

**Universität
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Traditio et Innovatio

**Darstellung und Charakterisierung von
niedrigkoordinierten Pniktogen-Stickstoffverbindungen**

Diplomarbeit

aus dem Fachgebiet Anorganische Chemie

der Mathematisch-Naturwissenschaftlichen Fakultät

Universität Rostock

von

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Darstellung und Charakterisierung von niedrigkoordinierten Pniktogen-Stickstoffverbindungen

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Anorganische Chemie

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Gutachter : Prof. Dr. Axel Schulz
Dr. Alexander Villinger

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Fabian Reiß

Rostock, den 12.07.2011

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1. Zielsetzung

Die vorliegende Arbeit aus dem Bereich der Elementorganischen Chemie behandelt die Synthese und Charakterisierung von niedrig koordinierten Pniktogen-Stickstoffverbindungen und gliedert sich in zwei Abschnitte. Als erstes Ziel dieser Arbeit galt die Untersuchung der basenassistenten Reaktion von Terphenylamin Ter-NH_2 ($\text{Ter-NH}_2 = 2,6\text{-bis-(2,4,6-trimethylphenyl)anilin}$) mit Pniktogen(III)chloriden ECl_3 ($\text{E} = \text{As, P}$) zu sterisch anspruchsvollen Amino(dichlor)pniktogen-Verbindungen R-N(H)-ECl_2 sowie deren Folgereaktionen zu 1,3-Dichloro-*cyclo*-1,3-dipnikta(III)-2,4-diazanen $[\text{R-N-E-Cl}]_2$. Dieser Teil sollte unter anderem Auskunft über das bei Raumtemperatur in Lösung vorliegende, molekulardynamische Gleichgewicht zwischen *cyclo*-1,3-Dipnikta-2,4-diazanen und dem entsprechenden Iminochlorpniktan geben.

Aufbauend auf den Erkenntnissen über das Reaktionsverhalten von Terphenylamin mit Phosphortrichlorid in Gegenwart von Basen sollte im zweiten Abschnitt eine Reihe von *N,N'*-Bis(terphenylamino)phosphenium-Salzen $[(\text{TerNH})_2\text{P}][\text{WCA}]$ mit unterschiedlichen, schwach koordinierenden Anionen ($\text{WCA} = \text{weakly coordinating anion}$) synthetisiert werden. Hierbei stand die Charakterisierung der Art und Stärke der Kation-Anion-Wechselwirkung sowohl in Lösung als auch im Festkörper im Vordergrund.

Die Untersuchung der Struktur sowie des chemischen und physikalischen Verhaltens der Verbindungen sollte durch schwingungsspektroskopische Methoden (UV/VIS-, IR-, Raman-Spektroskopie) und multinukleare Kernresonanzspektroskopie (^{31}P -, ^{13}C -, ^{19}F -, ^{11}B - und ^1H -NMR) in Lösung zum einen, zum anderen mit Hilfe der Röntgendiffraktometrie an geeigneten Einkristallen erfolgen. Anhand dieser Daten sollten die Bindungsverhältnisse der synthetisierten Verbindungen aufgeklärt und charakterisiert werden. Dadurch sollte sowohl der Zusammenhang zwischen Struktur und chemischer Bindung als auch die Ladungsverteilung und Reaktivität erklärt werden.

2. Allgemeiner Teil

2.1 Abkürzungen

Die in der vorliegenden Arbeit verwendeten Abkürzungen sind in *Tabelle 1* aufgeführt.

Ar ^F	fluorierter Arylligand	NMR	<i>nuclear magnetic resonance</i>
CB	Carborat	Ph	Phenyl-
CI	chemische Ionisation	R ^F	fluorierter Alkyligand
Dipp	2,6-Di- <i>iso</i> propylphenyl-	Raman	Raman-Spektroskopie
DSC	<i>differential scanning calorimetry</i>	RT	Raumtemperatur
DBU	1,8-Diazabicyclo[5.4.0]undec-7-en	s	stark, <i>strong</i>
ESI	Elektronen Spray Ionisation	T	Temperatur
H-BB	Wasserstoffbrückenbindung	<i>t</i> -Bu	<i>tert</i> -Butyl-
<i>i</i> -Pr	<i>iso</i> -Propyl-	Ter	Terphenyl-, 2,6-Bis(2,4,6-trimethyl-phenyl)-
IR	Infrarot-Spektroskopie	THF	Tetrahydrofuran
LDA	Lithiumdiisopropylamid	Triflat	Trifluormethansulfonat
m	mittel, <i>medium</i>	UV/VIS	Ultraviolett/Visuell-Spektroskopie
Me	Methyl-	w	schwach, <i>weak</i>
Mes*	Supermesityl-, 2,4,6-Tri- <i>tert</i> -butylphenyl-	WCA	schwachkoordinierendes Anion, <i>weakly coordinating anion</i>
MS	Massenspektrometrie	X-Ray	Röntgendiffraktometrie
<i>n</i> -BuLi	<i>n</i> -Butyllithium		

Tabelle 1: Verwendete Abkürzungen.

2.2 Maßeinheiten

Messgrößen wurden in den international geltenden Einheiten (SI) angegeben, davon abweichende Maßeinheiten und ihre Umrechnungen in SI-Einheiten sind in der *Tabelle 2* aufgeführt.

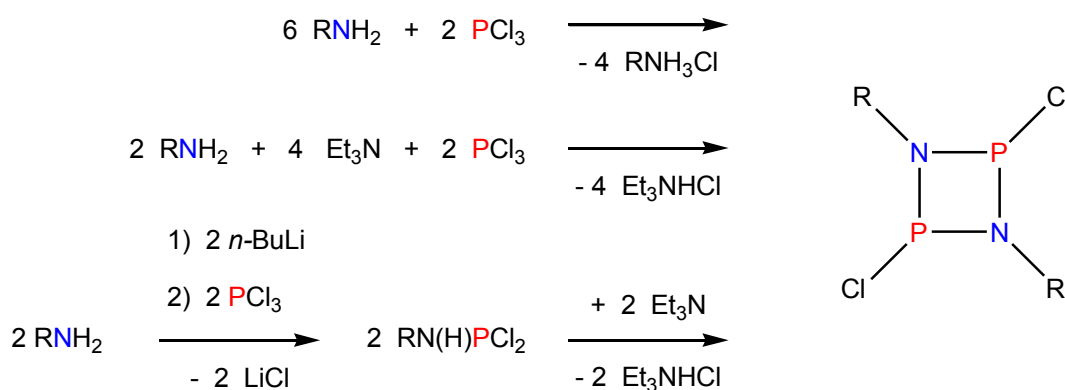
Größe	Symbol	Bezeichnung	Umrechnung in SI-Einheit
Länge	Å	Ångström	$1 \text{ Å} = 100 \text{ pm}$
Temperatur	°C	Grad Celsius	$X \text{ °C} = (x + 273.15) \text{ K}$
Zeit	d	Tag	$1 \text{ d} = 86400 \text{ s}$
	h	Stunde	$1 \text{ h} = 3600 \text{ s}$

Tabelle 2: Vom SI-System abweichende Einheiten.

3. Bisheriger Kenntnisstand

3.1 Binäre viergliedrige Pniktogen(III)-Stickstoff-Ringe

Bereits im Jahre 1894 wurde von Michaelis und Schroeter die Reaktion von Anilinhydrochlorid mit Phosphortrichlorid unter Rückflussbedingungen zu einem viergliedrigen Phosphor(III)-Stickstoff-Ring $[\text{Ph-N-P-Cl}]_2$ beschrieben.^[1] Dieser Arbeit folgte eine große Zahl analoger Synthesen von sogenannten *cyclo*-1,3-Diphospha-2,4-diazanen $[\text{R-N-P-R}']_2$ (R = Aryl, Alkyl; R' = Halogen, Aryl, Alkyl). Dabei stellte sich die basenunterstützte Kondensationsreaktion von Halogenphosphanen mit primären Aminen unter Halogenwasserstoff-Abspaltung als vielfältige Synthesemethode heraus.



Schema 1: Mögliche Synthesemethoden von *cyclo*-1,3-Diphospha-2,4-diazanen.

Burford *et al.* nehmen an, dass es durch den Einsatz von sterisch anspruchsvollen Substituenten R bzw. R' möglich ist, die monomere Spezies der $[\text{R-N-P-R}']_2$ -Derivate zu isolieren. Diese These wird durch das Iminochlorphosphan $\text{Mes}^*\text{-N=P-Cl}$ untermauert, dass sowohl in Lösung als auch im Festkörper als rotes Monomers vorliegt, wohingegen bereits die unerheblich weniger sterisch anspruchsvolle Dipp substituierte Verbindung nur als farbloses Dimer $[\text{Dipp-N-P-Cl}]_2$ isoliert werden kann. Des Weiteren konnte gezeigt werden, dass sich 1,3-Dichlor-*cyclo*-1,3-dipnikta(III)-2,4-diazane $[\text{R-N-E-Cl}]_2$ in Gegenwart von Lewis-Säuren (z.B. GaCl_3) in das entsprechende Trimer $[\text{R-N-P-Cl}]_3$ überführen lassen. Die Ringerweiterung geschieht durch formale Insertion eines R-N=P-Cl Fragmentes in eine N-P-Bindung des Dimers.^[2]

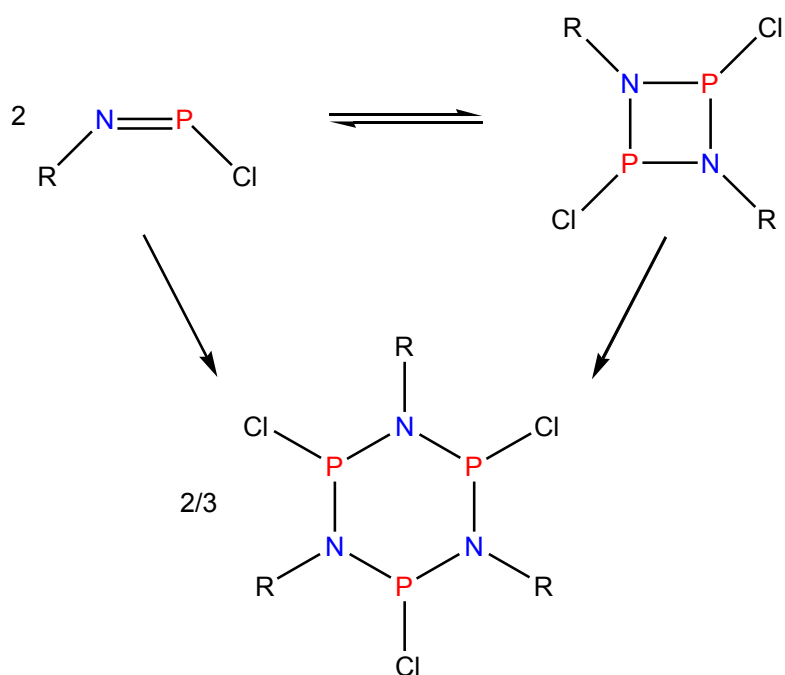
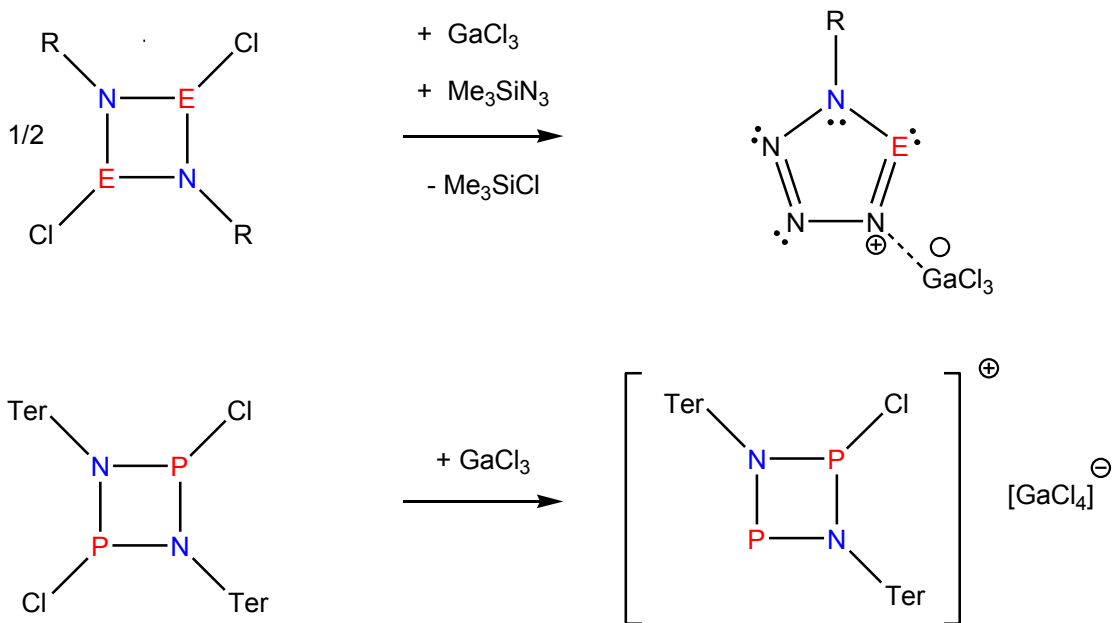


Abbildung 1: Monomer, Dimer und Trimer der Iminochlorosphane.

Im Vergleich zum Phosphor treten die schwereren Elemente der 15. Hauptgruppe, wie am Beispiel von $[t\text{-Bu-N-E-Cl}]_2$ ($E = \text{As, Sb}$) zu erkennen ist, in fester Phase ausschließlich in Form ihrer dimeren Spezies auf. Dies ist der geringeren Doppelbindungsstabilität $E=N$ und der niedrigeren Spannung des E_2N_2 -Ringes zuzuschreiben.^[3,4] Anhand von temperaturabhängigen $^1\text{H-NMR}$ -Untersuchungen konnte jedoch gezeigt werden, dass das kinetisch stabilisierte $[\text{Mes}^*\text{-N-As-Cl}]_2$ in Dichlormethan gelöst bei $23\text{ }^\circ\text{C}$ in einem Monomer/Dimer-Verhältnis von 1:1,7 vorliegt.^[5] Ausgehend von den cyclischen Pniktogen(III)-Stickstoff-Verbindungen ist es in einer Reihe Lewis-Säure-assistierter Reaktionen gelungen, unter Halogenabstraktion/austausch neuartige, kationische und neutrale Elementorganische-Verbindungen zu synthetisieren.^[6]



Schema 2: Beispielreaktionen von Pniktogen(III)-Stickstoff-Ringen (E = As, P; R = sterischer Rest wie z.B. Ter oder Mes*).

3.2 NPN-Kationen

Auf der Grundlage von massenspektrometrischen Untersuchungen an verschiedenen 2-substituierten 2-Phospha-1,3-diazacyclohexan-Verbindungen (R = Phenyl, Ethyl, Methyl, Cl; *Schema 3*) konnten R. Hutchins *et al.* im Jahre 1972 zeigen, dass die freien Elektronenpaare der Stickstoffatome in Abhängigkeit ihrer Position einen stabilisierenden Effekt in Bezug auf die Bildung von Phosphenium-Kationen $[(\text{R}_2\text{N})_2\text{P}]^+$ erzeugen.^[7] Wie in *Abbildung 2* verdeutlicht, werden NPN-Kationen durch Mesomerie stabilisiert, wenn die nichtbindenden Elektronenpaare parallel zum leeren p_z -Orbital des Phosphors ausgerichtet sind. In dieser Darstellung wird außerdem die isovalenzelektronische Beziehung zu den Singulett-Carbenen deutlich.

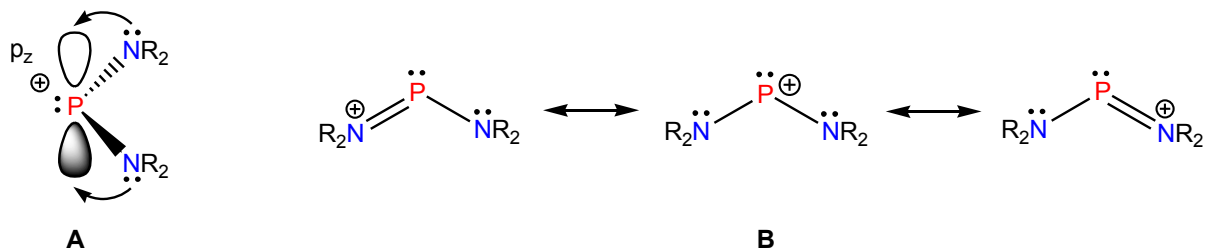
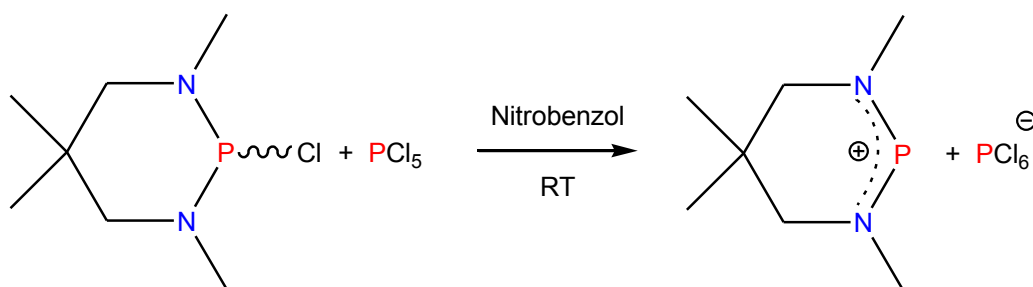


Abbildung 2: **A** Donorstabilisierung; **B** drei mögliche Resonanzformeln eines Phosphenium-Kations.

Die gewinkelte Struktur entspricht einer trigonal planaren Pseudostruktur, die im Einklang mit dem VSEPR-Modell für das AX₂E₁-System steht. Diese besondere strukturelle und elektronische Situation der NPN-Kationen macht sie zu schwachen σ -Donatoren und guten π -Akzeptoren mit ambidentem nukleophilem Charakter. Demzufolge besitzen sie den Carbenen gegenüber eine inverse Reaktivität, die in der Übergangsmetall-Katalyse von Interesse sein könnte.^[8] Auf der Grundlage ihrer Erkenntnisse gelang es R. Hutchins *et al.* wie in *Schema 3* gezeigt, die ersten Phosphenium-Ionen in Nitrobenzol zu synthetisieren.



Schema 3: Darstellung von 5,5,*N,N'*-Tertramethyl-1,3-diazacyclohexyl-2-phosphenium-hexachlorophosphat.

Jedoch erst die Entdeckung der donorstabilisierten Carbene von Arduengo *et al.*^[9] im Jahre 1991 und deren Einsatz als Liganden in Olefinmetatase-Katalysatoren von Grubbs *et al.*^[10] verhalf den niedervalenten Phosphor(III)-Verbindungen zu einem erhöhten Interesse. Seither wurde eine Vielzahl von *N*-heterocyclischen Phosphenium-Kationen mit einer großen Bandbreite stickstoffgebundener Substituenten synthetisiert.^[11] Zwar werden diese an die Carbene angelehnten Kationen formal durch eine zusätzliche 6π -Elektronen-Aromatizität stabilisiert, jedoch liegt dieser Energiegewinn nur im Bereich einiger kJ/mol und scheint nicht essentiell zur Stabilität beizutragen.^[12] Deshalb ist es verwunderlich, dass bisher nur wenige Beispiele acyclischer sekundärer Aminophosphenium-Kationen [(RNH)₂P]⁺ bekannt sind. Die bislang einzigen Systeme konnten mithilfe von kinetischer Stabilisierung durch den Einsatz des sterisch anspruchsvollen Mes*-Substituenten von E. Niece *et al.* [(Mes**NH*)₂P][AlCl₄]^[13], N. Burford *et al.* [(Mes**NH*)₂P][GaCl₄]^[14] und V. Romanenko *et al.* [(Mes**NH*)₂P][OTf]^[15] nachgewiesen werden. Die isomorphen Kristallstrukturen von [(Mes**NH*)₂P][AlCl₄] und [(Mes**NH*)₂P][GaCl₄] (*Abbildung 3*) sowie die ¹H-NMR-Daten von [(Mes**NH*)₂P][OTf] und [(Mes**NH*)₂P][GaCl₄] deuten auf eine starke Koordination durch das Anion in Form von NH...X-Wasserstoffbrückenbindungen hin. Die Synthese, Isolation und Charakterisierung von „nackten“ [(RNH)₂P]⁺-Kationen ist bislang nicht bekannt und deshalb Gegenstand dieser Arbeit.

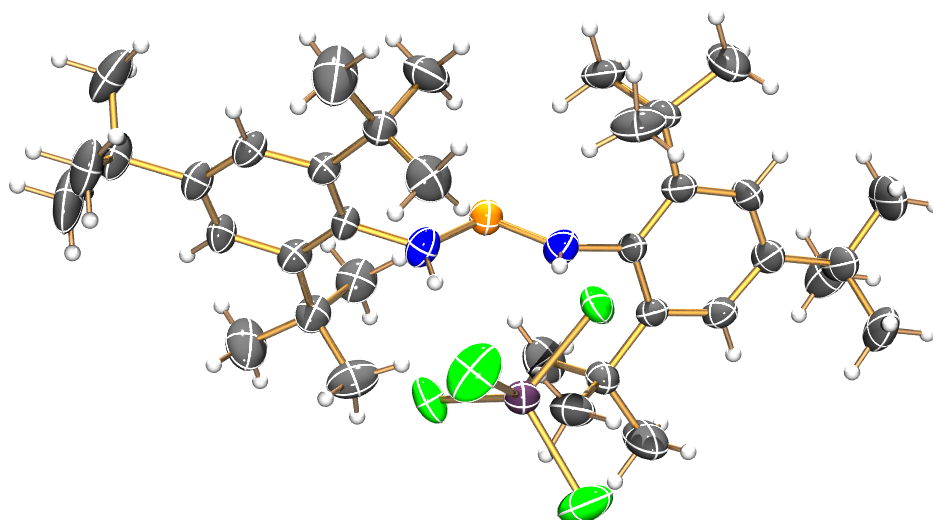


Abbildung 3: ORTEP-Darstellung der Molekülstruktur von $[(\text{Mes}^*\text{NH})_2\text{P}][\text{GaCl}_4]$ im Kristall. Verschiebungsellipsoide sind bei 60% Wahrscheinlichkeit gezeichnet. Wasserstoffbrücke mit 3,430Å (Farbcode: P orange, N blau, C grau, Cl grün, Ga Lila).

3.3 Schwachkoordinierende Anionen

Bei der Synthese von „nackten“, reaktiven kationischen Systemen stellt sich neben der Frage der kinetischen Stabilisierung durch sterisch anspruchsvolle Substituenten, auch die Frage nach der Wahl eines geeigneten, möglichst schwachkoordinierenden Anions (WCA = engl. weakly coordinating anion). Als allgemeines Konzept für WCA's gilt, dass ein möglichst einfach negativ geladenes Molekül mit chemisch inerten nicht nukleophilen funktionellen Gruppen seine Ladung auf eine möglichst große Oberfläche delokalisiert. Des Weiteren lässt sich feststellen, dass ein Anion vorrangig mit seiner basischsten Gruppe an das Kation koordiniert und diese demzufolge die Achillesferse für die Stabilität eines WCA's darstellt. In einem idealen „*nichtkoordinierenden Anion*“ müsste folglich das Wechselspiel von sterischen und elektronischen Effekten die Basizität auf ein Minimum reduzieren.^[16]

Die ersten Vertreter der nicht klassischen Anionen sind die korrespondierenden Basen der starken Brønsted-Säuren Trifluormethansulfonsäure $[\text{O}_3\text{SCF}_3]^-$ und Trifluoressigsäure $[\text{O}_2\text{CCF}_3]^-$ sowie die Anionen starker Lewis-Säuren wie z.B. $[\text{AlX}_4]^-$ oder $[\text{MF}_6]^-$ (X = Cl – I; M = P, As, Sb). Diese Anionen sind jedoch aufgrund ihres geringen sterischen Anspruchs und ihren basischen funktionellen Gruppen in vielen Fällen zur Koordination sowie der Ausbildung von Wasserstoffbrückenbindungen befähigt (*Abbildung 3*).

Die erste Gruppe von Anionen bei denen das Konzept der WCA's konsequent angewandt wurde, sind die Borate, bei denen vom $[\text{BF}_4]^-$ -Ion ausgehend die Fluoratome durch inerte fluoriierte Phenylgruppen substituiert wurden. Daraus entstand die Klasse der Tetraarylborat $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^[17] und $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ -Ionen ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$)^[18], die bereits in der homogenen Katalyse ihre Anwendung gefunden haben. Eine Reihe weiterer Substitutionen durch fluoriierte Alkylgruppen sowohl am Bor-Zentrum als auch an den Phenylsubstituenten der Anionen führten zu einer Vielzahl von Borat-Anionen. Diese haben jedoch aufgrund von meist komplexen, vielstufigen Synthesen weniger Verbreitung gefunden.

Als zweite Gruppe von schwachkoordinierenden Anionen sind die auf Borpolyedern basierenden *closo*-Carborate $[\text{CHB}_{11}\text{H}_{11}]^-$ ^[19] und $[\text{CHB}_9\text{H}_9]^-$ zu nennen. Diese gegen Luft und Wasser stabilen WCA's konnten von Reed *et al.*^[20] und Stibr *et al.*^[21] durch Substitution der Wasserstoffatome gegen kurze Alkylreste und/oder Halogenatome in neuartige gut kristallisierende Anionen überführt werden. Mit diesen auch gegen starke Oxidationsmittel stabilen Anionen, konnten die stärksten bekannten Brønsted-Säuren^[22], freie Silylium-Ionen^[23] und Fulleren-Kationen^[24] synthetisiert werden. Aufgrund ihrer aufwendigen Synthese zählen sie zu den teuersten Anionen, die ihren Einsatz überwiegend in der Grundlagenforschung finden.

Die dritte Gruppe sind die Perfluoralkoxy- $[\text{M}(\text{OR}^{\text{F}})_n]^-$ und Perfluoraryloxymetallate $[\text{M}(\text{OAr}^{\text{F}})_n]^-$ ($\text{R}^{\text{F}} =$ fluorierter Alkylrest, $\text{Ar}^{\text{F}} =$ fluorierter Arylrest) bei denen stark Lewis-saure und oxophile Metallatome wie B^{III} , Al^{III} , Nb^{V} , Ta^{V} und La^{III} als Zentralatome der sogenannten at-Komplexe zum Einsatz kommen. Die teil- und perfluorierten Alkoxy-metallate z.B. $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ besitzen vergleichbare koordinierende Eigenschaften wie die Carborane. In neuester Zeit konnte jedoch gezeigt werden, dass sich dieses Anion in Gegenwart der sehr starken Lewis-Säure $[\text{Mes}^*\text{-N}\equiv\text{P}]^+$ zur schwächeren freien Lewis-Säure $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_3]_2$ zersetzt (*Schema 4*).^[25]



Schema 4: Zersetzung des Alkoxyaluminat-Anions zur freien Lewis-Säure.

Des Weiteren konnte gezeigt werden, dass einige Vertreter der Aryloxymetallate zur Abspaltung von Alkoholatgruppen sowie zur Koordination durch ihre Sauerstoffatome neigen.^[26]

Als Gegenstand dieser Arbeit wurden im Rahmen der Synthese von „nackten“ N,N' -Bis(terphenylamino)phosphenium-Kationen $[(\text{TerNH})_2\text{P}]^+$ ausgewählte Vertreter der WCA's auf ihre koordinierenden Eigenschaften hin untersucht.

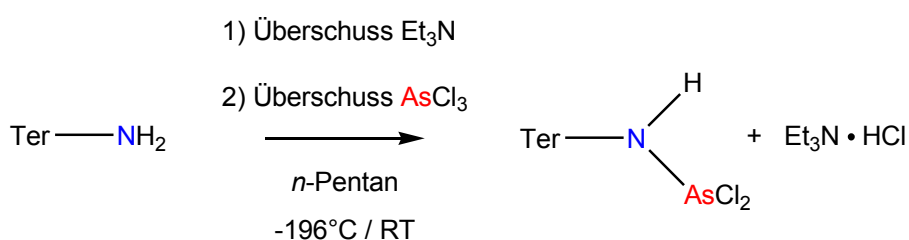
4. Ergebnisse und Diskussion

4.1 Synthese von sterisch abgeschirmten 1,3-Dichlor-2,4-bis-*m*-terphenyl-*cyclo*-1,3-dipnikta-2,4-diazanen [*m*-TerNPnCl]₂, (Pn = P, As)

Fabian Reiß, Alexander Villinger, Axel Schulz, Nico Weding

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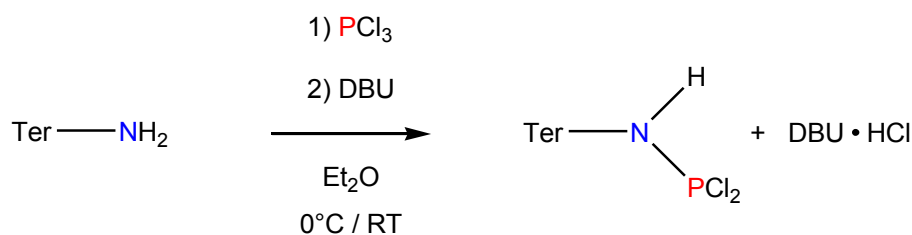
In dieser Arbeit wurden basenassistierte Reaktionen ausgehend von Terphenylamin Ter-NH₂ und Pniktogen(III)chloriden (ECl₃; E = As, P) über Amino(dichlor)pniktogen-Verbindungen R-N(H)-ECl₂ zu 1,3-Dichlor-*cyclo*-1,3-dipniktogen(III)-2,4-diazanen [R-N-E-Cl]₂ in Abhängigkeit von den Reaktionsbedingungen Temperatur, Lösungsmittel und Base untersucht. Nach literaturbekannten Vorschriften für primäre Amine lässt sich eine ECl₂-Gruppe über die Reaktion von Ter-NH₂ mit einem Überschuss an Triethylamin und ECl₃ erhalten.^[27] Während diese Bedingungen mit Arsenrichlorid in guten Ausbeuten (67 %) zu Terphenylamino(dichlor)arsan führten, konnte bei dem Einsatz von Phosphortrichlorid lediglich ein Produktgemisch von Ter-N(H)-PCl₂, Ter-N(PCl₂)₂, (*cis* und *trans*) [Ter-N-P-Cl]₂ sowie [(TerNH)₂P]Cl mittels ³¹P-NMR-Spektroskopie beobachtet werden.



Schema 5: Synthese von Terphenylamino(dichlor)arsan.

Die Reaktion von Terphenylamin mit einem großen Überschuss an Triethylamin und PCl₃ bei niedrigen Temperaturen in *n*-Pentan hingegen führt zu dem doppelt substituierten Terphenylamino-bis-(dichlor)phosphan Ter-N(PCl₂)₂ mit einer Ausbeute von 67 %. Da die Verwendung von Et₃N als Base nicht zum gewünschten Terphenylamino(dichlor)phosphan führte, wurden weitere Untersuchungen mit *n*-Butyllithium (*n*-BuLi) und 1,8-Diazabicyclo[5.4.0]undec-7-en (DBU) als Basen angestellt. Die in Diethylether bei 0°C durchgeführten Synthesen ergaben in sehr guten Ausbeuten (> 90 %) das gesuchte Ter-

N(H)-PCl_2 und führten in analogen Reaktionen mit AsCl_3 ebenfalls in guten Ausbeuten (> 70 %) zum Terphenylamino(dichlor)arsan.



Schema 6: Synthese von Terphenylamino(dichlor)phosphan.

Alle Verbindungen konnten als farblose kristalline Substanz aus *n*-Pentan und *n*-Hexan umkristallisiert werden. Während Terphenylamino-bis-(dichlor)phosphan $\text{Ter-N(PCl}_2)_2$ bei 199 °C schmilzt und durch Sublimation bei 180 °C (10^{-3} mbar) gereinigt werden kann, besitzen die Amino(dichlor)pniktogene Ter-N(H)-ECl_2 mit 153 °C (E = As) und 159 °C (E = P) niedrigere Schmelzpunkte. Die Singulett Signale im $^{31}\text{P-NMR}$ der Phosphane liegen mit 182,3 ppm für $\text{Ter-N(PCl}_2)_2$ und 159,4 ppm für Ter-N(H)-PCl_2 im Bereich von analogen, dreifachkoordinierten Phosphorverbindungen (166.6 ppm für $(\text{Me}_3\text{Si})_2\text{N-N}(\text{SiMe}_3)\text{-PCl}_2$, 155 ppm für Dipp-N(H)-PCl_2 , 165 ppm für $\text{Dipp-N(PCl}_2)_2$).^[28]

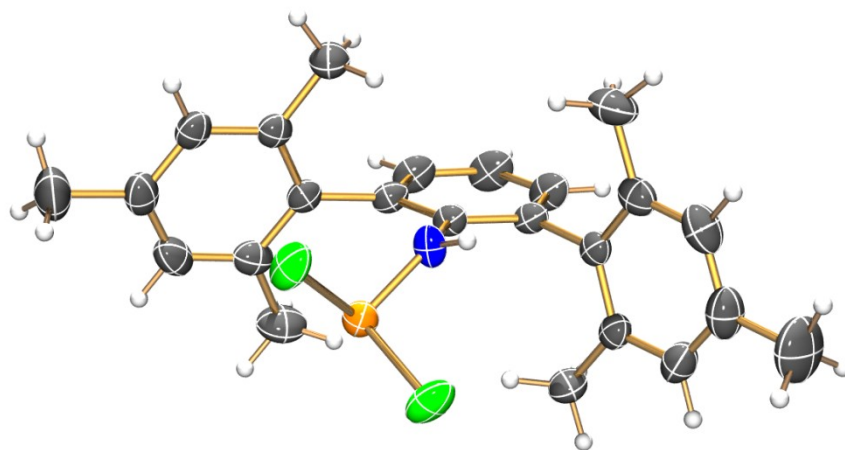
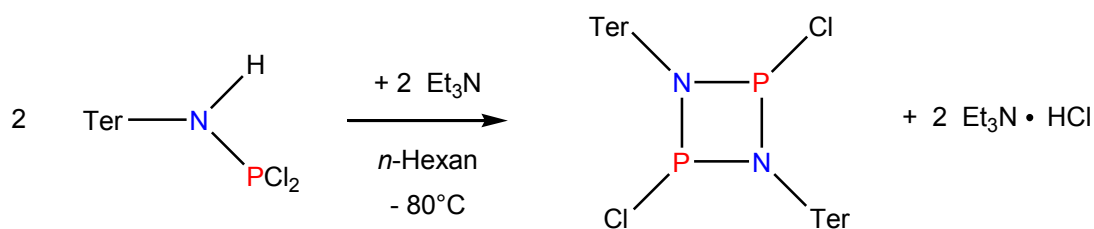


Abbildung 4: ORTEP-Darstellung der Molekülstruktur von Ter-N(H)-PCl_2 im Kristall. Verschiebungsellipsoide sind bei 60 % Wahrscheinlichkeit gezeichnet. (Farbcode: P orange, N blau, C grau, Cl grün).

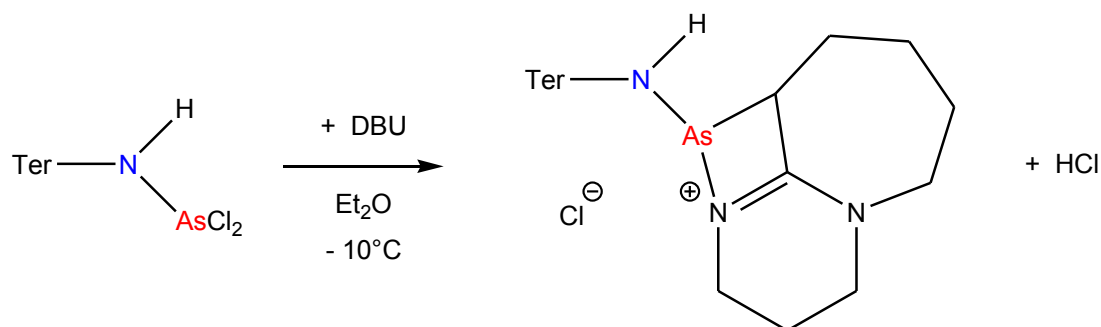
Interessanterweise führt die höhere Reaktivität der Phosphor-Spezies bei der Folgereaktion von Ter-N(H)-PCl_2 mit Et_3N in *n*-Hexan geradewegs zu 1,3-Dichlor-2,4-bis-terphenyl-*cyclo*-1,3-diphospha-2,4-diazen $[\text{Ter-N-P-Cl}]_2$ mit einer Ausbeute von 83 %,

wohingegen mit dem analogen Amino(dichlor)arsan unter diesen Bedingungen keine Reaktion zu beobachten ist.



Schema 7: Synthese von 1,3-Dichlor-2,4-terphenyl-*cyclo*-1,3-diphospha-2,4-diazen.

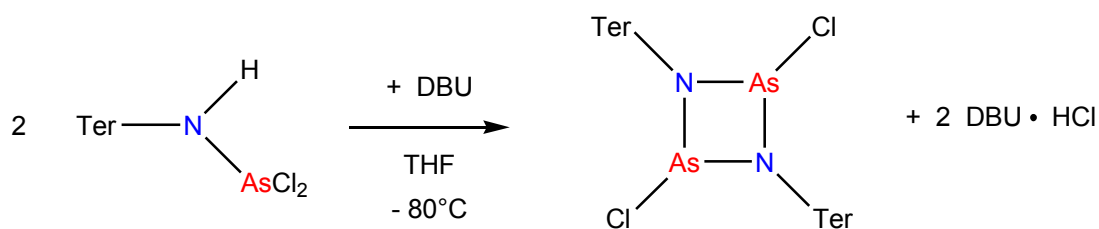
Da die Reaktion von Ter-N(H)-AsCl₂ mit frischem Lithiumdiisopropylamid (LDA) in Diethylether bei -50 °C zu dem unerwarteten Terphenylamino-diisopropylamino(chlor)arsan geführt hat (Ausbeute 83 %), wurde klar, dass eine starke, aber nicht nukleophile Base zur HCl-Eliminierung benötigt wird, da sonst der nukleophile Angriff am Arsen-Zentrum bevorzugt ist. Ein ähnliches Problem trat bei der Umsetzung von Terphenylamino(dichlor)arsan mit DBU in Diethylether bei -10 °C auf. Hierbei konnte anhand von Kristallen aus dem entstandenen komplexen Produktgemisch mithilfe der Röntgendiffraktometrie 2-Terphenylamino-2-arsa-3,7-diaza-tricyclo[5.4.1.0^{3,12}]dodec-3(12)-enylumchlorid als ein Syntheseprodukt identifiziert werden; jedoch war eine präparative Isolation dieser Verbindung nicht möglich.



Schema 8: Identifiziertes Nebenprodukt 2-Terphenylamino-2-arsa-3,7-diaza-tricyclo[5.4.1.0^{3,12}]dodec-3(12)-enylum chlorid.

Ein denkbarer Reaktionsmechanismus für die Bildung dieser Verbindung ist zunächst ein nukleophiler Chlorid-Austausch durch ein Stickstoffatom der Base, gefolgt von einer Chlorwasserstoff-Abspaltung und einer As-C-Verknüpfung. Eine vergleichbare Insertion einer PN-Einheit in eine CH-Bindung wurde bereits von Niecke *et al.* beschrieben.^[29] Aus einer weiteren Reaktion von Ter-N(H)-AsCl₂ mit DBU in THF bei einer niedrigeren

Temperatur (-80 °C) konnte das gewünschte 1,3-Dichlor-2,4-terphenyl-*cyclo*-1,3-diarsa-2,4-diazan [Ter-N-As-Cl]₂ mit einer Ausbeute von 52 % isoliert werden.



Schema 9: Synthese von 1,3-Dichlor-2,4-terphenyl-*cyclo*-1,3-diarsa-2,4-diazan.

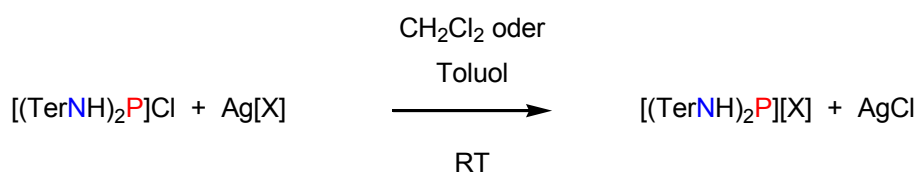
Die beiden *cyclo*-1,3-Dipnicta-2,4-diazane [R-N-E-Cl]₂ wurden als farblose (E = P) bzw. gelbe (E = As) kristalline Substanz mit überraschend hohen Schmelzpunkten von 285 °C (E = P) und 259 °C (E = As) isoliert. Interessanterweise liegt die Phosphor-Spezies in Lösung in einem *cis/trans*-Isomerengemisch vor (³¹P-NMR: 227,4 ppm für das *cis*, 264,1 ppm für das *trans*-Isomer), wohingegen die Arsen-Spezies sowohl in Lösung als auch im Festkörper nur als *trans*-Isomer auftritt. Wie von Stahl hervorgehoben wurde sind die meisten *cyclo*-Diphosph(III)azane in ihrer *cis*-Form thermodynamisch stabiler und ihre *trans*-Isomere sind die kinetisch bevorzugten Produkte.^[30] Erstaunlicherweise konnte bei den vorliegenden *cyclo*-1,3-Dipnicta-2,4-diazanen trotz ihrer sterisch anspruchsvollen Substituenten keine monomere Spezies beobachtet werden.

4.1 Das *N,N'*-Bis(terphenylamino)phosphenium-Kation – Ein empfindlicher Sensor für Wechselwirkungen mit verschiedenen Anionen

Fabian Reiß, Axel Schulz, Alexander Villinger

Manuskript eingereicht bei *Dalton Trans.*

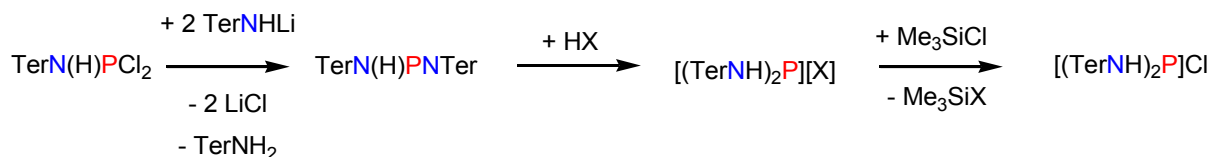
In dieser Arbeit wurden die Anion-Kation-Wechselwirkungen zwischen dem als Sonde gewählten *N,N'*-Bis(terphenylamino)phosphenium-Kation $[(\text{Ter-NH})_2\text{P}]^+$ und einer Auswahl von Anionen F^- , Cl^- , $[\text{CF}_3\text{CO}_2]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{GaCl}_4]^-$, $[\text{SbF}_6]^-$, $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ sowie dem Carborat $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ anhand von spektroskopischen und strukturellen Daten untersucht. Das $[(\text{TerNH})_2\text{P}]^+$ -Kation wurde als Messfühler ausgewählt, da es durch die beidseitige Terphenylsubstituierung eine besondere sterische Stabilisierung erfährt, aber dennoch über eine breite Palette von Bindungsmodi zum Anion, wie z.B. Wasserstoffbrückenbindungen, Ionenpaar-, und van-der-Waals-Wechselwirkungen, verfügt. Als geeignete Precursor-Verbindung wurde *N,N'*-Bis(terphenylamino)chlorphosphan $[(\text{TerNH})_2\text{P}]\text{Cl}$ gewählt, um über eine klassische Salzeliminierungsreaktion mit $\text{Ag}[\text{X}]$ -Salzen (X = schwachkoordinierendes Anion) einen einfachen Zugang zu den gewünschten Verbindungen zu erhalten (*Schema 10*).^[31] Die Synthese über Silber-Salze wurde mit den Anionen $[\text{CF}_3\text{CO}_2]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$, $[\text{SbF}_6]^-$ sowie dem Carborat $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ untersucht und führte mit der Ausnahme von $[\text{SbF}_6]^-$ zu den gewünschten Phosphenium-Salzen in guten Ausbeuten (20-70 %).



Schema 10: Synthese von $[(\text{TerNH})_2\text{P}][\text{X}]$ -Salzen über eine Salzeliminierungsreaktion (X = schwachkoordinierendes Anion).

Jedoch stellte sich die direkte Synthese von $[(\text{TerNH})_2\text{P}]\text{Cl}$ über gängige basenassistierte Reaktion von Phosphortrichlorid mit Terphenylamin als problematisch dar, da sie, wie in der vorangegangenen Arbeit erwähnt, zu einer Vielzahl von Nebenprodukten

wie Ter–N(H)–PCl₂, Ter–N(PCl₂)₂, (*cis* und *trans*) [Ter–N–P–Cl]₂ sowie TerN(H)P=NTer führt. Aus diesem Grund wurde eine mehrstufige Synthesestrategie ausgehend von Terphenylamin und Phosphortrichlorid über *N,N'*-Bis(terphenylaminoimino)phosphan TerN(H)P=NTer entwickelt, die gleichzeitig einen weiteren Zugang zu *N,N'*-Bis(terphenylamino)phosphenium-Salzen über Protonierungsreaktionen ermöglicht (*Schema 11*).



Schema 11: Synthese von [TerNH)₂P][X]-Salzen über Protonierungsreaktionen (X = Cl[−], [CF₃CO₂][−], [CF₃SO₃][−], [B(C₆F₅)₄][−]) sowie Synthese von [(TerNH)₂P]Cl über Silylethereliminierung im Fall von X = [CF₃CO₂][−], [CF₃SO₃][−].

Des Weiteren konnte gezeigt werden, dass die Silylethereliminierungsreaktionen des Trifluoracetat- und Triflat-Salzes mit Trimethylsilylchlorid zu *N,N'*-Bis(terphenylamino)-chlorphosphan führen (*Schema 11*). Als weitere Synthese von [(TerNH)₂P][X]-Salzen wurden Reaktionen von [(TerNH)₂P]Cl mit GaCl₃ und SbCl₅ sowie [(TerNH)₂P]F mit SbF₅ untersucht. Erstaunlicherweise führte lediglich die Umsetzung mit Galliumtrichlorid zum gewünschten Salz, wohingegen die mit Antimon(V)halogenid zu Ter–N(H)–PCl₂ bzw. Ter–N(H)–PF₂ führten.

Die erhaltenen Verbindungen wurden mit Hilfe von ^1H -NMR-, ^{31}P -NMR-, IR- und UV/VIS-Spektroskopie sowie DSC-Messungen untersucht und mit literaturbekannten Angaben für die analogen Mes*-substituierten Verbindungen verglichen (Tabelle 3).

Tabelle 3: Spektroskopische Daten von $[(\text{TerNH})_2\text{P}][\text{X}]$ ($\text{X} = \text{F}^-$, Cl^- , $[\text{CF}_3\text{CO}_2]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{GaCl}_4]^-$, $[\text{SbF}_6]^-$, $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ und $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$) und zum Vergleich $\text{TerN}(\text{H})\text{PNTer}$, $[(\text{Mes}^*\text{NH})_2\text{P}][\text{X}]$ ($\text{X} = [\text{GaCl}_4]^-$, $[\text{CF}_3\text{SO}_3]^-$).

Verbindung	T_{dec} °C	$^{31}\text{P}\{^1\text{H}\}$ ppm	^1H (NH) ^[g] ppm	ν_{NH} cm^{-1}	ν_{PN} cm^{-1}	VIS nm	UV nm
TerN(H)PNTer	311	278.0	6.34	3364 3289	1412	406 336	289 247
$[(\text{TerNH})_2\text{P}]\text{F}$	225	119.7 ^[a]	3.79	3334 3292	1418	- -	292 249
$[(\text{TerNH})_2\text{P}]\text{Cl}$	265 ^[e]	129.9	4.08	3309 3285	1419	- -	297 248
$[(\text{TerNH})_2\text{P}][\text{CF}_3\text{CO}_2]$	190 ^[f]	116.7	4.38	3314 3298	1422	- -	290 250
$[(\text{TerNH})_2\text{P}][\text{CF}_3\text{SO}_3]$	255	261.0	9.67	3341 3234	1426	438 363	292 246
$[(\text{TerNH})_2\text{P}][\text{B}(\text{C}_6\text{F}_5)_4]$	244	249.1	7.31	- 3287	1419	422 358	296 260
$[(\text{TerNH})_2\text{P}][\text{GaCl}_4]$	215	250.0	7.38	3333 3261	1416	438 361	- 255
$[(\text{TerNH})_2\text{P}][\text{SbF}_6]$ ^[d]	-	249.0	7.39	- -	-	- -	- -
$[(\text{TerNH})_2\text{P}][\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]$	273	249.0	7.2	3319 3255	1426	435 360	297 246
$[(\text{TerNH})_2\text{P}][\text{CHB}_{11}\text{H}_5\text{Br}_6]$	225	249.6	7.41	3330 3173	1428	435 358	296 245
$[(\text{Mes}^*\text{NH})_2\text{P}][\text{GaCl}_4]$ ^[b]	152	272.0	9.94	- 3175	1419	- -	- -
$[(\text{Mes}^*\text{NH})_2\text{P}][\text{CF}_3\text{SO}_3]$ ^[c]	-	279.7	11.6	- -	-	- -	- -

[a] Dublett durch ^{31}P - ^{19}F Kopplung; [b] entnommen aus Referenz [14]; [c] entnommen aus Referenz [15]; [d] Nur über X-Ray Messung charakterisiert; [e] Zersetzungspunkt = Schmelzpunkt, [f] Schmelzpunkt = 177°C, [g] Signal der NH Gruppe der Terphenylamino-Funktion, breites Duplett durch ^1H - ^{31}P Kopplung.

Alle Verbindungen sind mit Zersetzungspunkten im Bereich von 190 °C für $[(\text{TerNH})_2\text{P}][\text{CF}_3\text{CO}_2]$ und 273 °C für $[(\text{TerNH})_2\text{P}][\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]$ erstaunlich thermisch stabil. Der Vergleich der Zersetzungstemperaturen beider Tetrachlorogallat-Salze von 215 °C (Ter) vs. 152 °C (Mes*) deutet auf eine bessere kinetische Stabilisierung durch den Terphenylsubstituenten hin.

Anhand der starken Hochfeldverschiebung der ^{31}P -NMR- und ^1H -NMR-Signale ($\delta[^{31}\text{P}]$: 117 – 130 ppm; $\delta[^1\text{H}]$: 3,8 – 4,4 ppm) für die Salze mit den stark nukleophilen Anionen F^- , Cl^- , $[\text{CF}_3\text{CO}_2]^-$ lässt sich erkennen, dass auch in Lösung eine kovalent polare Bindung zum Phosphoratom aufrechterhalten wird. Bei allen weiteren Salzen mit der Ausnahme von $[\text{CF}_3\text{SO}_3]^-$ weisen die nahezu identischen Tieffeldverschiebungen von $\delta[^{31}\text{P}]$: 249 – 250 ppm und $\delta[^1\text{H}]$: 7,20 – 7,41 ppm auf ein vollständig dissoziiertes Salz hin. Einzig das Triflat-Salz weist mit seiner sehr starken Tieffeldverschiebung von $\delta[^{31}\text{P}]$: 261 ppm und $\delta[^1\text{H}]$: 9,67 ppm auf das Ausbilden eines Ionenpaares über eine Wasserstoffbrückenbindung (H-BB) $\text{NH}\cdots\text{O}(\text{O}_2)\text{SCF}_3$ hin. Interessanterweise zeigt auch hier der Vergleich mit den Mes*-analogen Verbindungen einen signifikanten Unterschied. Zwar bildet das $[\text{CF}_3\text{SO}_3]^-$ -

Anion im Vergleich zum $[\text{GaCl}_4]^-$ mit dem Supermesityl substituierten Kation die stärkeren H-BB aus, jedoch zeigt sich, dass der sterische Anspruch des Terphenyl-Substituenten im entsprechenden $[\text{GaCl}_4]$ -Salz groß genug ist, um eine Wasserstoffbrückenbindung zu unterbinden.

Der *Tabelle 3* lässt sich außerdem entnehmen, dass die kovalenten Verbindungen keine VIS-Aktivität aufweisen, wohingegen die Bildung der ionischen Verbindungen mit einer deutlichen orangen Färbung aufgrund von $n_{\text{NPN}} + \pi_{\text{aryl}} \rightarrow \pi^*_{\text{NPN}}$ Anregungen einhergeht.

Für die Untersuchung der Struktur-Eigenschaftsbeziehung wurden Einkristalle aus gesättigten Salzlösungen gezüchtet und mit Hilfe der Einkristall-Röntgendiffraktometrie vermessen. Eine Auswahl an Strukturparametern der verschiedenen Verbindungen ist in *Tabelle 4* dargestellt.

Tabelle 4: Ausgewählte Strukturdaten von $[(\text{TerNH})_2\text{P}][\text{X}]$ ($\text{X} = \text{F}^-, \text{Cl}^-, [\text{CF}_3\text{CO}_2]^-, [\text{CF}_3\text{SO}_3]^-, [\text{B}(\text{C}_6\text{F}_5)_4]^-, [\text{GaCl}_4]^-, [\text{SbF}_6]^-, [\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ und $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$) sowie zum Vergleich $[(\text{Mes}^*\text{NH})_2\text{P}][\text{ECl}_4]$ ($\text{E} = \text{Ga}, \text{Al}$).

Verbindung	N1–P / Å	N2–P / Å	N1–C1 / Å	< N–P–N / °	< τ_{aryl} / ° ^[c]
$[(\text{TerNH})_2\text{P}]\text{F}$	1.704(6)	1.663(1)	1.38(2)	91.6(4)	54.3
$[(\text{TerNH})_2\text{P}]\text{Cl}$	1.697(2)	1.591(2)	1.412(2)	94.6(1)	56.3
$[(\text{TerNH})_2\text{P}][\text{CF}_3\text{CO}_2]$	1.675(2)	1.687(2)	1.423(3)	94.84(9)	65.4
$[(\text{TerNH})_2\text{P}][\text{CF}_3\text{SO}_3]$	1.623(3)	1.609(3)	1.443(4)	104.9(1)	89.3
$[(\text{TerNH})_2\text{P}][\text{B}(\text{C}_6\text{F}_5)_4]$	1.630(3)	1.623(3)	1.440(4)	99.6(2)	87.4
$[(\text{TerNH})_2\text{P}][\text{GaCl}_4]$	1.635(1)	1.626(1)	1.428(2)	99.6(6)	74.5
$[(\text{TerNH})_2\text{P}][\text{SbF}_6]$	1.635(2)	1.635(2)	1.426(3)	98.0(2)	79.3
$[(\text{TerNH})_2\text{P}][\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^{\text{[a]}}$	1.628(3)	1.635(3)	1.431(4)	98.5(2)	89.9
	1.619(3)	1.637(3)	1.435(4)	96.9(2)	89.9
$[(\text{TerNH})_2\text{P}][\text{CHB}_{11}\text{H}_5\text{Br}_6]$	1.625(3)	1.630(3)	1.426(4)	96.3(1)	69.4
$[(\text{Mes}^*\text{NH})_2\text{P}][\text{GaCl}_4]$	1.601(3)	1.601(3)	1.469(4)	105.2(2)	37.0
$[(\text{Mes}^*\text{NH})_2\text{P}][\text{AlCl}_4]^{\text{[b]}}$	1.611	1.611	1.474	103.7	-

[a] zwei unabhängige Moleküle; [b] keine Standardabweichung angegeben, siehe Referenz [13]. [c] τ_{aryl} = Torsionswinkel zwischen den zwei Ebenen, die von den zentralen Phenylringen des Terphenyl bzw. des Supermesityl Substituenten aufgespannt werden.

Bei allen $[(\text{TerNH})_2\text{P}][\text{X}]$ -Verbindungen liegt der zwischen den zwei Ebenen der zentralen Phenylringe aufgespannte Torsionswinkel im Bereich von $\tau_{\text{aryl}} = 54 - 90^\circ$. Dies führt zu einer „Tasche“, die von den vier 2,4,6-Trimethylphenylsubstituenten in 2 und 6 Position der zentralen Phenylringe gebildet wird. In dieser „Tasche“ befindet sich die N(H)PN(H)-Einheit, welche so gegen weitere Reaktionen wie z.B. Dimerisierung geschützt wird. In allen kovalent gebundenen Verbindungen $[(\text{TerNH})_2\text{P}][\text{X}]$ ($\text{X} = \text{F}^-, \text{Cl}^-, [\text{CF}_3\text{CO}_2]^-$) befindet sich das Phosphoratom in einer trigonal pyramidalen Umgebung, wohingegen in allen ionischen Verbindungen sowohl die Stickstoffatome als auch der Phosphor annähernd

trigonal planar koordiniert vorliegen. Dies verdeutlichen die bei den kovalenten Verbindungen kleineren NPN-Bindungswinkel ($91 - 95^\circ$) im Vergleich zu den ionischen $[(\text{TerNH})_2\text{P}][\text{X}]$ -Substanzen ($96 - 105^\circ$). Der Vergleich der N–P-Bindungslängen mit den Summen der Kovalenzradien zeigt mit einem Bereich von $1,704(6) \text{ \AA}$ für $[(\text{TerNH})_2\text{P}]\text{F}$ bis $1,609(3) \text{ \AA}$, für $[(\text{TerNH})_2\text{P}][\text{CF}_3\text{SO}_3]$ vs. $\Sigma r_{\text{cov}}(\text{P}-\text{N}) = 1.82$ und $\Sigma r_{\text{cov}}(\text{P}=\text{N}) = 1.62 \text{ \AA}^{[32]}$, dass sowohl in den kovalenten als auch in den ionischen Verbindungen ein ausgeprägter partieller Doppelbindungscharakter vorliegt.

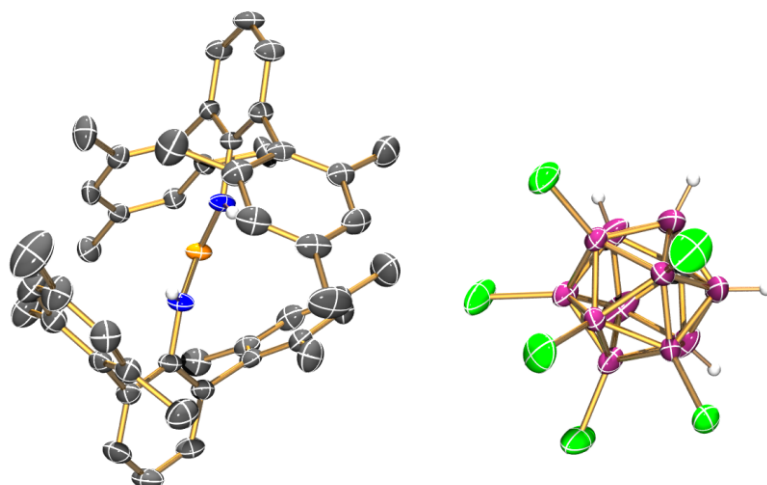


Abbildung 5: ORTEP-Darstellung der Molekülstruktur von $[(\text{TerNH})_2\text{P}][\text{CHB}_{11}\text{H}_5\text{Br}_6]$ im Kristall. Verschiebungsellipsoide sind bei 60 % Wahrscheinlichkeit gezeichnet (Farbcode: P orange, N blau, C grau, Br grün, B Magenta).

Wie in *Abbildung 6* verdeutlicht, zeigt eine Untersuchung der geringsten P–Y-Abstände ($\text{Y} = \text{Donoratom des Anions}$), dass das $[(\text{TerNH})_2\text{P}]^+$ -Kation drei verschiedene Arten von Wechselwirkungen mit seinem Anion eingeht: (i) die polare kovalente Bindung zum Phosphor wird bei kleinen nukleophilen Anionen wie F^- , Cl^- , $[\text{CF}_3\text{CO}_2]^-$ ausgebildet. (ii) Wasserstoffbrückenbindungen können von mittelgroßen Anionen wie dem $[\text{CF}_3\text{SO}_3]^-$ sowie von großen Anionen wie $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ und $[\text{GaCl}_4]^-$, die in der Lage sind teilweise in die Terphenyltasche einzutreten, ausgebildet werden. (iii) Schwache van-der-Waals-Wechselwirkungen zu randständigen H–C_{aryl}-Bindungen werden von Anionen wie $[\text{SbF}_6]^-$, $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ und $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ ausgebildet, die schlichtweg zu groß sind, um Zugang zur zentralen N(H)PN(H)-Einheit zu erhalten.

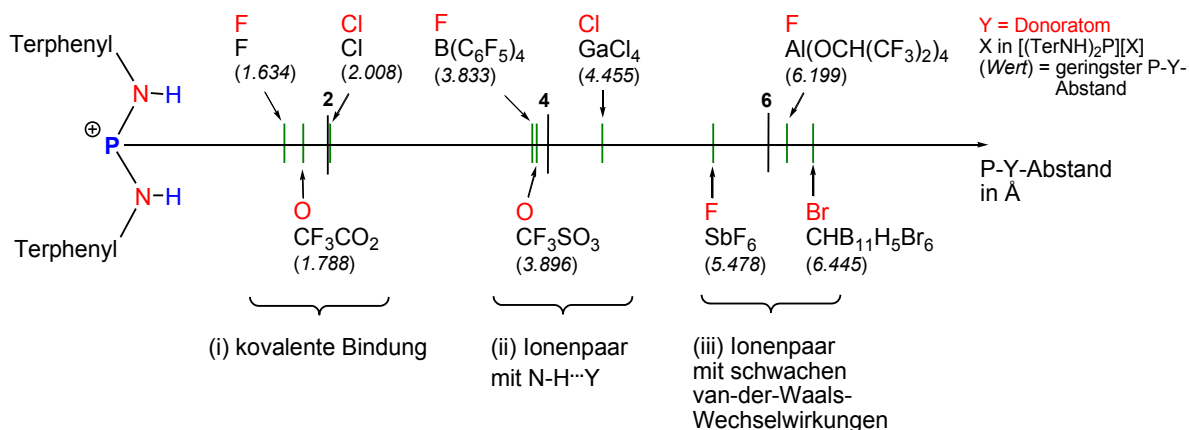


Abbildung 6: Wechselwirkungsmodi zwischen $[(\text{TerNH})_2\text{P}]^+$ und den verschiedenen Anionen.

Interessanterweise stellt sich der NPN-Bindungswinkel als sensitiv für die Stärke der Wasserstoffbrückenbindung heraus, und bietet so eine Möglichkeit, die Interaktion des Kations mit den verschiedenen Anionen zu untersuchen. So ist bei dem nahezu „nackten“ $[(\text{TerNH})_2\text{P}][\text{CHB}_{11}\text{H}_5\text{Br}_6]$ -Salz (*Abbildung 5*) der Winkel mit $96,3(1)^\circ$ am kleinsten und im $[(\text{TerNH})_2\text{P}][\text{CF}_3\text{SO}_3]$ mit der stärksten H-BB mit $104,9(1)^\circ$ am größten. Auch hier zeigt der Vergleich der beiden Tetrachlorogallat-Salze mit $99,61(6)^\circ$ (Ter) vs. $105,2(2)^\circ$ (Mes*), dass in der Mes*-substituierten Verbindung eine stärkere Wasserstoffbrückenbindung ausgebildet wird. Wie in *Abbildung 7* veranschaulicht, wird in der $[(\text{Mes}^*\text{NH})_2\text{P}][\text{GaCl}_4]$ -Verbindung durch zwei Chloratome des Anions eine H-Brücke aufgebaut, wohingegen im analogen $[(\text{TerNH})_2\text{P}][\text{GaCl}_4]$ -Salz lediglich ein Chloratom in eine Wasserstoffbrücke involviert ist. Dies zeigt deutlich, dass die vom Terphenyl aufgespannte „Tasche“ einen größeren Schutz der β -Atome bietet, während der Mes*-Substituent einen grösseren Tolman-Winkel und somit den größeren sterischen Einfluss am α -Atom aufweist (Tolman-Winkel für Mes* 228° vs. Ter 206°).^[33]

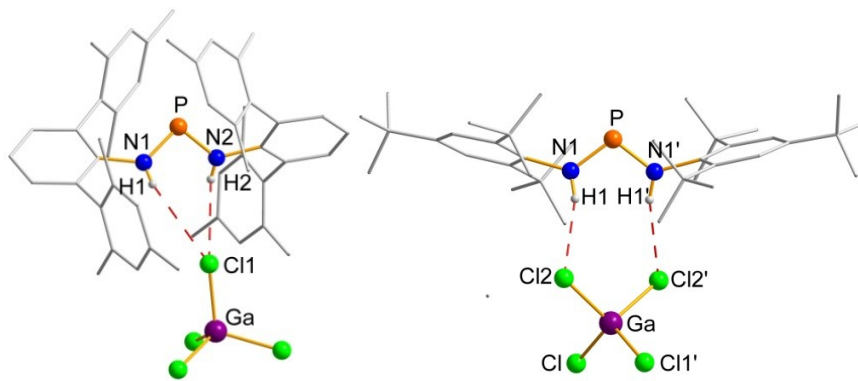


Abbildung 7: Darstellung der Wasserstoffbrückenbindungen in $[(\text{TerNH})_2\text{P}][\text{GaCl}_4]$ und $[(\text{Mes}^*\text{NH})_2\text{P}][\text{GaCl}_4]$.

5. Originalpublikationen

Dieses Kapitel beinhaltet die im Kapitel 4 beschriebenen Originalpublikationen.

5.1 Synthesis of sterically encumbered 2,4-bis-*m*-terphenyl-1,3-dichloro-2,4-cyclo-dipnictadiazanes [*m*-TerNPnCl]₂, (Pn = P, As)

Fabian Reiß, Axel Schulz, Alexander Villinger, Nico Weding

Dalton Trans. **2010**, 39, 9962 – 9972

Der eigene Beitrag liegt bei ca. 20%.

Zu dieser Publikation ist ein „*Electronic Supplementary Information File*“ mit ausführlichen kristallographischen und experimentellen Informationen online verfügbar.

Synthesis of sterically encumbered 2,4-bis-*m*-terphenyl-1,3-dichloro-2,4-*cyclo*-dipnictadiazanes [*m*-TerNPnCl]₂, (Pn = P, As)†

Fabian Reiß,^a Axel Schulz,^{*a,b} Alexander Villinger^{*a} and Nico Weding^{a,b}

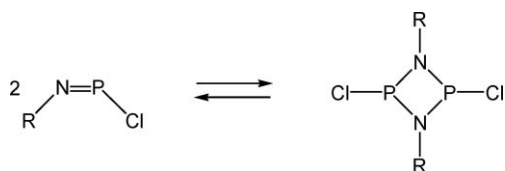
Received 22nd June 2010, Accepted 26th July 2010

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The reaction of *m*-terphenyl amine (2,6-bis-(2,4,6-trimethylphenyl)aniline, *m*-Ter = *m*-terphenyl = 2,6-bis-(2,4,6-trimethylphenyl)) and ECl₃ (E = P, As) in the presence of different bases (Et₃N, *n*-BuLi, LDA, DBU) and under different reaction conditions was studied. The reaction with excess Et₃N yielded *m*-Ter-N(H)-AsCl₂ for E = As, while for E = P *m*-Ter-N(PCl₂)₂ was formed. *m*-Ter-N(H)-ECl₂ was obtained in the reaction of *m*-terphenyl amine with *n*-BuLi and ECl₃ for E = As and P. Further treatment of *m*-Ter-N(H)-PCl₂ with Et₃N led to the formation of 1,3-dichloro-*cyclo*-1,3-diphospha-2,4-diazane, a synthesis protocol which cannot be applied to the analogous arsenic species. 1,3-dichloro-*cyclo*-1,3-diarsa-2,4-diazane was isolated when DBU was added to *m*-Ter-N(H)-AsCl₂ at low temperature (−80 °C).

Introduction

Four-membered pnictogen-nitrogen heterocycles of the type [R-N-E-Cl]₂ (E = group 15 element) are known as 1,3-dichloro-*cyclo*-1,3-dipnicta(III)-2,4-diazanes.¹ As early as 1894 Michaelis and Schroeter discovered the first *cyclo*-1,3-diphospha(III)-2,4-diazane when they treated aniline hydrochloride with an excess of PCl₃ for 48 h under reflux conditions (Scheme 1).² Pnictogen-nitrogen heterocycle chemistry has been developed to an important field in inorganic chemistry. In particular, the phosphorus species play a major role in preparative phosphorus-nitrogen chemistry. They have been utilized for the preparation of macrocycles, polymers, main-group complexes and ring transformation reactions.^{3–5}



Scheme 1 Dimerization of iminophosphanes.

1,3-Dichloro-*cyclo*-1,3-dipnicta(III)-2,4-diazanes can show a monomer-dimer equilibrium between the iminochloropnictane, R-N=E-Cl, and the *cyclo*-1,3-dipnicta(III)-2,4-diazane, [R-N-E-Cl]₂, depending on the organic group R, the solvent and the state of aggregation, which has been addressed in a series of papers.^{6,7} For example, Burford *et al.* proposed that dependent upon steric strain in derivatives of [R-N-P-X]₂ (X = halogen) the dimer can be destabilized with respect to the monomer.⁷ The

sensitivity of this equilibrium is best illustrated by the fact that Mes**N*=P-Cl (Mes* = 2,4,6-tri-*tert*-butylphenyl) is observed as the iminophosphane monomer in the solid state,⁸ while slightly smaller substituents such as 2,6-diisopropylphenyl or *m*-terphenyl allow dimerization.^{5,7}

Furthermore, for all heavier group 15 elements, only the dimers have been experimentally observed, *e.g.* for *t*Bu-N=E-Cl (E = As, Sb),^{9,10} showing that for the heavier elements the dimer is more stable. This trend can be attributed to less stable E=N double bonds and decreasing steric strain within the E₂N₂ ring. Experimentally known is the stable monomeric Mes**N*=P-Cl,⁸ while the heavier arsenic analogue forms a dimer in the solid state.¹¹ The arsenic dimer was first described by Burford *et al.*, and the authors already speculated on the reversible dissociation, which was experimentally proven by temperature dependent ¹H NMR experiments displaying a dimer/monomer ratio of 1 : 1.7.¹² The analogous multiple-bonded compounds of antimony (iminostibanes) and bismuth (iminobismuthanes) have yet to be reported.

Valuable starting materials for the synthesis of 1,3-dichloro-*cyclo*-1,3-dipnicta(III)-2,4-diazanes, [R-N-E-Cl]₂, include substituted amino(dichloro)pnictanes, R-N(H)-ECl₂. Amino(dichloro)pnictanes are known to easily eliminate HCl, which can be triggered by bases such as Et₃N, leading to 1,3-dichloro-*cyclo*-1,3-dipnicta(III)-2,4-diazanes.¹⁴

Here we report on the synthesis of sterically encumbered 2,4-bis-*m*-terphenyl-1,3-dichloro-*cyclo*-2,4-dipnictadiazanes [*m*-Ter-N-E-Cl]₂, (E = P, As; *m*-Ter = *m*-terphenyl = 2,6-bis-(2,4,6-trimethylphenyl)), the diversity of products depending on the reaction conditions (temperature, bases, solvents) and their spectroscopic characterization.

Results and discussion

The synthesis of 2,4-bis-*m*-terphenyl-1,3-dichloro-*cyclo*-2,4-dipnictadiazanes [*m*-Ter-N-E-Cl]₂ (E = P, As) via *m*-terphenyl-amino(dichloro)pnictanes, *m*-Ter-N(H)ECl₂ (E = P, As), has been studied starting from *m*-terphenylamine *m*-Ter-NH₂.^{13–15}

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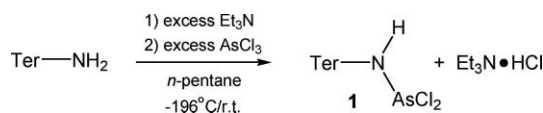
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† Electronic supplementary information (ESI) available: Additional experimental details. CCDC reference numbers 781907–781916. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00700e

m-Ter-NH₂ can be obtained in a four step synthesis starting from mesityl bromide (see supporting information†).¹⁶

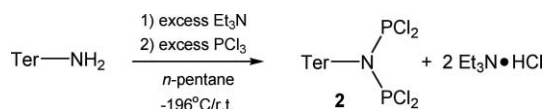
Synthesis and properties of *m*-terphenyl-amino(dichloro)pnictanes, *m*-Ter-N(H)ECl₂ (E = P, As)

According to known literature procedures for primary amines bearing other organic groups, introduction of the ECl₂ moiety can be achieved by reaction of *m*-Ter-NH₂ with an excess of triethylamine and ECl₃.^{1,3,4,7b,8,17} While this procedure nicely works for arsenic (Scheme 2) resulting in the formation of *m*-terphenyl-amino(dichloro)arsane (**1**) in good yields (67%), a complex reaction mixture is obtained when the analogous reaction is carried out with PCl₃. From the reaction mixture *m*-Ter-N(H)PCl₂, *m*-Ter-N(PCl₂)₂, (*cis* and *trans*) [*m*-Ter-N-P-Cl]₂ and [*m*-Ter-N(H)]₂PCl were identified by means of ³¹P NMR spectroscopy. It was not possible to isolate *m*-terphenyl-amino(dichloro)phosphane from this mixture.



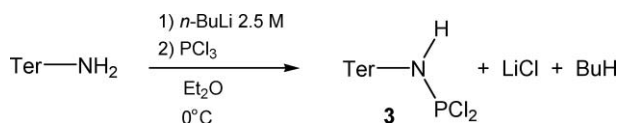
Scheme 2 Synthesis of **1** (procedure 1).

Furthermore, the reaction of *m*-Ter-NH₂ with a large excess of triethylamine and PCl₃ yields *N,N*-bis-dichlorophosphino-*m*-terphenyl-amine, *m*-Ter-N(PCl₂)₂ (**2**), with an isolated yield of 67% (Scheme 3).



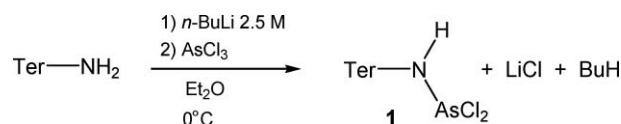
Scheme 3 Synthesis of **2**.

Since the utilization of Et₃N as base in the reaction with *m*-Ter-NH₂ and PCl₃ did not lead to the desired *m*-terphenyl-amino(dichloro)phosphane (**3**), *m*-Ter-N(H)PCl₂, *n*-BuLi was used to form the lithiated *m*-terphenylamine, *m*-Ter-N(H)Li, in diethyl ether at 0 °C, which gave in a smooth reaction with PCl₃ in high yields (93%) compound **3** (Scheme 4). For the analogous reaction with AsCl₃ (Scheme 5), species **1** was isolated with a yield of 77%, which is slightly less compared to the phosphorus analogue but *ca.* 10% better than in the reaction with Et₃N. The same holds for 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) as base, which also gives **3**, when only one equivalent is used (see below).



Scheme 4 Synthesis of **3**.

Compounds **1**, **2** and **3** can easily be re-crystallized from *n*-pentane or *n*-hexane. While **2** melts at 199 °C, amino(dichloro)pnictanes **1** and **3** melt at 153 and 159 °C, respectively. Compound **2** sublimes at 180 °C (10⁻³ mbar), which can be used for purification. The δ³¹P values of **2** and **3** (a singlet resonance at 182.3 and 159.4 ppm, respectively) are in the range

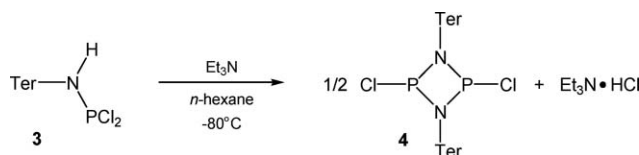


Scheme 5 Synthesis of **1** (Procedure 2, see Scheme 2).

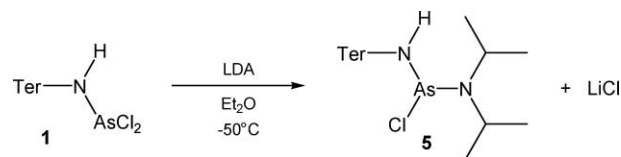
expected on the basis of numerous data from the literature for aminophosphanes (*cf.* 166.6 ppm for (Me₃Si)₂N-N(SiMe₃)-PCl₂, 155 ppm for Dipp-N(H)PCl₂, 165 ppm for Dipp-N(PCl₂)₂, Dipp = 2,6-diisopropylphenyl).¹⁷⁻²⁰ In the respective ¹H NMR spectra, the proton attached to the nitrogen is found at 5.43 (**1**) and 5.22 (**3**) ppm, respectively (*cf.* 5.48 ppm in Mes^{*}N(H)AsCl₂, 5.32 ppm in Mes^{*}N(H)PCl₂).^{11,21}

Synthesis and properties of 1,3-dichloro-*m*-terphenyl-cyclo-1,3-dipnicta-2,4-diazane, [*m*-Ter-N-E-Cl]₂ (E = P, As)

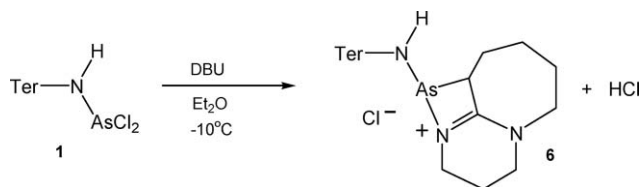
Interestingly, when Et₃N is added to a solution of **3** in *n*-hexane, the 1,3-dichloro-*m*-terphenyl-cyclo-1,3-diphospha-2,4-diazane (**4**) is formed in good yields (83%) (Scheme 6), while in case of the arsenic analogue (**1**) no reaction occurred. To obtain the 1,3-dichloro-*m*-terphenyl-cyclo-1,3-diarsa-2,4-diazane different type of bases such as diisopropylamide (LDA) and DBU were utilized in different solvents (Schemes 7, 8, and 9).



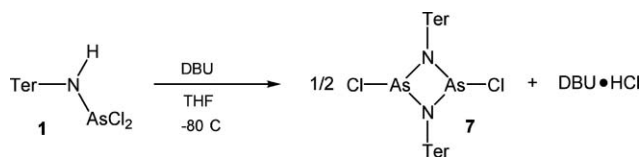
Scheme 6 Synthesis of **4**.



Scheme 7 Synthesis of **5**.



Scheme 8 Synthesis of **6**.



Scheme 9 Synthesis of **7**.

Firstly, to a solution of **1** in diethyl ether, a solution of LDA (Scheme 7), freshly prepared from diisopropylamine and *n*-BuLi

in diethyl ether, was added dropwise at $-50\text{ }^{\circ}\text{C}$ resulting in a yellow suspension. Removal of the solvent and drying *in vacuo* resulted in a colorless residue, which was extracted with *n*-hexane. Concentration *in vacuo* and storage at $-25\text{ }^{\circ}\text{C}$ resulted in the deposition of colorless crystals of *m*-terphenyl-amino-diisopropylamino(chloro)arsane (**5**) in good yields (83%). The unexpected formation of **5** clearly demonstrates that a strong but non-nucleophilic base is needed to achieve the elimination of HCl, otherwise only a nucleophilic substitution at the arsenic center is preferred.

A similar problem was encountered when DBU was used as strong but less nucleophilic base in diethyl ether. Here the addition of a solution of **1** in diethyl ether to a solution of DBU in diethyl ether at $-10\text{ }^{\circ}\text{C}$ lead to a complex reaction mixture from which 2-*m*-terphenyl-amino-2-arsa-3,7-diazatricyclo[5.4.1.0^{3,12}]dodeca-3(12)-enylum chloride (**6**) could be identified by single crystal X-ray diffraction (Scheme 8). A preparative separation was not successful. The formation of **6** can be explained by a nucleophilic substitution at the arsenic atom (Cl⁻ exchange by N atom of DBU) followed by a HCl elimination and As-C linkage. A similar reaction involving the insertion of a PN fragment into a CH bond has been reported by Niecke *et al.* when they treated bromobis(arylimino)phosphorane with silver triflate in the presence of DBU.²²

In a second reaction DBU was used in THF at considerably lower temperature ($-80\text{ }^{\circ}\text{C}$), which gave in a straightforward reaction 1,3-dichloro-*m*-terphenyl-*cyclo*-1,3-diarsa-2,4-diazane (**7**) in moderate yields (52%, Scheme 9).

Both *cyclo*-1,3-dipnicta-2,4-diazanes [*m*-Ter-N-E-Cl]₂ (**4** and **7**, Schemes 6 and 9) can be isolated as colourless (E = P) or yellow (E = As) crystalline materials with fairly high melting and decomposition points, respectively (**4**: 285 $^{\circ}\text{C}$, **7**: 259 $^{\circ}\text{C}$). *Cyclo*-dipnict(III)azanes can exist as *cis* or *trans* isomers. While for the phosphorus species **4** in solution a *cis* and a *trans* isomer was observed (³¹P NMR: 227.4 for the *cis*, 264.1 ppm for the *trans* isomer), only the *trans* isomer is found for the arsenic compound **7** as shown in a NMR study.¹ In the solid state for phosphorus only the *cis* and for arsenic^{1,7a,23} only the *trans* isomer could be detected as illustrated by X-ray studies (see

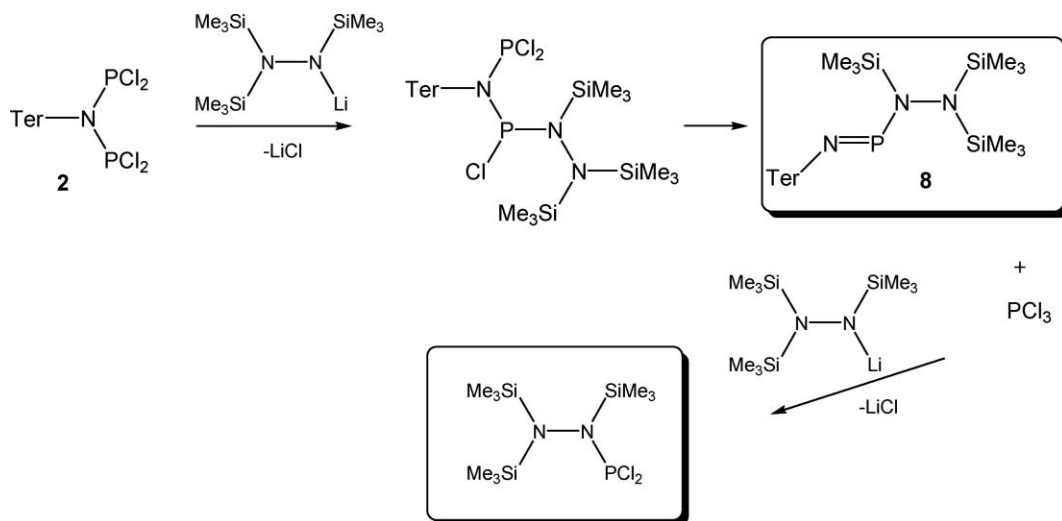
below). As pointed out by Stahl,⁴ most *cyclo*-diphosph(III)azanes are thermodynamically more stable as the *cis* isomer while the *trans* isomer is the kinetically favored product. It should be mentioned, that in contrast to the Mes* substituted analogue, **7** does not dissociate at ambient temperature in CH₂Cl₂ to form the monomeric imino(chloro)arsane.¹²

Synthesis of *N,N',N'*-[tris-(trimethylsilyl)]hydrazino-*m*-terphenyl-imino-phosphane (**8**)

In a series of experiments we studied the reaction of **2** with *N*-lithio-*N,N',N'*-[tris(trimethylsilyl)]hydrazide, Li[N(SiMe₃)₂–N(SiMe₃)₂], in order to see if it is possible to eliminate PCl₃ to generate 1,3-dichloro-*m*-terphenyl-*cyclo*-1,3-diphospha-2,4-diazane (**4**). At a first glance, this reaction yielded surprising products. Two species could be isolated: *N,N',N'*-[tris(trimethylsilyl)]hydrazino-*m*-terphenyl-imino-phosphane (**8**) and the known *N,N',N'*-[tris(trimethylsilyl)]hydrazino-dichlorophosphane, (Me₃Si)₂N–N(SiMe₃)–PCl₂.²⁰ It can be assumed that upon LiCl formation in a first reaction step the amino(hydrazine)-chlorophosphane is formed, which indeed implies the elimination of PCl₃ yielding **8** as shown in Scheme 10.

X-ray crystallography. The structures of compounds **1–6** and **8**, including the starting materials *m*-terphenyl-azide (*m*-Ter–N₃) and *m*-terphenylene (*m*-Ter–H) have been determined. Tables 1 and 2 present the X-ray crystallographic data. Selected molecular parameters are listed in Fig. 1–7. The molecular structures of the starting materials *m*-Ter–N₃ and *m*-Ter–H, are shown in the supporting information file (Schemes S1 and S2). X-ray quality crystals of all considered species were selected in Kel-F-oil (Riedel deHaen) or Fomblin YR-1800 (Alfa Aesar) at ambient temperature. All samples were cooled to $-100(2)\text{ }^{\circ}\text{C}$ during the measurement.

General structural trends. In all aminoarsane/phosphane derivatives, as expected, the central nitrogen atom is almost trigonal planar, and the pnictogen atom trigonal pyramidal coordinated. The sum of the bond angles at the amino nitrogen atom is always very close to 360 $^{\circ}$ indicating a planar environment and hence a formal sp²-hybridisation. Hence the lone pair localized



Scheme 10 Synthesis of **8**.

Table 1 Crystallographic details of compound 1–3

	1	1	2	3
Chem. formula	C ₂₄ H ₂₆ AsCl ₂ N	C ₂₄ H ₂₆ AsCl ₂ N	C ₂₄ H ₂₅ Cl ₄ NP ₂	C ₂₄ H ₂₆ Cl ₂ NP
Form. weight/g mol ⁻¹	474.28	474.28	531.19	430.33
Colour	Colourless	Colourless	Colourless	Colourless
Cryst. system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	24.301(5)	9.017(2)	16.571(3)	9.227(2)
<i>b</i> /Å	10.580(2)	29.293(6)	17.535(4)	28.933(6)
<i>c</i> /Å	8.842(2)	9.309(2)	17.726(4)	9.378(2)
α /°	90.0	90.0	90.0	90.0
β /°	90.0	108.09(3)	90.0	115.25(3)
γ /°	90.0	90.0	90.0	90.0
<i>V</i> /Å ³	2273.3(8)	2337.3(8)	5150.7(18)	2264.4(8)
<i>Z</i>	4	4	8	4
ρ_c /g cm ⁻³	1.386	1.348	1.370	1.262
μ /mm ⁻¹	1.740	1.692	0.597	0.367
$\lambda_{\text{Mo-K}\alpha}$ /Å	0.71073	0.71073	0.71073	0.71073
<i>T</i> /K	173(2)	173(2)	173(2)	173(2)
Measured reflns.	49272	42147	42834	82257
Indep. Reflins.	10714	8395	7492	8171
Reflns. with <i>I</i> > 2 σ (<i>I</i>)	9203	6382	5347	6390
<i>R</i> _{int}	0.0290	0.0412	0.0463	0.0328
<i>F</i> (000)	976	976	2192	904
<i>R</i> ₁ (R [<i>F</i> ² > 2 σ (<i>F</i> ²)])	0.0251	0.0409	0.0441	0.0470
w <i>R</i> ₂ (<i>F</i> ²)	0.0608	0.0978	0.1265	0.1188
GooF	1.021	1.057	1.061	1.050
Parameters	264	273	286	263

Table 2 Crystallographic details of compound 4–6 and 8

	4	5	6	8
Chem. formula	C ₄₈ H ₅₀ Cl ₂ N ₂ P ₂	C ₃₀ H ₄₀ AsClN ₂	C ₃₃ H ₄₁ AsClN ₃	C ₃₃ H ₅₂ N ₃ PSi ₃
Form. weight/g mol ⁻¹	787.74	539.01	590.06	606.02
Colour	Colourless	Colourless	Colourless	Yellow
Cryst. system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	19.912(4)	10.960(2)	10.158(2)	10.684(2)
<i>b</i> /Å	8.808(2)	11.400(2)	11.122(2)	11.033(2)
<i>c</i> /Å	24.420(5)	11.530(2)	14.580(3)	16.094(3)
α /°	90.00	86.53(3)	96.83(3)	86.43(3)
β /°	102.56(3)	87.06(3)	100.13(3)	82.08(3)
γ /°	90.00	83.06(3)	110.10(3)	75.71(3)
<i>V</i> /Å ³	4180.5(15)	1426.0(5)	1493.8(5)	1820.1(6)
<i>Z</i>	4	2	2	2
ρ_c /g cm ⁻³	1.252	1.255	1.312	1.106
μ /mm ⁻¹	0.268	1.305	1.253	0.199
$\lambda_{\text{Mo-K}\alpha}$ /Å	0.71073	0.71073	0.71073	0.71073
<i>T</i> /K	173(2)	173(2)	173(2)	173(2)
Measured reflns.	31428	24284	48634	18998
Indep. Reflins.	3656	4136	12631	7942
Reflns. with <i>I</i> > 2 σ (<i>I</i>)	3041	3336	9234	6071
<i>R</i> _{int}	0.0363	0.0377	0.0356	0.0285
<i>F</i> (000)	1664	568	620	656
<i>R</i> ₁ (R [<i>F</i> ² > 2 σ (<i>F</i> ²)])	0.0383	0.0375	0.0384	0.0426
w <i>R</i> ₂ (<i>F</i> ²)	0.0982	0.0921	0.0915	0.1193
GooF	1.028	1.081	1.008	1.064
Parameters	250	404	357	376

at this nitrogen atom is found in a p-type atomic orbital (AO). Small delocalization of this p-AO lone pair occurs, which is also known as hyperconjugation, leading to relatively shorter E–N bond lengths.²⁰ The E–N bond lengths of 1.819–1.858 Å for E = As and 1.657–1.713 Å for P, respectively, are always slightly shorter than expected for an E–N single bond (*cf.* $\Sigma r_{\text{cov}}(\text{N–P}) = 1.80$, $\Sigma r_{\text{cov}}(\text{N=P}) = 1.61$, $\Sigma r_{\text{cov}}(\text{N–As}) = 1.91$, $\Sigma r_{\text{cov}}(\text{N=As}) = 1.71$ Å).^{18,24} The sum of the bond angles at the arsenic atom ranges between

286–296° and at the phosphorus atom between 284–307°, in accord with structural data of known aminoarsane/phosphane derivatives.^{8,11,18,21} As depicted in Fig. 1–7, in all *m*-terphenyl substituted aminoarsanes, the N–ER₂ moiety adopts an almost central position inside the pocket formed by the *m*-terphenyl group. The bulky *m*-terphenyl group prevents all considered species from significant intermolecular interactions. For example in the solid state structures of **1** and **3** neither inter- nor intramolecular

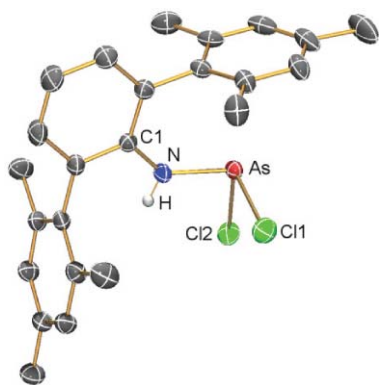


Fig. 1 ORTEP drawing of the molecular structure of **1** in the crystal (orthorhombic structure). Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms except NH are omitted for clarity. Selected bond lengths (Å) and angles (°): As–N 1.819(1), As–Cl2 2.2270(4), As–Cl1 2.2325(6), N–C1 1.407(1), N–As–Cl2 90.86(3), N–As–Cl1 101.36(3), Cl2–As–Cl1 94.59(2), C1–N–As 130.21(7).

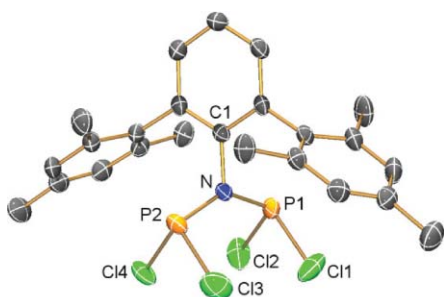


Fig. 2 ORTEP drawing of the molecular structure of **2** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Aryl hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–N 1.713(2), P2–N 1.708(2), P1–Cl1 2.0411(9), P1–Cl2 2.0592(8), P2–Cl4 2.0440(8), P2–Cl3 2.0643(9), N–C1 1.474(2); N–P1–Cl1 105.78(6), N–P1–Cl2 104.91(6), Cl1–P1–Cl2 96.58(4), N–P2–Cl4 105.49(6), N–P2–Cl3 103.92(6), Cl4–P2–Cl3 96.97(3), C1–N–P2 111.2(1), C1–N–P1 111.0(1), P2–N–P1 137.80(9).

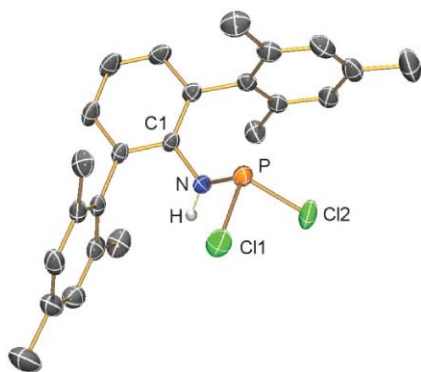


Fig. 3 ORTEP drawing of the molecular structure of **3** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms except NH are omitted for clarity. Selected bond lengths (Å) and angles (°): P–N 1.657(1), P–Cl2 2.0678(7), P–Cl1 2.0726(6), N–C1 1.426(2), N–H1 0.81(2); N–P–Cl2 100.91(5), N–P–Cl1 100.05(5), Cl2–P–Cl1 96.53(4), C1–N–P 122.8(1).

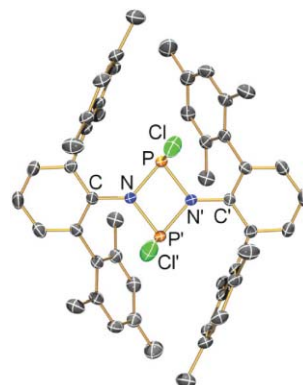


Fig. 4 ORTEP drawing of the molecular structure of **4** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): P–N' 1.709(2), P–N 1.731(2), P–Cl 2.1256(9), P–P' 2.612(1), N–C1 1.431(2), N–P' 1.709(2); N'–P–N 80.93(8), N'–P–Cl 108.66(6), N–P–Cl 95.12(6), N'–P–P' 40.90(6), N–P–P' 40.28(5), Cl–P–P' 102.15(2), C1–N–P' 132.8(1), C1–N–P 128.3(1), P'–N–P 98.83(8), N'–P–N–P' –5.4(1).

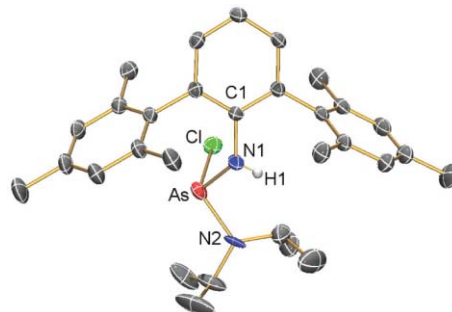


Fig. 5 ORTEP drawing of the molecular structure of **5** in the crystal. Thermal ellipsoids with 30% probability at 173 K. Hydrogen atoms except NH are omitted for clarity. Only one part of the two splitted positions is shown. Selected bond lengths (Å) and angles (°): N1–C1 1.394(2), As–N1 1.789(3), As–N2 1.85(2), As–Cl 2.333(4), N1–As–N2 96.0(4), N1–As–Cl 99.2(1), N2–As–Cl 101.6(3), As–N1–C1 127.4(2).

hydrogen bonding is observed. Significant hydrogen bonding is known for smaller substituents.^{5b,16}

m-Terphenyl-amino(dichloro)arsane (**1**), crystallizes from n-hexane in both the orthorhombic space group $Pna2_1$ with four formula units per unit cell and the monoclinic space group $P2_1/c$ also with four formula units per unit cell. Apparently, the orthorhombic crystals precipitate from hot n-pentane solution, while the monoclinic species are generated at lower temperatures. We want to focus the discussion on the orthorhombic crystals. The orthorhombic structure consists of well separated *m*-Ter-N(H)AsCl₂ molecules with no significant intermolecular contacts.

While the central phenyl ring of the terphenyl group, the H and the N atom lie in one plane, the As atom is slightly shifted out of this plane (\angle As–N–Cl–C = 20.38°). Moreover, the AsCl₂ unit in **1** is twisted towards H (\angle H–N–As–Cl1 = 75.69(2) vs. \angle H–N–As–Cl2 11.17°), resulting in a C₁ symmetric molecule (Fig. 1). The As–N distance amounts to 1.819(1) Å indicating some double bond character (*cf.* sum of the covalent radii $d_{\text{cov}}(\text{As–N}) = 1.91$ Å) introduced by hyperconjugation (see above), while slightly increased As–Cl distances are found ($d(\text{As–Cl2}) = 2.2270(4)$, $d(\text{As–Cl1}) = 2.2325(6)$ Å; *cf.* sum of the covalent radii

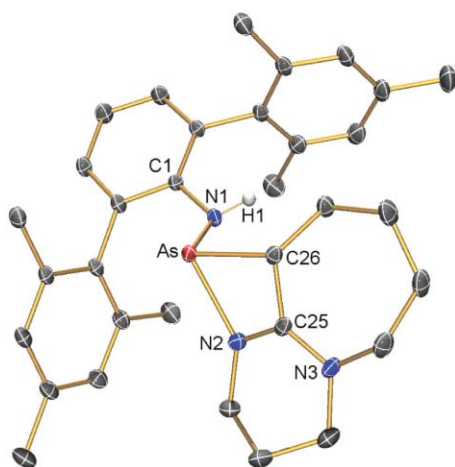


Fig. 6 ORTEP drawing of the cation of **6** in the crystal. Thermal ellipsoids with 30% probability at 173 K. Hydrogen atoms except NH and chloride ion omitted for clarity. Selected bond lengths (Å) and angles (°): As–N1 1.858(1), As–C26 2.003(2), As–N2 2.087(1), As–Cl 2.6078(7), N1–C1 1.403(2), N2–C25 1.310(2), N3–C25 1.332(2), N1–As–C26 98.23(6), N1–As–N2 94.09(5), C26–As–N2 67.47(5), N1–As–Cl 93.94(4), C26–As–Cl 88.63(4), N2–As–Cl 155.64(4), C1–N1–As 121.64(9).

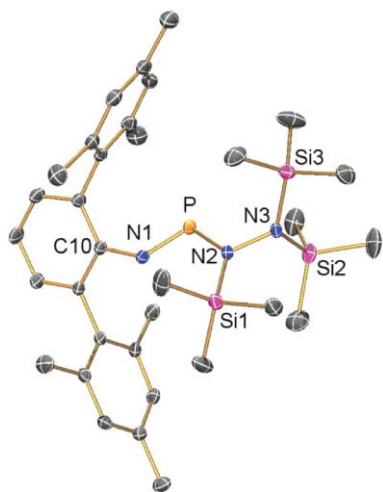


Fig. 7 ORTEP drawing of the molecular structure of **8** in the crystal. Thermal ellipsoids with 30% probability at 173 K. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P–N1 1.560(2), P–N2 1.660(1), Si1–N2 1.789(2), Si2–N3 1.750(2), Si3–N3 1.757(2), N2–N3 1.473(2), N1–P–N2 104.22(8), C10–N1–P 125.7(1), N3–N2–P 112.4(1), N3–N2–Si1 119.4(1), P–N2–Si1 128.15(8), N2–N3–Si2 115.3(1), N2–N3–Si3 116.0(1), Si2–N3–Si3 126.19(9).

$d_{\text{cov}}(\text{As–Cl}) = 2.20 \text{ \AA}$ ²⁴ due to partial delocalization of the electron density of the nitrogen lone pair into the σ^* As–Cl bonds.

N,N-Bis(dichlorophosphino)-*m*-terphenyl-aniline, *m*-Ter-*N*(PCL₂)₂ (**2**). crystallizes in the orthorhombic space group *Pbca* with eight formula units per unit cell. No significant intermolecular contacts are observed. The asymmetric unit consists of one molecule with two almost eclipsed PCL₂ moieties. The phosphorus atom sits in trigonal pyramidal environment with Cl–P–Cl angles between 96–97° and N–P–Cl angles between 103 and 106°. The P–N–P angle of 137.80(9)° is rather large, in accord with that in O₂Cl(O)P–N–P(Cl₂)–NR₂ (<PNP = 134.0(2), R = isopropyl).²⁵ The experimentally determined P1–N bond

length of 1.713(2) and P2–N 1.708(2) Å, respectively, is slightly shorter than expected for a typical P–N single bond (*cf.* $\Sigma r_{\text{cov.}} = 1.80$ (1.76) Å,²⁴ 1.704(1) and 1.703(1) in p-C₆H₄[N(PCl₂)₂]₂)²⁶ but comparable with the 1.704(2) Å in (Me₃Si)₂N–(Me₃Si)N–PPh₂.²⁰

m-Terphenyl-amino(dichloro)phosphane (**3**). crystallizes in the monoclinic space group *P2₁/c* with four formula units per cell. No significant intermolecular contacts are observed. In contrast to the arsenic species (**1**), the H atom is located outside the plane formed by the central phenyl ring and the N atom (<H–N–C1–C2 = 23.2°). Furthermore, the P–N–C1 angle of 122.8(1)° is considerably smaller compared to the As–N–C1 angle (130.21(7)°) in **1**, which may be attributed to the larger space demand of the pnictogen lone pair and AsCl₂ unit in **1**. Moreover, the larger ionic bond character in **1** may also contribute to a larger C–N–As angle. The P–N distance of 1.657(1) Å is slightly shorter as in **2** (1.713(2), 1.708(2) Å) but comparable with the 1.6451(9) Å in (Me₃Si)₃Si–N(SiMe₃)–PCl₂.^{2b} The average P–Cl bond lengths amounts to 2.070 Å, in accord with the value of 2.052 Å found for **2**.

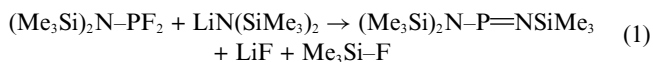
1,3-Dichloro-*m*-terphenyl-cyclo-1,3-diphospha-2,4-diazane (**4**). crystallizes in the monoclinic space group *C2/c* with four formula units per unit cell. No significant intermolecular contacts are observed. The asymmetric unit consists of a half molecule, which lies on a twofold crystallographic axis, with the whole molecule generated by the symmetry operation $-x, y, -z+1/2$ as depicted in Fig. 4. Cyclo-diphospha(III)-diazanes can exist as *cis* or *trans* isomers with the *cis* isomer being mostly the thermodynamically more stable isomer. Compound **4** adopts the *cis* configuration with respect to the position of the chlorine atoms. In general, the *cis* isomers have puckered P₂N₂ rings,⁴ whereas the rings in the *trans* isomers are planar. In contrast to this observation, the P₂N₂ ring in **4** is almost planar although being the *cis* isomer (deviation from planarity: N'–P–N–P' –5.4(1)°), but slightly distorted with two longer P–N bond lengths (P–N 1.731(2) Å) and two considerably shorter P–N distances (P–N' 1.709(2) Å; *cf.* 1.695(10) in [Ph–N–P–Cl]₂,²⁷ $\Sigma r_{\text{cov.}} = 1.80$ (1.76) Å).²⁴ Compared to [Ph–N–P–Cl]₂ the P–Cl bond lengths are slightly elongated (**4**: 2.1256(9) vs. [Ph–N–P–Cl]₂: 2.087(8) Å). The N–P–N' angle with 80.93(8)° is significantly smaller compared to the P–N–P' (98.83(8)°) angle. The N'–P–Cl amounts to 108.66(6)°, while the N–P–Cl angle is decreased to 95.12(6)°.

m-Terphenyl-amino-diisopropylamino(chloro)arsane (**5**). crystallizes in the triclinic space group *P1* with two formula units per unit cell. The AsCIN(Pr)₂ unit in **5** was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.7144(9)/0.2856(9)). As illustrated in Fig. 5, the pyramidal As atom is located outside the plane formed by the central phenyl ring and the N1 atom (deviation from planarity: 46.73°), and is attached to N1 and N2 with different distances ($d(\text{As–N1}) = 1.789(3)$, $d(\text{As–N2}) = 1.85(2) \text{ \AA}$). The N1–C1 distance amounts to 1.394 Å, which is slightly shorter than that found in **1** ($d(\text{N–C1}) = 1.407(1) \text{ \AA}$). While the N1–As–Cl angle of 99.2(1)° and the N2–As–Cl angle of 101.6(3)° are almost identical, the As–N1–C1 angle with 127.4(2)° is rather large but comparable with 130.21(7)° As–N1–C1 angle in **1**.

2-*m*-Terphenyl-amino-2-arsa-3,7-diaza-tricyclo[5.4.1.0^{3,12}]do-dec-3(12)-enylidium chloride (**6**). crystallizes in the triclinic space group *P1* with two formula units per unit cell. The asymmetric unit consists of one ion pair with six H⋯Cl contacts in the range

2.7–3.1 Å (cf. $\Sigma r_{\text{vdw}}(\text{H} \cdots \text{Cl}) = 3.01 \text{ \AA}$). As illustrated in Fig. 6, the pyramidal As atom forms a tricycle with the DBU moiety, which can only be accommodated by a very small N2–As–C26 angle of 67.47(5)° and rather large As–N2 (2.087(1) Å) and As–Cl (2.6078(7) Å) bond lengths. In comparison, the As–N1 distance amounts to 1.858(1) Å (cf. $d(\text{As–N})$ 1.819(1) in **1**, $\Sigma r_{\text{cov}}(\text{As–N}) = 1.91 \text{ \AA}$).²⁴ But also the N1–As–N2 (94.09(5)°) and N1–As–C26 (98.23(6)°) angles are fairly small, while the C1–N1–As angle of 121.64(9)° is larger but also significantly smaller than those found in **1** (130.21(7)°) and **6** (127.4(2)°), in accord with structural data of arsetanes.²⁸ It should be noted that compound **6** can be regarded as a rare example of an azaarsetane cation. Only one example of a cationic species, bearing an azaarsetene-1-yl-phosphonium ion, has been published by Grützmacher *et al.* displaying similar structural features.²⁹

N,N',N'-[tris-(trimethylsilyl)]hydrazino-*m*-terphenyl-imino-phosphane (**8**). crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. The asymmetric unit consists of one molecule of **8**. As shown in Fig. 7, the P=N double bond in hydrazino-*m*-terphenyl-imino-phosphane **8** is kinetically stabilized by the steric demand of the adjacent (Me₃Si)N–N(SiMe₃)₂ and *m*-terphenyl groups. Steric protection by these two groups is responsible for the impossibility of dimerization. It was not until 1973 that Flick and Niecke were able to prove the existence of a phosphorus(III) compound with the structural feature of a phosphazene, –P=N–.³⁰ This first iminophosphane, a phosphazene with phosphorus(III) in the coordination number two, was obtained from the reaction of bis(trimethylsilyl)amino(difluoro)phosphane with lithium-bis(trimethylsilyl)amide (eqn (1)). Meanwhile, phosphorus-nitrogen compounds with a two-coordinated phosphorus(III) atom represent a well-established class of organophosphorus compounds.^{18,31,32}



While the C10–N1–P–N2–N3 unit is almost planar ($\angle(\text{N3–N2–P–N1}) = 177.1^\circ$), the central phenyl ring of the *m*-terphenyl group is twisted by -53.56° . The hydrazine moiety adopts a staggered conformation with two perpendicular planes (Si1–N2–P plane perpendicular to Si2–N3–Si3 plane).^{20,34a,b} Both nitrogen atoms (N2 and N3) are in an ideal planar environment ($\Sigma \angle(\text{N2}) = 359.96^\circ$, $\Sigma \angle(\text{N3}) = 357.55^\circ$) with a N–N bond length of 1.473(2) Å, typical for a single bond. A short P–N1 distance with 1.560(2) Å, in accord with the P=N double bond, and a longer along P–N2 (1.660(1) Å) distance were found (cf. $\Sigma r_{\text{cov}}(\text{P–N}) = 1.80$ (1.76) Å).^{24,33} The latter distance is still significantly shorter as expected for a P–N single bond, which can be attributed to hyperconjugative effects along the P–N–Si units.^{5b,34} The short PN distance along with the presence of an almost planar C10–N–P–N–N unit indicate electronic delocalization, which might be the driving force for this unusual arrangement.

Conclusion

The synthesis of sterically encumbered dipnictadiazanes was achieved by treatment of *m*-terphenyl amine and ECl₃ (E = P and As) with bases such as Et₃N, *n*-BuLi, DBU or LDA. Depending on the base and reaction conditions used different products were obtained and fully characterized. While the reaction with an excess

of Et₃N yielded for E = As *m*-Ter–N(H)–AsCl₂, for E = P *m*-Ter–N(PCl₂)₂ was obtained. *m*-Ter–N(H)–PCl₂ was formed in the reaction with *n*-BuLi, a reaction protocol which can also be used to generate *m*-Ter–N(H)–AsCl₂.

Treatment of *m*-Ter–N(H)–PCl₂ with Et₃N resulted in the formation of *cyclo*-1,3-diphospha-2,4-diazane, while no reaction was observed in the analogous reaction with the arsenic species. To obtain the analogous *cyclo*-1,3-diarsa-2,4-diazane, *m*-Ter–N(H)–AsCl₂ was reacted with LDA yielding, however, *m*-Ter–N(H)–As(Cl)N(^{*i*}Pr)₂. Only the reaction with DBU at low temperature resulted in the formation of the *cyclo*-1,3-diarsa-2,4-diazane in good yields.

This paper demonstrates the difficulties with the preparation of *cyclo*-1,3-diarsa-2,4-diazane and *cyclo*-1,3-diphospha-2,4-diazane depending on the used stoichiometry, solvents and bases due to the competition of different reaction channels.

Experimental

General Information

All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane was purified according to a literature procedure,³⁵ dried over P₄O₁₀ and freshly distilled prior to use. Diethyl ether, tetrahydrofuran (THF) and benzene were dried over Na/benzophenone and freshly distilled prior to use. *n*-Pentane and *n*-hexane were dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. Acetone, ethanol and methanol were freshly distilled prior to use. *p*-Toluenesulfonylazide MePhSO₂N₃, 1-iodo-2,6-bis-(2,4,6-trimethylphenyl)-benzene Mes₂PhI, 1-azido-2,6-bis-(2,4,6-trimethylphenyl)benzene Mes₂PhN₃, 2,6-bis-(2,4,6-trimethylphenyl)aniline Mes₂PhNH₂ and *N*-lithio-2,6-bis-(2,4,6-trimethylphenyl)anilide Mes₂PhNHLi have been previously reported in literature and were prepared according to modified procedures.^{36,37,14,15c} Lithium-*N,N,N'*-[tris(trimethylsilyl)]hydrazide Li[(Me₃Si)₂NN(SiMe₃)] was prepared according to literature procedures.^{38,39} *p*-Toluenesulfonylchloride MePhSO₂Cl, (Acros, 99%), 1,3-dichlorobenzene (Merck, 99%), mesitylbromide MesBr (AlfaAesar, 99%), Iodine I₂ (Apolda, 99%), sodium hydroxide NaOH (Germed, 99%), sodium sulfite Na₂SO₃ (Germed, 99%), magnesium sulfate MgSO₄ (Acros, 97%), sodium azide NaN₃ (Acros, 99%) and *n*-BuLi (1.6M or 2.5M, Acros), were used as received. Arsenic trichloride AsCl₃ (Merck, 99%), phosphorous trichloride PCl₃ (Acros, 97%), 1,8-diazabicyclo[5.4.0]undec-7-en DBU (Merck, 99%), triethylamine (Merck, 97%) and diisopropylamine (Aldrich, 99%) were freshly distilled prior to use.

NMR

²⁹Si INEPT, ¹⁴N{¹H}, ³¹P{¹H}, ¹³C{¹H}, ¹³C DEPT, and ¹H NMR spectra were obtained with a Bruker AVANCE 250, 300 or 500 spectrometer and were referenced internally to the deuterated solvent (¹³C, C₆D₆: $\delta_{\text{reference}} = 128 \text{ ppm}$, CD₂Cl₂: $\delta_{\text{reference}} = 54 \text{ ppm}$, CDCl₃: $\delta_{\text{reference}} = 77 \text{ ppm}$) or to protic impurities in the deuterated solvent (¹H, C₆D₅H: $\delta_{\text{reference}} = 7.16 \text{ ppm}$, CDHCl₂: $\delta_{\text{reference}} = 5.31 \text{ ppm}$, CHCl₃: $\delta_{\text{reference}} = 7.26 \text{ ppm}$). C₆D₆ was dried over

Na/benzophenone and freshly distilled prior to use. CD₂Cl₂ and CDCl₃ were dried over P₄O₁₀ and freshly distilled prior to use.

IR

Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device was used.

Raman

Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm) was used.

CHN analyses

Analysator Flash EA 1112 from Thermo Quest was used.

MS

Finnigan MAT 95-XP from Thermo Electron was used.

Melting points

are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20 °C min⁻¹ (clearing-points are reported).

Syntheses

Synthesis of [2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)arsane (1). To a stirred solution of 2,6-bis-(2,4,6-trimethylphenyl)aniline Ter-NH₂ (3.295 g, 10.0 mmol) in Et₂O (50 mL), *n*-BuLi (2.5M, 10.1 mmol, 4.04 mL) was added dropwise at ambient temperature over a period of five minutes. The resulting yellow solution was stirred for one hour and was then added dropwise to a stirred solution of AsCl₃ (1.467 g, 11.0 mmol) in Et₂O (10 mL) at ambient temperature over a period of one hour, resulting in a colourless suspension, which is then stirred for two hours at ambient temperature. The colourless suspension is filtered (F4) and the residue is washed by repeated backdistillation of the solvent. Removal of solvent *in vacuo* results in a colourless residue, which is extracted with *n*-hexane (30 mL) and filtered (F4) resulting in a champagne coloured solution. Removal of solvent and drying *in vacuo* yields 3.634 g (7.66 mmol, 77%) of **1** as a colourless crystalline solid. Mp 153 °C. Anal. calc.% (found): C, 60.78 (60.07); H, 5.53 (5.52); N, 2.95 (2.69). ¹H NMR (25 °C, CD₂Cl₂, 300.13 MHz): δ = 2.12 (s, 12H, *o*-CH₃), 2.37 (s, 6H, *p*-CH₃), 5.43 (s, 1H, NH), 7.04–7.16 (m, 7H). ¹³C{¹H} NMR (25 °C, CD₂Cl₂, 75.5 MHz): δ = 20.8 (2, CH, *o*-CH₃), 21.6 (s, CH, *p*-CH₃), 122.6 (CH), 129.1 (CH), 129.9 (CH), 130.3, 134.6, 138.4, 140.0, 140.7. IR (ATR, 32 scans): 3320 (m), 3031 (w), 2971 (w), 2944 (w), 2913 (m), 2852 (w), 2731 (w), 1610 (w), 1583 (w), 1487 (w), 1441 (m), 1435 (m), 1416 (s), 1373 (m), 1356 (s), 1299 (w), 1356 (s), 1299 (w), 1279 (w), 1263 (s), 1223 (s), 1180 (w), 1097 (m), 1068 (m), 1032 (m), 1013 (m), 1007 (m), 962 (w), 894 (w), 846 (s), 868 (s), 855 (s), 800 (s), 794 (s), 742 (m), 724 (m), 640 (m), 587 (m), 565 (m), 548 (m), 542 (m). Raman (150 mW, 25 °C, 12 scans, cm⁻¹): = 3323 (1), 3050 (4), 3034 (4), 3020 (4), 2919 (6), 2859 (3), 2813 (3), 2732 (1), 1612 (6), 1585 (5), 1481 (3), 1381 (3), 1306 (7), 1287 (2), 1265 (3), 1225 (3), 1183 (2), 1162 (1), 1070 (3), 1007 (2), 947 (1), 870 (1), 744 (1), 730 (1), 642 (2), 579 (5), 552 (2), 523 (2), 470 (2), 408 (2), 343 (10), 332 (6), 309 (2), 272 (2), 253 (2), 235 (3), 170 (3),

145 (4), 132 (8). MS (EI, *m/z*): 91 (20.1), 289 (61.3), 326 (24.5) [Ter-NH₂-3H]⁺, 329 (25.6) [Ter-NH₂]⁺, 437 (5.41) [Ter-NAs-Cl]⁺, 473 (4.63) [M]⁺.

Synthesis of *N,N*-bis-dichlorophosphane-2,6-bis-(2,4,6-trimethylphenyl)aniline (2). 2,6-Bis-(2,4,6-trimethylphenyl)aniline (Ter-NH₂ = (Mes)₂Ar-NH₂) (1.647 g, 5.0 mmol) and triethylamine (5.463 g, 54 mmol) were dissolved in *n*-pentane (50 mL). PCl₃ (6.170 g, 45 mmol) was then condensed onto the frozen solution at -196 °C *in vacuo*. The mixture is warmed to ambient temperature and stirred for three days. The resulting colourless suspension is filtered (F4) and the residue is extracted two times by repeated backdistillations of the solvent. Removal of solvent and drying *in vacuo* yields 1.775 g (3.34 mmol, 67%) of **2** as colourless crystals. **2** can be sublimed at 180 °C. Mp 199 °C (dec.). Anal. calc.% (found): C, 54.26 (54.22); H, 4.74 (4.83); N, 2.64 (2.57). ³¹P{¹H} NMR (25 °C, CD₂Cl₂, 202.5 MHz): δ = 183.3. ¹H NMR (25 °C, CD₂Cl₂, 500.13 MHz): δ = 2.07 (s, 12H, *o*-CH₃), 2.34 (s, 6H, *p*-CH₃), 6.99 (s, 4H, *m*-CH-Mes), 7.21 (dm, 2H, ³*J*(¹H-¹H) = 7.5 Hz, *m*-CH), 7.50 (tt, 1H, ⁶*J*(¹H-³¹P) = 2.4 Hz, ³*J*(¹H-¹H) = 7.5 Hz, *p*-CH). ¹³C{¹H} NMR (25 °C, CD₂Cl₂, 125.8 MHz): δ = 21.5 (s, *o*-CH₃), 22.3 (m, *p*-CH₃), 129.4 (s, CH), 130.0 (t, *J*(¹³C-³¹P) = 3.0 Hz, CH), 132.3 (t, *J*(¹³C-³¹P) = 2.1 Hz, CH), 135.5 (s), 137.4 (s), 139.2 (s), 140.3 (t, *J*(¹³C-³¹P) = 25.6 Hz), 142.2 (t, *J*(¹³C-³¹P) = 6.5 Hz). Raman (100 mW, 25 °C, 8 scans, cm⁻¹): = 3082 (2), 3051 (4), 3018 (4), 2920 (10), 2585 (3), 2734 (2), 1612 (6), 1578 (3), 1482 (2), 1378 (3), 1307 (7), 1189 (2), 1170 (2), 1076 (4), 1007 (2), 848 (1), 738 (2), 677 (3), 576 (6), 558 (5), 527 (3), 504 (10), 488 (3), 468 (3), 460 (3), 410 (6), 338 (3), 282 (4), 249 (2), 197 (2). IR (ATR, 32 scans, 25 °C, cm⁻¹): 2947(w), 2915 (w), 2854 (w), 2731 (w), 1729(w), 1609 (w), 1453 (w), 1402 (w), 1376 (w), 1270 (w), 1186 (w), 1167 (w), 1152 (w), 1073 (w), 1029 (w), 900 (s), 847 (s), 806 (m), 779 (w), 752 (w), 736 (w), 714 (w), 675 (m), 596 (w), 583 (w), 556 (w), 529 (m). MS (EI, *m/z*, >10⁰):, 41 (11) [C₃H₃]⁺, 44 (11), 55 (10), 57 (15), 69 (10), 101 (17) [PCl₂]⁺, 141 (11), 149 (19), 171 (10), 282 (12), 297 (18) [Ter-N-2Me]⁺, 299 (12) [TerN-2Me+2H]⁺, 310 (43), 326 (82) [TerN-H]⁺, 342 (42) [M-Mes-2H]⁺, 357 (100) [TerNP]⁺, 393 (62) [Ter-NPCl]⁺, 529 (17) [M-PCl₂]⁺, 531 (22) [M]⁺.

Synthesis of [2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)phosphane (3). To a stirred solution of 2,6-bis-(2,4,6-trimethylphenyl)aniline Ter-NH₂ (3.555 g, 10.8 mmol) in Et₂O (60 mL), PCl₃ (neat, 2.200 g, 16.0 mmol) was added dropwise at -40 °C over a period of five minutes. To the resulting colourless solution, DBU (neat, 1.640 g, 10.8 mmol) was added dropwise over a period of 10 min at this temperature. The resulting colourless suspension was warmed to ambient temperatures, and stirred for 12 h. The solvent was removed *in vacuo*, and the colourless residue is extracted with *n*-hexane (50 mL) and washed several times by repeated backdistillations of the solvent and filtered (F4). The solvent is removed and the resulting colourless residue was dried *in vacuo* yields 4.503 g (10.5 mmol, 97%) of **3** as a colourless crystalline solid. Mp 146 °C. Anal. calc.% (found): C, 66.98 (67.23); H, 6.09 (6.32); N, 3.52 (3.14). ³¹P{¹H} NMR (25 °C, CD₂Cl₂, 121.5 MHz): δ = 159.4. ¹H NMR (25 °C, CD₂Cl₂, 300.13 MHz): δ = 2.02 (s, 12H, *o*-CH₃), 2.33 (s, 6H, *p*-CH₃), 5.22 (s, 1H, NH), 6.98 (s, 4H, *m*-Mes), 7.04 (m, 2H, *m*-CH), 7.19 (m, 1H, *p*-CH). ¹³C{¹H} NMR (25 °C, CD₂Cl₂, 75.5 MHz): δ = 20.8 (d, ⁶*J*(¹³C-³¹P) = 1.5 Hz, *o*-CH₃), 21.5 (s, *p*-CH₃), 124.4 (s,

CH), 129.3 (s, CH), 130.3 (s, CH), 131.6 (d, $J(^{13}\text{C}-^{31}\text{P}) = 3.8$ Hz), 134.9 (d, $J(^{13}\text{C}-^{31}\text{P}) = 3.0$ Hz), 137.6 (d, $J(^{13}\text{C}-^{31}\text{P}) = 5.1$ Hz), 137.8 (d, $J(^{13}\text{C}-^{31}\text{P}) = 4.1$ Hz), 139.0 (s). IR (ATR, 25 °C, cm^{-1}): 3327 (w), 2969 (w), 2943 (w), 2914 (w), 2853 (w), 1610 (w), 1573 (w), 1486 (w), 1421 (s), 1375 (m), 1358 (m), 1260 (m), 1217 (m), 1100 (w), 1070 (w), 1008 (w), 917 (m), 852 (s), 819 (w), 797 (m), 774 (m), 754 (s), 716 (w), 644 (m), 595 (w), 557 (m). Raman (75 mW, 25 °C, 3000 scans, cm^{-1}): = 3054 (4), 3017 (5), 2916 (10), 2858 (3), 2730 (1), 1613 (8), 1538 (4), 1482 (2), 1441 (3), 1380 (4), 1306 (10), 1218 (2), 1183 (2), 1166 (1), 1072 (2), 1010 (2), 947 (1), 735 (1), 645 (1), 578 (7), 558 (3), 521 (4), 480 (3), 440 (4), 403 (4), 332 (3), 264 (4), 234 (3), 151 (4). MS (EI, m/z , >10%): 49 (12), 57 (13) $[\text{C}_4\text{H}_9]^+$, 69 (11), 84 (13), 313 (14) $[\text{Ter} - \text{H}]^+$, 314 (16) $[\text{TerNH} - \text{Me}]^+$, 328 (100) $[\text{TerNH}]^+$, 358 (23) $[\text{M} - 2\text{Cl}]^+$, 394 (7) $[\text{M} - \text{Cl}]^+$, 429 (36) $[\text{M}]^+$.

Synthesis of 1,3-dichloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)-phenyl]-cyclo-1,3-diphospha-2,4-diazane (4). To a stirred solution of *N*-dichlorophosphane-2,6-bis-(2,4,6-trimethylphenyl)-aniline Ter-NHPCl_2 (2.152 g, 5.0 mmol) in *n*-hexane (50 mL), a solution of triethylamine Et_3N (0.759 g, 7.5 mmol) in *n*-hexane (10 mL) was added dropwise at -80 °C, resulting in a colourless suspension, which was slowly warmed to ambient temperature over a period of two hours. Stirring for one day at ambient temperature results in a pale yellowish suspension. The solvent is removed *in vacuo*, and the yellowish residue is extracted with *n*-hexane (50 mL) and filtered (F4). Removal of solvent and drying *in vacuo* results in a pale yellowish solid. Recrystallisation from a minimum of dichloromethane at 5 °C results in the deposition of colourless crystals. Removal of solvent by decantation and drying *in vacuo* yields 1.640 g (2.081 mmol, 83%) of **4** as a colourless, crystalline solid. Smp. 285 °C. Anal. calc.% (found): C, 73.18 (73.20); H, 6.40 (6.84); N, 3.56 (3.50). (NMR: *cis/trans* mixture, approx. 1 : 3) $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 121.5 MHz): $\delta = 227.4$ (s, *cis*), 264.1 (s, *trans*). ^1H NMR (25 °C, CD_2Cl_2 , 300.13 MHz): $\delta = 1.84$ (d, 12H, $^7J(^{31}\text{P}-^1\text{H}) = 1.7$ Hz, *trans*, *o*- CH_3), 1.90 (s, 12H, *cis*, *o*- CH_3), 2.35 (s, 6H, *cis*, *p*- CH_3), 2.46 (s, 6H, *trans*, *p*- CH_3), 6.72–6.86 (m, 6H, *cis/trans*), 7.01 (m, 1H, $^3J(^1\text{H}-^1\text{H}) = 7.6$ Hz, *cis*, *p*-CH), 7.06 (t, 1H, $^3J(^1\text{H}-^1\text{H}) = 7.6$ Hz, *trans*, *p*-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 75.5 MHz): $\delta = 21.0$ (s, *o*- CH_3), 21.3 (t, $J(^{13}\text{C}-^{31}\text{P}) = 2.7$ Hz, *o*- CH_3), 21.8 (s, *p*- CH_3), 21.9 (t, $J(^{13}\text{C}-^{31}\text{P}) = 3.7$ Hz, *p*- CH_3), 123.7 (s, CH), 124.8 (s, CH), 128.8 (s, CH), 129.1 (s, CH), 131.3 (s, CH), 131.6 (s, CH), 132.4 (t, $J(^{13}\text{C}-^{31}\text{P}) = 1.9$ Hz), 134.4 (s), 134.6 (s), 135.2 (t, $J(^{13}\text{C}-^{31}\text{P}) = 2.8$ Hz), 135.7 (t, $J(^{13}\text{C}-^{31}\text{P}) = 2.9$ Hz), 136.1 (t, $J(^{13}\text{C}-^{31}\text{P}) = 2.8$ Hz), 137.9 (s), 138.3 (t, $J(^{13}\text{C}-^{31}\text{P}) = 4.4$ Hz), 138.8 (t, $J(^{13}\text{C}-^{31}\text{P}) = 3.5$ Hz), 138.9 (t, $J(^{13}\text{C}-^{31}\text{P}) = 3.5$ Hz). Raman (150 mW, 25 °C, 8 scans, cm^{-1}): = 3047 (2), 3013 (2), 2918 (10), 2855 (2), 2732 (1), 1612 (4), 1583 (3), 1485 (1), 1431 (2), 1378 (2), 1305 (5), 1287 (2), 1166 (1), 1094 (1), 1007 (1), 942 (1), 740 (1), 577 (4), 562 (2), 540 (3), 524 (2), 483 (1), 438 (2), 387 (1), 338 (1), 264 (1), 227 (2), 203 (2). IR (ATR, 25 °C, cm^{-1}): 2972 (w), 2943 (w), 2914 (w), 2852 (w), 1610 (m), 1573 (w), 1417 (s), 1373 (m), 1357 (m), 1262 (w), 1219 (m), 1070 (w), 1032 (w), 1007 (w), 911 (m), 889 (m), 850 (w), 796 (m), 753 (m), 740 (w), 700 (w), 643 (w), 558 (w), 550 (w). MS (EI, m/z , >10%): 36 (17), 41 (13) $[\text{C}_3\text{H}_5]^+$, 44 (33), 57 (17) $[\text{C}_4\text{H}_5]^+$, 69 (11), 296 (12) $[\text{Ter} - \text{Me} - 2\text{H}]^+$, 310 (40) $[\text{Ter} - 3\text{H}]^+$, 326 (50) $[\text{Ter} - \text{N} - \text{H}]^+$, 342 (64) $[\text{Ter} - \text{NP} - \text{Me}]^+$, 358 (100) $[\text{Ter} - \text{NPr}]^+$, 393 (25) $[\text{Ter} - \text{NPrCl}]^+$, 671

(13) $[\text{Ter}_2\text{N}_2\text{P}]^+$, 716 (14) $[\text{M} - 2\text{Cl}]^+$, 735 (18) $[\text{M} - \text{Me} - \text{H}]^+$, 751 (27) $[\text{M} - \text{Cl}]^+$, 786 (32) $[\text{M}]^+$.

Synthesis of [2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-diisopropylamino(chloro)arsane (5). To a stirred solution of *N*-[2,4-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)arsane (1.206 g, 2.54 mmol) in diethyl ether (15 mL), a solution of lithium diisopropylamide LDA (2.55 mmol, freshly prepared from diisopropylamine (0.258 g, 2.55 mmol) and *n*-BuLi (2.5M, 2.55 mmol, 1.02 mL) in diethyl ether (15 mL) at -20 °C) is added dropwise at -50 °C over a period of 30 min. The resulting yellow suspension was warmed to ambient temperature and stirred for three hours. Removal of solvent and drying *in vacuo* results in a colourless residue, which was extracted with *n*-hexane (25 mL) and filtered (F4), resulting in a colourless solution. Concentration *in vacuo* and storage at -25 °C resulted in the deposition of colourless crystals. Removal of supernatant by decantation and drying *in vacuo* yields 1.181 g (2.19 mmol, 83%) of **5** as a colourless crystalline solid. Mp 128 °C. Anal. calc.% (found): C, 66.85 (66.71); H, 7.48 (7.48); N, 5.20 (4.67). ^1H NMR (25 °C, CD_2Cl_2 , 250.13 MHz): $\delta = 0.76$ (d, 6H, CH_3 , $^3J(^1\text{H}-^1\text{H}) = 6.7$ Hz), 0.97 (d, 6H, CH_3 , $^3J(^1\text{H}-^1\text{H}) = 6.7$ Hz), 2.08 (s, 6H, CH_3), 2.11 (s, 6H, CH_3), 2.31 (s, 6H, CH_3), 3.14 (sept, 2H, CH, $^3J(^1\text{H}-^1\text{H}) = 6.7$ Hz), 5.05 (s, 1H, NH), 6.94–7.03 (m, 7H, *m/p*-CH-Ph, *m*-CH-Mes). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 75.5 MHz): $\delta = 20.6$ (s, CH_3), 21.0 (s, CH_3), 21.4 (s, CH_3), 24.2 (s, $\text{CH}(\text{CH}_3)_2$), 25.8 (s, $\text{CH}(\text{CH}_3)_2$), 48.2 (s, $\text{CH}(\text{CH}_3)_2$), 121.2 (s, aryl-CH), 129.3 (s, aryl-CH), 129.4 (s, aryl-CH), 129.8 (s, aryl-CH), 130.3, 135.7, 137.9, 138.2, 138.4, 140.8. IR (ATR, 32 scans): 3338 (w), 3303 (w), 2960 (s), 2916 (m), 2860 (w), 2726 (w), 1611 (w), 1585 (w), 1485 (w), 1454 (m), 1434 (m), 1418 (s), 1378 (m), 1365 (m), 1306 (w), 1284 (w), 1258 (m), 1242 (m), 1224 (m), 1191 (m), 1168 (s), 1152 (s), 1118 (s), 1096 (m), 1074 (m), 1032 (w), 1014 (m), 944 (s), 884 (w), 848 (s), 814 (m), 805 (m), 791 (m), 759 (s), 744 (m), 718 (m), 647 (m), 604 (w), 577 (w), 565 (m), 550 (m). Raman (200 mW, 25 °C, 251 scans, cm^{-1}): = 3341 (1), 3051 (4), 3015 (4), 2961 (6), 2920 (10), 2864 (4), 2755 (2), 2735 (2), 1612 (3), 1586 (2), 1484 (1), 1441 (2), 1422 (1), 1380 (2), 1305 (4), 1285 (2), 1245 (1), 1261 (1), 1225 (3), 1182 (1), 1076 (1), 1007 (1), 946 (1), 850 (1), 642 (1), 743 (1), 722 (1), 644 (1), 603 (1), 578 (1), 550 (1), 520 (1), 465 (1), 447 (2), 407 (1), 359 (1), 336 (1), 306 (1), 281 (1), 248 (1), 230 (1), 177 (1), 130 (1). MS (CI, isobutane, m/z): 102 $[\text{N}(\text{iPr})_2]^+$, 330 $[\text{Ter} - \text{NH}_3]^+$, 402 $[\text{Ter} - \text{NAs}]^+$, 438 $[\text{M} - \text{N}(\text{iPr})_2]^+$, 503 $[\text{M} - \text{Cl}]^+$, 538 $[\text{M}]^+$.

Synthesis of 2-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-2-arsa-3,7-diaza-tricyclo[5.4.1.0^{3,12}]dodec-3(12)-enylum chloride (6). To a stirred solution of *N*-[2,4-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)-arsane (0.949 g, 2.0 mmol) in diethyl ether (20 mL), a solution of DBU (0.335 g, 2.2 mmol) in diethyl ether (10 mL) is added dropwise at -10 °C over a period of 10 min. The resulting yellow suspension is warmed to ambient temperature and is stirred for ten hours. The resulting colourless suspension is filtered (F4) and the solvent is removed *in vacuo*, resulting in a colourless froth. Recrystallisation from diethyl ether (10 mL) at -25 °C gave a mixture of several compounds from which 2-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-2-arsa-3,7-diaza-tricyclo[5.4.1.0^{3,12}]dodec-3(12)-enylum chloride **6** could be identified by an X-ray crystallographic analysis. A preparative separation was not successful.

Synthesis of 1,3-dichloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)-phenyl]-cyclo-1,3-diarsa-2,4-diazane (7). To a stirred solution of *N*-[2,4-bis-(2,4,6-trimethylphenyl)phenyl]amino-(dichloro)-arsane (4.743 g, 10.0 mmol) in tetrahydrofuran (50 mL), a solution of DBU (1.675 g, 11.0 mmol) in tetrahydrofuran (15 mL) is added dropwise at $-80\text{ }^{\circ}\text{C}$ over a period of 15 min. The resulting yellow suspension is warmed to ambient temperature over a period of four hours. The solvent is removed *in vacuo* and the yellowish residue is extracted with benzene (40 mL) and filtered (F4), resulting in a champagne coloured solution. Removal of solvent *in vacuo* results in a yellowish residue, which is recrystallized from dichloromethane (25 mL) at $-25\text{ }^{\circ}\text{C}$ over a period of 16 h. Removal of the supernatant by syringe and drying *in vacuo* yields 2.285 g (5.22 mmol, 52%) of **7** as a yellowish crystalline solid. Mp $259\text{ }^{\circ}\text{C}$ (dec.). Anal. calc.% (found): C, 65.84 (65.79); H, 5.76 (5.73); N, 3.20 (3.20). ^1H NMR ($25\text{ }^{\circ}\text{C}$, CD_2Cl_2 , 250.13 MHz): $\delta = 1.92$ (s, 6H, CH_3), 2.00 (s, 6H, CH_3), 2.44 (s, 6H, CH_3), 6.65 (m, 2H, *m*-CH-Ph), 6.77 (s, 2H, *m*-CH-Mes), 6.83 (s, 2H, *m*-CH-Mes), 6.91 (m, 1H, *p*-CH-Ph). ^{13}C $\{^1\text{H}\}$ NMR ($25\text{ }^{\circ}\text{C}$, CD_2Cl_2 , 75.5 MHz): $\delta = 20.8$ (s, CH_3), 21.9 (s, CH_3), 22.0 (s, CH_3), 122.5 (s, aryl-CH), 129.3 (s, aryl-CH), 129.7 (s, aryl-CH), 131.4 (s, aryl-CH), 131.5, 135.3, 138.2, 138.9, 138.9, 139.7. IR (ATR, 32 scans): 3063 (w), 3034 (w), 2975 (w), 2915 (m), 2853 (w), 2732 (w), 1610 (w), 1574 (w), 1481 (w), 1449 (m), 1402 (s), 1377 (m), 1225 (s), 1187 (m), 1097 (w), 1080 (m), 1032 (m), 1003 (m), 952 (w), 874 (s), 846 (s), 820 (s), 791 (s), 753 (s), 744 (s), 672 (m), 644 (m), 588 (m), 568 (m), 559 (m), 546 (m), 535 (m). Raman (100 mW, $25\text{ }^{\circ}\text{C}$, 161 scans, cm^{-1}): = 3039 (5), 2982 (3), 2919 (10), 2859 (3), 2734 (2), 1611 (3), 1577 (3), 1477 (1), 1412 (3), 1377 (2), 1302 (3), 1267 (3), 1189 (1), 1160 (1), 1088 (1), 1031 (1), 1005 (1), 947 (1), 740 (1), 689 (1), 565 (2), 518 (1), 460 (1), 424 (2), 380 (1), 314 (3), 274 (1), 233 (1), 177 (2), 145 (2). MS (CI, m/z): 330 [Ter – NH_3] $^+$, 708 [M – Cl – Mes – CH_3 + 2H] $^+$, 804 [M – 2Cl] $^+$, 839 [M – Cl] $^+$, 876 [M + H] $^+$.

Synthesis of *N,N,N'*-[Tris-(trimethylsilyl)]hydrazino-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]imino-phosphane (8). A solution of *N*-lithio-*N,N,N'*-[tris(trimethylsilyl)]hydrazide (0.534 g, 2.1 mmol) in diethyl ether (10 mL) was added dropwise to a stirred solution of *N,N*-bis-dichlorophosphane-2,6-bis-(2,4,6-trimethylphenyl)aniline (**1**) (0.531 g, 1.0 mmol) in diethyl ether (20 mL) at $0\text{ }^{\circ}\text{C}$ over a period of ten minutes, resulting in a yellow solution and a colourless precipitate. The slurry was then warmed to ambient temperature and stirring was continued for two hours. The solvent was removed *in vacuo*, and the yellow residue was extracted in 10 ml *n*-hexane and filtered (F4). The solution was concentrated to incipient crystallization. Crystallization at $-45\text{ }^{\circ}\text{C}$, filtration (F4) and drying *in vacuo* yields 0.575 g (95%) of **8** as a yellow crystalline solid. Mp $155\text{ }^{\circ}\text{C}$ (dec.). Anal. calc.% (found): C, 65.40 (64.85); H, 8.65 (8.94); N, 6.93 (6.93). $^{31}\text{P}\{^1\text{H}\}$ NMR ($25\text{ }^{\circ}\text{C}$, CD_2Cl_2 , 121.5 MHz): $\delta = 322.6$. ^1H NMR ($25\text{ }^{\circ}\text{C}$, CD_2Cl_2 , 500.13 MHz): $\delta = -0.11$ (s, 9H, $\text{NSi}(\text{CH}_3)_3$), -0.06 (s, 18H, $\text{N}(\text{Si}(\text{CH}_3)_2)_2$), 2.00 (s, 12H, *o*- CH_3), 2.25 (s, 6H, *p*- CH_3), 6.83 (s, 4H, *m*-CH-Mes), 6.97–6.99 (m, 3H). $^{29}\text{Si}\{^1\text{H}\}$ NMR ($25\text{ }^{\circ}\text{C}$, CD_2Cl_2 , 99.4 MHz): $\delta = 11.8$ (s, $\text{N}(\text{Si}(\text{CH}_3)_2)_2$), 15.1 (s, $\text{NSi}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($25\text{ }^{\circ}\text{C}$, CD_2Cl_2 , 75.5 MHz): $\delta = 1.10$ ($\text{NSi}(\text{CH}_3)_3$), 2.39 (d, $J(^{13}\text{C}-^{31}\text{P}) = 1.8\text{ Hz}$, $\text{N}[\text{Si}(\text{CH}_3)_2]$), 21.3–21.4 (m, *o*- CH_3 /*m*- CH_3), 121.6 (CH), 128.5 (CH), 129.1

(CH), 131.5 (d, $J(^{13}\text{C}-^{31}\text{P}) = 8.0\text{ Hz}$), 136.6 (s), 136.9 (s), 138.9 (s), 145.1 (d, $J(^{13}\text{C}-^{31}\text{P}) = 13.5\text{ Hz}$). Raman (50 mW, $25\text{ }^{\circ}\text{C}$, 8 scans, cm^{-1}): = 3045 (3), 3018 (3), 2960 (5), 2905 (10), 1614 (2), 1585 (4), 1415 (8), 1380 (2), 1297 (7), 1096 (2), 1036 (1), 957 (1), 643 (2), 577 (3), 524 (2), 449 (2), 391 (2), 331 (1), 235 (3). IR (ATR, $25\text{ }^{\circ}\text{C}$, cm^{-1}): 2953 (m), 2910 (w), 2854 (w), 1612 (w), 1580 (w), 1574 (w), 1411 (m), 1374 (w), 1293 (m), 1248 (s), 1090 (w), 1032 (w), 953 (s), 921 (s), 834 (s), 817 (s), 768 (s), 753 (s), 739 (w), 679 (m), 666 (m), 641 (m), 619 (m), 599 (m), 588 (m). MS (EI, m/z , $>10\%$): 41 (21) [C_3H_5] $^+$, 43 (23), 49 (21), 57 (35) [C_4H_6] $^+$, 73 (84) [SiMe_3] $^+$, 84 (25), 97 (13), 112 (23), 130 (16) [$\text{N}(\text{SiMe}_3)_2$ + H] $^+$, 146 (23) [$(\text{SiMe}_3)\text{N} - \text{SiMe}_2 + \text{H}$] $^+$, 205 (27) [PN(TMS) – N(TMS)] $^+$, 232 (24) [N(SiMe₃) – N(SiMe₃)₂ – Me] $^+$, 247 (14) [N(SiMe₃) – N(SiMe₃)₂] $^+$, 277 (100) [P – N(SiMe₃) – N(SiMe₃)₂ – H] $^+$, 329 (32) [Ter – NH] $^+$, 310 (18) [Ter – 3H] $^+$, 358 (71) [Ter – NP] $^+$, 386 (14) [M – (SiMe₃)₃] $^+$, 430 (34) [M – N(SiMe₃)₂ – Me] $^+$, 445 (32) [M – N(SiMe₃)₂] $^+$, 590 (91) [M – Me] $^+$, 605 (81) [M] $^+$.

X-ray Structure Determination. X-ray quality crystals of all compounds were selected in Kel-F-oil (Riedel deHaen) or Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 173(2) K during measurement. The data was collected on a Bruker-Nonius Apex X8 CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$). The structures were solved by direct methods (*SHELXS-97*)⁴⁰ and refined by full-matrix least squares procedures (*SHELXL-97*)⁴¹. Semi-empirical absorption corrections were applied (*SADABS*)⁴². All non hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model. All N bound hydrogen were refined freely. The AsClN(*i*Pr)₂ unit in **5** was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.7144(9)/0.2856(9)).

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5.2 The *N,N*-Bis-terphenyl-amino-phosphenium Cation - A Sensitive Probe For The Interactions With Different Anions

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The *N,N*-Bis-terphenyl-amino-phosphenium Cation - A Sensitive Probe For The Interactions With Different Anions[†]

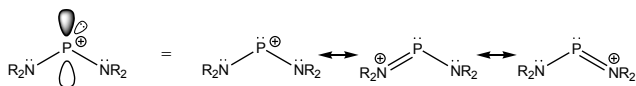
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Abstract. A series of salts containing the terphenyl-substituted bis(amino)phosphenium cation with different anions (F⁻, Cl⁻, [CF₃CO₂]⁻, [CF₃SO₃]⁻, [B(C₆F₅)₄]⁻, [GaCl₄]⁻, [SbF₆]⁻, [Al(OCH(CF₃)₂)₄]⁻ and the carborate [CHB₁₁H₅Br₆]⁻) has been prepared utilizing different synthetic protocols. All products have been fully characterised spectroscopically and by single-crystal X-ray diffraction studies. A detailed analysis of the interionic interactions and their influence on the molecular structure of the phosphenium cation displays a strong dependency on the capability of the anion to enter the pocket generated by the bulky terphenyl substituents.

Introduction

The first dicoordinate phosphorus cation, observed in so called phosphamethine cyanines, was reported by Dimroth and Hoffmann as early as 1964.¹ The term phosphenium ions has been introduced to indicate a positive charge at the two-coordinate phosphorus center with a formally vacant 3p orbital.² Phosphenium cations are related to carbenes of the type R¹-C-R² where isovalence electronic P⁺ replaces the central carbon. As is well-known, carbenes are stabilized best when R¹ and R² are atoms or groups such as NR₂ which can serve as π-electron donors to the carbon.³ The same holds true for isovalence electronic phosphenium analogs (Scheme 1).

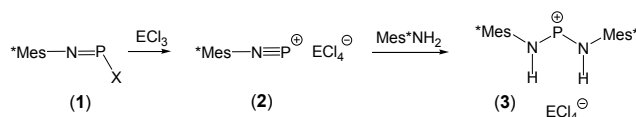


Scheme 1. Stabilization of phosphenium ions by π-electron donors as in [R₂N-P-NR₂]⁺ (R = substituent)

Parry *et al.* reported the first examples of acyclic phosphenium ions [(Me₂N)₂P]⁺ and [(Me₂N)(Cl)P]⁺ which were obtained by chloride abstraction from the corresponding amino(chloro)phosphanes employing Lewis acids such as ECl₃ (E = Fe, Al, Ga).⁴ Structural data of acyclic phosphenium ions are still limited to only a few amino substituted examples: [(Pr₂N)₂P]⁺[X]⁻ (X = [AlCl₄]⁻, [GaCl₄]⁻, [B(C₆F₅)₄]⁻).^{5,6}

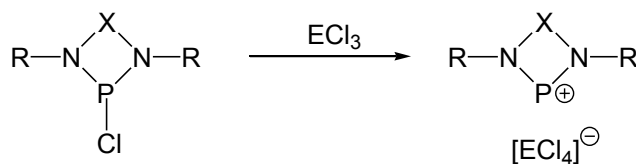
Niecke and Kroher showed that electrophilic attack of AlCl₃ on the P=N double bond of the amino(imino)phosphane R₂N-P=NR (R = Me₃Si) generates the internal salt R₂N-P⁽⁺⁾-N(Al⁽⁻⁾Cl₃)R with a formal positive charge at the phosphorus atom and the negative charge at the aluminium atom.⁷ This internal salt readily eliminates Me₃Si-Cl upon heating leading to a four-membered (Cl₂)Al⁽⁻⁾-N(Me₃Si)-P⁽⁺⁾-N(Me₃Si) heterocycle. Moreover, it was shown that reaction of the chloro(imino)phosphane 2,4,6-^tBu₃C₆H₂-N=P-Cl with AlCl₃, leads to the stable salt [2,4,6-^tBu₃C₆H₂-N≡P]⁺[AlCl₄]⁻ bearing a formal PN triple bond,⁸ instead of the expected phosphanylium adduct, 2,4,6-^tBu₃C₆H₂-N(Al⁽⁻⁾Cl₃)-P⁽⁺⁾-Cl. Detailed studies have shown that structure and reactivity of iminophosphanes 2,4,6-^tBu₃C₆H₂-N=P-X are considerably

dependent on the substituent X bonded to the two-coordinated phosphorus *e.g.* with respect to *cis/trans* conformation.⁹



Scheme 2. Synthesis of Mes*3[EC₁₄] (E = Al, Ga).^{10,11}

The only known aryl substituted bis(amino)phosphenium cation **3** (R = ^tBu, E = Al, Scheme 2) was introduced by Niecke¹⁰ and coworkers and further studied by Burford *et al.*¹¹ As shown in Scheme 2 the phosphadiazonium cation [Mes*NP]⁺ (**2**) reacts quantitatively with Mes*NH₂ (Mes* = 2,4,6-tri-^tbutylphenyl-), yielding ECl₄⁻ salts with the bis(amino)phosphenium cation (Mes***3**). The solid-state structures of Mes*3[GaCl₄] and Mes*3[AlCl₄] were confirmed by X-ray crystallography and structural parameters of the cation are essentially identical.



Scheme 3. Synthesis of phosphorus carbene analogs by chloride abstraction: (i) X = (CH₂)₂ 1,3,2-diazaphospholenium ion with (R = alkyl, aryl, E = Al, Ga); (ii) X = P-Cl chloro-*cyclo*-1,3-diphospha-2,4-diazanium ion with (R = Ter, E = Ga).^{13,15}

Salts containing a five-membered heterocyclic cation with a formal bis(amino)phosphenium fragment (R₂N-P⁽⁺⁾-NR₂) are called 1,3,2-diazaphospholenium ions.^{12,13} They are isoelectronic with imidazolyl carbenes,¹⁴ are stabilized by similar electronic factors and can be obtained by chloride abstraction with Lewis acids in 2-chloro-1,3,2-diazaphospholenes (Scheme 3).¹³ Chloride abstraction was also successfully applied in the isolation of salts bearing the

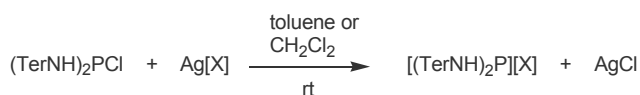
cyclo-1,3-diphospha-2,4-diazanium ion, which can also be regarded as carbene analog (Scheme 3).¹⁵

The structure and bonding of bis(amino)phosphenium ions has been intensively studied.^{2b,10,11} In solution especially ³¹P NMR spectroscopy is a powerful tool for the identification of phosphonium ions. As might be anticipated from the low coordination number and the presence of a formal positive charge at phosphorus, the ³¹P chemical shifts of phosphonium ions are rather deshielded and fall in the range +100 to +520 ppm.^{2b} For instance in [(Me₂N)(^tBu)P]⁺ a strongly deshielded ³¹P chemical shift is observed (513 ppm)¹⁶ which can be ascribed to the inability of the ^tBu to donate π-electrons. Steric effects also play a role in determining the ³¹P chemical shifts. Interestingly, ³¹P chemical shifts of the bis(amido)-substituted cations increase with increasing ligand size.^{2b} This trend has been interpreted on the basis of progressive twisting of the R₂N groups with respect to the P⁺ center, thereby reducing the N(2p)-P(3p) overlap with increasing steric strain.¹⁶ To the best of our knowledge the influence of the anion with respect to the cation structure and physical properties has not been studied comprehensively. As model system we have chosen the *N,N*-bis-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-phosphenium ion ([TerNH₂]⁺), R = mesityl in Scheme 2) since its salts are usually easily obtained and allow hydrogen bonding although bearing the sterically demanding terphenyl group. To get further insight into the anion influence we have prepared [(TerNH₂)₂P]⁺ (Ter3) with the following formal counterions: F⁻, Cl⁻, [CF₃CO₂]⁻,¹⁷ [CF₃SO₃]⁻,¹⁸ [B(C₆F₅)₄]⁻,^{19,20,21} [GaCl₄]⁻,^{11,19,22} [SbF₆]⁻,²³ [Al(OCH(CF₃)₂)₄]⁻¹⁹ and the carborate [CHB₁₁H₅Br₆]⁻.^{19,24} Here, we want to report on the anion influence resulting in small differences in the structural data set, but may have a huge influence on physical properties such as melting points or NMR data.

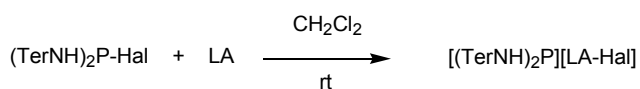
Results and Discussion

Synthesis and spectroscopic studies

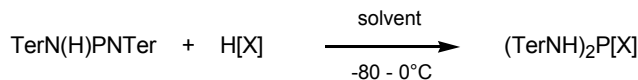
Convenient synthetic routes to salts bearing the [(TerNH₂)₂P]⁺ ion (Ter3) include salt-elimination reactions of (TerNH₂)₂P-Cl with Ag[X] (X = weakly coordinating anion,¹⁹ Scheme 4), halogen abstraction by the action of a Lewis acid such as GaCl₃ or SbCl₅ (Scheme 5) or protonation of imino(amino)phosphane TerN(H)P=NTer (Scheme 6). A synthetic protocol analogous to the generation of Mes*3-salts as illustrated in Scheme 2 cannot be applied to obtain Ter3-salts since the starting material Ter-N=P-Cl is not accessible.



Scheme 4. Synthesis of Ter3-salts via salt elimination (X = [CF₃CO₂]⁻, [CF₃SO₃]⁻, [B(C₆F₅)₄]⁻, [Al(OCH(CF₃)₂)₄]⁻, [CHB₁₁H₅Br₆]⁻ and [SbF₆]⁻).

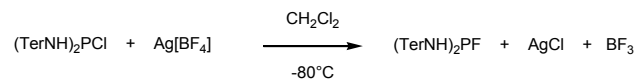


Scheme 5. Synthesis of Ter3-salts via halide abstraction [LA-Hal] = [GaCl₄]⁻.



Scheme 6. Synthesis of Ter3-salts via protonation of terphenyl-substituted imino(amino)phosphane (X = Cl⁻, [CF₃CO₂]⁻, [CF₃SO₃]⁻, [B(C₆F₅)₄]⁻).²⁵

For the salt elimination reaction usually the silver salts are utilized. These reactions were carried out either in toluene or CH₂Cl₂ at ambient temperatures. The formation of Ter3 cation is easily followed by UV/VIS due to its prominent orange color (Table 1). The application of this methods is restricted to the synthesis of salts containing the weakly coordinating anions X = [CF₃CO₂]⁻, [CF₃SO₃]⁻, [B(C₆F₅)₄]⁻, [Al(OCH(CF₃)₂)₄]⁻ and [CHB₁₁H₅Br₆]⁻. Interestingly, while this reaction nicely works with Ag[B(C₆F₅)₄]⁻, for the non-fluorinated species Ag[B(C₆H₅)₄]⁻ no reaction was observed. In case of the fluoro-metallate anions [SbF₆]⁻ and [BF₄]⁻ the synthesis was not successful even if temperatures below -80 °C were applied. Initially, the Ter3 cation is formed as indicated by the orange color which, however, quickly diminishes when the temperature is raised to ambient temperatures. For Ter3[SbF₆] only a very few orange crystals could be isolated besides the major product which was identified as 2,6-bis(2,4,6-trimethylphenyl)anilinium hexafluoroantimonate [TerNH₃][SbF₆].^{26a} The synthesis of Ter3[BF₄] does not work due to a rapid Cl/F exchange reaction (Scheme 8) even at low temperatures, albeit the Ter3 cation was also observed initially. Obviously, the [(TerNH₂)₂P]⁺ ion (Ter3) is the stronger Lewis acid compared to BF₃; hence fluoride ion exchange is observed.



Scheme 8. Reaction of Ter3Cl with Ag[BF₄]

Halide abstraction was attempted with GaCl₃ and SbCl₅ starting from Ter3Cl as well as with SbF₅ in the reaction with Ter3F. Only the reaction with GaCl₃ gave in good yields the desired product Ter3[GaCl₄], while for SbF₅ and SbCl₅ only Ter-N(H)-PF₂ and Ter-N(H)-P-Cl₂, respectively, could be identified as the major product. The protonation reaction of terphenyl-substituted imino(amino)phosphane was successfully applied in the preparation of Ter3[X] (X = Cl⁻, [CF₃CO₂]⁻, [CF₃SO₃]⁻, [B(C₆F₅)₄]⁻). It is noteworthy that a large excess of acid during protonation or hydrolysis leads to the formation of the ammonium salts [TerNH₃][X] for all Ter3[X].

Very pure Ter3Cl is obtained in the silylether elimination reaction of Ter3[X] (X = [CF₃CO₂]⁻ and [CF₃SO₃]⁻) with Me₃SiCl. Here the driving force is the formation of Me₃SiOC(O)CF₃ and Me₃SiOS(O₂)CF₃, respectively. It is interesting to mention, that Ter3[Cl] is not directly accessible from TerNH₂ and PCl₃ in the presence of bases such as Et₃N, DBU, and ⁿBuLi due to the formation of by-products (e.g. TerN(H)-P-Cl₂, [TerN-PCl]₂, TerN(H)-P=N-Ter). Thus the best way to Ter3Cl goes via TerN(H)-P-Cl₂ and 2 equiv. of Ter-NHLi leading to TerN(H)-P=N-Ter (60 % yield). Protonation with HCl yields directly Ter3[Cl] (Scheme 6).

Table 1 Spectroscopic data (Mp., ³¹P, ¹H, ν_{NH}, ν_{PN} and UV/VIS) of Ter3[X] (X = F⁻, Cl⁻, [CF₃CO₂]⁻, [CF₃SO₃]⁻, [B(C₆F₅)₄]⁻, [GaCl₄]⁻, [SbF₆]⁻, [Al(OCH(CF₃)₂)₄]⁻ and [CHB₁₁H₅Br₆]⁻), and for comparison TerN(H)PNTer, Mes*3[Y] (Y = [GaCl₄]⁻, [F₃CSO₃]⁻)

Compound	T _{dec} °C	³¹ P{ ¹ H} ppm	¹ H (NH) ppm	ν _{NH} cm ⁻¹	ν _{PN} cm ⁻¹	VIS nm		UV nm		
TerN(H)PNTer	311	278.0	6.34	3364	3289	1412	406	336	289	247
Ter3F	225	119.7 ^a	3.79	3334	3292	1418	-	-	292	249
Ter3Cl	265 ^e	129.9	4.08	3309	3285	1419	-	-	297	248
Ter3[CF ₃ CO ₂]	190 ^f	116.7	4.38	3314	3298	1422	-	-	290	250
Ter3[CF ₃ SO ₃]	255	261.0	9.67	3341	3234	1426	438	363	292	246
Ter3[B(C ₆ F ₅) ₄]	244	249.1	7.31	-	3287	1419	422	358	296	260
Ter3[GaCl ₄]	215	250.0	7.38	3333	3261	1416	438	361	-	255
Ter3[SbF ₆] ^d	-	249.0	7.39	-	-	-	-	-	-	-
Ter3[Al(OCH(CF ₃) ₂) ₄]	273	249.0	7.2	3319	3255	1426	435	360	297	246
Ter3[CHB ₁₁ H ₅ Br ₆]	225	249.6	7.41	3330	3173	1428	435	358	296	245
Mes*3[GaCl ₄] ^b	152	272.0	9.94	-	3175	1419	-	-	-	-
Mes*3[CF ₃ SO ₃] ^c	-	279.7	11.6	-	-	-	-	-	-	-

^a duplet due to ³¹P-¹⁹F coupling; ^b taken from reference ¹¹; ^c taken from reference ^{9c}; ^d was only characterized by Xray and NMR studies due to fast decomposition; ^e decomposition temperature = m.p.; ^f m.p. 177°C.

All Ter3[X] compounds have been fully characterized by CHN-analysis, ³¹P and ¹H NMR spectroscopy, IR and UV/VIS spectroscopy and X-ray structure analysis. Table 1 summarizes the spectroscopic data.

According to UV/VIS studies all ionic Ter3[X] species are orange at ambient temperatures due to a n_{NPN}→π_{NPN}* excitation. Besides this strong n_{NPN}→π_{NPN}* excitation, which is not observed for the covalently bound species, a couple of other π_{ter}→π*_{ter} excitations are observed. The PN stretching mode, which is influenced by the substituent, structural situation around the NPN unit and the extent of the hydrogen bonding, is found in the typical region between 1400-1500 cm⁻¹ (cf. [Mes*NP]⁺[GaCl₄]⁻: 1494; Mes*N=P-Cl: 1437 cm⁻¹).²⁷

All Ter3[X] compounds are astonishingly thermally stable, moisture sensitive but stable under argon atmosphere over a long period as solids and in solvents such as CH₂Cl₂, benzene or toluene at ambient temperature. They can be prepared in bulk and are long stable when stored in a sealed tube. While the covalently bound Ter3[X] (X = F⁻, Cl⁻, [CF₃CO₂]⁻) can be handled in air for a short time, all Ter3[X] salts decompose quickly as indicated by the color change from orange to colorless. For example, it was shown that e.g. Ter3[Al(OCH(CF₃)₂)₄] slowly hydrolyses over a period of 7 days in the freezer (-25 °C) yielding the internal salt (TerNH)₂P⁽⁺⁾(H)-O-Al⁽⁻⁾(OCH(CF₃)₂)₃.^{26b}

Besides Ter3Cl and Ter3[CF₃CO₂] for which a true melting point was found (265 °C and 177°C), DSC studies displayed only decomposition points ranging between 190°C (Ter3[CF₃CO₂]) and 273°C (Ter3[Al(OCH(CF₃)₂)₄]). It is interesting to note that Mes*3[GaCl₄] is thermally significantly less stable than its terphenyl substituted counterpart (152 vs. 215 °C). It can be assumed that the terphenyl group provides a better kinetic protection.

Xray studies (see below) and computations clearly reveal the dominant polar covalent bonding in Ter3[X] (X = F⁻, Cl⁻, [CF₃CO₂]⁻) and ion pair formation in all the other species. Solution NMR data display a similar picture. While a strong upfield shift is observed for Ter3[X] (X = F⁻, Cl⁻, [CF₃CO₂]⁻) in the ¹H (δ[¹H]: 3.8 - 4.4) and ³¹P NMR spectra (δ[³¹P]: 117 - 130), for all other species except from Ter3[CF₃SO₃] the analogous resonances are found in the downfield

region expected for phosphonium ions^{2b} at δ[³¹P]: 249 - 250 and δ[¹H]: 7.2 - 7.4, respectively. Since for all ionic species almost the same chemical shifts are observed, it can be assumed that in solution solvated ions are present with the exception of Ter3[CF₃SO₃] for which ion pairing is indicated. In the ¹H spectrum of Ter3[CF₃SO₃] the hydrogen shift is found at 9.67 ppm which can be attributed to strong NH...O(O₂)SCF₃ hydrogen bonds being responsible for the ion pairing. Also the considerably downfield shift in the ³¹P spectrum (261 vs. 250 ppm, Table 1) supports this argument along with the Xray data for the solid state. In contrast to Ter3[GaCl₄], which forms separated ions in solution, the analogous Mes*3[GaCl₄] forms ion pairs as indicated by the ¹H and ³¹P NMR data (Table 1, δ[¹H]: 7.38 vs. 9.94). As shown below in the Mes*3[GaCl₄] compound stronger hydrogen bonds is observed compared to Ter3[GaCl₄]. In agreement with ion pairing for Ter3[CF₃SO₃] also Mes*3[CF₃SO₃] displays an even stronger downfield shift (δ[¹H]: 9.67 vs. 11.60).

Structural Elucidation

Suitable crystals for single-crystal X-ray diffraction studies of Ter3[X] compounds ([X] = F⁻, Cl⁻, [CF₃CO₂]⁻, [CF₃SO₃]⁻, [B(C₆F₅)₄]⁻, [GaCl₄]⁻, [SbF₆]⁻, [Al(OCH(CF₃)₂)₄]⁻ and the carborate [CHB₁₁H₅Br₆]⁻), Mes*3[GaCl₄] and (TerNH)₂P(H)OAl(OCH(CF₃)₂)₃.^{26b} were obtained by crystallization of saturated solutions at low temperature. Due to a strong disorder problem in the structure of TerN(H)PNTer we abstain from a detailed discussion. Crystallographic and further details are given in the supporting information.

While the salt Ter3[B(C₆F₅)₄] crystallised as a solvate with one molecule of CH₂Cl₂ per formula unit, Ter3[Al(OCH(CF₃)₂)₄] with 1/2 molecule fluorobenzene and Ter3[CHB₁₁H₅Br₆] with 1.5 molecules of benzene, all other Ter3[X] compounds crystallised solvent-free. The molecular structures of all considered Ter3[X] species and for comparison Mes*3[GaCl₄], and (TerNH)₂P(H)OAl(OCH(CF₃)₂)₃ are shown in Figures 1-3 and Figure S0 (Supporting Information). Selected bond lengths and angles are summarized in Table 2 together with the previously reported structural data for Mes*3[ECl₄] (E = Al, Ga).^{10,11} For Mes*3[GaCl₄] we have repeated the structural analysis to get a consistent set of structural data of equal quality.

Table 2 Selected structural data of Ter3[X] (X = F⁻, Cl⁻, [CF₃CO₂]⁻, [CF₃SO₃]⁻, [B(C₆F₅)₄]⁻, [GaCl₄]⁻, [SbF₆]⁻, [Al(OCH(CF₃)₂)₄]⁻ and [CHB₁₁H₅Br₆]⁻), and for comparison Mes*3[EC₄] (E = Ga, Al) and [(TerNH)₂P(H)OAl(OCH(CF₃)₂)₃]

Compound	N1–P / Å	N2–P / Å	N1–C1 / Å	<N–P–N / °	<τ _{aryl} / ° ^c
Ter3F	1.704(6)	1.663(1)	1.38(2)	91.6(4)	54.3
Ter3Cl	1.697(2)	1.591(2)	1.412(2)	94.6(1)	56.3
Ter3[CF ₃ CO ₂]	1.675(2)	1.687(2)	1.423(3)	94.84(9)	65.4
Ter3[CF ₃ SO ₃]	1.623(3)	1.609(3)	1.443(4)	104.9(1)	89.3
Ter3[B(C ₆ F ₅) ₄]	1.630(3)	1.623(3)	1.440(4)	99.6(2)	87.4
Ter3[GaCl ₄]	1.635(1)	1.626(1)	1.428(2)	99.61(6)	74.5
Ter3[SbF ₆]	1.635(2)	1.635(2)	1.426(3)	98.0(2)	79.3
Ter3[Al(OCH(CF ₃) ₂) ₄] ^a	1.628(3)	1.635(3)	1.431(4)	98.5(2)	89.9
Ter3[CHB ₁₁ H ₅ Br ₆]	1.619(3)	1.637(3)	1.435(4)	96.9(2)	89.9
Ter3[CHB ₁₁ H ₅ Br ₆]	1.625(3)	1.630(3)	1.426(4)	96.3(1)	69.4
(TerNH) ₂ P(H)OAl(OCH(CF ₃) ₂) ₃	1.625(2)	1.627(2)	1.435(2)	115.09(9)	35.3
Mes*3[GaCl ₄]	1.601(3)	1.601(3)	1.469(4)	105.2(2)	37.0
Mes*3[AlCl ₄] ^b	1.611	1.611	1.474	103.7	-

^a two independent molecules; ^b no standard deviations available, see reference ¹⁰; ^c τ_{aryl} = torsion angle between the two planes composed of the central aryl of the terphenyl or Mes* group.

For all Ter3[X] species the central phenyl rings of the terphenyl group attached to the nitrogen atom try to form an almost orthogonal arrangement (torsion angles between 54 – 90°, Table 2) leading to the formation of a pocket generated by four aryl-substituents (in 2 and 6 position) in which the N(H)PN(H) moiety is embedded and sterically protected (Figure 2). Thus for instance, dimerization *e.g.* for TerN(H)PNTer and formation of *cyclo*-diphosphadiazanes is impossible. The N(H)PN(H) moiety is not coplanar to the central aryl rings of the terphenyl group located but twisted (*e.g.* C1_{aryl}–C2_{aryl}–N–P dihedral angles in Ter3[GaCl₄] between 29 - 38°). Thus delocalization of NPN π electron density into the central aryls is limited.

As displayed in Table 2 and Figure 1 in all covalently bound Ter3[X] (X = F⁻, Cl⁻, [CF₃CO₂]⁻) species the phosphorus atom adopts a trigonal pyramidal environment. In all other species the structure consist of separated [Ter3]⁺ and [X]⁻ ions with several different interionic contacts (see below). Here both nitrogen atoms and the di-coordinated phosphorus atom of the N(H)PN(H) moiety

sit in a trigonal planar environment with PN bond lengths ranging from 1.619 – 1.635 Å, which are significantly shorter than those found for the covalently bound Ter3[X] species (*cf.* Ter3[F]: 1.704(6) and 1.663(1) Å, Table 2). For Ter3[CF₃SO₃] a slightly shorter PN bond length is found with 1.609(3) Å along with a considerably larger NPN angle which can be attributed to strong NH···O hydrogen bonds (see below). The short PN bond lengths (average 1.628 Å) of the ionic Ter3[X] species indicate partial double bond character and lie in the expected range for amino(imino)phosphanes, for example P=N 1.545(6) and P=N 1.632(6) in MeN(H)–P=N–Mes* (Σ*r*_{cov}(P–N) = 1.82 and Σ*r*_{cov}(P=N) = 1.62 Å).^{9d,28,29} It is interesting to note, that already for the covalently bound Ter3[X] species partial PN double bond character can be discussed due to hyperconjugation.³⁰ As expected for the covalently bound Ter3[X] species small NPN angles between 91 - 95° were observed, while significantly larger NPN angles are measured for the ionic Ter3[X] compounds (NPN 96 - 100°) except from Ter3[CF₃SO₃] for which a larger angle was measured (104.9°).

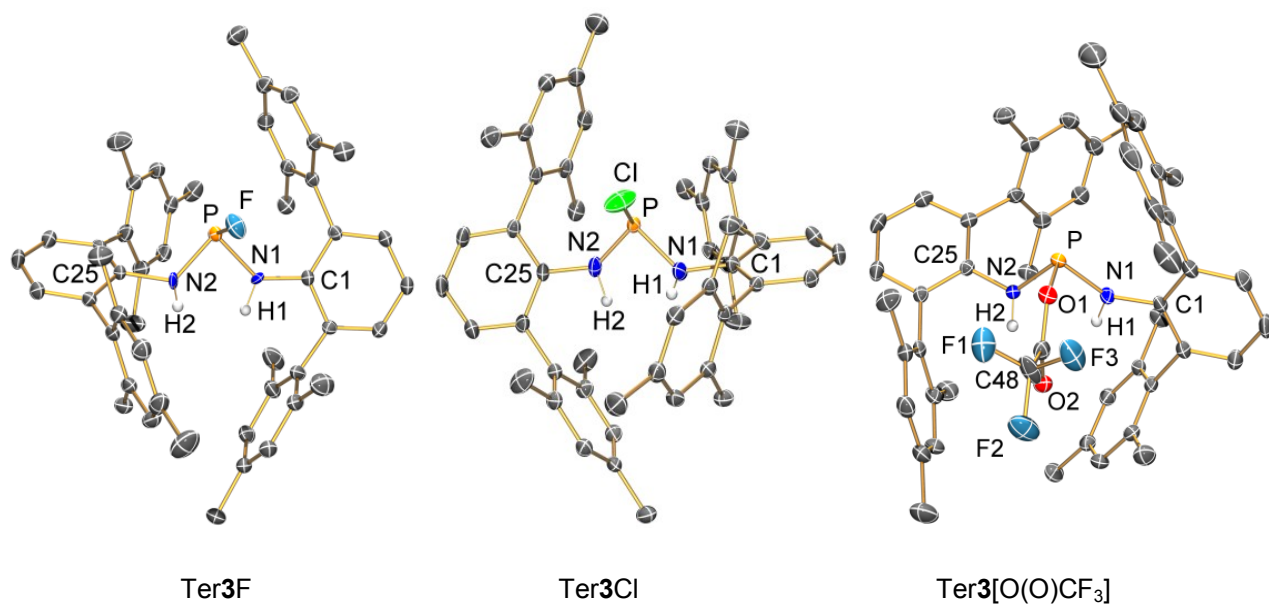
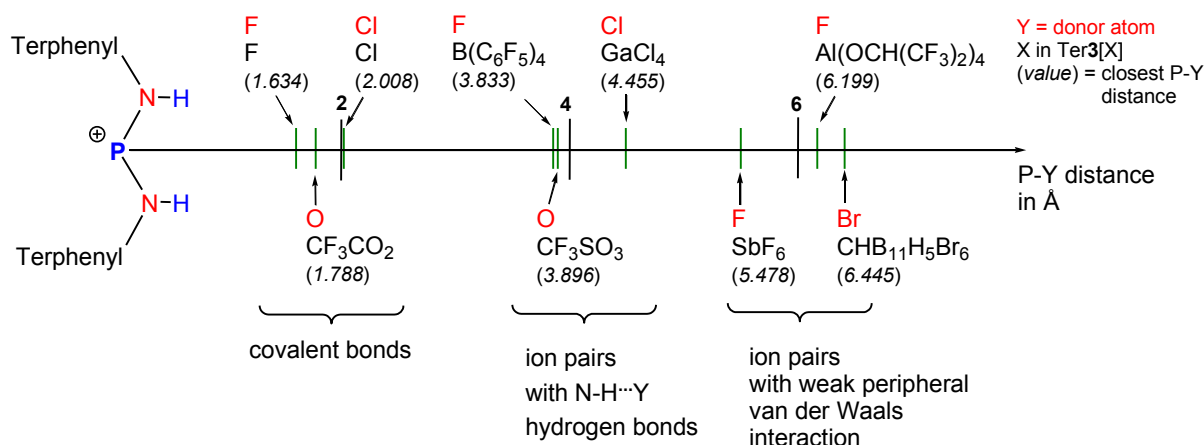


Fig. 1 ORTEP drawing of covalently bound Ter3[X] species (X = F⁻, Cl⁻, [CF₃CO₂]⁻). Thermal ellipsoids with 30% probability at 173 K (hydrogen atoms of the terphenyl group omitted).

For the interaction between the formal fragments $[\text{Ter}3]^+$ and $[\text{X}]^-$ in $\text{Ter}3[\text{X}]$ three strategies are employed: (i) Polar covalent bonding with the phosphorus atom of $[\text{Ter}3]^+$ is found for small nucleophilic anions such as F^- , Cl^- , and $[\text{CF}_3\text{CO}_2]^-$ (Figure 1). (ii) $\text{NH}\cdots\text{Y}$ hydrogen bonding ($\text{Y} = \text{F}, \text{Cl}, \text{O}$; Y donor atom of $[\text{X}]^-$) is found for medium sized anions which are small enough to enter the pocket generated by the terphenyl groups ($[\text{CF}_3\text{SO}_3]^-$), and larger complex anions ($[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{GaCl}_4]^-$), that are capable of partially entering the terphenyl pocket (Figure 2). (iii) Only weak van der Waals interactions with peripheral H-C_{aryl} atoms are observed for large weakly coordinating anions ($[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$, $[\text{SbF}_6]^-$, and $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$), which are simply too big to allow access to the

terphenyl pocket and thus formation of hydrogen bonds is impossible (Figure 3, Scheme 9).

As depicted in Scheme 9 the P–Y distances ($\text{Y} = \text{atom of } [\text{X}]^-$ closest to P) are found in the range between 1.634 ($\text{Y} = \text{F}$, $\text{Ter}3\text{F}$) - 2.008 Å ($\text{Y} = \text{Cl}$, $\text{Ter}3\text{Cl}$) for the covalent species with a typical P–Y single bond (cf. $d(\text{P-F}) = 1.634(3)$ vs. $\Sigma r_{\text{cov}} = 1.66$ Å; $d(\text{P-Cl}) = 2.008(2)$ vs. $\Sigma r_{\text{cov}} = 2.04$ Å; $d(\text{P-O1}) = 1.789(2)$ vs. $\Sigma r_{\text{cov}} = 1.72$ Å), 3.833 ($\text{Y} = \text{F}$, $\text{Ter}3[\text{B}(\text{C}_6\text{F}_5)_4]$) to 4.455 Å ($\text{Y} = \text{Cl}$, $\text{Ter}3[\text{GaCl}_4]$) for species with strong $\text{NH}\cdots\text{Y}$ hydrogen bonds, and 5.478 ($\text{Y} = \text{F}$, $\text{Ter}3[\text{SbF}_6]$) - 6.445 ($\text{Y} = \text{Br}$, $\text{Ter}3[\text{CHB}_{11}\text{H}_5\text{Br}_6]$) for weak van der Waals interaction with peripheral H_{Ter} atoms.



Scheme 9. Interactions between $[\text{Ter}3]^+$ and $[\text{X}]^-$ fragments.

Interestingly, while the PN distances exhibit only insignificant deviations for all ionic $\text{Ter}3[\text{X}]$ species (besides slightly smaller values for $\text{Ter}3[\text{CF}_3\text{SO}_3]$), the NPN angle is a sensitive measure for the magnitude of $\text{NH}\cdots\text{Y}$ hydrogen bonds ($\text{Y} = \text{halogen}, \text{O}$). The stronger these hydrogen bonds are, the larger the NPN angles will be observed e.g. $96.3(1)^\circ$ in $\text{Ter}3[\text{CHB}_{11}\text{H}_5\text{Br}_6]$ with no hydrogen bond at all vs. $104.9(1)^\circ$ in $\text{Ter}3[\text{CF}_3\text{SO}_3]$ with the strongest hydrogen

bond found in the series $\text{Ter}3[\text{X}]$. Also the comparison between $\text{Ter}3[\text{GaCl}_4]$ (99.6°) and $\text{Mes}^*3[\text{GaCl}_4]$ (105.2°) supports this argument since significantly shorter $\text{NH}\cdots\text{Cl}$ contacts are found in $\text{Mes}^*3[\text{GaCl}_4]$ (see below, Table 2, Figure 2), which might be the reason for the different behavior in solution (ion pairing vs. solvated ions, see above).

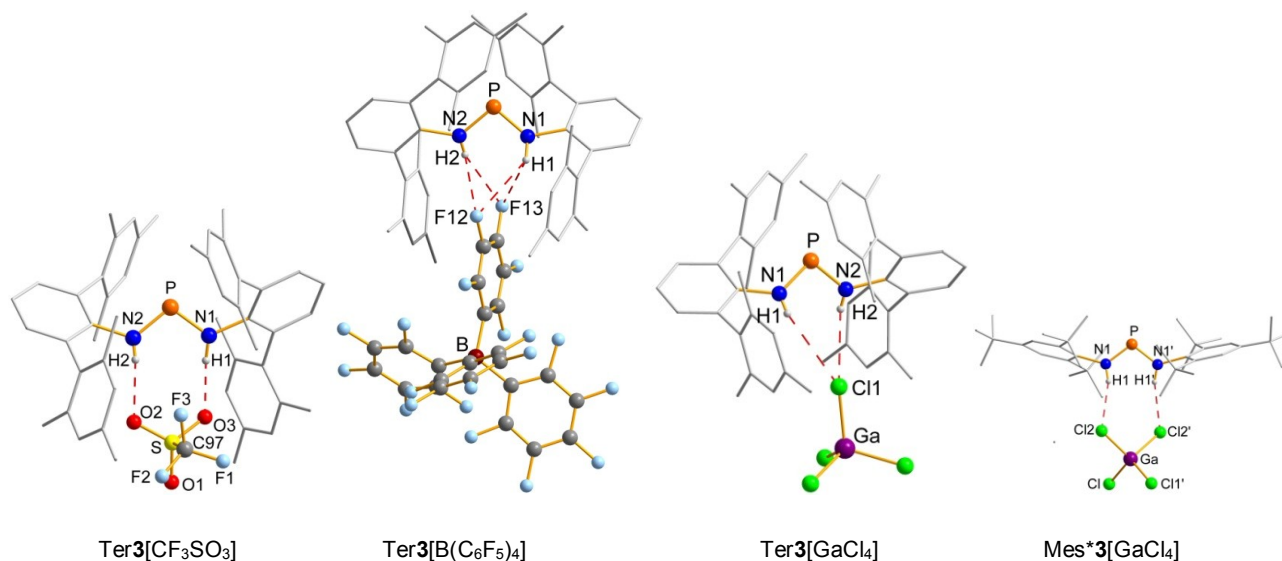


Fig. 2 Hydrogen bonds in $\text{R}3[\text{X}]$ ($\text{R} = \text{Ter}, \text{Mes}^*$).

Let us focus further on the hydrogen bonds. The hydrogen bond may most generally be considered as a three-centre four-electron interaction that stabilizes and is associated with spectroscopic and structure-defining effects.³¹ The classification into weak, strong and very strong is somewhat subjective. However, it is their directionality that makes hydrogen bonds important as crystal structure directors as can be seen in Figure 2. In all three Ter3[X] species ($X = [\text{CF}_3\text{SO}_3]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, and $[\text{GaCl}_4]^-$) the $\text{NH}\cdots\text{Y}$ hydrogen bonds can be classified as strong hydrogen bonds since they dominate the interionic interaction. The strongest hydrogen bonds amongst these three species can be assumed for Ter3[CF₃SO₃] with $\text{N}\cdots\text{O}$ distances of 2.746 (N1–O3) and 2.830 Å (N2–O2) resulting amongst other structural changes into a larger NPN angle (see above). Especially interesting are the hydrogen bonds in Ter3[B(C₆F₅)₄] with $\text{N}\cdots\text{F}$ distances of 3.075 (N1–F13) and 3.228 (N2–F12) Å, since in this case only one C₆F₅ ring of the anion is inside the terphenyl pocket which is reminiscent to the key-lock principle known from biology. Due the parallel arrangement of this C₆F₅ ring with one aryl of both terphenyl groups, further weak van der Waals interaction between $\text{C}_{\text{aryl}}\cdots\text{F}$ (shortest distance 3.547 Å), $\text{C}_{\text{aryl}}\cdots\text{C}$ (shortest distance 3.457 Å) and weak $\text{C}_{\text{methyl}}\cdots\text{H}\cdots\text{F}$ – C_{anion} hydrogen bonds (shortest $\text{C}_{\text{methyl}}\cdots\text{F}$ – C_{anion} 3.327 Å) can be assumed. In case of Ter3[GaCl₄] it is interesting to compare the $\text{N}\cdots\text{H}\cdots\text{Cl}$ – GaCl_3 hydrogen bond and its implication with that in Mes*3[GaCl₄] with respect to steric strain. While in Ter3[GaCl₄] only one Cl atom forms two $\text{N}\cdots\text{H}\cdots\text{Cl}$ bond (N1–Cl1 3.796 and N2–Cl1 3.505 Å), in Mes*3[GaCl₄] two Cl atoms form, in a bidentate fashion, one $\text{N}\cdots\text{H}\cdots\text{Cl}$ bond each, which are identical due to symmetry (3.430 Å, Figure 2). The shorter $\text{N}\cdots\text{H}\cdots\text{Cl}$ distances along with the increase of the NPN angle (Table 2) indicate stronger hydrogen bonds in Mes*3[GaCl₄]. Obviously, in Ter3[GaCl₄] the terphenyl pocket provides less space compared to the situation in Mes*3[GaCl₄] and hence only one Cl atom fits into the pocket. The

strong $\text{N}\cdots\text{H}\cdots\text{Cl}$ – GaCl_3 hydrogen bond in Ter3[GaCl₄] is also manifested by a considerable Ga–Cl bond lengthening for the Cl1 atom (Figure 2) involved in the hydrogen bond (*cf.* Ga1–Cl1 2.1928(4) vs. Ga1–Cl3 2.1632(5), Ga1–Cl4 2.1652(4), Ga1–Cl2 2.1743(4) Å). Also in Mes*3[GaCl₄] two significantly different Ga–Cl bond lengths are found for Ga1–Cl1 2.155(1) and Ga1–Cl2 2.1872(9) Å, with Cl2 and Cl2' additionally involved in hydrogen bonds. The quintessence of this comparison is the fact, that the Mes* group provides a larger steric protection for the α atom attached to the Mes* group (*e.g.* larger Tolman angle for Mes* 228° vs. Ter 206°),³² while the terphenyl group is capable of embedding a larger moiety and thus better protecting the β atom such as for the N(H)PN(H) unit in R3[X] (R = Mes*, Ter) compounds.

It should be noted that besides the discussed interionic hydrogen bonds, short $\text{O2}\cdots\text{N1}$ (3.046) and $\text{O2}\cdots\text{N2}$ (2.885 Å) distances in Ter3[CF₃CO₂] suggesting intramolecular $\text{NH}\cdots\text{O2}$ hydrogen bonds (Figure 1).

Finally, Ter3[X] ($X = [\text{SbF}_6]^-$, $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ and $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$) crystallize poorly³³ indicating only very weak interionic interaction. It is known that cations with C–H bonds in the presence of fluoro-ligand containing anions usually crystallize better, likely through the formation of many assisting H–F contacts (*e.g.* $[\text{Ag}(\text{C}_2\text{H}_4)][\text{Al}(\text{OR}^{\text{F}})_4]$ ($\text{R}^{\text{F}} = \text{C}(\text{CF}_3)_3$),³⁴ or $[\text{H}(\text{OEt}_2)_2][\text{Al}(\text{OR}^{\text{F}})_4]$ ³⁵ salts). For all three Ter3[X] many assisting $\text{C}_{\text{methyl}}\cdots\text{H}\cdots\text{Y}$ ($\text{Y} = \text{F}, \text{Br}$) contacts are detected ($< \Sigma r_{\text{vdw}}(\text{H}\cdots\text{Y})$; 2.9 Å for $\text{Y} = \text{F}$, 3.3 for $\text{Y} = \text{Br}$)³⁶ of which only a few (shortest contacts) are shown for the ion pairs in Figure 3. However, these dispersive interactions are weak and not structure determining. Therefore, the structural parameters of the [Ter3]⁺ cation within the framework of an ensemble of large and weakly coordinating anions such as $[\text{SbF}_6]^-$, $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ and $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ are almost identical (Table 2).

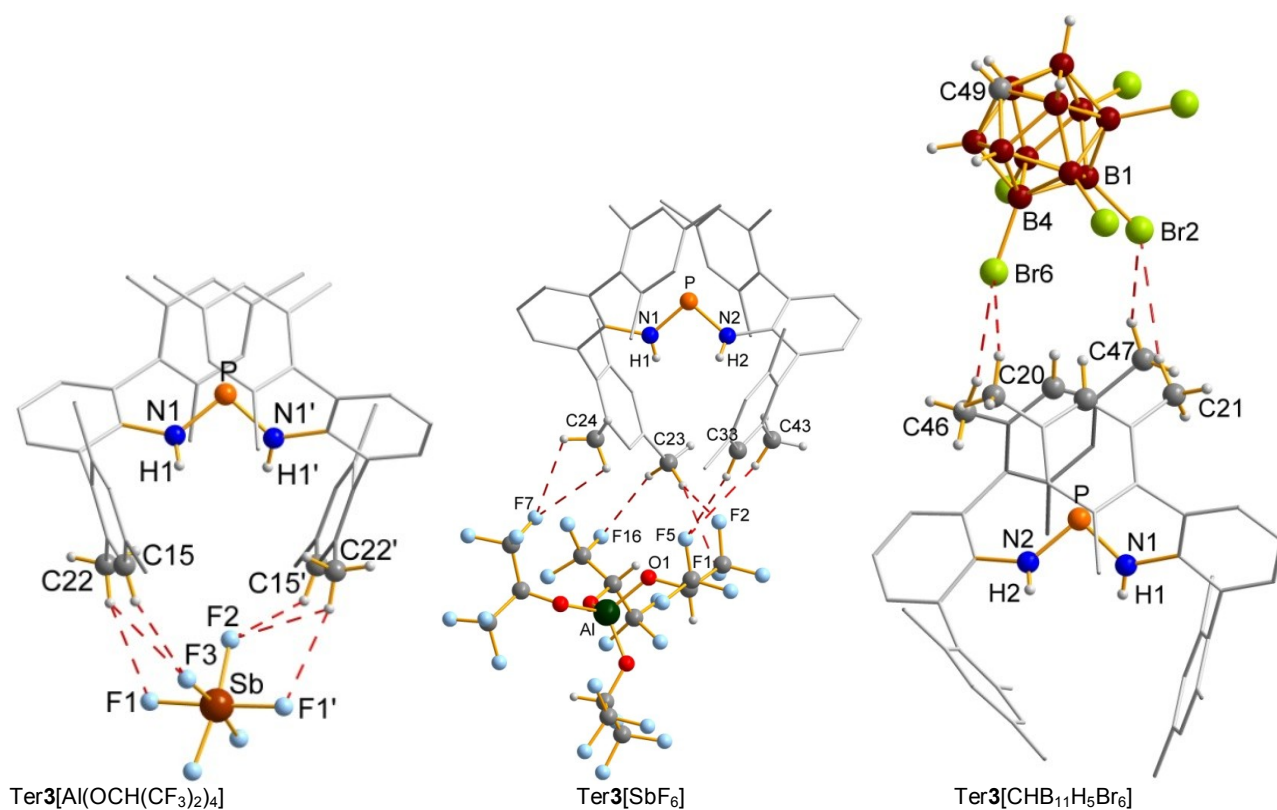


Fig. 3 Weak interionic van der Waals interactions in Ter3[X]. Only the interactions of one ion pair are depicted.

Conclusions

Different synthetic routes to salts bearing the *N,N*-bis-terphenyl-amino-phosphonium cation ($[\text{Ter3}]^+$) have been studied. Simple salt-elimination reactions of $(\text{TerNH})_2\text{P}-\text{Cl}$ with $\text{Ag}[\text{X}]$ (X = weakly coordinating anion) or protonation of $\text{TerN}(\text{H})\text{PNTer}$ with strong acids offer a generally applicable and economic access to $\text{Ter3}[\text{X}]$ compounds with a wide range of anions. Most $\text{Ter3}[\text{X}]$ compounds were obtained in good yields and purity and are suitable starting materials for further synthesis.

Systematic single-crystal X-ray diffraction studies of $\text{Ter3}[\text{X}]$ compounds with the focus on the cation \cdots anion interaction have revealed that depending on the size of the anion the pocket formed by the terphenyl can be entered to certain degree resulting (besides covalent bonding) in strong interionic hydrogen bonds which are structure-defining ($[\text{X}]^- = [\text{CF}_3\text{SO}_3]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, and $[\text{GaCl}_4]^-$). For those ions ($[\text{SbF}_6]^-$, $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ and $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$) that are too big to fit into the terphenyl pocket many $\text{C}_{\text{methyl}}-\text{H}\cdots\text{Y}$ ($\text{Y} = \text{F}, \text{Br}$) contacts are detected which can be described as weak dispersive interactions that are not structure determining.

Solution NMR data suggest dissociation of ionic $\text{Ter3}[\text{X}]$ in contrast to analogous Mes^* species for which ion pairing is observed. This different solution behavior can be attributed to the better steric protection provided by the terphenyl substituent preventing from stronger hydrogen bonds. The only exception in the series of ionic $\text{Ter3}[\text{X}]$ species represents $\text{Ter3}[\text{CF}_3\text{SO}_3]$ for which ion pairing in solution was found due to very strong hydrogen bonding.

In conclusion it was shown that the Ter3 cation can be used as sensitive probe for the examination of anion properties as well as kind and degree of cation \cdots anion interactions.

Experimental Section

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane was purified according to a literature procedure,³⁷ dried over P_4O_{10} , followed by CaH_2 , and was freshly distilled and degassed prior to use. Diethyl ether, tetrahydrofuran (THF), toluene and benzene were dried over $\text{Na}/\text{benzophenone}$, *n*-hexane was dried over $\text{Na}/\text{benzophenone}/\text{tetraglyme}$. All solvents were freshly distilled prior to use. *n*-butyllithium $^n\text{BuLi}$ (Acros, 2.5M), silver tetrafluoroborate AgBF_4 (Acros, 99%), gallium trichloride GaCl_3 (abcr, 99.9%), antimony pentafluoride SbF_5 (Acros, 99%), antimony pentachloride SbCl_5 (Acros, 99%), sodium tetraphenylborate $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ (Acros, 99.5%) and silver hexafluoroantimonate AgSbF_6 (abcr, 98%) were used as received. Phosphorous trichloride PCl_3 (Acros, 97%), trifluoromethanesulfonic acid $\text{CF}_3\text{SO}_3\text{H}$ (Merck, 98%) and trifluoroacetic acid $\text{CF}_3\text{CO}_2\text{H}$ (Solvay, 99%) were freshly distilled prior to use. 2,6-Bis-(2,4,6-trimethylphenyl)aniline TerNH_2 , 2,6-bis-(2,4,6-trimethylphenyl)-phenyl]amino-(dichloro)phosphane $\text{TerN}(\text{H})\text{PCl}_2$, silver *closo*-7,8,9,10,11,12-hexabromocarboranate $\text{Ag}[\text{CHB}_{11}\text{H}_5\text{Br}_6]$, silver triflate $\text{Ag}[\text{CF}_3\text{SO}_3]$, silver trifluoroacetate $\text{Ag}[\text{CF}_3\text{CO}_2]$, silver tetrakis(1,1,1,3,3,3-hexafluoro-2-isopropoxy)-aluminate $\text{Ag}[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]$ and silver tetrakis(pentafluorophenyl)borate toluene trisolvate $\text{Ag}(\text{toluene})_3[\text{B}(\text{C}_6\text{F}_5)_4]$, were prepared according to literature procedures.^{38,39,40,41,21c} Bis-diethyl ether oxonium tetrakis(pentafluorophenyl)borate $[(\text{Et}_2\text{O})_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ and silver tetraphenylborate $\text{Ag}[\text{B}(\text{C}_6\text{H}_5)_4]$

have been previously reported in literature and were prepared according to modified procedures.^{42,43}

NMR: $^{31}\text{P}\{^1\text{H}\}$, $^{19}\text{F}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, ^{13}C DEPT, and ^1H NMR spectra were obtained on a Bruker AVANCE 250, 300 or 500 spectrometer and were referenced internally to the deuterated solvent (^{13}C , CD_2Cl_2 : $\delta_{\text{reference}} = 54$ ppm, $\text{DMSO}-d_6$: $\delta_{\text{reference}} = 40$ ppm) or to protic impurities in the deuterated solvent (^1H , CDHCl_2 : $\delta_{\text{reference}} = 5.31$ ppm, $\text{DMSO}-d_5 = 2.5$ ppm). CD_2Cl_2 was dried over P_4O_{10} and freshly distilled prior to use. $\text{DMSO}-d_6$ was dried over CaH_2 and freshly distilled prior to use.

IR: Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device was used.

Raman: Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm) was used.

CHN analyses: Analysator Flash EA 1112 from Thermo Quest was used.

MS: Finnigan MAT 95-XP from Thermo Electron was used.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20°C/min (clearing-points are reported).

DSC: DSC 823e from Mettler-Toledo (Heating-rate 5 °C/min) was used.

UV/VIS: Lambda 19 Perkin Elmer, Software Lambda-SPX 1. Samples were measured in CH_2Cl_2 at ambient temperature. Settings: Scan: 200-800nm, Interval 0.5nm, Scan speed 120nm/min, Smooth 1, Slit 1nm

Ter3F: To a stirred suspension of $(\text{TerNH})_2\text{PCl}$ (0.500g, 0.69mmol) in CH_2Cl_2 (5mL), a powder of silver tetrafluoridoborate AgBF_4 (0.136g, 0.70mmol) was added in small portions at a temperature of -80°C over a period of 20 minutes. The orange solution was allowed to warm to ambient temperature for 30 minutes, resulting in the precipitation of silver chloride. This mixture was degasified three times by freeze-pump-warm procedure. The precipitate was removed by filtration (F4) and the solvent was removed *in vacuo*. The resulting yellow residue was washed four times with *n*-hexane (4mL), dried *in vacuo* and solved in toluene (4mL). The second fraction of a fractional crystallisation, with storage at -25°C over 12 h, was collected and washed with toluene (0.5mL). Removal of solvent by syringe and drying *in vacuo* yields 0.098g (0.14mmol, 20%) of *N,N*-bis-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-fluoro-phosphane **Ter3F** as a colourless powder. Mp. 225°C (dec.). Anal. calc. % (found): C 81.55 (80.43); H 7.41 (7.46); 3.96 (3.90). $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 121.5MHz): $\delta = 119.70$ (d, $^1J(^{19}\text{F}-^{31}\text{P}) = 1084\text{Hz}$). $^{19}\text{F}\{^1\text{H}\}$ NMR (25°C, CD_2Cl_2 , 282.4MHz): $\delta = -63.15$ (d, $^1J(^{19}\text{F}-^{31}\text{P}) = 1084\text{Hz}$). ^1H NMR (25 °C, CD_2Cl_2 , 300.13MHz): $\delta = 1.57$ (s, 12H, *o*-CH₃), 1.73 (s, 12H, *o*-CH₃), 2.28 (s, 12H, *p*-CH₃), 3.79 (br. s, 2H, NH), 6.70-6.84 (m, 12H, *m*-CH), 6.85-6.91 (m, 2H, *p*-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 62.9MHz): $\delta = 20.0$ (s, *o*-CH₃), 20.43 (br. s, *o*-CH₃), 21.56 (s, *o*-CH₃), 122.0 (s, CH), 128.8 (d, $J(^{13}\text{C}-^{31}\text{P}) = 10.1\text{Hz}$), 129.7 (s, CH), 130.9 (m, CH), 135.6 (s, CH), 137.2-137.5 (m), 137.5 (s). IR (ATR, 25 °C, cm^{-1}): 3334 (m), 3292 (m), 3000 (m), 2945 (m), 2915 (m), 2853 (m), 2731 (w), 1611 (m), 1583 (m), 1553 (w), 1530 (w), 1513 (w), 1486 (m), 1418 (s), 1373 (s), 1305 (m), 1265 (m), 1225 (s), 1183 (m), 1097 (w), 1073 (m), 1031 (m), 1006 (m),

946 (m), 928 (m), 889 (s), 861 (m), 846 (s), 836 (s), 796 (m), 751 (s), 697 (s), 662 (m), 650 (m), 637 (m), 597 (m), 563 (m), 549 (m). Raman (400 mW, 25 °C, 3 accumulations, cm^{-1}): 3049 (1), 3012 (1), 2949 (1), 2917 (1), 2856 (1), 2732 (1), 1613 (3), 1587 (3), 1484 (3), 1449 (3), 1379 (4), 1305 (5), 1288 (3), 1182 (3), 1165 (3), 1159 (3), 1078 (3), 1007 (3), 947 (3), 892 (2), 837 (3), 752 (3), 740 (3), 699 (3), 662 (3), 636 (3), 579 (4), 560 (3), 522 (3), 414 (3), 395 (3), 369 (3), 336 (3), 275 (3). MS (CI, m/z , >10 %, $[\text{M}]^+$ = $[\text{TerN(H)PN(H)Ter}]^+$): 329 (11) $[\text{TerNH}_2]^+$, 330 (60) $[\text{TerNH}_3]^+$, 705 (14) $[\text{M} + \text{F} - \text{H}]^+$, 706 (19) $[\text{M} + \text{F}]^+$, 707 (100) $[\text{M} + \text{F} + \text{H}]^+$. UV-VIS (25 °C, CH_2Cl_2): λ = 292 (s), 249 (s). Crystals suitable for X-ray crystallographic analysis were obtained by concentration of a dichloromethane solution of Ter3F to incipient crystallisation and storage at -25 °C overnight.

Ter3Cl: An excess of gaseous hydrogen chloride HCl is passed through a stirred yellow suspension of TerN(H)PNter (1.31g, 1.90mmol) in Et₂O (80mL) at a temperature of 0 °C over a period of one hour. After this the solution was allowed to warm to ambient temperature and stirred for one hour. The solvent was removed *in vacuo*, and the yellow residue was extracted four times with toluene (40mL) and filtered (F4). The resulting light yellow solution was concentrated to incipient crystallisation and stored at -1 °C for two days, which results in the deposition of colourless crystals. Removal of solvent by syringe and drying *in vacuo* yields 0.77g (1.10mmol, 58%) of Ter3Cl as a colorless crystalline solid. Mp. 265 °C. Anal. calc. % (found): C, 79.70 (79.26); H, 7.25 (6.84); N, 3.87 (4.07). ³¹P{¹H} NMR (25 °C, CD₂Cl₂, 121.5MHz): δ = 129.9. ¹H NMR (25 °C, CD₂Cl₂, 300.13MHz): δ = 1.68 (s, 12H, *o*-CH₃), 1.85 (s, 12H, *o*-CH₃), 2.39 (s, 12H, *p*-CH₃), 4.08 (d, 2H, NH, ²*J*(¹H-³¹P) = 3.6Hz), 6.80-6.94 (m, 12H, *m*-CH), 6.95-7.01 (m, 2H, *p*-CH). ¹³C{¹H} NMR (25 °C, CD₂Cl₂, 75.5MHz): δ = 20.30 (s, *o*-CH₃), 20.68 (d, *o*-CH₃, *J*(¹³C-³¹P) = 2.2Hz), 21.61 (s, *p*-CH₃), 122.68 (d, *p*-CH, *J*(¹³C-³¹P) = 2.2Hz), 129.00 (d, *m*-CH-Mes, *J*(¹³C-³¹P) = 2.8Hz), 131.64 (d, *J*(¹³C-³¹P) = 3.3Hz), 135.08 (s), 137.34 (d, *J*(¹³C-³¹P) = 1.7Hz), 137.25 (d, *J*(¹³C-³¹P) = 3.9Hz), 137.67 (s), 137.75 (d, *J*(¹³C-³¹P) = 2.2Hz). IR (ATR, 25 °C, cm^{-1}): 3309 (m), 3285 (m), 2971 (w), 2945 (w), 2914 (m), 2853 (w), 2731 (w), 1610 (m), 1582 (w), 1486 (w), 1419 (s), 1373 (s), 1303 (m), 1284 (m), 1260 (m), 1254 (m), 1242 (m), 1222 (s), 1183 (m), 1098 (w), 1073 (m), 1031 (m), 1006 (m), 931 (m), 895 (s), 861 (m), 846 (s), 797 (m), 770 (s), 752 (s), 664 (m), 639 (m), 597 (m), 563 (m), 549 (m). Raman (500 mW, 25 °C, 750 scans, cm^{-1}): 3312 (1), 3286 (1), 3052 (2), 3015 (2), 2917 (3), 2857 (2), 2731 (1), 1613 (3), 1586 (2), 1482 (2), 1443 (2), 1380 (2), 1304 (3), 1232 (1), 1183 (2), 1162 (1), 1079 (2), 1007 (2), 948 (1), 838 (1), 741 (1), 664 (1), 579 (2), 561 (2), 523 (2), 415 (2), 386 (2), 336 (2), 275 (2), 240 (2). MS (CI, m/z , >10 %, $[\text{M}]^+$ = $[\text{TerN(H)PN(H)Ter}]^+$): 330 (15) $[\text{TerNH}_3]^+$, 687 (100) $[\text{M} - \text{Cl}]^+$, 743 (20) $[\text{isobutene} + \text{M}]^+$. UV-VIS (25 °C, CH_2Cl_2): λ = 297 (s), 248 (s). Crystals of Ter3Cl suitable for X-ray crystallographic analysis were obtained in moderate yield by prolonged storage of dichloromethane solutions at -1 °C.

Ter3[B(C₆F₅)₄]: To a stirred solution of (TerNH₂)₂PCl (0.180g, 0.25mmol) in toluene (15mL), a solution of Ag[B(C₆F₅)₄] · 2 toluene (0.243g, 0.25mmol) in toluene (15mL) was added dropwise at ambient temperatures over a period of 15 minutes. The orange solution was allowed to stir for one hour. The solvent was removed *in vacuo*, and the orange residue was dissolved in CH₂Cl₂ (10mL) and filtered (F4). The resulting orange solution was concentrated to incipient crystallisation and stored at -1 °C overnight, which results in the deposition of orange crystals. Removal of solvent by syringe

and drying *in vacuo* yields 0.125g (0.092mmol, 37%) of dichloromethane solvate Ter3[B(C₆F₅)₄] as an orange crystalline solid. Mp. 244 °C (dec.). Anal. calc. % (found): C, 60.39 (60.40); H, 3.75 (3.68); N, 1.93 (1.86). ³¹P{¹H} NMR (25 °C, CD₂Cl₂, 121.5MHz): δ = 249.1. ¹H NMR (25 °C, CD₂Cl₂, 300.13MHz): δ = 1.76 (s, 24H, *o*-CH₃), 2.25 (s, 12H, *p*-CH₃), 6.94 (s, 8H, *m*-CH-Mes), 7.14 (d, 4H, *m*-CH, ³*J*(¹H-¹H) = 7.74Hz), 7.31 (d, 2H, NH, ²*J*(¹H-³¹P) = 12.3Hz), 7.36-7.43 (m, 2H, *p*-CH). ¹¹B{¹H} NMR (25 °C, CD₂Cl₂, 96.29MHz): δ = -16.60. ¹⁹F{¹H} NMR (25 °C, CD₂Cl₂, 282.38MHz): δ = -132.78 (m), -163.75 (m), -167.49 (m). ¹³C{¹H} NMR (25 °C, CD₂Cl₂, 75.5MHz): δ = 20.65 (s, *o*-CH₃), 21.32 (s, *p*-CH₃), 129.08 (s, *p*-CH), 130.61 (s, *m*-CH-Mes), 131.08 (s, *m*-CH), 132.26 (d, *J*(¹³C-³¹P) = 3.3Hz), 132.59 (d, *J*(¹³C-³¹P) = 4.4Hz), 132.76 (d, *J*(¹³C-³¹P) = 3.0Hz), 137.52 (d, *J*(¹³C-³¹P) = 6.0Hz), 141.23 (s), 148.7 (d, *o*-CF, ¹*J*(¹³C-¹⁹F) = 238Hz), 138.8 (d, *p*-CF, ¹*J*(¹³C-¹⁹F) = 240Hz), 136.9 (d, *m*-CF, ¹*J*(¹³C-¹⁹F) = 241Hz), 125 (*ipso*-C). IR (ATR, 25 °C, cm^{-1}): 3287 (w), 2974 (w), 2919 (w), 2859 (w), 2738 (w), 1642 (w), 1611 (w), 1558 (w), 1511 (s), 1461 (s), 1419 (m), 1379 (m), 1340 (m), 1308 (m), 1239 (s), 1203 (m), 1154 (m), 1081 (s), 1033 (m), 977 (s), 954 (s), 857 (m), 806 (m), 774 (m), 756 (s), 738 (s), 681 (m), 660 (s), 630 (m), 610 (m), 600 (m), 572 (m), 556 (m). Raman (1500 mW, 25 °C, 700 scans, cm^{-1}): 3065 (1), 3019 (1), 2922 (2), 2861 (1), 2739 (1), 1644 (1), 1611 (3), 1584 (3), 1480 (2), 1422 (3), 1381 (2), 1301 (3), 1260 (2), 1216 (4), 1187 (3), 1079 (3), 1009 (2), 968 (5), 843 (2), 732 (1), 658 (1), 598 (2), 583 (3), 556 (2), 521 (2), 491 (2), 448 (2), 267 (2). MS (ESI-TOF, m/z , >10 %): 679 (100) $[\text{B(C}_6\text{F}_5)_4]^-$. MS (CI, m/z , >10 %, $[\text{M}]^+$ = $[\text{TerN(H)PN(H)Ter}]^+$): 330 (100) $[\text{TerNH}_3]^+$, 526 (40) $[\text{TerNP(C}_6\text{F}_5)_4]^+$, 687 (41) $[\text{M}]^+$, 855 (35) $[\text{M} + \text{C}_6\text{F}_5]^+$. UV-VIS (25 °C, CH_2Cl_2): λ = 422 (w), 358 (m), 296 (m), 260 (s). Crystals of Ter3[B(C₆F₅)₄] suitable for X-ray crystallographic analysis were obtained in moderate yield by prolonged storage of a saturated dichloromethane solution at ambient temperature.

Ter3[CF₃CO₂]: To a stirred yellow solution of TerN(H)PNter (0.343g, 0.50mmol) in toluene (10mL), a solution of trifluoroacetic acid (0.057g, 0.50mmol) in toluene (1mL) was added dropwise at -80 °C over a period of five minutes. The solution was allowed to warm to ambient temperature and stirred for one hour. The solvent was removed *in vacuo*, and the yellow residue was dissolved in dichloromethane (5mL). The resulting yellow solution was concentrated to incipient crystallisation and stored at ambient temperature overnight, which results in the deposition of pale yellow crystals. The supernatant was removed, and the crystalline residue was washed with dichloromethane (0.5mL) and dried *in vacuo* yields 0.196g (0.24mmol, 48%) of Ter3[CF₃CO₂]. Mp. 177 °C. Dec. 190 °C. Anal. calc. % (found): C, 74.98 (74.89); H, 6.54 (6.55); N, 3.50 (3.36). ³¹P{¹H} NMR (25 °C, CD₂Cl₂, 121.5MHz): δ = 116.7. ¹H NMR (25 °C, CD₂Cl₂, 300.13MHz): δ = 1.75 (m, 24H, *o*-CH₃), 2.36 (s, 12H, *p*-CH₃), 4.38 (d, 2H, NH, ²*J*(¹H-³¹P) = 4.5Hz), 6.78 – 6.92 (m, 12H, *m*-CH), 6.93 – 7.00 (m, 2H, *p*-CH). ¹⁹F{¹H} NMR (25 °C, CD₂Cl₂, 282.4MHz): δ = -75.25 (s). ¹³C{¹H} NMR (25 °C, CD₂Cl₂, 75.5MHz): δ = 20.35 (m, *o*-CH₃), 21.56 (s, *p*-CH₃), 122.52 (s, *p*-CH), 129.10 (s, *m*-CH-Mes), 130.19 (*m*-CH), 130.81 (d), 135.24 (d), 137.17 (br. s), 137.58 (s), 137.67 (s), 137.93 (s). IR (ATR, 25 °C, cm^{-1}): 3354 (w), 3314 (w), 3298 (w), 3250 (w), 2946 (w), 2917 (m), 2856 (w), 1875 (w), 1756 (m), 1611 (m), 1487 (w), 1434 (m), 1422 (s), 1368 (m), 1288 (w), 1264 (m), 1241 (w), 1209 (s), 1157 (s), 1142 (s), 1133(s), 1075 (m), 1031 (m), 1007 (m), 949 (m), 933 (m), 899 (s), 848 (s), 798 (m), 777 (m), 754 (s), 731 (m), 704 (m), 696 (m), 661 (m), 648 (m), 629 (m), 614 (m), 596 (m), 550 (m). Raman (1500 mW, 25 °C, 700 scans, cm^{-1}): 3316 (1), 3300 (1), 3048

(3), 3011 (3), 2915 (3), 2859 (2), 2733 (2), 2550 (1), 1759 (1), 1611 (4), 1588 (3), 1484 (2), 1445 (2), 1381 (3), 1306 (5), 1229 (3), 1185 (1), 1164 (1), 1077 (2), 1007 (2), 949 (1), 824 (1), 739 (1), 662 (2), 577 (3), 554 (2), 521 (2), 489 (1), 415 (1), 330 (2), 276 (2), 249 (2), 234 (2). MS (CI, m/z, >10 %, $[M]^+$ = $[\text{TerN}(\text{H})\text{PN}(\text{H})\text{Ter}]^+$): 330 (100) $[\text{TerNH}_3]^+$, 358 (26) $[\text{TerNP}]^+$, 671 (15) $[\text{M} - \text{CH}_4]^+$, 687 (77) $[M]^+$, 705 (21) $[\text{M} + \text{F} - \text{H}]^+$. UV-VIS (25°C, CH_2Cl_2): λ = 290 (s), 250 (s). Crystals suitable for X-ray crystallographic analysis were obtained by concentration of a dichloromethane solution of $\text{Ter3}[\text{CF}_3\text{CO}_2]$ to incipient crystallisation and storage at ambient temperature overnight.

Ter3[GaCl₄]: To a stirred suspension of $(\text{TerNH})_2\text{PCl}$ (0.180g, 0.25mmol) in dichloromethane (6mL), a solution of gallium trichloride GaCl_3 (0.053g, 0.30mmol) in dichloromethane (2mL) was added dropwise at ambient temperature over a period of ten minutes. The pale yellow suspension was allowed to stir for one hour, resulting in an orange solution. This solution was concentrated to incipient crystallisation and stored at -1°C overnight, which results in the deposition of orange crystals. The supernatant was removed, and the crystalline residue was washed with dichloromethane (0.5mL) and dried *in vacuo* yields 0.105g (0.12mmol, 47%) of $\text{Ter3}[\text{GaCl}_4]$ as an orange crystalline solid. Mp. 215°C (dec.). Anal. calc. % (found): C(measured with lead oxide), 64.10 (64.53); H 5.83 (5.92); N 3.11 (3.14). $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 121.5MHz): δ = 250. ^1H NMR (25 °C, CD_2Cl_2 , 300.13MHz): δ = 1.80 (s, 24H, *o*-CH₃), 2.32 (s, 12H, *p*-CH₃), 7.04 (br. s, 8H, *m*-CH-Mes), 7.15 (d, 4H, *m*-CH, $^3J(\text{H}^1\text{H}^1\text{H}) = 7.6\text{Hz}$), 7.38(d, 2H, NH, $^2J(\text{H}^1\text{H}^31\text{P}) = 12.5\text{Hz}$), 7.39 – 7.44 (m, 2H, *p*-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 75.5MHz): δ = 20.83 (br. s, *o*-CH₃), 21.53 (s, *p*-CH₃), 129.12 (s, *p*-CH), 130.64 (s, *m*-CH-Mes), 131.14 (s, *m*-CH), 132.23 (d, $J(^{13}\text{C}^31\text{P}) = 3.3\text{Hz}$), 132.72 (d, $J(^{13}\text{C}^31\text{P}) = 4.4\text{Hz}$), 132.86 (d, $J(^{13}\text{C}^31\text{P}) = 2.8\text{Hz}$), 137.57 (d, $J(^{13}\text{C}^31\text{P}) = 3.9\text{Hz}$), 141.21 (s). IR (ATR, 25 °C, cm^{-1}): 3333 (w), 3261 (m), 3052 (w), 2975 (m), 2945 (m), 2916 (m), 2844 (m), 2737 (w), 1609 (m), 1573 (m), 1557 (m), 1478 (m), 1436 (s), 1416 (m), 1380 (m), 1342 (m), 1300 (m), 1292 (m), 1254 (m), 1201 (m), 1164 (m), 1129 (m), 1068 (m), 1032 (m), 1007 (m), 950 (s), 939 (s), 852 (s), 800 (s), 780 (m), 753 (s), 737 (m), 652 (m), 627 (m), 598 (m), 571 (m), 562 (m), 544 (m). Raman (1500 mW, 25 °C, 669 scans, cm^{-1}): 3264 (1), 3057 (1), 3023 (1), 2917 (3), 2857 (1), 2737 (1), 1611 (3), 1582 (3), 1480 (2), 1420 (3), 1380 (2), 1310 (3), 1268 (2), 1216 (5), 1187 (3), 1073 (3), 1007 (2), 963 (4), 840 (2), 730 (2), 658 (2), 598 (2), 583 (3), 521 (2), 489 (2), 415 (2), 361 (2), 269 (2), 230 (1), 207 (1). MS (CI, m/z, >10 %, $[M]^+$ = $[\text{TerN}(\text{H})\text{PN}(\text{H})\text{Ter}]^+$): 358 (16) $[\text{TerNP}]^+$, 671 (21) $[\text{M} - \text{CH}_4]^+$, 687 (100) $[M]^+$. UV-VIS (25°C, CH_2Cl_2): λ = 438 (m), 361 (m), 255 (s). Crystals suitable for X-ray crystallographic analysis were obtained by concentration of a dichloromethane solution of $\text{Ter3}[\text{GaCl}_4]$ to incipient crystallisation and storage at ambient temperature overnight.

Ter3[CF₃SO₃]: To a stirred solution of $\text{TerN}(\text{H})\text{PNTer}$ (0.342g, 0.50mmol) in toluene (22mL), a solution of $\text{CF}_3\text{SO}_3\text{H}$ (0.075g, 0.50mmol) in toluene (4mL) was added dropwise at -80°C over a period of ten minutes. The resulting yellow solution was allowed to warm to ambient temperature and stirred for 30 minutes. The solvent was removed *in vacuo*, and the yellow residue was dissolved in dichloromethane (5mL). This solution was concentrated to incipient crystallisation and stored at -25°C overnight, which results in the deposition of orange crystals. The supernatant was removed, and the crystalline residue was washed with dichloromethane (0.5mL) and dried *in vacuo* yields 0.08g (0.10mmol, 20%) of $\text{Ter3}[\text{CF}_3\text{SO}_3]$ as an

orange crystalline solid. Mp. 255°C (dec.). Anal. calc. % (found): C 70.31 (70.44); H 6.26 (6.80); N 3.35 (3.32). $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 121.5MHz): δ = 261 (br. s). ^1H NMR (25 °C, CD_2Cl_2 , 300.13MHz): δ = 1.74 (s, 24H, *o*-CH₃), 2.33 (s, 12H, *p*-CH₃), 6.94 (s, 8H, *m*-CH-Mes), 7.01 (d, 4H, *m*-CH, $^3J(\text{H}^1\text{H}^1\text{H}) = 7.7\text{Hz}$), 7.34 (m, 2H, *p*-CH), 9.67 (d, 2H, NH, $^2J(\text{H}^1\text{H}^31\text{P}) = 12.3\text{Hz}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 75.5MHz): δ = 20.86 (d, *o*-CH₃, $J(^{13}\text{C}^31\text{P}) = 2.2\text{Hz}$), 21.56 (s, *p*-CH₃), 128.66 (s, *p*-CH), 129.66 (s, *m*-CH-Mes), 131.34 (s, *m*-CH), 132.90 (d, $J(^{13}\text{C}^31\text{P}) = 8.8\text{Hz}$), 133.64 (br. s), 135.46 (d, $J(^{13}\text{C}^31\text{P}) = 5.5\text{Hz}$), 137.55 (d, $J(^{13}\text{C}^31\text{P}) = 2.8\text{Hz}$), 139.60 (s). $^{19}\text{F}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 282.38MHz): δ = -78.67 (s). IR (ATR, 25 °C, cm^{-1}): 3341 (w), 3234 (w), 2917 (m), 2857 (w), 2734 (w), 1612 (w), 1575 (w), 1566 (w), 1506 (w), 1441 (m), 1426 (m), 1379 (m), 1293 (m), 1269 (m), 1223 (s), 1168 (s), 1077 (w), 1024 (s), 1010 (s), 969 (m), 850 (s), 803 (m), 754 (m), 744 (m), 636 (s), 596 (m), 563 (m), 551 (m), 541 (m). Raman (400 mW, 25 °C, 750 scans, cm^{-1}): 3055 (3), 3017 (2), 2919 (4), 2858 (2), 2733 (1), 1613 (4), 1682 (3), 1582 (3), 1484 (2), 1435 (3), 1378 (2), 1306 (1), 1214 (5), 1189 (2), 1083 (3), 1031 (2), 1009 (2), 982 (5), 855 (2), 797 (1), 739 (2), 654 (2), 579 (2), 554 (2), 523 (2), 415 (2), 384 (2), 330 (2), 265 (2), 232 (2). MS (CI, m/z, >10 %, $[M]^+$ = $[\text{TerN}(\text{H})\text{PN}(\text{H})\text{Ter}]^+$): 330 (100) $[\text{TerNH}_3]^+$, 687 (13) $[M]^+$. UV-VIS (25°C, CH_2Cl_2): λ = 438 (w), 363 (m), 292 (s), 246(s). Crystals suitable for X-ray crystallographic analysis were obtained by concentration of a dichloromethane solution of $\text{Ter3}[\text{CF}_3\text{SO}_3]$ to incipient crystallisation and storage at -25°C overnight.

Ter3[Al(OCH(CF₃)₂)₄]: To a stirred solution of $(\text{TerNH})_2\text{PCl}$ (0.175g, 0.24mmol) in dichloromethane (4mL), a solution of $\text{Ag}[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]$ (0.200g, 0.25mmol) in dichloromethane (2mL) was added dropwise at ambient temperature over a period of ten minutes. The orange solution was allowed to stir for 30 minutes and was then filtered (F4). The solvent was removed *in vacuo* and the resulting orange precipitate was washed four times with *n*-hexane (4mL). This precipitate was dissolved in dichloromethane (2mL) and filtered (F4). Removal of solvent by syringe and drying *in vacuo* yields 0.232g (0.17mmol, 70%) of *N,N*-bis-(2,6-bis-(2,4,6-trimethylphenyl)phenyl)amino-phosphonium tetrakis(1,1,1,3,3,3-hexafluoro-2-isopropoxy)aluminate $\text{Ter3}[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]$ as a shiny orange microcrystalline solid. Mp. 273°C (dec.). Anal. calc. % (found): C 52.11 (52.74); H 4.08 (4.08); 2.03 (1.97). $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 121.5MHz): δ = 249 (br. s). ^1H NMR (25 °C, CD_2Cl_2 , 300.13MHz): δ = 1.79 (s, 24H, *o*-CH₃), 2.31 (s, 12H, *p*-CH₃), 4.51 (m, 4H, *iso*-propoxy), 7.02 (s, 8H, *m*-CH-Mes), 7.15 (d, 4H, *m*-CH, $^3J(\text{H}^1\text{H}^1\text{H}) = 7.7\text{Hz}$), 7.29 (br. d, 2H, NH, $^2J(\text{H}^1\text{H}^31\text{P}) = 12.3\text{Hz}$), 7.42 (t, 2H, *p*-CH, $^3J(\text{H}^1\text{H}^1\text{H}) = 7.7\text{Hz}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 75.5MHz): δ = 20.75 (s, *o*-CH₃), 21.47 (s, *p*-CH₃), 71.47 (m, *iso*-propoxy), 121.71 (s, CF₃), 125.51 (s, CF₃) 129.16 (s, *p*-CH), 130.70 (s, *m*-CH-Mes), 131.14 (s, *m*-CH), 132.25 (d, $J(^{13}\text{C}^31\text{P}) = 3.3\text{Hz}$), 132.52 (d, $J(^{13}\text{C}^31\text{P}) = 4.4\text{Hz}$), 132.90 (d, $J(^{13}\text{C}^31\text{P}) = 2.8\text{Hz}$), 137.60 (d, $J(^{13}\text{C}^31\text{P}) = 3.9\text{Hz}$), 141.33 (s). $^{19}\text{F}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 282.38MHz): δ = -77.38 (s). IR (ATR, 25 °C, cm^{-1}): 3479 (w), 3378 (w), 3319 (w), 3255 (w), 2948 (w), 2919 (w), 2860 (w), 2737 (w), 1610 (w), 1603 (w), 1574 (w), 1488 (w), 1441 (m), 1426 (m), 1375 (m), 1290 (m), 1261 (m), 1211 (s), 1178 (s), 1099 (s), 1034 (m), 1009 (m), 957 (m), 890 (m), 852 (s), 798 (m), 754 (m), 736 (m), 727 (m), 685 (s), 650 (m), 630 (m), 597 (m), 566 (m), 550 (m). Raman (1500 mW, 25 °C, 700 scans, cm^{-1}): 3067 (2), 3021 (1), 2920 (2), 2866 (2), 2743 (1), 1611 (3), 1586 (3), 1480 (2), 1428 (5), 1383 (2), 1380 (4), 1289 (3), 1270 (3), 1221 (5), 1185 (3), 1073 (3), 1009 (3), 978 (4), 842 (2), 784 (1), 759 (1), 730 (2), 658 (2), 597 (2), 577 (2), 556 (2), 519 (2), 489 (2), 415 (2), 361 (2), 330

(2), 271 (2), 236 (1). MS (CI, m/z, >10 %, [M]⁺ = [TerN(H)PN(H)Ter]⁺): 329 (32) [TerNH₂]⁺, 330 (20) [TerNH₃]⁺, 705 (100) [M + F - H]⁺. UV-VIS (25°C, CH₂Cl₂): λ = 435 (w), 360 (m), 297 (m), 271 (s), 246 (s). Crystals suitable for X-ray crystallographic analysis were obtained by concentration of a fluorobenzene solution of Ter3[Al(OCH(CF₃)₂)₄] to incipient crystallisation and storage at -25°C for two days. Storage for longer time also produced additional crystals of (TerNH)₂P(H)OAl(OCH(CF₃)₂)₃ as a result of hydrolysis.

Ter3[CHB₁₁H₅Br₆]: To a stirred suspension of (TerNH)₂PCl (0.180g, 0.25mmol) in CH₂Cl₂ (5mL), a powder of Ag[CHB₁₁H₅Br₆] (0.230g, 0.32mmol) was added in one portion at ambient temperature. The orange suspension was stirred for one hour and filtered (F4). The solvent was removed *in vacuo* and the resulting orange precipitate was washed four times with benzene (2mL). The resulting deep orange oil was covered with a layer of benzene and stored at ambient temperature overnight, which results in the deposition of orange crystals. Removal of solvent by syringe and drying *in vacuo* yields 0.129g (0.10mmol, 40%) of Ter3[CHB₁₁H₅Br₆]. Mp. 225°C (dec.). Anal. calc. % (found): C 45.12 (45.65); H 4.48 (4.61); N 2.15 (1.84). ³¹P{¹H} NMR (25 °C, CD₂Cl₂, 121.5MHz): δ = 249.6 (br. s) ¹H NMR (25 °C, CD₂Cl₂, 300.13MHz): δ = 1.80 (s, 24H, o-CH₃), 2.31 (s, 12H, p-CH₃), 1.00–3.50 (m br. s, carboranate-BH/CH), 7.03 (s, 8H, m-CH-Mes), 7.15 (d, 4H, m-CH, ³J(¹H-¹H) = 7.74Hz), 7.41 (d, 2H, NH), 7.42 (t, 2H, p-CH, ³J(¹H-¹H) = 7.65Hz). ¹¹B NMR (25°C, CD₂Cl₂, 96.3MHz): δ = -1.90 (br. s, 1B, B₁₂), -9.92 (br. s, 5B, B₇₋₁₁), -20.1 (d, 5B, ¹J(¹H-¹¹B) = 167Hz). ¹³C{¹H} NMR (25 °C, CD₂Cl₂, 75.5MHz): δ = 20.82 (br. s, o-CH₃), 21.55 (s, p-CH₃), 129.16 (s, p-CH), 130.68 (s, m-CH-Mes), 131.17 (s, m-CH), 132.25 (d, J(¹³C-³¹P) = 3.3Hz), 132.55 (d, J(¹³C-³¹P) = 4.4Hz), 132.90 (d, J(¹³C-³¹P) = 2.8Hz), 137.58 (d, J(¹³C-³¹P) = 3.9Hz), 141.26 (s). IR (ATR, 25 °C, cm⁻¹): 3330 (w), 3173 (w), 3052 (w), 2946 (w), 2916 (m), 2855 (w), 2601 (m), 1611 (m), 1556 (w), 1510 (m), 1435 (s), 1428 (m), 1378 (m), 1290 (w), 1240 (m), 1199 (m), 1176 (m), 1126 (m), 1076 (w), 1002 (s), 990 (s), 952 (s), 932 (s), 857 (s), 805 (s), 744 (s), 679 (m), 633 (s), 596 (m), 563 (m), 549 (m). Raman (400 mW, 25°C): Due to fluorescence behaviour not measurable. MS (CI, m/z, >10 %): 330 (100) [TerNH₃]⁺, 386 (15) [isobutene + TerNH₃]⁺. UV-VIS (25°C, CH₂Cl₂): λ = 435 (w), 358 (m), 296 (w), 245 (s). Crystals suitable for X-ray crystallographic analysis were obtained by concentration of a benzene solution of Ter3[CHB₁₁H₅Br₆] to a deep orange oil and storage at ambient temperature overnight.

Ter[SbF₆]: To a stirred suspension of (TerNH)₂PCl (0.180g, 0.25mmol) in CH₂Cl₂ (5mL), a suspension of Ag[SbF₆] (0.103g, 0.30mmol) in dichloromethane (10mL) was added over a period of 20 minutes at -80°C. The orange solution was allowed to warm to ambient temperature for 30 minutes, resulting in the precipitation of silver chloride. The solvent was removed *in vacuo* and the residue was dissolved in CH₂Cl₂ (3mL) and filtered (F4). The resulting solution was concentrated to incipient crystallisation and stored at -1°C overnight, which results in the deposition of colourless crystals and a few orange crystals. The colourless crystals were identified as [TerNH₃][SbF₆] and the orange crystals were identified as Ter3[SbF₆] by X-ray structure determinations.

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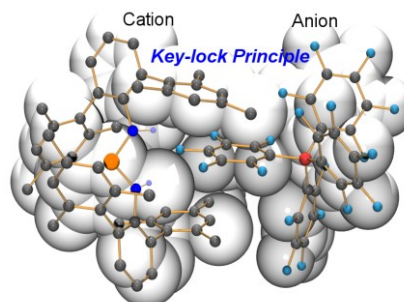
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Graphical Abstract



6. Zusammenfassung

Es wurden die Reaktionen des sterisch anspruchsvollen Terphenylamins mit ECl_3 ($\text{E} = \text{P}, \text{As}$) und verschiedenen Basen wie LDA, Et_3N , DBU und $n\text{-BuLi}$ untersucht. Dabei konnte eine große Anzahl von verschiedenen Produkten synthetisiert und charakterisiert werden. So führt die Reaktion von Et_3N mit AsCl_3 zu R-N(H)-AsCl_2 , wohingegen mit PCl_3 $\text{R-N(PCl}_2)_2$ gebildet wird. Bei dem Einsatz von $n\text{-BuLi}$ wird in beiden Fällen Amino(dichlor)pniktane R-N(H)-ECl_2 ($\text{E} = \text{P}, \text{As}$) gebildet. Ausgehend von den Amino(dichlor)pniktanen konnten viergliedrige sterisch abgeschirmte 1,3-Dichloro-2,4-bis-terphenyl-*cyclo*-1,3-dipnicta-2,4-diazane $[\text{TerNPnCl}]_2$ ($\text{Pn} = \text{P}, \text{As}$) aufgebaut werden. Hierbei führte Et_3N im Falle von $\text{E} = \text{P}$ zum gewünschten Produkt, eine Reaktion die mit AsCl_3 nicht beobachtet werden konnte. Erst der Einsatz von DBU in THF bei $-80\text{ }^\circ\text{C}$ führte zum $[\text{TerNAsCl}]_2$. Erstaunlicherweise ist in beiden Fällen in Lösung sowie im Festkörper nur die dimere Spezies beobachtet worden. Dies ist ein deutliches Zeichen für den großen sterischen und elektronischen Unterschied zwischen den Terphenyl- und Supermesitylsubstituenten.

Mit Hilfe unterschiedlicher Synthesemethoden, wie der einfachen Salzeliminierungsreaktion von $[(\text{TerNH})_2\text{P}]\text{Cl}$ mit $\text{Ag}[\text{X}]\text{-Salzen}$ ($\text{X} =$ schwachkoordinierendes Anion) sowie der Protonierung von TerN(H)P=N Ter mit starken Säuren, konnte eine Reihe von Salzen, die das N,N' -Bis(terphenylamino)phosphenium-Kation $[(\text{TerNH})_2\text{P}]^+$ enthalten, synthetisiert und vollständig charakterisiert werden. In einer systematischen Studie der strukturellen Daten wurden die Anion-Kation-Wechselwirkungen in Abhängigkeit von der Größe der Anionen untersucht. So gehen kleine nukleophile Anionen wie F^- , Cl^- , $[\text{CF}_3\text{CO}_2]^-$ kovalente Bindungen zum Phosphoratom ein, wohingegen große Anionen wie $[\text{CF}_3\text{SO}_3]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ und $[\text{GaCl}_4]^-$ in der Lage sind, in die Terphenyltasche einzutreten und Wasserstoffbrückenbindungen auszubilden. Andere Anionen wie $[\text{SbF}_6]^-$, $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ und $[\text{CHB}_{11}\text{H}_5\text{Br}_6]^-$ sind zu groß, um mit der N(H)PN(H) -Einheit zu interagieren, und bilden daher nur schwache van-der-Waals-Wechselwirkungen zu randständigen H-C_{aryl} -Bindungen des Kations aus. Die Auswertung der $^{31}\text{P-NMR}$ - und $^1\text{H-NMR}$ -Daten, der in CD_2Cl_2 gelösten Salze zeigte, dass die Terphenyltasche im Vergleich zu den analogen $[(\text{Mes}^*\text{NH})_2\text{P}][\text{X}]\text{-Verbindungen}$ ($\text{X} = [\text{CF}_3\text{SO}_3]^-$, $[\text{GaCl}_4]^-$), eine bessere sterische Abschirmung ermöglicht, da sie, mit Ausnahme der kovalent gebundenen Verbindungen und des über Wasserstoffbrückenbindungen assoziierten $[\text{CF}_3\text{SO}_3]^-$ -Salzes, zu „nackten“ $[(\text{TerNH})_2\text{P}]^+$ -Kationen führt.

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