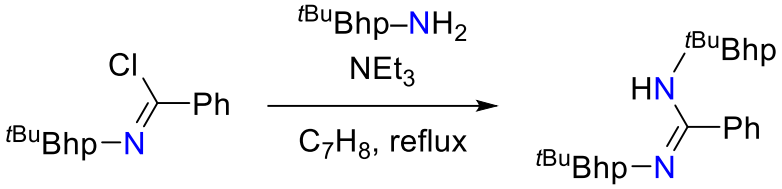
Figure 41. continued.

$^{13}C\{^{1}H\}$ NMR spectrum





5.5.3 $^{t\mathrm{Bu}}$Bhp–NC(Ph)N(H)–$^{t\mathrm{Bu}}$Bhp (**4**)



The reaction protocol is based on previously published procedures.[81,82,84]

In a 500 mL Schlenk flask, the imidoyl chloride (13.76 g, 22.77 mmol) and amine (10.99 g, 22.81 mmol) are dissolved in anhydrous toluene (250 mL). After adding triethylamine (3.70 g, 36.55 mmol), the mixture is left stirring at 135 °C (oil bath) for 10 d. Afterwards, toluene (250 mL) is added and the mixture is washed with a saturated aqueous solution of sodium bicarbonate (100 mL) and water (3 x 150 mL). The organic layer is dried over $MgSO_4$ and volatiles are removed at the rotary evaporator. The brown sticky solid is washed with methanol (200 mL), recrystallized from ethyl acetate to remove residual amide and amine and eventually dried at 130 °C (oil bath) and 10^{-3} mbar for 24 h. Yield: 15.11 g (14.40 mmol, 63.2 %).

Crystals suitable for single-crystal XRD were obtained from a saturated solution in 1,2-dimethoxyethane at room temperature.

Formula: $C_{79}H_{72}N_2$. M = 1049.46 g/mol. Mp. 238–240 °C. EA found (calcd.) in %: C 90.12 (90.42), H 6.74 (6.92), N 2.56 (2.67). ^{1}H NMR (CD_2Cl_2, 500.1 MHz): δ = 1.08 (s, 9 H, *t*Bu), 1.11 (s, 9 H, *t*Bu), 4.99 (s, 1 H, N*H*), 5.94 (s, 2 H, C*H*Ph$_2$), 5.95 (s, 2 H, C*H*Ph$_2$), 6.61 (s, 2 H, C*H*), 6.97 (m, 47 H, C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ = 31.5 (s, C(*C*H$_3$)$_3$), 34.6 (s, *C*(CH$_3$)$_3$), 35.1 (s, *C*(CH$_3$)$_3$), 52.1 (s, *C*HPh$_2$), 53.8 (s, *C*HPh$_2$), 126.1 (s, *C*H), 126.2 (s, *C*H), 126.5 (s, *C*H), 126.8 (s, *C*H), 127.5 (s, *C*H), 128.4 (s, *C*H), 128.8 (s, *C*H), 129.4 (s, *C*H), 129.8 (s, *C*H), 130.0 (s, *C*H), 130.4 (s, *C*H), 134.0 (s, $C_{quat.}$), 135.8 (s, $C_{quat.}$), 142.9 (s, $C_{quat.}$), 143.4 (s, $C_{quat.}$), 143.9 (s, $C_{quat.}$), 144.5 (s, $C_{quat.}$), 145.2 (s, $C_{quat.}$), 146.2 (s, $C_{quat.}$), 149.6 (s, $C_{quat.}$), 155.6 (s, $C_{quat.}$). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3421 (vw), 3390 (vw), 3083 (vw), 3058 (w), 3025 (w), 2959 (w), 2901 (w), 2866 (w), 1949 (vw), 1879 (vw), 1801 (vw), 1737 (vw), 1644 (m), 1599 (w), 1578 (w), 1519 (vw), 1492 (m), 1469 (m), 1447 (m), 1412 (w), 1393 (w), 1362 (w), 1337 (vw), 1298 (w), 1282 (w), 1265 (w), 1243 (w), 1187 (w), 1156 (w), 1131 (w), 1113 (w), 1076 (w), 1049 (vw), 1030 (w), 1001 (w), 983 (vw), 948 (w), 911 (w), 894 (w), 863 (w), 835 (w), 814 (vw), 775 (w), 760 (m), 738 (m), 696 (vs), 645 (m), 633 (w), 622 (m), 606 (m), 585 (m), 548 (w), 517 (w), 507 (w), 490 (w), 480 (w), 470 (m), 441 (w).

Raman (633 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3401 (1), 3392 (1), 3197 (1), 3162 (1), 3060 (4), 3045 (2), 3031 (1), 3004 (1), 2952 (1), 2901 (2), 2863 (1), 2830 (1), 2779 (1), 2710 (1), 1646 (4), 1599 (4), 1584 (2), 1494 (1), 1466 (1), 1455 (1), 1315 (1), 1304 (1), 1267 (1), 1203 (1), 1185 (1), 1171 (2), 1160 (1), 1077 (1), 1031 (3), 1002 (10), 840 (1), 833 (1), 766 (1), 750 (1), 685 (1), 647 (1), 636 (1), 619 (1), 606 (1), 527 (1), 306 (1), 265 (1), 251 (1), 240 (2), 213 (2), 204 (1), 179 (1), 157 (2), 134 (2). MS (APCI +, m/z): 1050 ($[M+H]^+$).

Figure 42. ^{1}H NMR, ^{13}C{^{1}H} NMR, IR and Raman spectra of **4** (solvent signals marked by asterisk).

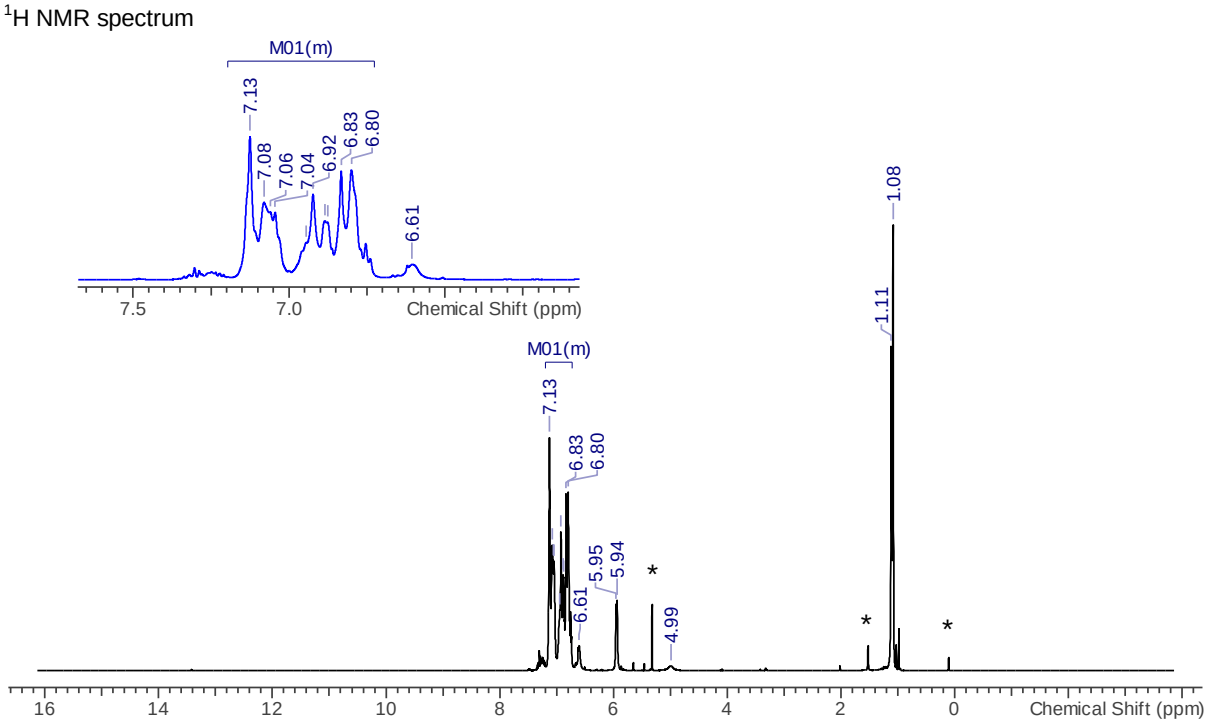
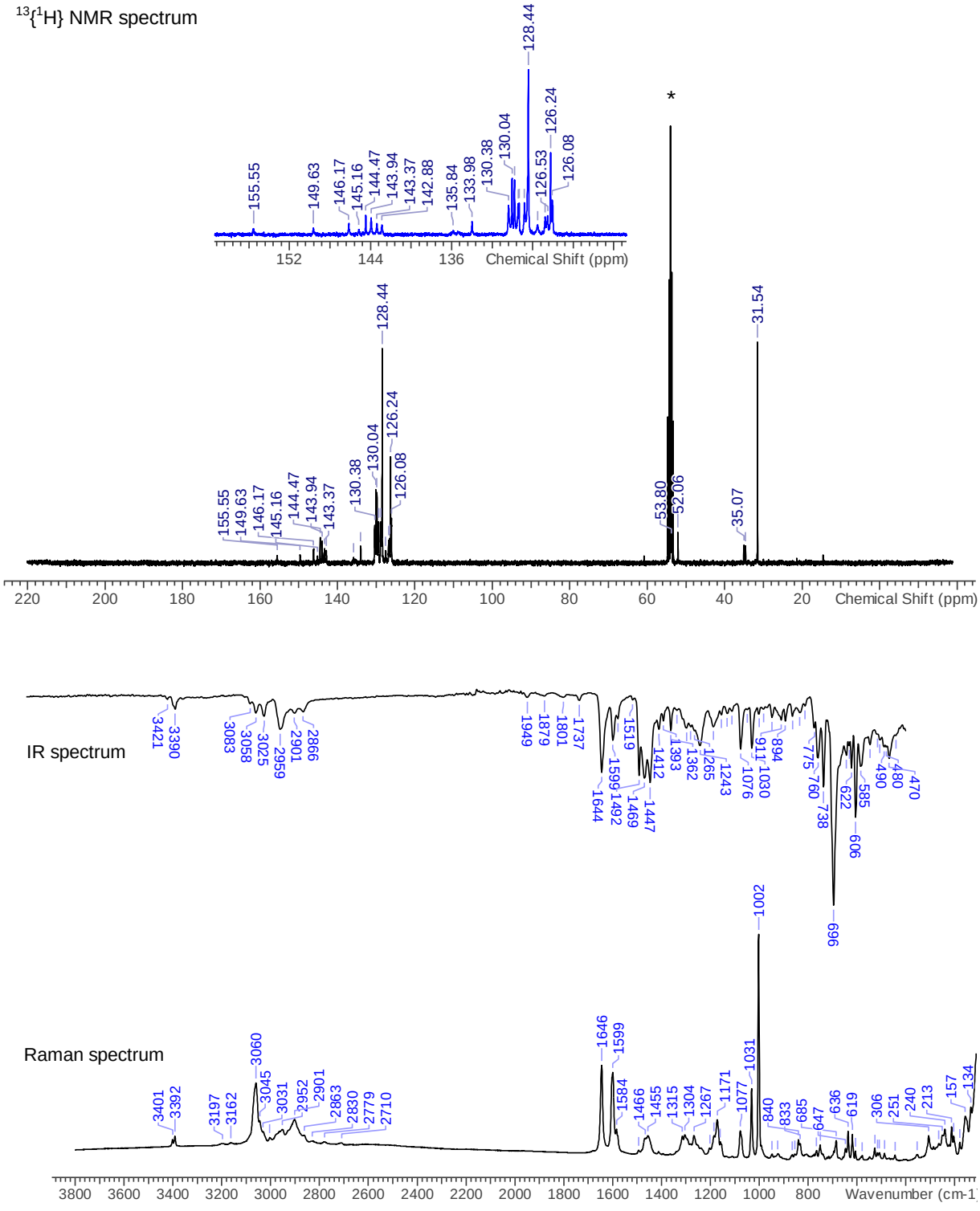
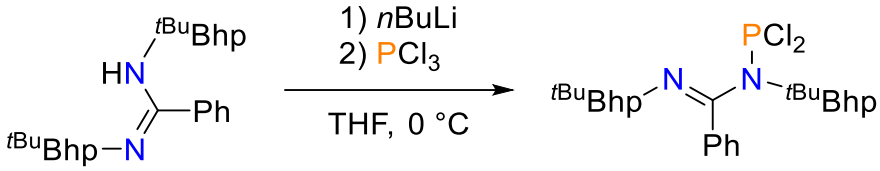


Figure 42. continued.



5.5.4 $^{t\mathrm{Bu}}$Bhp–NC(Ph)N(PCl$_2$)–$^{t\mathrm{Bu}}$Bhp (**5**)



In a 50 mL Schlenk flask, the amidine (2.25 g, 2.14 mmol) is dissolved in anhydrous THF (30 mL). After adding *n*BuLi (2.5 M in hexane, 0.94 mL, 2.35 mmol) at 0 °C (ice bath), the resulting orange-red solution is stirred at room temperature for 1 h. Afterwards, the mixture is cooled again to 0 °C (ice bath) and PCl_3 (0.40 mL, 4.57 mmol) is added via syringe, leading to an immediate color change to light yellow. The mixture is warmed to ambient temperature and left stirring overnight. The next day, all volatiles are removed *in vacuuo* (10^{-3} mbar) and the resulting solid is dissolved in anhydrous benzene (30 mL) and filtered over celite. Concentrating the solution leads to a pale yellow solid, which is isolated and eventually dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 2.25 g (1.95 mmol, 91.1 %).

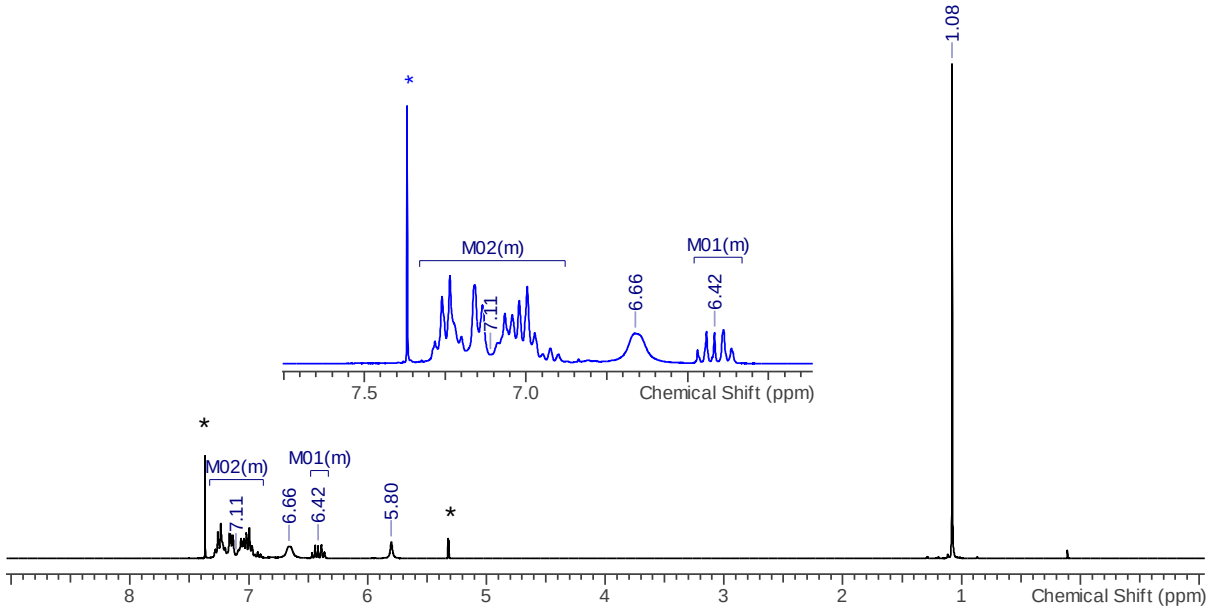
Crystals suitable for single-crystal XRD were obtained from a saturated solution in 1,2-dimethoxyethane at room temperature.

Formula: $C_{79}H_{71}Cl_2N_2P$. M = 1150.32 g/mol. Mp. 240–243 °C. EA found (calcd.) in %: C 82.54 (82.49), H 6.23 (6.22), N 2.66 (2.44). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.08 (s, 18 H, *t*Bu), 5.80 (s, 4 H, C*H*Ph$_2$), 6.42 (m, 4 H, C*H*), 6.66 (s, 8 H, C*H*), 7.11 (m, 37 H, C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ = 31.2 (s, C(*C*H$_3$)$_3$), 35.0 (s, *C*(CH$_3$)$_3$), 52.4 (s, *C*HPh$_2$), 126.6 (s, *C*H), 127.7 (s, *C*H), 128.4 (s, *C*H), 128.7 (s, *C*H), 130.2 (s, *C*H), 130.4 (s, *C*H), 131.4 (s, *C*H), 137.0 (s, $C_{quat.}$), 138.9 (s, $C_{quat.}$), 143.7 (s, $C_{quat.}$), 145.3 (s, $C_{quat.}$), 148.9 (s, $C_{quat.}$), 160.8 (d, J = 25 Hz, $C_{quat.}$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ = 112.9 (s, *P*Cl$_2$). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3084 (vw), 3059 (w), 3026 (w), 2962 (w), 2863 (w), 1804 (vw), 1602 (m), 1575 (w), 1494 (m), 1474 (w), 1445 (m), 1414 (w), 1393 (w), 1362 (w), 1340 (w), 1329 (w), 1296 (m), 1253 (w), 1243 (w), 1181 (w), 1156 (w), 1140 (w), 1105 (w), 1088 (w), 1078 (w), 1031 (w), 1002 (w), 975 (w), 950 (w), 915 (w), 895 (w), 860 (w), 833 (w), 814 (vw), 798 (w), 781 (w), 763 (m), 740 (m), 726 (w), 697 (vs), 649 (w), 633 (w), 622 (w), 606 (m), 579 (m), 548 (w), 524 (w), 493 (m), 480 (m), 466 (m), 445 (m), 423 (w). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3066 (2), 3061 (2), 3055 (2), 3047 (2), 3042 (1), 3028 (1), 3003 (1), 2925 (1), 2902 (1), 2891 (1), 2863 (1), 1601 (4), 1584 (1), 1339 (1), 1305 (1), 1298 (1), 1182 (1), 1171 (1), 1161 (1), 1088 (1), 1029 (3), 1002 (10), 990 (1), 834 (1), 807 (1), 744 (1), 618 (1), 491 (1), 351 (1), 332 (1),

301 (1), 252 (1), 237 (1), 231 (1), 219 (1), 186 (1), 163 (3), 144 (1), 123 (2), 105 (3). MS (CI +, m/z): 1117 ([M–Cl]$^+$), 1050 ([M–PCl_2+2H]$^+$).

Figure 43. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, IR and Raman spectra of **5** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

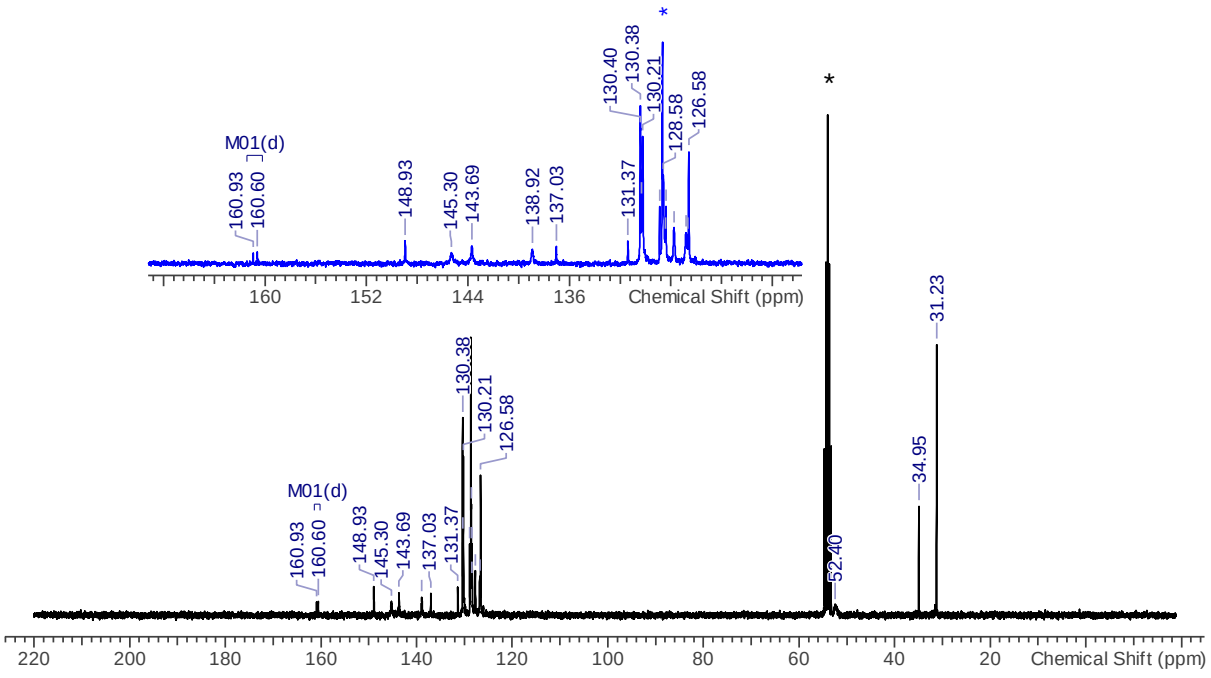
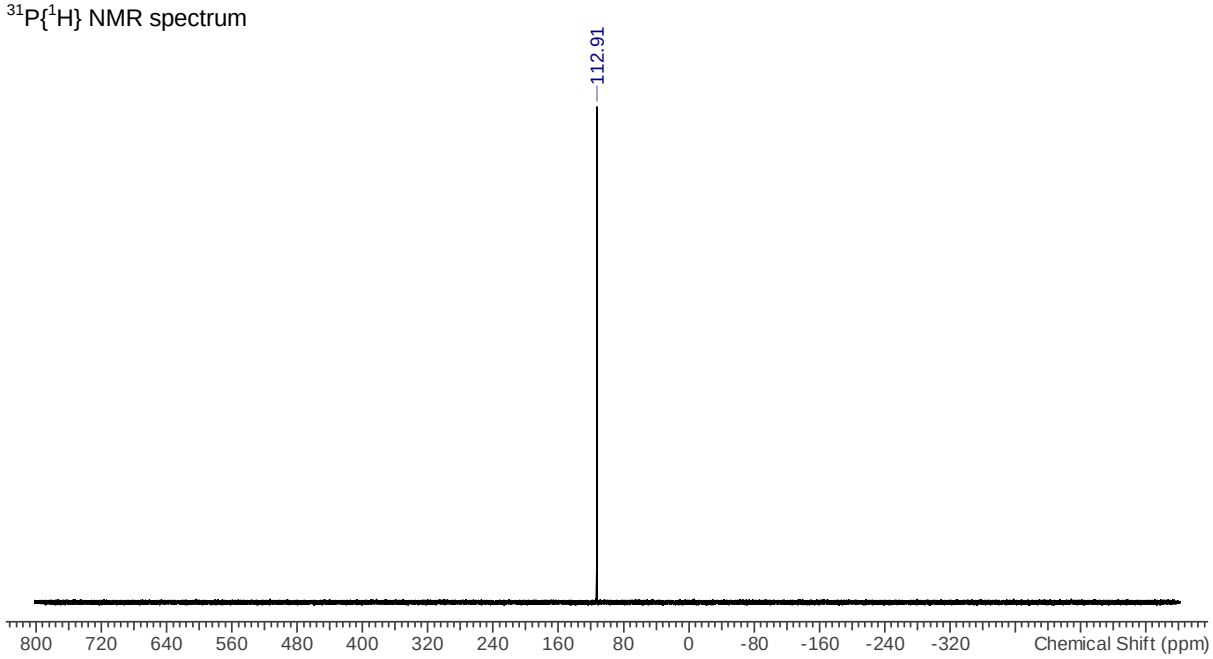
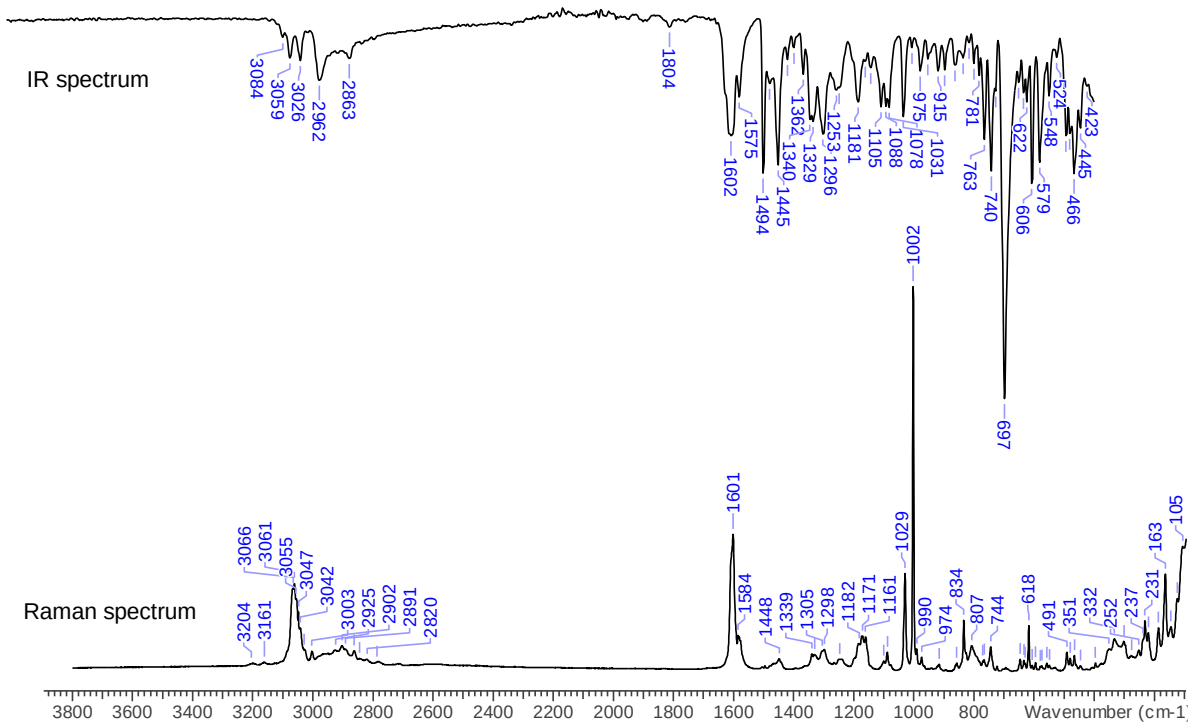


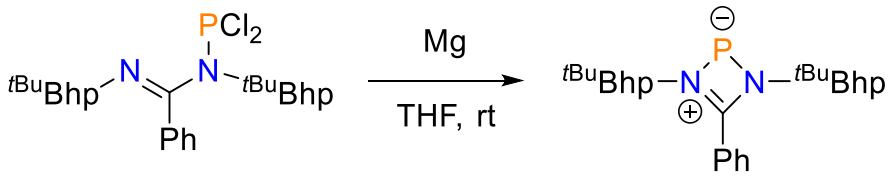
Figure 43. continued.

$^{31}P\{^{1}H\}$ NMR spectrum





5.5.5 $^{t\mathrm{Bu}}$Bhp–[NC(Ph)NP]–$^{t\mathrm{Bu}}$Bhp (**6**)



In a 50 mL Schlenk flask, the dichlorophosphorusamidinate (1.91 g, 1.66 mmol) and magnesium turnings (1.31 g, 53.81 mmol) are dissolved in anhydrous THF (30 mL). The reaction can be accelerated by sonication in an ultrasonic bath (37 kHz), resulting in a color change from pale yellow to orange, and the mixture is left stirring at room temperature. The reaction progress should be monitored via ^{31}P NMR spectroscopy. Upon full conversion (~ 4–6 h), all volatiles are removed *in vacuuo* (10^{-3} mbar) and the solid material is dried for an additional 30 min. Anhydrous benzene (30 mL) is added, residues are allowed to settle and insoluble components are removed by filtration over celite. The solution is concentrated, yielding an orange solid, which is isolated and eventually dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 1.30 g (1.20 mmol, 72.6 %).

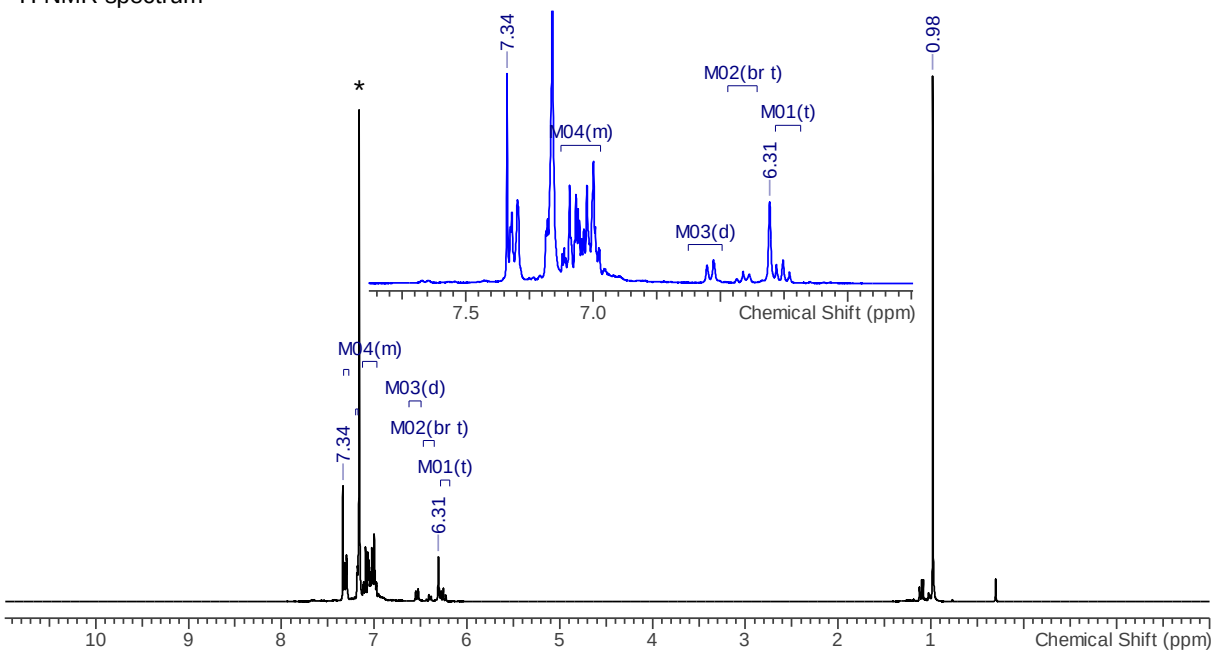
Crystals suitable for single-crystal XRD were obtained from a saturated solution in 1,2-dimethoxyethane at room temperature.

Formula: $C_{79}H_{71}N_2P$. M = 1079.42 g/mol. Mp. 226–229 °C. EA found (calcd.) in %: C 87.45 (87.91), H 6.24 (6.63), N 2.33 (2.60). ^{1}H NMR (C_6D_6, 500.1 MHz): δ = 0.98 (s, 18 H, *t*Bu), 6.25 (t, $^3J(^1H,^1H)$ = 7.7 Hz, 2 H, *m*-H (Ph)), 6.31 (s, 4 H, C*H*Ph$_2$), 6.41 (t, $^3J(^1H,^1H)$ = 7.5 Hz, 1 H, *p*-H (Ph)), 6.54 (d, $^3J(^1H,^1H)$ = 7.6 Hz, 2 H, *o*-H (Ph)), 7.04 (m, 28 H, C*H*), 7.18 (s, 4 H, C*H*), 7.31 (d, $^3J(^1H,^1H)$ = 7.5 Hz, 8 H, C*H*), 7.34 (s, 4 H, C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): δ = 31.4 (s, C(*C*H$_3$)$_3$), 35.1 (s, *C*(CH$_3$)$_3$), 52.2 (s, *C*HPh$_2$), 126.5 (s, *C*H), 127.0 (s, *C*H), 127.2 (s, *C*H), 128.7 (s, *C*H), 128.8 (s, *C*H), 129.1 (s, *C*H), 130.2 (s, *C*H), 135.5 (s, *C*$_{quat.}$), 141.9 (s, *C*$_{quat.}$), 144.0 (s, *C*$_{quat.}$), 146.5 (s, *C*$_{quat.}$), 150.8 (s, *C*$_{quat.}$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ = 407.9 (s, N*P*N). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3084 (vw), 3059 (w), 3024 (w), 2962 (w), 2869 (w), 2811 (vw), 1593 (w), 1509 (w), 1492 (m), 1476 (w), 1447 (m), 1414 (w), 1393 (w), 1364 (m), 1329 (w), 1296 (w), 1255 (w), 1200 (w), 1181 (w), 1156 (w), 1136 (w), 1107 (w), 1076 (w), 1031 (w), 1002 (vw), 993 (vw), 983 (vw), 950 (vw), 919 (w), 895 (w), 864 (w), 808 (vw), 791 (vw), 761 (w), 736 (w), 719 (m), 695 (vs), 684 (m), 655 (w), 635 (w), 622 (w), 604 (s), 583 (w), 548 (w), 532 (w), 499 (w), 472 (w), 435 (w), 408 (w). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3057 (2), 1632 (1), 1594 (10), 1573 (1), 1510 (10), 1476 (1), 1461 (1), 1436

(5), 1363 (1), 1342 (1), 1330 (1), 1182 (5), 1158 (1), 1138 (1), 1092 (2), 1032 (1), 1003 (4), 996 (9), 990 (3), 945 (1), 770 (1), 633 (1), 620 (1), 592 (1), 479 (1), 404 (1), 361 (1), 333 (1), 298 (1), 239 (1), 183 (1), 172 (1), 155 (1), 126 (3). UV/Vis (benzene, 0.06 mM): 430 nm (ε = 13517 M^{-1} cm^{-1}). MS (CI +, m/z): 1050 ($[M–P+2H]^+$).

Figure 44. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, IR, Raman and UV/Vis spectra of **6** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

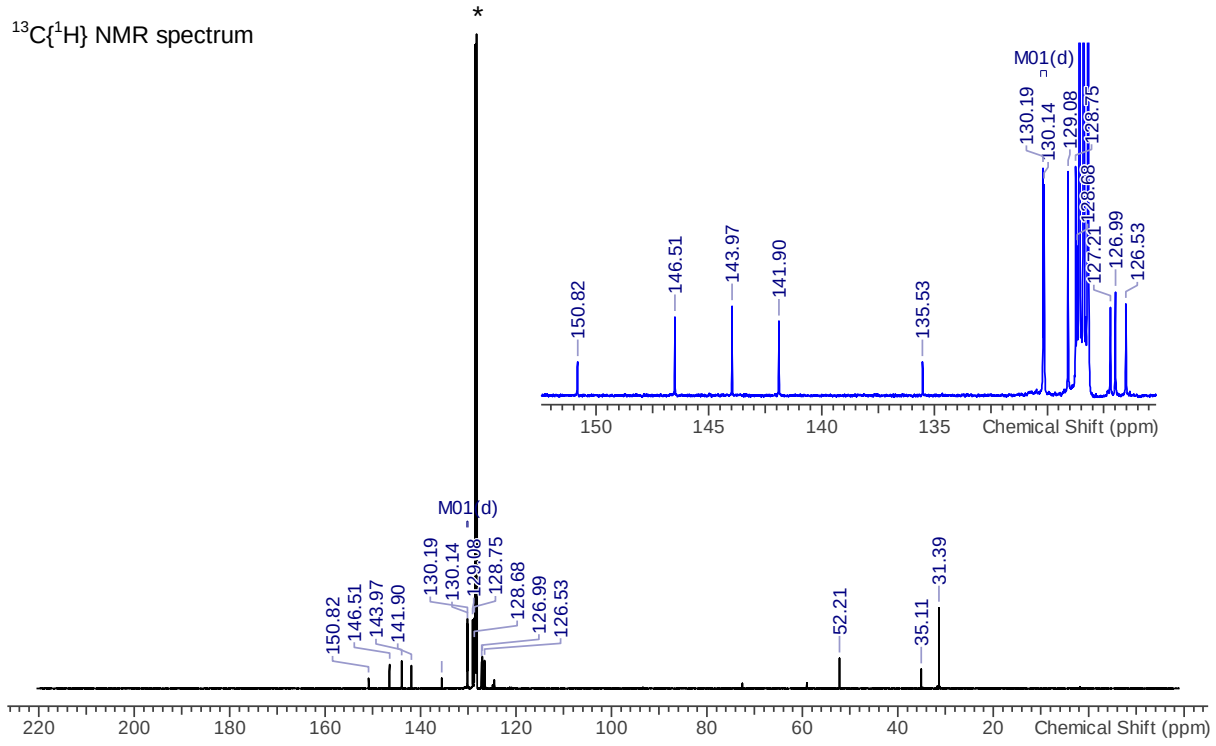


Figure 44. continued.

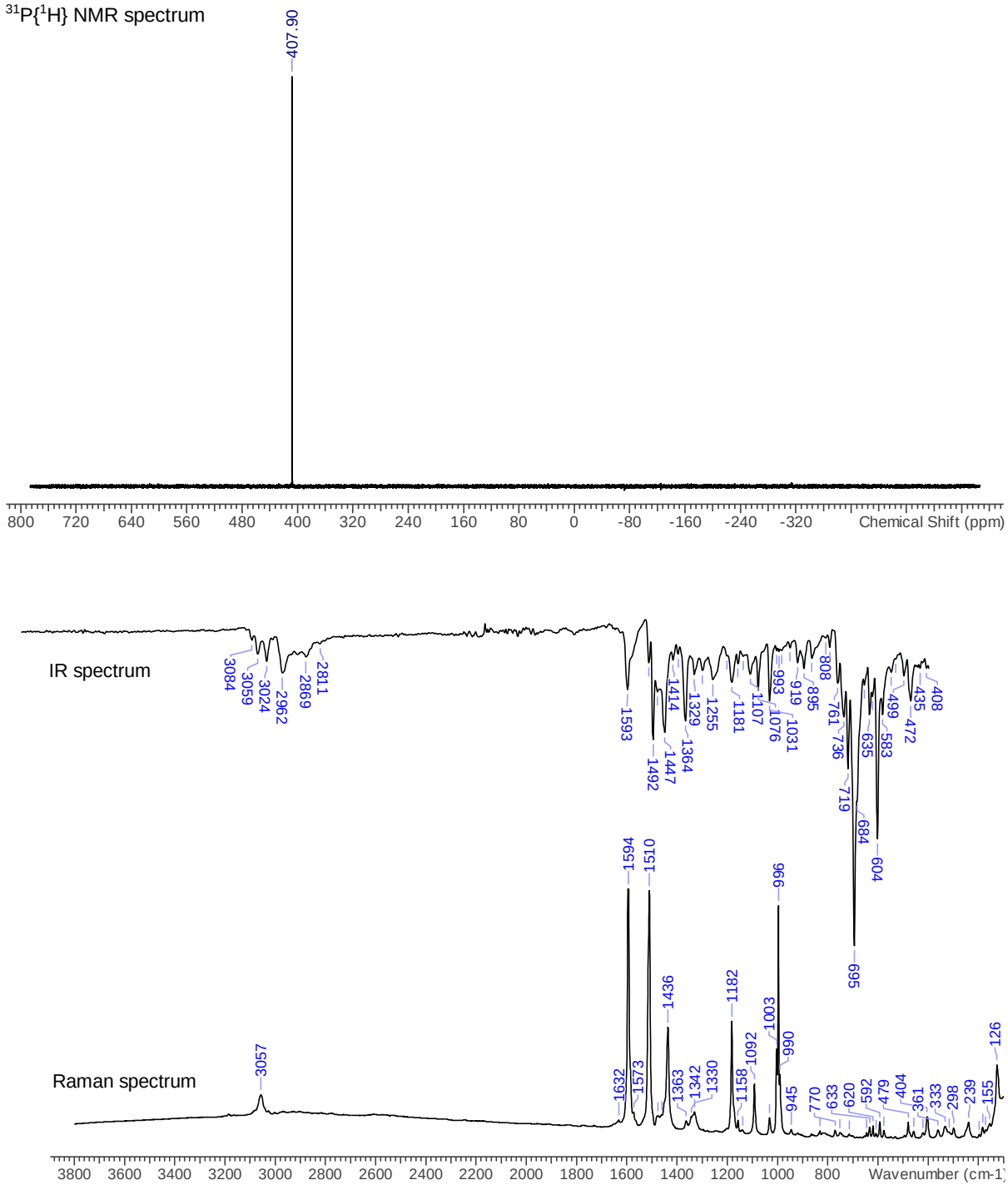
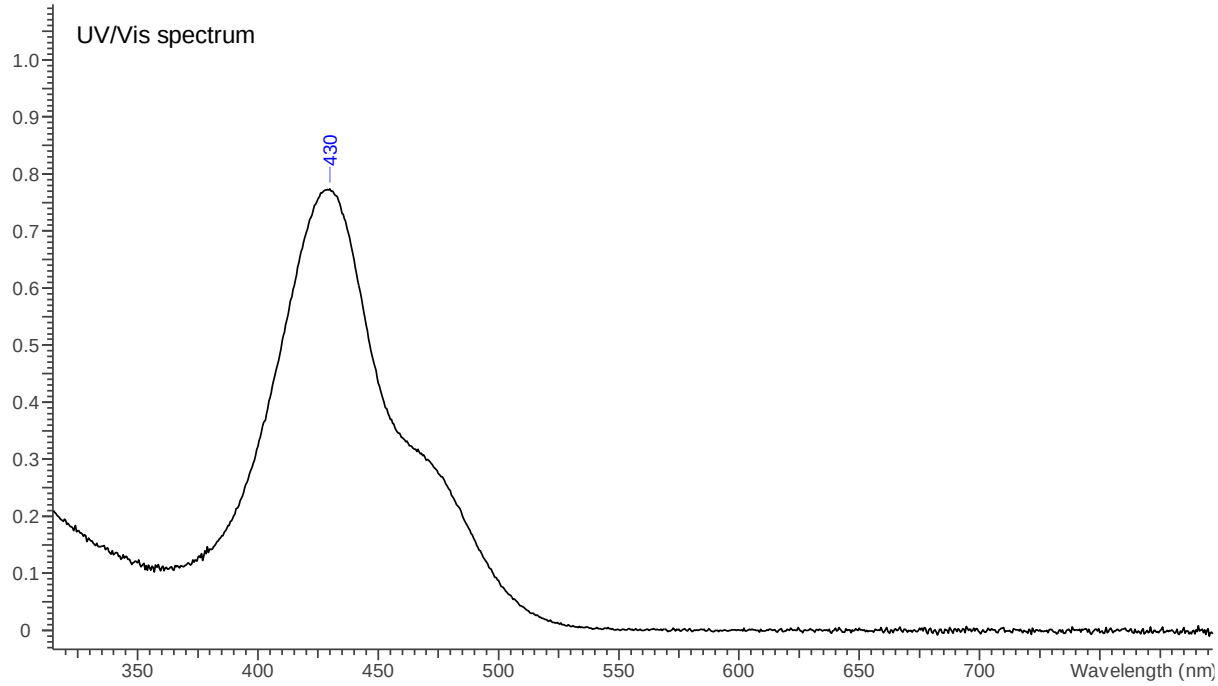
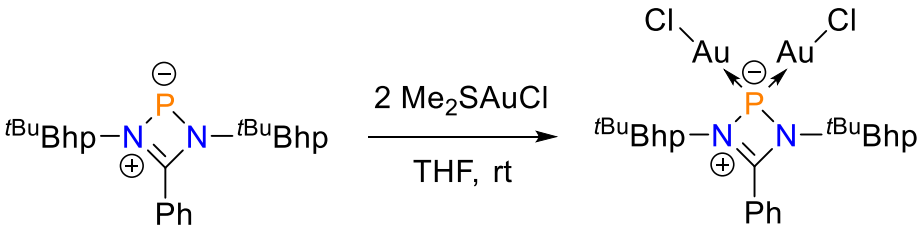


Figure 44. continued.



5.5.6 $^{t\mathrm{Bu}}$Bhp–[NC(Ph)NP]–$^{t\mathrm{Bu}}$Bhp • 2 AuCl (**8**)



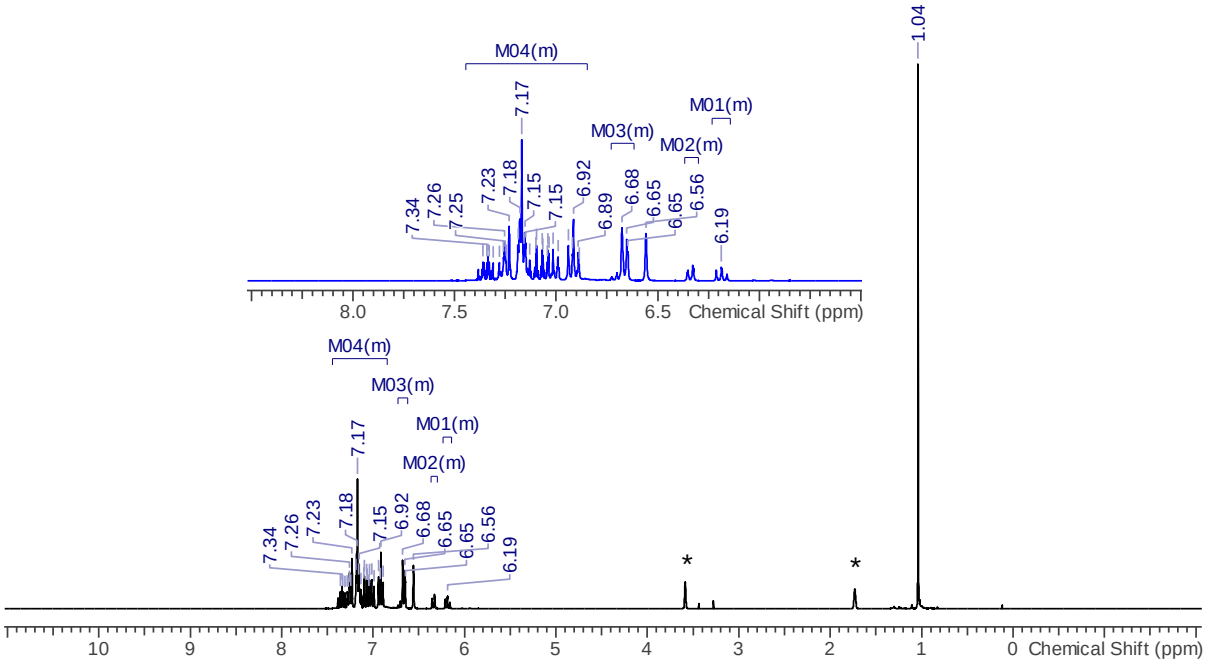
A suspension of chloro(dimethyl sulfide)gold(I) (0.08 g, 0.28 mmol) in anhydrous THF (5 mL) is added dropwise to a solution of **6** (0.15 g, 0.14 mmol) in anhydrous THF (3 mL), resulting in a color change from orange to golden yellow. After stirring for 30 min, volatiles are removed *in vacuuo* (10^{-3} mbar). The solid is dissolved in anhydrous fluorobenzene (5 mL), filtered and concentrated, yielding **8** as colorless crystals. If necessary, filtration is repeated multiple times to remove gold precipitations. The crystals are eventually dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 0.13 g (0.08 mmol, 60.1 %).

Crystals suitable for single-crystal XRD were obtained from a saturated solution in fluorobenzene at room temperature.

Formula: $C_{79}H_{71}Au_2Cl_2N_2P•3(C_6H_5F)$. M = 1832.57 g/mol. Mp. 110 °C (decomp.). EA found (calcd.) in %: C 63.90 (63.58), H 4.55 (4.73), N 1.47 (1.53). ^{1}H NMR (THF-d_8, 300.1 MHz): δ = 1.04 (s, 18 H, *t*Bu), 6.19 (m, 2 H, *m*-H (Ph)), 6.34 (m, 2 H, *o*-H (Ph)), 6.56 (s, 4 H, C*H*Ph_2), 6.66 (m, 8 H, *p*-H (Ph)), 7.13 (m, 37 H, *m*-H + *o*-H + *p*-H (Ph)). ^{13}C{^{1}H} NMR (THF-d_8, 75.5 MHz): δ = 31.0 (s, C(*C*H_3)$_3$), 35.5 (s, *C*(CH_3)$_3$), 53.3 (s, *C*HPh_2), 116.0 (d, *J* = 20.9 Hz, *C*H), 127.5 (d, *J* = 19.3 Hz, *C*H), 129.4 (d, *J* = 5.5 Hz, *C*H), 129.8 (s, *C*H), 130.4 (s, *C*H), 130.5 (s, *C*H), 130.9 (s, *C*H), 141.8 (s, $C_{quat.}$), 141.9 (s, $C_{quat.}$), 145.4 (s, $C_{quat.}$), 152.9 (s, $C_{quat.}$), 162.3 (s, $C_{quat.}$), 165.6 (s, $C_{quat.}$). ^{31}P{^{1}H} NMR (THF-d_8, 121.5 MHz): δ = 262.7 (s, N*P*N). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3119 (vw), 3102 (vw), 3086 (w), 3059 (w), 3028 (w), 2954 (w), 2904 (w), 2869 (w), 1595 (m), 1566 (vw), 1523 (w), 1492 (m), 1478 (m), 1455 (m), 1445 (m), 1414 (w), 1379 (m), 1364 (w), 1332 (w), 1309 (m), 1263 (m), 1233 (m), 1214 (s), 1173 (m), 1152 (m), 1103 (m), 1078 (m), 1064 (m), 1031 (w), 991 (m), 983 (m), 950 (w), 915 (w), 897 (w), 874 (w), 860 (w), 851 (w), 831 (w), 804 (m), 791 (w), 767 (m), 752 (m), 738 (s), 717 (m), 697 (vs), 686 (s), 651 (m), 633 (m), 625 (m), 602 (m), 581 (m), 561 (m), 532 (w), 517 (m), 509 (m), 499 (s), 476 (m), 464 (s), 443 (m), 425 (w), 402 (m). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3062 (3), 3015 (2), 1596 (10), 1524 (8), 1478 (3), 1466 (2), 1451 (2), 1444 (2), 1332 (1), 1184 (1), 1170 (1), 1031 (2), 1006 (4), 995 (2), 834 (1), 829 (1), 806 (2), 769 (1), 748 (1), 738 (1), 659 (1), 653 (1), 637 (1), 632 (1), 620 (1), 583 (1), 465 (2), 397 (1), 345 (2), 335 (1), 316 (1), 299 (1), 270 (1), 252 (1), 239 (1), 230 (1), 217 (1), 177 (4), 162 (1). MS (CI +, m/z): 1050 ([M–P$(AuCl)_2$+2H]$^{+}$).

Figure 45. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, IR and Raman spectra of **8** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

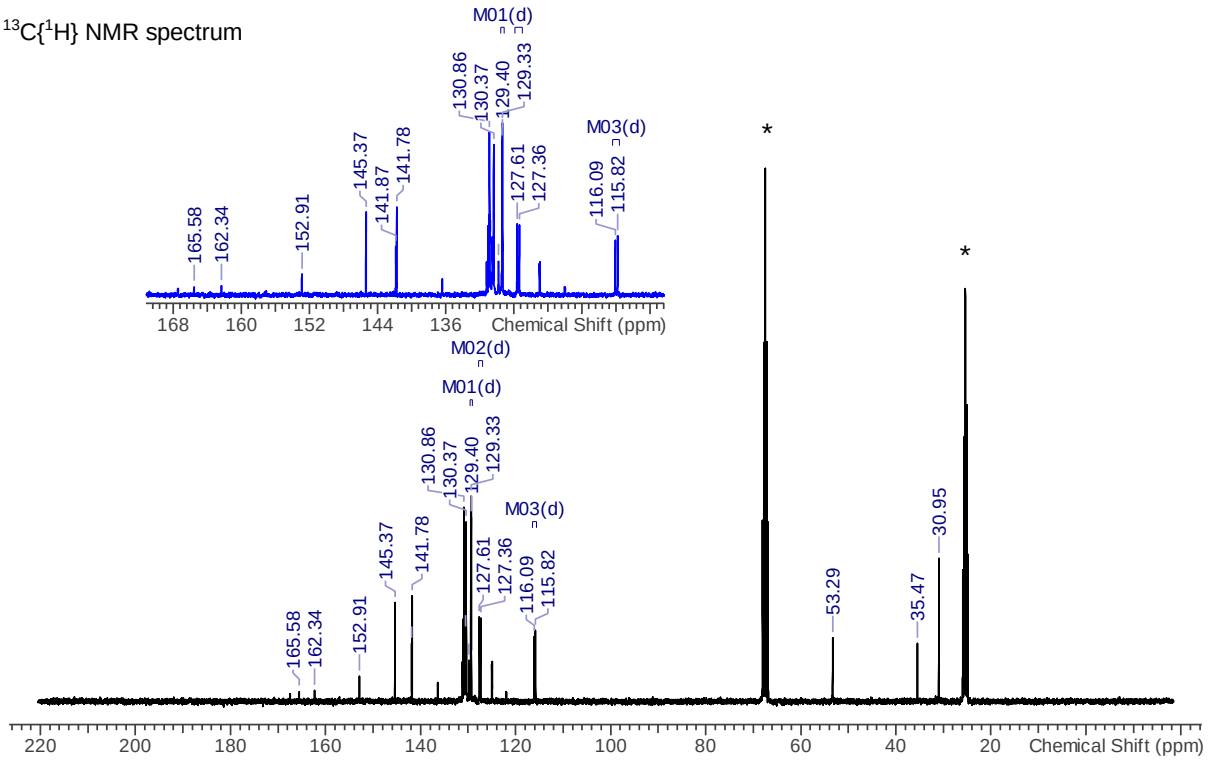
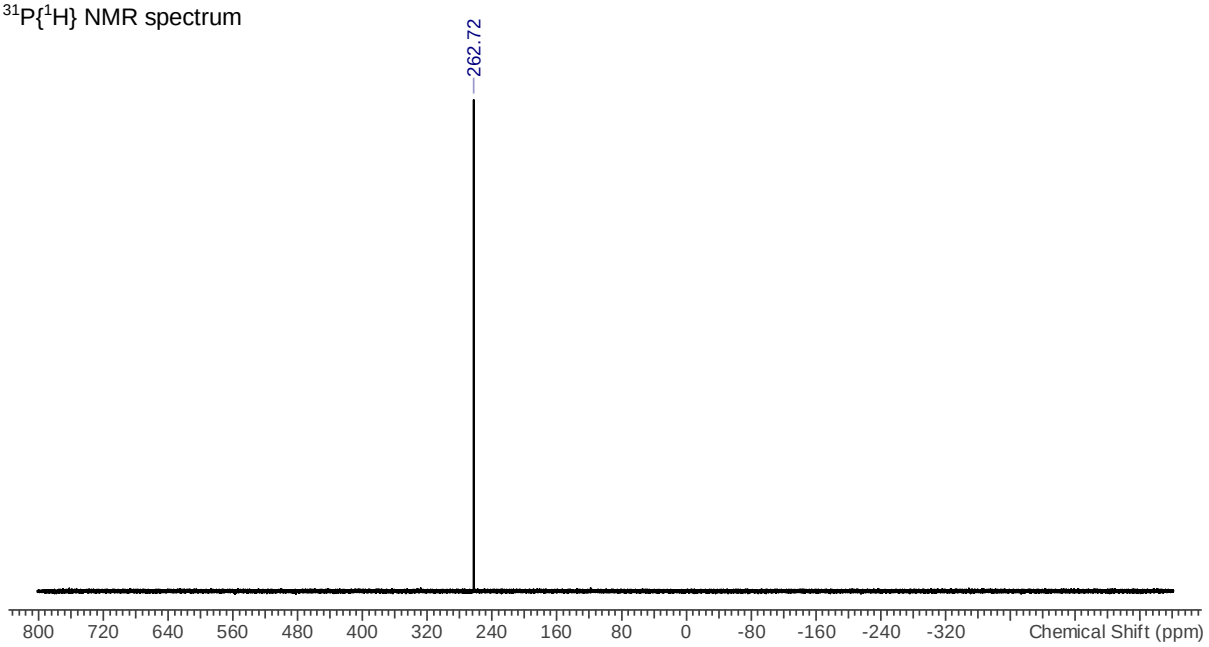
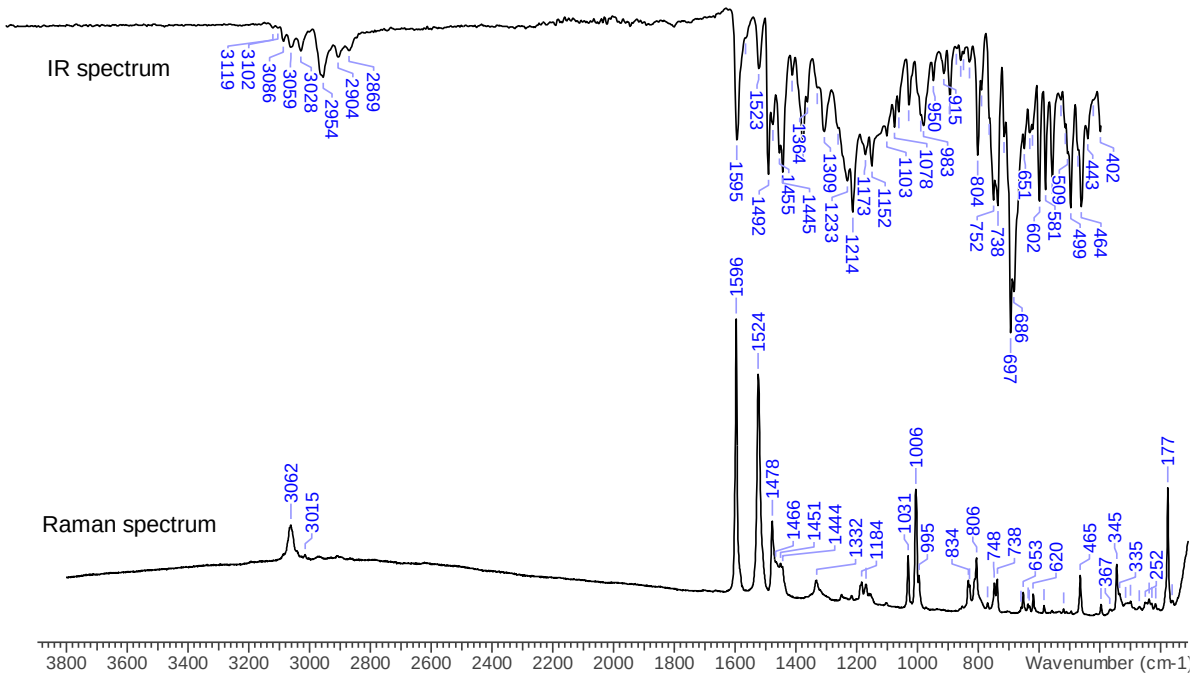


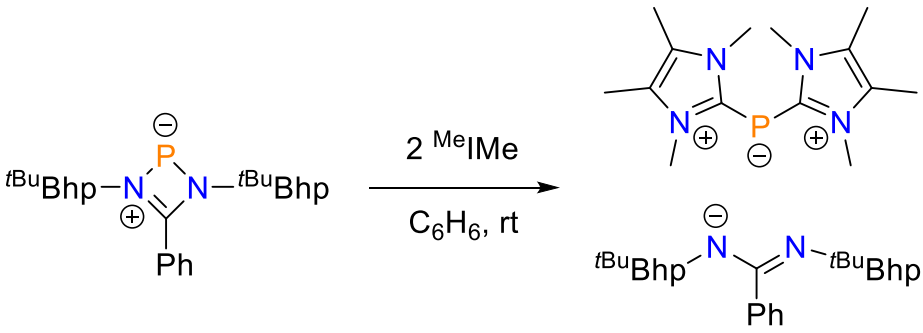
Figure 45. continued.

$^{31}P\{^{1}H\}$ NMR spectrum





5.5.7 [(^{Me}IMe)$_2$P][^{tBu}Bhp–NC(Ph)N–^{tBu}Bhp] (**9**)



A solution of ^{Me}IMe (0.05 g, 0.37 mmol) in anhydrous THF (3 mL) is added dropwise to a solution of **6** (0.20 g, 0.19 mmol) in anhydrous THF (3 mL), resulting in a color change from orange to yellow. After stirring for 1 h, volatiles are removed *in vacuuo* (10^{-3} mbar). The solid is dissolved in anhydrous benzene (8 mL), filtered and concentrated, resulting in yellow block-shaped crystals, which are dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 0.15 g (0.12 mmol, 60.7 %).

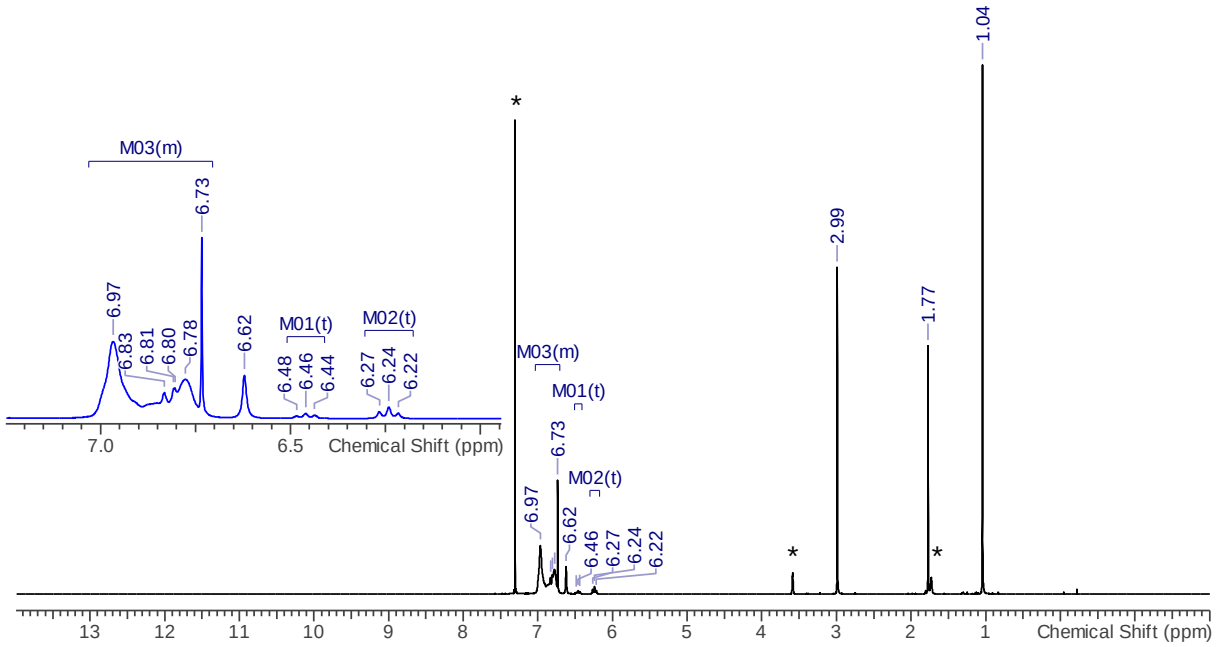
Crystals suitable for single-crystal XRD were obtained from a saturated solution in benzene at room temperature.

Formula: $C_{93}H_{95}N_4P$. M = 1299.78 g/mol. Mp. 135–138 °C. EA found (calcd.) in %: C 85.53 (85.94), H 7.68 (7.37), N 4.69 (4.31). ^{1}H NMR (THF-d$_8$, 300.1 MHz): δ = 1.04 (s, 18 H, *t*Bu), 1.77 (s, 12 H, C(C*H*$_3$) (^{Me}IMe)), 2.99 (s, 12 H, N(C*H*$_3$) (^{Me}IMe)), 6.24 (t, ^3J(^{1}H,^{1}H) = 7.4 Hz, 2 H, *o*-H (Ph)), 6.46 (t, ^3J(^{1}H,^{1}H) = 7.2 Hz, 1 H, *p*-H (Ph)), 6.62 (s, 4 H, C*H*Ph$_2$), 6.80 (m, 46 H, C*H*). ^{13}C{^{1}H} NMR (THF-d$_8$, 62.9 MHz): δ = 8.9 (s, C(*C*H$_3$) (^{Me}IMe)), 32.2 (s, C(*C*H$_3$)$_3$), 33.4 (d, ^3J(^{13}C,^{31}P) = 8.2 Hz, N(*C*H$_3$) (^{Me}IMe)), 34.5 (s, *C*(CH$_3$)$_3$), 52.3 (s, *C*HPh$_2$), 124.9 (s, *C*H), 125.9 (s, *C*H), 126.0 (s, *C*H), 126.9 (d, J(^{13}C,^{31}P) = 2.8 Hz, C$_{quat.}$), 127.8 (s, *C*H), 129.1 (s, *C*H), 130.7 (s, *C*H), 131.1 (s, *C*H), 136.7 (s, C$_{quat.}$), 138.0 (s, C$_{quat.}$), 147.0 (s, C$_{quat.}$), 149.2 (s, C$_{quat.}$), 157.5 (s, C$_{quat.}$), 157.9 (s, C$_{quat.}$), 158.9 (s, C$_{quat.}$). ^{31}P{^{1}H} NMR (THF-d$_8$, 121.5 MHz): δ = –112.2 (s, C*P*C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3389 (vw), 3081 (vw), 3055 (w), 3024 (w), 2960 (w), 2950 (w), 2900 (w), 2863 (w), 1639 (w), 1597 (w), 1577 (w), 1492 (m), 1480 (m), 1439 (m), 1387 (m), 1360 (w), 1303 (m), 1235 (vs), 1181 (s), 1123 (s), 1109 (s), 1074 (m), 1031 (m), 981 (s), 950 (w), 919 (w), 911 (w), 901 (w), 851 (w), 827 (w), 810 (w), 789 (w), 779 (w), 763 (m), 738 (m), 717 (m), 697 (s), 678 (s), 635 (m), 622 (m), 606 (m), 589 (m), 579 (m), 563 (m), 554 (m), 524 (m), 499 (m), 470 (m). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3098 (1), 3059 (3), 3052 (3), 3038 (1), 3024 (1), 2995 (1), 2949 (1), 2932 (2), 2902 (2), 2898 (2),

2861 (1), 2773 (1), 2704 (1), 1660 (1), 1639 (1), 1605 (6), 1584 (1), 1500 (2), 1488 (1), 1458 (5), 1444 (3), 1421 (2), 1412 (2), 1399 (7), 1388 (6), 1377 (3), 1353 (1), 1318 (1), 1302 (2), 1284 (1), 1275 (1), 1254 (1), 1229 (1), 1198 (1), 1170 (2), 1155 (1), 1138 (1), 1103 (2), 1095 (2), 1080 (1), 1030 (2), 1002 (10), 992 (5), 972 (1), 952 (1), 921 (1), 854 (1), 837 (1), 828 (1), 781 (1), 766 (1), 750 (1), 740 (1), 720 (1), 700 (4), 690 (1), 680 (2), 646 (2), 635 (2), 625 (1), 619 (1), 608 (1), 601 (1), 587 (1), 579 (1), 563 (1), 553 (1), 527 (1), 487 (1), 454 (1), 353 (1), 316 (1), 304 (2), 284 (1), 274 (2), 247 (3), 224 (2), 212 (3), 186 (2), 167 (2), 146 (3), 136 (3). MS (ESI +, m/z): 279 ($[(^{Me}IMe)_2P]^+$). MS (ESI –, m/z): 1048 ($[^{tBu}Bhp–NC(Ph)N–^{tBu}Bhp]^-$).

Figure 46. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, IR and Raman spectra of **9** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

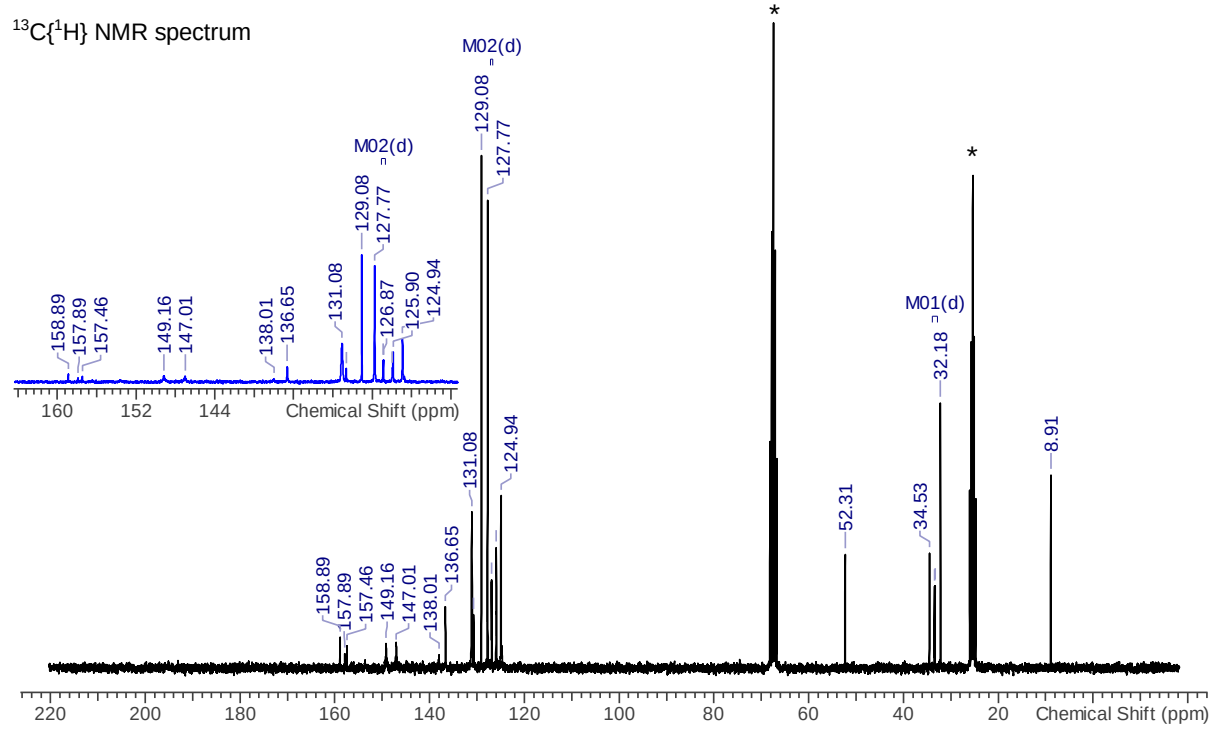
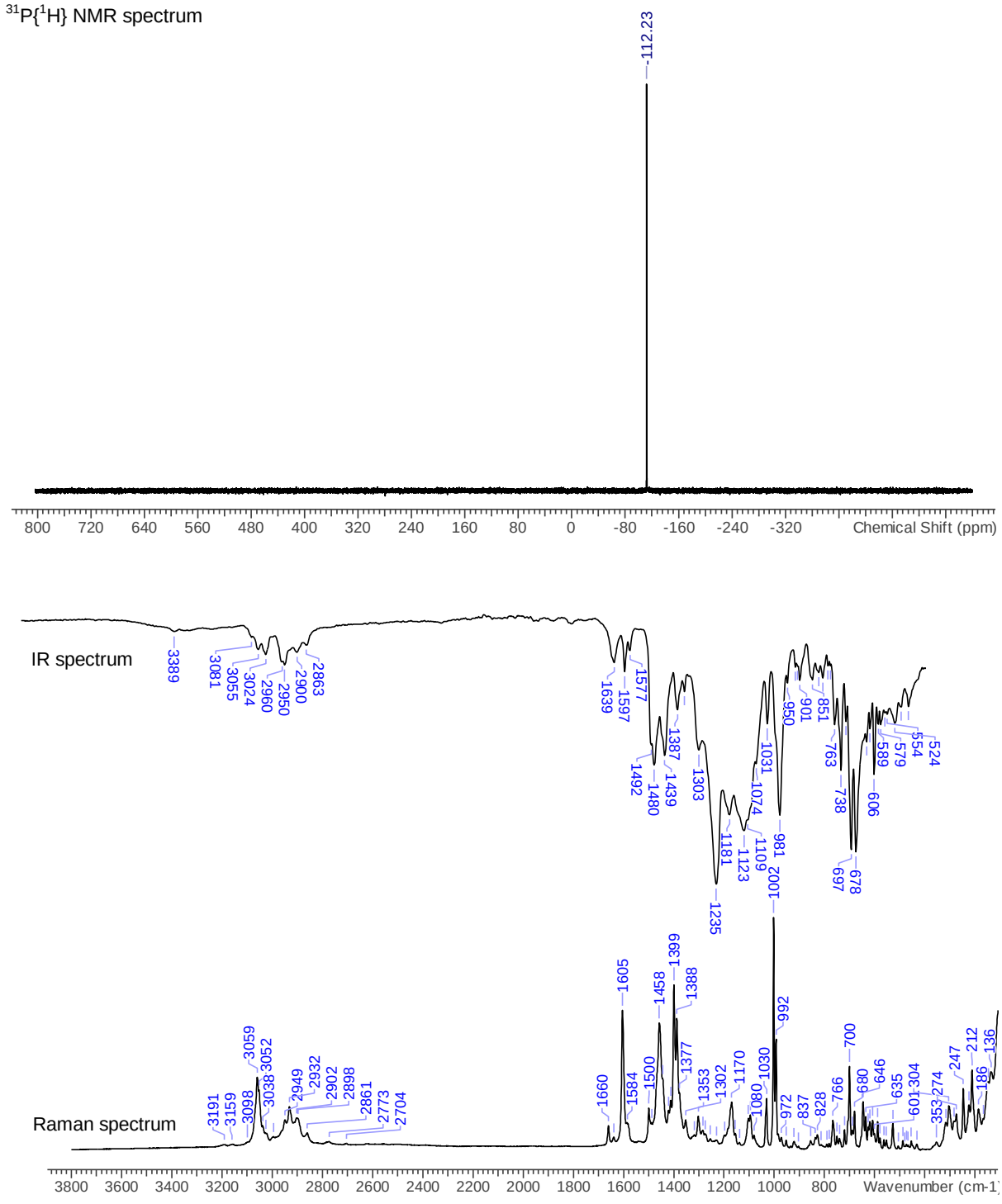
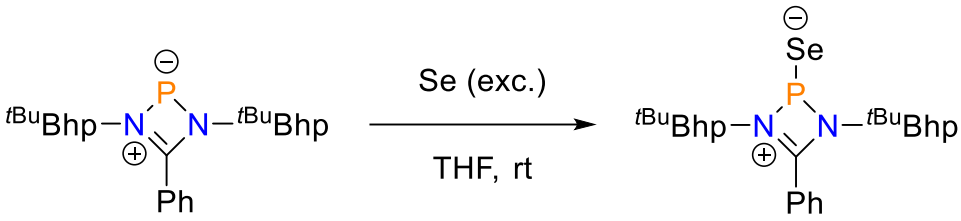


Figure 46. continued.



5.5.8 $^{t\mathrm{Bu}}$Bhp–[NC(Ph)NP(Se)]–$^{t\mathrm{Bu}}$Bhp (**11a**)

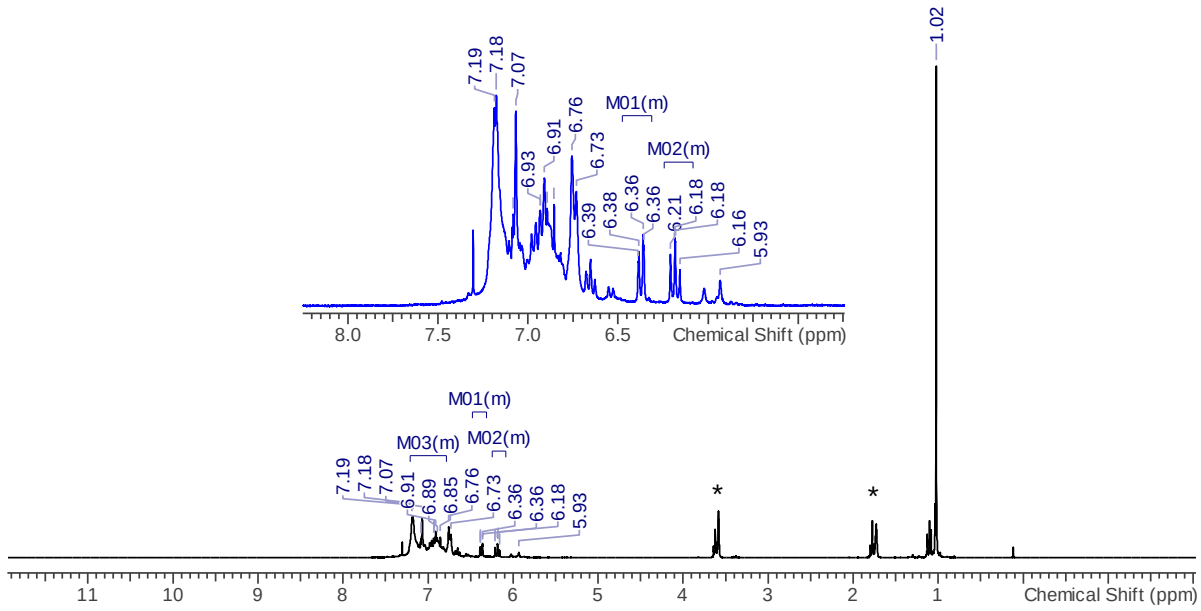


6 (0.25 g, 0.23 mmol) and black selenium (0.10 g, 1.27 mmol) are mixed together in anhydrous THF (5 mL). After stirring for 1 h, the mixture is filtered and volatiles are removed in vacuo (10^{-3} mbar), resulting in a light orange solid. Yield: 0.16 g (0.14 mmol, 58.4 %).

Formula: $C_{79}H_{71}N_2PSe$. M = 1158.40 g/mol. Mp. 157–160 °C. EA found (calcd.) in %: C 81.91 (81.52), H 6.18 (6.55), N 2.42 (2.18). ^{1}H NMR (THF-d$_8$, 300.1 MHz): δ = δ = 1.02 (s, 18 H, *t*Bu), 5.93 (s, 1 H, *p*-H (Ph)), 6.18 (m, 2 H, *m*-H (Ph)), 6.37 (m, 2 H, *o*-H (Ph)), 6.73 (s, 4 H, C*H*Ph$_2$), 6.76 (s, 4 H, *m*-H), 7.04 (m, 40 H, C*H*). ^{13}C{^{1}H} NMR (THF-d$_8$, 75.5 MHz): δ = 31.2 (s, C(*C*H$_3$)$_3$), 35.3 (s, *C*(CH$_3$)$_3$), 52.4 (s, *C*HPh$_2$), 126.8 (s, *C*H), 128.9 (s, *C*H), 129.0 (s, *C*H), 130.5 (s, *C*H), 130.6 (s, *C*H), 131.0 (s, *C*H), 133.0 (s, *C*$_{quat.}$), 133.4 (s, *C*H), 143.2 (s, *C*$_{quat.}$), 145.1 (s, *C*$_{quat.}$), 146.4 (s, *C*$_{quat.}$), 146.8 (s, *C*$_{quat.}$), 150.4 (s, *C*$_{quat.}$). ^{31}P{^{1}H} NMR (THF-d$_8$, 202.5 MHz): δ = 311.9 (s, N*P*N). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3098 (vw), 3059 (w), 3024 (w), 2960 (w), 2904 (w), 2867 (w), 1810 (vw), 1752 (vw), 1637 (vw), 1597 (w), 1581 (w), 1534 (w), 1492 (m), 1461 (m), 1445 (m), 1406 (m), 1362 (w), 1334 (w), 1309 (w), 1253 (w), 1202 (w), 1177 (w), 1156 (w), 1136 (w), 1099 (w), 1076 (w), 1031 (m), 1004 (w), 979 (w), 969 (w), 948 (w), 915 (w), 895 (w), 860 (w), 835 (w), 810 (vw), 796 (w), 785 (w), 761 (m), 736 (m), 697 (vs), 647 (w), 633 (w), 622 (m), 604 (s), 579 (m), 554 (m), 530 (w), 505 (m), 466 (m), 451 (m), 427 (w). Raman (785 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 1600 (2), 1583 (1), 1531 (1), 1484 (1), 1444 (1), 1396 (1), 1308 (1), 1248 (1), 1183 (1), 1170 (1), 1156 (1), 1098 (1), 1078 (1), 1031 (3), 1002 (10), 991 (1), 981 (1), 953 (1), 911 (1), 860 (1), 833 (2), 809 (1), 767 (1), 745 (1), 727 (1), 706 (1), 685 (1), 647 (1), 635 (1), 617 (2), 605 (1), 576 (1), 558 (1), 529 (1), 506 (1), 489 (1), 470 (1), 453 (1), 429 (1), 407 (1), 384 (1), 355 (1), 330 (1), 298 (1), 266 (2), 238 (3), 214 (3), 171 (2), 146 (5). MS (ESI +, m/z): 1158 ([M]$^+$).

Figure 47. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, IR and Raman spectra of **11a** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

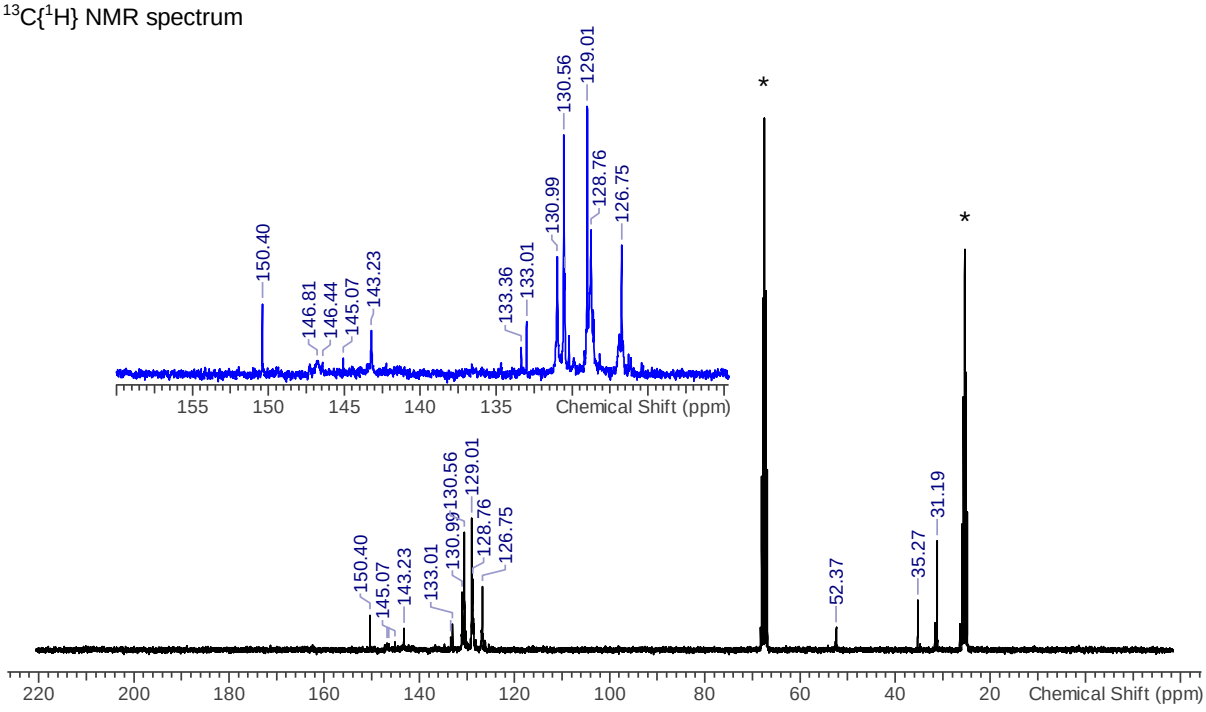
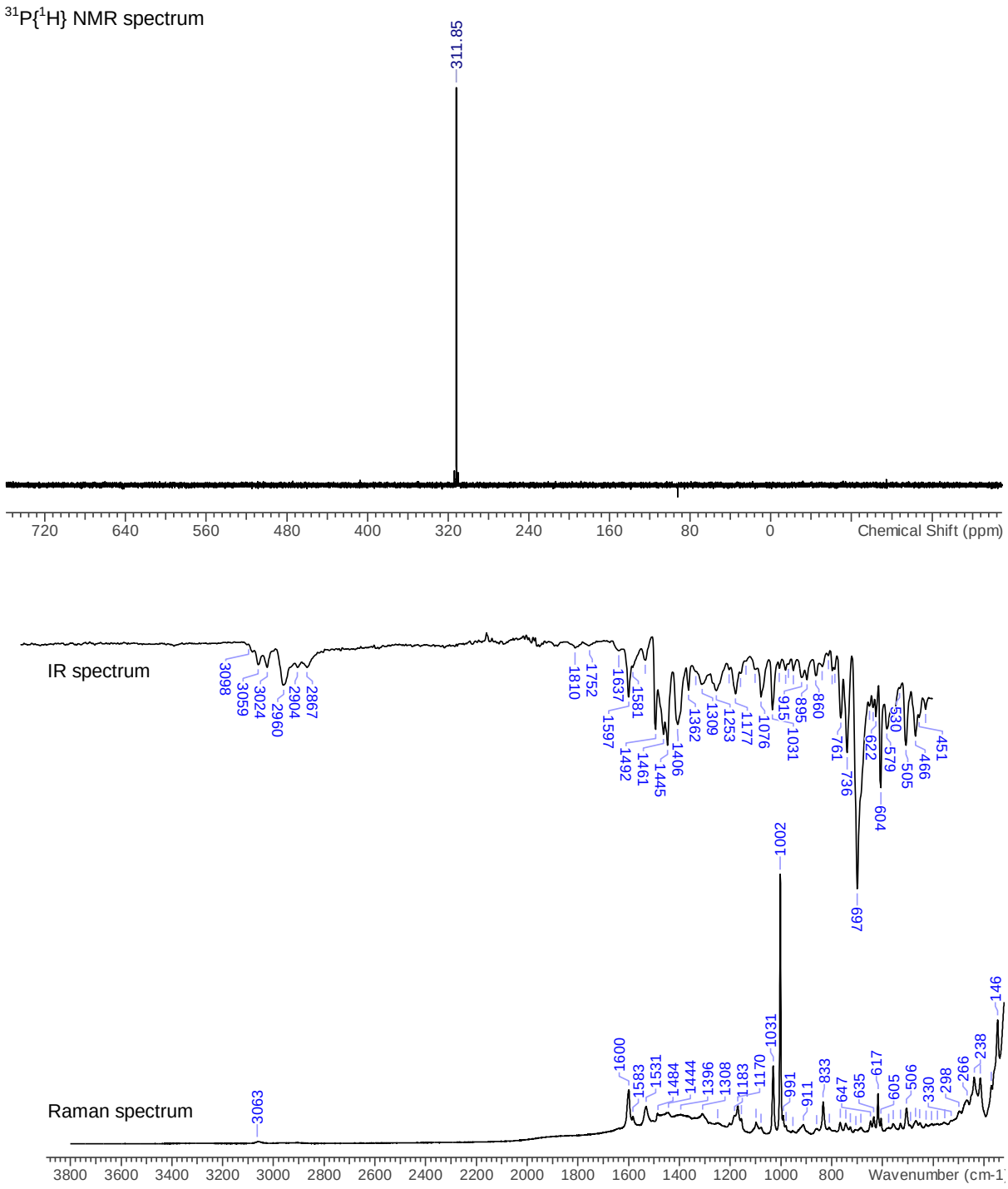
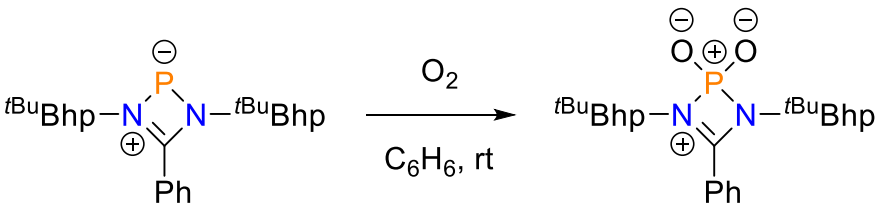


Figure 47. continued.



5.5.9 $^{t\mathrm{Bu}}$Bhp–[NC(Ph)NP(O$_2$)]–$^{t\mathrm{Bu}}$Bhp (**12**)



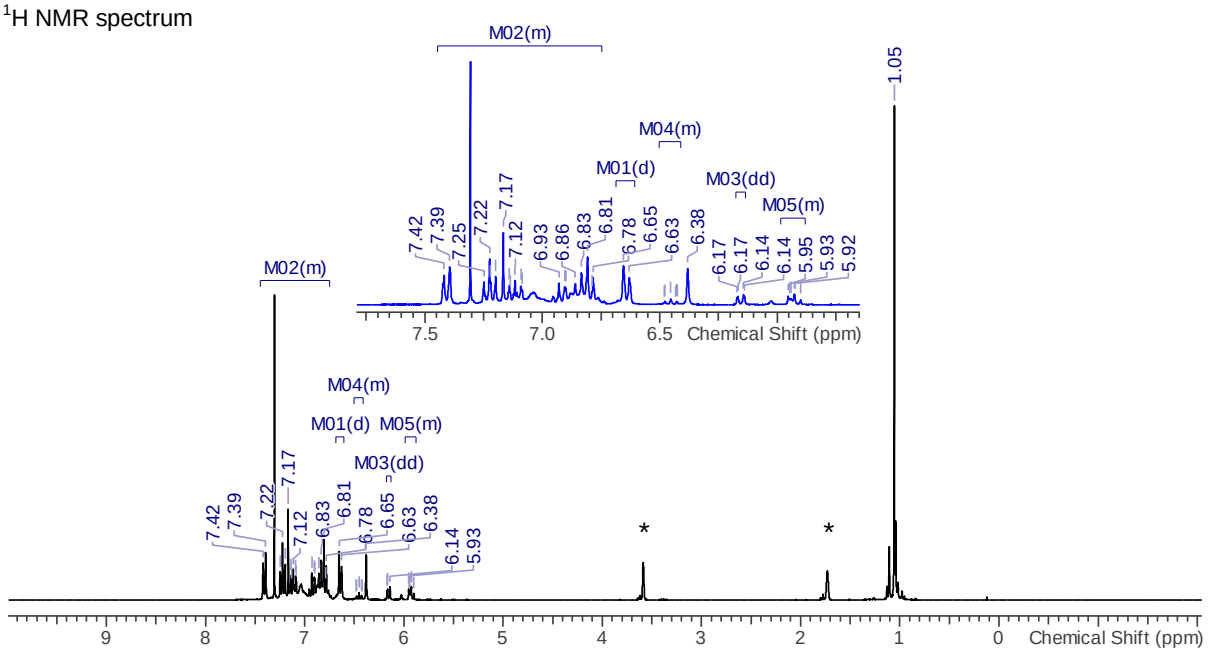
The colorless product formed during a crystallization attempt from a solution of **6** in anhydrous benzene at room temperature in an apparent reaction with atmospheric oxygen. Therefore, no explicit reaction protocol or yield is given.

Crystals suitable for single-crystal XRD were obtained from a saturated solution in benzene at room temperature.

Formula: $C_{79}H_{71}N_2PO_2$. M = 1111.42 g/mol. Mp. 287–290 °C (decomp.). EA found (calcd.) in %: C 85.59 (85.37), H 6.82 (6.44), N 2.49 (2.52). ^{1}H NMR (THF-d$_8$, 300.1 MHz): δ = δ = 1.05 (s, 18 H, *t*Bu), 5.93 (m, 2 H, *m-H* (Ph)), 6.15 (dd, $^3J(^1H,^1H)$ = 8.4 Hz, $^4J(^1H,^1H)$ = 1.2 Hz, 2 H, *o-H* (Ph)), 6.38 (s, 4 H, C*H*Ph$_2$), 6.45 (m, 1 H, *p-H* (Ph)), 6.64 (d, $^3J(^1H,^1H)$ = 7.2 Hz, 8 H, *p-H* (Bhp)), 7.15 (m, 36 H, C*H*). ^{13}C{^{1}H} NMR (THF-d$_8$, 75.5 MHz): δ = 31.2 (s, C(*C*H$_3$)$_3$), 35.3 (s, *C*(CH$_3$)$_3$), 52.0 (s, *C*HPh$_2$), 126.7 (s, *C*H), 126.9 (s, *C*H), 128.9 (s, *C*H), 129.1 (s, *C*H), 129.3 (s, *C*H), 130.3 (s, *C*H), 130.8 (s, *C*H), 141.3 (s, *C*$_{quat.}$), 142.6 (s, *C*$_{quat.}$), 145.1 (s, *C*$_{quat.}$), 146.4 (s, *C*$_{quat.}$), 147.2 (s, *C*$_{quat.}$), 151.2 (s, *C*$_{quat.}$). ^{31}P{^{1}H} NMR (THF-d$_8$, 121.5 MHz): δ = 4.9 (s, N*P*N). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3084 (w), 3059 (w), 3026 (w), 2962 (w), 2954 (w), 2902 (w), 2865 (w), 1639 (w), 1626 (w), 1614 (w), 1597 (w), 1577 (w), 1531 (w), 1492 (m), 1474 (w), 1463 (m), 1445 (m), 1406 (w), 1360 (w), 1350 (w), 1338 (w), 1303 (w), 1237 (m), 1200 (w), 1181 (m), 1154 (w), 1127 (m), 1076 (m), 1031 (m), 983 (w), 948 (w), 917 (w), 895 (w), 857 (w), 835 (w), 812 (w), 796 (w), 763 (m), 738 (m), 697 (vs), 678 (m), 649 (w), 635 (w), 622 (m), 606 (m), 581 (m), 565 (m), 546 (w), 530 (w), 519 (w), 499 (w), 480 (m), 456 (m), 420 (w), 410 (w). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3188 (1), 3164 (1), 3062 (4), 3046 (2), 3004 (1), 2968 (1), 2948 (1), 2928 (1), 2904 (1), 2862 (1), 2786 (1), 1598 (4), 1585 (1), 1535 (2), 1488 (1), 1475 (1), 1454 (1), 1448 (1), 1354 (1), 1337 (1), 1307 (1), 1299 (1), 1239 (1), 1205 (1), 1172 (1), 1161 (1), 1125 (2), 1112 (1), 1030 (3), 1002 (10), 991 (5), 836 (1), 767 (1), 743 (1), 648 (1), 637 (1), 618 (1), 478 (1), 270 (1), 250 (1), 241 (1), 229 (1), 175 (1), 161 (1). MS (ESI +, m/z): 1111 ([M]$^+$).

Figure 48. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, IR and Raman spectra of **12** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

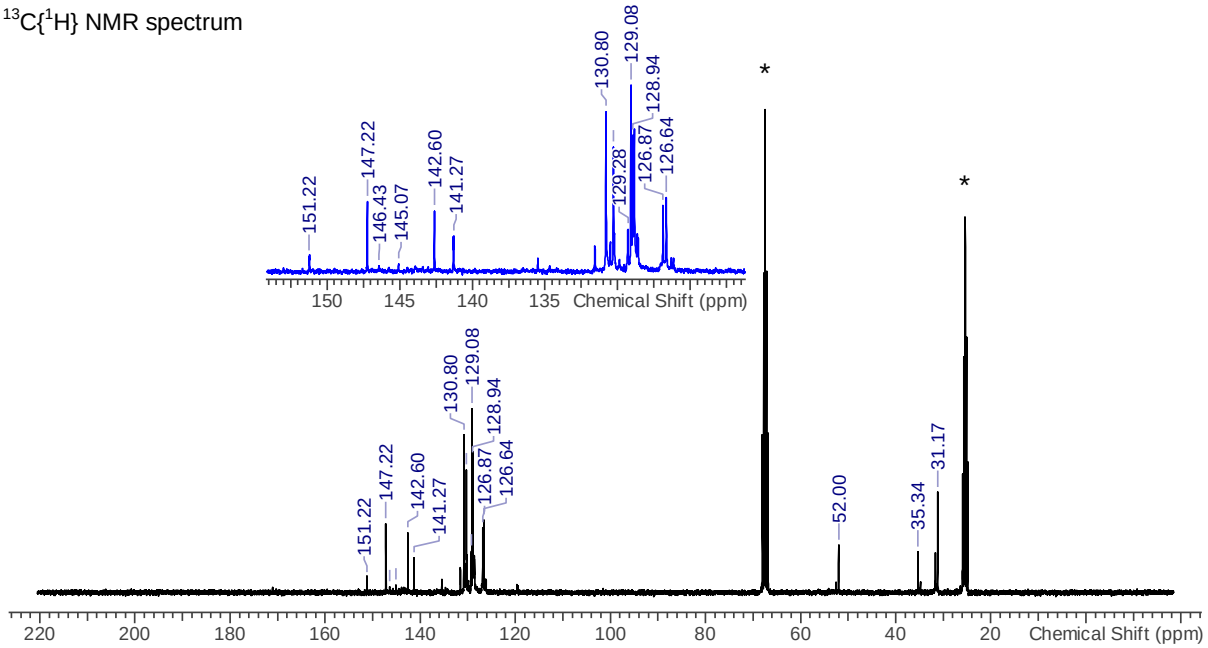
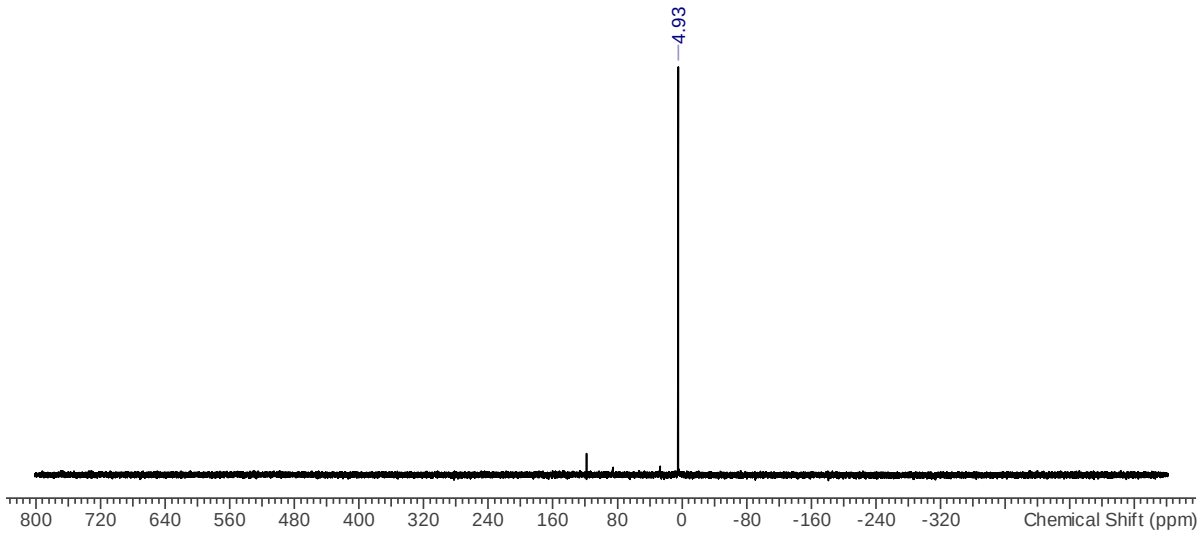
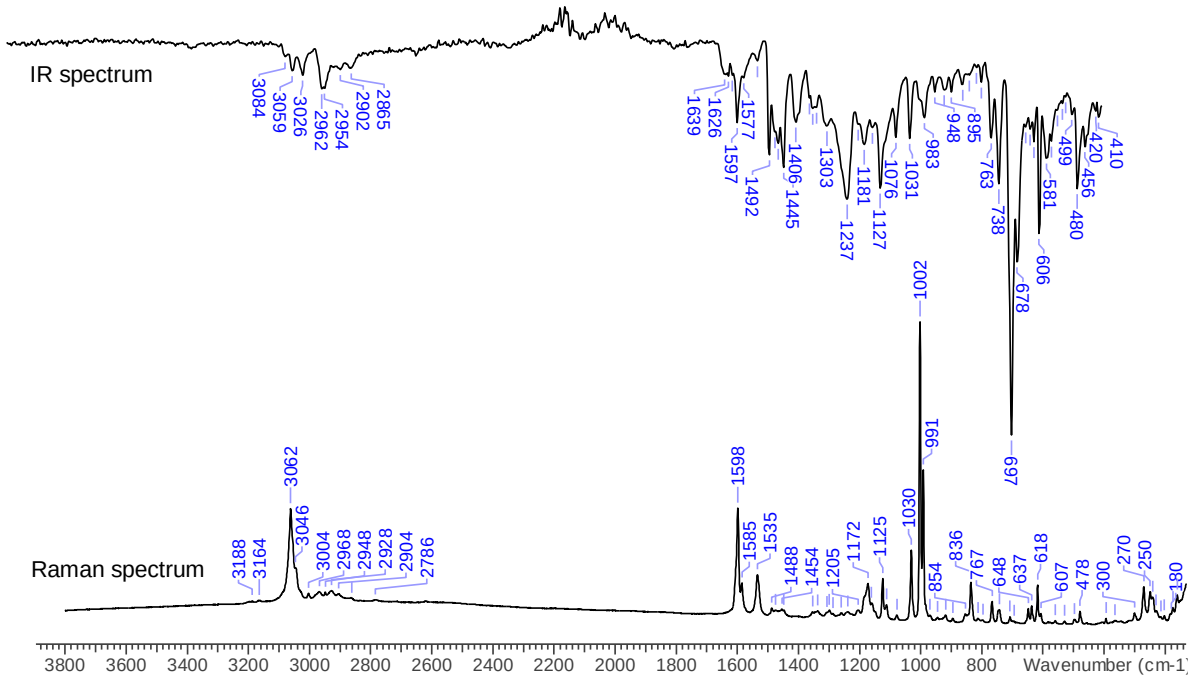


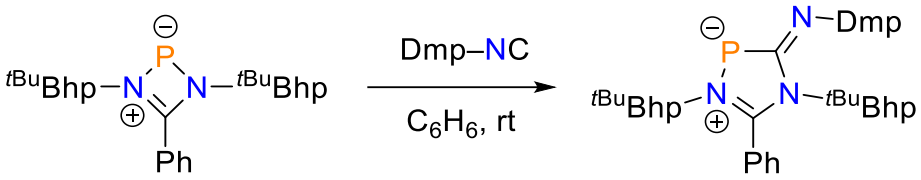
Figure 48. continued.

$^{31}P\{^{1}H\}$ NMR spectrum





5.5.10 $^{t\mathrm{Bu}}$Bhp–[NC(Ph)NC(NDmp)P]–$^{t\mathrm{Bu}}$Bhp (**13**)



6 (0.20 g, 0.19 mmol) and Dmp–NC (0.03 g, 0.19 mmol) are dissolved together in anhydrous benzene (4 mL), resulting in a blood-red mixture. After stirring for 1 h, volatiles are removed *in vacuuo* (10^{-3} mbar). The residue is dissolved in anhydrous diethyl ether (5 mL), filtered and concentrated. The red crystals are eventually dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 0.11 g (0.1 mmol, 49.2 %).

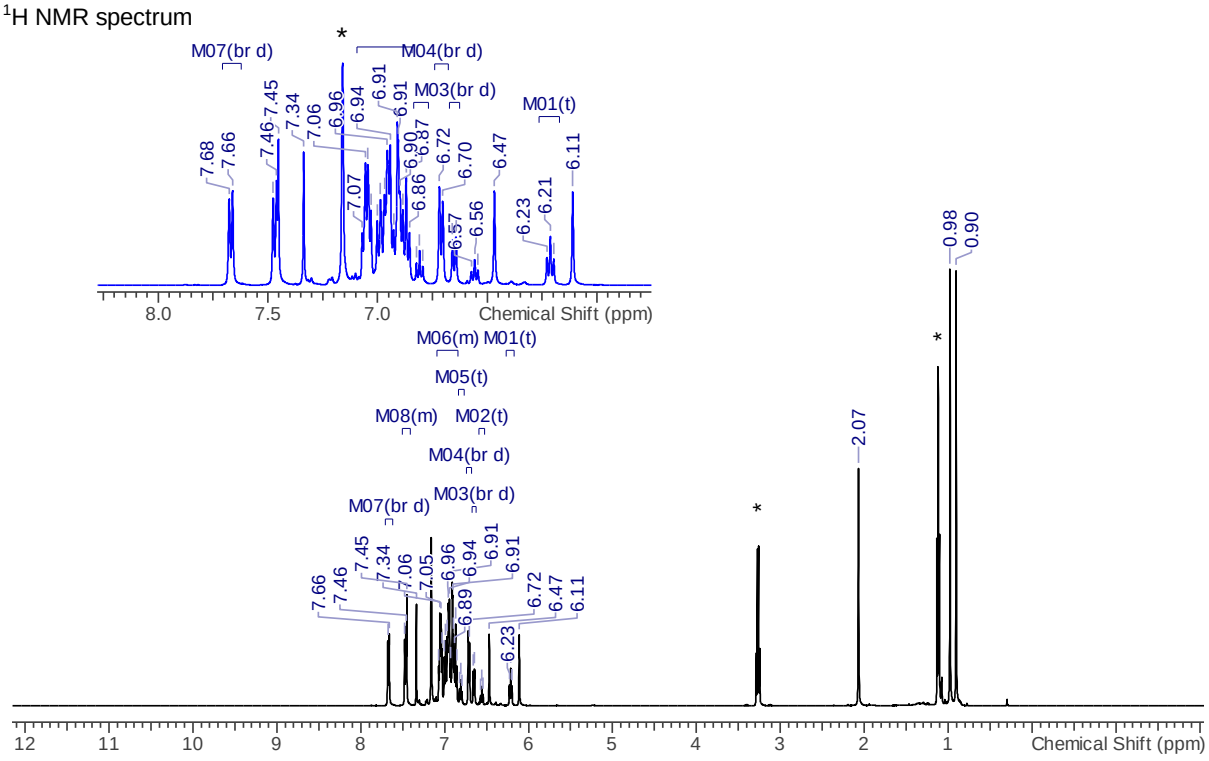
Crystals suitable for single-crystal XRD were obtained from a saturated solution in diethyl ether at room temperature.

Formula: $C_{88}H_{80}N_3P$. M = 1210.60 g/mol. Mp. 235 °C (decomp.). EA found (calcd.) in %: C 87.07 (87.31), H 7.02 (6.66), N 3.14 (3.47). ^{1}H NMR (C_6D_6, 500.1 MHz): δ = 0.90 (s, 9 H, *t*Bu), 0.98 (s, 9 H, *t*Bu), 2.07 (s, 6 H, C*H*$_3$ (Dmp)), 6.11 (s, 2 H, C*H*Ph$_2$), 6.32 (t, J(^{1}H,^{1}H) = 7.9 Hz, 2 H), 6.47 (s, 2 H, C*H*Ph$_2$), 6.56 (t, J(^{1}H,^{1}H) = 7.6 Hz, 1 H), 6.65 (d, J(^{1}H,^{1}H) = 7.9 Hz, 2 H), 6.71 (d, J(^{1}H,^{1}H) = 7.6 Hz, 4 H), 6.81 (t, J(^{1}H,^{1}H) = 7.4 Hz, 1 H), 6.95 (m, 30 H), 7.34 (s, 2 H), 7.46 (m, 6 H), 7.67 (d, J(^{1}H,^{1}H) = 7.6 Hz, 4 H). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ = 19.2 (s, *C*H$_3$ (Dmp)), 31.1 (s, C(*C*H$_3$)$_3$), 31.2 (s, C(*C*H$_3$)$_3$), 34.9 (s, *C*(CH$_3$)$_3$), 35.0 (s, *C*(CH$_3$)$_3$), 52.1 (s, *C*HPh$_2$), 53.1 (s, *C*HPh$_2$), 126.8 (s, *C*H), 127.3 (s, *C*H), 128.3 (s, *C*H), 128.7 (s, *C*H), 128.9 (s, *C*H), 129.0 (s, *C*H), 129.3 (s, *C*H), 129.3 (s, *C*H), 130.1 (s, *C*H), 130.3 (s, *C*H), 130.5 (s, *C*H), 130.8 (s, *C*H), 131.5 (s, *C*H), 135.5 (s, *C*$_{quat.}$), 135.8 (s, *C*$_{quat.}$), 140.5 (s, *C*$_{quat.}$), 142.7 (s, *C*$_{quat.}$), 143.7 (s, *C*$_{quat.}$), 144.4 (s, *C*$_{quat.}$), 145.0 (s, *C*$_{quat.}$), 145.4 (s, *C*$_{quat.}$), 148.8 (s, *C*$_{quat.}$), 151.0 (s, *C*$_{quat.}$), 151.2 (s, *C*$_{quat.}$), 151.4 (s, *C*$_{quat.}$). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ = 152.9 (s, N*P*C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3389 (vw), 3102 (vw), 3084 (vw), 3059 (w), 3026 (w), 2956 (w), 2925 (w), 2859 (w), 2115 (vw), 1948 (vw), 1886 (vw), 1806 (vw), 1750 (vw), 1641 (w), 1597 (w), 1577 (w), 1558 (w), 1492 (m), 1465 (m), 1447 (m), 1412 (w), 1393 (w), 1381 (w), 1362 (w), 1305 (m), 1237 (s), 1181 (s), 1150 (m), 1119 (s), 1078 (m), 1033 (m), 983 (m), 950 (w), 917 (w), 892 (w), 860 (w), 845 (w), 831 (w), 808 (w), 761 (m), 740 (m), 728 (m), 697 (vs), 660 (m), 649 (m), 635 (m), 622 (m), 606 (s), 579 (m), 557 (w), 530 (m), 499 (w), 472 (m), 439 (w). Raman (785 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 1598 (8), 1585 (3), 1561 (3), 1505 (8), 1470 (6), 1438 (10), 1424 (6), 1413 (6), 1377 (5), 1299 (3), 1253 (3), 1223 (2), 1187 (2), 1183 (2), 1170

(2), 1160 (2), 1120 (2), 1096 (2), 1077 (2), 1059 (3), 1033 (2), 1004 (7), 968 (1), 925 (2), 917 (1), 893 (3), 862 (3), 857 (3), 848 (4), 836 (4), 811 (1), 767 (1), 755 (2), 748 (3), 737 (2), 728 (2), 691 (2), 672 (3), 664 (2), 650 (2), 645 (2), 619 (2), 604 (2), 597 (2), 583 (3), 563 (2), 544 (2), 538 (2), 528 (2), 512 (2), 502 (2), 493 (2), 476 (2), 462 (4), 447 (3), 426 (2), 411 (2), 406 (2), 399 (3), 366 (3), 352 (2), 325 (2), 300 (2), 282 (2), 238 (2), 226 (3), 218 (2), 193 (2), 178 (3), 162 (3), 138 (4), 132 (5). UV/Vis (benzene, 0.11 mM): 508 nm (ε = 5501 M^{-1} cm^{-1}). MS (ESI +, m/z): 1211 ($[M+H]^+$).

Figure 49. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, IR, Raman and UV/Vis spectra of **13** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

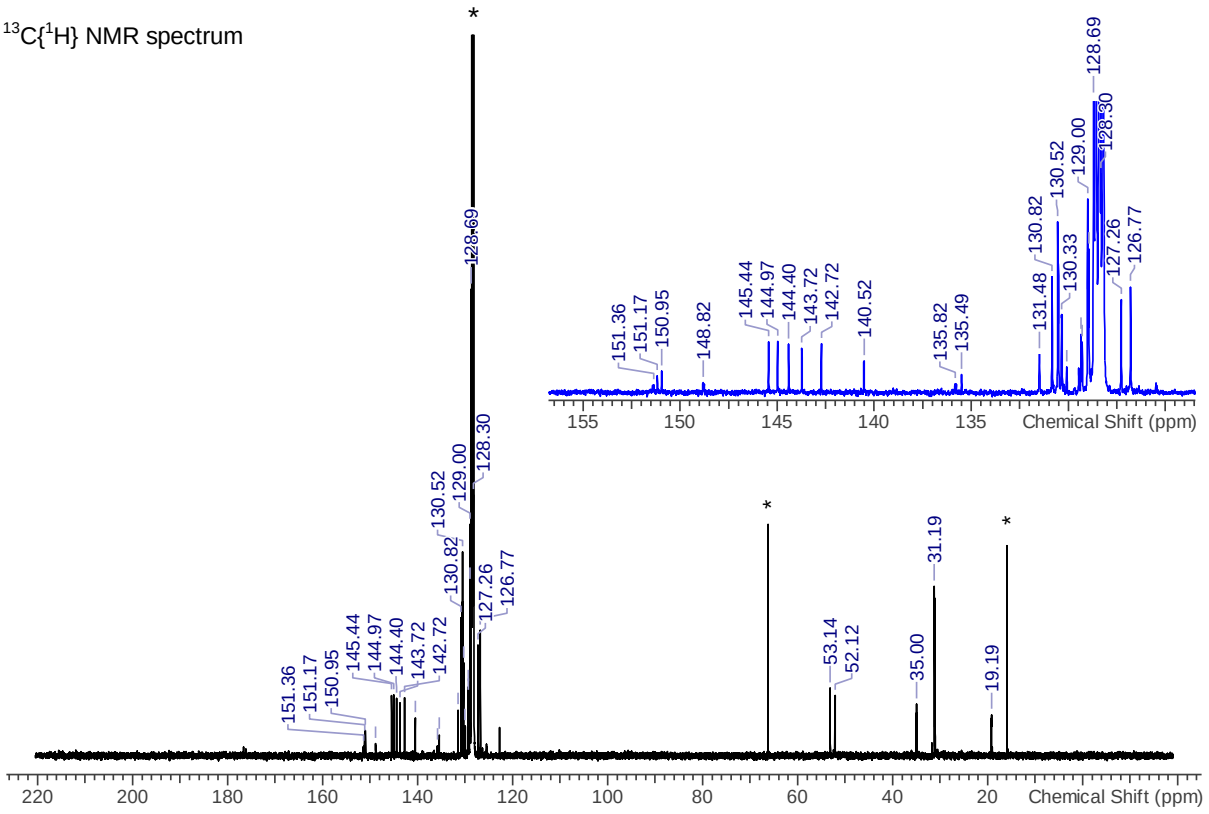


Figure 49. continued.

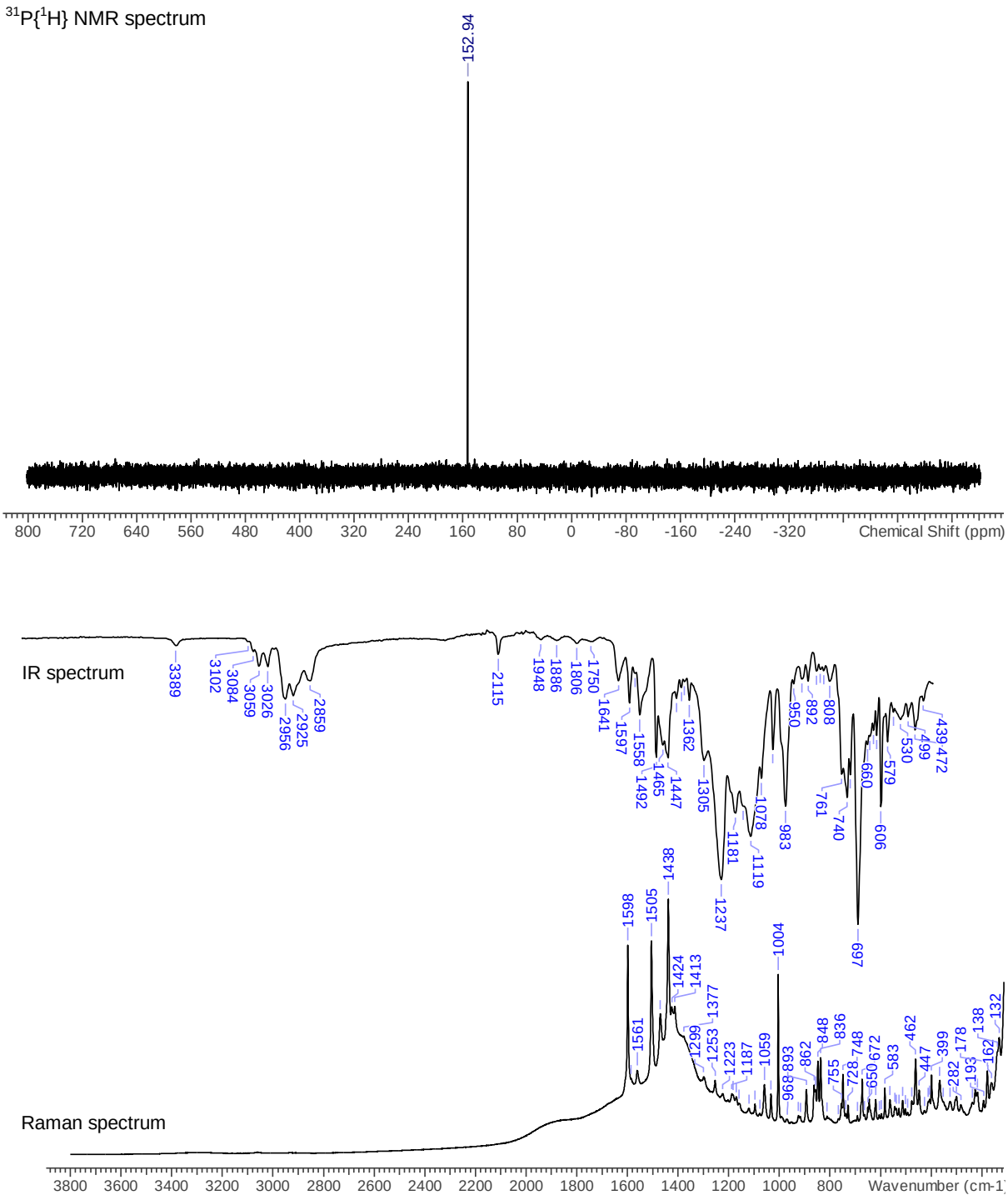
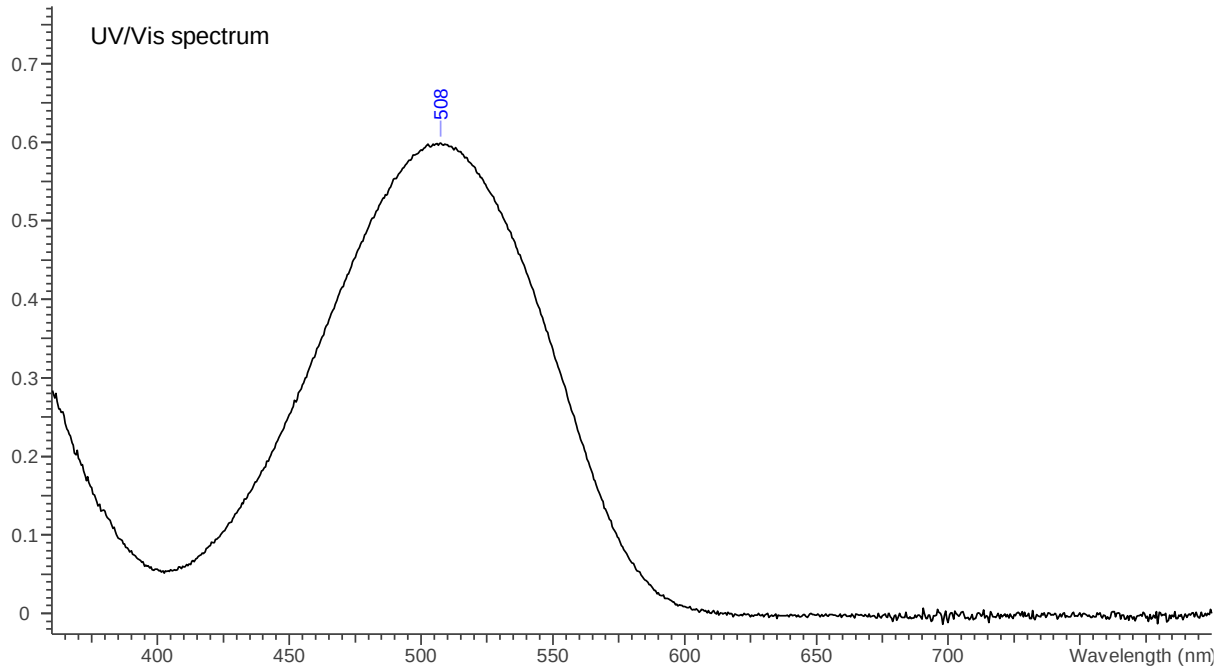
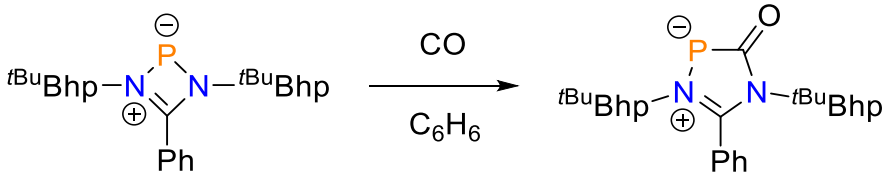


Figure 49. continued.



5.5.11 $^{t\mathrm{Bu}}$Bhp–[NC(Ph)NC(O)P]–$^{t\mathrm{Bu}}$Bhp (**14**)



CO (1 bar) is bubbled through a solution of **6** (0.25 g, 0.23 mmol) in anhydrous benzene (20 mL) for 1 h (color change to yellow starts after 5 min). After flushing the flask with argon, the mixture is left stirring at room temperature overnight. The next day, volatiles are removed *in vacuuo* (10^{-3} mbar) and the yellow solid is dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 0.18 g (0.16 mmol, 68.5 %).

Crystals suitable for single-crystal XRD were obtained from a saturated solution in toluene at room temperature.

Formula: $C_{80}H_{71}N_2PO$. M = 1107.43 g/mol. Mp. 250–253 °C (decomp.). EA found (calcd.) in %: C 86.48 (86.77), H 6.62 (6.46), N 2.33 (2.53). ^{1}H NMR (C_6D_6, 500.1 MHz): δ = 0.92 (s, 9 H, *t*Bu), 0.94 (s, 9 H, *t*Bu), 6.02 (s, 2 H, C*H*Ph$_2$), 6.11 (s, 2 H, C*H*Ph$_2$), 6.51 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 1 H, *p-H* (Ph)), 6.56 (d, $^3J(^1H,^1H)$ = 7.6 Hz, 2 H, C*H*), 6.74 (d, $^3J(^1H,^1H)$ = 7.6 Hz, 4 H, C*H*), 6.98 (m, 30 H, C*H*), 7.39 (s, 2 H, *m-H*), 7.43 (s, 2 H, *m-H*), 7.51 (d, $^3J(^1H,^1H)$ = 7.5 Hz, 4

H, C*H*), 7.70 (d, $^{3}J(^{1}H,^{1}H)$ = 7.6 Hz, 4 H, C*H*). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 62.9 MHz): δ = 31.1 (s, C(*C*H_3)$_3$), 31.2 (s, C(*C*H_3)$_3$), 35.0 (s, *C*(CH$_3$)$_3$), 35.0 (s, *C*(CH$_3$)$_3$), 52.4 (s, *C*HPh$_2$), 53.0 (s, *C*HPh$_2$), 126.6 (s, *C*H), 127.2 (s, *C*H), 127.4 (s, *C*H), 129.0 (s, *C*H), 129.1 (s, *C*H), 129.2 (s, *C*H), 130.2 (s, *C*H), 130.3 (s, *C*H), 130.5 (s, *C*H), 130.6 (s, *C*H), 130.8 (s, *C*H), 133.0 (s, $C_{quat.}$), 140.7 (s, $C_{quat.}$), 141.5 (s, $C_{quat.}$), 142.1 (s, $C_{quat.}$), 143.3 (s, $C_{quat.}$), 143.9 (s, $C_{quat.}$), 145.0 (s, $C_{quat.}$), 145.1 (s, $C_{quat.}$), 145.4 (s, $C_{quat.}$), 151.2 (s, $C_{quat.}$), 151.5 (s, $C_{quat.}$). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 202.5 MHz): δ = 132.7 (s, N*P*C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3391 (vw), 3104 (vw), 3084 (vw), 3059 (w), 3026 (w), 3001 (vw), 2960 (w), 2923 (w), 2855 (w), 1962 (vw), 1952 (vw), 1944 (vw), 1890 (vw), 1880 (vw), 1804 (vw), 1766 (vw), 1645 (w), 1624 (w), 1597 (m), 1577 (w), 1492 (m), 1465 (m), 1447 (m), 1412 (w), 1393 (w), 1379 (w), 1362 (w), 1336 (w), 1299 (w), 1282 (w), 1255 (w), 1177 (w), 1154 (w), 1113 (w), 1076 (m), 1031 (m), 1004 (w), 981 (w), 969 (vw), 948 (w), 921 (w), 895 (w), 862 (w), 841 (w), 833 (w), 812 (vw), 800 (w), 763 (m), 738 (m), 728 (m), 697 (vs), 647 (w), 633 (w), 622 (w), 606 (m), 583 (m), 546 (w), 507 (w), 493 (w), 470 (m). Raman (785 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 1596 (2), 1583 (1), 1505 (2), 1469 (1), 1463 (1), 1441 (2), 1426 (1), 1307 (1), 1248 (1), 1201 (1), 1187 (1), 1169 (1), 1156 (1), 1032 (3), 1002 (10), 990 (1), 922 (1), 917 (1), 869 (1), 853 (1), 848 (1), 834 (4), 804 (2), 763 (1), 748 (2), 743 (2), 646 (1), 634 (1), 617 (2), 610 (1), 529 (1), 457 (1), 421 (1), 405 (1), 394 (1), 354 (1), 335 (2), 301 (4), 285 (3), 248 (2), 234 (2), 220 (2), 212 (3), 199 (2), 187 (2), 176 (4), 162 (4), 149 (3), 130 (5). MS (ESI +, m/z): 1107 ([M]$^{+}$).

Figure 50. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, IR and Raman spectra of **14** (solvent signals marked by asterisk).

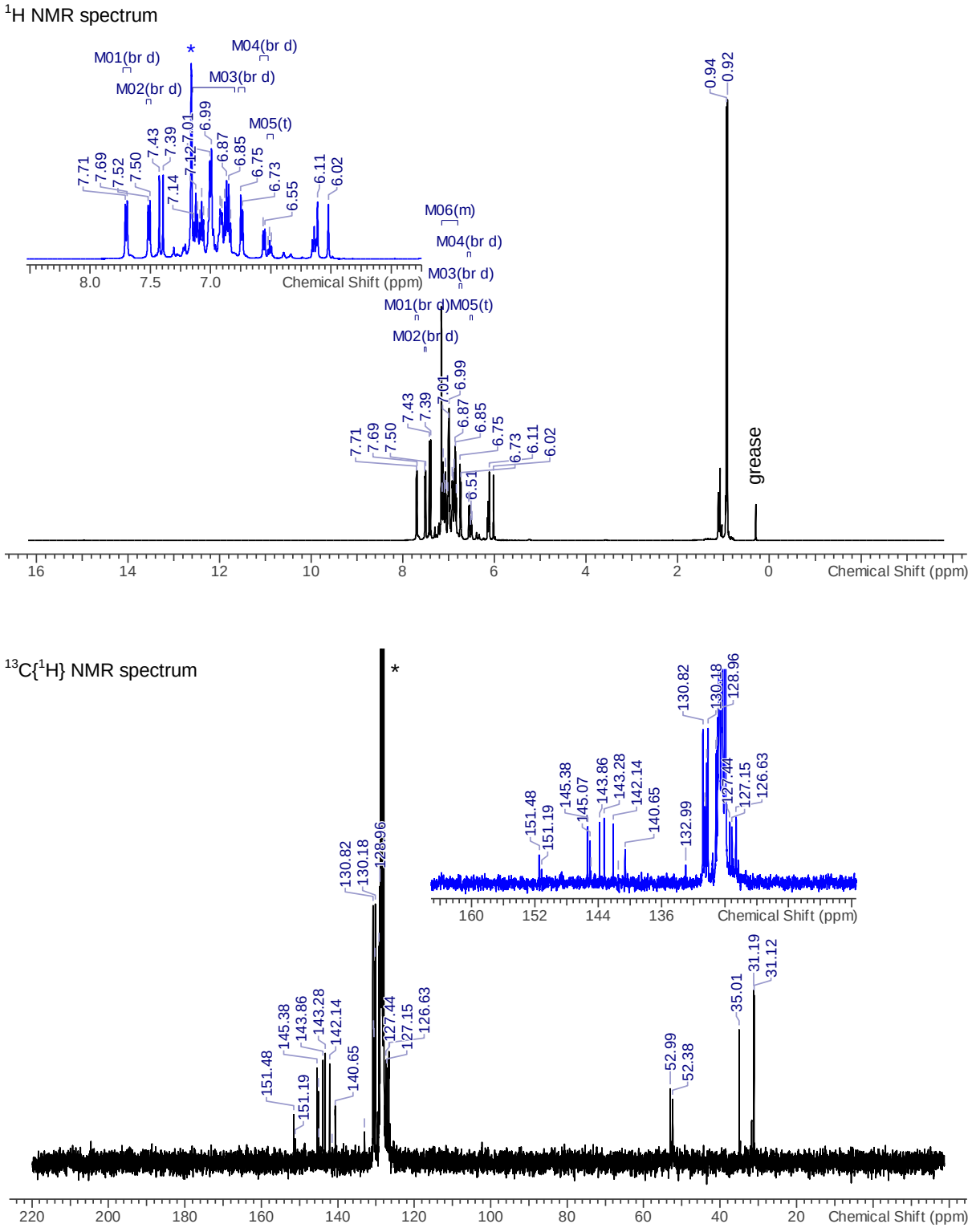
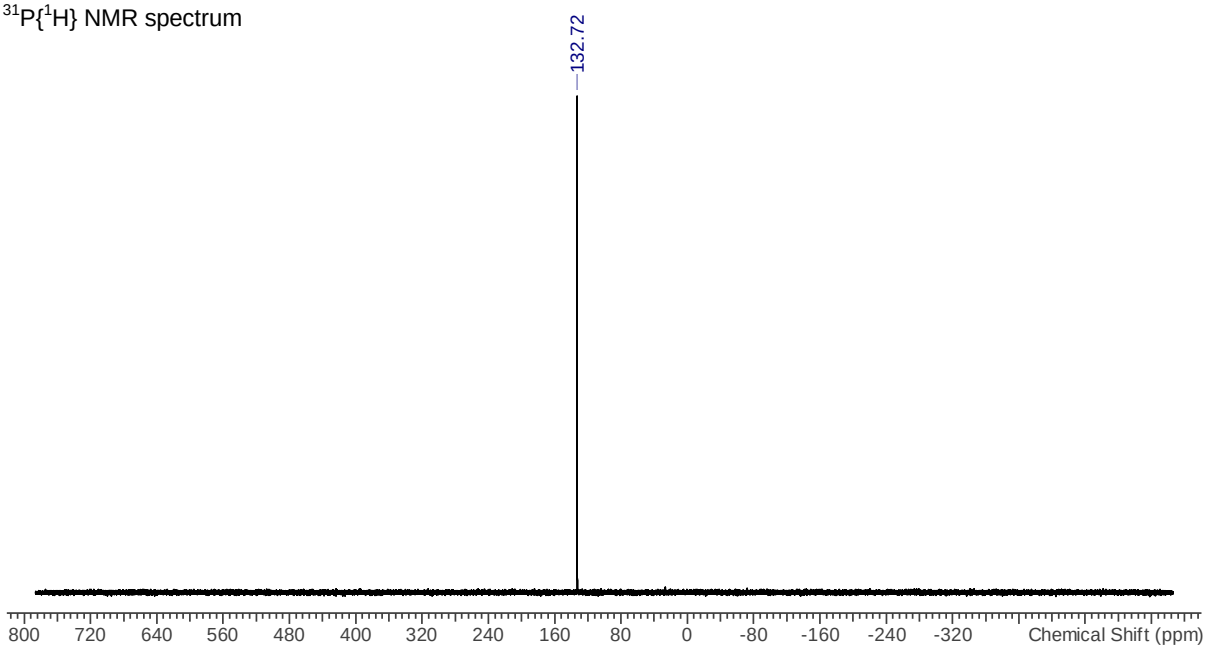
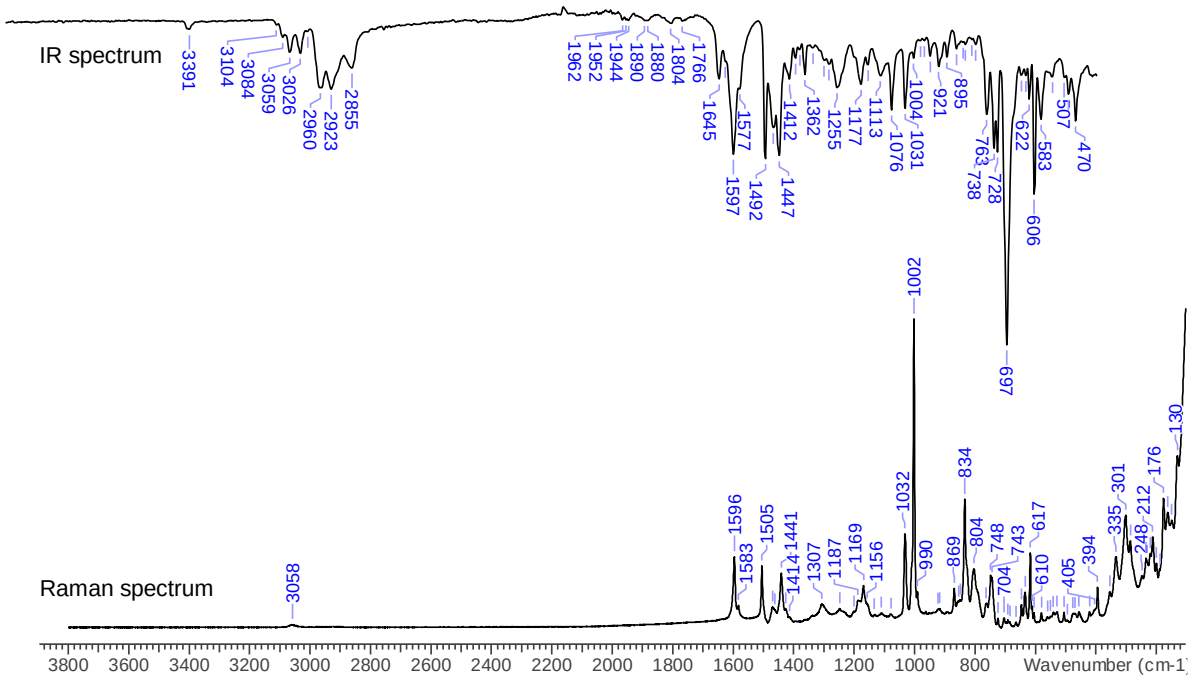


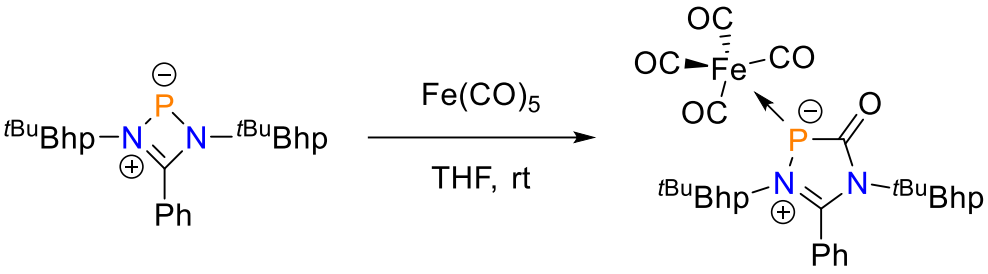
Figure 50. continued.

$^{31}P\{^{1}H\}$ NMR spectrum





5.5.12 $^{t\mathrm{Bu}}$Bhp–[NC(Ph)NC(O)P(Fe(CO)$_4$)]–$^{t\mathrm{Bu}}$Bhp (**15**)



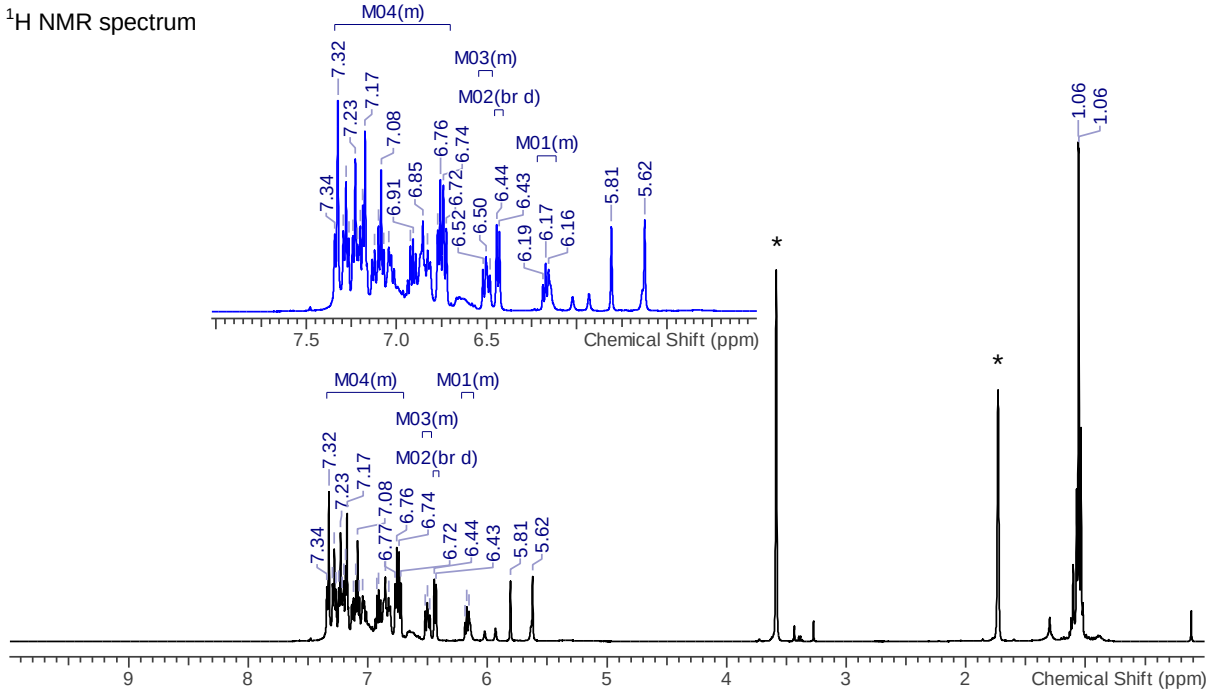
$Fe(CO)_5$ (0.05 mL, 0.38 mmol) is added to a solution of **6** (0.20 g, 0.19 mmol) in anhydrous THF (5 mL) and the mixture is left stirring at room temperature overnight. The next day, volatiles are removed *in vacuuo* (10^{-3} mbar). The residue is dissolved in anhydrous diethyl ether (10 mL), filtered and concentrated. The dark red crystals are eventually dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 0.08 g (0.06 mmol, 34.8 %).

Crystals suitable for single-crystal XRD were obtained from a saturated solution in diethyl ether at room temperature. The refined data showed a disorder with respect to iron-coordinated (69 %) and non-coordinated (31 %) heterocycle.

Formula: $C_{84}H_{71}FeN_2O_5P$. M = 1275.32 g/mol. Mp. 150 °C (decomp.). EA found (calcd.) in %: C 79.45 (79.11), H 5.23 (5.61), N 1.78 (2.20). ^{1}H NMR (THF-d_8, 500.1 MHz): δ = 1.06 (s, 9 H, *t*Bu), 1.06 (s, 9 H, *t*Bu), 5.62 (s, 2 H, C*H*Ph$_2$), 5.81 (s, 2 H, C*H*Ph$_2$), 6.17 (m, 3 H, C*H*), 6.44 (d, $J(^1H,^1H)$ = 7.8 Hz, 4 H, C*H*), 6.50 (m, 4 H, C*H*), 7.08 (m, 38 H, C*H*). ^{13}C{^{1}H} NMR (THF-d_8, 202.5 MHz): δ = 31.1 (s, C(*C*H$_3$)$_3$), 31.2 (s, C(*C*H$_3$)$_3$), 35.4 (s, *C*(CH$_3$)$_3$), 35.5 (s, *C*(CH$_3$)$_3$), 52.8 (s, C*H*Ph$_2$), 52.9 (s, C*H*Ph$_2$), 126.9 (s, *C*H), 127.0 (s, *C*H), 127.4 (s, *C*H), 127.5 (s, *C*H), 127.7 (s, *C*H), 128.7 (s, *C*H), 128.7 (s, *C*H), 128.8 (s, *C*H), 128.9 (s, *C*H), 129.1 (s, *C*H), 129.1 (s, *C*H), 129.4 (s, *C*H), 130.2 (s, *C*H), 130.4 (s, *C*H), 130.5 (s, *C*H), 130.8 (s, *C*H), 131.3 (s, *C*H), 140.0 (s, $C_{quat.}$), 141.9 (s, $C_{quat.}$), 142.2 (s, $C_{quat.}$), 142.9 (s, $C_{quat.}$), 143.7 (s, $C_{quat.}$), 144.1 (s, $C_{quat.}$), 145.0 (s, $C_{quat.}$), 145.0 (s, $C_{quat.}$), 151.8 (s, $C_{quat.}$), 152.3 (s, $C_{quat.}$), 215.0 (s, N*C*O). ^{31}P{^{1}H} NMR (THF-d_8, 202.5 MHz): δ = 171.7 (s). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3100 (vw), 3082 (vw), 3060 (w), 3025 (w), 3003 (vw), 2964 (w), 2928 (w), 2905 (w), 2870 (w), 2042 (m), 1974 (m), 1946 (s), 1908 (s), 1872 (w), 1664 (w), 1597 (m), 1581 (w), 1509 (w), 1493 (m), 1475 (m), 1445 (m), 1413 (w), 1402 (w), 1394 (w), 1363 (w), 1306 (m), 1237 (s), 1199 (m), 1177 (m), 1153 (m), 1119 (m), 1105 (m), 1078 (m), 1031 (m), 1024 (w), 1002 (w), 983 (m), 948 (w), 922 (w), 896 (w), 858 (w), 851 (w), 842 (w), 829 (w), 810 (w), 799 (w), 767 (m), 762 (m), 741 (m), 727 (m), 697 (vs), 642 (w), 624 (m), 616 (s), 605 (vs), 581 (m), 562 (m), 553 (m),

536 (w), 526 (m), 513 (m), 504 (m), 497 (m), 487 (w), 475 (m), 446 (w), 435 (w), 426 (m), 412 (w), 407 (w). Raman (785 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 1600 (2), 1584 (1), 1508 (2), 1478 (1), 1447 (1), 1401 (1), 1298 (1), 1247 (1), 1170 (1), 1156 (1), 1118 (1), 1079 (1), 1031 (3), 1024 (2), 1003 (8), 992 (1), 925 (1), 857 (2), 853 (1), 843 (2), 832 (3), 821 (1), 810 (1), 768 (1), 747 (1), 727 (1), 646 (1), 642 (2), 636 (1), 630 (1), 618 (4), 605 (1), 583 (1), 563 (1), 526 (1), 514 (2), 498 (2), 483 (2), 476 (1), 459 (1), 446 (1), 435 (4), 426 (4), 408 (1), 401 (2), 386 (1), 368 (1), 339 (3), 297 (2), 272 (2), 255 (3), 239 (4), 218 (3), 204 (3), 195 (2), 176 (5), 154 (7), 149 (7), 132 (10). MS (ESI +, m/z): 1108 ($[M–Fe(CO)_4+H]^+$).

Figure 51. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, IR and Raman spectra of **15** (solvent signals marked by asterisk).



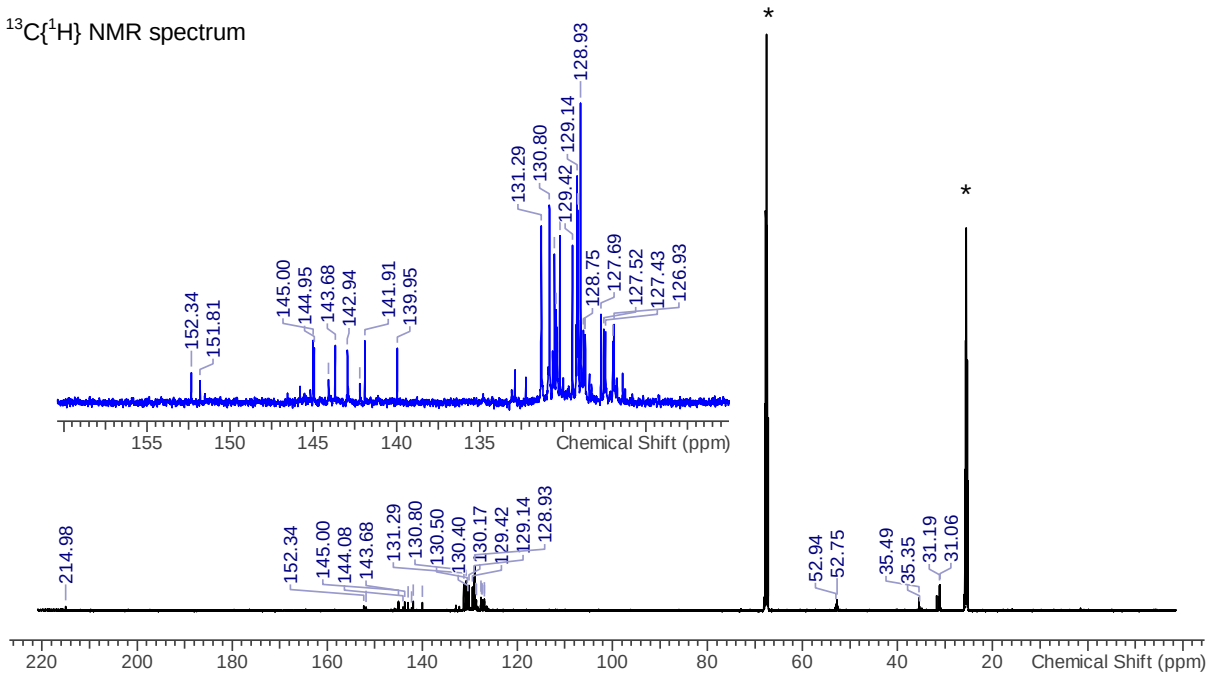
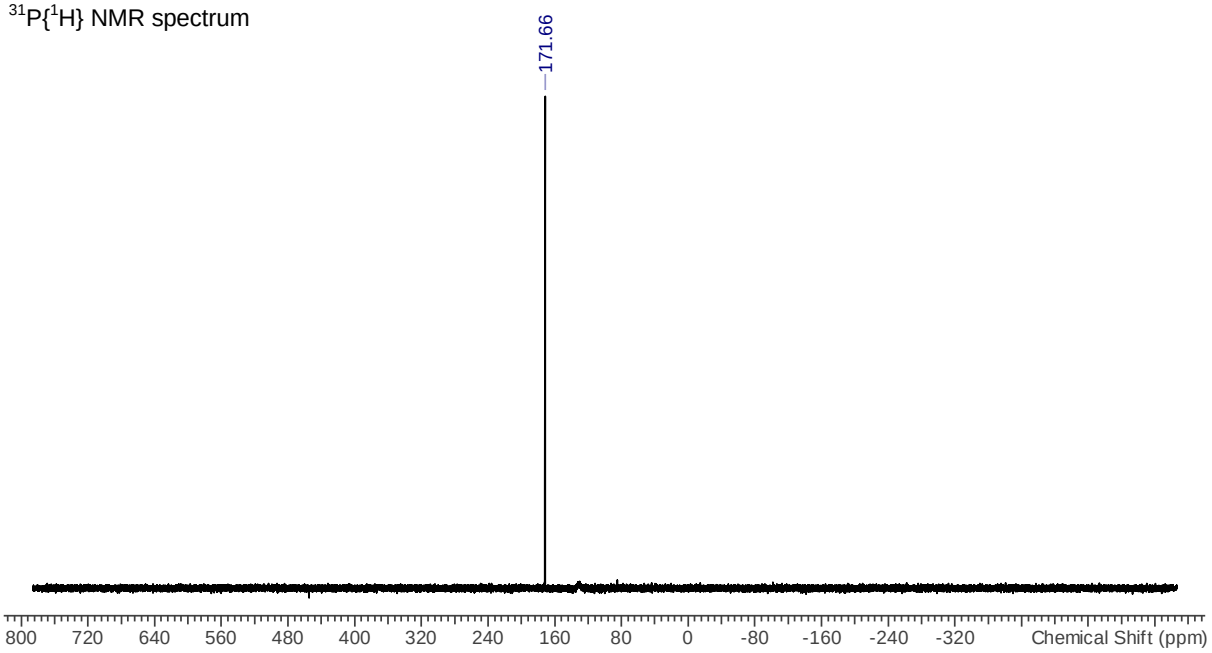
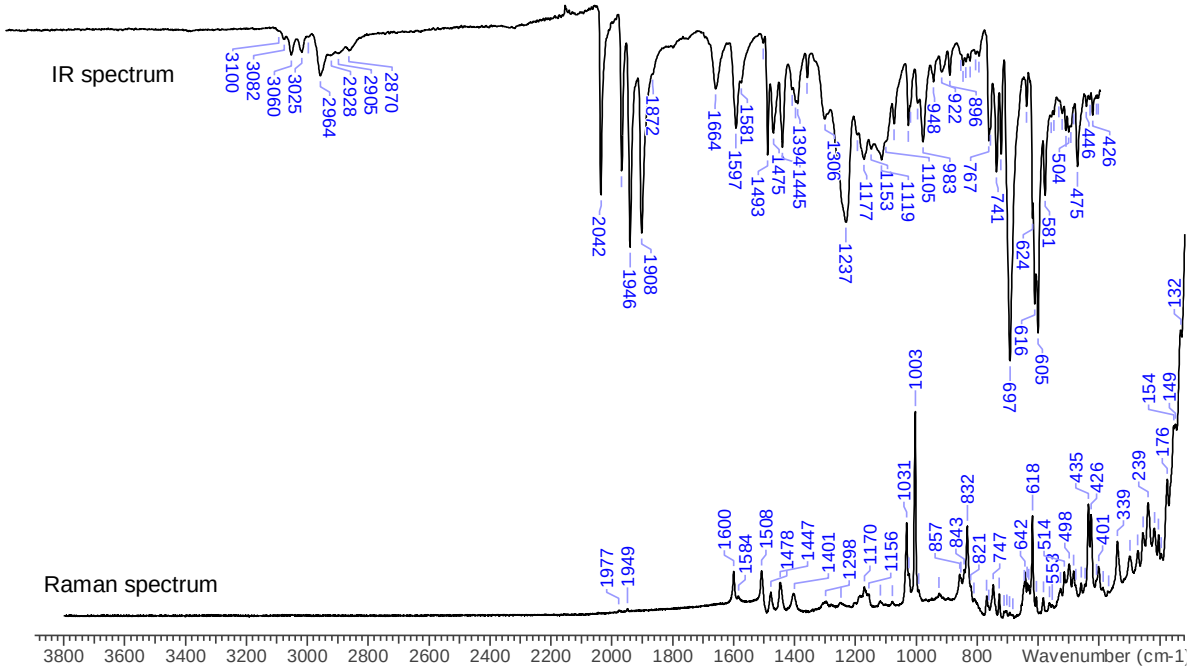


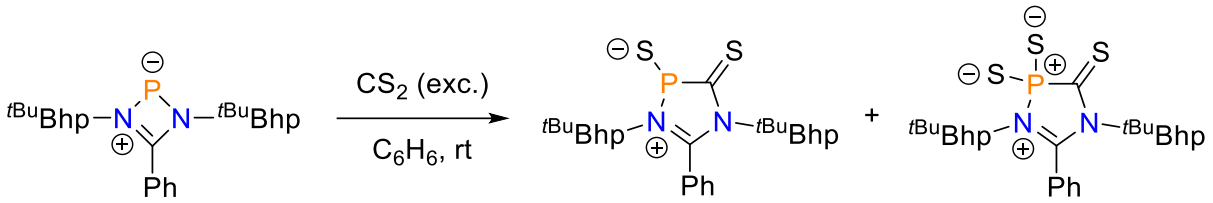
Figure 51. continued.

$^{31}P\{^{1}H\}$ NMR spectrum





5.5.13 $^{t\mathrm{Bu}}$Bhp–[NC(Ph)NC(S)P(S/S$_2$)]–$^{t\mathrm{Bu}}$Bhp (**16/17**)



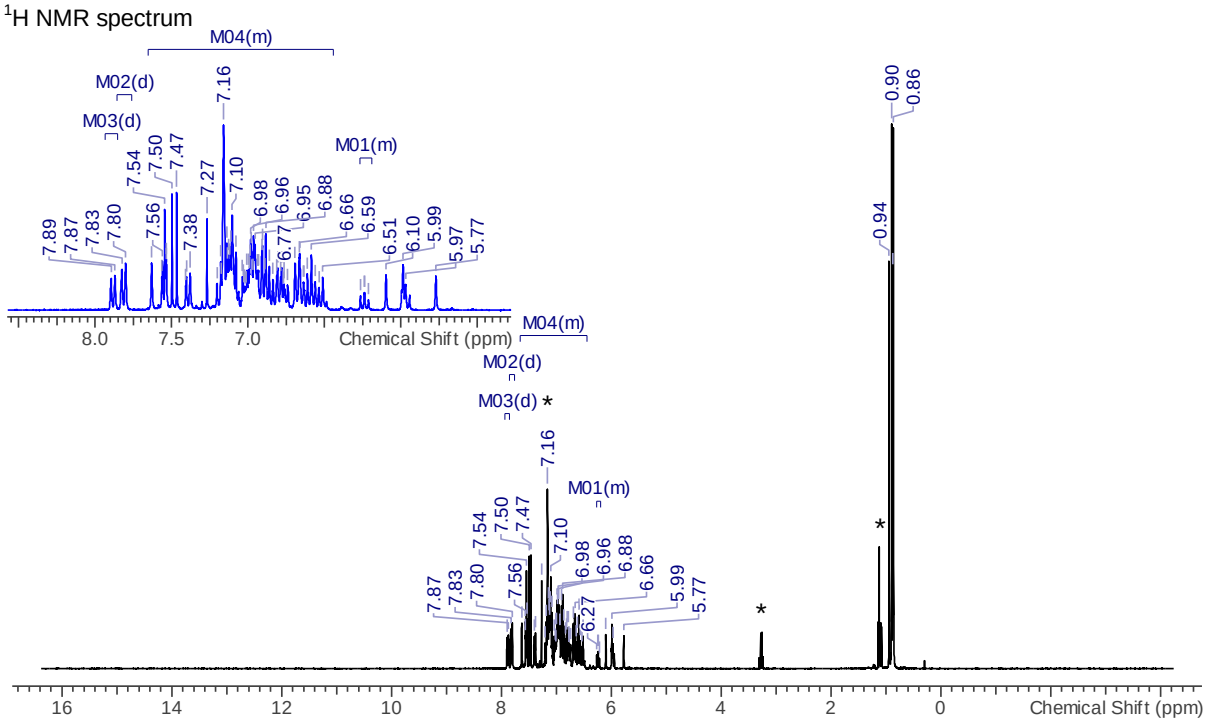
An excess of CS_2 (0.02 mL, 0.33 mmol) is added to a solution of **6** (0.20 g, 0.19 mmol) in anhydrous benzene (5 mL) via syringe, resulting in a color change to dark red. After stirring for 1 h, volatiles are removed *in vacuuo* (10^{-3} mbar). The residue is dissolved in anhydrous diethyl ether (5 mL), filtered and concentrated, yielding crystals of an inseparable mixture of two insertion products.

Crystals suitable for single-crystal XRD were obtained from a saturated solution in diethyl ether at room temperature.

Formula: $C_{80}H_{71}N_2PS_2/C_{80}H_{71}N_2PS_3$. M = 1155.56/1187.62 g/mol. ^{1}H NMR (C_6D_6, 300.1 MHz): δ = 0.86 (s, 9 H, *t*Bu), 0.87 (s, 9 H, *t*Bu), 0.90 (s, 9 H, *t*Bu), 0.94 (s, 9 H, *t*Bu), 5.77 (s, 2 H, C*H*Ph$_2$), 5.97 (s, 2 H, C*H*Ph$_2$), 5.99 (s, 2 H, C*H*Ph$_2$), 6.10 (s, 2 H, C*H*Ph$_2$), 6.24 (m, 2 H, C*H*), 7.07 (m, 88 H, C*H*), 7.81 (d, $^3J(^1H,^1H)$ = 7.4 Hz, 4 H, C*H*), 7.88 (d, $^3J(^1H,^1H)$ = 7.2 Hz, 4 H, C*H*). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ = 99.9 (s, *P*S$_2$), 192.9 (s, *P*S). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3086 (vw), 3059 (vw), 3026 (vw), 2999 (vw), 2962 (vw), 2867 (vw), 1597 (vw), 1581 (vw), 1492 (w), 1474 (w), 1445 (w), 1412 (vw), 1393 (vw), 1346 (w), 1305 (m), 1228 (vs), 1181 (s), 1119 (s), 1033 (w), 981 (s), 919 (w), 895 (w), 808 (w), 742 (m), 717 (m), 697 (m), 664 (m), 647 (m), 622 (w), 604 (m), 587 (w), 579 (w), 524 (m), 497 (w), 468 (w), 453 (w), 431 (w), 410 (w). Raman (785 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 1595 (5), 1584 (2), 1508 (4), 1481 (2), 1445 (3), 1436 (2), 1395 (2), 1351 (3), 1310 (1), 1249 (2), 1222 (3), 1202 (2), 1188 (2), 1166 (2), 1156 (2), 1145 (2), 1131 (2), 1093 (2), 1077 (2), 1053 (2), 1032 (4), 1003 (10), 992 (2), 966 (2), 957 (2), 926 (2), 862 (2), 848 (2), 832 (4), 818 (2), 794 (3), 763 (2), 744 (2), 735 (3), 731 (3), 714 (2), 712 (2), 706 (2), 702 (2), 663 (3), 652 (2), 644 (2), 631 (2), 619 (4), 612 (3), 605 (2), 590 (4), 578 (2), 568 (4), 549 (3), 528 (3), 493 (2), 465 (2), 454 (3), 446 (3), 430 (3), 406 (3), 394 (4), 389 (4), 376 (3), 361 (2), 347 (2), 324 (2), 301 (4), 279 (3), 255 (3), 248 (3), 217 (4), 205 (6), 188 (9), 173 (4), 151 (4), 125 (8).

Figure 52. ^{1}H NMR, ^{31}P{^{1}H} NMR, IR and Raman spectra of **16/17** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{31}P{^{1}H} NMR spectrum

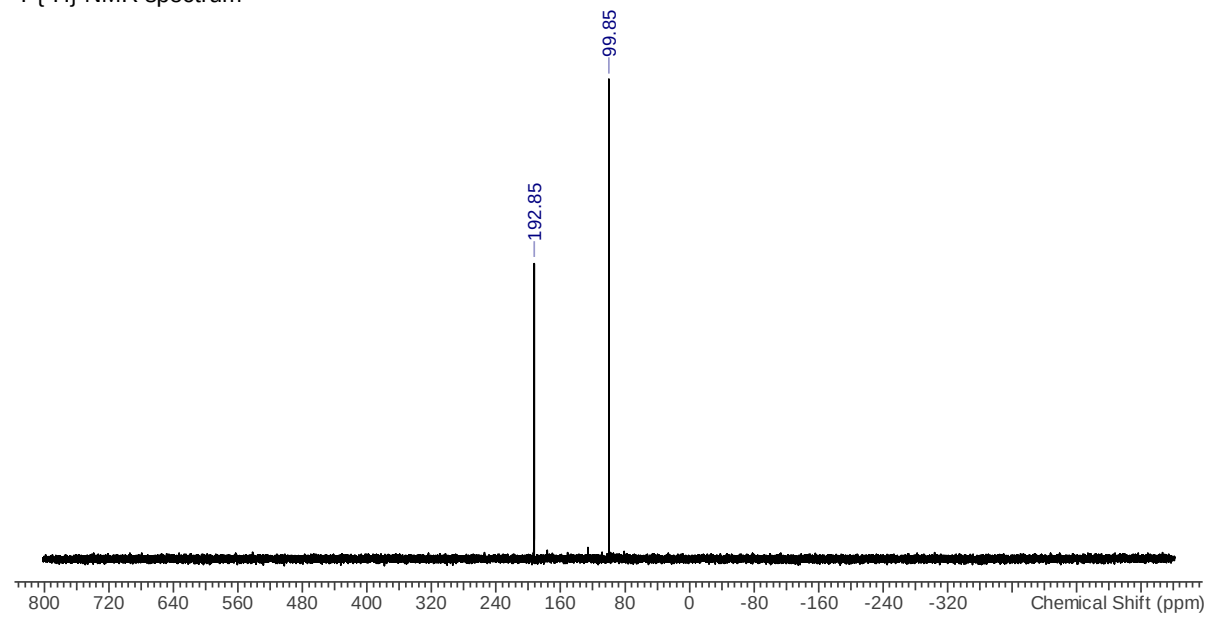
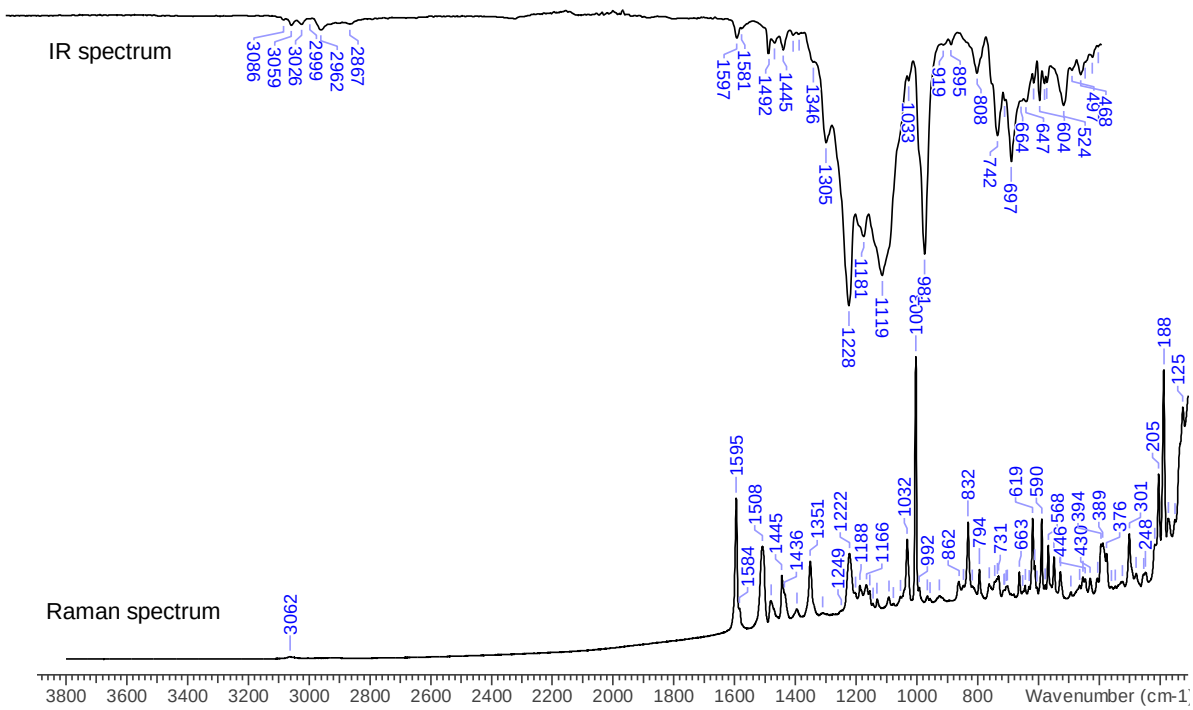
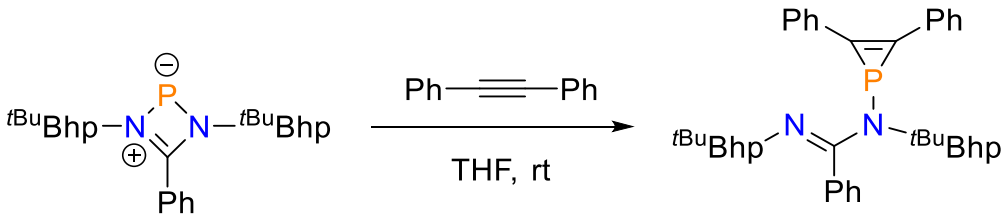


Figure 52. continued.



5.5.14 $^{t\mathrm{Bu}}$Bhp–NC(Ph)N(P(C$_{14}$H$_{10}$))–$^{t\mathrm{Bu}}$Bhp (**18**)



6 (0.20 g, 0.19 mmol) and diphenylacetylene (0.03 g, 0.19 mmol) are dissolved in anhydrous THF (5 mL), resulting in a yellow mixture. After stirring for 2 h, volatiles are removed *in vacuo* (10^{-3} mbar, 50 °C, 1 h). The residue is dissolved in anhydrous diethyl ether (5 mL), filtered and concentrated. The colorless crystals are eventually dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 0.13 g (0.10 mmol, 55.9 %).

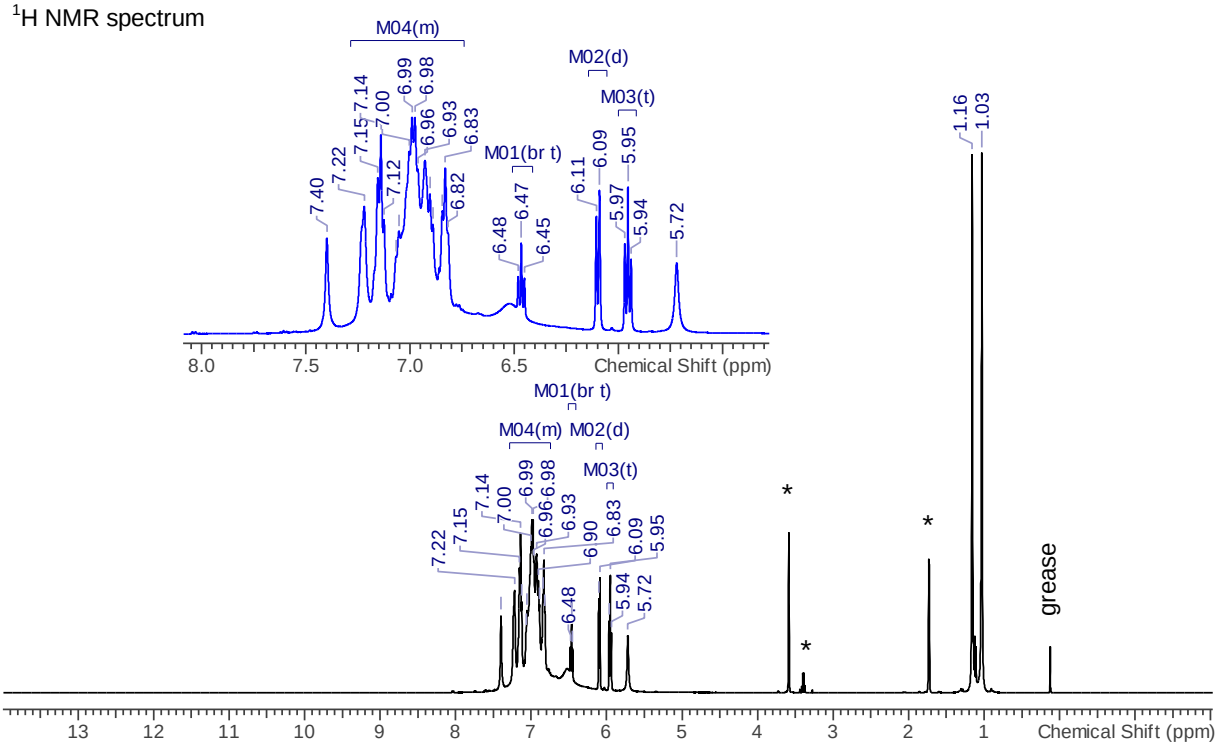
Crystals suitable for single-crystal XRD were obtained from a saturated solution in diethyl ether at room temperature.

Formula: $C_{93}H_{81}N_2P$. M = 1257.66 g/mol. Mp. 180–183 °C. EA found (calcd.) in %: C 89.31 (88.82), H 6.52 (6.49), N 2.25 (2.23). ^{1}H NMR (THF-d$_8$, 500.1 MHz): δ = 1.03 (s, 9 H, *t*Bu), 1.16 (s, 9 H, *t*Bu), 5.72 (s, 2 H, C*H*Ph$_2$), 5.95 (t, $J(^1H,^1H)$ = 7.9 Hz, 2 H), 6.10 (d, $J(^1H,^1H)$ =

7.6 Hz, 2 H), 6.47 (t, $J(^1H,^1H)$ = 7.5 Hz, 2 H), 6.99 (m, 53 H, C*H*), 7.40 (s, 2 H, C*H*Ph_2). $^{13}C\{^1H\}$ NMR (THF-d_8, 125.8 MHz): δ = 31.5 (s, C(CH_3)$_3$), 31.6 (s, C(CH_3)$_3$), 34.8 (s, C(CH_3)$_3$), 35.3 (s, C(CH_3)$_3$), 52.1 (s, $CHPh_2$), 53.1 (s, $CHPh_2$), 126.3 (s, *C*H), 126.4 (s, *C*H), 126.7 (s, *C*H), 127.0 (s, *C*H), 127.4 (s, *C*H), 128.4 (s, *C*H), 128.5 (s, *C*H), 128.8 (s, *C*H), 128.9 (s, *C*H), 129.0 (s, *C*H), 129.6 (s, *C*H), 130.1 (s, *C*H), 130.4 (s, *C*H), 131.0 (s, $C_{quat.}$), 131.3 (s, *C*H), 134.4 (s, $C_{quat.}$), 138.9 (s, $C_{quat.}$), 141.7 (s, $C_{quat.}$), 143.9 (s, $C_{quat.}$), 145.0 (s, $C_{quat.}$), 145.2 (s, $C_{quat.}$), 145.5 (s, $C_{quat.}$), 145.8 (s, $C_{quat.}$), 147.6 (s, $C_{quat.}$), 149.2 (s, $C_{quat.}$), 161.4 (d, $^1J(^{13}C,^{31}P)$ = 12 Hz, *C*P*C*). $^{31}P\{^1H\}$ NMR (THF-d_8, 202.5 MHz): δ = –96.4 (s, C*P*C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3084 (vw), 3059 (w), 3026 (w), 2958 (w), 2904 (vw), 2861 (vw), 1944 (vw), 1878 (vw), 1804 (vw), 1715 (vw), 1599 (w), 1583 (w), 1564 (m), 1492 (m), 1476 (w), 1443 (m), 1414 (vw), 1393 (vw), 1362 (w), 1303 (m), 1233 (vs), 1181 (s), 1125 (s), 1086 (s), 1031 (m), 981 (s), 950 (w), 938 (w), 915 (w), 892 (w), 862 (w), 855 (w), 843 (w), 835 (w), 814 (w), 802 (w), 779 (w), 756 (m), 738 (s), 690 (vs), 666 (m), 649 (m), 635 (m), 622 (m), 606 (m), 592 (m), 579 (m), 569 (m), 554 (m), 538 (m), 515 (m), 499 (m), 470 (m), 445 (m), 423 (w). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3066 (2), 3054 (2), 3044 (1), 2999 (1), 2966 (1), 2953 (1), 2942 (1), 2915 (1), 2904 (1), 2860 (1), 1717 (10), 1688 (1), 1598 (6), 1585 (3), 1568 (2), 1492 (1), 1455 (1), 1445 (1), 1285 (2), 1279 (2), 1246 (1), 1203 (1), 1186 (1), 1180 (1), 1170 (1), 1155 (1), 1135 (3), 1088 (1), 1032 (3), 1001 (9), 964 (1), 923 (1), 913 (1), 836 (1), 768 (1), 687 (1), 679 (1), 665 (1), 636 (1), 620 (1), 608 (1), 559 (1), 477 (1), 298 (1), 288 (1), 278 (1), 269 (1), 252 (1), 236 (1), 213 (1), 179 (2), 166 (1), 139 (2), 133 (2). MS (ESI +, m/z): 1258 ($[M+H]^+$).

Figure 53. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, IR and Raman spectra of **18** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

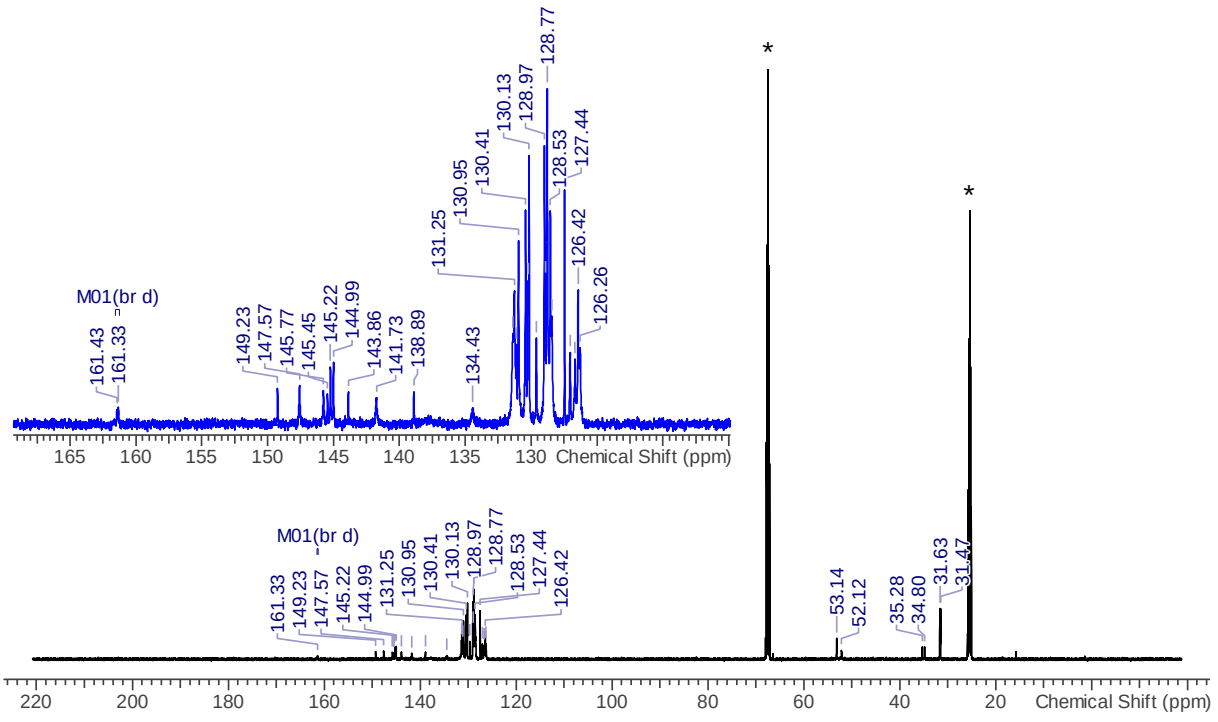
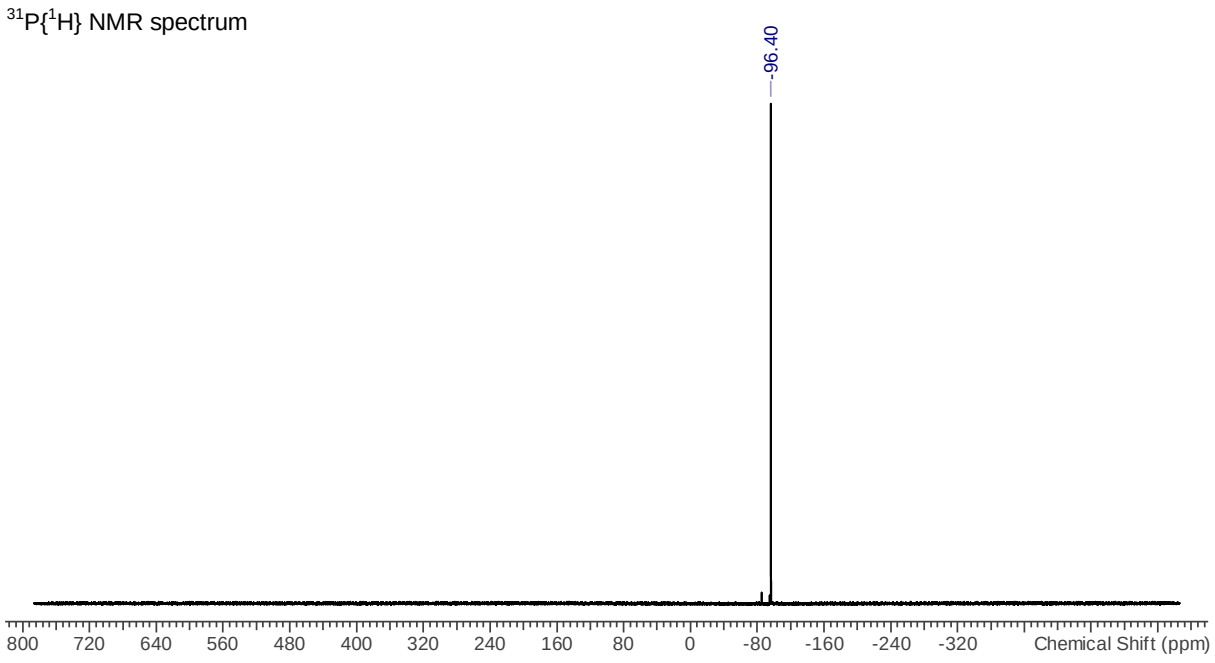
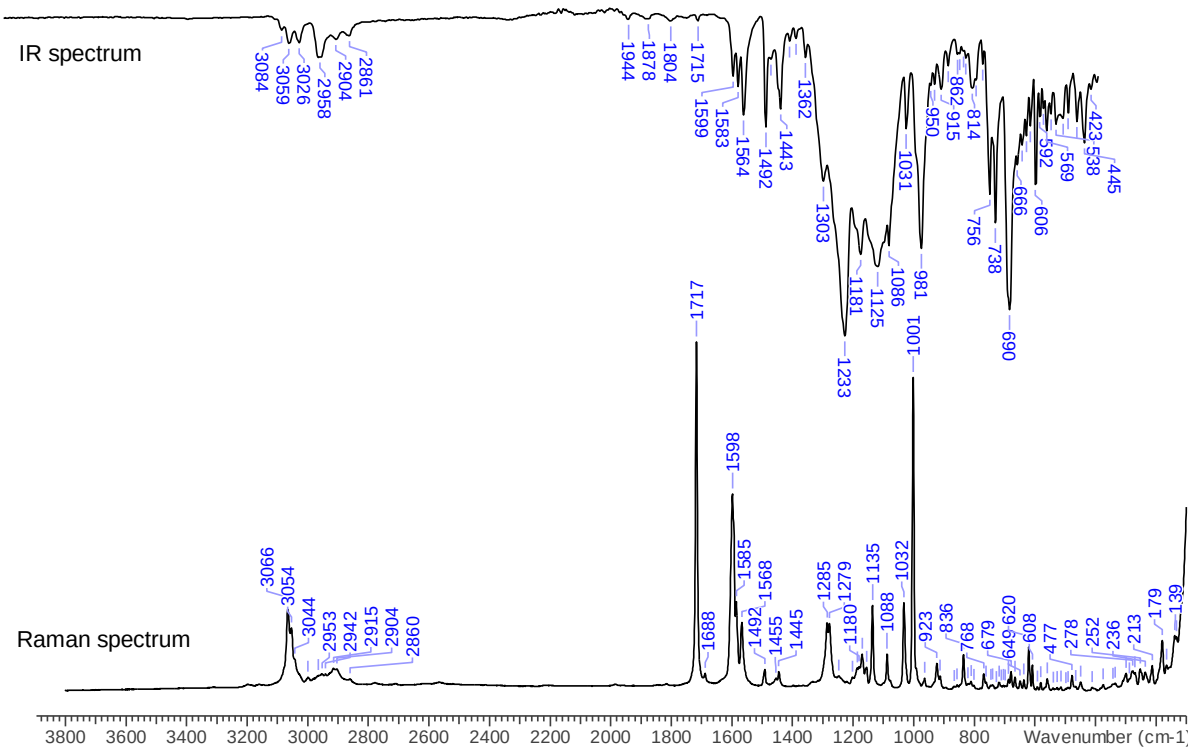
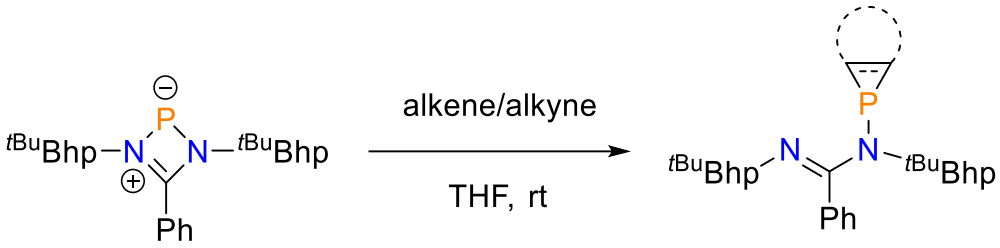


Figure 53. continued.





5.5.15 $^{t\mathrm{Bu}}$Bhp–NC(Ph)N(P(R))–$^{t\mathrm{Bu}}$Bhp (**19-22**)



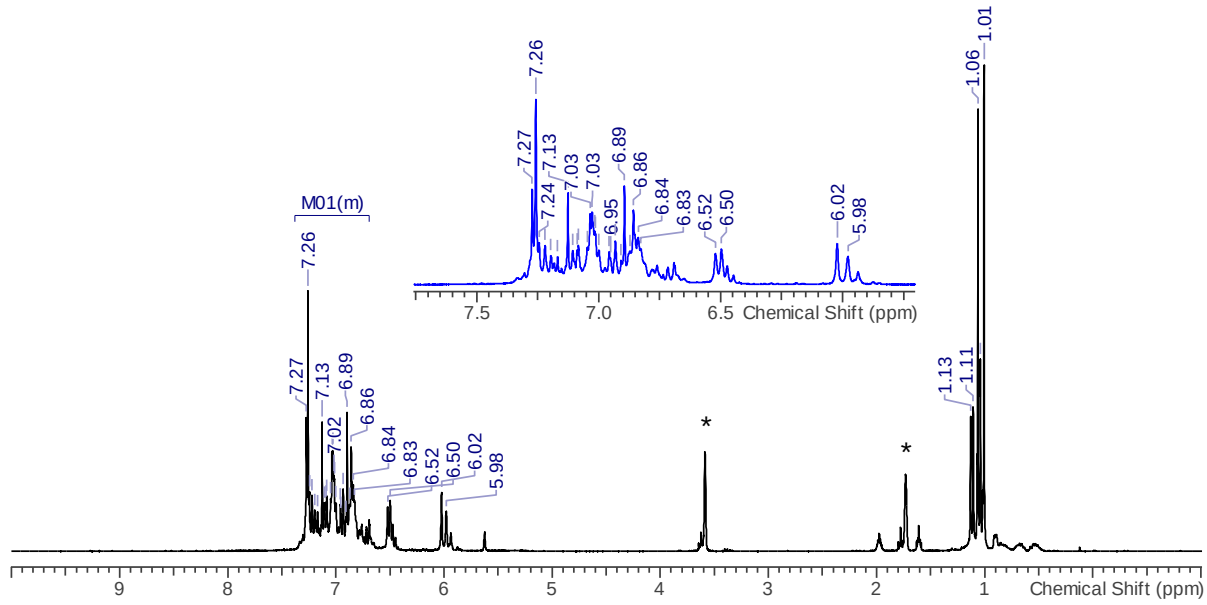
All reactions are carried out following similar protocols.

An excess of alkene/alkyne (5 eq.) is added to a solution of **6** (0.10 g, 0.10 mmol) in anhydrous THF (5 mL) and the mixture is left stirring for 1 h (except for BTMSA, which is left stirring overnight). Afterwards, volatiles are removed *in vacuuo* (10^{-3} mbar) and the residue is dried at 80 °C (oil bath) and 10^{-3} mbar for 1 h.

R = Cyclohexene (19): Formula: $C_{85}H_{81}N_2P$. M = 1161.57 g/mol. ^{1}H NMR (THF-d_8, 300.1 MHz): δ = 1.01 (s, 9 H, *t*Bu), 1.04 (s, 4 H, C*H*$_2$ (Cy)), 1.06 (s, 9 H, *t*Bu), 1.11 (s, 4 H, C*H*$_2$ (Cy)), 1.13 (s, 2 H, C*H* (Cy)), 5.98 (s, 2 H, C*H*Ph$_2$), 6.02 (s, 2 H, C*H*Ph$_2$), 6.50 (s, 2 H, *m*-*H*), 6.52 (s, 2 H, *m*-*H*), 7.06 (m, 45 H, C*H*). ^{13}C{^{1}H} NMR (THF-d_8, 75.5 MHz): δ = 22.9 (s, *C*H$_2$ (Cy)), 22.9 (s, *C*H$_2$ (Cy)), 23.5 (s, *C*H$_2$ (Cy)), 23.6 (s, *C*H$_2$ (Cy)), 27.1 (s, *C*H (Cy)), 27.7 (s, *C*H (Cy)), 31.3 (s, C(*C*H$_3$)$_3$), 31.7 (s, C(*C*H$_3$)$_3$), 34.8 (s, *C*(CH$_3$)$_3$), 35.1 (s, *C*(CH$_3$)$_3$), 52.5 (s, *C*HPh$_2$), 53.1 (s, *C*HPh$_2$), 126.5 (s, *C*H), 126.7 (s, *C*H), 127.1 (s, *C*H), 128.1 (s, *C*H), 128.6 (s, *C*H), 128.7 (s, *C*H), 128.9 (s, *C*H), 130.2 (s, *C*H), 130.5 (s, *C*H), 130.9 (s, *C*H), 131.8 (s, *C*H), 133.6 (s, *C*$_{quat.}$), 134.7 (s, *C*$_{quat.}$), 141.5 (s, *C*$_{quat.}$), 144.0 (s, *C*$_{quat.}$), 144.8 (s, *C*$_{quat.}$), 145.3 (s, *C*$_{quat.}$), 145.4 (s, *C*$_{quat.}$), 145.7 (s, *C*$_{quat.}$), 146.6 (s, *C*$_{quat.}$), 148.3 (s, *C*$_{quat.}$). ^{31}P{^{1}H} NMR (THF-d_8, 121.5 MHz): δ = –95.5 (s, C*P*C). MS (ESI +, m/z): 1162 ([M]$^+$), 1050 ([M–P(Cy)+H]$^+$].

Figure 54. ^{1}H NMR, ^{13}C{^{1}H} NMR and ^{31}P{^{1}H} NMR spectra of **19** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

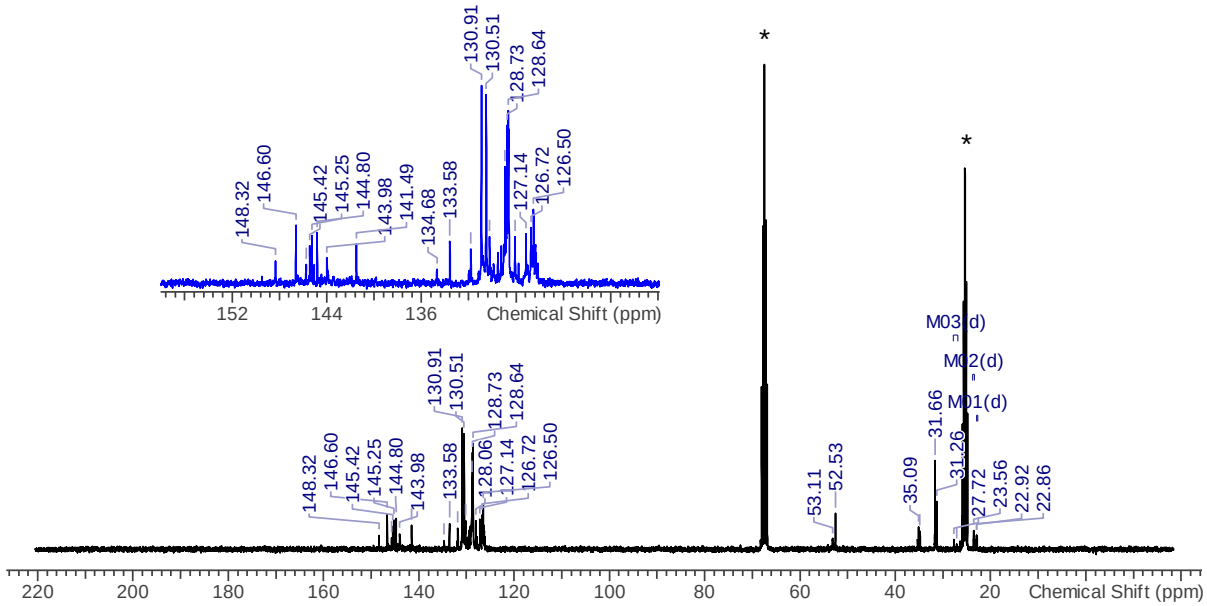
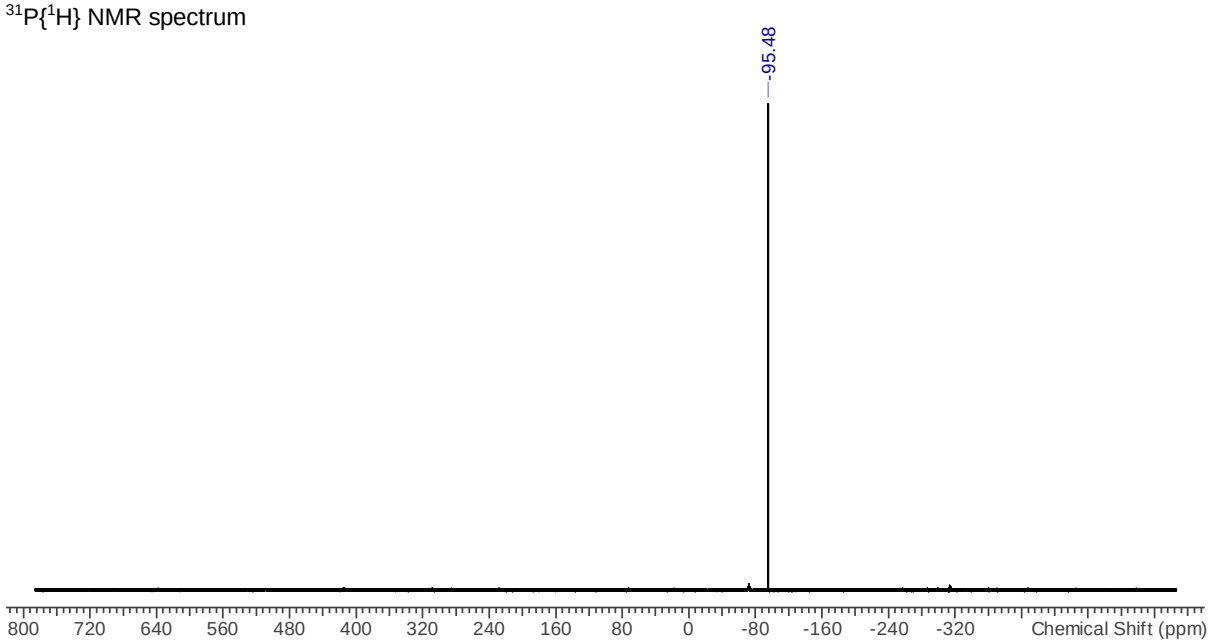


Figure 54. continued.

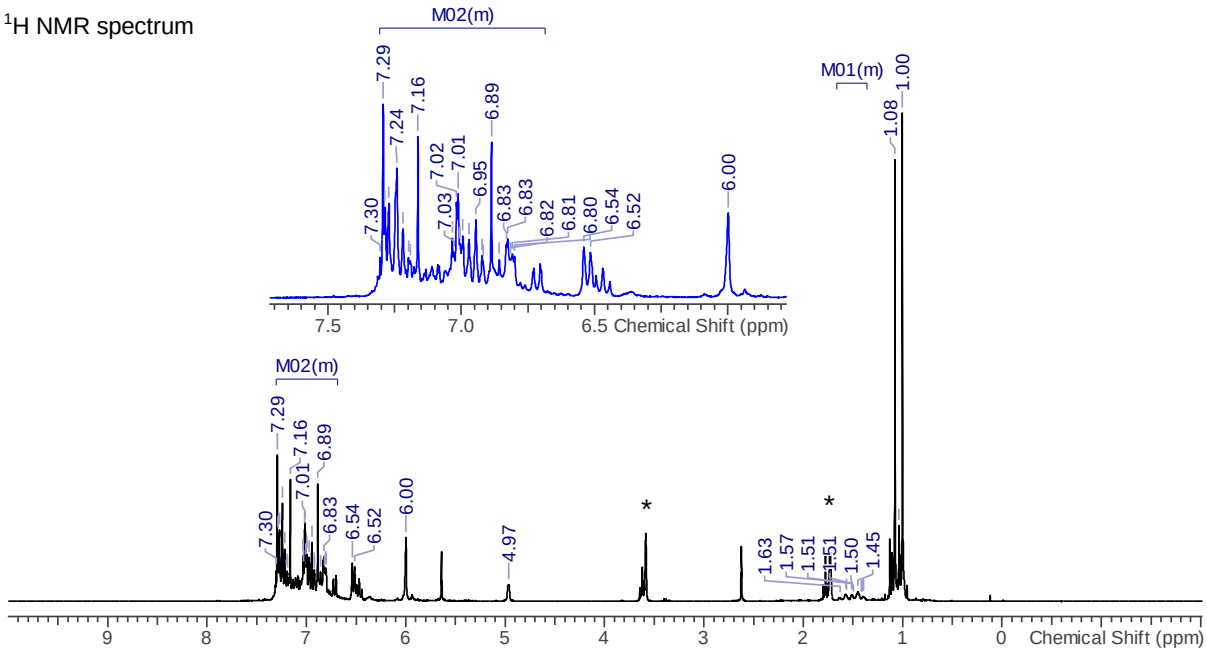
$^{31}P\{^{1}H\}$ NMR spectrum



R = 1,4-Cyclohexadiene (20): Formula: $C_{85}H_{79}N_2P$. M = 1159.55 g/mol. ^{1}H NMR (THF-d_8, 300.1 MHz): δ = 1.00 (s, 9 H, *t*Bu), 1.04 (s, 2 H, C*H* (Cy)), 1.08 (s, 9 H, *t*Bu), 1.48 (m, 4 H, CH_2 (Cy)), 4.97 (s, 2 H, C*H* (Cy)), 6.00 (s, 4 H, C*H*Ph_2), 6.52 (s, 2 H, *m-H*), 6.54 (s, 2 H, *m-H*), 7.07 (m, 45 H, C*H*). $^{13}C\{^{1}H\}$ NMR (THF-d_8, 75.5 MHz): δ = 22.6 (s, *C*H_2 (Cy)), 22.8 (s, *C*H_2 (Cy)), 26.4 (s, *C*H (Cy)), 26.5 (s, *C*H (Cy)), 26.9 (s, *C*H (Cy)), 27.5 (s, *C*H (Cy)), 31.3 (s, C(*C*H_3)$_3$), 31.7 (s, C(*C*H_3)$_3$), 34.8 (s, *C*(CH_3)$_3$), 35.1 (s, *C*(CH_3)$_3$), 52.6 (s, *C*HPh_2), 53.1 (s, *C*HPh_2), 126.6 (s, *C*H), 127.2 (s, *C*H), 128.0 (s, *C*H), 128.6 (s, *C*H), 128.8 (s, *C*H), 128.9 (s, *C*H), 129.3 (s, *C*H), 130.5 (s, *C*H), 130.9 (s, *C*H), 131.0 (s, *C*H), 131.8 (s, *C*H), 132.0 (s, $C_{quat.}$), 133.5 (s, $C_{quat.}$), 141.4 (s, $C_{quat.}$), 143.9 (s, $C_{quat.}$), 144.7 (s, $C_{quat.}$), 145.3 (s, $C_{quat.}$), 145.4 (s, $C_{quat.}$), 145.8 (s, $C_{quat.}$), 146.5 (s, $C_{quat.}$), 148.2 (s, $C_{quat.}$). $^{31}P\{^{1}H\}$ NMR (THF-d_8, 121.5 MHz): δ = –92.8 (s, C*P*C). MS (ESI +, m/z): 1160 ($[M]^+$),

Figure 55. ^{1}H NMR, ^{13}C{^{1}H} NMR and ^{31}P{^{1}H} NMR spectra of **20** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

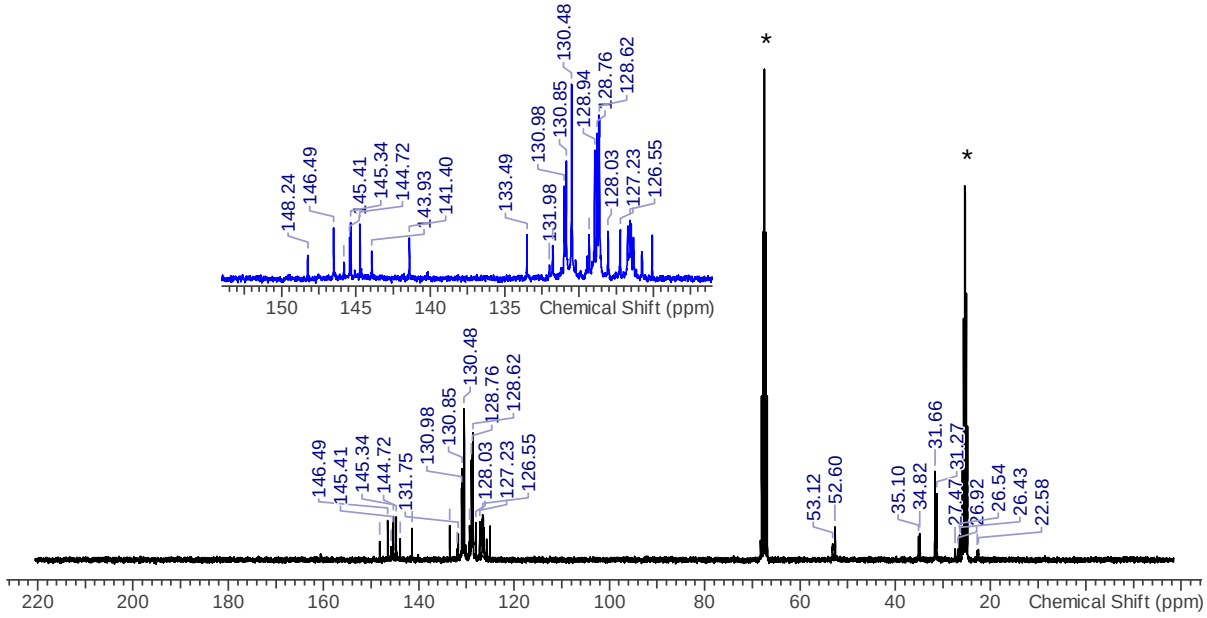
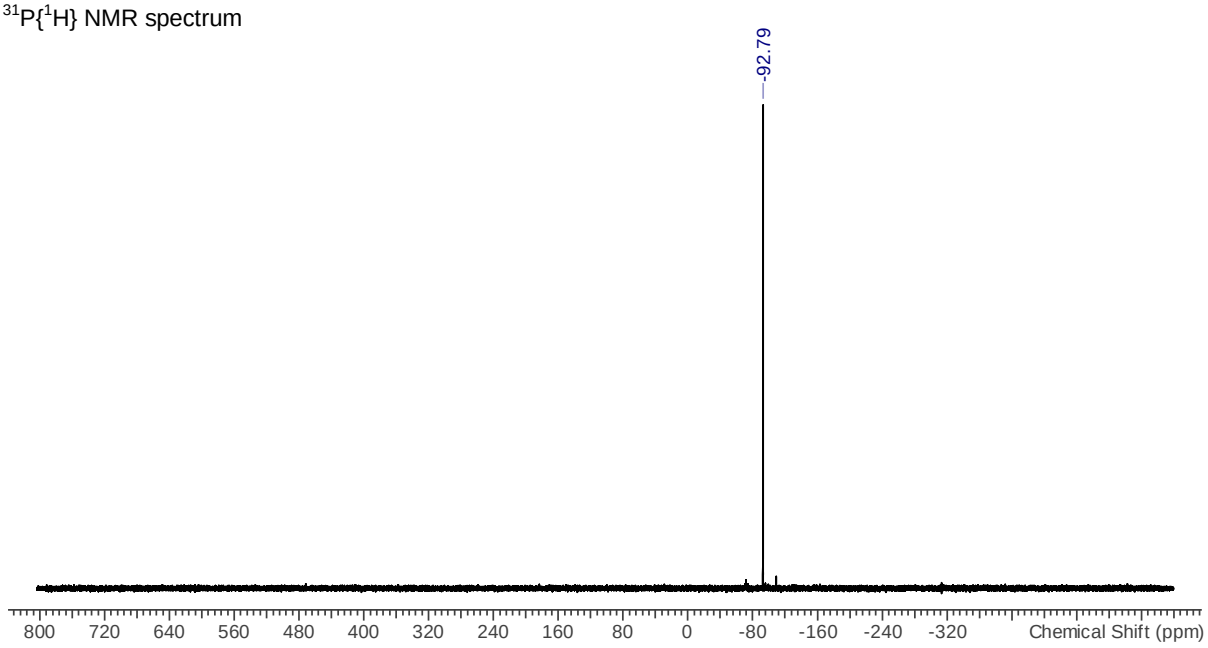


Figure 55. continued.

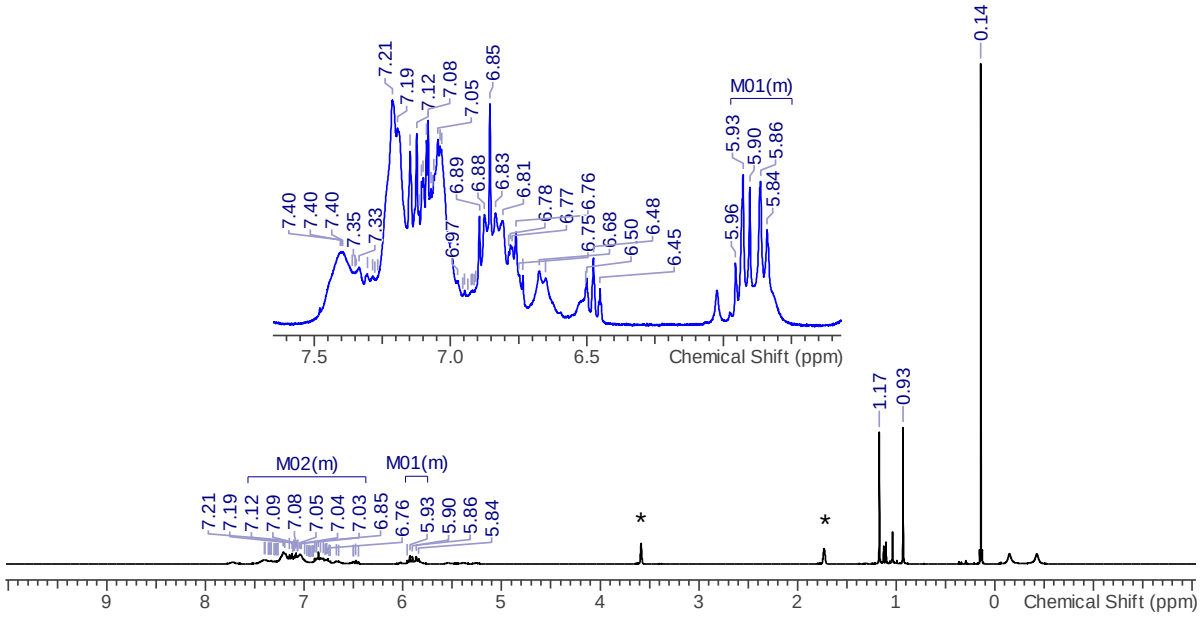
$^{31}P\{^{1}H\}$ NMR spectrum



R = BTMSA (21): Formula: $C_{87}H_{89}N_2PSi_2$. M = 1249.83 g/mol. ^{1}H NMR (THF-d_8, 300.1 MHz): δ = 0.14 (s, 18 H, Si(CH_3)$_3$), 0.93 (s, 9 H, *t*Bu), 1.17 (s, 9 H, *t*Bu), 5.89 (m, 8 H, C*H*), 7.03 (m, 45 H, C*H*). $^{13}C\{^{1}H\}$ NMR (THF-d_8, 75.5 MHz): δ = –0.9 (s, Si(*C*H$_3$)$_3$), –0.0 (s, Si(*C*H$_3$)$_3$), 31.4 (s, C(*C*H$_3$)$_3$), 31.6 (s, C(*C*H$_3$)$_3$), 34.7 (s, *C*(CH$_3$)$_3$), 35.2 (s, *C*(CH$_3$)$_3$), 52.5 (s, *C*HPh$_2$), 52.9 (s, *C*HPh$_2$), 114.2 (s, $C_{quat.}$), 126.7 (s, *C*H), 126.8 (s, *C*H), 127.1 (s, *C*H), 128.6 (s, *C*H), 128.6 (s, *C*H), 129.0 (s, *C*H), 130.2 (s, *C*H), 130.2 (s, *C*H), 130.5 (s, *C*H), 130.6 (s, *C*H), 131.3 (s, *C*H), 134.7 (s, $C_{quat.}$), 137.9 (s, $C_{quat.}$), 140.5 (s, $C_{quat.}$), 143.4 (s, $C_{quat.}$), 143.8 (s, $C_{quat.}$), 145.1 (s, $C_{quat.}$), 145.5 (s, $C_{quat.}$), 146.0 (s, $C_{quat.}$), 146.4 (s, $C_{quat.}$), 148.4 (s, $C_{quat.}$). $^{31}P\{^{1}H\}$ NMR (THF-d_8, 121.5 MHz): δ = –109.0 (s, C*P*C). ^{29}Si INEPT NMR (THF-d_8, 59.6 MHz): δ = 21.2 (dec, $^{2}J(^{29}Si,^{1}H)$ = 7.4 Hz, TMS). MS (ESI –, m/z): 1249 ([M–H]$^-$),

Figure 56. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR and ^{29}Si INEPT NMR spectra of **21** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

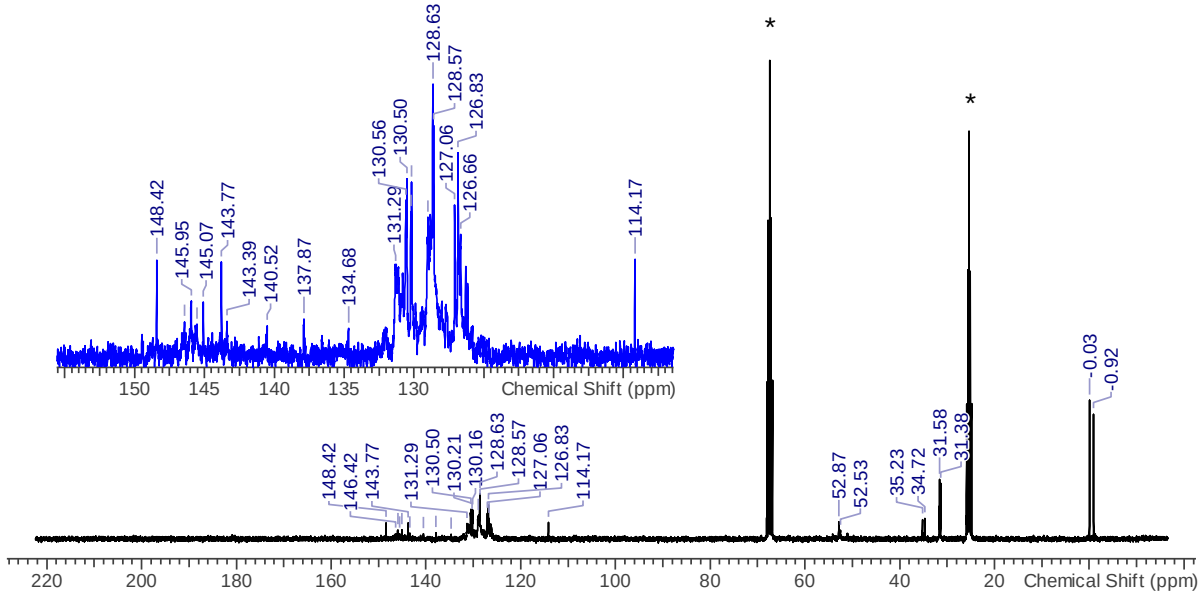
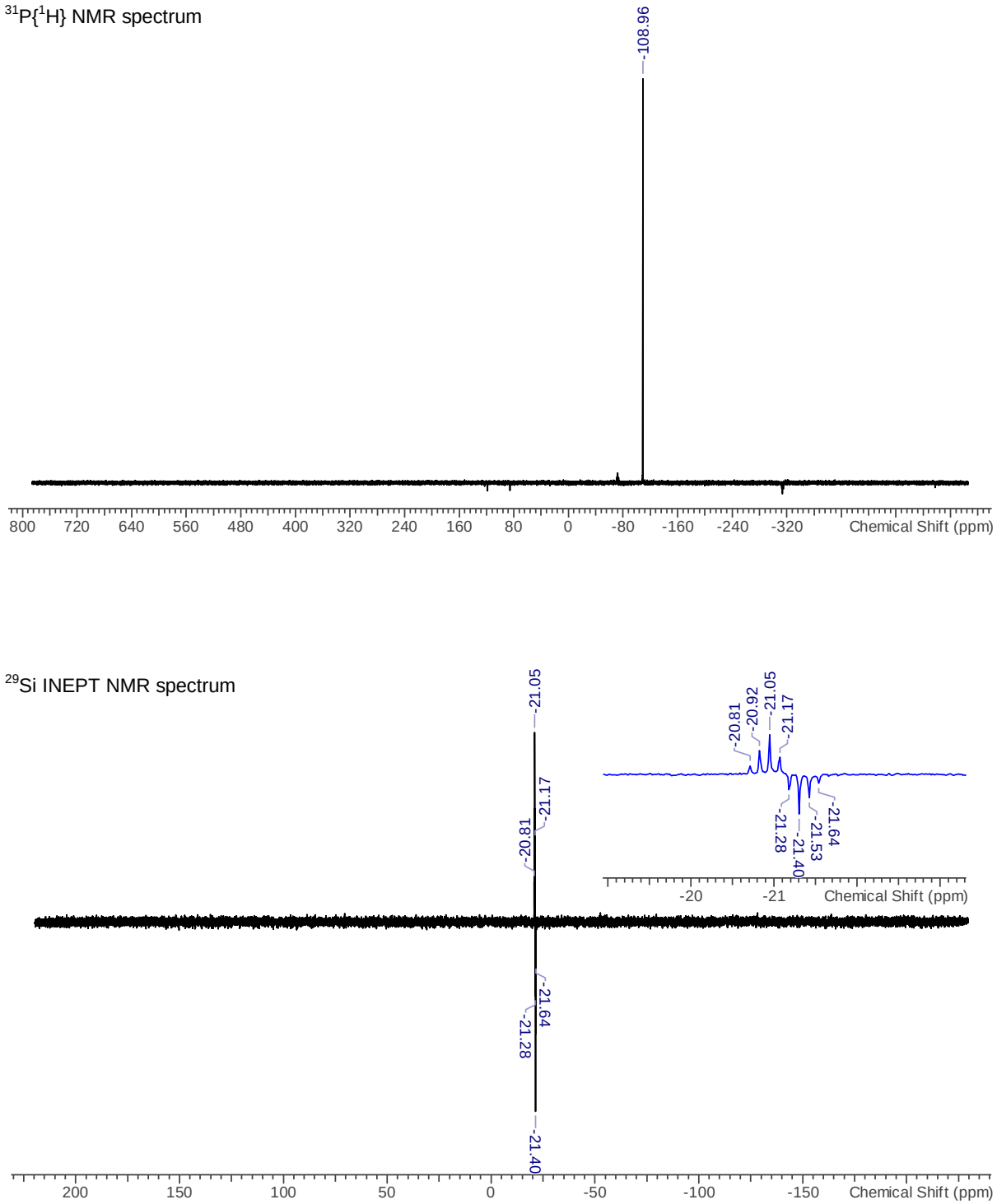


Figure 56. continued.

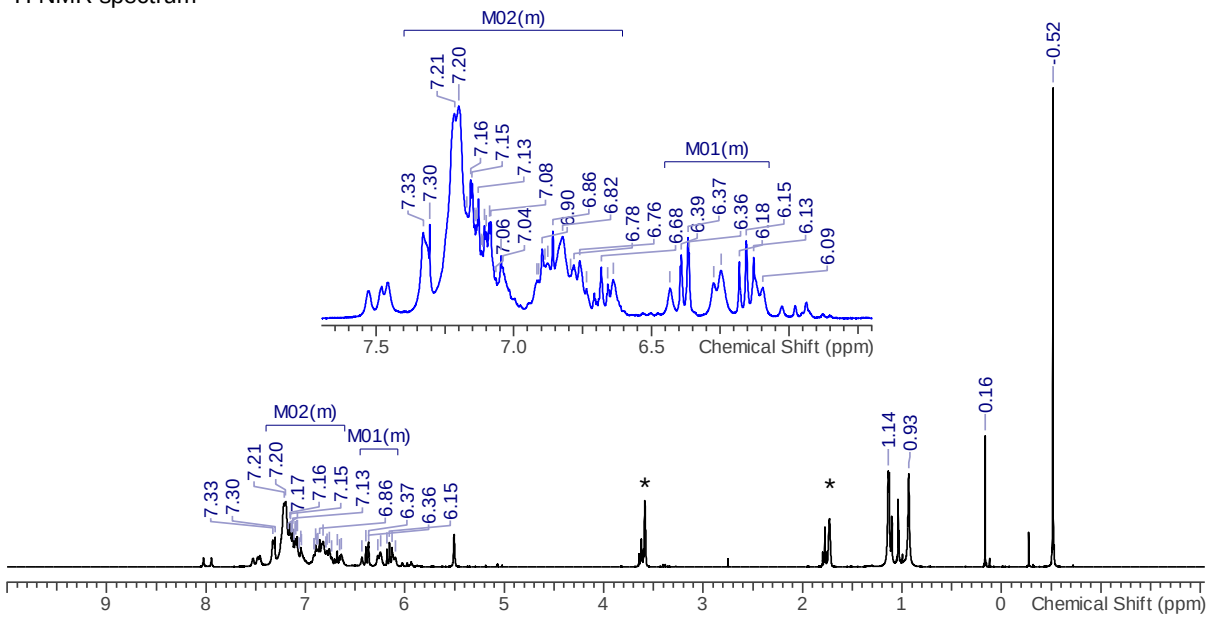


R = TMSA (22): Formula: $C_{84}H_{81}N_2PSi$. M = 1177.64 g/mol. ^{1}H NMR (THF-d_8, 300.1 MHz): δ = –0.52 (s, 9 H, Si(C*H*$_3$)$_3$), 0.16 (s, 1 H, *H*CP), 0.93 (s, 9 H, *t*Bu), 1.14 (s, 9 H, *t*Bu), 6.26 (m, 10 H, C*H*), 7.06 (m, 43 H, C*H*). ^{13}C{^{1}H} NMR (THF-d_8, 75.5 MHz): δ = –1.6 (s, Si(*C*H$_3$)$_3$), –0.1 (s, H*C*P), 31.3 (s, C(*C*H$_3$)$_3$), 31.7 (s, C(*C*H$_3$)$_3$), 34.8 (s, *C*(CH$_3$)$_3$), 35.2 (s, *C*(CH$_3$)$_3$), 51.9 (s, *C*HPh$_2$), 53.3 (s, *C*HPh$_2$), 125.9 (s, *C*H), 127.0 (s, *C*H), 127.5 (s, *C*H), 128.2 (s, *C*H), 128.4

(s, *C*H), 128.8 (s, *C*H), 129.8 (s, *C*H), 130.7 (s, *C*H), 131.0 (s, *C*H), 131.3 (s, *C*H), 131.5 (s, *C*H), 132.5 (s, $C_{quat.}$), 135.3 (s, $C_{quat.}$), 137.8 (s, $C_{quat.}$), 141.4 (s, $C_{quat.}$), 143.8 (s, $C_{quat.}$), 144.5 (s, $C_{quat.}$), 145.6 (s, $C_{quat.}$), 146.5 (s, $C_{quat.}$), 148.1 (s, $C_{quat.}$), 149.5 (s, $C_{quat.}$), 150.3 (s, $C_{quat.}$). $^{31}P\{^{1}H\}$ NMR (THF-d_8, 121.5 MHz): δ = –118.2 (s, C*P*C). ^{29}Si INEPT NMR (THF-d_8, 59.6 MHz): δ = –8.2 (dec, $^{2}J(^{29}Si,^{1}H)$ = 7.4 Hz, TMS). MS (ESI +, m/z): 1178 ($[M]^+$).

Figure 57. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR and ^{29}Si INEPT NMR spectra of **22** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

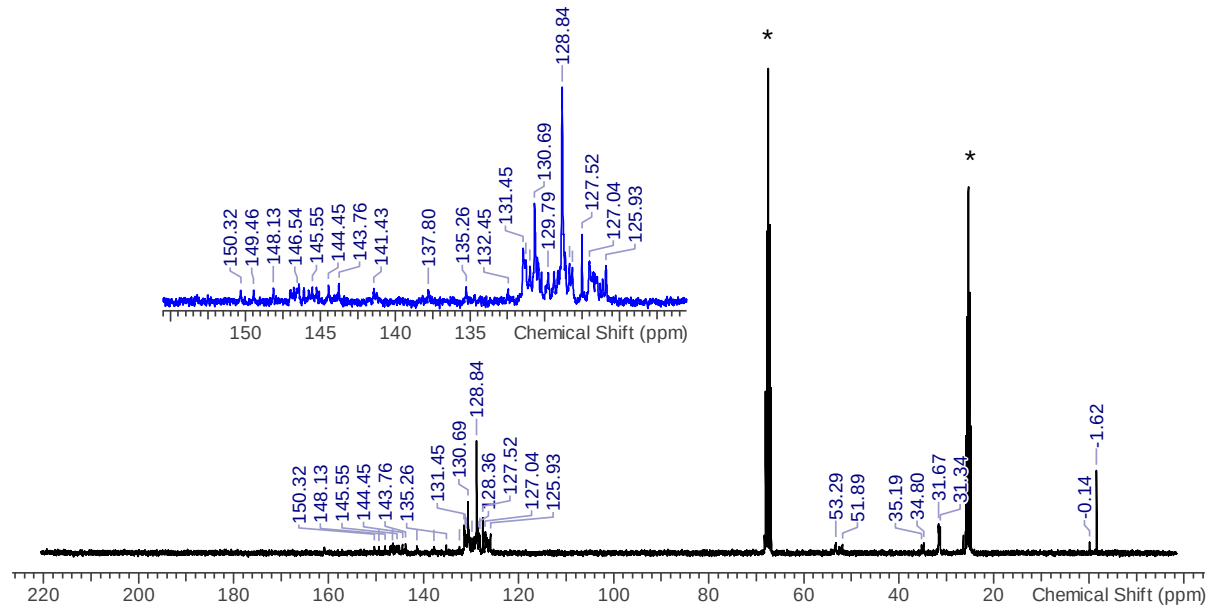
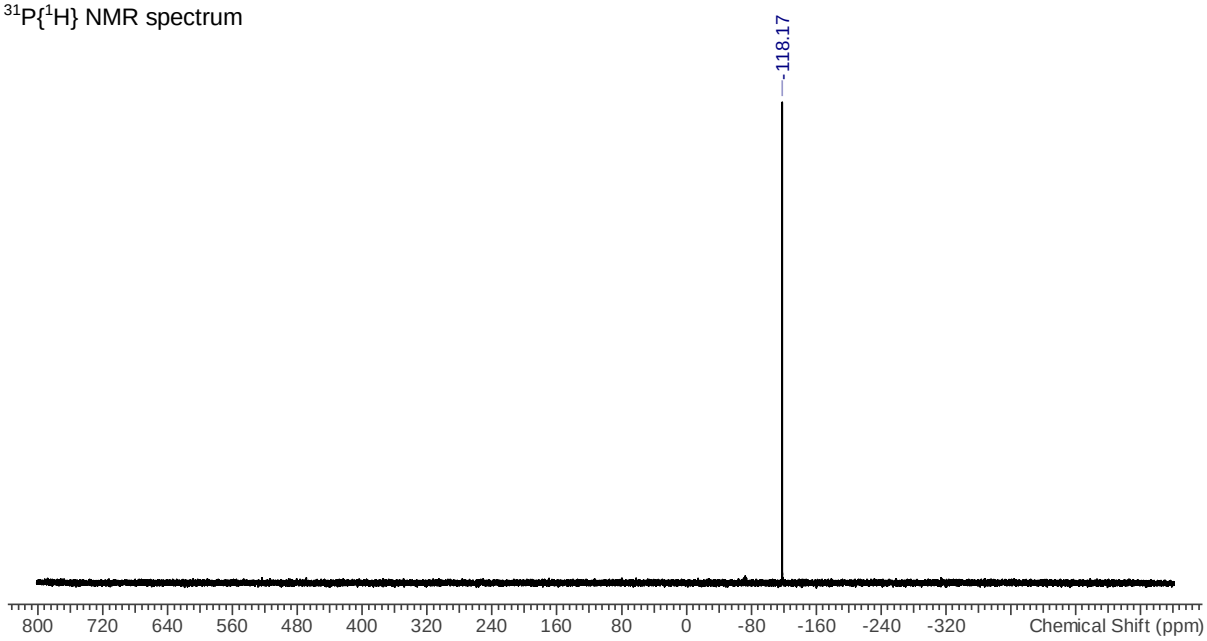
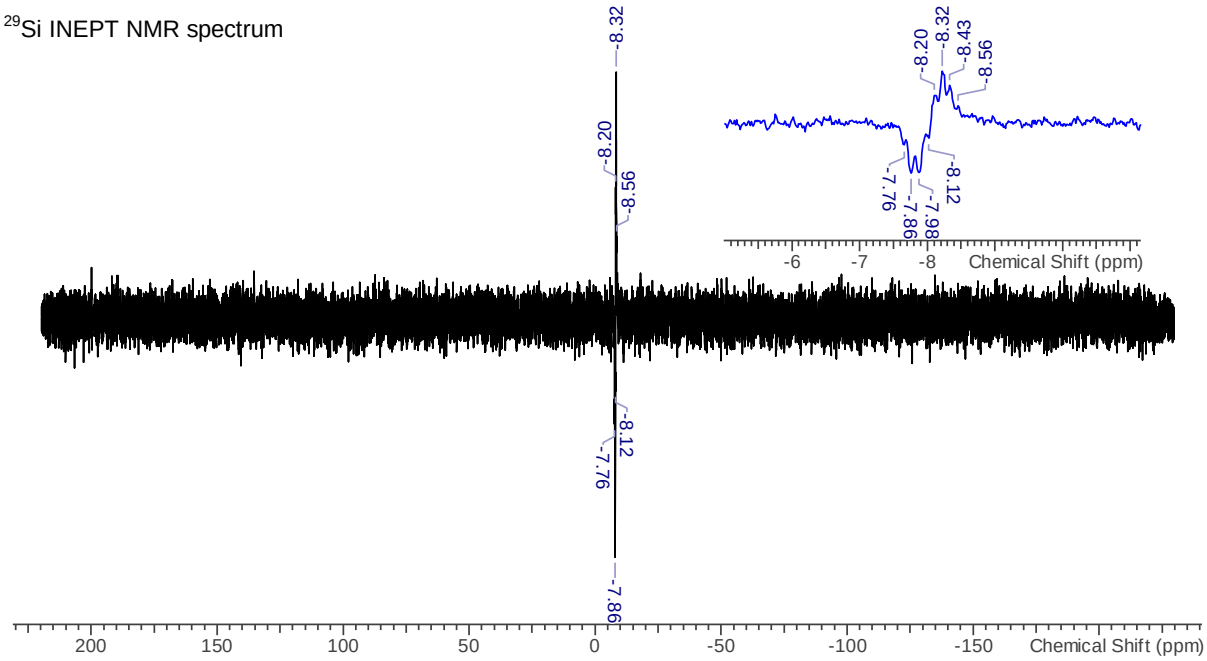


Figure 57. continued.

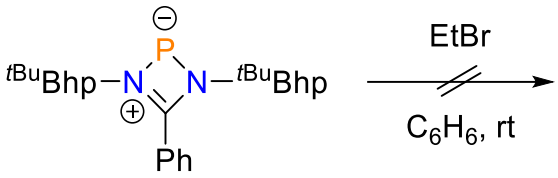
$^{31}P\{^{1}H\}$ NMR spectrum



^{29}Si INEPT NMR spectrum



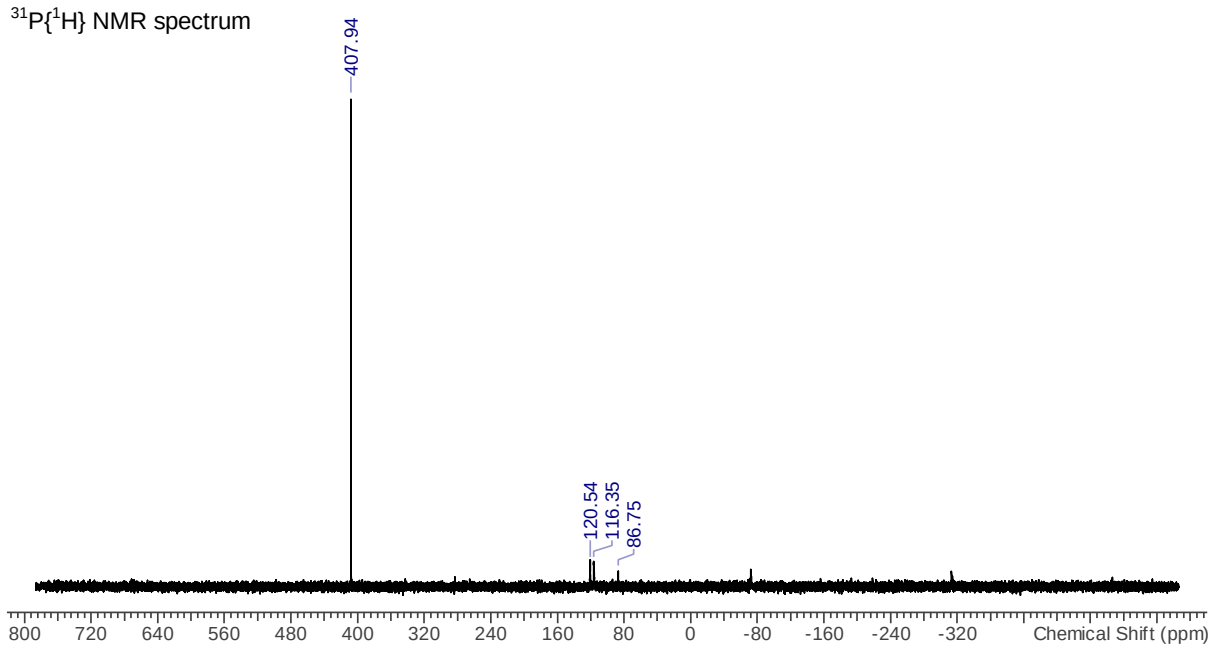
5.5.16 $^{t\mathrm{Bu}}$Bhp–[NC(Ph)NP]–$^{t\mathrm{Bu}}$Bhp (**6**) + EtBr



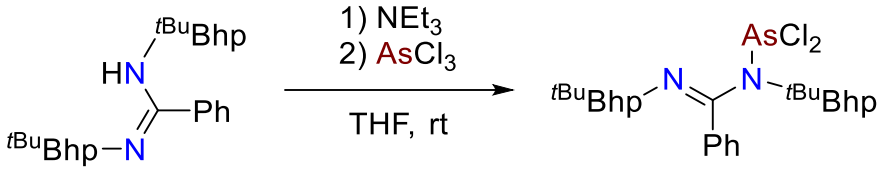
An excess of bromoethane (0.1 mL, 1.34 mmol) is added to a solution of **6** (0.21 g, 0.20 mmol) in anhydrous benzene and the mixture is left stirring at room temperature. A $^{31}P\{^{1}H\}$ NMR spectrum after 8 d reveals no significant changes.

$^{31}P\{^{1}H\}$ NMR (THF-d_8, 202.5 MHz): δ = –407.9 (s, N*P*N), 120.5 (s), 116.4 (s), 86.8 (s).

Figure 58. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **6** with EtBr.



5.5.17 $^{t\mathrm{Bu}}$Bhp–NC(Ph)N($AsCl_2$)–$^{t\mathrm{Bu}}$Bhp (**23**)



A solution of the amidine (0.50 g, 0.48 mmol) in anhydrous THF (15 mL) is cooled to 0 °C (ice bath). NEt_3 (0.3 mL, 2.16 mmol) and $AsCl_3$ (0.1 mL, 1.19 mmol) are added consecutively, whereupon the color of the mixture changes to pale yellow. After stirring overnight at room temperature, volatiles are removed *in vacuuo* (10^{-3} mbar) and the yellow solid is dried for 1 h at 80 °C. Anhydrous Et_2O (30 mL) is added, the mixture is filtered and the product is extracted (3x) via evaporation-condensation-cycles. Volatiles are again removed *in vacuuo* and the product is washed with minimal amounts of anhydrous Et_2O and eventually dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 0.33 g (0.28 mmol, 58.3 %).

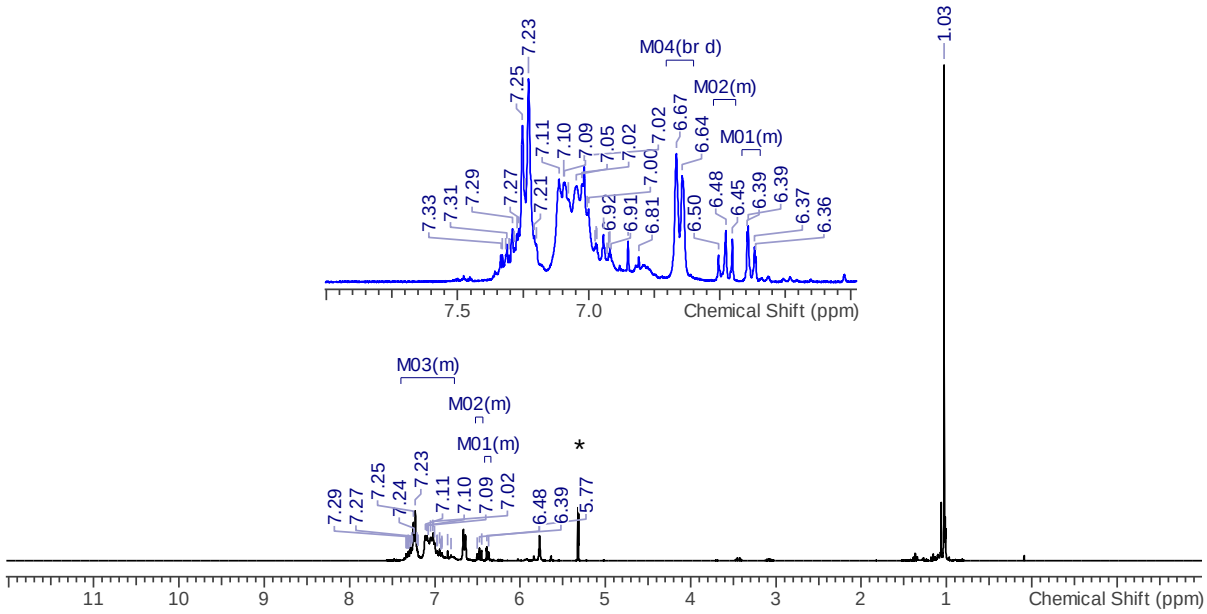
Crystals suitable for single-crystal XRD were obtained from a saturated solution in dichloromethane at room temperature.

Formula: $C_{79}H_{71}Cl_2N_2As$. M = 1194.27 g/mol. Mp. 260–265 °C. EA found (calcd.) in %: C 79.64 (79.45), H 5.63 (5.99), N 2.84 (2.35). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.03 (s, 18 H, *t*Bu), 5.77 (s, 4 H, C*H*Ph_2), 6.38 (m, 2 H, C*H*), 6.47 (m, 2 H, C*H*), 6.62 (d, $J(^1H,^1H)$ = 6.8 Hz, 8 H, C*H*), 7.12 (m, 37 H, C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 62.9 MHz): δ = 31.2 (s, C(CH_3)$_3$), 34.9 (s, *C*(CH_3)$_3$), 52.2 (s, *C*HPh_2), 126.6 (s, *C*H), 127.8 (s, *C*H), 128.7 (s, *C*H), 128.9 (s, *C*H), 130.3 (s, *C*H), 130.5 (s, *C*H), 131.5 (s, *C*H), 136.9 (s, $C_{quat.}$), 139.4 (s, $C_{quat.}$), 143.7 (s, $C_{quat.}$), 145.3 (s, $C_{quat.}$), 148.9 (s, $C_{quat.}$), 164.0 (s, N*C*N). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3084 (vw), 3057 (w), 3026 (w), 2999 (vw), 2964 (w), 2921 (w), 2863 (w), 2797 (w), 1892 (vw), 1806 (vw), 1771 (vw), 1645 (vw), 1620 (m), 1608 (m), 1573 (m), 1517 (vw), 1494 (m), 1472 (w), 1463 (w), 1447 (m), 1414 (w), 1395 (vw), 1362 (w), 1336 (w), 1307 (m), 1235 (s), 1181 (m), 1125 (m), 1078 (m), 1033 (w), 983 (m), 950 (w), 928 (w), 917 (w), 892 (w), 864 (w), 855 (w), 829 (w), 810 (w), 789 (w), 761 (m), 734 (m), 695 (vs), 633 (w), 622 (m), 604 (m), 585 (m), 577 (m), 546 (w), 528 (w), 495 (w), 472 (m), 458 (w). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3065 (3), 3056 (3), 3050 (3), 3026 (2), 3001 (2), 2979 (2), 2967 (2), 2941 (2), 2927 (2), 2904 (2), 1605 (4), 1584 (3), 1506 (3), 1480 (3), 1465 (3), 1452 (3), 1349 (2), 1343 (3), 1334 (3), 1311 (3), 1300 (3), 1282 (3), 1245 (2), 1198 (2), 1187 (3), 1172 (3), 1157 (2), 1109 (2), 1078 (2), 1032 (4), 1002 (10), 993 (2), 954 (3), 894 (2), 857 (2), 838 (3), 809 (2), 767 (2), 759 (2), 751 (2), 727

(3), 710 (2), 649 (2), 637 (2), 618 (3), 606 (2), 584 (2), 557 (2), 530 (2), 498 (2), 488 (2), 476 (2), 451 (2), 360 (2), 304 (2), 284 (2), 271 (2), 248 (3), 229 (3), 215 (2), 155 (2). MS (CI +, m/z): 1050 ($[M–AsCl_2+2H]^+$).

Figure 59. ^{1}H NMR, ^{13}C{^{1}H} NMR, IR and Raman spectra of **23** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

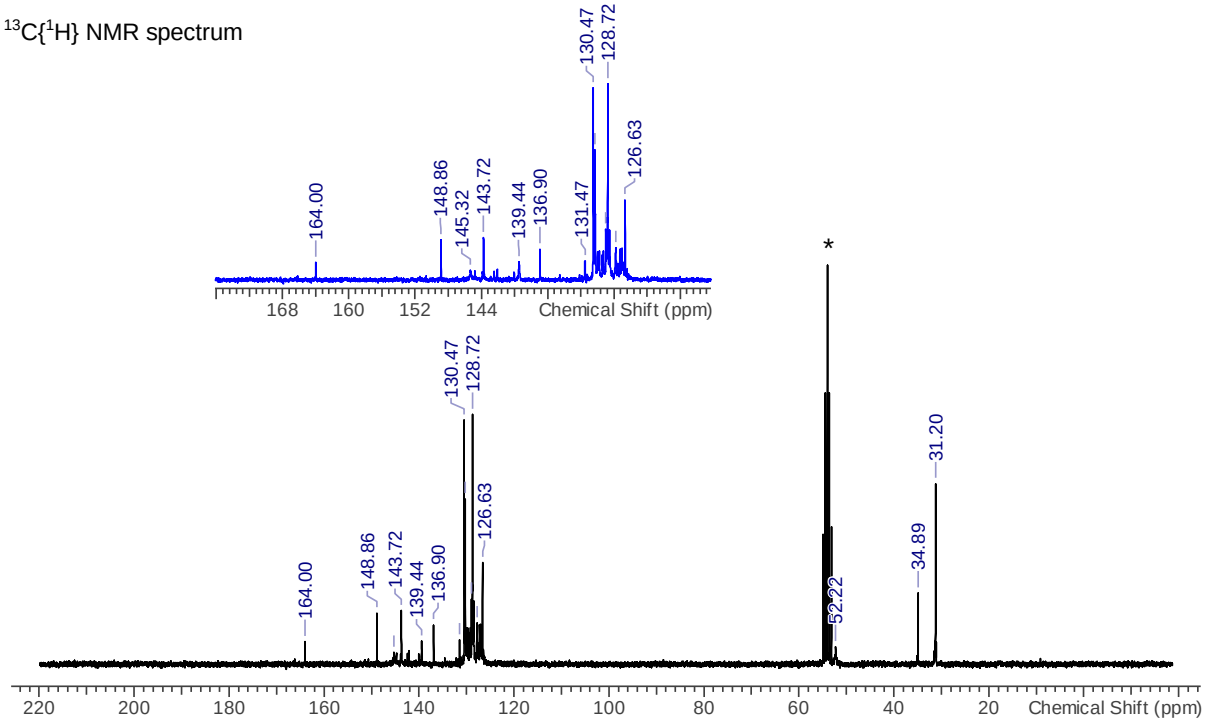
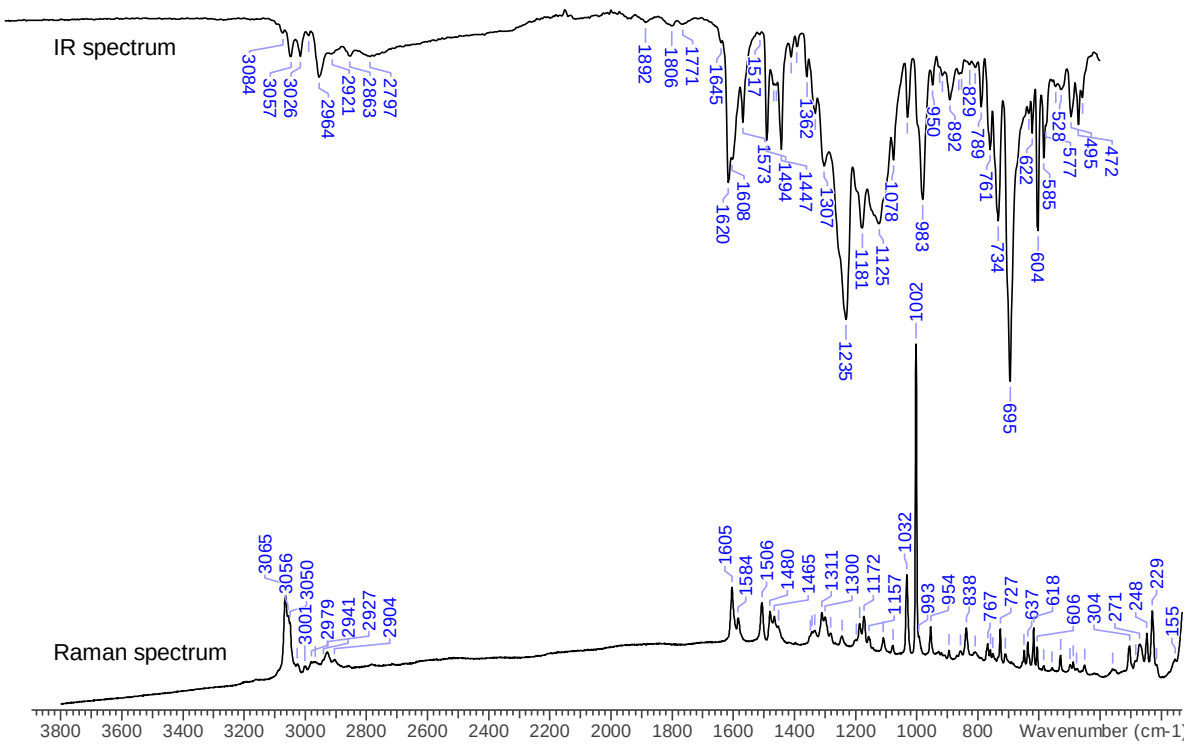
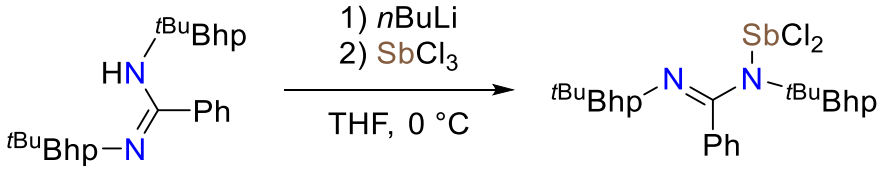


Figure 59. continued.



5.5.18 $^{t\mathrm{Bu}}$Bhp–NC(Ph)N($SbCl_2$)–$^{t\mathrm{Bu}}$Bhp (**24**)



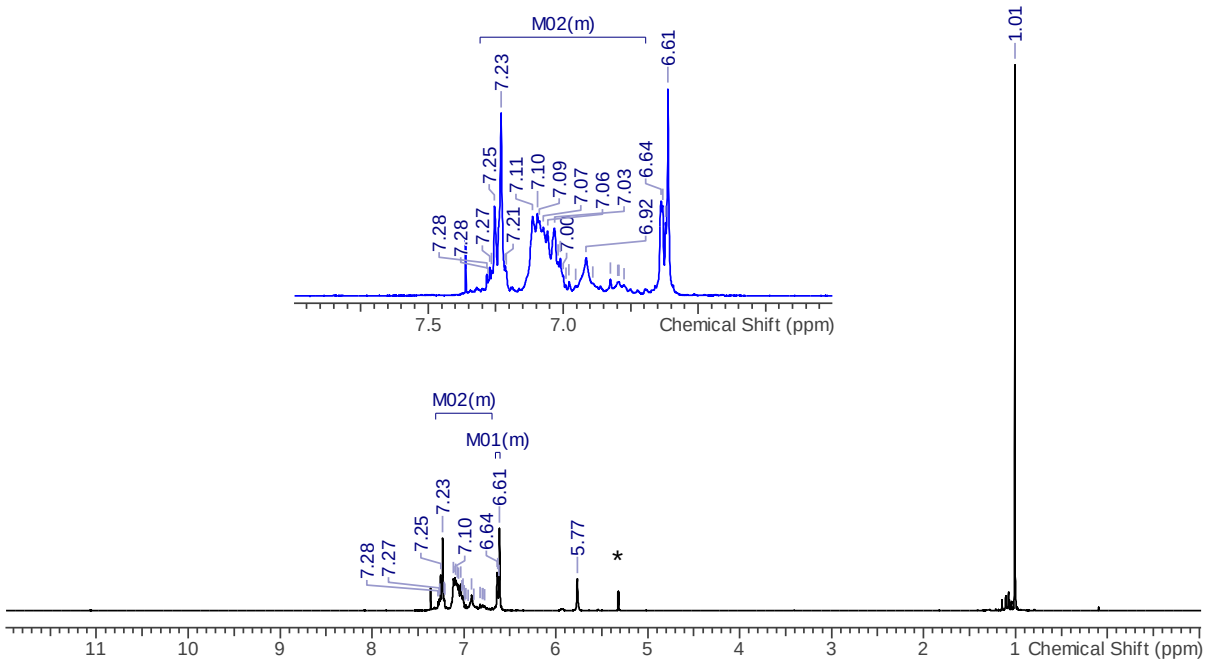
A solution of the amidine (0.51 g, 0.48 mmol) in anhydrous THF (12 mL) is cooled to 0 °C (ice bath), whereupon *n*BuLi (2.5 M in hexane, 0.2 mL, 0.55 mmol) is added. The mixture is left stirring at room temperature for 1 h, whereupon a solution of $SbCl_3$ (0.13 g, 0.57 mmol) in anhydrous THF (5 mL) is added at –80 °C. The pale yellow mixture is left stirring at room temperature overnight. Volatiles are removed in vacuuo and the solid is dried for 2 h at 80 °C. Afterwards, anhydrous benzene (15 mL) is added and the mixture is filtered over celite. Removal of the solvent yields the product as a pale beige solid, which is dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 0.32 g (0.26 mmol, 54.2 %).

Crystals suitable for single-crystal XRD were obtained from a saturated solution in diethyl ether at room temperature.

Formula: $C_{79}H_{71}Cl_2N_2Sb$. M = 1241.11 g/mol. Mp. 322–328 °C. EA found (calcd.) in %: C 76.71 (76.45), H 5.77 (5.77), N 2.44 (2.26). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.01 (s, 18 H, *t*Bu), 5.77 (s, 4 H, C*H*Ph$_2$), 6.61 (s, 4 H, C*H*), 6.62 (m, 8 H, C*H*), 7.11 (m, 37 H, C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ = 31.2 (s, C(*C*H$_3$)$_3$), 34.8 (s, *C*(CH$_3$)$_3$), 52.3 (s, *C*HPh$_2$), 126.7 (s, *C*H), 127.2 (s, *C*H), 127.8 (s, *C*H), 128.7 (s, *C*H), 129.0 (s, *C*H), 130.4 (s, *C*H), 130.7 (s, *C*H), 137.1 (s, $C_{quat.}$), 139.3 (s, $C_{quat.}$), 144.0 (s, $C_{quat.}$), 145.0 (s, $C_{quat.}$), 148.6 (s, $C_{quat.}$), 167.2 (s, N*C*N). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3084 (vw), 3059 (w), 3026 (w), 2999 (vw), 2964 (w), 2923 (w), 2865 (w), 1645 (vw), 1618 (m), 1606 (m), 1573 (w), 1521 (w), 1494 (m), 1472 (w), 1465 (w), 1447 (m), 1414 (w), 1395 (w), 1375 (w), 1364 (w), 1336 (w), 1299 (w), 1286 (w), 1261 (w), 1243 (w), 1204 (vw), 1181 (w), 1154 (vw), 1105 (vw), 1078 (w), 1033 (w), 1002 (vw), 993 (vw), 971 (vw), 950 (w), 917 (w), 895 (w), 864 (w), 855 (w), 831 (vw), 814 (vw), 789 (w), 761 (m), 732 (m), 697 (vs), 647 (w), 633 (w), 622 (w), 604 (m), 585 (m), 577 (m), 557 (w), 548 (w), 495 (w), 472 (m), 460 (w). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3198 (1), 3161 (1), 3078 (2), 3063 (4), 3004 (2), 2965 (2), 2930 (2), 2901 (2), 2860 (2), 1601 (5), 1582 (2), 1524 (2), 1488 (1), 1452 (1), 1444 (1), 1379 (1), 1295 (1), 1245 (1), 1195 (1), 1188 (1), 1169 (2), 1155 (1), 1096 (1), 1075 (1), 1030 (2), 1002 (10), 989 (1), 971 (1), 941 (1), 917 (1), 856 (1), 843 (1), 833 (2), 817 (1), 807 (1), 767 (1), 748 (1), 642 (1), 630 (1), 619 (1), 349 (2), 317 (1), 302 (1), 290 (1), 279 (1), 251 (1), 235 (1), 219 (1), 210 (1), 202 (2), 188 (1), 172 (1), 142 (2), 125 (3). MS (CI +, m/z): 1050 ([M–$SbCl_2$+2H]$^+$).

Figure 60. ^{1}H NMR, ^{13}C{^{1}H} NMR, IR and Raman spectra of **24** (solvent signals marked by asterisk).

^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum

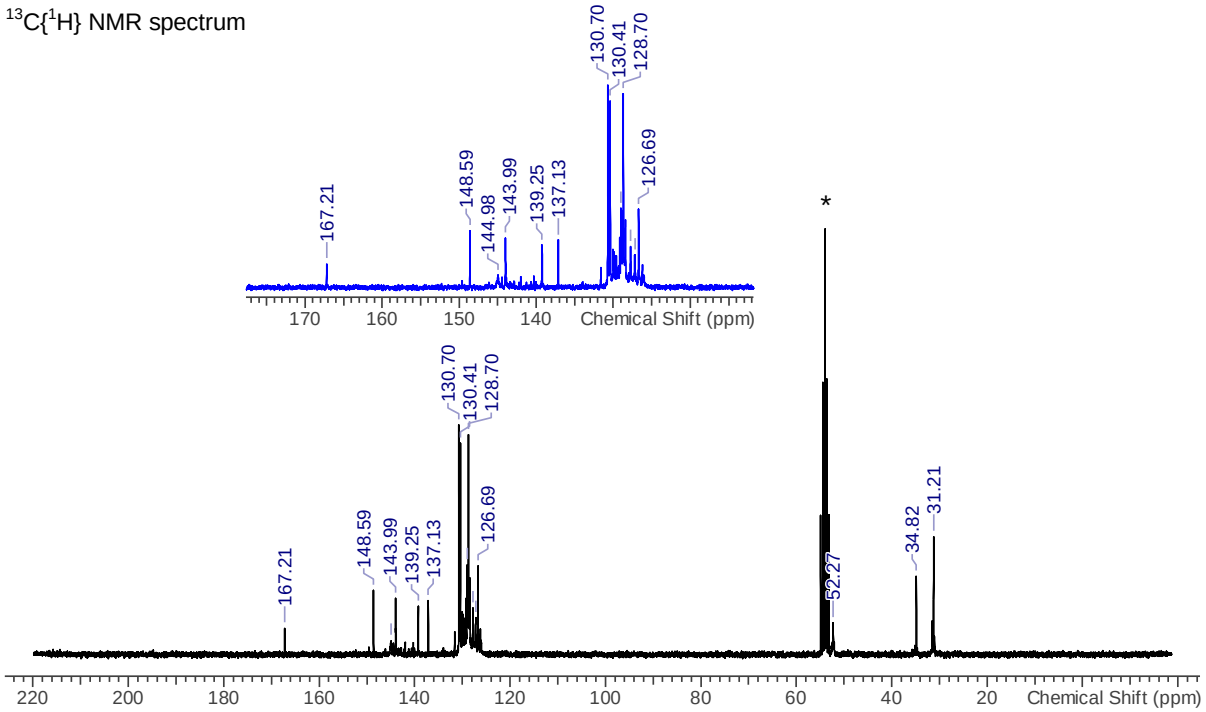
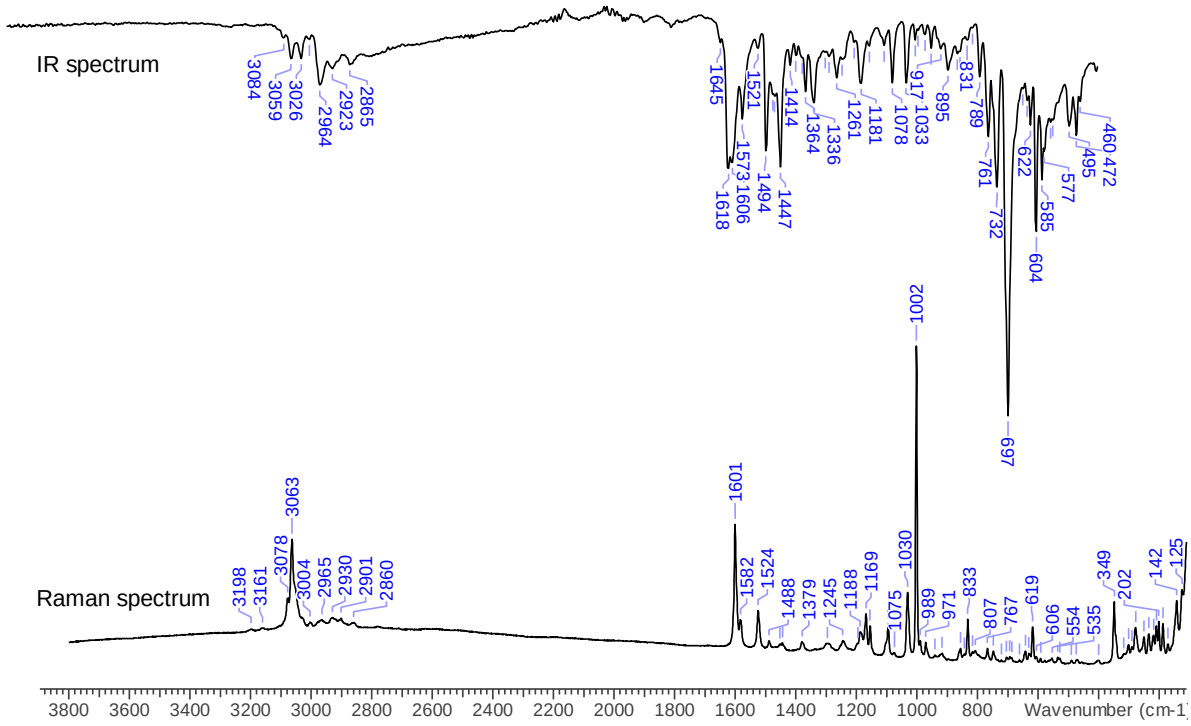
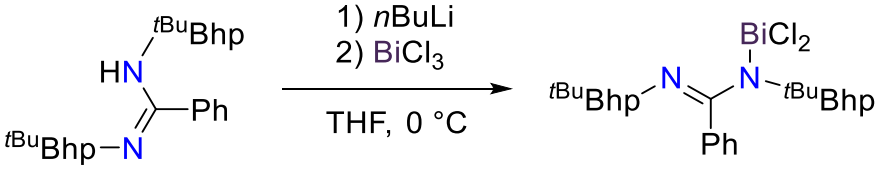


Figure 60. continued.



5.5.19 $^{t\mathrm{Bu}}$Bhp–NC(Ph)N($BiCl_2$)–$^{t\mathrm{Bu}}$Bhp (**25**)



A solution of the amidine (0.50 g, 0.48 mmol) in anhydrous THF (12 mL) is cooled to 0 °C (ice bath), whereupon *n*BuLi (2.5 M in hexane, 0.2 mL, 0.53 mmol) is added. The mixture is left stirring at room temperature for 1 h, whereupon a solution of $BiCl_3$ (0.19 g, 0.59 mmol) in anhydrous THF (5 mL) is added at –80 °C. The yellow mixture is left stirring at room temperature for 2 d. Volatiles are then removed *in vacuuo* (10^{-3} mbar) and the solid is dried for 2 h at 80 °C. Afterwards, anhydrous benzene (15 mL) is added and the mixture is filtered over celite. The solvent is removed *in vacuuo* and the product is washed with minimal amounts of anhydrous diethyl ether, yielding a yellow solid, which is eventually dried at 50 °C (oil bath) and 10^{-3} mbar for 1 h. Yield: 0.13 g (0.10 mmol, 20.8 %).

Crystals suitable for single-crystal XRD were obtained from a saturated solution in diethyl ether at room temperature.

Formula: $C_{79}H_{71}Cl_2N_2Bi$. M = 1328.33 g/mol. Mp. 211–217 °C. EA found (calcd.) in %: C 71.81 (71.43), H 5.39 (5.39), N 1.96 (2.11). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 0.98 (s, 18 H, *t*Bu), 5.89 (s, 4 H, C*H*Ph$_2$), 6.61 (d, $J(^1H,^1H)$ = 7.2 Hz, 8 H, C*H*), 6.89 (s, 4 H, *m*-*H*), 7.09 (m, 25 H, C*H*), 7.28 (m, 12 H, C*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz): δ = 31.5 (s, C(*C*H$_3$)$_3$), 34.5 (s, *C*(CH$_3$)$_3$), 51.9 (s, *C*HPh$_2$), 126.7 (s, *C*H), 127.0 (s, *C*H), 127.4 (s, *C*H), 128.7 (s, *C*H), 129.4 (s, *C*H), 130.5 (s, *C*H), 130.6 (s, *C*H), 136.7 (s, $C_{quat.}$), 139.6 (s, $C_{quat.}$), 144.0 (s, $C_{quat.}$), 145.7 (s, $C_{quat.}$), 149.0 (s, $C_{quat.}$), 167.1 (s, N*C*N). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3100 (vw), 3084 (vw), 3059 (w), 3026 (w), 3003 (vw), 2962 (w), 2933 (w), 2902 (w), 2865 (w), 1890 (vw), 1808 (vw), 1645 (vw), 1599 (w), 1579 (w), 1511 (w), 1492 (m), 1484 (m), 1443 (m), 1414 (w), 1379 (m), 1364 (m), 1334 (w), 1313 (w), 1303 (w), 1288 (w), 1274 (w), 1251 (w), 1243 (w), 1181 (w), 1154 (w), 1107 (w), 1094 (w), 1076 (w), 1031 (w), 1004 (w), 969 (w), 950 (w), 938 (w), 923 (w), 897 (w), 860 (w), 833 (w), 796 (w), 779 (w), 763 (m), 748 (w), 732 (m), 699 (vs), 647 (w), 622 (w), 606 (m), 592 (m), 579 (w), 565 (w), 554 (w), 521 (w), 507 (w), 493 (w), 472 (m), 447 (w), 425 (w). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3059 (3), 2976 (1), 2969 (1), 2931 (1), 2906 (1), 1599 (2), 1582 (1), 1511 (1), 1485 (1), 1480 (1), 1465 (1), 1451 (1), 1380 (1), 1299 (1), 1287 (1), 1277 (1), 1242 (1), 1189 (1), 1184 (1), 1169 (2), 1155 (1), 1105 (1), 1093 (1), 1033 (2), 1029 (2), 1001 (10), 989 (1), 964 (1), 955 (1), 857 (1), 832 (1), 819 (1), 805 (1), 767 (1), 748 (1), 647 (1), 640 (1), 630 (1), 618 (2), 606 (1), 313 (3), 302 (1), 268 (1), 251 (2), 236 (2), 219 (1), 207 (1), 183 (2), 169 (1), 156 (1), 142 (2). MS (CI +, m/z): 1050 ([M–BiCl$_2$+2H]$^+$).

Figure 61. ^{1}H NMR, ^{13}C{^{1}H} NMR, IR and Raman spectra of **25** (solvent signals marked by asterisk).

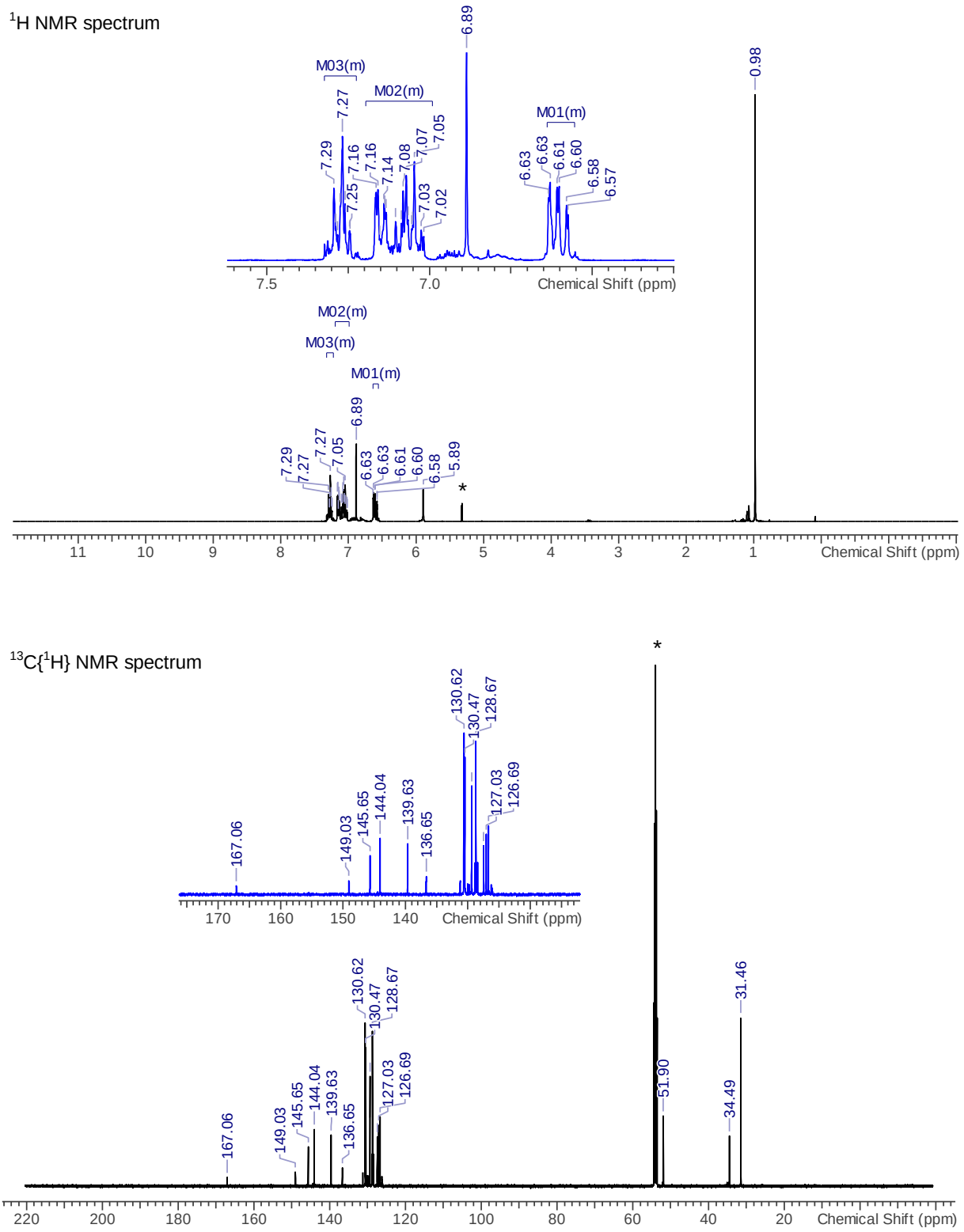
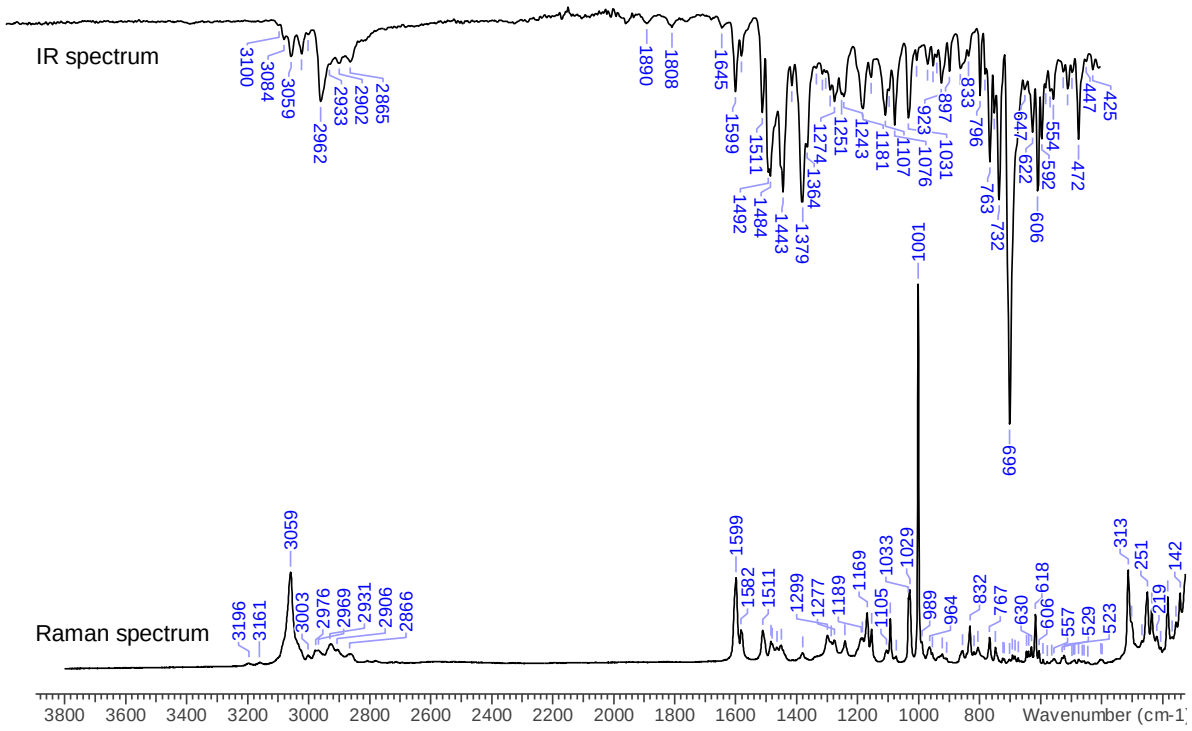
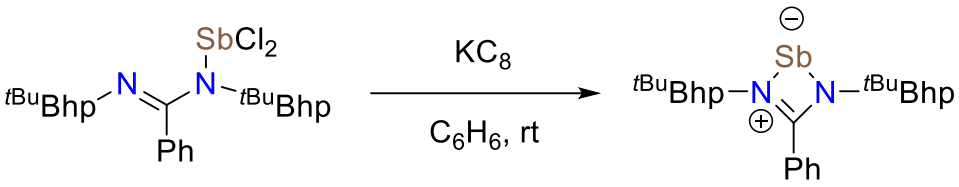


Figure 61. continued.



5.5.20 $^{t\mathrm{Bu}}$Bhp–[NC(Ph)NSb]–$^{t\mathrm{Bu}}$Bhp (**26**)



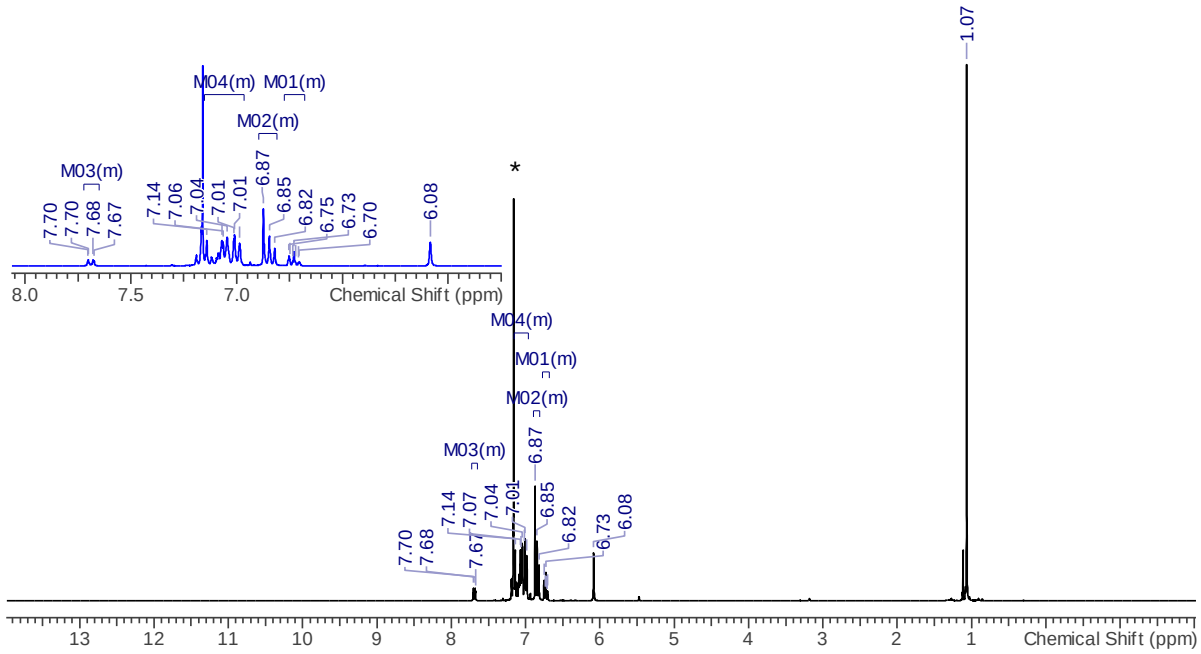
The dichloroantimonyamidinate (0.20 g, 0.16 mmol) and KC_8 (0.10 g, 0.74 mmol) are dissolved in anhydrous benzene (10 mL) and stirred with a glass stir bar overnight at room temperature. The next day, insoluble components are removed via a celite-packed frit and the solvent is removed *in vacuuo* (10^{-3} mbar). The yellow residue is eventually dried at 80 °C and 10^{-3} mbar for 1 h. Yield: 0.06 g (0.05 mmol, 31.8 %).

(Due to the low amount of product, only a ^{1}H NMR spectrum was measured and the residual solid was used for crystallization attempts.)

Formula: $C_{79}H_{71}N_2Sb$. M = 1170.21 g/mol. ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.07 (s, 18 H, *t*Bu), 6.08 (s, 4 H, C*H*Ph$_2$), 6.73 (m, 4 H, *p-H* (CH*Ph*$_2$), 6.86 (m, 12 H, C*H*), 7.05 (m, 31 H, C*H*), 7.69 (m, 2 H, C*H*).

Figure 62. ^{1}H NMR spectrum of **26** (solvent signal marked by asterisk).

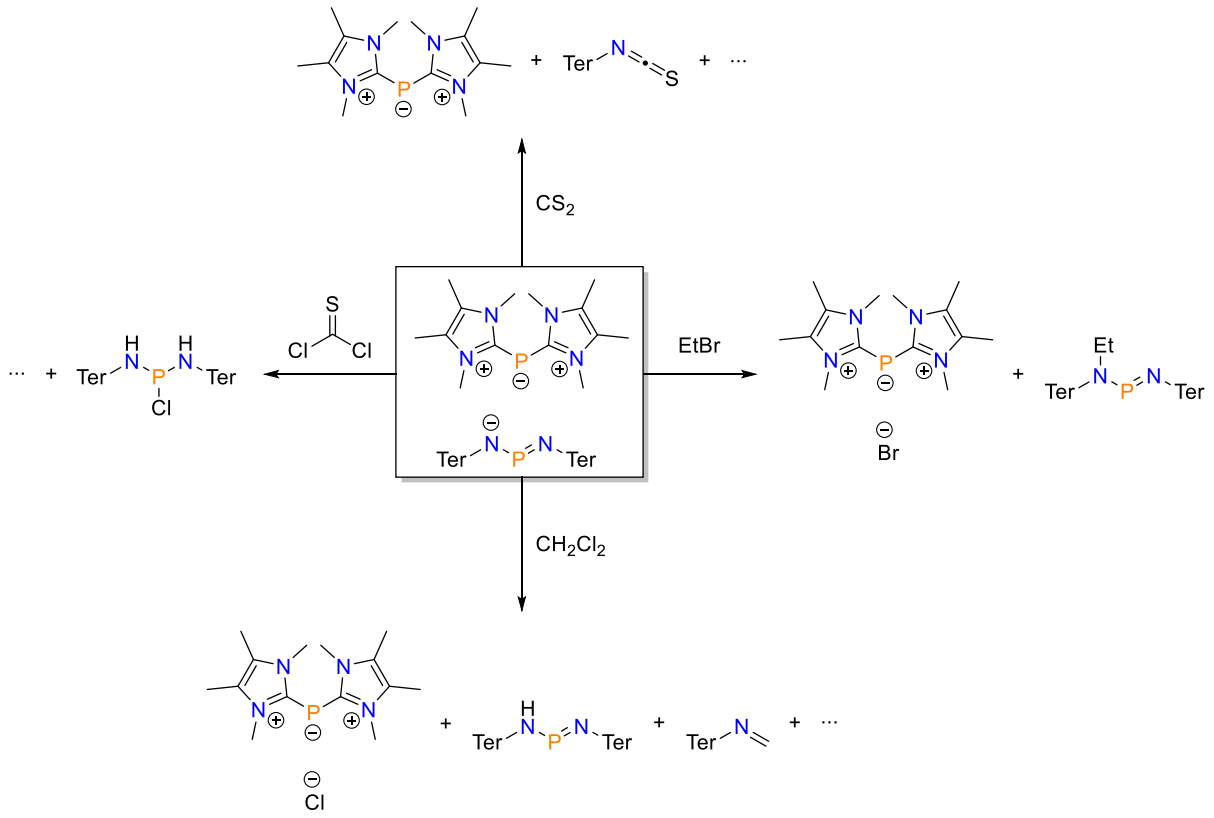
^{1}H NMR spectrum



5.6 Discontinued projects

Apart from the project presented in this thesis, additional investigations were carried out on two unrelated projects.

In the first part, the previously isolated ion pair [(^{Me}IMe)$_2$P][Ter–NPN–Ter][103] was to be tested in the activation of small molecules. However, initial experiments (Scheme 46) usually led to complex product mixtures. Only a few products could be identified, based on ^{31}P NMR spectra and isolated single crystals. The presence of the phosphamethine cyanine cation [(^{Me}IMe)$_2$P]$^+$ in almost all cases indicates its low electrophilicity. Furthermore, decomposition products of the [Ter–NPN–Ter]$^-$ anion, like an isothiocyanate (Figure 63) and a methyleneimine (Figure 64), underline its fragility. While salts of the type [(^{Me}IMe)$_2$P][X] (X = halogen) are soluble in acetonitrile, but insoluble in benzene, terphenyl-based compounds are soluble in benzene, but insoluble in acetonitrile, allowing for partial separation of the complex mixtures. It should be noted, that the depicted reactions did not take place when K[Ter–NPN–Ter] was used. In this regard, the larger phosphamethine cyanine cation leads to a more nucleophilic anion. However, due to unselective reactivity, this project was eventually abandoned.



Scheme 46. Reactions of a weakly interacting ion pair with a selection of small molecules.

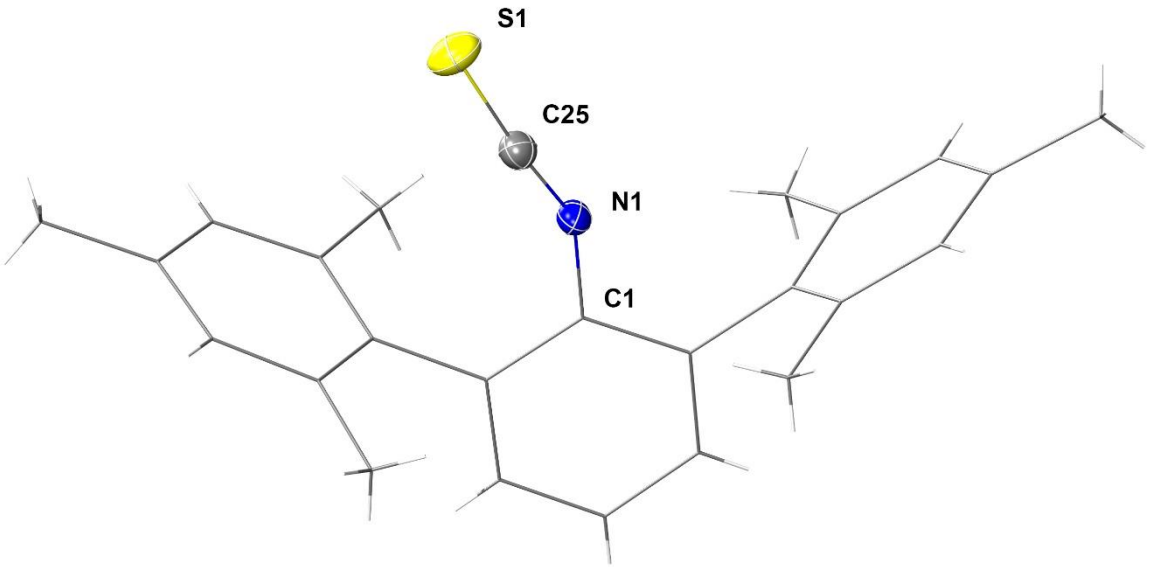


Figure 63. Molecular structure of Ter–NCS in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Ter substituent is depicted as wireframe. Selected bond lengths (in Å) and angles (in °): C1–N1 = 1.397(2), N1–C25 = 1.176(2), C25–S1 = 1.577(2), C1–N1–C25 = 149.7(2), N1–C25–S1 = 174.2(2), C1–N1–C25–S1 = 175(1).

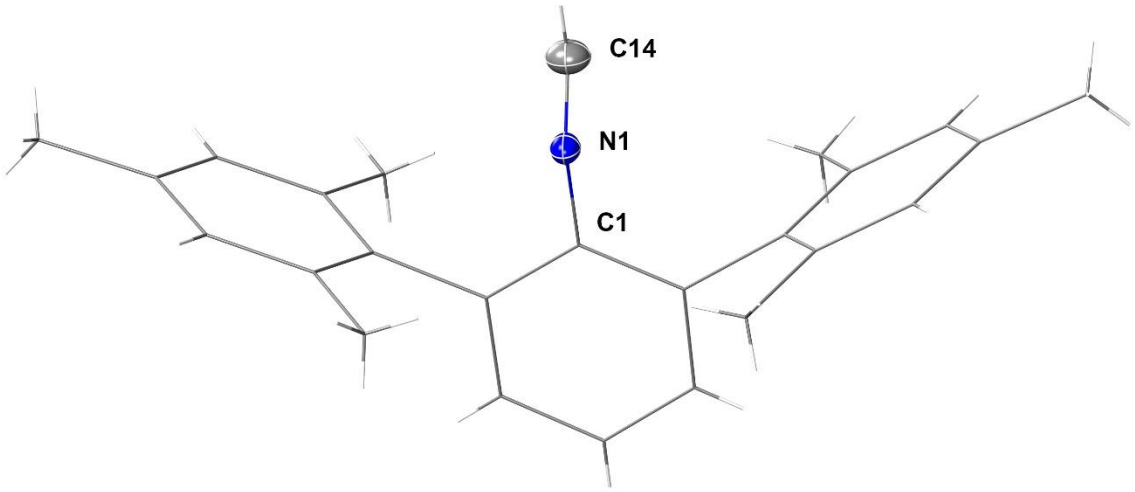


Figure 64. Molecular structure of Ter–N(CH_2) in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Ter substituent is depicted as wireframe. Selected bond lengths (in Å) and angles (in °): C1–N1 = 1.428(3), N1–C14 = 1.252(3), C1–N1–C14 = 118.6(2).

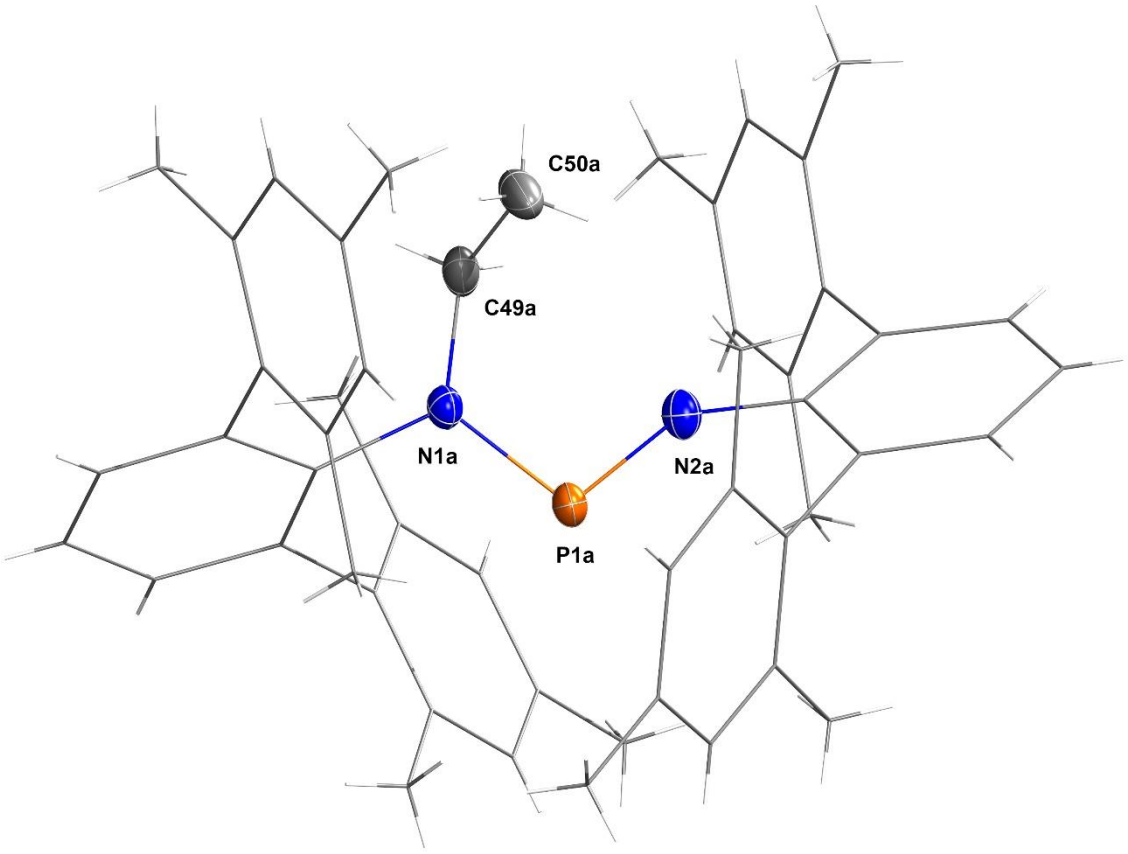
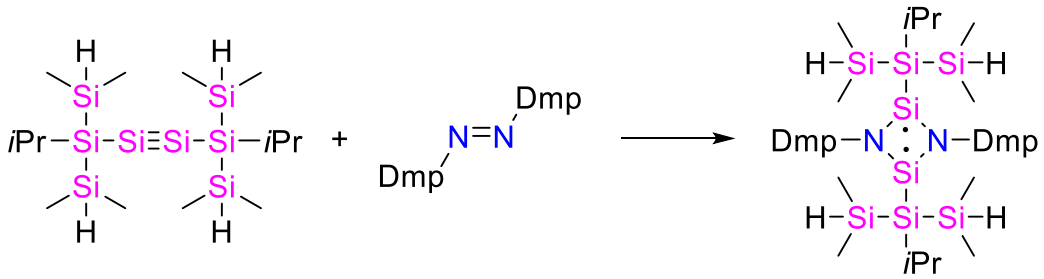


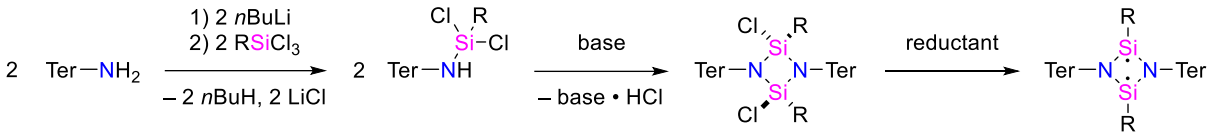
Figure 65. Molecular structure of Ter–N(Et)PN–Ter in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Ter substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): N1a–C49a = 1.478(5), C49a–C50a = 1.511(5), N1a–P1a = 1.681(6), P1a–N2a = 1.536(8), N1a–C49a–C50a = 115.0(3), C49a–N1a–P1a = 121.5(3), N1a–P1a–N2a = 102.1(3), N2a–P1a–N1a–C49a = 0.5(6).

In a second project, a new pathway to a symmetric N_2Si_2 biradical, previously reported by SEKIGUCHI et al. (Scheme 47),[22] was to be established and the reactivity of the biradical further investigated.



Scheme 47. Addition of a disilyne and a diazene to yield a symmetric biradical by SEKIGUCHI et al.[22]

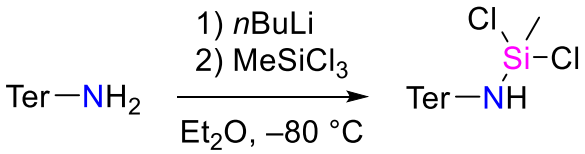
Therefore, two different aminosilanes were synthesized, with the next intended steps being the cyclization and reduction to the envisaged biradical (Scheme 48).



Scheme 48. Attempted synthesis of a N_2Si_2 biradical (R = Me, Ph).

While the aminosilanes (Figure 66 and 68) could be prepared in good yields (70–80 %), the subsequent cyclization proved to be challenging. A variety of bases/reductants was employed, but no changes were observed for NEt_3 (excess, CH_2Cl_2, 7 d, rt), DABCO (1 eq., CH_2Cl_2, 1 d, rt), KH (1–2 eq., THF, 3 weeks, 60 °C) or Mg (excess, THF, 3 weeks, rt). Meanwhile $Li[N(TMS)_2]$ (1 eq., THF, 1 d, rt) and DBU (excess, CH_2Cl_2) led to different products, as evidenced by ^{29}Si INEPT NMR spectra. The reaction with DBU stands out, as several signals appear and disappear over the course of 8 days. However, no products could be isolated and further characterized, which likewise led to the discontinuation of this project.

5.6.1 Ter–N(H)Si(Cl)$_2$Me (**ts225**)



In a 50 mL Schlenk flask, terphenyl amine (1.55 g, 4.70 mmol) is dissolved in anhydrous diethyl ether (20 mL) and cooled to –80 °C. Afterwards, *n*BuLi (2.5 M in hexane, 2.1 mL, 5.25 mmol) is added dropwise and the light yellow mixture is left stirring at room temperature for 1 h. Trichloromethylsilane (0.80 g, 5.35 mmol) is then added dropwise at –80 °C and the white mixture is left stirring at room temperature overnight. The next day, all volatiles are removed *in vacuuo* and solids are dried for another 3 h at 10^{-3} mbar. Anhydrous benzene (10 mL) is added and the suspension is filtered over a celite-packed frit. Volatiles are again removed *in vacuuo*, resulting in an off-white solid. Yield: 1.61 g (3.65 mmol, 77.5 %).

Crystals suitable for single-crystal XRD were obtained from a saturated solution in diethyl ether at room temperature.

Formula: $C_{25}H_{29}Cl_2NSi$. M = 442.50 g/mol. Mp. 123–125 °C. EA found (calcd.) in %: C 68.29 (67.86), H 6.57 (6.61), N 3.07 (3.17). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = –0.15 (s, 3 H, Me), 2.08 (s, 12 H, *o*-C*H*$_3$), 2.32 (s, 6 H, *p*-C*H*$_3$), 3.82 (s, 1 H, N*H*), 6.99 (m, 6 H, *m*-*H*), 7.10 (dd, $^3J(^1H,^1H)$ = 8.3 Hz, $^3J(^1H,^1H)$ = 6.4 Hz, 1 H, *p*-*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz): δ = 5.9 (s, Me), 20.8 (s, *C*H$_3$), 21.4 (s, *C*H$_3$), 122.7 (s, *C*H), 129.2 (s, *C*H), 130.4 (s, *C*H), 132.7 (s, $C_{quat.}$), 135.9 (s, $C_{quat.}$), 137.9 (s, $C_{quat.}$), 138.2 (s, $C_{quat.}$), 139.9 (s, $C_{quat.}$). ^{29}Si INEPT NMR (CD_2Cl_2, 59.6 MHz): δ = –2.1 (q, $^2J(^{29}Si,^1H)$ = 9 Hz). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3465 (vw), 3356 (vw), 3292 (w), 2980 (w), 2961 (w), 2936 (w), 2908 (w), 2846 (w), 2723 (vw), 1722 (vw), 1675 (vw), 1605 (w), 1582 (w), 1484 (w), 1420 (m), 1373 (m), 1301 (w), 1280 (w), 1258 (m), 1237 (w), 1223 (m), 1180 (w), 1091 (w), 1075 (m), 1029 (m), 1005 (m), 943 (m), 933 (m), 847 (s), 803 (s), 795 (s), 773 (m), 752 (s), 713 (m), 686 (w), 674 (w), 635 (m), 592 (m), 559 (m), 547 (s), 528 (vs), 508 (s), 497 (s), 456 (m), 419 (m), 405 (m). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3051 (1), 3012 (3), 2999 (3), 2985 (3), 2919 (9), 2861 (2), 2733 (1), 1613 (3), 1594 (1), 1569 (1), 1487 (1), 1445 (1), 1407 (1), 1384 (5), 1379 (4), 1307 (6), 1243 (1), 1185 (1), 1166 (2), 1080 (1), 1027 (1), 1007 (6), 950 (1), 937 (1), 885 (1), 851 (1), 806 (1), 791 (1), 776 (1), 762 (1), 743 (1), 717 (1), 638 (1), 581 (9), 561 (8), 553 (3), 533 (1), 523 (3), 511 (2), 500 (1), 484 (1), 478 (1), 458 (4), 408 (1), 370 (1), 330 (2), 285 (1), 272 (1), 250 (2), 227 (3), 218 (2), 179 (1), 144 (3). MS (CI +, isobutane, m/z): 442 $[M+H]^+$, 406 $[M–Cl]^+$, 329 $[Ter\text{-}NH_2]^+$.

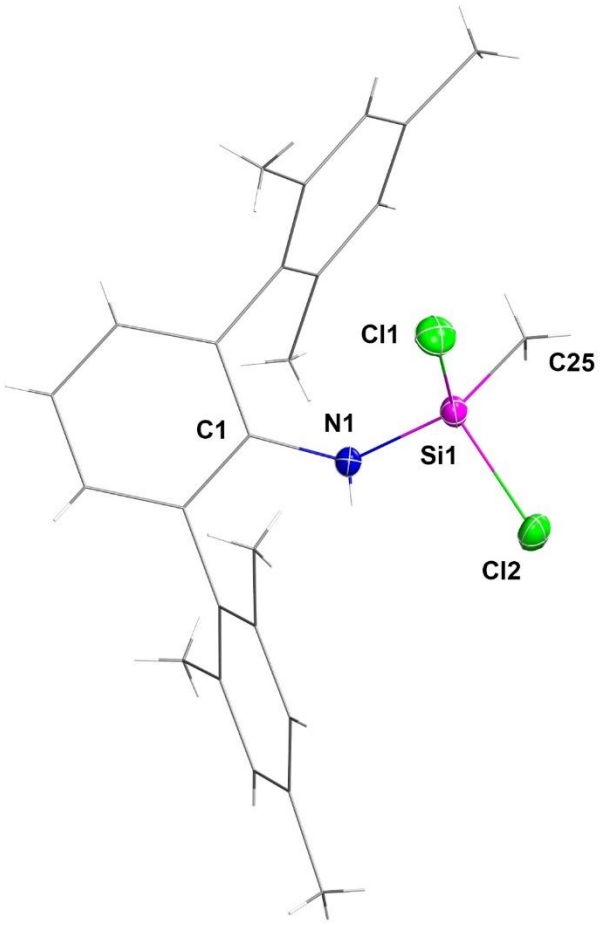
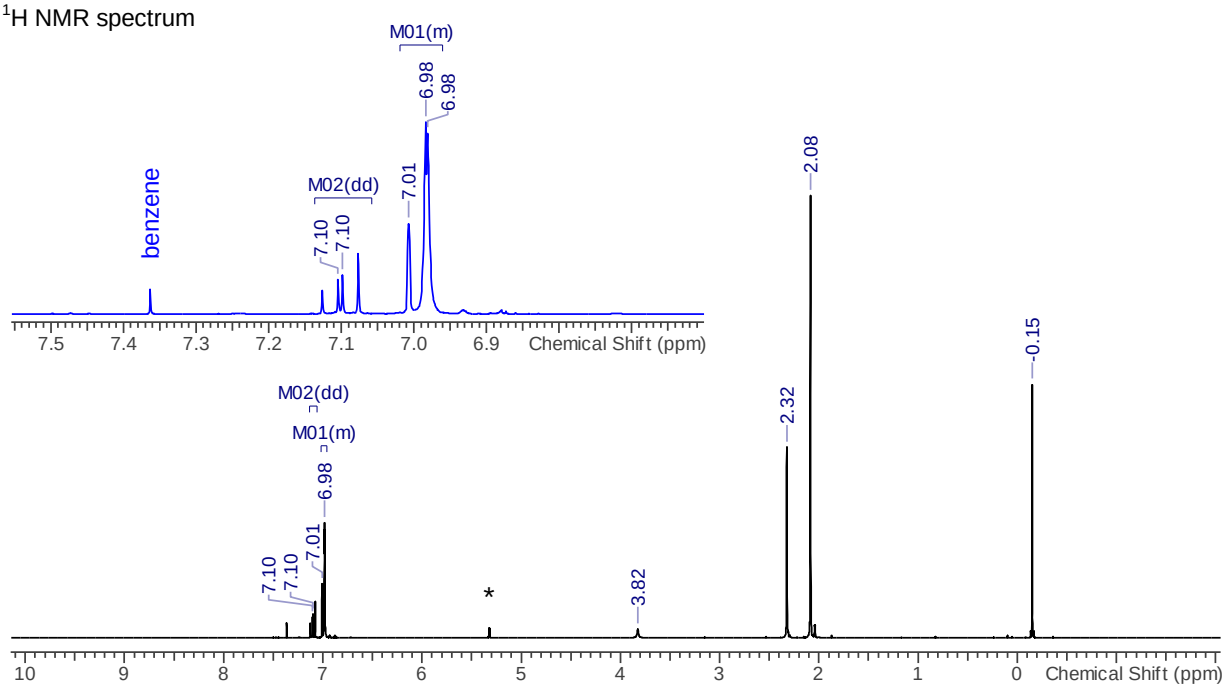


Figure 66. Molecular structure of Ter–N(H)Si(Cl)$_2$Me in the single crystal. Ellipsoids are set at 50 % probability (123(2) K). The Ter and Me substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): C1–N1 = 1.412(2), N1–Si1 = 1.703(1), Si1–Cl1 = 2.0518(7), Si1–Cl2 = 2.0608(6), Si1–C25 = 1.829(2), C1–N1–Si1 = 135.4(1), N1–Si1–Cl1 = 111.52(5), N1–Si1–Cl2 = 101.65(5), N1–Si1–C25 = 119.37(8), Cl1–Si1–C25 = 108.92(7), Cl2–Si1–C25 = 107.46(6).

Figure 67. ^{1}H, $^{13}C\{^{1}H\}$, ^{29}Si INEPT NMR, IR and Raman spectra of Ter–N(H)Si(Cl)$_2$Me (solvent signal marked by asterisk).

^{1}H NMR spectrum



$^{13}C\{^{1}H\}$ NMR spectrum

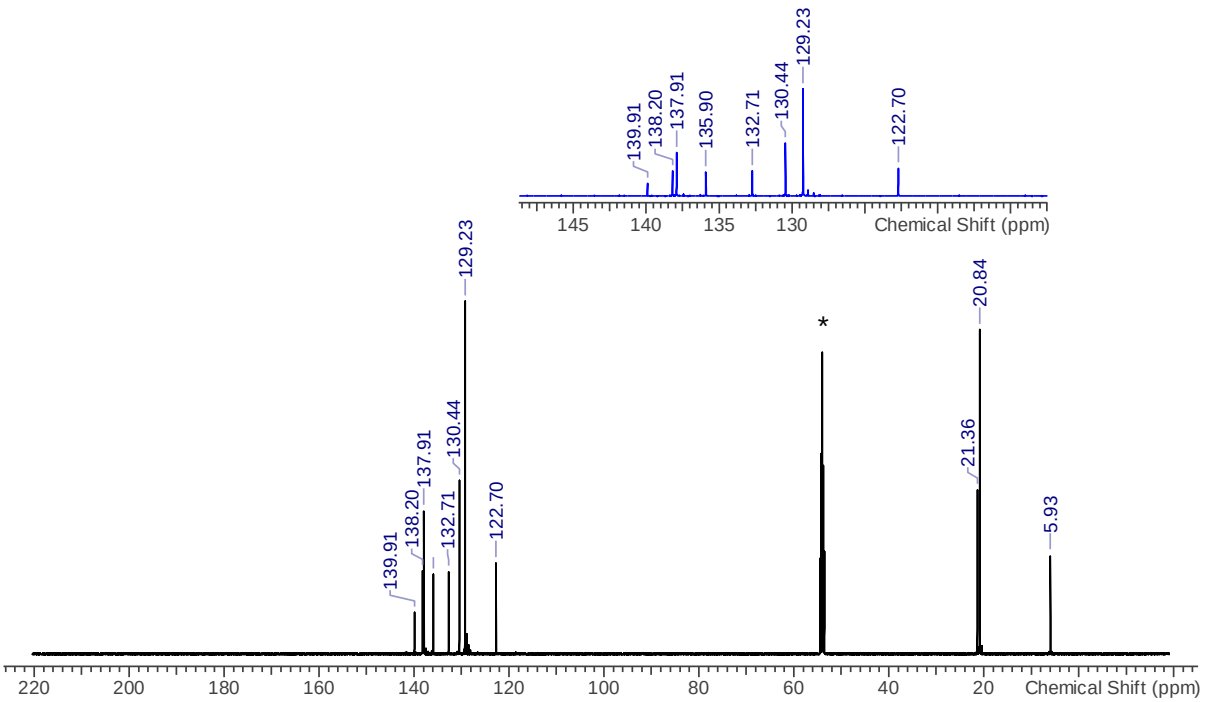
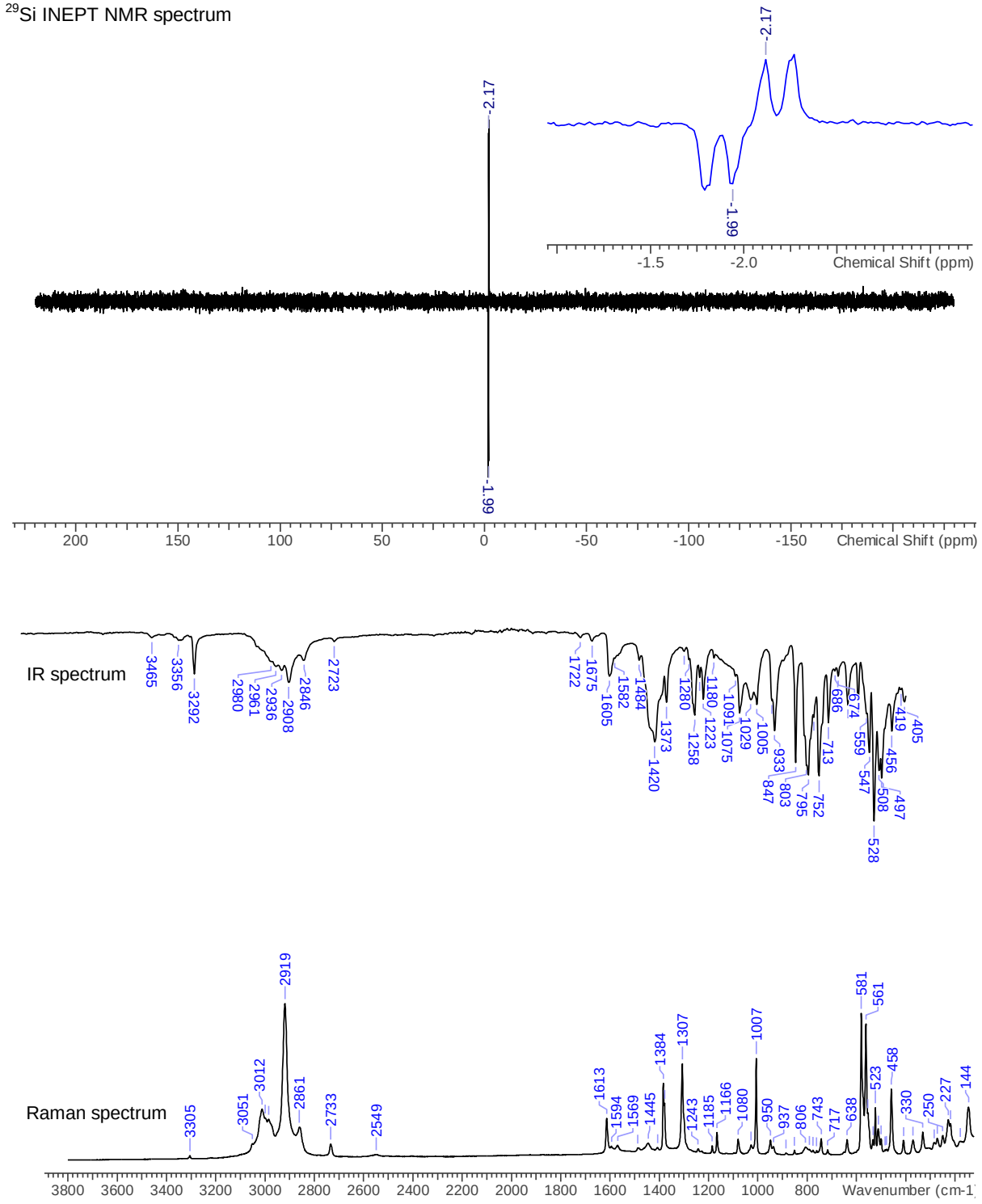
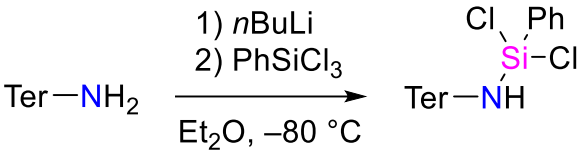


Figure 67. continued.



5.6.2 Ter–N(H)Si(Cl)$_2$Ph (**ts234**)



In a 25 mL Schlenk flask, terphenyl amine (0.50 g, 1.53 mmol) is dissolved in anhydrous diethyl ether (8 mL) and cooled to –80 °C. Afterwards, *n*BuLi (2.5 M in hexane, 0.7 mL, 1.68 mmol) is added dropwise and the light yellow mixture is left stirring at room temperature for 1 h. Trichlorophenylsilane (0.36 g, 1.69 mmol) is then added dropwise at –80 °C and the white mixture is left stirring at room temperature overnight. The next day, all volatiles are removed *in vacuuo* and solids are dried for another 3 h at 10^{-3} mbar. Anhydrous benzene (10 mL) is added and the suspension is filtered over a celite-packed frit. Volatiles are again removed *in vacuuo*, leaving a yellowish gel. Yield: 0.53 g (1.06 mmol, 69.3 %).

Crystals suitable for single-crystal XRD were obtained from a saturated solution in diethyl ether at room temperature.

(**Note**: Even small amounts of Trichlorophenylsilane (Bp. 201 °C) inhibit crystallization. However, the gelatinous product may be used without further purification.)

Formula: $C_{30}H_{31}Cl_2NSi$. M = 504.57 g/mol. Mp. 98–100 °C. EA found (calcd.) in %: C 71.79 (71.41), H 6.19 (6.19), N 2.71 (2.78). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 2.06 (s, 12 H, *o*-C*H*$_3$), 2.26 (s, 6 H, *p*-C*H*$_3$), 4.08 (s, 1 H, N*H*), 6.83 (m, 4 H, *m-H* (Mes)), 6.99 (d, 1 H, ^3J = 0.9 Hz, *m-H*), 7.02 (s, 1 H, *m-H*), 7.10 (m, 3 H, *m-H* + *p-H* (Ph)), 7.20 (m, 2 H, *o-H* (Ph)), 7.39 (m, 1 H, *p-H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ = 20.9 (s, *C*H$_3$), 21.4 (s, *C*H$_3$), 123.1 (s, *C*H), 128.2 (s, *C*H), 129.2 (s, *C*H), 130.6 (s, *C*H), 131.6 (s, *C*H), 132.3 (s, $C_{quat.}$), 133.5 (s, *C*H), 135.8 (s, $C_{quat.}$), 137.4 (s, $C_{quat.}$), 137.6 (s, $C_{quat.}$), 138.0 (s, $C_{quat.}$), 139.3 (s, $C_{quat.}$). ^{29}Si INEPT NMR (CD_2Cl_2, 59.6 MHz): δ = –17.8 (d, J = 14 Hz). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3467 (vw), 3372 (vw), 3337 (vw), 3290 (w), 3039 (w), 2992 (w), 2961 (w), 2936 (w), 2908 (w), 2846 (w), 2721 (vw), 1605 (w), 1599 (w), 1586 (w), 1482 (w), 1424 (s), 1373 (m), 1332 (w), 1303 (w), 1282 (w), 1256 (m), 1221 (m), 1184 (w), 1177 (w), 1153 (w), 1114 (m), 1091 (m), 1075 (m), 1029 (m), 1005 (m), 995 (w), 945 (m), 933 (m), 877 (w), 845 (m), 801 (m), 787 (m), 750 (s), 738 (s), 703 (m), 692 (s), 633 (m), 616 (w), 596 (m), 565 (s), 557 (s), 545 (s), 514 (vs), 483 (s), 460 (m), 419 (m). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3304 (2), 3073 (2), 3056 (3), 3020 (2), 3006 (1), 2967 (1), 2947 (1), 2917 (4), 2858 (1), 2731 (1), 1613 (3), 1591 (4), 1572 (1), 1484

(1), 1441 (2), 1403 (1), 1380 (3), 1307 (10), 1289 (2), 1270 (1), 1226 (2), 1189 (2), 1183 (2), 1165 (1), 1160 (1), 1118 (2), 1089 (3), 1029 (2), 1007 (3), 997 (10), 949 (1), 939 (1), 738 (1), 706 (2), 636 (3), 597 (1), 577 (10), 560 (4), 524 (4), 516 (2), 484 (2), 462 (2), 420 (1), 400 (3), 347 (2), 335 (3), 324 (3), 275 (4), 243 (4), 222 (3), 205 (2), 179 (2), 162 (4), 136 (7). MS (CI +, isobutane, m/z): 504 $[M+H]^+$, 468 $[M–Cl]^+$, 329 $[Ter\text{-}NH_2]^+$.

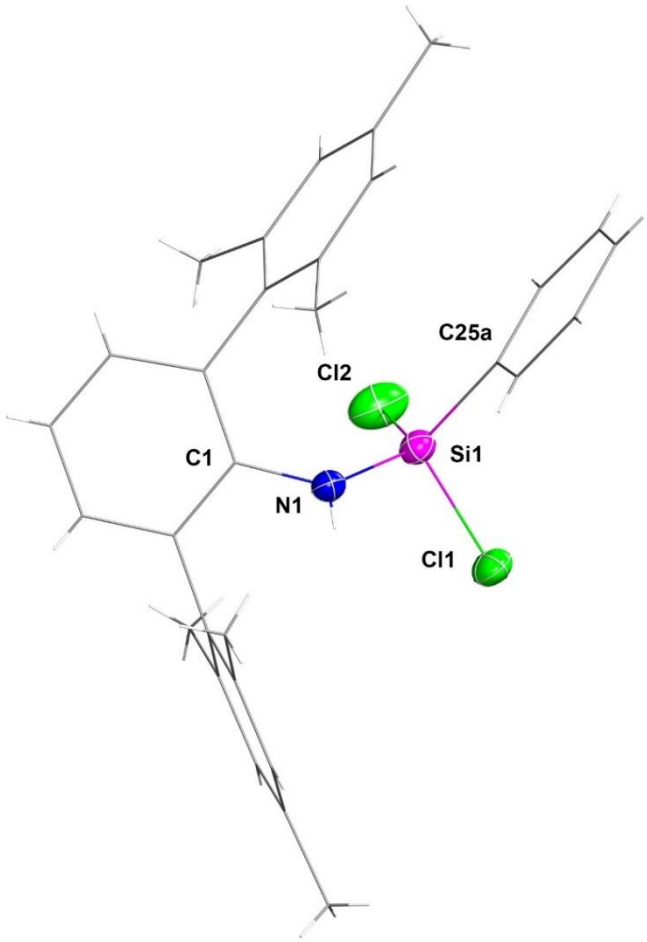
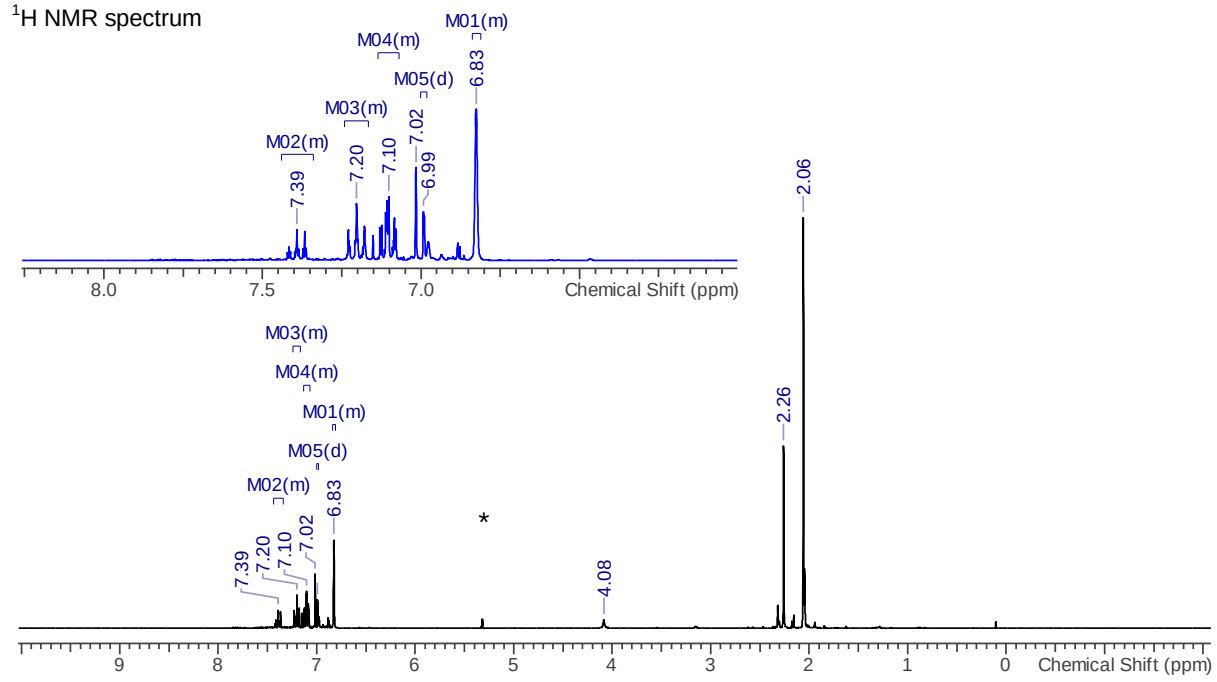


Figure 68. Molecular structure of Ter–N(H)Si(Cl)$_2$Ph in the single crystal. Ellipsoids are set at 50 % probability (173(2) K). The Ter and Ph substituents are depicted as wireframe. Selected bond lengths (in Å) and angles (in °): C1–N1 = 1.416(2), N1–Si1 = 1.697(2), Si1–Cl1 = 2.0652(7), Si1–Cl2 = 2.0359(7), Si1–C25a = 1.866(6), C1–N1–Si1 = 137.9(1), N1–Si1–Cl1 = 101.24(6), N1–Si1–Cl2 = 113.46(6), N1–Si1–C25a = 116.6(3), Cl1–Si1–C25a = 106.9(3), Cl2–Si1–C25a = 111.7(3).

Figure 69. ^{1}H, $^{13}C\{^{1}H\}$, ^{29}Si INEPT NMR, IR and Raman spectra of Ter–N(H)Si(Cl)$_2$Me (solvent signal marked by asterisk).



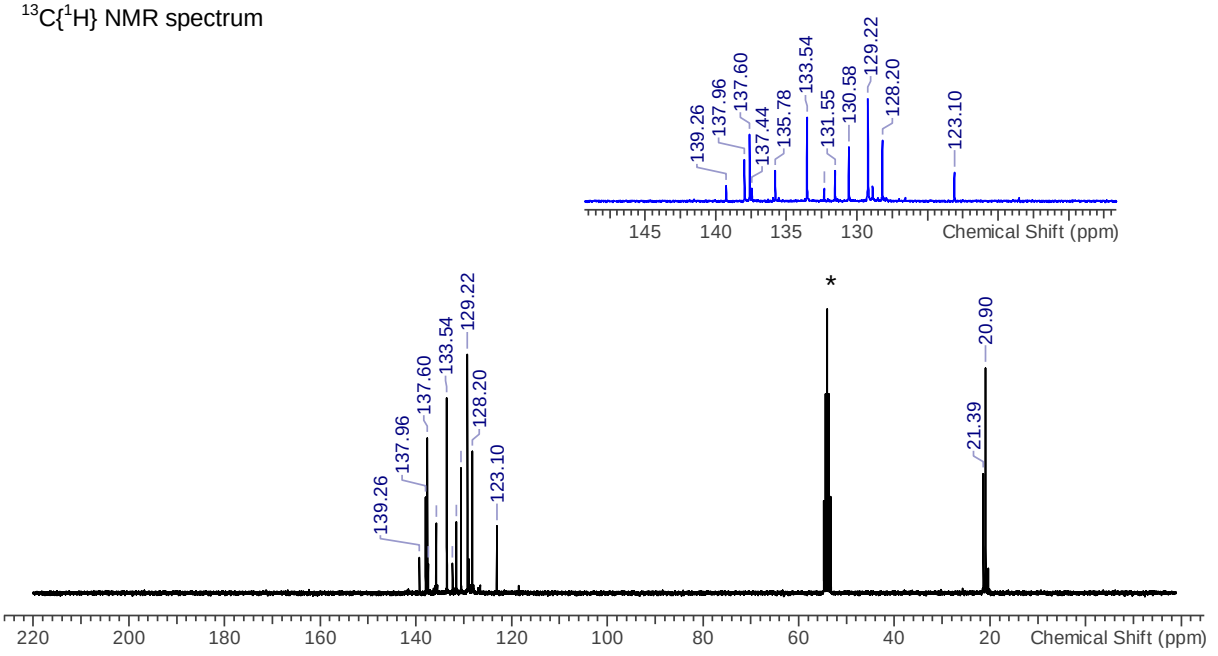
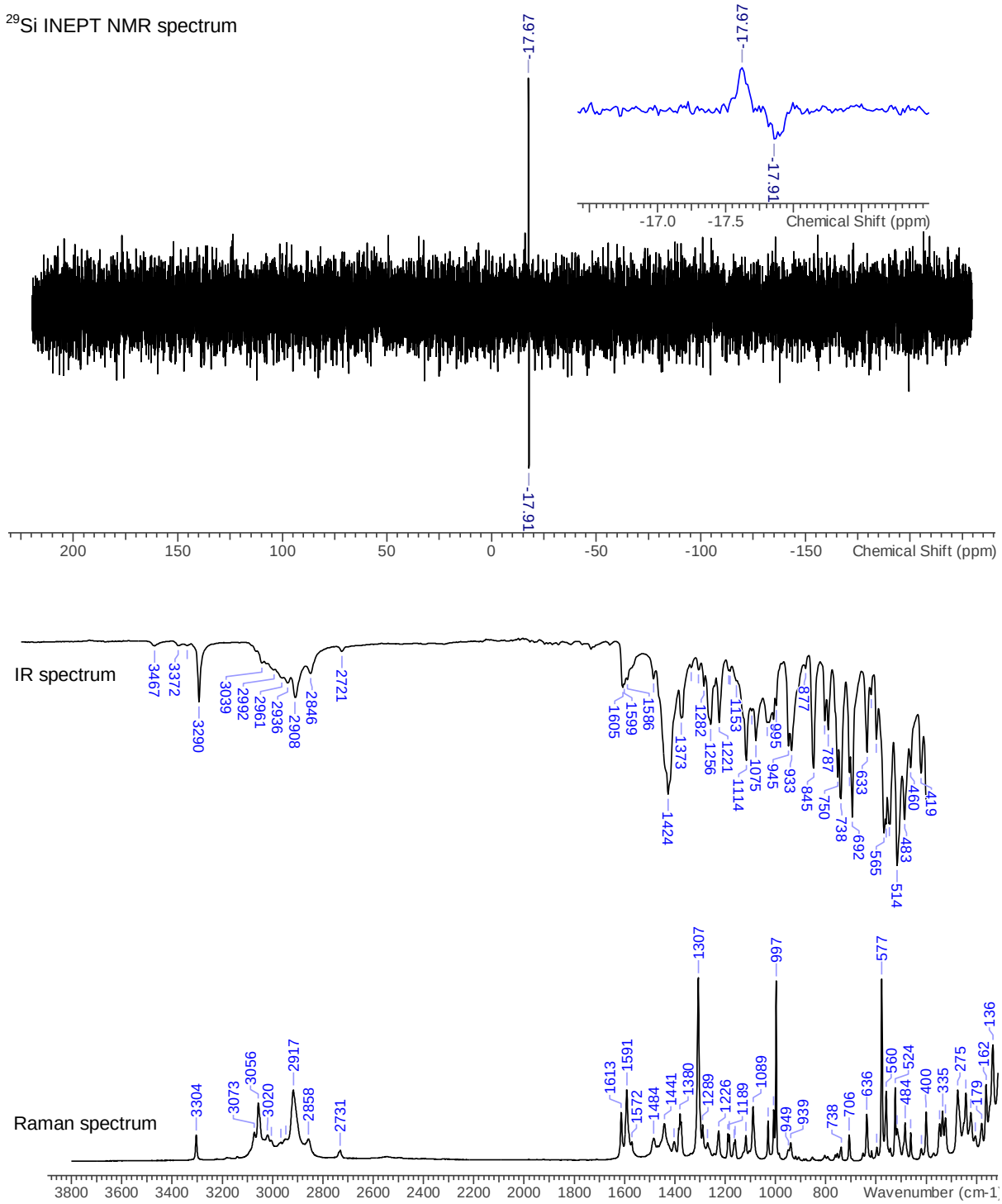


Figure 69. continued.



5.7 Additional computational data

5.7.1 CASSCF computations

The wave function of a biradical must be described by at least two determinants, since the frontier orbitals are nearly degenerate. In the following, the orbitals of the active space of **6**, **13** and **14** are illustrated and their occupation numbers are given.

Table 19. Most important configurations that contribute to the CASSCF(2,2)/def2-TZVP wave function of **6** ($|c_i^2|>0.01$).

#	**configuration**	$\mathbf{c_i^2}$
1	20	0.95
2	02	0.05

Table 20. Most important configurations that contribute to the CASSCF(2,2)/def2-TZVP wave function of **13** ($|c_i^2|>0.01$).

#	**configuration**	$\mathbf{c_i^2}$
1	20	0.98
2	02	0.02

Table 21. Most important configurations that contribute to the CASSCF(2,2)/def2-TZVP wave function of **14** ($|c_i^2|>0.01$).

#	**configuration**	$\mathbf{c_i^2}$
1	20	0.97
2	02	0.03

Figure 70. CASSCF(2,2)/def2-TZVP orbitals of **6** with their orbital occupancies (hydrogens omitted for clarity).

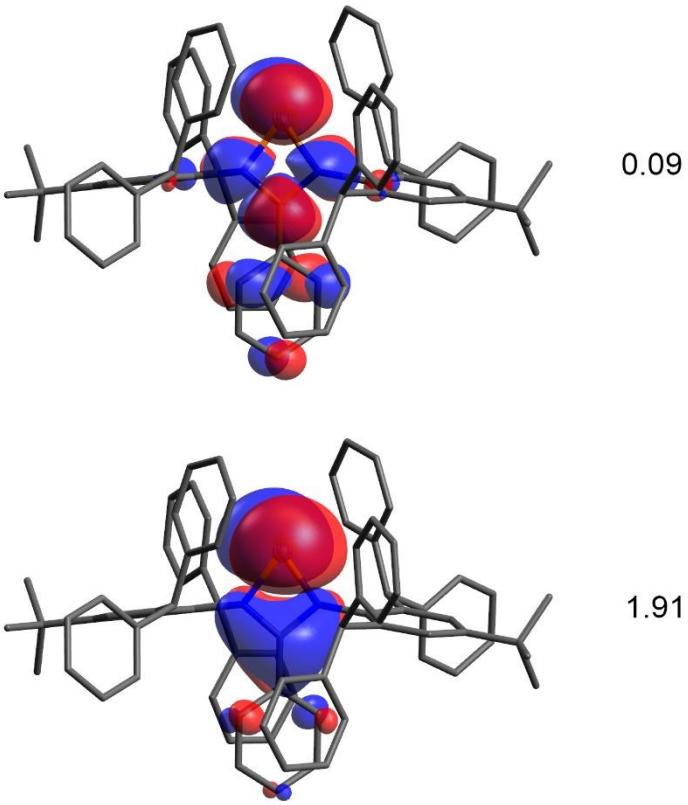


Figure 71. CASSCF(2,2)/def2-TZVP orbitals of **13** with their orbital occupancies (hydrogens omitted for clarity).

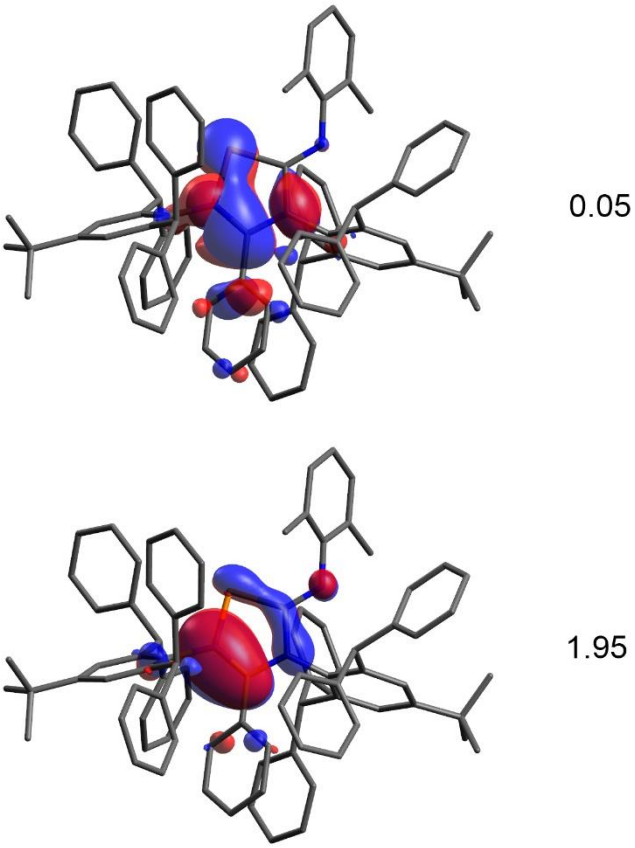
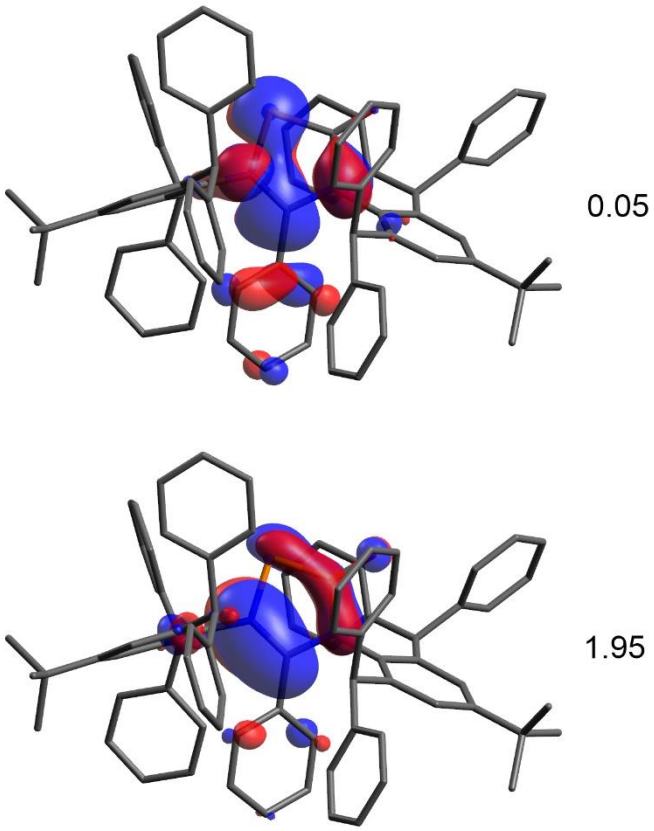
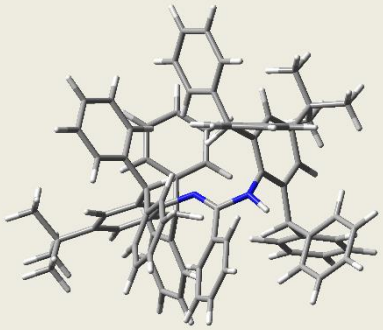


Figure 72. CASSCF(2,2)/def2-TZVP orbitals of **14** with their orbital occupancies (hydrogens omitted for clarity).



5.7.2 Optimized structures (PBE-D3/def2-TZVP)

^{tBu}Bhp–NC(Ph)N(H)–^{tBu}Bhp (4)



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C	1.65641600	1.00131800	-0.08037800
N	-0.96691600	-1.07303500	1.30330400
C	0.78598800	-0.03625400	2.56588300
C	2.98325400	0.53336300	0.04734600
C	1.43392500	2.31999800	-0.54245400
C	-1.97190500	-1.09794800	0.29406500
H	-1.31671100	-1.21385100	2.25003100
C	0.98705200	-1.09503800	3.46360800
C	1.12297400	1.26902800	2.95178600
C	4.03700400	1.40575700	-0.24073200
C	3.27463800	-0.92072300	0.38517200
C	2.51527100	3.17325700	-0.76056300
C	0.00340300	2.72441600	-0.87500400
C	-3.15123800	-0.36195300	0.52138400
C	-1.81260300	-1.84913500	-0.87776500
H	0.75405000	-2.11583100	3.15443600
C	1.51654400	-0.85000500	4.72953300
C	1.63495200	1.51146100	4.22534800
H	0.98355600	2.09231000	2.25071400
H	5.05295900	1.00931500	-0.17828200
C	3.83976000	2.74034100	-0.61010800
H	2.30333400	-1.43961100	0.41499500
C	3.92095000	-1.17142600	1.74148300
C	4.04744000	-1.55884200	-0.76919900
H	2.30360600	4.19623600	-1.07201600
H	-0.64983400	2.19277900	-0.16545400
C	-0.26213600	4.20838800	-0.67799100
C	-0.38753200	2.21296400	-2.25773900
C	-3.22422600	0.53438400	1.75485300
C	-4.19224200	-0.45401500	-0.40131000
C	-2.87421700	-1.90043200	-1.78773200
C	-0.49770100	-2.57175800	-1.12337600
H	1.69510600	-1.68271300	5.41066100
C	1.83363000	0.45335500	5.11549100
H	1.88800500	2.53113700	4.52005900

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C    3.98094500   -2.49405200    2.21028200
C    4.45015800   -0.15909000    2.54651100
C    5.41331100   -1.85333100   -0.70024300
C    3.36278400   -1.82493200   -1.96391000
C   -0.50260700    4.68261400    0.62053300
C   -0.26496100    5.12848800   -1.73249200
C    0.51496200    2.22723200   -3.32969500
C   -1.68020100    1.72087300   -2.47849800
H   -2.25883700    1.06851900    1.79744600
C   -4.28892200    1.61312100    1.63704500
C   -3.31186500   -0.27161500    3.04390300
H   -5.09936500    0.12034300   -0.21197700
C   -4.08341000   -1.23352900   -1.56211600
H   -2.73096400   -2.48070800   -2.69765200
H    0.27685900   -1.82317300   -0.87916600
C   -0.26975900   -3.74539800   -0.18366400
C   -0.28085200   -2.91264500   -2.58944500
H    2.25046700    0.64329300    6.10575500
C    5.89996500    3.72474000    0.42216600
C    5.89889700    3.06246300   -2.00501400
C    4.62930900    5.07417600   -1.24815300
H    3.55897200   -3.29370500    1.59780900
C    4.56152400   -2.79732700    3.43926700
C    5.03410500   -0.45931200    3.78119200
H    4.38863200    0.87785200    2.21581400
H    5.95918200   -1.66366600    0.22567500
C    6.07746400   -2.40211400   -1.80152400
C    4.01779800   -2.38295900   -3.05948100
H    2.30120900   -1.58269200   -2.04060900
H   -0.51026200    3.97400900    1.45337300
C   -0.73430900    6.03569500    0.86269300
C   -0.49124400    6.48708400   -1.49421800
H   -0.09999100    4.77508900   -2.75150700
H    1.53771000    2.57015300   -3.16350200
C    0.12665100    1.78922800   -4.59803200
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H   -2.38700400    1.66793200   -1.64746300
C   -3.97019100    2.80529400    0.97174400
C   -5.58736600    1.44700800    2.13189200
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C   -0.37829700   -4.21608200   -3.08704800
C    0.02293200   -1.87036400   -3.47884700
H    5.31565200    4.14677400    1.25307900
H    6.78142100    4.36426400    0.26099500
H    6.25467200    2.73080500    0.72909400
H    6.25168600    2.04889800   -1.76929300
H    6.78062600    3.69521100   -2.18997100
H    5.31413500    3.00531100   -2.93464500
H    4.04770300    5.08852700   -2.18157400
H    5.52550200    5.69224400   -1.40417700
H    4.02565400    5.54996500   -0.46141700
H    4.59356400   -3.83302700    3.78299000
C    5.09711600   -1.77704200    4.23147900
H    5.43448500    0.34877000    4.39630900
H    7.14390800   -2.62492200   -1.73156900
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H    3.45486100   -2.59355200   -3.97094800
H   -0.92683800    6.38036800    1.88031200
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H   -0.48953800    7.18876200   -2.33038000
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C   -1.16896200    1.31485600   -4.81010000
H   -3.07211500    0.87750900   -3.88893400
H   -2.95799400    2.95518600    0.58821600
C   -4.92608600    3.80457900    0.79333200
C   -6.54915300    2.44444900    1.95178500
H   -5.84631300    0.53287700    2.66905700
C   -2.67904500   -0.55870500    5.37516100
H   -2.04273800    1.09040600    4.13705200
C   -4.09342900   -2.19724500    4.30545100
H   -4.54553900   -1.83904000    2.22216500
C   -5.88106600    0.02752700   -2.81864500
C   -6.35306100   -2.22535800   -1.82056000
C   -4.89306700   -2.02224900   -3.84242000
H   -2.33960300   -4.04341800    0.33777300
C   -1.05845700   -5.45332000    1.35621500
C    1.30018500   -5.26416800    0.88817300
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H    5.55298400   -2.00970700    5.19536100
H    5.90235400   -3.11035000   -3.83626900
H   -0.90903500    8.00622400   -0.01355200
H   -1.47211200    0.95905900   -5.79615200
H   -4.65250600    4.72599000    0.27640300
C   -6.22329300    3.62435400    1.28035500
H   -7.55725300    2.29957000    2.34429900
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H   -4.66226300   -3.12787600    4.34391300
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H   -4.09417400   -1.46747000   -4.35615500
H   -5.76801700   -2.05197700   -4.50771900
H   -1.88694000   -5.93901200    1.87532400
C    0.24989100   -5.89252200    1.56377200
H    2.32734800   -5.60381700    1.03586900
H   -0.24621300   -5.49984900   -4.81656700
C    0.13953000   -3.43510900   -5.32083400
H    0.47253400   -1.30267500   -5.50450100
H   -6.97439700    4.40400100    1.14413500
H   -3.44798700   -2.32074600    6.36465000
H    0.45127400   -6.72067800    2.24519600
H    0.30795300   -3.63963200   -6.37956300
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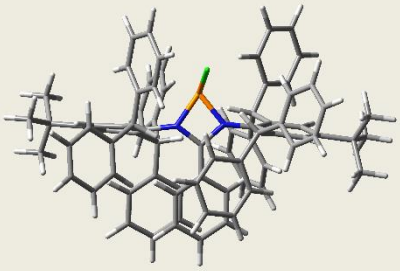
[$^{t\mathrm{Bu}}$Bhp–[NC(Ph)N(PCl)]–$^{t\mathrm{Bu}}$Bhp]$^{+}$



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C	2.41183900	-0.09076900	0.31651600
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C	0.06840200	0.00441700	-1.91402000
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C	-0.98449500	-0.75244500	-3.95823400
C	0.21914600	-0.56150000	-4.64382800
C	1.34291100	-0.07498200	-3.97229500
C	1.27574500	0.20417600	-2.61366600
C	3.45255100	0.84051000	0.47673000
C	4.75949000	0.36532700	0.62288900
C	5.05387100	-1.00030800	0.66336700
C	3.99415500	-1.89523500	0.46353100
C	2.68184500	-1.47667100	0.23997400
C	-3.08108000	1.57625500	-0.23635400
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C	-3.22076400	-0.82431100	0.28699400
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C	6.88978600	-2.35957800	-0.35419800
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C	-7.41176900	-0.89192600	-0.54379500
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C	-2.55257300	-3.26198900	-0.21182900
C	3.17277600	2.33633400	0.49480300
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C     0.75233700   -3.88622400   -3.61273700
C     1.96644100   -3.83210500   -4.30165500
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C     1.96832300   -6.05369100    1.28949300
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C     2.06753800    4.68658100    3.28304000
C     2.38747300    3.96366500    4.43729900
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C     4.27241600    3.07628500   -1.65294000
C     5.27761700    3.72041100   -2.37310200
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C    -3.12657700   -3.20260700   -1.48592600
C    -3.03555400   -4.29029400   -2.36165300
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C     0.31991800    3.56386500   -3.60701200
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H     2.15604900    0.57093100   -2.08893000
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H     4.18502500   -2.96973100    0.46225700
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H    -5.18226400   -1.66744500    0.19716500
H     8.48714800   -0.84182400    1.24737500
H     7.55388700    0.25359100    0.21098100
H     7.24965500    0.20492000    1.96765300
H     7.48342500   -2.84920100    2.29350700
H     5.78350400   -3.28924500    2.02367300
H     6.18471000   -1.87659900    3.02662600
H     6.88560800   -1.73714200   -1.26098700
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H    -6.47974600    1.94247400   -2.32591900
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H    -3.66450000   -2.30687200   -1.79923900
H    -3.49584600   -4.22704900   -3.34918900
H    -2.30060800   -6.30085500   -2.65535300
H    -1.25585200   -6.41844100   -0.38894800
H    -1.42351800   -4.49924500    1.15590600
H    -2.13042800   -1.18507300    3.30531200
H    -3.29593300   -1.73524200    5.42070300
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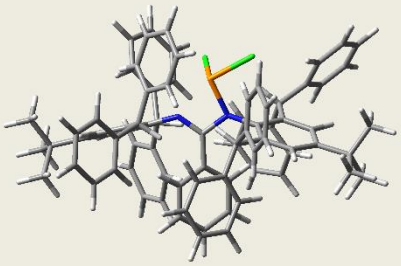
^{tBu}Bhp–NC(Ph)N(PCl$_2$)–^{tBu}Bhp (5)



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C	3.23847000	1.03042000	0.43033300
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C	-3.39703400	-0.81245600	-0.02386200
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C	-0.76982500	-0.82989000	-2.50575500
C	4.51056400	-1.37304800	-0.18104500
C	2.37728600	-2.69873700	-0.00456300
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C	2.53748000	2.34838600	0.73581100
C	-4.00288300	1.74184300	-0.98245100
C	-1.72464600	2.64492700	-0.42817900
C	-4.66335600	-0.50395500	-0.51579500
C	-3.10978700	-2.22171800	0.49006900
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C	1.37242000	0.43341600	-3.76978500
C	-0.62417800	-0.91916800	-3.88857400
H	-1.59873200	-1.33971900	-2.02389600
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C	2.78811300	-3.52309300	-1.22072100
C	2.49401700	-3.46220200	1.31358900
H	5.18146000	1.90086400	0.32900700
H	1.65525000	2.39213600	0.06978200
C	1.98788500	2.41788400	2.15394000
C	3.39468700	3.55381800	0.37496800
H	-4.22892200	2.75741600	-1.30508600
C	-4.99369200	0.76215800	-1.01654900
H	-0.89932700	2.33825100	0.23626300
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H    -1.35144000   -1.49462400   -4.46283200
C     6.79849500   -0.20471900   -0.30011400
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C     3.69410400   -4.58728900   -1.13591700
C     1.76222400   -4.64843600    1.47988300
C     3.26999400   -3.00990700    2.38555600
C     2.45148800    1.58518100    3.17635800
C     0.96512200    3.33236900    2.44348500
C     4.06652500    4.30954900    1.34179100
C     3.55602100    3.89695700   -0.97510000
C    -6.41231600    1.03113500   -1.52444200
C    -0.00467500    3.90440000   -1.76558000
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C    -2.81720300    4.96894500   -0.46677200
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C    -5.00279500   -2.14156100    2.17457700
C    -4.73816400   -4.16281400    0.89498700
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C    -3.22097300   -3.22804300   -1.85010700
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H     1.56376500   -2.35619400   -2.56147700
C     2.65363200   -3.88031400   -3.62277500
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C     1.88243900    1.64011100    4.45149300
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C    -3.22146100    4.87426400    2.28876400
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H    -4.67988300   -1.12882400    2.41769100
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C    -5.82413100   -4.73048900    1.56902200
H    -4.21529600   -4.74605600    0.13657200
H    -0.78984300   -3.63747600    0.48780500
C    -0.77200400   -4.50604400   -1.49456700
C    -2.68017600   -3.99762800   -2.88015700
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C     2.57038400   -4.88782600    3.74654000
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H    -7.75906300    0.21957700   -3.03735000
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H    -7.60384700    2.60273900   -2.42045600
H    -5.89253400    2.66503800   -2.89352800
H    -7.35191000   -0.19998200    0.03867600
H    -8.43673000    0.99623500   -0.70937200
H    -7.19522700    1.51894300    0.45932000
H     1.42618500    5.01418900   -2.92925300
C     0.09128800    3.85734900   -4.18110300
H    -1.37222800    2.59163700   -5.13973000
H    -3.78588600    6.89449600   -0.39221900
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C    -6.50489300   -4.00409700    2.54455300
H    -6.13559500   -5.74796200    1.32557200
H     0.19545800   -4.99200900   -1.36267800
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H    -3.22107000   -4.09654300   -3.82334500
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H     0.54894100    4.18122700   -5.11729400
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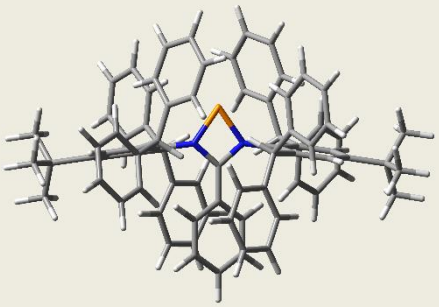
$^{t\text{Bu}}$Bhp–[NC(Ph)NP]–$^{t\text{Bu}}$Bhp (6)



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C	-3.94092600	-2.18878500	0.25831200
C	-1.48247900	-2.78648300	0.01517900
C	4.72218200	-0.05517900	0.06096700
C	3.10271200	-1.96819100	-0.44605400
C	3.94073200	2.20370600	0.26546000
C	1.47979100	2.79990900	0.01695100
H	-1.99199000	0.84594300	2.20906700
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C    2.99842400   -1.23292000   -2.90193200
C    2.34959700    5.18245900   -0.36038800
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C   -2.64181800   -6.04595900   -2.59767600
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H    6.01392100    3.58907500    1.60295700
H    6.22162500    3.82227700   -0.15157300
H    5.25670400   -4.44529000    2.88347400
C    6.25482000   -4.57971500    0.97001100
H    7.00561700   -4.53384100   -1.05492100
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C    1.89354600   -2.60307800   -4.56565100
H    2.81403500   -0.69435400   -4.98252300
H    3.11225100    7.15218400   -0.80060900
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H    2.03730400    4.73170300   -4.20207300
H   -1.71863200    4.95040600    2.64945700
C   -0.12486600    4.09019500    3.83627100
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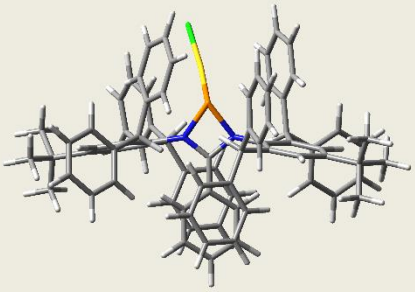
^{tBu}Bhp–[NC(Ph)NP]–^{tBu}Bhp • AuCl (7)



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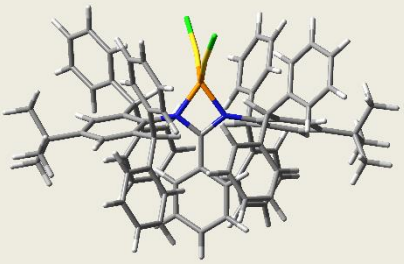
^{tBu}Bhp-[NC(Ph)NP]-^{tBu}Bhp • 2 AuCl (8)



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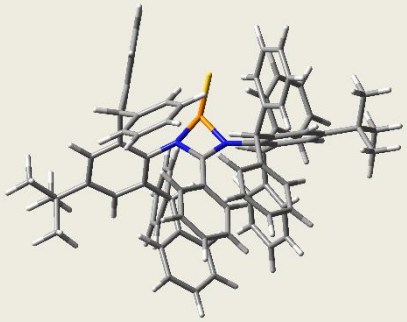

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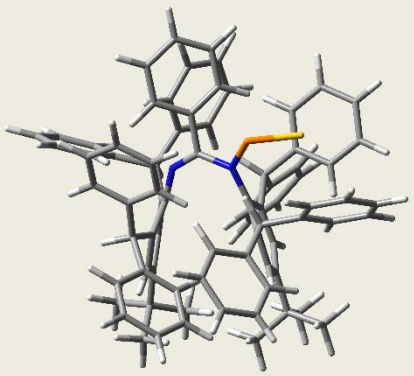
$^{t\text{Bu}}$Bhp–NC(Ph)N(PS)–$^{t\text{Bu}}$Bhp (10b)



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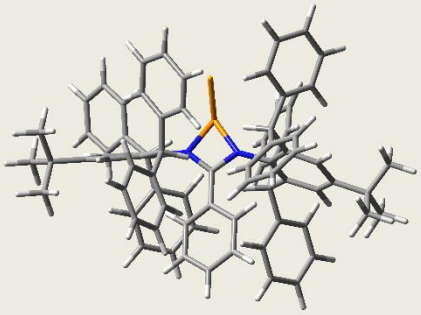

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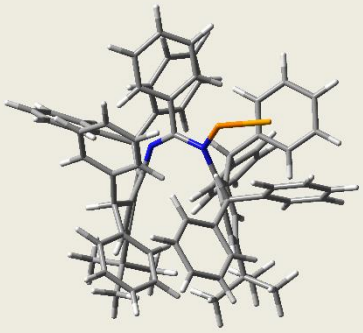

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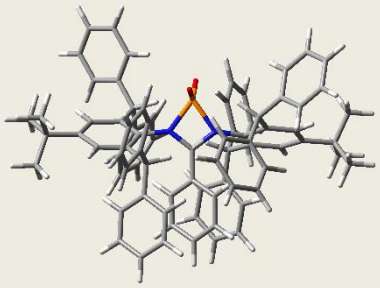

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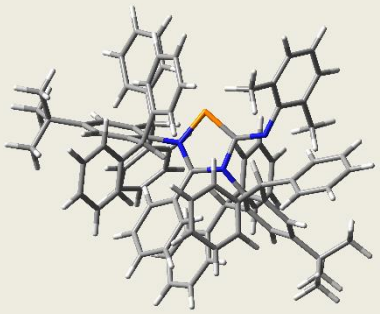
^{tBu}Bhp-[NC(Ph)NC(NDmp)P]-^{tBu}Bhp (13)



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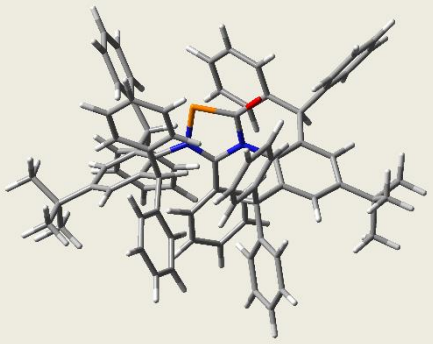

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H    3.89827015    1.50374209    2.95427667
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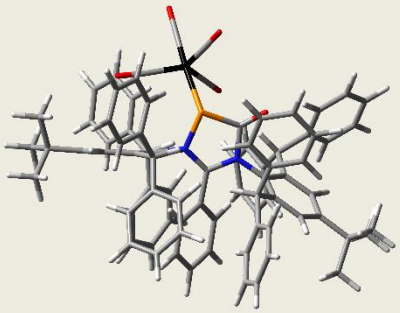
^{tBu}Bhp-[NC(Ph)NC(O)P(Fe(CO)$_4$)]-^{tBu}Bhp (15)



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O	1.42133300	0.13454800	5.62100800
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C	3.07498200	1.18997900	-0.28550900
C	-0.47899100	0.26042000	-1.81277700
C	-3.07834100	1.53216900	-0.12031800
C	-3.60375300	-0.84083200	0.18603100
C	4.07608700	-1.13837500	-1.44987800
C	1.91389500	-2.38646300	-1.24706200
C	4.40345900	1.09679100	-0.69720700
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C	0.21158200	1.26696700	-2.50289800
C	-1.42303500	-0.52291500	-2.49739800
C	-4.39992000	1.75205200	-0.50107800
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C	-3.24596200	-2.26016800	0.61080000
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C	4.93647300	-0.05611000	-1.28083600
H	1.08766300	-2.39429200	-0.51738600
C	2.75374800	-3.64257200	-0.97350100
C	1.29641500	-2.45598300	-2.64229200
H	5.04360300	1.96349200	-0.52606800
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C	3.56945500	3.14238100	1.23840900

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H    -3.05074300    7.26302900   -0.75435700
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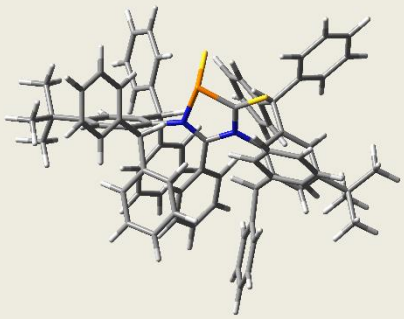

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N	-1.15759000	-0.16385400	0.75729600
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C	-0.74429000	-1.05858700	-2.14141400
C	0.84977500	0.76910200	-2.10992400
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C	5.02009900	0.09592600	-0.79894800
H	1.32343000	-2.53718000	-0.17461900
C	2.94620800	-3.49426100	0.79375200
C	2.50547800	-3.37625500	-1.71083200
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H	1.63132400	1.86484000	1.74864300
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C	3.47518100	2.74072700	2.28974900
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C	-3.41360100	-1.06454500	0.53891100
H	-1.37092800	-1.77373000	-1.61414000
C	-0.68333000	-1.08639300	-3.53075900
C	0.89428000	0.74284300	-3.50155000
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C    -4.76912300   -0.87825900    0.25375300
C    -2.95740100   -2.43527700    1.03124900
H    -1.27314200   -1.82540800   -4.07385400
C     0.13049800   -0.18233200   -4.21474200
H     1.51359400    1.46851700   -4.02855000
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C     6.37428200    1.49281200   -2.37175100
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C     2.53814100   -4.80396600    2.80652400
C     4.78753900   -4.55066700    1.97813100
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H     2.85053900   -5.33767300   -0.87845800
C     2.69558500   -5.41364100   -3.02761700
C     2.31576400   -3.30773700   -4.13484700
H     2.17302900   -1.58039800   -2.85937000
H     3.43533000    3.13104100   -1.29821300
C     2.28846500    4.94587500   -1.50712100
C     0.65192800    5.37455500    0.21433300
H     0.52990500    3.89338900    1.78336000
H     4.56294300    4.09895100    1.00485800
C     5.35824600    4.10294500    3.00596500
C     4.20867100    2.71228700    4.60625500
H     2.52592500    1.59191000    3.84835300
H    -4.68209000    2.28699400   -0.91529800
C    -5.26408100    0.31447800   -0.27503000
H    -1.11459400    2.27981700   -0.12512500
C    -1.85207800    2.55544600   -2.11442800
C    -2.70217400    3.68853900   -0.03005200
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H    -2.05861900   -2.28132000    1.65025700
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C    -2.53106700   -3.32061100   -0.13039200
H     0.16692100   -0.19341900   -5.30499100
H     6.99179800   -1.81512100   -1.50439200
H     7.90135700   -0.73866300   -2.58206100
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H    5.66330400    1.30453500   -3.18970800
H    1.83370200   -5.19208100    3.54376200
C    3.90153200   -5.07110900    2.92517200
H    5.85735200   -4.74873300    2.06397800
H    2.84922700   -6.49363800   -3.06663900
C    2.50300900   -4.69024300   -4.20526100
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C    1.29735900    5.76460900   -0.96366400
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H    4.08202300    2.34284800    5.62535300
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C   -0.89760300    3.49803700   -2.52693200
C   -2.57714600    1.87548400   -3.09695600
C   -3.32251700    4.65663900   -0.82975400
C   -2.66044500    3.88957300    1.35554900
C   -4.24361500   -2.46386900    3.19181400
C   -4.67374000   -4.24995900    1.62973400
C   -3.23353500   -3.36949000   -1.34293900
C   -1.37458600   -4.09928700   -0.00172100
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H    1.00954900    6.68872000   -1.46736900
H    5.91100500    3.95487200    5.09116400
C   -6.91978600    0.86291500   -2.06943400
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C   -7.60351100   -0.68039500   -0.22698300
H   -0.31977400    4.03195500   -1.77336900
C   -0.69441800    3.77664000   -3.87510100
C   -2.37247300    2.14924800   -4.45391700
H   -3.31136400    1.12338500   -2.80792100
H   -3.36278400    4.52391100   -1.91152200
C   -3.87910000    5.80417200   -0.25721400
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H   -7.97999100    1.04658700   -2.29976900
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H   -6.68323800    2.65957700    0.03927100
H   -7.13184100    1.53922500    1.34216100
H   -7.30932300   -1.56163900   -0.81622000
H   -8.65847600   -0.46695800   -0.45107100
H   -7.53402800   -0.94153800    0.83896400
H    0.05064200    4.52096900   -4.16346400
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H   -5.36659500   -2.51250800    5.02858700
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C   -1.59288200   -4.89362600   -2.27213600
H    0.02395100   -5.44233500   -0.94787700
H   -1.28860800    3.32415000   -5.90869700
H   -4.24823900    6.90173100    1.56858100
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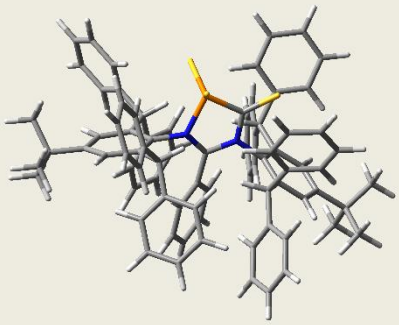
$^{t\text{Bu}}$Bhp–[NC(Ph)NC(S)P(S$_2$)]–$^{t\text{Bu}}$Bhp (17)



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C	-0.02525600	0.01288000	-0.03697900
C	2.80321200	-1.63442000	-0.16696100
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C	1.86199700	-2.82127800	-0.00964500
C	4.67530600	0.42652900	-0.27943700
C	3.02911900	2.15416600	0.53887100
C	-2.46497400	0.30746300	0.06900000
C	-0.75389000	-0.77791700	-2.28425000
C	1.03998600	0.83947300	-2.14373900
H	4.34298400	-2.86551400	-0.98560900
C	5.06169200	-0.85262200	-0.69469200
H	0.82455800	-2.44985300	-0.03047300
C	2.05362100	-3.47481700	1.35561500
C	1.97465300	-3.79224300	-1.18393600
H	5.39225100	1.24521900	-0.33899900
H	1.92976700	2.24676200	0.48860600
C	3.58590600	3.21140100	-0.42728800
C	3.39657100	2.46678600	1.98844300
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C     5.01766900    2.61691700    3.78790200
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H   -7.26021700    2.00759600   -3.38213300
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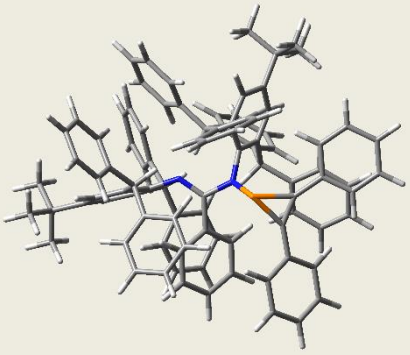
^{tBu}Bhp–NC(Ph)N(P($C_{14}H_{10}$))–^{tBu}Bhp (18)



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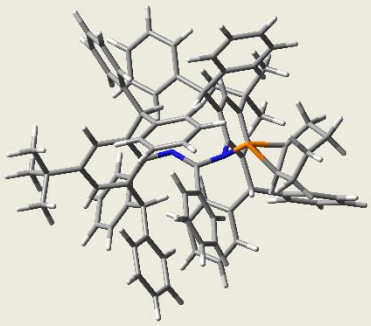
$^{t\text{Bu}}$Bhp–NC(Ph)N(P(C$_6$H$_{10}$))–$^{t\text{Bu}}$Bhp (19)



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C	3.37290900	-1.88919000	-2.15149000
C	2.85354900	-0.94662600	-3.20184600
C	3.93486700	-3.25553700	-2.55435400
C	4.22033700	-3.37162000	-4.05683200
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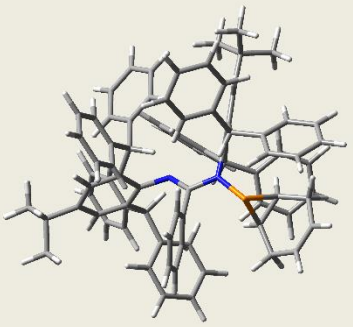
^{tBu}Bhp–NC(Ph)N(P(C$_6$H$_8$))–^{tBu}Bhp (20)



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C	0.93694300	2.71491400	1.59984900
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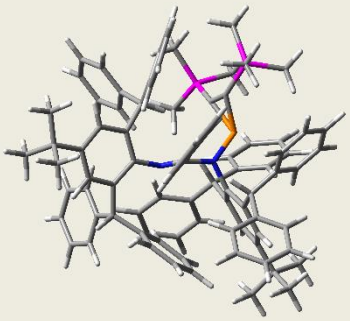
^{tBu}Bhp–NC(Ph)N(P(BTMSA))–^{tBu}Bhp (21)



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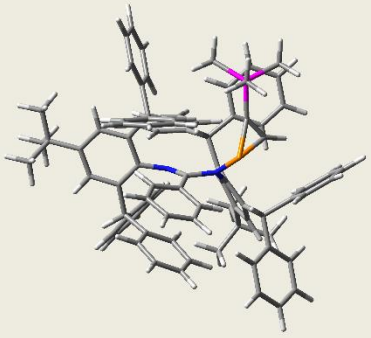
^{tBu}Bhp-NC(Ph)N(P(TMSA))-^{tBu}Bhp (22)



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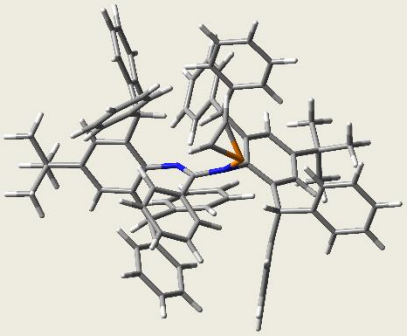
$^{t\mathrm{Bu}}$Bhp–NC(Ph)N(P(C$_2$H$_2$))–$^{t\mathrm{Bu}}$Bhp



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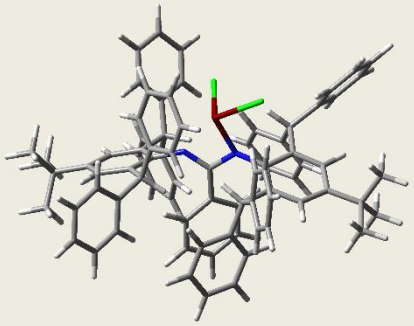
$^{t\text{Bu}}$Bhp–NC(Ph)N(AsCl$_2$)–$^{t\text{Bu}}$Bhp (23)



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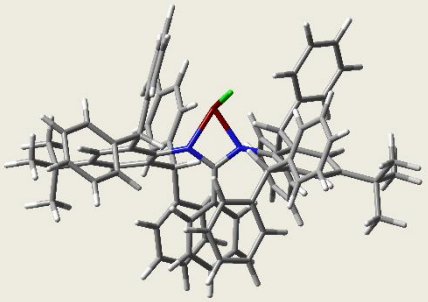
[$^{t\text{Bu}}$Bhp–[NC(Ph)N(AsCl)]–$^{t\text{Bu}}$Bhp]$^{+}$



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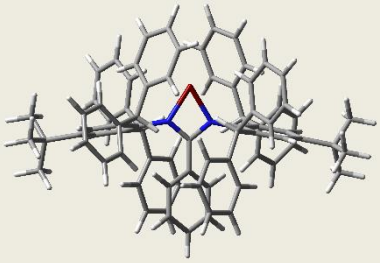
[$^{t\text{Bu}}$Bhp–[NC(Ph)NAs]–$^{t\text{Bu}}$Bhp]



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C	-1.09162600	0.51869800	4.14452200
C	1.09591100	-0.50201000	4.14112600
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C    -5.30970900    3.23425100   -0.93523300
C    -4.33069900    3.41372000    1.25934200
C    -1.75295000   -3.78706400   -2.14671700
C    -2.31832600   -5.16050700   -0.24632100
C    -1.54276000   -2.95153400    2.70294900
C     0.29427000   -3.94833400    1.51088700
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C     2.03489700   -3.24160900   -2.29122200
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C     1.75504500    3.80974400   -2.14418100
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C     1.54297700    2.96818900    2.70457900
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H    -1.86573600    4.04620400   -1.53970600
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C    -2.53204700    1.27295800   -4.16326600
H    -3.51348600    0.20286400   -2.56418000
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C    -5.37401800    4.24815700    1.66149000
H    -3.53268900    3.15910500    1.96137400
H    -1.36214300   -2.84524400   -2.54340800
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C    -2.70724900   -6.18991200   -1.10731500
H    -2.36794100   -5.30556500    0.83473100
H    -2.46734300   -2.37354700    2.70860000
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H     5.24969400   -2.84803400   -1.97575300
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C     1.58821900   -3.40035800   -3.60020200
C     2.51689300   -1.24887700   -4.17333400
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H     2.39252700    5.31706500    0.83832000
C     2.72713400    6.20464100   -1.10289700
C     2.13903400    4.83821500   -3.00408000
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C    -0.84523400    4.40685000    2.70975400
C     0.98727100    3.40212600    3.91135800
H     2.46585000    2.38747600    2.71151300
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H    -8.45302000   -1.18508000    0.93165700
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H    -2.72076800    0.48623700   -4.89586500
H    -7.14670100    4.32159200   -1.24459900
C    -6.39392900    4.57579100    0.76442400
H    -5.38907300    4.64741900    2.67735600
H    -2.05235700   -4.67714000   -4.08743100
C    -2.61881500   -6.02073800   -2.49037000
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H     8.34917700    1.76368500   -0.30705000
H     7.57501400    3.54388200    1.23286600
H     5.93442300    3.55655900    1.91271000
H     6.18580300    3.88032900    0.17853600
H     5.38142700   -4.62421500    2.66593200
C     6.37606800   -4.56520100    0.74716100
H     7.11857300   -4.32332000   -1.26721500
H     1.03847300   -4.30159200   -3.87621700
C     1.82038500   -2.39765300   -4.54673700
H     2.70890700   -0.46155000   -4.90441000
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H    -1.47949400    2.54442600   -5.55724000
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H    -2.91749700   -6.82703600   -3.16237500
H     0.63658100   -4.44233800    4.86546800
H     7.19192200   -5.21999800    1.05729500
H     1.46079500   -2.51416200   -5.57027000
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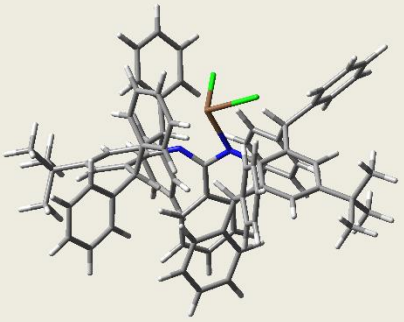
$^{t\text{Bu}}$Bhp–NC(Ph)N(SbCl$_2$)–$^{t\text{Bu}}$Bhp (24)



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C	-1.32699800	0.54252200	2.45814800
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C	-4.65260400	0.94583100	-0.17338900
C	-2.57014900	2.33050900	-0.61818200
C	3.96035400	1.77666600	1.18577500
C	1.67809300	2.65066800	0.62133900
C	4.65130400	-0.45821400	0.72153000
C	3.12123300	-2.20536800	-0.26614400
H	-2.03699800	1.10860300	1.86212400
C	-1.49894700	0.47297500	3.83715500
C	0.47404800	-0.90473100	4.01646300
H	1.49762700	-1.33890900	2.18155800
H	-5.01480900	-2.35119300	0.49702600
C	-5.32128600	-0.24912300	0.13204700
H	-1.33398000	-2.47661900	0.27593700
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C	-3.43027900	3.53019300	-0.24230200
H	4.16983100	2.79635600	1.50753200
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C    -0.20361400    3.84193400    4.34878700
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C     3.57922300    6.00278600   -1.39097100
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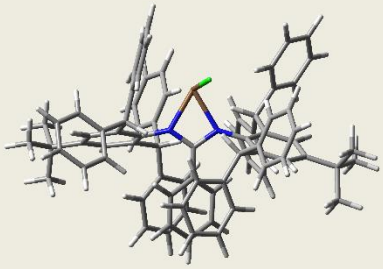
[$^{t\mathrm{Bu}}$Bhp–[NC(Ph)N(SbCl)]–$^{t\mathrm{Bu}}$Bhp]$^{+}$



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C	-5.17562500	0.87891300	-0.28424000
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C	2.91912400	-1.44442100	-0.67554400
C	4.24931000	-1.43644400	-1.09141400
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C    -4.06644600   -3.91409600   -0.95332100
C    -5.02447100   -4.82944300   -1.39050600
C    -6.13126700   -5.11851300   -0.58920800
C    -6.27012100   -4.49048300    0.65022500
C    -5.30870600   -3.57657300    1.08574800
C     3.18092200    3.52932600   -1.10094000
C     3.07546500    4.76579400   -1.74674200
C     2.42228500    5.83086800   -1.12799500
C     1.85697800    5.64834600    0.13819600
C     1.96147600    4.41471100    0.77720700
C     3.48089000    1.17239100    3.21191100
C     4.23863000    1.22398200    4.37964300
C     5.13213200    2.28004100    4.58204300
C     5.25518100    3.27231300    3.60967000
C     4.48626200    3.21988100    2.44317200
C     3.55656900   -3.99806400    0.88979300
C     4.39374800   -5.05176300    1.24962900
C     4.69052000   -6.05849900    0.32576200
C     4.13935000   -5.99943900   -0.95347900
C     3.29531100   -4.94306700   -1.31124000
C     0.17252500   -3.73183500   -1.99770800
C    -0.51180700   -4.05929000   -3.16815900
C    -0.03983900   -3.60609800   -4.40263500
C     1.11078200   -2.81729500   -4.45146600
C     1.79504600   -2.49342000   -3.27772000
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H     1.57890500    1.44329000   -1.93169100
H     1.43994400    1.86262700   -4.36387200
H    -0.30730800    0.73043600   -5.72812500
H    -1.92594700   -0.81900100   -4.64207800
H    -1.81539300   -1.21697400   -2.20210200
H    -5.62422100   -1.18528800    0.17178800
H    -4.35528000    2.83773800   -0.64356000
H     4.64787000   -2.35515800   -1.52411300
H     5.22557200    1.60851300    0.02332300
H    -8.64514400    0.57944100   -0.45740100
H    -7.45952000   -0.62187100   -1.00338600
H    -7.58670300   -0.20893700    0.72687200
H    -7.97041500    2.81675900    0.37337000
H    -6.26834700    3.32468200    0.40196400
H    -6.84576200    2.09892400    1.55295100
H    -6.54350100    1.10317400   -2.66695300
H    -7.79704600    2.23099900   -2.09478000
H    -6.09298200    2.73324600   -2.11303200
H     7.62372500   -0.76555300   -3.23293200
H     6.07854100   -1.63540500   -3.13471800
H     6.09124900    0.11834700   -3.43702700
H     8.35599700    0.78056300   -1.45479700
H     7.37922400    1.10148800   -0.01088900
H     6.87064700    1.74083800   -1.59707300
H     6.76638400   -2.54135600   -0.81054400
H     8.30221500   -1.65681800   -0.94858200
H     7.24917800   -1.40288600    0.46592200
H     1.35298100   -2.67087100    0.05379700
H     1.72208000    1.81581600    1.29456800
H    -2.22586800   -2.51602700    0.18309900
H    -0.74039000    2.09009800   -0.21600700
H     0.07768100    4.32446500   -1.27058200
H     0.36064700    5.35689500   -3.49256400
H    -1.18466200    4.75123400   -5.36456900
H    -2.98288700    3.07158200   -4.97011600
H    -3.25090500    2.02759300   -2.75033700
H    -0.78163300    2.53741700    2.11028600
H    -1.14232400    4.20664400    3.90429400
H    -2.49328800    6.25348100    3.44680100
H    -3.45687900    6.61044100    1.17743500
H    -3.07294100    4.94576600   -0.61964300
H    -2.60585300   -4.42275400    2.21210100
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H    -2.01163600   -4.54302000    4.60923300
H    -1.90049300   -2.47234200    5.99232500
H    -2.40187700   -0.26654100    4.93740600
H    -3.07674600   -0.15658900    2.54747100
H    -3.20076600   -3.68828300   -1.58184300
H    -4.90506000   -5.32213300   -2.35668100
H    -6.88029500   -5.83572000   -0.92699500
H    -7.13006400   -4.71436100    1.28313800
H    -5.42112000   -3.09573100    2.05961200
H     3.70449600    2.70935300   -1.59422100
H     3.51365500    4.89407700   -2.73783800
H     2.34628800    6.79689500   -1.62894500
H     1.32796500    6.46751000    0.62744400
H     1.52208300    4.28403500    1.76823400
H     2.81843800    0.31650200    3.04240900
H     4.13885800    0.43790800    5.12973400
H     5.73030400    2.32505300    5.49288900
H     5.95319900    4.09777600    3.75723500
H     4.58246400    4.00730700    1.69449400
H     3.34560300   -3.20417100    1.60909500
H     4.81951100   -5.08765300    2.25376600
H     5.34762200   -6.88339100    0.60438400
H     4.36391000   -6.77952300   -1.68262100
H     2.86733200   -4.91149900   -2.31380100
H    -0.18244200   -4.10877100   -1.03453700
H    -1.40679000   -4.68265700   -3.11902000
H    -0.56701600   -3.86603300   -5.32168700
H     1.48084300   -2.45096700   -5.41027200
H     2.69347400   -1.87583000   -3.32536400
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[$^{t\text{Bu}}$Bhp-[NC(Ph)NSb]-$^{t\text{Bu}}$Bhp] (26)

Sb	-0.01296200	0.02912600	-2.10365900
N	-1.09632000	0.10146100	-0.22967900
N	1.08689400	-0.07149900	-0.23799300
C	-0.00186900	0.01076200	0.56378900
C	-2.38198600	-0.39580600	0.06890100
C	2.37634700	0.41541500	0.06207400
C	0.00168800	0.00701500	2.01948300
C	-3.47219500	0.49469400	0.01368900
C	-2.59887600	-1.76911500	0.31396800
C	3.46139300	-0.48674100	0.00156600
C	2.60447400	1.78082700	0.31798000
C	-1.07792600	0.55086900	2.74371800
C	1.08395800	-0.53912300	2.73794200
C	-4.75792700	0.02079000	0.28391800
C	-3.19668100	1.94144700	-0.37144700
C	-3.90236000	-2.19804800	0.57073700
C	-1.45779200	-2.77460000	0.22720800
C	4.74428400	-0.02330300	0.27634900
C	3.17484200	-1.92917000	-0.39057900
C	3.91406000	2.20251600	0.58522700
C	1.47084200	2.79406900	0.23208900
H	-1.91394700	0.99886700	2.20982500
C	-1.07388100	0.54342700	4.13411800
C	1.08461100	-0.53676400	4.12839500
H	1.91873900	-0.98448800	2.19995800
H	-5.58341100	0.73035800	0.25822500
C	-4.99724800	-1.32549100	0.58430300
H	-2.31765600	2.25473000	0.21901000
C	-2.77442000	2.08742200	-1.83057200
C	-4.33078600	2.87847800	0.00364300
H	-4.06357000	-3.26437200	0.73824600
H	-0.63891000	-2.27756000	-0.32431100
C	-1.86552800	-3.96351000	-0.64080800
C	-0.88692500	-3.21448400	1.56749200
H	5.56865800	-0.73663000	0.24458900
C	4.99699500	1.32168400	0.59227300
H	2.29619400	-2.23994600	0.20167400
C	4.30542700	-2.87329600	-0.02262400
C	2.74776700	-2.06421500	-1.84900200
H	4.07722300	3.26467600	0.76465700
H	0.65230100	2.30269300	-0.32513700

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C     1.88839000    3.98324700   -0.63065800
C     0.89416000    3.23149200    1.57021100
H    -1.91399400    0.98191200    4.67492600
C     0.00654600    0.00200200    4.83579500
H     1.92674100   -0.97692000    4.66468000
C    -6.39538900   -1.87043200    0.89204400
C    -2.15164400    3.27605300   -2.24161900
C    -2.98681200    1.07927300   -2.78232400
C    -5.36137500    3.19065800   -0.89107600
C    -4.37734700    3.41591200    1.29693600
C    -1.79514600   -3.83989600   -2.03491800
C    -2.33515900   -5.16345300   -0.09323200
C    -1.51057700   -2.95155000    2.79071600
C     0.32043800   -3.93069400    1.57505500
C     6.42816800    1.76868800    0.90445400
C     4.35675100   -3.40986800    1.27091900
C     5.32977900   -3.19034600   -0.92269000
C     2.10960200   -3.24306500   -2.26359400
C     2.97173200   -1.05513700   -2.79687900
C     2.36005800    5.17999600   -0.07815900
C     1.82471500    3.86257700   -2.02542000
C    -0.31396400    3.94644400    1.57326700
C     1.51192800    2.96618600    2.79586400
H     0.00845900    0.00002800    5.92686700
C    -7.46442200   -0.76964600    0.87806300
C    -6.76997900   -2.92998300   -0.16435900
C    -6.38672300   -2.52347200    2.28936800
H    -1.98794900    4.07262700   -1.51245300
C    -1.72605400    3.44597200   -3.55553800
C    -2.55630000    1.24756200   -4.10563900
H    -3.48744300    0.15538600   -2.48640500
H    -5.32993700    2.78762800   -1.90509800
C    -6.41906900    4.01438400   -0.49978100
C    -5.43074400    4.24187000    1.69039700
H    -3.57447400    3.18072800    2.00013200
H    -1.41072800   -2.90820300   -2.46190800
C    -2.19305500   -4.88850800   -2.86371000
C    -2.74083700   -6.21261700   -0.92189600
H    -2.36798700   -5.28245700    0.99159200
H    -2.43845000   -2.37900400    2.80821500
C    -0.94263300   -3.38975900    3.99013800
C     0.88814300   -4.37268500    2.76829100
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H     0.81223800   -4.15386200    0.62526500
C     6.94974800    0.97340300    2.11875600
C     7.32731800    1.48489100   -0.31621200
C     6.51089400    3.26579400    1.23157400
H     3.55904400   -3.17012900    1.97839700
C     5.40882600   -4.23973900    1.65946100
C     6.38616000   -4.01833200   -0.53633700
H     5.29476900   -2.78767200   -1.93672800
H     1.93615400   -4.04038700   -1.53750700
C     1.67995100   -3.40229200   -3.57769700
C     2.53704000   -1.21229800   -4.11988400
H     3.48483100   -0.13913500   -2.49781200
H     2.38910800    5.29611000    1.00704900
C     2.77383800    6.22923300   -0.90265400
C     2.23062600    4.91130600   -2.85015800
H     1.43899000    2.93303300   -2.45605000
H    -0.80170200    4.16967700    0.62137000
C    -0.88768500    4.38586000    2.76458400
C     0.93815500    3.40208400    3.99334000
H     2.43947600    2.39315400    2.81637700
H    -7.25637100    0.01161300    1.62378500
H    -8.44531400   -1.20681500    1.11470700
H    -7.54360400   -0.28841500   -0.10778100
H    -6.78469700   -2.48699000   -1.17070800
H    -7.76910200   -3.34124500    0.04588500
H    -6.05478300   -3.76424500   -0.17540300
H    -6.11822600   -1.78812600    3.06190800
H    -5.66535600   -3.35078000    2.34516800
H    -7.38274200   -2.92618900    2.52849400
H    -1.22101200    4.36921000   -3.84397200
C    -1.91702900    2.42521300   -4.49290000
H    -2.71798600    0.44665300   -4.82940800
H    -7.21446400    4.24759100   -1.20983500
C    -6.45794700    4.54238400    0.79222600
H    -5.44823200    4.65527700    2.70052600
H    -2.12573200   -4.77739700   -3.94802000
C    -2.67255000   -6.07894000   -2.30993700
H    -3.10518000   -7.14156000   -0.47922700
H    -1.43806100   -3.15865900    4.93450700
C     0.25474400   -4.10444900    3.98533000
H     1.82522200   -4.93253700    2.74677700
H     7.98192500    1.27301700    2.35601100
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H     6.94645000   -0.10846500    1.92609100
H     6.32433200    1.16043700    3.00391100
H     6.97165800    2.03757900   -1.19785600
H     7.33980100    0.41546300   -0.56869300
H     8.36261300    1.79541200   -0.10828200
H     7.55258900    3.53512500    1.45852400
H     5.89966200    3.52464300    2.10869100
H     6.18061200    3.88827700    0.38709700
H     5.43022800   -4.65204300    2.66996000
C     6.42990900   -4.54532100    0.75594500
H     7.17661900   -4.25561300   -1.25054900
H     1.16327500   -4.31819300   -3.86887100
C     1.88243000   -2.38036800   -4.51102900
H     2.70841700   -0.41096100   -4.84094500
H     3.14006400    7.15565000   -0.45627600
C     2.71175900    6.09877100   -2.29133700
H     2.16811900    4.80280800   -3.93501900
H    -1.82543900    4.94445900    2.73968300
C    -0.25955900    4.11624400    3.98408600
H     1.42888100    3.16935000    4.93977100
H    -1.57149300    2.55007300   -5.52010300
H    -7.28160400    5.19009700    1.09652600
H    -2.98372500   -6.90089500   -2.95691300
H     0.69706700   -4.44482100    4.92301600
H     7.25253500   -5.19612300    1.05642200
H     1.53400300   -2.49674900   -5.53825800
H     3.02920300    6.92093000   -2.93503700
H    -0.70647400    4.45473000    4.92027800
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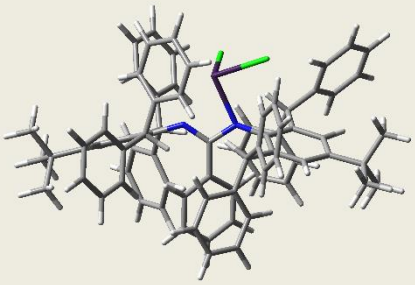
$^{t\text{Bu}}$Bhp–NC(Ph)N(BiCl$_2$)–$^{t\text{Bu}}$Bhp (25)



Cl	0.55645900	-2.44816100	-2.78871100
Bi	0.37398800	-0.01032900	-2.32949000
Cl	2.75899100	0.66054100	-2.97572100
N	-1.15340300	-0.10031500	-0.35632300
N	1.07082800	-0.12089700	-0.12009700
C	-0.13726700	-0.09408200	0.49403500
C	-2.52778500	-0.16922400	-0.09036300
C	2.33395600	0.20470800	0.42563400
C	-0.30310600	-0.11297600	1.97176600
C	-3.17592300	-1.37984700	0.21956800
C	-3.30298200	1.01091800	-0.24077500
C	2.63061000	1.51030600	0.87881500
C	3.36952300	-0.76691300	0.39831100
C	-1.38506100	0.54540100	2.58063900
C	0.58063100	-0.84408200	2.77759300
C	-4.56402000	-1.38353600	0.41019700
C	-2.41286500	-2.69381000	0.27422300
C	-4.68189000	0.95423500	-0.06454700
C	-2.59180100	2.32160500	-0.55840500
C	3.91648300	1.79542200	1.35585600
C	1.62508700	2.65291600	0.80894000
C	4.63420600	-0.42563700	0.86920700
C	3.10927800	-2.18752500	-0.09796000
H	-2.07486500	1.13246500	1.98093300
C	-1.58231500	0.46041000	3.95552800
C	0.37169200	-0.94145400	4.15207400
H	1.42025400	-1.36549400	2.32848700
H	-5.03184500	-2.33181600	0.67261300
C	-5.34398400	-0.23616800	0.27392900
H	-1.35165600	-2.45422500	0.45062700
C	-2.86581200	-3.53411600	1.46265000
C	-2.45885200	-3.43966400	-1.05835800
H	-5.25109000	1.87849500	-0.16931000
H	-1.72764100	2.38099500	0.12776100
C	-2.00924600	2.35437800	-1.96255600
C	-3.45364700	3.54109100	-0.25986200
H	4.11612500	2.81553200	1.68233300
C	4.93759200	0.84696100	1.37030800
H	0.82551000	2.33530300	0.11789100
C	0.94600000	2.99252200	2.13073100
C	2.27207100	3.88942900	0.17378800

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H     5.41681100   -1.18402300    0.81029400
H     2.33908900   -2.12488300   -0.88066800
C     4.33787600   -2.81761800   -0.75127900
C     2.51962500   -3.03889800    1.01653700
H    -2.42132800    0.98764900    4.41059400
C    -0.71166100   -0.29307700    4.74600900
H     1.05943100   -1.53901500    4.75175200
C    -6.85908300   -0.22716400    0.49350600
C    -2.39415400   -3.20758600    2.74183000
C    -3.77443700   -4.59198500    1.33400700
C    -1.76532200   -4.65259400   -1.18706300
C    -3.13318400   -2.94256500   -2.17862700
C    -2.59662000    1.65566300   -3.02610000
C    -0.85939600    3.12018900   -2.21904900
C    -4.09623300    4.27503000   -1.26238700
C    -3.64788900    3.91878600    1.07696000
C     6.35751100    1.15637200    1.85032000
C    -0.16110700    3.85504500    2.11617500
C     1.40499600    2.52281300    3.36453900
C     2.55824900    5.05043500    0.90185800
C     2.62941300    3.84415000   -1.18177500
C     4.88728800   -2.20671900   -1.89029300
C     4.93240600   -3.99027900   -0.27281500
C     1.33007800   -3.74638200    0.80441900
C     3.13339000   -3.12118400    2.27588100
H    -0.87572200   -0.36831500    5.82229600
C    -7.40171200   -1.62017100    0.83927400
C    -7.55924700    0.26508900   -0.78909800
C    -7.19149800    0.73131800    1.65583100
H    -1.68542100   -2.38679500    2.85789600
C    -2.81524600   -3.92042000    3.86316900
C    -4.20112300   -5.30621100    2.45696600
H    -4.14237000   -4.86711300    0.34407200
H    -1.23912700   -5.06213200   -0.32333000
C    -1.74061600   -5.34382900   -2.39565100
C    -3.11076300   -3.63295500   -3.39421300
H    -3.68289700   -2.00355200   -2.10211900
H    -3.47879000    1.04134100   -2.83661000
C    -2.05142800    1.72412900   -4.31297000
C    -0.30985000    3.18775400   -3.50248100
H    -0.38699900    3.67609900   -1.40581800
H    -3.95309000    4.00034000   -2.30856900
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C    -4.91717700    5.35903400   -0.93734200
C    -4.46461400    4.99934500    1.40449900
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H    -3.64021900   -3.22301700   -4.25639600
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H    -5.74363300    6.57241700    0.64870600
H    -0.79594700    4.08081400    5.45700900
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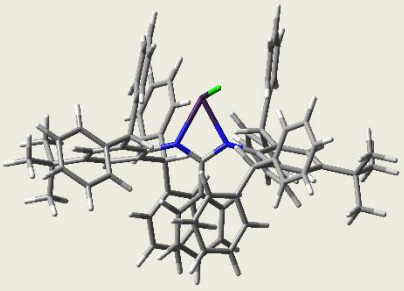
[^{tBu}Bhp–[NC(Ph)N(BiCl)]–^{tBu}Bhp]$^{+}$



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C	-4.49772900	-1.05623300	1.06969700
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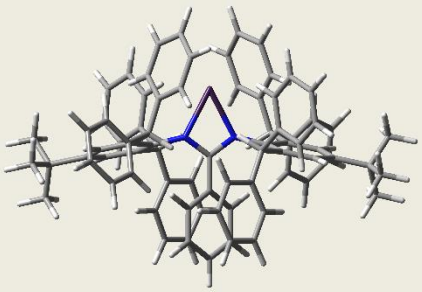
[$^{t\text{Bu}}$Bhp–[NC(Ph)NBi]–$^{t\text{Bu}}$Bhp]



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C	1.46553100	2.79372300	0.38832400
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C	-1.06540300	0.56107300	4.22551900
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H	1.90422300	-1.00948300	2.29149600
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C	-2.78375300	2.05532400	-1.74515200
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H	-4.06599900	-3.25953000	0.90477400
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C    -1.77932500    3.41027400   -3.49984400
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H     2.44849000    2.38812600    2.96653600
H    -7.25843100    0.02244900    1.74723000
H    -8.44774400   -1.20209300    1.25337200
H    -7.54747600   -0.29750500    0.01956600
H    -6.78846000   -2.50553200   -1.01925500
H    -7.76955300   -3.35006400    0.20689600
H    -6.05412900   -3.77090500   -0.01214500
H    -6.11995000   -1.76194900    3.20512300
H    -5.66850100   -3.33253900    2.50528300
H    -7.38548300   -2.90493300    2.68456300
H    -1.30219400    4.34184800   -3.80817600
C    -1.94134800    2.36548100   -4.41663500
H    -2.69708900    0.36165900   -4.71512100
H    -7.22331000    4.22089200   -1.13226400
C    -6.45311400    4.54849000    0.85945000
H    -5.43071900    4.69231400    2.75888000
H    -1.94459000   -4.91051600   -3.75441900
C    -2.63456700   -6.13021100   -2.10784600
H    -3.20771100   -7.11037500   -0.26938800
H    -1.45011000   -3.15534000    5.09420400
C     0.24807500   -4.09673600    4.15044500
H     1.82453300   -4.92169000    2.91765800
H     7.98459300    1.26838000    2.48631200
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H     6.95289600   -0.11085900    2.03978100
H     6.32719000    1.14304400    3.13273400
H     6.97214900    2.07436900   -1.05742400
H     7.34604800    0.44583100   -0.44878700
H     8.36371800    1.82358900    0.02955200
H     7.54616000    3.54071500    1.61591000
H     5.89376100    3.51502700    2.26722200
H     6.17169400    3.90124600    0.54996800
H     5.43195700   -4.68289200    2.72737800
C     6.44342400   -4.53975300    0.82201100
H     7.20218500   -4.21283800   -1.17423100
H     1.26150100   -4.31332100   -3.82230000
C     1.90760200   -2.33876400   -4.42934700
H     2.67188800   -0.33802000   -4.72701300
H     3.24262300    7.11511600   -0.26369100
C     2.64581700    6.14740100   -2.10132000
H     1.93195500    4.94028500   -3.74704100
H    -1.81653900    4.94049300    2.91752900
C    -0.24270700    4.11246400    4.15171200
H     1.45219900    3.16700900    5.09714600
H    -1.60197100    2.47991100   -5.44706700
H    -7.27457000    5.20138700    1.15856200
H    -2.93595800   -6.96509200   -2.74282800
H     0.68846100   -4.43546600    5.08964700
H     7.26645000   -5.19273800    1.11657800
H     1.56342900   -2.44946400   -5.45859200
H     2.94736100    6.98303700   -2.73526800
H    -0.68376600    4.45117000    5.09061000
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