Universität Rostock

Traditio et Innovatio

Synthesis and Characterization of new CN-based transition metal complexes

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vorgelegt von Omar Mowafaq Younis AL-Ramadhani, geb. am 03.08.1976 in Mosul, Iraq
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Dekan: Prof. Dr. Klaus Neymeyr, Mathematisch-Naturwissenschaftliche Fakultät,
Universität Rostock.

1. Gutachter: Prof. Dr. Axel Schulz, Universität Rostock
2. Gutachter: Prof. Dr. Uwe Rosenthal, Leibniz-Institut für Katalyse (LIKAT), Rostock

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ERKLÄRUNG

Ich versichere hiermit an Eides statt, dass ich die vorliegende Arbeit selbstständig angefertigt und ohne fremde Hilfe verfasst habe. Dazu habe ich keine außer den von mir angegebenen Hilfsmitteln und Quellen verwendet und die den benutzten Werken inhaltlich und wörtlich entnommenen Stellen habe ich als solche kenntlich gemacht.

Rostock, 21.04.2016

……………………….
Omar Younis

Affectionately Dedicated to

The spirit of My Father

My Dear Mother

My Own Family

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encouragement. They are the most important people in my life and they have been with me every step of the way.

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Omar

Zusammenfassung

Wegen seiner ambidenten Natur ist Tricyanophosphan ($P(CN)_3$) ein interessanter Baustein für den Aufbau von höhermolekularen Strukturen. Metalle können entweder am Stickstoff oder/und Phosphor koordinieren, was zu einer 3:1 Donor-Stöchiometrie führt. Mit Blick auf die Koodinationschemie ist ebenfalls Tetracyanopyrrolid (TCP^-) interessant, da es mit fünf Donorzenten ausgestattet ist: zwei Cyanid-Gruppen in 2- und zwei in 3-Position sowie ein Stickstoffatom im Pyrrolidring. Somit ist das TCP^- -Anion ein sehr vielseitiger Ligand und sehr gut geeignet, Koordinationspolymere zu bilden. Demzufolge scheint es aus koordinationschemischer Sicht interessant zu sein, das neutrale $P(CN)_3$ und anionische TCP^- als neue CN-basierte Liganden in der Übergangsmetallchemie zu verwenden.

Im ersten Teil der vorliegenden Arbeit wurde das Koordinationsverhalten von Tricyanophosphin untersucht, um CN-reiche Phosphorverbindungen zu erhalten, ausgehend von Umsetzungen von $P(CN)_3$ mit schwachkoordinierenden Anionen (WCAs), Lewis-Basen, Übergangsmetallkomplexen und Raumtemperatur-Ionischen Flüssigkeiten (RT-ILs). Die meisten der erhaltenen Verbindungen waren Polymere, weil sie in den meisten Lösungmitteln unlöslich waren. Alle präparierten Verbindungen wurden mittels der üblichen Analytik charakterisiert.

Im zweiten Teil dieser Arbeit wurden neue Übergangsmetallkomplexe synthetisiert, die das Tetracyanopyrrolid-Anion $[C_4(CN)_4N]^-$ $(TCP)^-$ ausgehend von Tetracyanopyrrol (HTCP) enthalten. Hervorzuheben ist dabei, dass ein neues 1D-Koordinationspolymer aus der Reaktion von HTCP mit $Mn(acac)_3$ isoliert werden konnte. Des Weiteren wurden neue TCP-Salze des Typs $[R_3NH]TCP$ (R = Me or ^{n}Pr) synthestisiert, ausgehend von der Reaktion von $[R_3NH]Cl$ mit HTCP in Wasser. Alle neuen Verbindungen wurden mittels Einkristall-Diffraktometrie und anderer Analytik charakterisiert.

Summary

Due to its ambident nature of tricyanophosphine, $P(CN)_3$, is an interesting building block for the formation of supramolecular architectures. Metals can either coordinate at nitrogen or/and phosphorus leading to a 3:1 donor stoichiometry. With respect to coordination chemistry tetracyanopyrrolide (TCP^-) is also interesting, because it is furnished with five donor centers: two cyanide group in 2- and two in 3- position and one pyrrolide N-ring atom. Therefore, the anion is an extremely versatile ligand with potential to form coordination polymers. Thus from the coordination chemistry view it seems interesting to utilize the neutral $P(CN)_3$ and the anionic TCP^- as new CN-based ligands in transition metal chemistry.

In the first part of this thesis the coordination behavior for tricyanophsphine was studied, for preparing CN-rich phosphorous compounds from the reaction of tricyanophosphine with weakly coordinating anions (WCAs), Lewis bases, transition metal complexes and room temperature ionic liquids (RT-ILs). Most of these obtained compounds were polymers because they were insoluble in most of the solvents. All prepared compounds were characterized by common analytics.

In the second part of this thesis the new transition metal complexes containing the tetracyanopyrrolide anion $[C_4(CN)_4N]^-$ (TCP) from tetracyanopyrrole (HTCP) were synthesized. Remarkably, a new 1D-coordination polymer from reaction of HTCP with $Mn(acac)_3$ could be isolated. Additionally, new TCP- salts of the type $[R_3NH]TCP$ (R= Me or ^{n}Pr) from reaction $[R_3NH]Cl$ with HTCP in water were synthesized. All new compounds were characterized by mean of X-ray crystallography and other analytics.

Table of contents

List of abbreviations

ATR	*Attenuated Total Reflection*
acac	acetylacetonate
BMIm	1-butyl-3-methylimidazolium
COD	Cyclooctapentadiene
DFT	*density functional theory*
DMAP	Dimethylaminopyridine
DMSO	Dimethylsulfoxide
DSC	*Differential Scanning Calometry*
DAN	1,8-Diaminonaphthalene
DMF	*N, N*-Dimethylformamide
EA	Elementalanalysis
EI	*electron impact*
Et_3N	Triethylamine
EtCN	Propionitrile
ESI	Electrospray-Ionasition
EMIm	1-ethyl-3-methylimidazolium
HTCP	Tetracyanopyrrole
HUMO	Highest Unoccupied Molecular Orbital
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital
m	*medium* (IR), *meta* (NMR), multiplett (NMR)
NMR	*Nuclear Magnetic Resonance*
o	*ortho*
p	*para*
ppm	*parts per million*
1,10-phen	1,10-phenanthroline
***p*-cymene**	1-methyl-4-(1-methyl ethyl)benzene
q	Quartet (NMR)
RT-ILs	Room Temperature Ionic Liquids
r_{cov}	covalent radius
δ	Chemical shift (NMR)
s	*strong* (IR), Singulett (NMR)
Triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
Tp^-	Hydridotris(3,5-dimethylpyrazolyl)borate
TMEDA	Tetramethylethylenediamine
TCP	Tetracyanopyrrolide
tcpc	Tricyanopyrrole-2-carboxamide
thf	Tetrahydrofuran
T_{dec}	Decomposition temperature
TGA	*Thermogravimetric analysis*
v:v	volume ratio
WCA	*weakly coordinating anion*
w	*weak* (IR)

Unit conversion

Quantity	**Symbol**	**Name**	**Conversion**
Frequency	MHz	Megahertz	1 MHz = 10^6 s^{-1}
	Hz	Hertz	1 Hz = 1s^{-1}
Length	Å	Angstrom	1 Å = 10^{-10} m
	µm	micrometer	1 µm = 10^{-6} m
	nm	nanometer	1 nm = 10^{-9} m
Power	mW	Milliwatt	1 mW = 10^{-3} kg·m^2·s^{-3}
Temperature	°C	degrees Celsius	x°C = (x + 273.15) K
Volume	mL	Milliliter	1 ml = 1cm^3 = 10^{-6} m^3
Heat	kJ	Kilojoule	1 kJ = $10^3$$m^2$· kg· s^{-2}
Wavenumber	cm^{-1}	reciprocal centimeter	1cm^{-1} = 100 m^{-1}
Time	h	hour	1h = 3600 s
	min	Minute	1min = 60 s
Pressure	bar	bar	1bar = 100,000 Pa
	hpa	hectopascal	1hPa = 100 Pa
Energy	eV	electron-volt	1eV = 1.6 x 10^{-19} J

1. Objective

The aim of this study was to examine the coordination chemistry of novel donor-acceptor complexes (with new CN linkers) containing anions such as tetracyanopyrrolide (TCP) and neutral phosphorus(III)cyanide. Surprisingly, the knowledge about the general coordination behavior of $P(CN)_3$ is very limited yet. Therefore the first coordination experiments for $P(CN)_3$ addressed the question of coordination control. Strong π-bases were used to force P-coordination, while first row or late transition metals were expected to bind *via* nitrogen. In addition, the nitrogen position may be blocked by formation of Lewis adducts with $B(C_6F_5)_3$. Finally, if $P(CN)_3$ shows a similar behavior like PF_3 in the coordination, indeed, the synthesis of homoleptic complexes was an intriguing synthetic goal.

With respect to coordination chemistry tetracyanopyrrolide is furnished with five donor centers, three of which are of different type: cyanide group in 2- and 3- position and the pyrrolide N-ring atom. Therefore the anion is an extremely versatile ligand with the potential to form coordination polymers. The utilization of tetracyanopyrrolide ions in combination with transition metal ions was investigated and additionally the possibility of π-bonding by the anionic pyrrolide system was tested, because the pyrrolide is considered π-iso-electronically to cyclopentadienide.

For characterization of all prepared compounds both vibrational spectroscopic methods (Raman and IR spectroscopy), multi-nuclear magnatic reasonance spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{19}F, INEPT ^{29}Si and ^{31}P) in solution, elemental analysis, thermal analysis (DSC/TGA), mass spectroscopy and X-Ray were applied.

2. Introduction

2.1 Phosphorus cyanide compounds

The first supposed connection between the cyanide and phosphorus is based on a publication by *H. Davy* from 1816.[1] *H. Davy* described the conversion of mercury cyanide with some elements, including phosphorus, whereby the respective compounds were formed, but were not isolated or characterized.

In 1835 *Cenedella* also described a supposed synthesis of phosphorus cyanide compound.[2] Similar to the method by *H.Davy*, elementary phosphorus reacted with $Hg(CN)_2$ by carefully heating in a glass tube, but the resulting product had clearly different properties than the later isolated and characterized phosphorus tricyanide. Therefore it was not established as a synthetic method.

$$2\ \mathrm{P} + 3\ \mathrm{Hg(CN)_2} \longrightarrow 2\ \mathrm{P(CN)_3} + 3\ \mathrm{Hg}$$

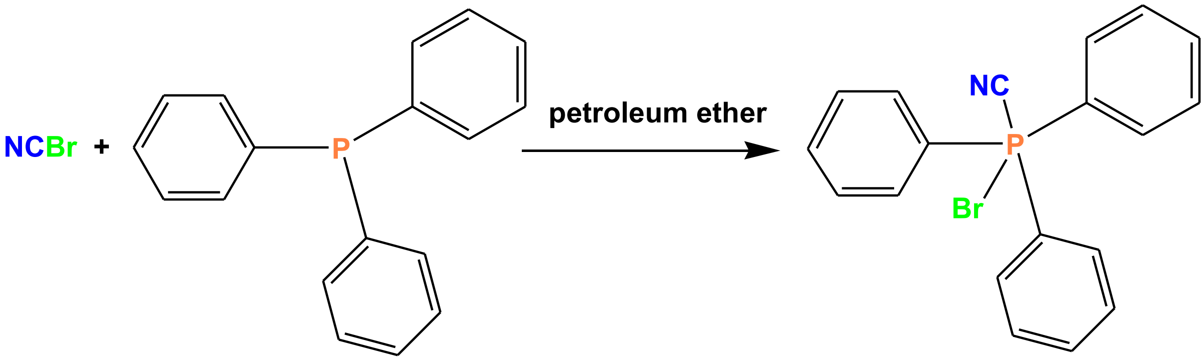
Scheme 1: Supposed formation of $P(CN)_3$ by *H. Davy* in1816[1] and *Cenedella* 1835.[2]

The first proper synthetic method and characterization of $P(CN)_3$ was published by *Hübner* and *Wehrhane* in 1863 and 1864.[3, 4] They filled AgCN, phosphorus and dried chloroform in a sealed vial, which was heated to 120 - 140 °C for 6 - 8 hours.

$$\mathrm{PCl_3} + 3\ \mathrm{AgCN} \xrightarrow[\mathrm{CHCl_3}]{\substack{6\text{ - }8\text{ h} \\ 120\text{ - }140\ ^{\circ}\mathrm{C}}} \mathrm{P(CN)_3} + 3\ \mathrm{AgCl}$$

Scheme 2: Preparation of $P(CN)_3$ by *Hübner* and *Wehrhane* 1863/64.[3, 4]

The first who succeeded in synthesizing a phosphorus^{V}cyanide were *Steinkopf* and *Buchheim* in 1921.[5] For the synthesis of a pentavalent phosphorus, which contained a cyanide, triphenylphosphine was reacted with cyanogen bromide in petroleum ether, obtaining triphenylphosphine bromide cyanide $PPh_3(Br)CN$.



Scheme 3: Formation of $PPh_3Br(CN)$ by *Steinkopf* and *Buchheim* 1921.[5]

One of the first synthetic methods for $[PX_6]^-$ anions by *Lange* and *Müller* was published in 1930.[6] Hydrogen fluoride was reacted with phosphorus pentoxide in the presence of ammonia and after recrystallization with ammonia- ammonium hexafluoridophosphate was obtained.

$$12\ HF + P_2O_5 \xrightarrow{-5\ H_2O} 2\ HPF_6 \xrightarrow{NH_3} [NH_4][PF_6]$$

Scheme 4: Synthesis method of the first P^V salt by *Lange* and *Müller* 1930.[6]

A method for the preparation of phosphorus pentacyanide was developed by *Gall* and *Schüppen* in 1930.[7] The conversion of phosphorus tricyanide with cyanogen was performed under high pressure and heating in a sealed tube. Recent studies have shown that $P(CN)_5$ is formed in oxidizing solvents, but in solvents such as chloroform or dichloromethane it decomposes to $P(CN)_3$ and $(CN)_2$.[8]

In 1958, Me_3SiCN was used by *Bither et al*. as a cyanation reagent for the first time.[9] By a substitution reaction proceeding from half-metal-halogen compounds were obtained the half-metal-cyanide compounds. For example, it was possible to synthesize bismuth tricyanide by the reaction of bismuth trichloride with Me_3SiCN.

$$BiCl_3 + 3\ Me_3Si(CN) \longrightarrow Bi(CN)_3 + 3\ Me_3SiCl$$

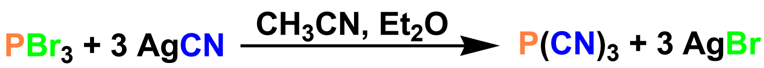
Scheme 5: First cyanation with Me_3SiCN by *Bither et al*. 1958.[9]

The salts of $[PCl_4]^-$ are based on a publication of *Masaguer* from 1957.[10] The reaction of PCl_3 with sulfuryl chloride has been described, whereby $[SO_2Cl]$ $[PCl_4]$ was obtained .

$$SO_2Cl_2 + PCl_3 \longrightarrow [SO_2Cl][PCl_4]$$

Scheme 6: Synthesis of the first P^{III} - salts of *Masaguer* 1957.[10]

Phosphorus tricyanide can be synthesized also by the method of *Bither et al.*[9] from reaction of PCl_3 with Me_3SiCN. A further alternative synthesis method for $P(CN)_3$ was developed by *Maier* in 1963.[11] The reaction of phosphorus bromide was carried out with silver cyanide in acetonitrile. The synthesis method according to *Maier* for $P(CN)_3$ and also to *Dillon* and *Platt* [12] is carried out in diethylether .



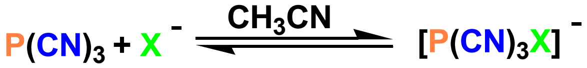
$$PBr_3 + 3\ AgCN \xrightarrow{CH_3CN,\ Et_2O} P(CN)_3 + 3\ AgBr$$

Scheme 7: Synthesis of $P(CN)_3$, starting from PBr_3 by *Maier* 1963.[11]

The effectiveness of the method of *Hübner* and *Wehrhane* was increased by *Jones* and *Coskran*.[13] They also used dried acetonitrile, but the reaction was carried out in a nitrogen atmosphere. Here, the product could already be obtained with good yield after two hours at room temperature.

In addition to the mentioned anion $[P(CN)_3X]^-$ also the cation $[P(CN)_4]^+$ was found, but only in solution along with other tetrapseudohalogenphosphonium cations.[8]

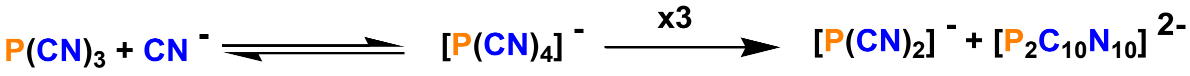
In 1980 *Wilkie et al.* reported the supposed compound potassium tetracyanidophosphate $K[P(CN)_4]$.[14] As described in 1981/82,[15, 16] it may be due the Lewis acidity of the phosphorus atom that leads to adduct formation with halides.



$$P(CN)_3 + X^- \xrightleftharpoons{CH_3CN} [P(CN)_3X]^-$$

Scheme 8: Adduct formation of $P(CN)_3$ with halides by *Dillon* 1981/82.[15, 16]

Further investigations by *Schmidpeter et al.*[17] have shown that the $[P(CN)_4]^-$ ion in solution is formed by adding CN^- to $P(CN)_3$, but then an intermolecular redox reaction of decomposition took place rapidly. This produced a dicyanophosphide, $[P(CN)_2]^-$ and the unusual anion $[P_2C_{10}N_{10}]^{2-}$.



Scheme 9: In-situ formation and decay of $[P(CN)_4]^-$

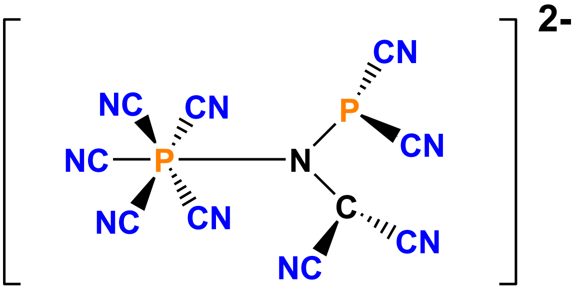
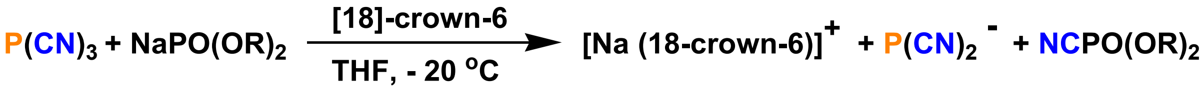


Figure 1: Schematic structure of the anion $[P_2C_{10}N_{10}]^{2-}$

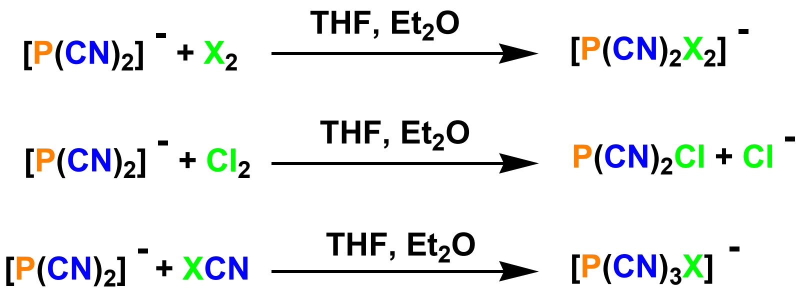
Dicyanophosphide is described for the first time by *Schmidpeter* and *Zwaschka* 1977. The synthesis and properties of this ion were reported.[18] It is prepared by reacting $P(CN)_3$ with dialkylphosphites, $NaPO(OR)_2$, and [18] crown-6 in THF, under cooling to −20 °C.



Scheme 10: Formation of dicyanophosphide anion.

Dicyanophosphide can be considered as a pseudohalide which means that to $P(CN)_3$ could be described as inter pseudo halogen compound. This is consistent with the electrophilic transmission of cyano residue on the dialkylphosphate during the above synthesis. Similarly, the addition of a halide to $[P(CN)_3X]^-$ according to scheme 8 is analogous to the formation of I_3^- from I_2 and I^-.

Substituting $[P(CN)_2]^-$ with X_2 (X = Br, I) by the oxidative addition was gave $[P(CN)_2X_2]^-$ anions also addition XCN instead of halogens to $[P(CN)_2]^-$ anion was gave $[P(CN)_3X]^-$ ion. By contrast, with Cl_2 under the same conditions only $P(CN)_2Cl$ is formed.[19]



Scheme 11: Reactions of $[P(CN)_2]^-$ with halogens and cyanogen halides.

Dicyanophosphide is angled; in the crystal [18] crown-6-K$[P(CN)_2]$ the nitrogen of the CN group coordinates to the K^+ ion, so that zigzag-shaped P-C-N ···K ··· N-C-P- chains are observed in crystal structure.[20]

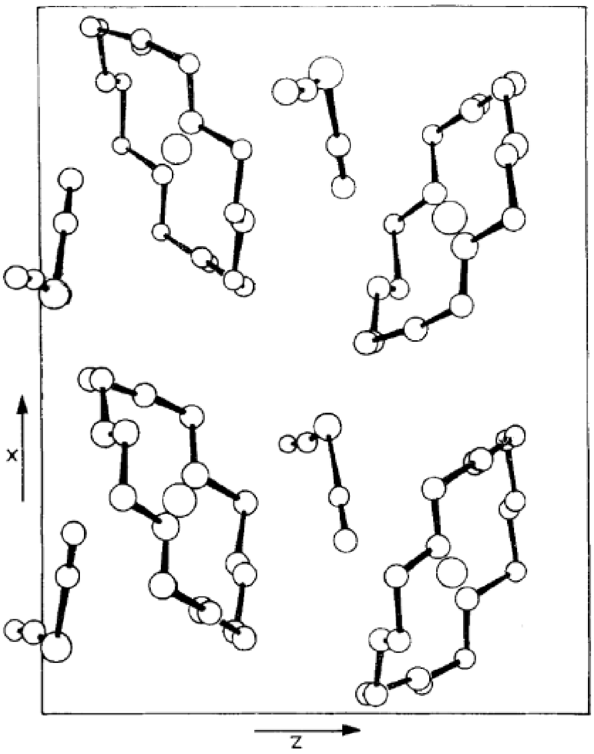
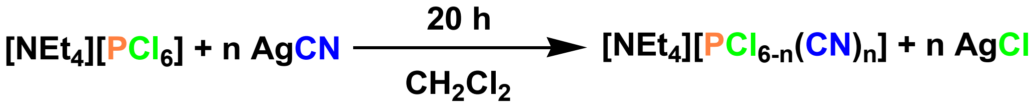


Figure 2: Crystal structure of [18]-crown-6-K$[P(CN)_2]$[20] with P-C-N ··· K ··· N-C-P-chains.

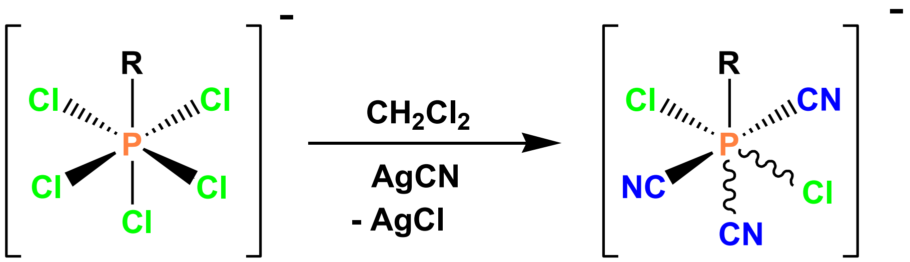
Dillon and *Platt* developed in 1982-83 synthetic methods for Phosphor^{V}cyanide halide compounds.[12, 21] Silver cyanide was at that time the conventional reagent for introducing cyanide. By the reaction of $[NEt_4][PCl_6]$ with AgCN in CH_2Cl_2 the mono-, di- and tricyanido derivatives were obtained (Scheme 12). The compound $[PCl_3(CN)_3]^-$ show at room temperature the greatest stability to hydrolysis in air and further substitutions. The authors attributed this to the lowering of the free T_{2g} 3d orbitals through the CN groups. Due to this lowering of the orbitals can held π interaction with the lone pairs of chlorine atoms, with the strengthening and stabilizing of the P– Cl bonds.



$$[NEt_4][PCl_6] + n\ AgCN \xrightarrow[CH_2Cl_2]{20\ h} [NEt_4][PCl_{6-n}(CN)_n] + n\ AgCl$$

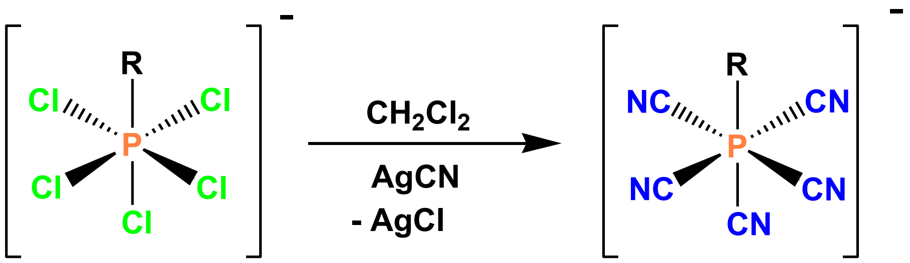
Scheme 12: Synthesis of $[PCl_{6-n}(CN)_n]^-$ anion (n = 1-3) by *Dillon and Platt* 1982/83.[12, 21]

Dillon et al. investigated in 1986/88 organochloridophosphate (V) anions.[22, 23] They discovered that the coordination behavior of $[PPhCl_5]^-$ and $[P(CCl_3)Cl_5]^-$ are not similar to $[PCl_6]^-$ towards the cyanation behavior using silver cyanide. The substitution at this two compounds ends also in the stable tricyanido form ($[PPhCl_2(CN)_3]^-$ or $[P(CCl_3)Cl_2(CN)_3]^-$).



Scheme 13: Cyanation investigation of *Dillon et al.* 1986/88[22, 23] only three chlorine atoms are substituted by CN; R=Ph, CCl_3.

In contrast, the authors found that inserting a small alkyl group, a complete substitution of halogen by cyanide takes place.



Scheme 14: Cyanation investigation of *Dillon et al.* 1986/88[22, 23] all chlorine atoms are substituted by CN; R = Me, Et.

The authors explained these results by the fact that the small alkyl group have a +I-effect that destabilizes the compound and makes the formation of a five-coordinate possible for the transition state, which supports a substitution. Electron-withdrawing substituent, with a –I-effect stabilizes, the hexa- coordinate phosphate anion, so that it is not possible to form a five-coordinate transition state. However, in contradiction to this, is the substitution of $[P(C_6F_5)Cl_5]^-$ by means of AgCN for $[P(C_6H_5)Cl(CN)_4]^-$,[23] although the pentafluorophenyl group with a significantly stronger −I-effect exerted as phenyl radical and should, therefore, be theoretically substituted only up to three times. One possible explanation for this is the fact that the pentafluorophenyl group accepts a larger space consumption and facilitates the dissociation of chlorido- ions.

In 1991 *Krolevets et al.* developed one of the most effective methods for the synthesis of phosphortricyanide.[24] By reacting phosphorus trichloride with Methoxydimethylsilylcyanide for 10 to 25 minutes at 30 - 50 °C $P(CN)_3$ is obtained with a yield of 97% . $(MeO)Me_2SiCN$ is in contrast with Me_3SiCN to a significantly stronger cyanating, by the +M-effect of the other group. The mesomeric effect leads to an increase of the electron density in the system, which in turn promotes a substitution.

$$\mathbf{PCl_3 + 3\ (MeO)Me_2SiCN \xrightarrow[30\ -\ 50\ ^{o}C]{10\ -\ 25\ min} P(CN)_3 + 3\ (MeO)Me_2SiCl}$$

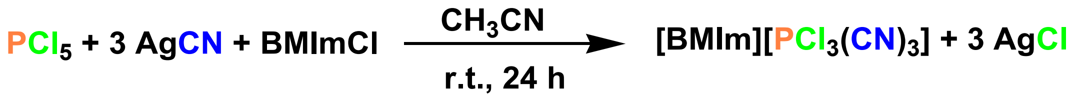
Scheme 15: Preparation of $P(CN)_3$, with $(MeO)Me_2SiCN$.[24]

K. Sievert and *K. Bläsing* in our group developed methods for catalytic syntheses of phosphorus^{V} cyanide compounds.[25] As cyanation reagent trimethylsilyl cyanide was used by addition of catalytic amounts of a variety of Lewis acids. This could be achieved at room temperature and in short times. By reaction of $[^{n}Bu_4N][PF_6]$ with Me_3SiCN the mono-, di-, tri- and tetracyanido phosphates are obtained.

$$\mathbf{[^{n}Bu_4N][PF_6] + n\ Me_3SiCN \xrightarrow[\substack{5\ mol\ \%\ .\ kat.\\ Me_3SiCN\ \ ex}]{25\ ^{o}C\ /\ 117\ ^{o}C} [^{n}Bu_4N][PF_{6-n}(CN)_n] + n\ Me_3SiF}$$

Scheme 16: Synthesis of $[PF_{6-n}(CN)_n]^-$ anion (n = 1-4) by *Sievert* and *Bläsing* 2014.[25]

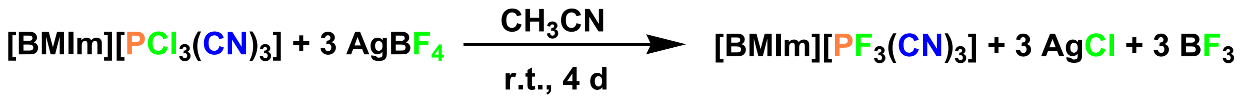
The first use of cyanide phosphate anion in ionic liquids derived from a patent by *The Nippon Synthetic Chemical Industry CO. LTD* from 2012.[26] By reacting phosphorus pentachloride, silver cyanide and BMImCl, will obtain the BMIm- salt of trichloridotricyanidophosphates at room temperature.



$$PCl_5 + 3\ AgCN + BMImCl \xrightarrow[\text{r.t., 24 h}]{CH_3CN} [BMIm][PCl_3(CN)_3] + 3\ AgCl$$

Scheme 17: Synthesis of [BMIm][$PCl_3(CN)_3$].[26]

By reacting the product with silver tetrafluoridoborate can also be accessed a to trifluoridotricyanidophosphate analogous anion. The characterization was carried out by mean of ^1H NMR, ^{31}P NMR, IR spectroscopy and mass spectrometry.



$$[BMIm][PCl_3(CN)_3] + 3\ AgBF_4 \xrightarrow[\text{r.t., 4 d}]{CH_3CN} [BMIm][PF_3(CN)_3] + 3\ AgCl + 3\ BF_3$$

Scheme 18: Synthesis of [BMIm][$PF_3(CN)_3$].

In the literature, significantly fewer from known, the compounds can be found to the other elements of group 15. All arsenic, antimony and bismuth compounds so far were only described as tricyanide $E(CN)_3$, which can be synthesized similar to the phosphorus trichloride from the element trichloride with a cyanation reagent. The characterization was carried out by mean of melting point and elemental analysis.[27] The molecular structure for arsenic tricyanide was published by *K. Emerson and D. Britton* in 1963.[28]

2.2 Tetracyanopyrrolide compounds

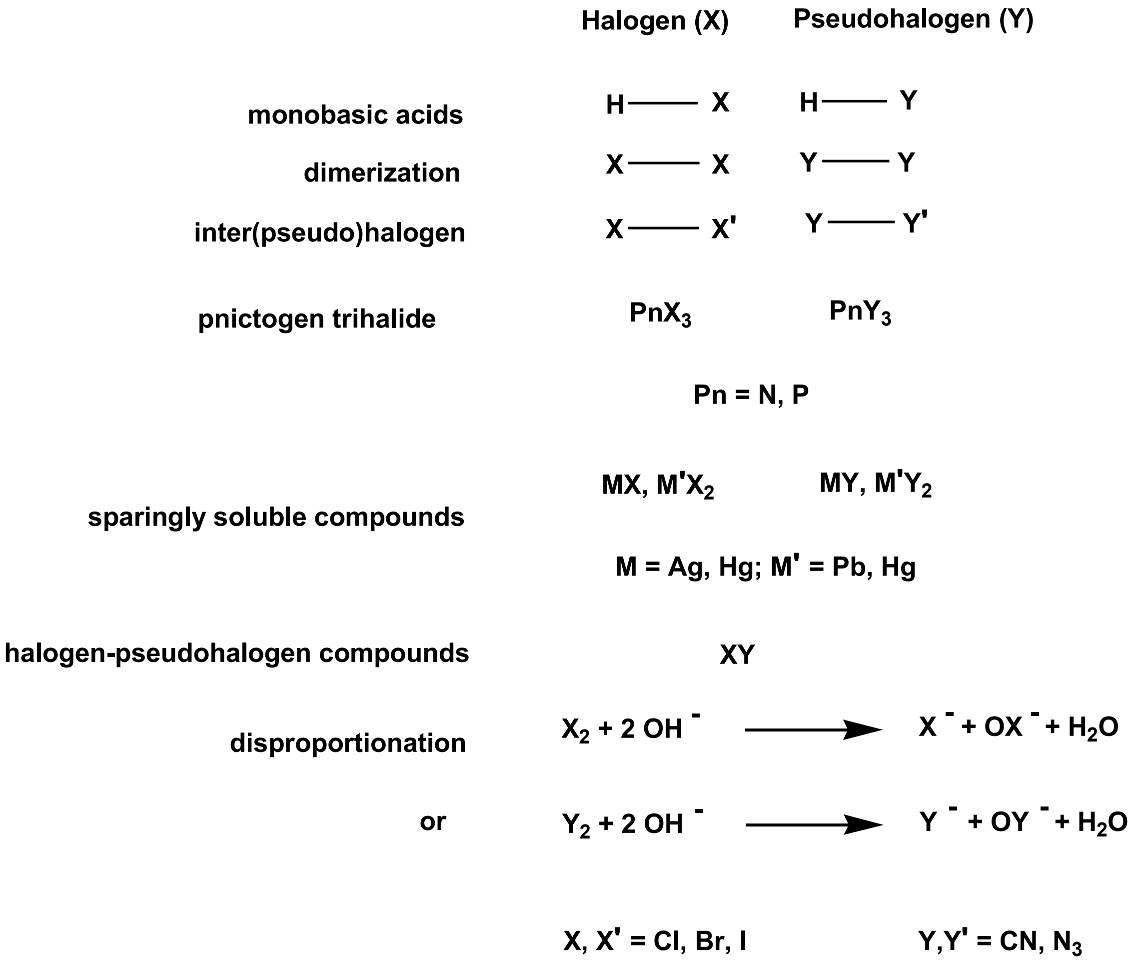
Cyanocarbons are a class of compounds that consist solely of C and N, known as neutral species and as anions. The functionality is mainly dominated by the high number of present cyano groups, which are strongly electron withdrawing groups and participate by resonance with the π system of the underlying carbon ring or chain.

Cyanocarbons are highly electron deficient and are only weakly basic and weakly coordinating.[29] Azole ring based on polynitriles[30] and cyano-substituted pyrroles[31] have been in the focus of theoretical investigations showing the aromaticity, the stability vs. oxidation and decreasing basicity with increasing number of CN groups.

The pentacyanocyclopentadienide anion $[C_5(CN)_5]^-$ is a prominent member due to its high symmetry. The coordination chemistry of $[C_5(CN)_5]^-$ has received substantial attention during the last years for the preparation of metal-organic coordination polymers.[32, 33, 34, 35] In contrast, the chemistry of its congener, in which a nitrogen atom replaces one ring carbon atom, namely the tetracyanopyrrolide anion (TCP) is still scarcely explored. Only some references about tetracyanopyrrolide were reported.[36, 37, 38]

The term *pseudohalogen* was introduced in 1925 for strongly bond, linear or planar univalent radicals (Y•, e.g., Y = CN, OCN, N_3, $SCSN_3$), which can form anions (Y^-), hydracids (H-Y), and neutral species (Y-Y, dipseudohalogens) as well as the interpseudohalogens (X-Y, X = halogen or pseudohalogen)[39, 40, 41] and has remained a widely used this concept ever since.

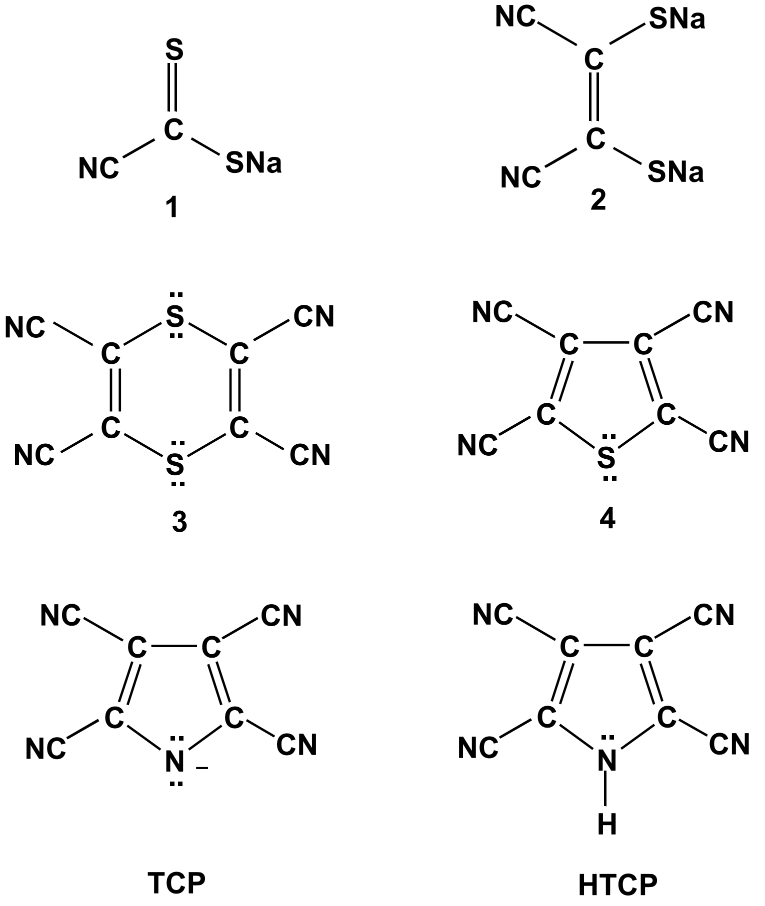
An extension of the concept of pseudohalogens means compounds also singly negatively charged ions form and fulfill the characteristics shown in scheme 19. These are molecules that are no longer linear but planar. An important example of pseudohalides is the $[CS_2N_3]^-$ ion.[42, 43, 44] Two examples of planar pseudohalides are dicyanamide ($[N(CN)_2]^-$) and the tricyanmethanide ($[C(CN)_3]^-$).[45, 46]



Scheme 19: The most important halogen and pseudohalogen compounds compared.

Some other known pseudohalogen acids are isocyanic (HNCO), cyanuric acid $C_3N_3(OH)_3$, fulminic acid (HCNO) as the thiocyanic (HSCN) and isothiocyanic acid (HNCS). In deprotonated form, they are known as the pseudohalides ago as cyanate (OCN^-), isocyanate (NCO^-), thiocyanate (SCN^-) (also called rhodanide), isothiocyanate (NCS^-) and fulminate (CNO^-), all with one negative charge. But selenocyanate ($SeCN^-$) or tellurocyanate ($TeCN^-$) belong to known pseudohalides. In these examples, already a trend becomes clear how to extend such systems. In the case of cyanide it became a cyanate by the addition of a chalcogen. Here this was varied from oxygen to tellurium. Similarly, it is possible to produce new pseudohalides and to extend the concept of pseudohalogens.[47, 48, 49]

The starting materials that are needed for the synthesis of tetracyanopyrrolide are sodium cyanide (NaCN), sodium azide (NaN_3) and carbon disulfide (CS_2). Both NaN_3 and NaCN in it are pseudohalogen compounds. Pseudohalogens are compounds which are no halogens, but behave as halogens or have specific properties that have also halogens. In the textbooks of inorganic chemistry pseudo-elements are discussed.[50] The chemistry of thiacyanocarbons (Scheme 20) was developed by *Bähr* and *Schleitzer* as early as 1955-1957.[51] They started from CS_2 and NaCN to obtain sodium cyanodithioformate, which dimerizes under oxidizing conditions to give disodium dimercaptomaleodinitrile (**2**) as shown in (Scheme 20). Both **1** or **2** can be oxidized to afford tetracyano-1,4-dithiin (**3**) in high yield.[51, 52] The reactive dithiin **3** extrudes sulfur at elevated temperatures to give tetracyanothiophene **4**.



Scheme 20: Thiacyanocarbons and tetracyanopyrrolides.

The free acid (HTCP) of the tetracyanopyrrolide (TCP) ion (Scheme 20) is easily obtained by ion exchange utilizing acidic amberlite resin. HTCP, which is a medium strong acid,[53] forms salts bearing the TCP anion upon addition of strong bases such as MOH (M = R_4N, alkali metal) or even ammonia.[54]

An other chemical term is binary CN compounds, which also include the tetracyanopyrrolide anion (TCP).[54,55] Compared to their hydrogen-containing analogues (amide, methanide, pyrrolide) it was found acceptable from the terms of Bronsted base contrary. While the pK_b value of the Pyrrolide base is − 3.51 and the pKa value of the pyrrole at 17.51,[56] the tetracyanopyrrolide shows only a weak basicity of (pK_b = 11.29) and the HTCP an acidity of (pKa = 2.71),[53] strong delocalization of the negative charge on the CN groups causes the high acidity and the easy deprotonation, respectively.

The tetracyanopyrrolide ion is not only a pseudohalide, but due to the low alkalinity and the associated good distribution of negative charge, it is a weakly coordinating anion (WCA^- −weakly coordinating anion). Typical representatives of weakly coordinating anion are singly charged complex anions such as $[BF_4]^-$, $[AlX_4]^-$ (X = Cl, Br, I), $[PnF_6]^-$(Pn = P, As, Sb), $[XSO_3]^-$(X = F, CF_3) or even $[ClO_4]^-$.[57, 58, 59, 60, 61]

The halogens can of course also be exchanged for pseudohalogens and obtained, for example, $[B(CN)_4]^-$ or $[P(N_3)_6]^-$.[62, 63] Pseudohalogens have the advantage that they are slightly larger and the negative charge can be better delocalized. With the formation of Lewis acid-base adducts the anions (Lewis base) may be greatly magnified by the Lewis acids bonded to them, and thus the concept for the synthesis of WCAs is extended.

K. Voss et al. in our group succeeded in the conversion of tricyanmelaminates with $B(C_6F_5)_3$ to tricyanmelaminate-borane adduct ($[TCMel{\cdot}3B]^-$).[64] Also here, the CN groups as donor groups are involved in the coordination to the borane. From the x-ray crystallographic structure determination of $Na_3[TCMel{\cdot}3B]$ and, however, $MMIm_3$ $[TCMel{\cdot}3B]$ shows that donor-acceptor interactions between the respective cations and the amidic and aromatic nitrogen atoms in the anion (Figure 3).

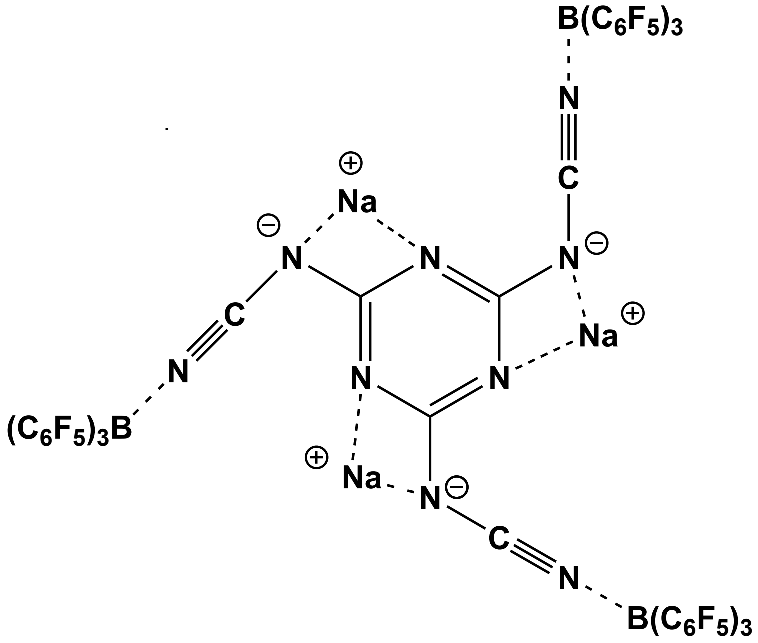


Figure 3: Coordination environment at tricyanmelaminate-borane adduct anion in Na_3[TCMel· 3B].[64]

The presentation of the first moisture- and air-stable ionic liquids led to a steady increase of interest in this class of compounds.[65] Today Ionic liquids (ILs) can be divided into classic ILs, which have a melting point below possess the boiling point of water (<100 ^{0}C) and the more important for many applications Room Temperature ILs (RT-ILs), which are even still liquid at room temperature (<25 ^{0}C). By combination of flow properties of liquids with more interesting properties, such as e.g. electrical conductivity, negligible vapor pressure and high heat capacity, the application is diversified now widely. Ionic Liquids find use as alternative solvents in the so-called "Green Chemistry" (e.g. Cellulose-processing),[66] in catalysis,[67] as a liquid heat storage media[68] and as electrolytes in batteries.[69]

Paul Walden presented in 1914 the first RT-IL, the triehtylammoniumnitrate, which has a melting point at 12 °C.[70] A breakthrough was the work of the research group led by *Wilkes* 1992, which succeeded in synthesizing hydrolytically stable RT-ILs.[71]

With CN-functionalized imidazolium, pyridinium, piperidinium and pyrrolidinium cations (Figure 4) ionic liquids based on CN-functionalized cations are more common in the literature, while about ionic liquids with CN-functionalized anions are known not so much.

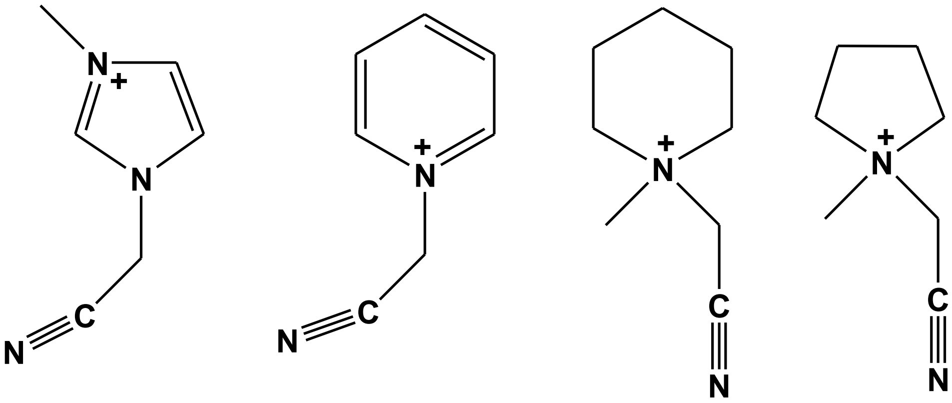


Figure 4: Selected examples of CN-functionalized imidazolium, pyridinium, Piperidinium and pyrrolidinium cations.

One application is known, however, ionic liquids that include the CN-containing 4,5-dicyano-triazolate anion (a) (Figure 5). These ionic liquids, which also are called "Armand's ligand", are effective stabilization reagents for the production of contaminant-free, especially chloride free, highly disperse catalysts.[72] Besides the already mentioned "Armand's ligand" only few more CN- functionalized anions are known which forming ionic liquids with weakly coordinating cations, such as e.g. tetracyanopyrrolide(b),[36] dicyanamide (c),[73] tricyanmethanide (d)[74] or tetracyanidoborate (e).[75] A special feature within the CN-functionalized ILs are the imidazolium-based ionic liquids with the tricyanmelaminate (f) as anion.[64] To the best knowledge , these are the first ionic liquids with a triply negatively charged anion.

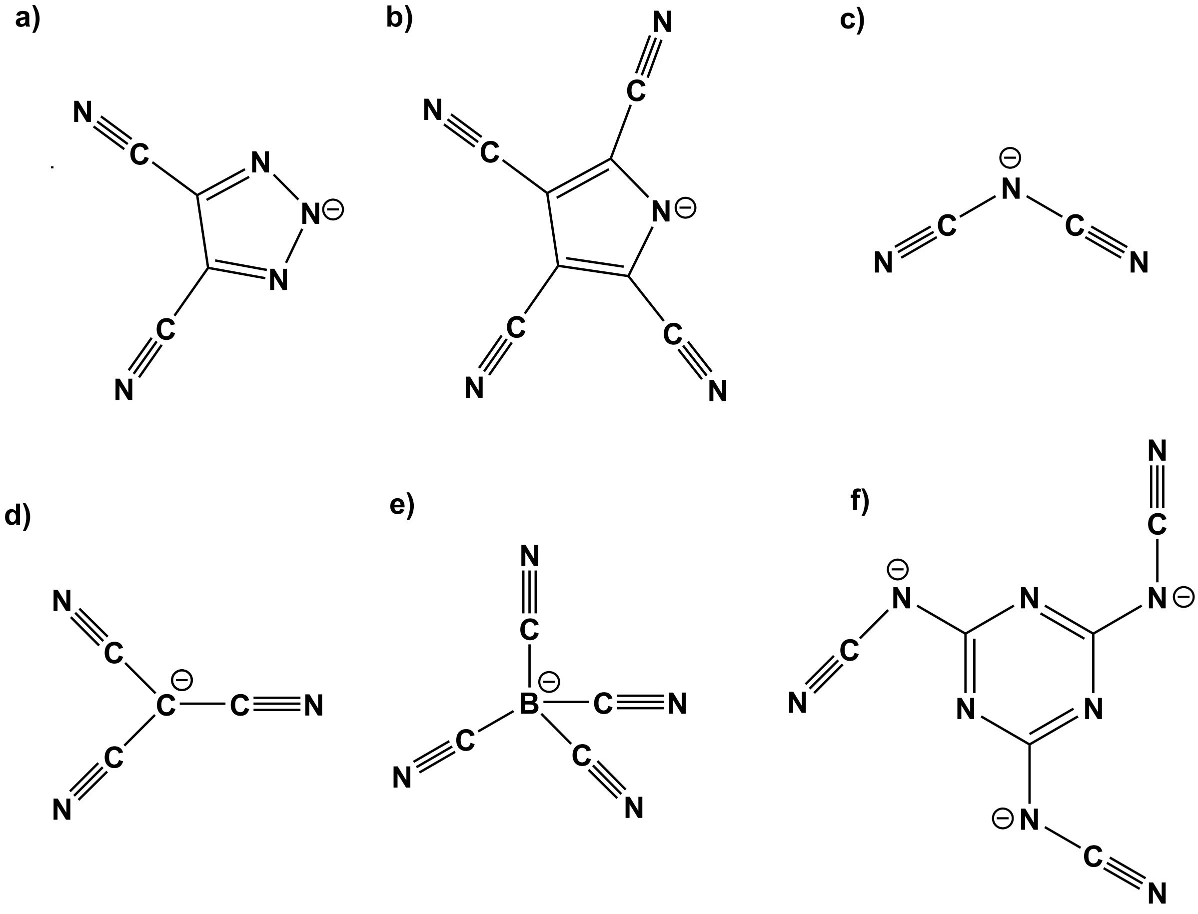
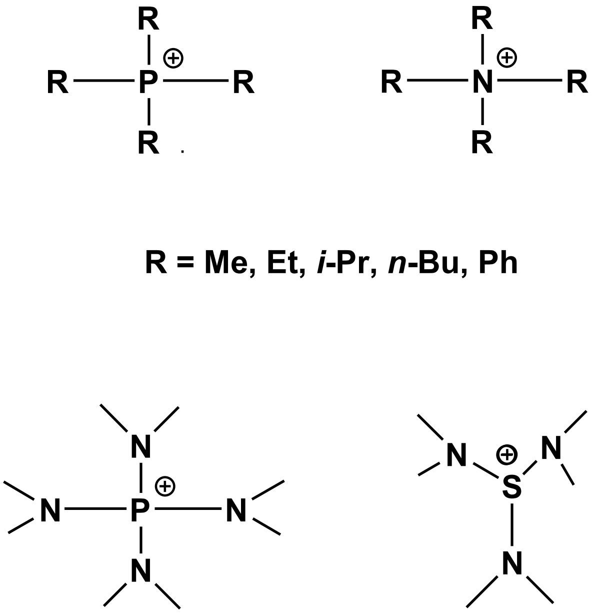


Figure 5: For ionic liquids suitable CN-functionalized anions: 4,5-dicyano-triazolate (a), tetracyanopyrrolide (b), dicyanamide (c), tricyanmethanide (d), tetracyanidoborate (e) and tricyanmelaminate (f).

Ammonium, sulfonium and phosphonium ions are also excellent as weak coordinating cations, if the positive charge is delocalized over a large area and these cations are chemically extremely robust. The first tetraalkylphosphonium compounds are already known since 1871 and were synthesized by *Hofmann*.[76]



Scheme 21: Selected examples of tetraalkylphosphonium, tetraalkylammonium, tetraaminophosphonium and triaminosulfonium cations.

By definition, the coordination polymers are inorganic polymers, in which metal centers and ligands are bridged together by coordinate bonds. The coordination units may extend base their choice in one, two or three dimensions.[77] By varying the metal centers and ligands leave interesting build polymeric structures with special chemical and physical properties. In addition to their high thermal stability they have more specific properties, such as for example luminescence, magnetism and porosity. Thus these are suitable coordination polymers used as materials in LEDs (Light-Emitting Diodes), superconductors and molecular storage media.[78]

Cyanide-bridged copper centers form coordination polymers, luminescence in it have a broad spectral range, co-ligands influence the frequency of the emitted radiation.[79] By bridging of transition metals (eg. nickel, iron, chromium) with cyanides ferromagnetic coordination polymers are could synthesized. Some of these coordination polymers, which also have permanent porosity, can show changes in the magnetic order or the color changing as a function of the load condition with guest molecules, such as in Co^{II}_3 $[Cr^{III}(CN)_6]_2$, was observed.[80]

In addition, a large number of coordination polymers are known from the anionic or neutral poly nitrile ligands are built. Among other things, can be found in the literature a set of coordination polymers with dicyanamide[81] and tricyanmethanide[82] as anionic ligands.

About tetracyanopyrrolide as ligand in coordination polymers, however, is very little known. The first three-dimensional coordination polymer network based on tetracyanopyrrolide was prepared in our group by *T. Jantz* 2012[83] from ion-exchange of [Me_4N][TCP] with sodium cations in acetonitrile, where the solid state indicated the unit cell contains six NaTCP and in addition seven THF solvent molecules, which are linked by numerous interactions. The Na^+ ions have either a 4N + 2O or a 3N + 3O coordination leading to a distorted octahedral environment for all sodium ions. Although, the pyrrolide nitrogen atom always takes part in the Na^+ coordination, either one (Figure 6 and 7) or two CN groups in (Figure 8) remain uncoordinated.

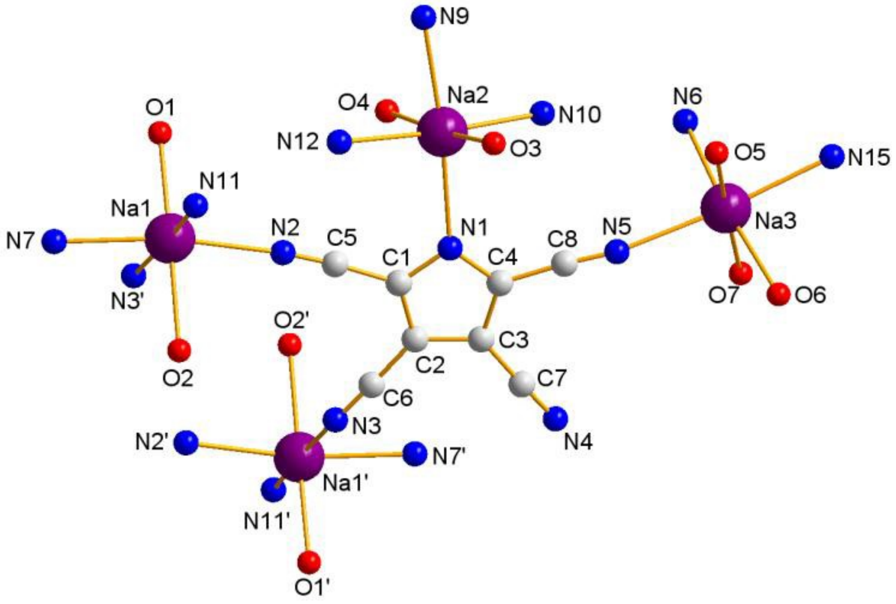


Figure 6: Ball-and-stick representation of a TCP-anion with the coordinating Na cations. Of the THF molecules only oxygen is shown.

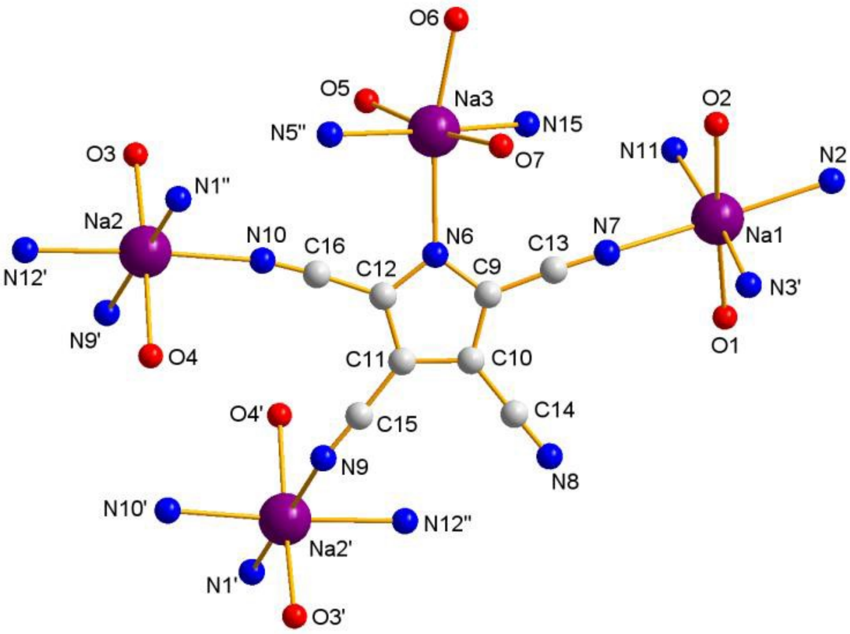


Figure 7: Ball-and-stick representation of a TCP-anion with the coordinating Na cations. Of the THF molecules only oxygen is shown.

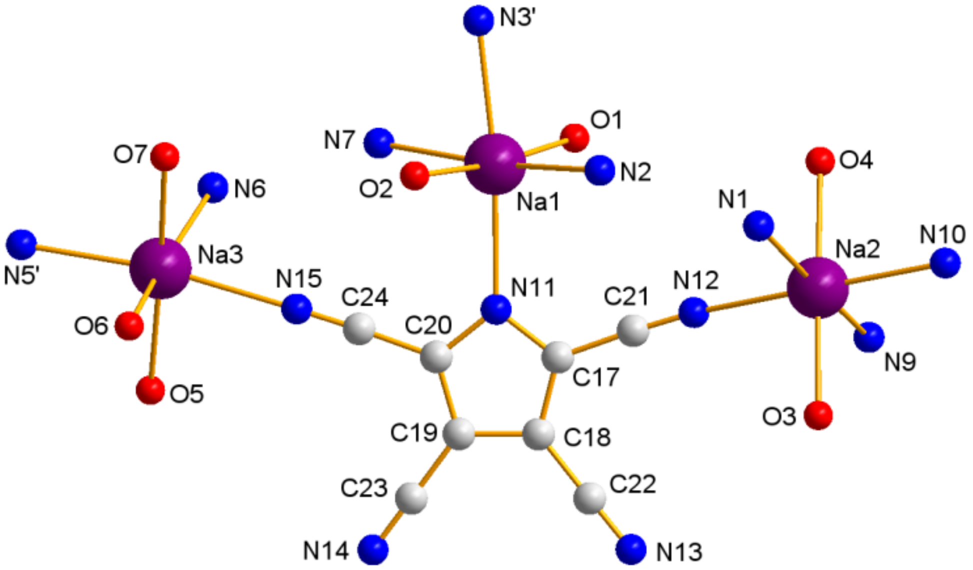
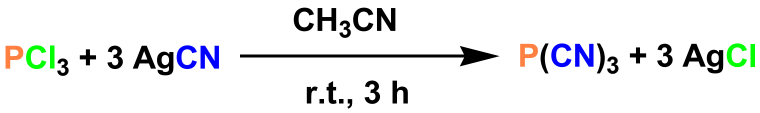


Figure 8: Ball-and-stick representation of a TCP-anion with the coordinating Na cations. Of the THF molecules only oxygen is shown.

3. Results and discussion

3.1 Synthesis of tricyanophosphine

The synthesis of tricyanophosphine was carried out following a literature method.[13] Phosphorus trichloride was added to a suspension of silver cyanide in acetonitrile. This immediately gave milky white precipitate, which is attributed to the formation of silver chloride. In order to avoid the formation of elemental silver, the reaction was carried out in absence of light.



$$PCl_3 + 3\ AgCN \xrightarrow[\text{r.t., 3 h}]{CH_3CN} P(CN)_3 + 3\ AgCl$$

Scheme 22: Synthesis of tricyanophosphine

After filtering off and washing the precipitate, the filtrate was dried in vacuo. It has arisen that an additional safety flask with a cooling bath is useful, since the $P(CN)_3$ starts to sublime under high vacuum at room temperature and in particular is supported from the solution of acetonitrile.

For purification, the crude product was dried initially at room temperature. Later under gentle warming it was sublimated under high vacuum at a bath temperature of 60 °C. Colorless crystals were formed in long white needles.

The **IR-ATR** and **Raman** spectrum of $P(CN)_3$ show a distinct CN band at 2204 cm^{-1}. This is in agreement with comparative data from the literature.[13, 84-85]

NMR spectra were recorded in deuterated dichloromethane. In **^{13}C NMR** spectrum is the split signal of the CN groups of $P(CN)_3$ by coupling with the phosphorus atom to the doublet ($\delta = 110.7$ ppm). In **^{31}P NMR** spectrum can be observed a singlet for the central phosphorus atom at −125.1 ppm.

The shift of the phosphorus atom to the high field falls here at lower than in acetonitrile ($\delta = -137.8$ ppm).[86] This is quite plausible, as in acetonitrile a weak coordinative interaction between the CN group of the solvent and the phosphorus atom of P $(CN)_3$ can be discussed. In addition mole mass investigations have shown that $P(CN)_3$ in acetonitrile solution is present as a dimer.[87] The situation is similar in the solid state, which is also an interaction between the CN groups and the phosphorus center of the $P(CN)_3$.[88] According to the isotropic chemical shift of the phosphorus atom in the ^{31}P MAS-NMR spectrum is ($\delta = -140.0$ ppm), with which is the effect similar to the acetonitrile solution.[89]

The shift of the phosphorus atom in 1-iodopropane is -129.7 ppm[86] and is therefore in a similar range to the value determined for dichloromethane. It is thus that $P(CN)_3$ is less coordinated, as expected in these solvents.

3.2 Reactions of $P(CN)_3$ with Weakly Coordinating Anions $(WCA)^-$ and Lewis bases

3.2.1 General

Weakly coordinating anions $(WCA)^-$ have achieved great interest in olefin polymerization, ionic liquids, stabilizing highly reactive intermediates and battery technology. This interest has led to basic research on the physical and chemical properties of anions containing bulky hydrocarbon and fluoro carbon functionalities over the last two decades.[90] *F. Reiss et al.* in our group was prepared a series of salts containing the terphenyl-substituted bis(amino)phosphenium cation $[(TerNH)_2P]^+$ with different weakly coordinating anions by salt-elimination reactions of $(TerNH)_2P\text{-}Cl$ with AgWCA ($WCA^- = [CF_3CO_2]^-$, $[CF_3SO_3]^-$, $[B(C_6F_5)_4]^-$, $[Al(OCH(CF_3)_2)_4]^-$, $[CHB_{11}H_5Br_6]^-$ and $[SbF_6]^-$ in dry toluene or dichloromethane.[91] So the reaction $P(CN)_3$ with weakly coordinating anions $(WCA)^-$ should be investigated.

Phosphines are known as Lewis bases, usually. But *Wilkie and Parry*[14] have already shown that $P(CN)_3$ do not react with Lewis acids like $AlCl_3$ or B_2H_6. On the other hand $P(CN)_3$ reacts with KCN to give $K[P(CN)_4]$. That is why reactions from $P(CN)_3$ with different Lewis bases should be investigated.

3.2.2 Reactions of $P(CN)_3$ with Weakly Coordinating Anions $(WCA)^-$

These reactions were carried out in expectation to the general reaction shown in scheme 23.

$$P(CN)_3 + Ag\,WCA \longrightarrow [P(CN)_2]^+\ WCA^- + AgCN$$

$WCA^- = [OOCCF_3]^-$, $[Al(OCH(CF_3)_2)_4]^-$, $[BF_4]^-$ and $[B(C_6F_5)_4]^-$

Scheme 23: General reaction of $P(CN)_3$ with weakly coordinating anions

A solution of AgWCA was added to a solution of $P(CN)_3$ in dry tetrahydrofuran or dichloromethane at room temperature. This gave immediately a white precipitate. In order to avoid the formation of elemental silver, the reaction was carried out in absence of light. After filtering off and washing the white precipitate the solvent was removed from the filtrate. The resulting residue was washed two times with tetrahydrofuran or dichloromethane and dried *in vacuo*.

In the reaction of $P(CN)_3$ with $Ag[Al(OCH(CF_3)_2)_4]$, there are changes in **^{13}P NMR** and **IR-ATR** spectra compared to the spectra from the starting materials but it was not possible to isolate any product.

With $P(CN)_3$ and $Ag[B(C_6F_5)_4]\bullet Et_2O$ at room temperature or low temperature (−70 °C), no reaction has occurred. After heating the solution for two hours the **^{19}F NMR** spectrum gave more signals compared to ^{19}F NMR spectrum of starting material.

The use of heating in this reaction could be led to decomposition of the anion, as well as, the melting point of $P(CN)_3$ is between 50 − 60 °C and when using the heating at 50 °C or up from this temperature could be led to decomposition of the $P(CN)_3$.

In all reactions except the reaction with $Ag[B(C_6F_5)_4]$ the presence of a distinct CN band at 2164 cm^{-1} in the IR-ATR spectrum of the white precipitate is observed. This agrees well with comparative data of $(AgCN)_\infty$ from the literature.[92] Where in the case of the $\nu(CN)$ mode, this is readily explained as a consequence of the change in the nature of the vibration when the trimeric units are linked into an infinite chain. The frequency of this mode is partly affected by the $\nu(MC)$ mode through coupling of the coordinates involved in these vibrations.[92] However, the frequency of the $\nu(CN)$ mode also increases as a result of "stiffening" of the CN bond when the cyano group acts as a σ-donor which gives a band at 2094 cm^{-1}.[93] In the case of the infinite chains, a greater frequency increase occurs relative to the monomer because the CN group is involved in a σ-donor interaction with both of the metal atoms that is bridges.[92] Nevertheless it could not be isolated any product which could result from AgCN elimination.

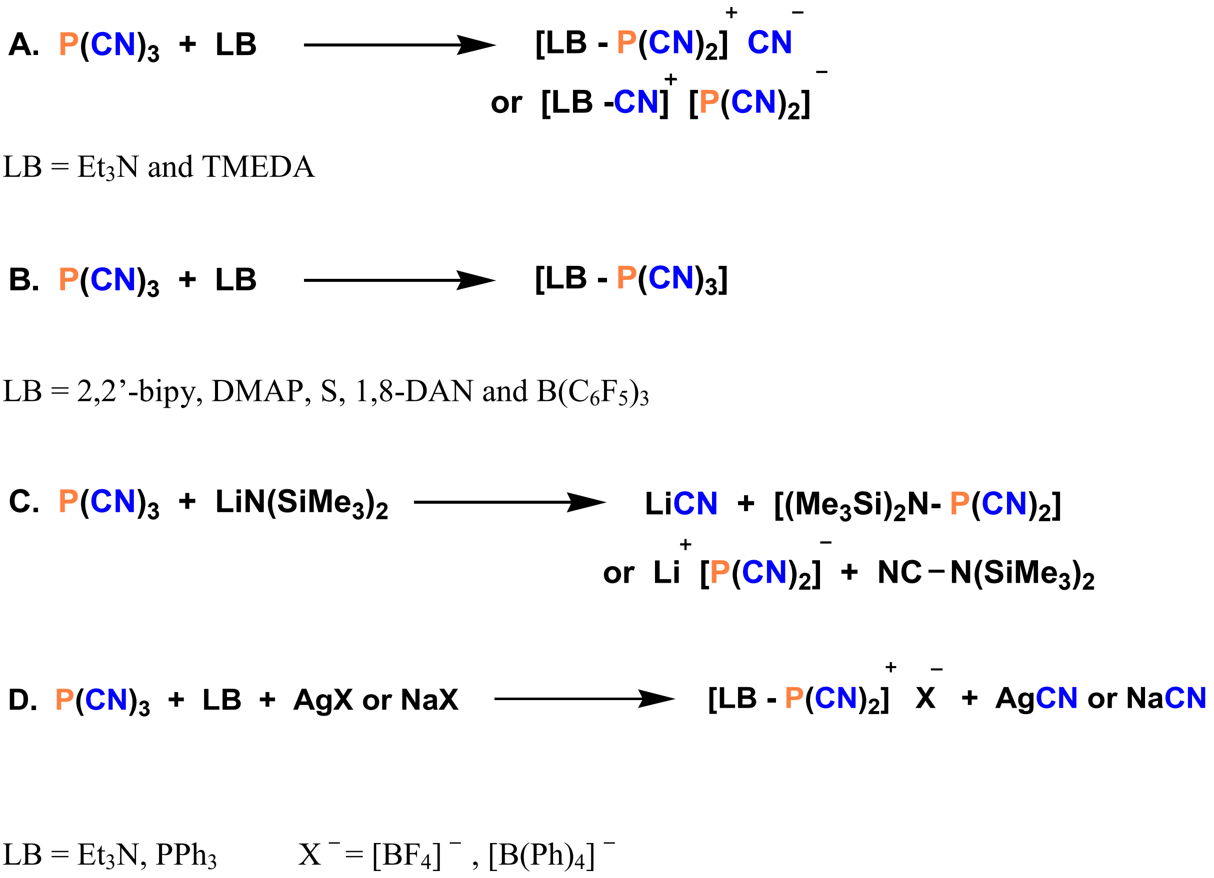
In addition, it is known that the $[Ag(CN)_2]^-$ moiety is a versatile rod-shaped building block for the construction of coordination polymers. However, AgCN is hardly used because its insolubility in common solvent presents serious difficulty in preparation and characterization of the intended products.[94] So we can see the insolubility in most of common solvents for the resulting residue in all reactions because the presence of the AgCN in the structure.

The resulting residue from the mixture after removal of the solvent for all of these reactions is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as CH_3CN or THF, but it shows a solubility in DMSO, and this confirms to the formation of the polymer.

Generally, in all reactions, there are no isolated products, only a mixture from products and starting materials. The crystals obtained from the reaction solutions were characterized always as $P(CN)_3$.

3.2.3 Reactions of $P(CN)_3$ with Lewis bases

These reactions were carried out in expectation to the general reactions shown in scheme 24.



A. $P(CN)_3 + LB \longrightarrow [LB-P(CN)_2]^{+}\ CN^{-}$ or $[LB-CN]^{+}\ [P(CN)_2]^{-}$

LB = Et_3N and TMEDA

B. $P(CN)_3 + LB \longrightarrow [LB-P(CN)_3]$

LB = 2,2’-bipy, DMAP, S, 1,8-DAN and $B(C_6F_5)_3$

C. $P(CN)_3 + LiN(SiMe_3)_2 \longrightarrow LiCN + [(Me_3Si)_2N-P(CN)_2]$ or $Li^{+}\ [P(CN)_2]^{-} + NC-N(SiMe_3)_2$

D. $P(CN)_3 + LB + AgX \text{ or } NaX \longrightarrow [LB-P(CN)_2]^{+}\ X^{-} + AgCN \text{ or } NaCN$

LB = Et_3N, PPh_3 $X^- = [BF_4]^-$, $[B(Ph)_4]^-$

Scheme 24: General reactions of $P(CN)_3$ with Lewis bases

The general reaction of **A** was carried out according to the following procedure. Lewis bases were added at −70 °C to a solution of $P(CN)_3$ in dry dichloromethane. The resulting yellow solution was warmed up to ambient temperature. After stirring overnight for the yellow solution at room temperature, resulting in a brown solution. The solvent was removed *in vacuo* and the residue was dried *in vacuo*.

In the reaction of $P(CN)_3$ with Et_3N and TMEDA, there is observed a change in ^{13}P NMR and IR-ATR spectra compared to the starting solution but that it was not possible to isolate any product, as well as, it seems the dicyano phosphide ion $[P(CN)_2]^-$unstable in the solution, and in these reactions may be tricyanophosphine behave as an interpseudohalogen compound, NC−$P(CN)_2$, with “positive cyanogen”.[18]

The resulting residue from the mixture after removal of the solvent from these reactions is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as CH_3CN or THF, but it shows a solubility in DMSO.

The general reaction of **B** was carried out according to the following procedure. A solution of Lewis base was added at room temperature or low temperature to a solution of $P(CN)_3$ in dry tetrahydrofuran or dichloromethane. After stirring overnight for the solution at room temperature, the solvent was removed *in vacuo* and the residue was dried *in vacuo*.

In the reaction of $P(CN)_3$ with 2,2'-bipyridine and sulfur at room temperature or low temperature (−70 °C), no reaction has occurred, where in **^{31}P NMR** and **IR-ATR** spectra show the same signal for $P(CN)_3$ and the same vibration for CN group at $P(CN)_3$.

With $P(CN)_3$ and $B(C_6F_5)_3$, there is observed a change in **^{11}B NMR** spectrum compared to ^{11}B NMR spectrum of $B(C_6F_5)_3$, but it was not possible to isolate any product.

In the reaction of $P(CN)_3$ with DMAP (DMAP = 4-dimethylaminopyridine) and 1,8- DAN (DAN = diaminonaphthalene), there are changes in **^{31}P NMR** and **IR-ATR** spectra at room temperature or low temperature compared to the spectra from the starting materials but that it was not possible to isolate any product.

The resulting residue from the mixture after removal of the solvent in all reactions is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as CH_3CN or THF, except the resulting residue from the reaction with $B(C_6F_5)_3$ and 1,8-diaminonaphthalene shows a good solubility in polar solvents such as CH_2Cl_2, CH_3CN and THF.

The reaction of **C** was carried out according to the following procedure. A solution of $LiN(SiMe_3)_2$ was added at −70 °C to a solution of $P(CN)_3$ in dry tetrahydrofuran. The resulting yellow solution was warmed up to ambient temperature. After stirring three hours for the yellow solution at room temperature, resulting in a yellow solution. The solvent was removed *in vacuo* and the residue was dried *in vacuo*.

The idea from this reaction was that on the one hand, the interaction of a Li^+ cation with the one CN group in $P(CN)_3$ to formation LiCN and on the other hand could generate the reaction of $(Me_3Si)_2N^+$ with $[P(CN)_2]^-$ to formation neutral product $[(Me_3Si)_2N{-}P(CN)_2]$.[95]

In the **^{31}P NMR** spectrum, there is a major signal at − 197.50 ppm was confirmed the formation of $[P(CN)_2]^-$ anion[17] and in **INEPT ^{29}Si NMR** spectrum a signal at −11.71 ppm was confirmed the presence of ***Si*** in product. In the **^{1}H NMR** spectrum shows a singlet signal at 0.3 ppm due to CH_3 group in trimethylsilyl. But unfortunately it was not possible to isolate any product.

The general reaction of **D** was carried out according to the following procedure. A solution of Lewis bases was added to a solution of $P(CN)_3$ in dry dichloromethane or tetrahydrofuran at − 70 °C. After stirring 30 min, a solution of silver tetraflouridoborate or sodium tetraphenylborate in dry dichloromethane or tetrahydrofuran was added at − 70 °C. After stirring overnight for the yellow solution at room temperature, the solvent was removed *in vacuo* and the residue was dried *in vacuo*.

The reaction $P(CN)_3$ with trimethylamine and sodium tetraphenylborate was achieved as described above. The yellow solution was concentrated and stored at −30 °C for four days resulting colorless crystals.

The isolated colorless crystals belong only to the triethylammoniumsalt of the tetraphenylborate. The proton could come from the solvent. **$[Et_3NH{\bullet}THF]^+$ $[B(Ph)_4]^-$** (Figure 9).

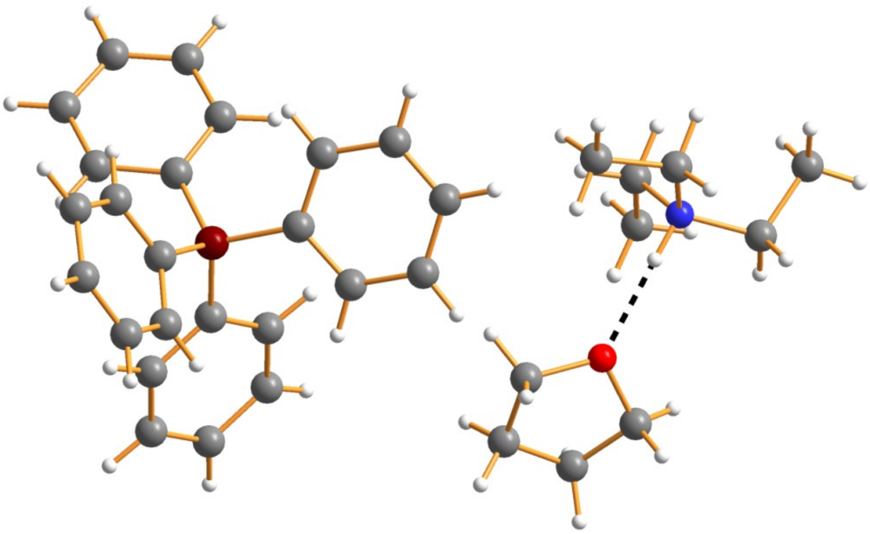


Figure 9: Ball and stick representation of **$[Et_3NH•THF]^+$ $[B(Ph)_4]^-$** with the color code: dark Red –Boron, blue –Nitrogen, red –Oxygen, gray – Carbon, white – Hydrogen.

In the reaction of $P(CN)_3$ with PPh_3 and $Na[B(Ph)_4]$, there is observed a change in **^{31}P NMR** spectrum compared to the spectra from the starting materials, but that it was not possible to isolate any product.

About the reaction of $P(CN)_3$ with Et_3N and $AgBF_4$, there is observed a change in **^{31}P NMR** spectrum, as well as, in the **IR-ATR** spectrum shows a vibration for CN group at 2164 cm^{-1} was confirmed the formation of AgCN, but that it was not possible to isolate any product.

Although the presence of more changes in **NMR** (**^{31}P**, **^{19}F** and **^{11}B**) and **IR-ATR** spectra compared to the spectra from the starting materials are observed, but in all reactions, there are no isolated products, only a mixture from products and starting materials.

3.2.4 Reaction of $P(CN)_3$ with triphenylphosphine (5)

It is known that pure $P(CN)_3$ is associated in solution[96] and that in the solid state[97] nitrogen atoms are significantly closer to the phosphorus atoms than van der Waals distances. These facts suggest internal acid-base interactions, with phosphorus as the acid center and nitrogen as the base.[98]

The reaction of $P(CN)_3$ with triphenylphosphine was carried out according to the following procedure. Triphenylphosphine was added at − 40 °C to a solution of $P(CN)_3$ in dry dichloromethane. After stirring overnight at room temperature, the orange brown solution was concentrated and stored at –30 °C for three days, which results colorless crystals.

Surprisingly, the product for the reaction of PPh_3 with $P(CN)_3$ in a dichloromethane solution was unexpected and was obtained as colorless crystals of the product $[Ph_3P{=}N{-}C(CN)_2{-}C(CN)_2{-}N{=}PPh_3]{\bullet}2CH_2Cl_2$ **(5)**. That means an oxidation from P(III) to P(V) has occurred.

The structure of the tetracyanodiiminophosphorane **(5)** consists of two PPh_3 units linked by a $-NC(CN)_2C(CN)_2N-$ bridge (Figure 10). The molecule has center symmetry, with the $N{-}PPh_3$ units adopting an anti-configuration along the $C1{-}C1^i$ bond. The P1−N1 bond length = 1.576(13) Å is consistent with a P=N double bond, with the P1−N1−C1 bond angle of 129.3(10)° being somewhat larger than the idealized 120° expected for an sp^2 nitrogen atom. The C1−N1 bond length of 1.409(19) Å is typical for a C−N single bond, while the terminal CN bond lengths are consistent with C≡N triple bonds.

Godfrey et al.[99] prepared dicyano triphenylphosphine from the reaction of PPh_3 with PhSeCN in diethyl ether. They obtained after several weeks crystals from acetone solution for the same reaction, these crystals were characterized as tetracyanodiiminophosphorane by mean of ^{31}P NMR and IR spectra.

The mechanism for the formation of $[Ph_3P{=}N{-}C(CN)_2{-}C(CN)_2{-}N{=}PPh_3]$ is unclear, but it seems that it forms $PPh_3(CN)_2$ in the first step from the reaction and then happened decomposition for this product. The elimination of $(CN)_2$ from $PPh_3(CN)_2$, followed by attack of PPh_3 at the nitrogen atom is likely to result in the initial formation of unsaturated bridged species, such as $Ph_3P{=}N{-}C{\equiv}C{-}N{=}PPh_3$. This unit would be susceptible to successive addition of $(CN)_2$ across the unsaturated carbon-carbon bonds, thus resulting finally in $[Ph_3P{=}N{-}C(CN)_2{-}C(CN)_2{-}N{=}PPh_3]$.[100]

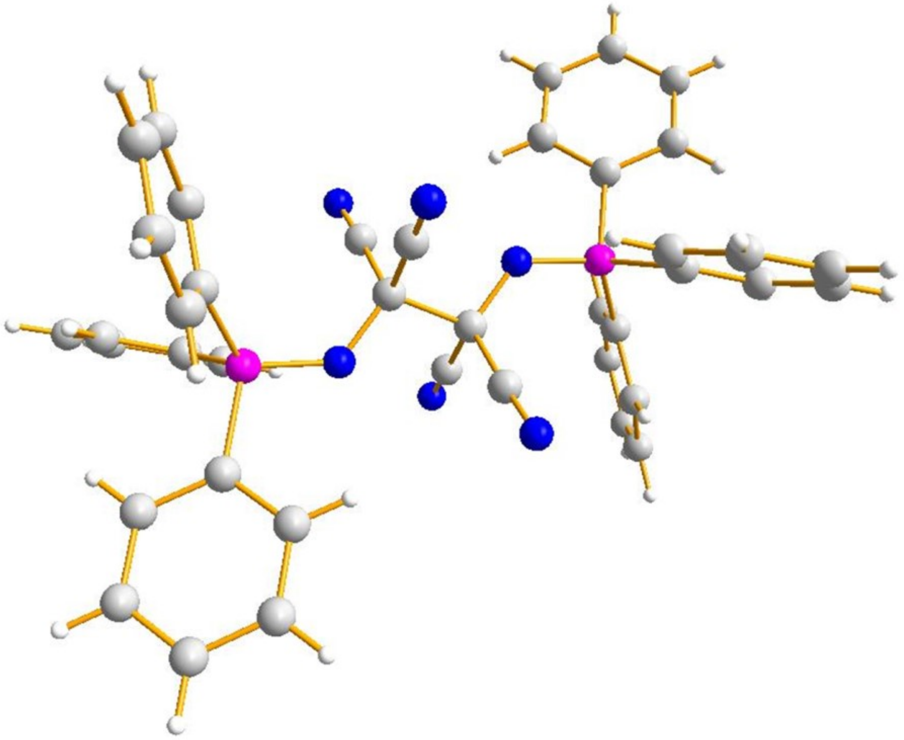


Figure 10: Ball and stick representation of **5** with the color Code: pink − Phosphorus, blue − Nitrogen, gray − Carbon, white − Hydrogen.

NMR spectra were recorded in deuterated dichloromethane. In **^{1}H NMR** spectrum of the product, the aromatic ring protons appear as a multiplet in the range 7.58−7.23 ppm and **^{13}C NMR** spectrum confirms the presence of the aromatic ring protons.

The **^{31}P NMR** spectrum shows one signal at 27.65 ppm due to triphenyl phosphine,[99] a significant down field shift was observed after coordination to the nitrogen atom as compared to free $P(CN)_3$ which gives a signal at −125.1 ppm.

In the **IR-ATR** spectrum, the vibration band at 2187 cm^{-1} confirms the presence of the CN groups, compared to IR spectrum of $P(CN)_3$ which gives a vibration band for CN group at 2204 cm^{-1}.

3.3 Reactions of $P(CN)_3$ with transition metal complexes

3.3.1 General

Phosphines are among the most important ligands in organometallic chemistry, with a wide range of steric and electronic properties. They have found widespread applications in transition metal-catalysed asymmetric syntheses. The catalytic activity of these complexes ranges from hydrogen transfer [101] to ring-closing metathesis.[102]

So that in a further part the possibility of using $P(CN)_3$ as a ligand in transition metal chemistry should be investigated.

3.3.2 Reaction of $P(CN)_3$ with dichloro(*p*-cymene)ruthenium(II)dimer

The reaction was carried out according to the following procedure. A solution of dichloro (*p*-cymene) ruthenium(II) dimer in dichloromethane (*p*-cymene=1-methyl-4-(1-methylethyl)benzene was added to a solution of $P(CN)_3$ in dichloromethane. After stirring overnight for the red solution at room temperature, diethyl ether was added with stirring after reducing the solvent to about **3** mL, the solvent was removed *in vacuo.*

For purification, the yellow precipitate was washed with dichloromethane two times and was dried *in vacuo*.

NMR spectra were recorded in deuterated dimethylsulfoxide. In **^{1}H NMR** spectrum of the product, the *p*-cymene signals are well-resolved and exhibit only H–H coupling. The aromatic ring protons appear as a multiplet in the range 7.05–7.10 ppm. The protons of isopropyl group $HC(Me)_2$ signals appear as a doublet at 1.16 ppm.

The **^{31}P NMR** spectrum shows one signal at − 11.33 ppm due to phosphine ligand, a significant down field shift was observed after coordination to the metal as compared to free $P(CN)_3$ which gives a signal at −125.1 ppm, as well as, **^{13}C NMR** and **mass** spectra confirm the presence of the *p*-cymene ring.

New strong vibration at 2143 cm^{-1} in the **IR-ATR** spectrum confirms the presence of the CN groups compared to IR-ATR spectrum of CN group at $P(CN)_3$ which gives a vibration at 2204 cm^{-1}. The stretching frequency of the cyanide band is shifted by about 60 cm^{-1}. It is apparent that the chloride ligands participate to enhance donation of the electron ion pairs from both the atoms in the CN moiety towards the ruthenium metal center, which are in fact anti-bonding with respect to C=N bond. Hence the *v*(C=N) frequency increases with increasing donation of these ion pairs.[103]

The compound is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as CH_3CN or THF, but it shows a good solubility in DMSO.

Unfortunately it was not possible to isolate crystals.

3.3.3 Reaction of $P(CN)_3$ with tetrakis(triphenylphosphine)palladium(0) (6)

The aim of this synthesis was the preparation of the homoleptic complex $Pd\{P(CN)_3\}_4$, considering that $P(CN)_3$ shows parallels to PF_3 in the coordination behavior, especially the calculated HOMO-LUMO gap is comparable to PF_3, which is a strong π-acceptor.

The reaction was carried out according to this procedure. A solution of $Pd(PPh_3)_4$ in tetrahydrofuran was added at −70 °C to a solution of an excess $P(CN)_3$ in tetrahydrofuran. This gave after stirring overnight at room temperature a yellow precipitate, removed by filtration and dissolved in dichloromethane. The yellow solution was concentrated and stored at −30 °C for one day, which results colorless crystals.

The product of the reaction of $Pd(PPh_3)_4$ with $P(CN)_3$ in a tetrahydrofuran was the unexpected complex $[Pd(PPh_3)_2(CN)_2]$. That means an oxidation from Pd(0) to Pd(II) has occurred, as well as, there is no coordination of phosphorous atom to metal ion.

The synthesized compound **6** crystallizes in the orthorhombic unit cell space group *pbca*. The crystal structure of $[Pd(PPh_3)_2(CN)_2]$ contains mononuclear complex with the central metal ion Pd^{2+} located in inversion center.

The crystal structure **6** (Figure 11) confirms the trans arrangement of the two triphenyl phosphine donors. The coordination geometry around the palladium atom is slightly distorted square planar where the $P{-}Pd{-}P^{i}$ angle is 180.00(8)° and the $C1{-}Pd{-}C1^{i}$ angle is 180.0(3)°. The plane of the CN group is oriented perpendicular to the palladium coordination plane. The

Pd−P bond lengths (2.314(11) Å) and Pd−C1 bond lengths (1.994(5) Å) fall in the range previously observed for the related palladium(II) complexes.[104]

NMR spectra were recorded in deuterated dichloromethane. In the **^{1}H NMR** spectrum, the signal of the aromatic ring protons appears as a multiplet in the range 7.38−7.59 ppm.

The **^{31}P NMR** spectrum shows one signal at 23.06 ppm due to triphenyl phosphine,[105] a significant down field shift was observed for coordination to the metal as compared to free $P(CN)_3$ which gives a signal at −125.1 ppm.

The C≡N group can be detected in the **Raman** spectrum, the band appears at 2144 cm^{-1}. In the **IR-ATR** spectrum, the band appears at 2131 cm^{-1}. These vibrations confirm of the CN groups coordinated to the metal, compared to IR and Raman spectra of $P(CN)_3$ which give a vibration band for CN group at 2204 cm^{-1} .

The compound **6** is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene, but it shows a good solubility in polar solvents such as CH_2Cl_2 and THF.

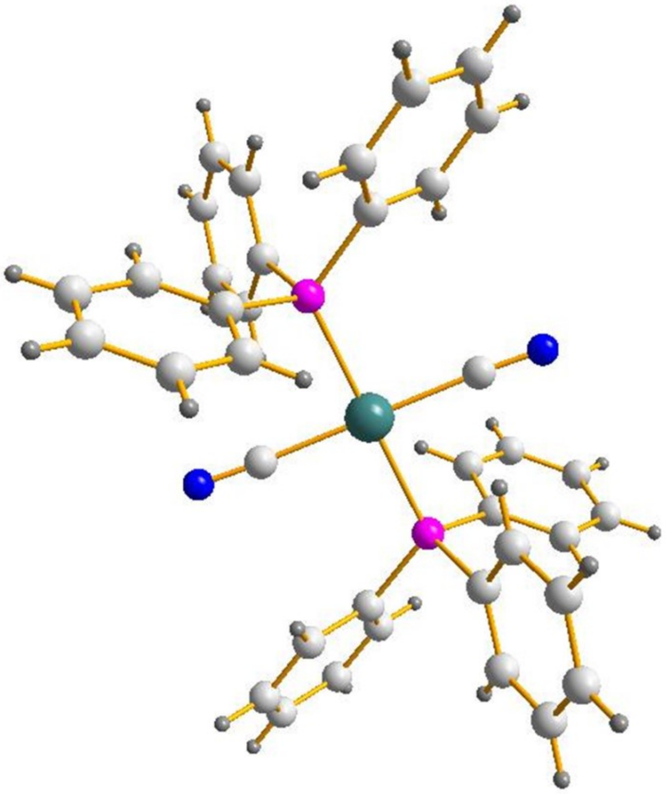


Figure 11: Ball and stick representation of **6** with the color code: dark green − Palladium, pink − Phosphorus, blue − Nitrogen, White − Carbon, gray − Hydrogen

3.3.4 Reaction of $P(CN)_3$ with 1,1,1-tris(diphenylphosphinomethyl)ethane nickel(0) (7)

The reaction was carried out according to the following procedure. A solution of 1, 1, 1-tris(diphenylphosphinomethyl)ethane (triphos = $CH_3C(CH_2PPh_2)_3$) in tetrahydrofuran was added to a solution of $Ni(COD)_2$ in tetrahydrofuran (COD = cyclooctadiene). After stirring four hours at room temperature, a solution of $P(CN)_3$ in tetrahydrofuran was added. This gave a brown precipitate after stirring overnight, which was removed by filtration.

To work up, the solvent was removed *in vacuo* and the residue was dissolved in dichloromethane and concentrated, diethyl ether was added dropwise and stored at room temperature for two days resulting red crystals.

The isolated red crystals are not the expected cyanophosphine complex but the mononuclear complex $[Ni(triphos)(CN)_2]$. That means an oxidation from Ni(0) to Ni(II) has occurred, as well as, there is no coordination of phosphorous atom to metal ion.

The synthesized compound **7** crystallizes in the monoclinic unit cell space group $P2_1/C$. The crystal structur of $[Ni(triphos)(CN)_2]$ contains mononuclear complex with the central metal ion Ni^{2+} located in inversion center.

The crystal structure **7** (Figure 12) shows an idealized square-pyramidal coordination of the nickel center with one of phosphorus donors occupying the apical position and with the other two phosphorus donors and the two co-ligands (CN groups) are forming the base of the pyramid. The apical Ni−P2 bond (2.36 (5) Å) was longer than the equatorial Ni−P bonds (2.19−2.20 (4) Å). The P−Ni−P angle are, by virtue of being part of the chelate cage, close to 90^o. The C−Ni−C angle spanned by the coordination atoms of the cyano groups is found at $84.97(7)^o$. The P−Ni−C angles fall in two classes. The angles referring to CN groups which are in an idealized *trans* position to each other show values between 156^o and 158^o, while angles referring to mutual idealized *cis* positions are in a range between $87^o - 110^o$. The deviations from the idealized square-pyramidal geometry are thus substantial.[106]

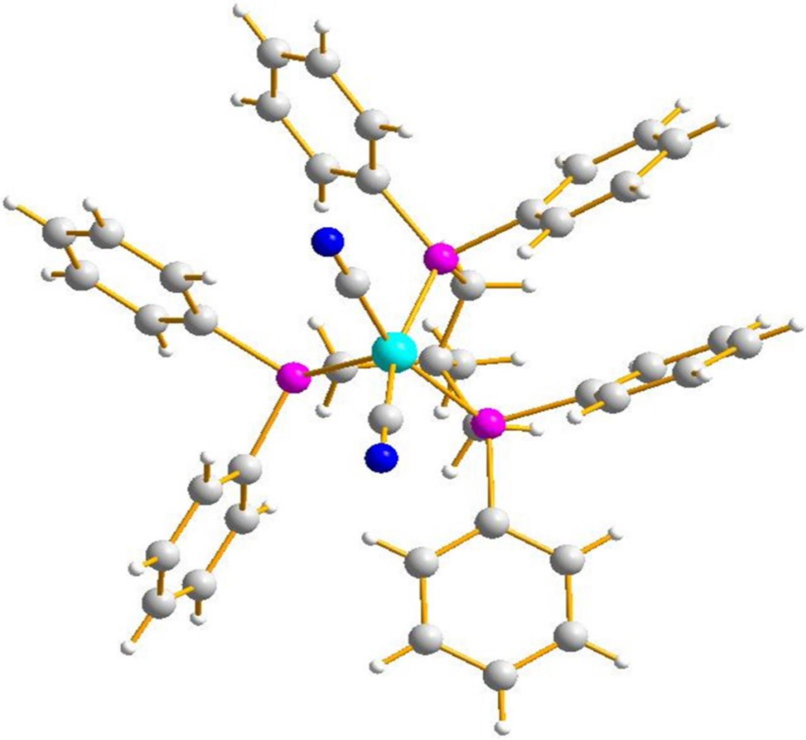


Figure 12: Ball and stick representation of **7** with the color code: dark blue– Nickel, pink– Phosphorus, blue–Nitrogen, gray – Carbon, white – Hydrogen.

NMR spectra were recorded in deuterated dichloromethane. The **^{1}H NMR** spectrum results confirm the presence of the 1,1,1-tris(diphenylphosphinomethyl)ethane ligand (triphos).

In the **^{31}P NMR** spectrum of the compound, the signal for the product was at a major chemical shift of $\delta = -3.70$ (1.0) ppm due to1,1,1-tris(diphenylphosphinomethyl)ethane ligand (triphos).

The C≡N group can be detected in the **Raman** spectrum, the band appears at 2123 cm^{-1}. In the **IR-ATR** spectrum, the band appears at 2116 cm^{-1}. These vibrations confirm of the CN groups coordinated to the metal, compared to IR and Raman spectra of $P(CN)_3$ which give a vibration band for CN group at 2204 cm^{-1}.

The compound **7** is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene, but it shows a good solubility in polar solvents such as CH_2Cl_2 and THF.

3.3.5 Reaction of $P(CN)_3$ with [hydridotris(3,5-dimethylpyrazolyl)borate tricarbonyltungsten(II)] and ferroceniumhexafluorophosphate

In this reaction the sevenfold coordinated tungsten(II) hydrotris(3,5-dimethylpyrazolyl)borate tricarbonyl phosphine complex was used. The tris(3,5-dimethylpyrazolyl)borate ligand is especially sterically demanding, with an estimated cone angle of 244°. The lable "tetrahedral enforcer" should use to describe this.[107]

The reaction was carried out according to the following procedure. Oxidation of the anionic tungsten (0) tricarbonyl reagent $[\ TpW(CO)_3]^-$ by ferrocenium hexafluorophosphate generates a neutral 17-electron radical tungsten (I). To prepare 7-coordinated phosphine complex after oxidizing the $TpW(CO)_3$ radical with ferrocenium, presumably a cationic 16-electron tungsten (II) intermediate $[\ Tp^-W(CO)_3]^+$ is generated, which has solvent coordinated in accord with 18-electron-rule guidelines. Addition of tricyano phosphine may be lead to formation of the 7-coordinated cationic complex. The residue was washed two times with diethyl ether to remove ferrocene and the residue was dried *in vacuo*. It was not possible to isolate crystals.

The **^{19}F NMR** spectrum of the residue, a doublet at −73.3 ppm to be detected for the fluorine atoms at the central phosphorus atom in the anion. In **^{31}P NMR** spectrum can be observed a septet at −144.5 ppm belongs to coordinate phosphorus atom of the hexafluorophosphate, as well as, one singlet signal at −65.68 ppm may be attributed to coordinate phosphorus atom with tungsten atom.

In **IR-ATR** spectrum, three bands appear at 1910, 1960 and 2045 cm^{-1} belongs to carbonyl group, as well as, one band at 2228 cm^{-1} for CN group, compared to IR spectrum of $P(CN)_3$ which gives a vibration band for CN group at 2204 cm^{-1} .

Surprisingly, **mass spectrum** (negative ions) shows the highest intensity peak at *m/z* = 144.964687 corresponding to the $[PF_6]^-$, but mass spectrum (positive ions) shows the highest intensity peak at *m/z* = 566.167 corresponding to the $TpW(CO)_3H^+$ with other peak at *m/z* = 542.167.

3.3.6 Reaction of $P(CN)_3$ with tris(propionitrile)tricarbonylmolybdenum(0)

The reaction was carried out according to the following procedure. A solution of $[Mo(CO)_3(EtCN)_3]$ was added to a solution of $P(CN)_3$ in dry dichloromethane. After stirring overnight for a yellow solution at room temperature the brown precipitate was removed by filtration, the solvent was removed *in vacuo* and the residue was dried *in vacuo*.

In this reaction, no changes in **^{31}P NMR** and **IR-ATR** spectra compared to the spectra from the starting materials are observed, while ^{31}P NMR spectrum for the brown precipitate did not give any signal because it was insoluble in most of the solvents. It was not possible to isolate any product.

3.4 Reactions of $P(CN)_3$ with Room Temperature Ionic Liquids (RT-ILs)

3.4.1 General

Room Temperature Ionic Liquids (RT-ILs) are salts with low melting points composed of an organic cation and either an organic or an inorganic anion.[108] In contrast to classical solvents, ionic liquids possess a series of outstanding advantages as electrolytes such as no vapor pressure, high thermal stability, wide range of solubility and wide electrochemical window.[109] *Hardacre et al.*[110] have shown that addition of N-methylimidazole (NMI) to a solution of PCl_3 in $[EMim]^+$ $[OTf]^-$ resulted in the formation of a yellow precipitate, probably of $[P(NMI)_3]Cl_3$ which rapidly hydrolysed when exposed to air.

So reactions from $P(CN)_3$ with different room temperature ionic liquids (RT-ILs) should be investigated.

3.4.2 Reaction of $P(CN)_3$ with 1-ethyl-3-methylimidazolium dicyanamide in dichloromethane

The reaction was carried out according to the following procedure. A solution of 1-ethyl-3-methylimidazolium dicyanamide was added to a solution of $P(CN)_3$ in dry dichloromethane at 0 °C. After stirring four hours at room temperature the color changed from yellow to brown. After stirring overnight at room temperature the solvent was removed *in vacuo.*

For purification the brown precipitate was washed two times with acetonitrile and was dried for 6 h *in vacuo*.

NMR spectra were recorded in deuterated acetonitrile. In **^{1}H NMR** and **^{13}C NMR** spectra show the signals belong to EMIm cation.

In the **^{31}P NMR** spectrum of the residue, there is a major chemical shift of $\delta = -194.82$ ppm (s, $[P(CN)_2]^-$),[17] compared to ^{31}P NMR spectrum of $P(CN)_3$ which gives a signal at −142 ppm.

New vibration at 2165 cm^{-1} in the **IR-ATR** spectrum confirms the presence of the CN groups compared to IR-ATR spectrum of CN group at $P(CN)_3$ which gives a vibration at 2204 cm^{-1}. By mean of **DSC** measurement the decompose temperature at 305 °C, at a heating rate of 10 K / min was determined.

The residue from the mixture after removal of the solvent is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene. It shows very poor solubility in common polar organic solvents such as MeCN or THF. In water, at the same time the residue is unstable and a water hydrolyzation takes place because ^{31}P NMR spectrum in D_2O shows new signals at 0.25 and 2.65 ppm and these signals refer to form phosphoroxide or phosphonic acid $[DPO(OD)_2]$.

3.4.3 Reaction of $P(CN)_3$ with 1-ethyl-3-methylimidazolium dicyanamide in tetrahydrofuran

The reaction was carried out according to the following procedure. A solution of 1-ethyl-3-methylimidazolium dicyanamide was added to a solution of $P(CN)_3$ in dry tetrahydrofuran at 0 °C. After stirring overnight for the deep brown oily solution at room temperature the solvent was removed *in vacuo* and the *deep brown oily precipitate* was dried *in vacuo*.

For purification the deep brown oily precipitate was washed six times with acetonitrile. The *brown precipitate* was separated by filtration and was dried for 12 h *in vacuo*. From the deep brown solution the solvent was removed *in vacuo* and the *deep brown precipitate* was dried *in vacuo*.

After stirring overnight, new vibration shows at 2173 cm^{-1} in the **IR-ATR** spectrum of the *deep brown oily precipitate* confirms the presence of the CN groups compared to IR-ATR spectrum of CN group at $P(CN)_3$ which gives a vibration at 2204 cm^{-1}.

In the ^{31}**P NMR** spectrum of the *deep brown oily precipitate* there is a major chemical shift of $\delta = -194.43$ ppm (s, $[P(CN)_2]^-$),[17] compared to ^{31}P NMR spectrum of $P(CN)_3$ which gives a signal at −142 ppm.

NMR spectra were recorded in deuterated acetonitrile. In ^{1}**H NMR** and ^{13}**C NMR** spectra of the *deep brown oily precipitate* show the signals belong to EMIm cation.

After washing with acetonitrile, the ^{31}**P NMR** spectrum of the *brown precipitate* was not clear because it was insoluble in deuterated acetonitrile. The ^{1}**H NMR** and **mass** spectra refer to EMIm cation but the ^{13}**C NMR** spectrum was not clear. A new vibration at 2172 cm^{-1} in the **IR-ATR** spectrum of the *brown precipitate* confirms the presence of the CN groups compared to IR-ATR spectrum of CN group at $P(CN)_3$ which gives a vibration at 2204 cm^{-1}, but when using high temperature at 200 ^{o}C for three hours, new vibration for CN group shows at 2166 cm^{-1}.

For filtrate after washing with acetonitrile and filtration, new vibration shows at 2170 cm^{-1} in the **IR-ATR** spectrum of the *deep brown precipitate* confirms the presence of the CN groups. In the ^{31}**P NMR** spectrum of the *deep brown precipitate* there is a major chemical shift of $\delta = -194.43$ ppm (s, $[P(CN)_2]^-$).[17] **NMR** spectra were recorded in deuterated acetonitrile. In ^{1}**H NMR** and ^{13}**C NMR** spectra show the signals belong to EMIm cation.

In **DSC/TGA** results of the *brown precipitate*, it can be seen is comparably stable before being heated to 257 ^{o}C and evaporation of some solvent in the compound causes the mass loss before 100 ^{o}C. The obvious mass loss of 39.5% between 257 and 335 ^{o}C, should be caused the decomposition of compound.

The *brown precipitate* is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene. It shows very poor solubility in common polar organic solvents such as MeCN or THF. In water, at the same time the *brown precipitate* is unstable and reacted under water (hydrolyzation) because ^{31}P NMR spectrum in D_2O shows new signals at 0.25 and 2.65 ppm and these signals refer to form phosphoroxide or phosphonic acid $[DPO(OD)_2]$.

3.4.4 Reaction of $P(CN)_3$ with silver dicyanoamide–tris(pentafluorphenyl) Borane•diether

The reaction was carried out according to the following procedure. A solution of $Ag[N\{CN{\bullet}B(C_6F_5)_3\}_2]{\bullet}2Et_2O$ in fluorobenzene was added to a solution of $P(CN)_3$ in fluorobenzene. After stirring overnight for the yellow solution at room temperature the solvent was removed *in vacuo* and the residue was dried *in vacuo*.

In the ^{31}**P NMR** spectrum of the residue there is a major chemical shift of $\delta = 142.88$ (1.0) ppm. Furthermore, there are signals at $\delta = 49.67$ (0.2) and 17.39 (0.2) ppm, which are associated to resulting by-products.

The ^{19}**F NMR** spectrum of the residue shows resonances shifted to lower frequency compared to $B(C_6F_5)_3$ in starting material, but similarly broad. The ^{11}**B NMR** spectrum shows a signal at −13.35 ppm compared to ^{11}B NMR spectrum of starting material which gives a signal at −12.10 ppm.[111]

A new vibration at 2222 cm^{-1} in the **IR-ATR** spectrum of the residue confirms the presence of the CN groups compared to IR-ATR spectrum of CN group at $P(CN)_3$ which gives a vibration at 2204 cm^{-1} and IR-ATR spectrum for CN group at $Ag[N\{CN{\bullet}B(C_6F_5)_3\}_2]$ which gives a vibration at 2291 cm^{-1}.[111, 112]

The residue is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene, but it shows a good solubility in polar solvents such as CH_3CN, that means it is not a polymer.

Unfortunately it was not possible to isolate any products or crystals from all reactions of $P(CN)_3$ with Room Temperature Ionic Liquids (RT-ILs).

3.5 Reactions of tetracyanopyrrolide

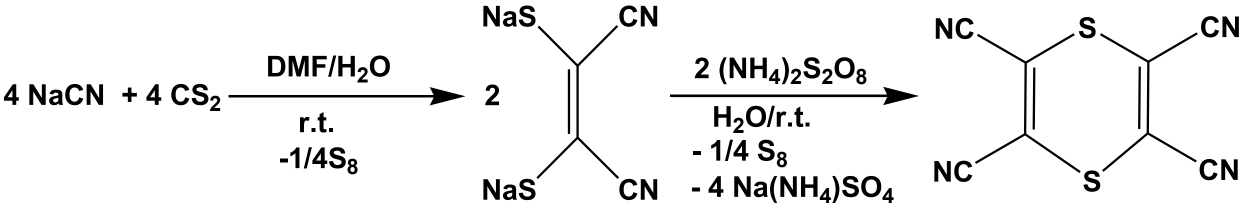
3.5.1 General

With respect to the coordination chemistry tetracyanopyrrolide is furnished with five donor centers, three of which are of different type: cyanide group in 2- and 3- position and the pyrrolide N ring atom. Therefore the anion is an extremely versatile ligand with potential to form coordination polymers and finally, the possibility of π-bonding by the anionic pyrrolide system will be tested, because the pyrrolide is considered π-iso electronically to cyclopentadienide.

In the following part the possibility of using the tetracyanopyrrolide anion as a ligand in transition metal chemistry should be investigated.

3.5.2 Synthesis of tetracyano-1,4-dithiin ($C_8N_4S_2$)

The synthesis of tetracyano-1,4-dithiin was carried out following a literature method.[51, 54-55] Carbon disulfide was added dropwise to a suspension of NaCN and DMF with stirring vigorously, H_2O was added and the mixture was stirred overnight at room temperature. The resulting sulfur was filtered off, under stirring ammonium peroxodisulfate as an oxidizing reagent was added and tetracyano-1,4-dithiin was obtained as product.



Yield: 67%

Scheme 25: Direct conversion of cyanide and carbon disulfide in DMF and subsequent oxidation by ammonium peroxodisulfate in water to dithiin.

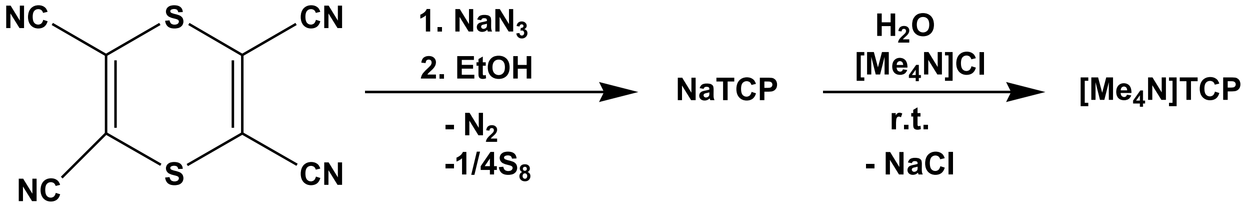
For purification, the crude product was dried at room temperature, several recrystallisations from a saturated dichloroethane solution of tetracyano-1,4-dithiin resulted yellow crystals, which were already isolated and discussed by *Martin Becker* in our group.[113]

The C≡N group can be detected in the **^{13}C NMR** spectrum, the signal appears at 125.4 ppm and in the **IR-ATR** spectrum the band appears at 2218 cm^{-1}. In the **Raman** spectrum, the band appears as a very sharp peak at 2220 cm^{-1}. This vibration in the IR and Raman spectra confirms the presence of the CN groups.

3.5.3 Synthesis of tetramethylammoniumtetracyanopyrrolide [Me$_4$N]TCP

The synthesis of tetramethylammoniumtetracyanopyrrolide was carried out following a literature method.[36] The dithiine was dissolved in ethanol and added to sodium azide. In addition faster vigorous evolution of gas is observed, since N_2 escapes. The solution is dark and sulfur deposits can be observed. For work up, the ethanol is removed and the brown residue was dissolved in water. The resulting sulfur was filtered off. To the resulting sodium-tetracyanopyrrolide (NaTCP) resulting from the reaction in byproducts separate, which was dissolved in water and filtrated. Tetramethylammoniumchloride ([Me$_4$N]Cl) as a saturated aqueous solution was added at 0 °C and the tetramethylammoniumtetracyanopyrrolide was obtained as product.

For purification, the crude product was dried at room temperature, several recrystallisations from a saturated isopropylalcohol solution pure tetramethylammoniumtetracyanopyrrolide was obtained as colorless crystals, which were already isolated and discussed by *Martin Becker* in our group.[113]



Yield: 70%

Scheme 26: Scheme of reaction steps from dithiin to [Me$_4$N]TCP.

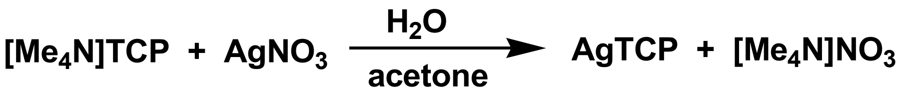
The C≡N group can be detected on the vibration in the **Raman** spectrum at 2233 cm^{-1}. In the **IR-ATR** spectrum, the band appears as a very sharp peak at 2220 cm^{-1}. This vibration in the

IR and Raman spectra confirms the presence of the CN groups. By **DSC** measurement the melting point at 272 °C and decompose temperature at 324 °C, at a heating rate of 10 K / min were determined.

Characteristic of the TCP anion are the four **^{13}C NMR** signals occurring at a shift of 119.7, 114.5, 112.4 and 102.0 ppm. It involves singlet signal as where the methyl group of the cation, which can be found at 54.4 ppm. The NMR spectrum was measured in DMSO-d_6, in which all pyrrolides solve very well, as all precursors. The NMR spectra are thus suitable for a direct signal comparison.

3.5.4 Synthesis of Silver tetracyanopyrrolide AgTCP

The synthesis of silver tetracyanopyrrolide was carried out following a literature method.[36] A solution of silver nitrate in water was added to a solution of tetramethylammonium tetracyanopyrrolide in mixture (H_2O and acetone). In order to avoid the formation of elemental silver, the reaction was carried out in absence of light. After stirring for 3 h, the precipitate was removed by filtration, washed three times with ethanol and was dried *in vacuo*.



$$[Me_4N]TCP + AgNO_3 \xrightarrow[\text{acetone}]{H_2O} AgTCP + [Me_4N]NO_3$$

Yield: 75%

Scheme 27: Synthesis of silver tetracyanopyrrolide

The **NMR** spectrum was recorded in deuterated dimethylsulfoxide. In the **^{13}C NMR** spectrum the signals of the TCP$^-$ anion appear at 119.8, 114.3, 112.3 and 102.1 ppm.

In the **IR-ATR** spectrum, the band appears as a very sharp peak at 2233 cm^{-1}. This vibration in the IR spectrum confirms the presence of the CN groups. By **DSC** measurement the melting point at 270 °C and decompose temperature at 313 °C, at a heating rate of 10 K / min were determined.

3.5.5 Synthesis of tetracyanopyrrole HTCP

Procedure 1

Simmons et al.[53,54] described the possibility of starting from tetramethylammoniumtetracyanopyrrolide to obtain the acidic compound (Scheme 28). A column was charged with Amberlyst 15 ion exchange resin. The column was washed with 10 mol% HCl, de-ionized water, acetone, and acetonitrile. Tetramethylammonium tetracyanopyrrolide was dissolved in acetonitrile and added slowly to the given column. Free pyrrole was eluted with acetonitrile.

For purification, the residue was eluted to column chromatography (Ethyl acetate / heptane (v: v = 3: 1)). After evaporating under reduced pressure, the precipitate was washed two times with dichloromethane under heating, and dried *in vacuo* at room temperature.

Martin Becker in our group has also carried out this reaction, the product was obtained by column chromatography and isolated from the water adduct as colorless crystals, which was already discussed.[113]

$$\textbf{[Me}_4\textbf{N]TCP} \xrightarrow[\textbf{CH}_3\textbf{CN}]{\textbf{10\% HCl}} \textbf{HTCP} + \textbf{[Me}_4\textbf{N]Cl}$$

Yield: 45%

Scheme 28: Ion exchange in which a $[Me_4N]^+$ ion is exchanged to a H^+ ion.

A **^{1}H NMR** spectrum appears a singlet signal at a shift of 11.03 ppm, which is attributed to the NH group in CD_3CN. In **^{13}C NMR** spectrum the typical TCP signals at shifts of 112.1, 108.8, 107.6 and 105.7 ppm in CD_3CN are seen, these signals in the ^{13}C NMR spectrum confirm the presence of the CN groups.

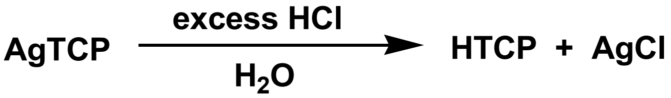
In the **IR-ATR** spectrum shows as a strong vibration band at 2243 cm^{-1} and this confirms the presence of the CN groups.

Procedure 2

Tetracyanopyrrole free from water was prepared for the first time by *Simmons* in 1962[53] and characterized by IR-ATR, elemental analysis and mass spectroscopy but the yield from this reaction was 20%. *Thomas Jantz* in our group in 2012[83] prepared tetracyanopyrrole containing two water molecular using ion-exchange column of $[Me_4N]TCP$ in acetonitrile with full characterization but the yield from this reaction was 54% .

So we deceided preparation tetracyanopyrrole free from water in high yield by new procedure as the following: excess hydrochloric acid was added to a suspension of silver tetracyanopyrrolide in water at room temperature. After stirring overnight, the suspension was filtrated and the solvent was removed under reduced pressure.

For purification, the precipitate was washed two times with dichloromethane under heating and was dried *in vacuo* for 6 h at room temperature. Sublimation of the residue at (150 °C) for 6 h gave tetracyanopyrrole as a white crystalline solid. The interesting in this procedure the yield was high 71% .



$$\mathbf{AgTCP} \xrightarrow[\mathbf{H_2O}]{\textbf{excess HCl}} \mathbf{HTCP + AgCl}$$

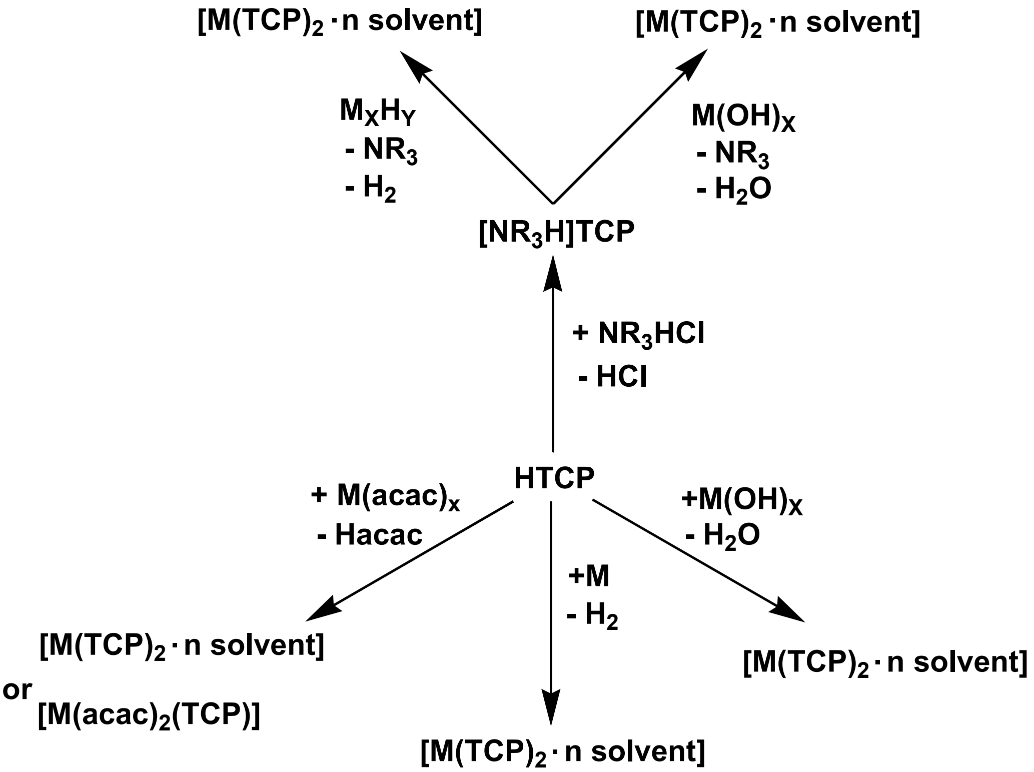
Yield: 71%

Scheme 29: Reaction of AgTCP with HCl in water for HTCP.

The C≡N group can be detected in the **Raman** spectrum, the band appears at 2252 cm^{-1}. In the **IR-ATR** spectrum, the band appears as a strong vibration band at 2244 cm^{-1}. This vibration in the IR and Raman spectra confirms the presence of the CN groups. By **DSC** measurement the melting point at 207 °C and decompose temperature at 237 °C, at a heating rate of 10 K / min were determined.

Characteristic of the TCP anion are the four **^{13}C NMR** signals occurring at a shift of 112.1, 108.7, 107.6 and 105.8 ppm in CD_3CN. These signals in the ^{13}C NMR spectrum confirm the presence of the CN groups. In **^{1}H NMR** spectrum shows a singlet signal at a shift of 11.09 ppm, which is attributed to the NH group in CD_3CN. The cyano groups thus provide a dramatic increase in the acidity of the nitrogen proton, which is also clearly reflected in the down field shift resonance signal in ^{1}H NMR spectrum shows (9.27 in the ^{1}H pyrrole [114] vs.11.9 ppm in the tetracyanopyrrole).

So we utilized the tetracyanopyrrole as a ligand to prepare new transition metal complexes shown in scheme 30.



M = Mg $^{2+}$, Fe $^{2+}$, Cu $^{2+}$, Zn $^{2+}$, Mn $^{3+}$ and Cr $^{3+}$

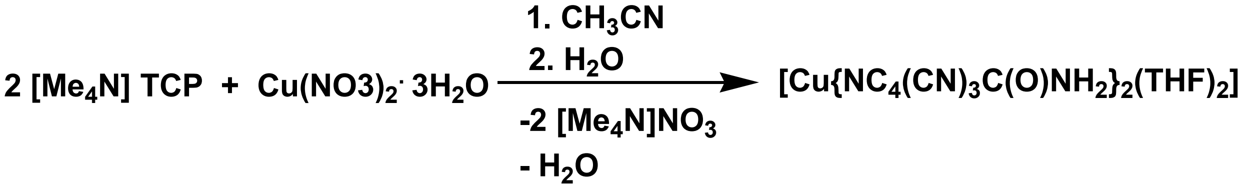
R = Me_3NHCl and $^{n}Pr_3NHCl$

Scheme 30: General representation for HTCP reactions.

3.5.6 Synthesis of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis(tetrahydrofuran)copper(II) $[Cu\{NC_4(CN)_3C(O)NH_2\}_2(THF)_2]$ (8)

A solution of $Cu(NO_3)_2{\bullet}3H_2O$ in water was added to a solution of tetramethylammonium-tetracyanopyrrolide in acetonitrile at room temperature. After stirring for 15 min, the acetonitrile was evaporated and the solution was filtered, the fitrate was evaporated to give a greenish yellow precipitate **8** (Scheme 31).

By vapor diffusion of diethyl ether into a tetrahydrofuran solution of a greenish yellow precipitate, crystals could be obtained as a by-product in small amounts.



$$2\,[Me_4N]\,TCP + Cu(NO3)_2 \cdot 3H_2O \xrightarrow[\substack{-2\,[Me_4N]NO_3 \\ -\,H_2O}]{\substack{1.\ CH_3CN \\ 2.\ H_2O}} [Cu\{NC_4(CN)_3C(O)NH_2\}_2(THF)_2]$$

Yield: 10%

Scheme 31: Synthesis of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis(tetrahydrofuran) copper(II).

In the **IR-ATR** spectrum appears a new vibration band for CN group at 2233 cm^{-1}, compared to IR spectrum of $[Me_4N]$TCP which gives a vibration band for CN group at 2220 cm^{-1}.

The compound **8** crystallizes in the monoclinic unit cell space group $P2_1/c$. The two CN distances are 1.13 Å and are therefore slightly larger than the sum of the covalent radii (Σr_{cov} C≡N 1.11 Å).[115] The CC distances in the ring differ only in third decimal place and are on average 1.40 Å. This value is between the sums of the covalent radii of a CC single (1.54 Å) and a C = C double bond (1.34 Å),[115] which is closer to a double bond. This also applies to the same size CN distances in five-membered ring (1.35 Å).

In the crystal structure of $[Cu\{NC_4(CN)_3C(O)NH_2\}_2(THF)_2]$ **(8)**, the copper(II) central atom is located in an inversion center and adopts an octahedral coordination (Figure 13). The equatorial positions are occupied by two symmetry related tcpc ligands, forming five-membered chelate rings in one plane, coordinating the metal center via the oxygen atom of the amide group and the N atom of the pyrrole ring. Two trans-positioned tetrahydrofuran molecules coordinate via their oxygen atoms almost perpendicular to this plane and complete the coordination geometry around the copper central atoms to an elongated octahedron.

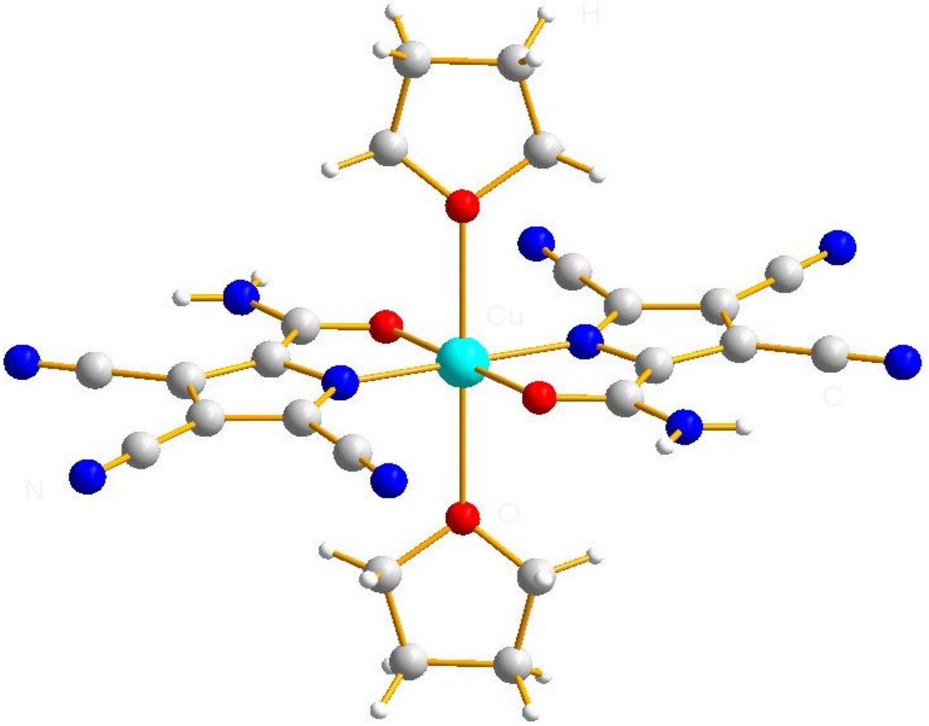


Figure 13: Ball and stick representation of **8** with the color code: dark blue – Copper, blue – Nitrogen, red – Oxygen, gray – Carbon, white – Hydrogen.

The distance between Cu–N(equat) and Cu–O(equat) was 1.97 Å and 1.99 Å while Cu–O(axial) was 2.47Å, that means clearly the Jahn-Teller effect is present.[37]

If water is not strictly excluded, the tetracyanopyrrolide anion can undergo hydrolysis under transformation of one cyano substituent to a carboxamide group, transforming tcp into tricyanopyrrole-2-carboxamide $(NC_4(CN)_3C(O)NH_2)^-$ (tcpc).

We observed that this reaction occurs in the presence of Cu^{2+} ions and converts tcp after one day at room temperature completely. From THF solutions, the copper(II) complex $[Cu\{NC_4(CN)_3C(O)NH_2\}_2(THF)_2]$ could be isolated, which incorporates the mononegative tricyanopyrrole-2-carboxamide as a chelating ligand. This copper(II)-assisted hydrolysis to the corresponding amide under mild conditions is well known.[116, 117]

3.5.7 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II) acetonitrile solvate $[Zn(TCP)_2{\bullet}4CH_3CN]{\bullet}2CH_3CN$ (9)

The reaction was carried out according to this procedure. A powder of zinc was added to a solution of tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight the unconsumed powder of zinc was removed by filtration, and the resulting solution was concentrated *in vacuo*. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at 8 °C for one day resulted colorless crystals of $[Zn(TCP)_2{\bullet}4CH_3CN]{\bullet}2CH_3CN$ (Scheme 32).

$$2HTCP + Zn \xrightarrow{CH_3CN} [Zn(TCP)_2 \cdot 4CH_3CN] \cdot 2CH_3CN + H_2$$

Yield: 44%

Scheme 32: Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II) acetonitrile solvate.

The synthesized compound **9** crystallizes in the triclinic unit cell space group *P*-1 . The crystal structure of $[Zn(TCP)_2{\bullet}4CH_3CN]{\bullet}2CH_3CN$ contains a mononuclear complex with the central metal ion Zn^{2+} located in inversion center. The central metal ion has octahedral six-coordination environment, by two-trans positioned (tcp) ligands and four molecules of acetonitrile in the equatorial plane (Figure 14). A sandwich structure with η^5−pyrrolide ligands as characteristic for bis(η^5−pyrrolide)zinc[37, 118-119] is not present, which obviously caused by the low electron density in the central C_4N ring due to the strong electron-withdrawing effect of the nitrile substituents.

The carbon-nitrogen bond length in the C≡N groups is on average 1.144 (11) Å.[120] The distances C1−C2 1.392 (18), C2−C3 1.409 (2) and C3−C4 1.397 (19) Å are also here between the values for a C−C single and double bond (Σr_{cov} C=C 1.34 and C−C 1.54 Å),[115] the distances C1− N1 1.361 (18), C4−N1 1.362 (17) Å and the exocyclic C−C bond lengths (1.421− 1.432 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.[36]

The average angle M−N−centroid (tcp ring) equals 180°, indicating that the metal atoms are essentially in the plane of the C_4N ring, which expected for a σ bonding situation. The bonds $M-N_{pyrrole}$ amount to 2.15 Å, while the bonds M−NCMe in the equatorial planes (average M−N 2.153 (13) Å).

The complex $[Zn(TCP)_2{\bullet}4CH_3CN]{\bullet}2CH_3CN$ adopt a similar structural arrangement as found for the complex $[Co\{C_5(CN)_5\}_2(H_2O)_2(THF)_2]$, $(C_5(CN)_5)^-$ = pentacyanocyclopentadienide anion), where the Co(II) atom is coordinated by the N atoms of nitrile groups of two trans positioned $C_5(CN)_5$ ligands.[33]

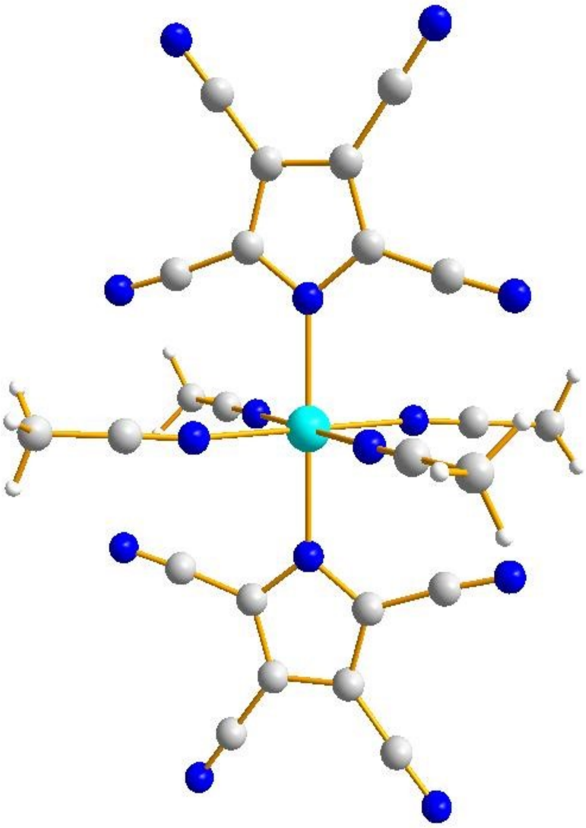


Figure 14: Ball and stick representation of **9** with the color code: dark blue – Zinc, blue – Nitrogen, gray – Carbon, white – Hydrogen.

By **TGA/DSC** measurement, the thermal decomposition of the synthesized compound occurs in two stages in the temperature rang 50–900 °C. The first mass loss of 8.74 % occurs between 350–475 °C is assigned to the release of the one solvate acetonitrile molecules (calculated weight loss 6.37 %). In the second stage started of decomposition for the compound at 497 °C and this decomposition caused results of low accuracy with the elemental analysis.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp peak at 2231 cm^{-1}. In the **IR-ATR** spectrum, the band appears as a strong vibration band at 2232 cm^{-1}, compared to IR spectrum of HTCP which gives a vibration band for CN group at 2244 cm^{-1} and in Raman spectrum at 2252 cm^{-1}.

Characteristic of the TCP anion are the four **^{13}C NMR** signals occurring at a shift of 112.8, 108.9, 108.2 and 104.8 ppm in CD_3CN. These signals in the ^{13}C NMR spectrum confirm the presence of the CN groups.

3.5.8 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II) acetonitrile solvate $[Fe(TCP)_2{\bullet}4CH_3CN]{\bullet}2CH_3CN$ (10)

The reaction was carried out according to the following procedure. A powder of iron was added to a solution of tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight the unconsumed powder of iron was removed by filtration, and the resulting solution was concentrated *in vacuo*. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at 8 °C for one day resulted colorless crystals of $[Fe(TCP)_2{\bullet}4CH_3CN]{\bullet}2CH_3CN$ (Scheme 33).

$$\mathrm{2HTCP + Fe \xrightarrow{CH_3CN} [Fe(TCP)_2{\cdot}4CH_3CN]{\cdot}2CH_3CN + H_2}$$

Yield: 45%

Scheme 33: Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II) acetonitrile solvate.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp peak at 2237 cm^{-1}. In the **IR-ATR** spectrum, the band appears as a strong vibration band at 2227 cm^{-1}, compared to IR spectrum of HTCP which gives a vibration band for CN group at 2244 cm^{-1} and in Raman spectrum at 2252 cm^{-1}.

Characteristic of the TCP anion are the four **^{13}C NMR** signals occurring at a shift of 112.9, 108.9, 108.2 and 104.8 ppm in CD_3CN. These signals in the ^{13}C NMR spectrum confirm the presence of the CN groups.

By **TGA/DSC** measurement, the thermal decomposition of the synthesized compound occurs in two stages in the temperature rang 50–900 °C. The first mass loss of 15.29 % occurs between 110–130 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 12.94 %). In the second stage started of decomposition for the compound at 360 °C and this decomposition caused results of low accuracy with the elemental analysis.

The synthesized compound **10** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure of $[Fe(TCP)_2•4CH_3CN]•2CH_3CN$ contains a mononuclear complex with the central metal ion Fe^{2+} located in inversion center. The central metal ion has octahedral six-coordination environment, by two axially bond (tcp) ligands and four molecules of acetonitrile in the equatorial plane (Figure 15).

The average angle M−N−centroid (tcp ring) equals 180°, indicating that the metal atoms are essentially in the plane of the C_4N ring and represents a multifunctional binary CN ligand, which is capable of forming classic coordination bonds through the ion pairs of the CN groups or the ring N atom. The bonds $M-N_{pyrrole}$ (average 2.178 (8) Å), while the bonds M−NCMe in the equatorial planes (average M−N 2.161 (9) Å).

The carbon-nitrogen bond length in the C≡N groups is on average 1.145 (15) Å.[120] The distances C1−C2 1.397 (13), C2−C3 1.408 (14) and C3−C4 1.398 (13) Å are also here between the values for a C-C single and double bond (Σr_{cov} C=C 1.34 and C−C 1.54 Å),[115] the distances C1−N1 1.363 (12), C4−N1 1.363 (12) Å and the exocyclic C−C bond lengths (1.421− 1.431 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.[36]

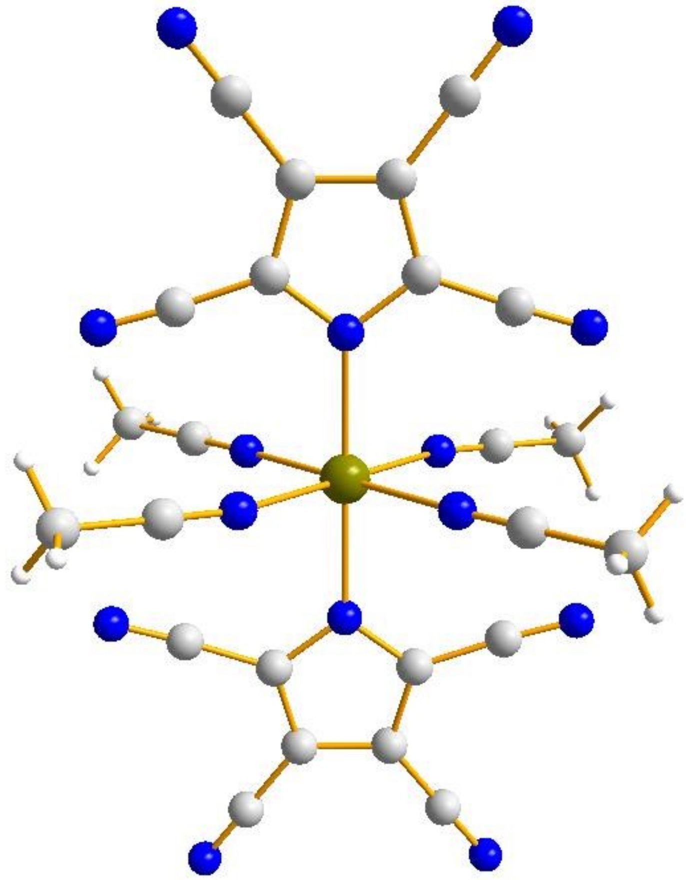


Figure 15: Ball and stick representation of **10** with the color code: dark green – Iron, blue – Nitrogen, gray – Carbon, white – Hydrogen.

The tendency for delocalization of the π-electron system towards the peripherial cyano groups is displayed in the exocyclic C–C bond lengths, which are only slightly longer than those within the aromatic ring. The two nitrile substituents in the positions 2 and 5 of the pyrrole ring cause a high sterical demand of this molecule when bond in the η^1 -N mode.[37]

3.5.9 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II) acetonitrile solvate [Mg(TCP)$_2$•4CH$_3$CN]•2CH$_3$CN (11)

The reaction was carried out according to this procedure. A solution of magnesium hydroxide in acetonitrile was added to a solution of tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight the resulting was filtrated and the resulting solution was concentrated *in vacuo*. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at 8 °C for one week resulted colorless crystals of [Mg(TCP)$_2$•4CH$_3$CN]•2CH$_3$CN (Scheme 34).

$$\mathbf{2HTCP + Mg(OH)_2 \xrightarrow{CH_3CN} [Mg(TCP)_2{\cdot}4CH_3CN]{\cdot}2CH_3CN + 2H_2O}$$

Yield: 64%

Scheme 34: Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II)acetonitrile solvate.

By **TGA/DSC** measurement, the thermal decomposition of the synthesized compound occurs in three stages in the temperature rang 50−800 °C. The first mass loss of 7.37 % occurs between 78−120 °C is assigned to the release of the one solvate acetonitrile molecules (calculated weight loss 6.81 %). The second mass loss of 16.51 % occuring between 125−152 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 13.62 %). In the third stage started of decomposition for the compound at 248 °C and this decomposition caused results of low accuracy with the elemental analysis.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears at 2235 cm^{-1}. In the **IR-ATR** spectrum, the band appears as a strong vibration band at 2227 cm^{-1}.

Characteristic of the TCP anion are the four **^{13}C NMR** signals occurring at a shift of 118.1, 112.7, 111.4 and 103.2 ppm in CD$_3$CN. These signals in the ^{13}C NMR spectrum confirm the presence of the CN groups.

The synthesized compound **11** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure of [Mg(TCP)$_2$•4CH$_3$CN]•2CH$_3$CN contains a mononuclear complex with the central metal ion Mg^{2+} located in inversion centre. In the centrosymmetry for

$[Mg(TCP)_2{\cdot}4CH_3CN]{\cdot}2CH_3CN$, the six coordinate magnesium atom has a regular octahedral geometry, by two trans positioned (tcp) ligands and four molecules of acetonitrile in the equatorial plane (Figure 16).

The average angle M−N−centroid (tcp ring) equals 180°, indicating that the metal atoms are essentially in the plane of the C_4N ring, the bonds $M{-}N_{pyrrole}$ (average 2.203 (8) Å). The bonds M−NCMe in the equatorial planes (average M−N 2.152 (9) Å).[121]

The carbon-nitrogen bond length in the C≡N groups is on average 1.144 (14) Å.[120] The distances C1−C2 1.393 (13), C2−C3 1.402 (14) and C3−C4 1.396 (13) Å are also here between the values for a C−C single and double bond (Σr_{cov} C=C 1.34 and C−C 1.54 Å),[115] the distances C1−N1 1.361 (12), C4−N1 1.365 (12) Å and the exocyclic C−C bond lengths (1.422− 1.432 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.[36]

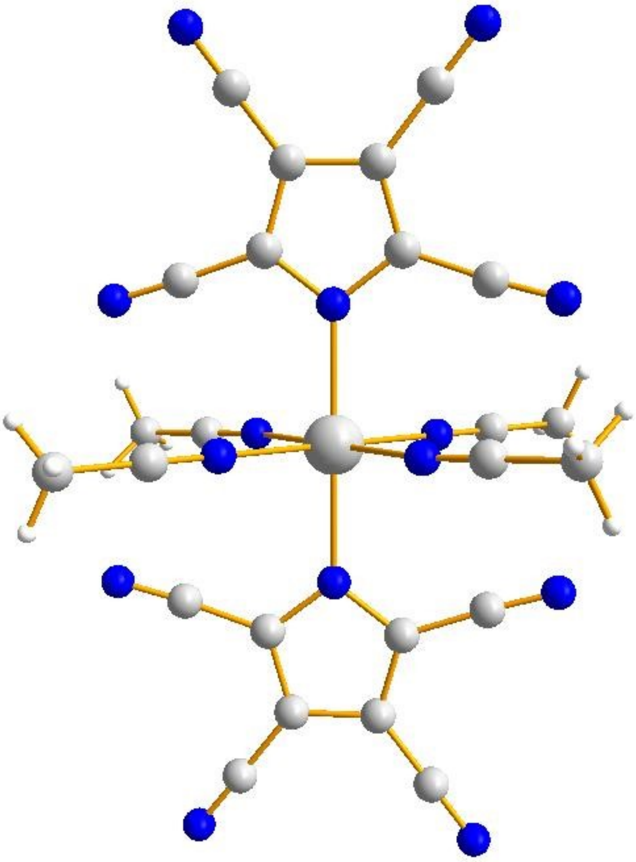


Figure 16: Ball and stick representation of **11** with the color code: dark gray − Magnesium, blue − Nitrogen, gray − Carbon, white − Hydrogen

The tendency for delocalization of the π-electron system towards the peripheral cyano groups is displayed in the exocyclic C−C bond lengths, which are only slightly longer than those within the aromatic ring. The two nitrile substituents in the positions 2 and 5 of the pyrrole ring cause a high sterical demand of this molecule when bond in the η^1 -N mode.[37]

3.5.10 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II) acetonitrile solvate [Cu(TCP)$_2$•4CH$_3$CN]•2CH$_3$CN (12)

The reaction was carried out according to the following procedure. A solution of tetracyanopyrrole in acetonitrile was added to a suspension solution of di(acetylacetonate)-copper(II) in acetonitrile at room temperature. After stirring overnight the resulting mixture was filtrated and the solution was concentrated *in vacuo*. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at 8 ^{o}C for one day resulted green crystals of [Cu(TCP)$_2$•4CH$_3$CN]•2CH$_3$CN (Scheme 35).

$$\mathbf{2\,HTCP + Cu(acac)_2 \xrightarrow{CH_3CN} [Cu(TCP)_2{\cdot}4CH_3CN]{\cdot}2CH_3CN + 2H(acac)}$$

Yield: 65%

Scheme 35: Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II)acetonitrile solvate.

The synthesized compound **12** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure of [Cu(TCP)$_2$•4CH$_3$CN]•2CH$_3$CN contains a mononuclear complex with the central metal ion Cu^{2+} located in inversion center. The geometry of the complex ion is elongated octahedral coordination (Figure 17) and the equatorial plane is formed by two N atoms of two tetracyanopyrrolide and two N atoms of two acetonitrile. The two other N atoms of two acetonitrile are located at the axial positions at a rather long distance, obviously as a result of Jahn-Teller distortion.[122]

The average angle M−N−centroid (tcp ring) equals 180^{o}, indicating that the metal atoms are essentially in the plane of the C$_4$N ring, the bonds M−N$_{\text{pyrrole}}$ (average 2.025 (10) Å).[123, 124]

The two bonds M−NCMe in the equatorial plane (average M−N 2.025 (11) Å), while the two bonds M−NCMe in the axial plane (average M−N 2.345 (12) Å).[122]

The carbon-nitrogen bond length in the C≡N groups is on average 1.145 (18) Å.[120] The distances C1−C2 1.394 (18), C2−C3 1.408 (18) and C3−C4 1.394 (17) Å are also here between the values for a C-C single and double bond (Σr_{cov} C=C 1.34 and C−C 1.54 Å),[115] the distances C1−N1 1.365 (16), C4−N1 1.363 (16) Å and the exocyclic C−C bond lengths (1.421− 1.433 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.[36]

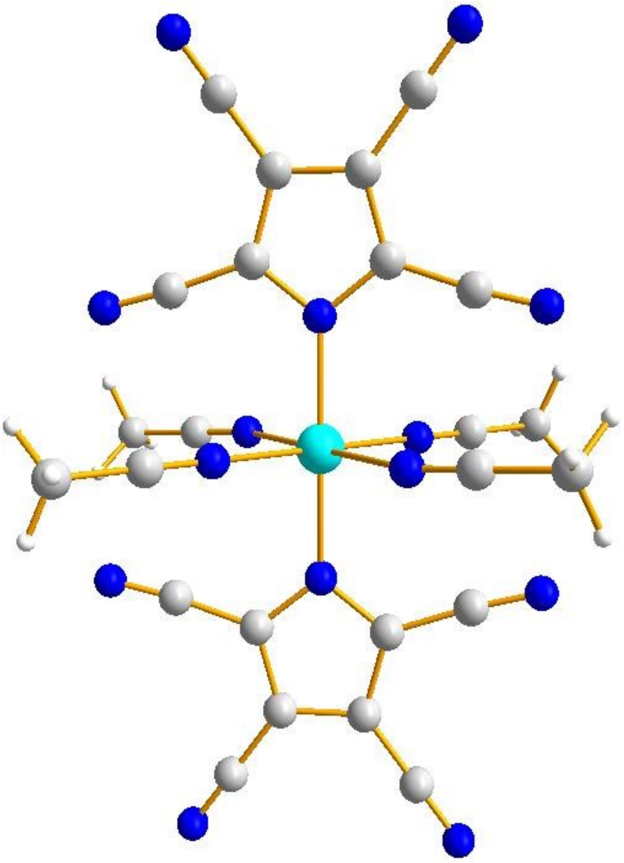


Figure 17: Ball and stick representation of **12** with the color code: dark blue − Copper, blue − Nitrogen, gray − Carbon, white − Hydrogen.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp peak at 2239 cm^{-1}. In the **IR-ATR** spectrum, the band appears as a strong vibration band at 2231 cm^{-1}.

By **TGA/DSC** measurement, the thermal decomposition of the synthesized compound occurs in three stages in the temperature rang 50−800 °C. The first mass loss of 10.57 % occurs between 59− 85 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 12.78 %). The second mass loss of 12.87 % occuring between 168−200 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 12.78 %). In the third stage started of decomposition for the compound at 452 °C and this decomposition caused results of low accuracy with the elemental analysis.

3.5.11 Synthesis of di(acetylacetonate)-1,5-N-µ-tetracyanopyrrolido manganese(III) [Mn(acac)$_2$TCP] (13)

The reaction was carried out according to this procedure. A solution of tri (acetylacetonate) manganese(III) in acetonitrile was added to a solution of tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight, the resulting was filtrated.

For purification, the yellow-black filtrate was evaporated to dryness to yield a yellow precipitate, washed two times with benzene and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by vapor diffusion of benzene into acetonitrile solution resulted yellow crystals of [Mn(acac)$_2$TCP] (Scheme 36).

$$\mathrm{HTCP} + \mathrm{Mn(acac)_3} \xrightarrow{\mathrm{CH_3CN}} [\mathrm{Mn(acac)_2TCP}] + \mathrm{H(acac)}$$

Yield: 72%

Scheme 36: Synthesis of di(acetylacetonate)-1,5-N-µ-tetracyanopyrrolidomanganese(III).

The synthesized compound **13** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure gave a 1D-coordination polymer di(acetylacetonate)− 1,5− N− µ−tetracyanopyrrolido manganese(III). The Mn^{3+} ions have either a $2N_{pyrrolide} + 4O_{acetylacetonate}$ coordination leading to a distorted octahedral environment. Although, the pyrrolide nitrogen atom always takes part in the Mn^{3+} coordination, either three CN groups remain uncoordinated (Figure 18).

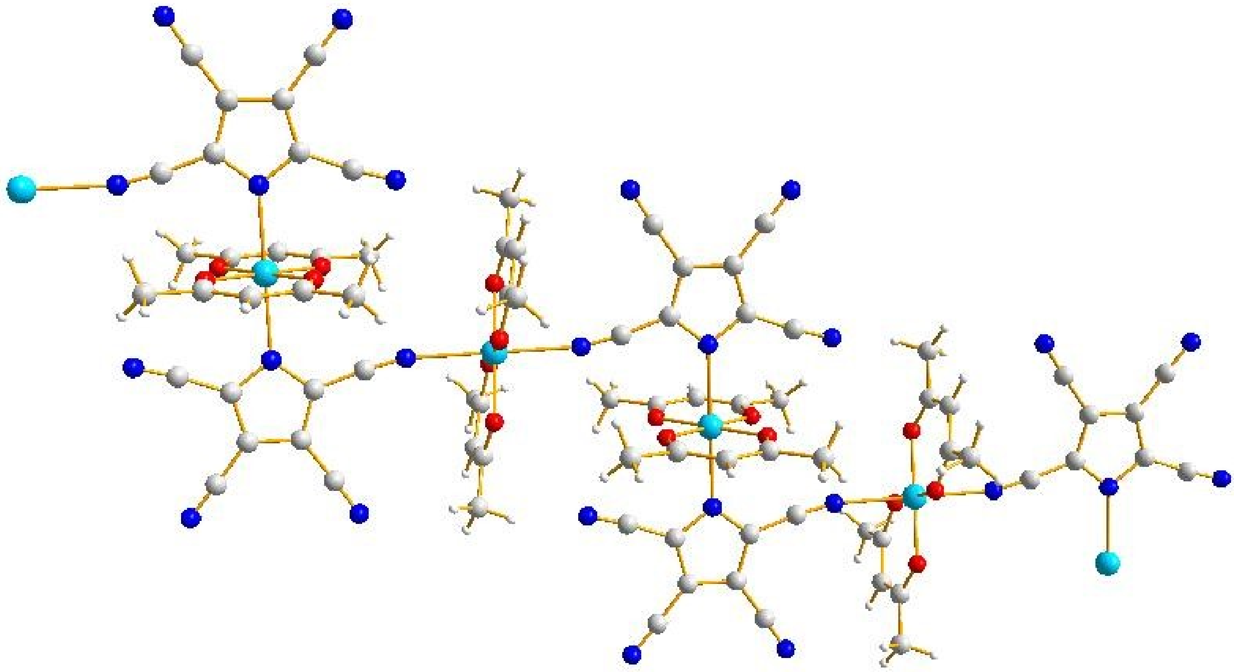


Figure 18: Ball and stick representation of **13** with the color code: dark blue − Manganese, blue − Nitrogen, red − Oxygen, gray − Carbon, white − Hydrogen.

The distances C1−C2 1.395 (2), C2−C3 1.405 (2) and C3−C4 1.397 (2) Å are also here between the values for a C−C single and double bond (Σr_{cov} C=C 1.34 and C−C 1.54 Å),[115] the distances C1−N1 1.356 (2), C4−N1 1.360 (19) Å and the exocyclic C−C bond lengths (1.421− 1.433 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.[36]

It is interesting to note that no significant difference in the CN bond lengths is observed depending on the coordination mode (1.141− 1.144 Å) and even the uncoordinated cyano groups are within this range ($\Sigma r_{cov}(C\equiv N) = 1.14$ Å).[120] The angle between the CN groups and the ring are between (174.8°−178.7°), and are almost planar to the ring. The angle between Mn and $N_{pyrrolide}$, Mn and $O_{acetylacetonate}$ always equal 180.0° and confirm the planarity.

Two different sets of Mn−N bond lengths are found: $d(\text{Mn}-\text{N}_{pyrrolide})$ = 2.29 Å and $d(\text{Mn}-\text{N}_{cyano})$ = 2.36 Å, this agrees well with comparative data from the literature.[125, 126] The bond lengths $\text{Mn}-\text{O}_{acetylacetonate}$ (average 1.899 (8) Å), are in agreement well with the corresponding distance in $[\text{Mn(acac)}_2(\text{OH}_2)_2\text{ClO}_4]\cdot 2\text{H}_2\text{O}$.[127]

The C≡N groups are confirmed by vibrational spectroscopy methods, **IR-ATR** and **Raman** spectra. In the Raman spectrum, the band appears at 2232 cm^{-1}, while in the IR spectrum, there are two bands appear at 2248 and 2232 cm^{-1}. By **DSC** measurement the melting point at 56−57 °C and decompose temperature at 210 °C, at a heating rate of 10 K / min were determined.

3.5.12 Synthesis of acetonitrile-di(acetylacetonate)tetracyanopyrrolido chromium(III) $[\text{Cr(acac)}_2\text{TCP}\cdot\text{CH}_3\text{CN}]\cdot 0.67\ \text{CH}_3\text{CN}$ (14)

The reaction was carried out according to the following procedure. A solution of tri(acetylacetonate)chromium(III) in acetonitrile was added to a solution of tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight the resulting was filtrated and the resulting solution was concentrated *in vacuo*. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at 8 °C for one week resulted brown crystals of $[\text{Cr(acac)}_2\text{TCP}\cdot\text{CH}_3\text{CN}]\cdot 0.67\ \text{CH}_3\text{CN}$ (Scheme 37).

$$\text{HTCP} + \text{Cr(acac)}_3 \xrightarrow{\text{CH}_3\text{CN}} [\text{Cr(acac)}_2\text{TCP}\cdot\text{CH}_3\text{CN}]\cdot 0.67\text{CH}_3\text{CN} + \text{H(acac)}$$

Yield: 38%

Scheme 37: Synthesis of acetonitrile-di(acetylacetonate)tetracyanopyrrolidochromium(III).

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp peak at 2240 cm^{-1}. In the **IR-ATR** spectrum, the band appears as a medium band at 2232 cm^{-1}.

The synthesized compound **14** crystallizes in the monoclinic unit cell space group *C2/C*. The crystal structure gave acetonitrile-di(acetylacetonate)tetracyanopyrrolidochromium (III). The central metal ion Cr^{3+} is coordinated by four O atoms of two acetylacetonate ligands in the equatorial plane and one N pyrrolide, one N acetonitrile in trans arrangement, displaying a slightly distorted octahedral geometry (Figure 19).

The carbon-nitrogen bond length in the C≡N groups is on average 1.139 (3) Å.[120] The distances C1−C2 1.382 (4), C2−C3 1.415 (3) and C3−C4 1.383 (4) Å are also here between the values for a C−C single and double bond (Σr_{cov} C=C 1.34 and C−C 1.54 Å),[115] the distances C1−N1 1.365 (3), C4−N1 1.364 (3) Å and the exocyclic C−C bond lengths (1.428−1.436 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.[36]

The angle between the CN groups and the ring are between (173.6°−178.6°), and are almost planar to the ring. The angle between Cr and $N_{pyrrolide}$, Cr and $O_{acetylacetonate}$ are between (177.1°−180.0°) and confirm the planarity.

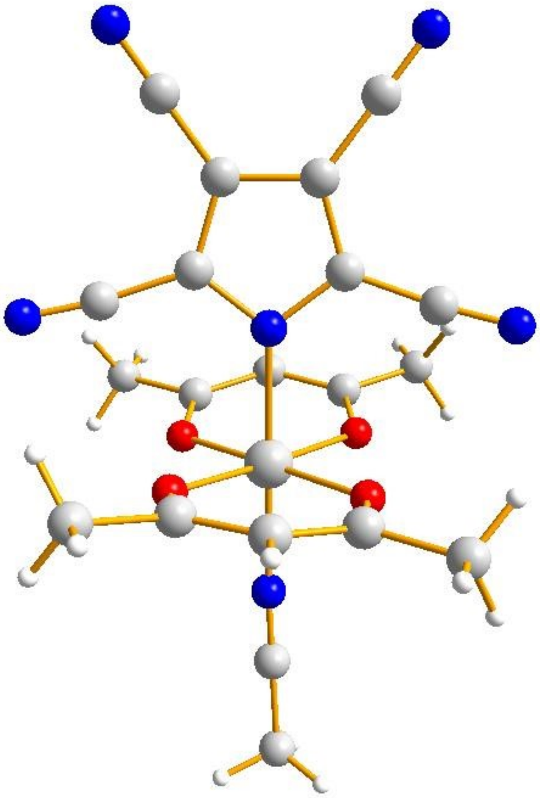


Figure 19: Ball and stick representation of **14** with the color code: dark gray − Chromium, blue −Nitrogen, red − Oxygen, gray − Carbon, white − Hydrogen

The bond Cr−$N_{pyrrole}$ was 2.066 (2) Å), The bond Cr−NCMe in the axial plane was 2.049(2) Å).[128] The bond lengths Cr−$O_{acetylacetonate}$ (average 1.934 (17) Å), are in good agreement with comparative data from the literature.[129]

By **TGA/DSC** measurement, the thermal decomposition of the synthesized compound occurs in two stages in the temperature rang 50− 800 °C. The first mass loss of 14.12 % occurs between 120− 180 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 16.93 %). In the second stage started of decomposition for the compound at 247 °C.

3.5.13 Reaction of HTCP with tri(acetylacetonate)manganese(III)

The aim of this synthesis was the preparation of tris(tetracyanopyrrolido)manganese(III), we utilized in this reaction different ratio to get on this product. The reaction was carried out according to this procedure. A solution of tri(acetylacetonate)manganese(III) in acetonitrile was added to a solution of an excess tetracyanopyrrole in acetonitrile at room temperature. After stirring overnight the resulting mixture was filtrated and the yellow-black solution was evaporated to dryness to yield a yellow precipitate, washed two times with benzene and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by vapor diffusion of benzene into acetonitrile solution but the resulting was two crystal structures from solution, first was 1% yellow crystals of [Mn(acac)$_2$TCP] **(13)** which already was discussed previously and second was 99% colorless crystals of [Mn(TCP)$_2$•4CH$_3$CN]•2CH$_3$CN **(15)**. That means a reduction from Mn(III) to Mn(II) has occurred.

The synthesized compound **15** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure of [Mn(TCP)$_2$•4CH$_3$CN]•2CH$_3$CN contains a mononuclear complex with the central metal ion Mn^{2+} located in inversion center. The central metal ion has octahedral six-coordination environment, by two axially bond (tcp) ligands and four molecules of acetonitrile in the equatorial plane (Figure 20).

The carbon-nitrogen bond length in the C≡N groups is on average 1.147 (13) Å.[120] The distances C1−C2 1.398 (11), C2−C3 1.408 (12) and C3−C4 1.397 (11) Å are also here between the values for a C−C single and double bond (Σr_{cov} C=C 1.34 and C−C 1.54 Å),[115] the distances C1−N1 1.361 (10), C4−N1 1.363 (10) Å and the exocyclic C−C bond lengths

(1.398– 1.429 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.[36]

The average angle M–N-centroid (tcp ring) equals 180°, indicating that the metal atoms are essentially in the plane of the C_4N ring, the bonds M–$N_{pyrrole}$ (average 2.260 (7) Å).[125] The bonds M–NCMe in the equatorial plane (average M–N 2.227 (8) Å).[130]

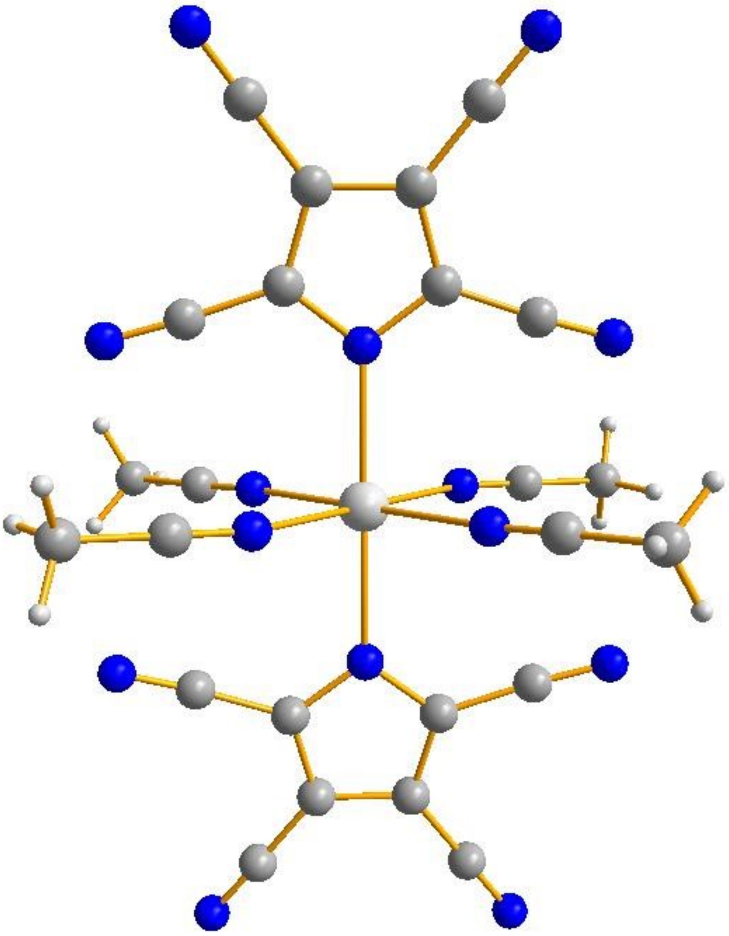


Figure 20: Ball and stick representation of **15** with the color code: dark gray – Manganese, blue – Nitrogen, gray – Carbon, white – Hydrogen.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp peak at 2236 cm^{-1}. In the **IR-ATR** spectrum, the band appears as a strong vibration band at 2233 cm^{-1}.

By **TGA/DSC** measurement, the thermal decomposition of the synthesized compound **15** occurs in two stages in the temperature rang 50–800 °C. The first mass loss of 13.89 % occurs between 50– 65 °C is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 12.95 %). In the second stage started of decomposition for the compound at 218 °C.

3.5.14 Synthesis of trimethylammoniumtetracyanopyrrolide [Me_3NH]TCP (16)

The synthesis of this reaction was carried out according to this procedure. A solution of trimethylammoniumchloride in water was added to a solution of tetracyanopyrrole in water at room temperature. After stirring overnight, the resulting was filtrated.

For purification, the yellow filtrate was evaporated to dryness to yield a yellow precipitate, washed two times with dichloromethane and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at room temperature for three days resulted colorless crystals of [Me_3NH]TCP (Scheme 38).

$$\mathrm{HTCP} + [\mathrm{Me_3N}]\mathrm{HCl} \xrightarrow{\mathrm{H_2O}} [\mathrm{Me_3NH}]\mathrm{TCP} + \mathrm{HCl}$$

Yield: 77%

Scheme 38: Synthesis of trimethylammoniumtetracyanopyrrolide.

By **TGA/DSC** measurement, the thermal decomposition of the synthesized compound occurs in two stages in the temperature rang 50– 800 °C. The first stage gave melting point at 184-185 °C, while in the second stage started the decomposition of the compound at 298 °C.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp at 2235 cm^{-1}. In the **IR-ATR** spectrum, there are two bands appear as a medium band at 2234 cm^{-1} and very strong band at 2224 cm^{-1}.

Characteristic of the TCP anion are the four **^{13}C NMR** signals occurring at a shift of 119.4, 114.3, 112.1 and 102.4 ppm. It involves singlet signal as where the methyl group of the cation, which can be found at 44.6 ppm.

A **^{1}H NMR** spectrum shows a singlet signal at a shift of 4.41 ppm, which is attributed to the methyl group, and a broad signal at 7.38 ppm, which is attributed to the NH group in CD_3CN.

The synthesized compound **16** crystallizes in the orthorhombic unit cell space group *pnma*. The crystal structure gave trimethylammoniumtetracyanopyrrolide (Figure 21). The carbon-nitrogen bond length in the C≡N groups is on average 1.148 (16) Å.[120] The distances C1−C2 1.399 (15), C2−C3 1.409 (15) and C3−C4 1.399 (15) Å are also here between the values for a C−C single and double bond (Σr_{cov} C=C 1.34 and C−C 1.54 Å),[115] the distances C1− N1 1.357 (15), C4−N1 1.357 (13) Å and the exocyclic C−C bond lengths (1.417−1.430 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.[36]

The distance between N6−H1 was 0.915 (18) Å[32] and the distance between N1….H1 was 1.955 (18) Å and the solid state structure of $[Me_3NH]$TCP consists of ion pairs of the monomer units, which are associated by H-bonding between the H atom of $[Me_3NH]^+$ ion and one of the N atoms of the TCP ion where was the distance between N1…..H1−N6 is 2.86 Å(Figure 21). [36]

The C_2v symmetry of the TCP anion is confirmed by the interatomic distances in the same molecule (for example, N1−C1 equal to N1−C4). It shows that the π-electrons thus all the atoms are highly delocalized and connected formal in five-membered ring by a double bond with each other, as in other aromatic systems.

The aromaticity is confirmed by the Hückel rule. The six π electrons satisfy the rule 4n + 2 and the molecule is completely planar. All dihedral angles are either 180 ° or 0 ° large. From the high symmetry of the anion follows that there can only be very weak interactions with the cation, which is why form layers and no mesh.

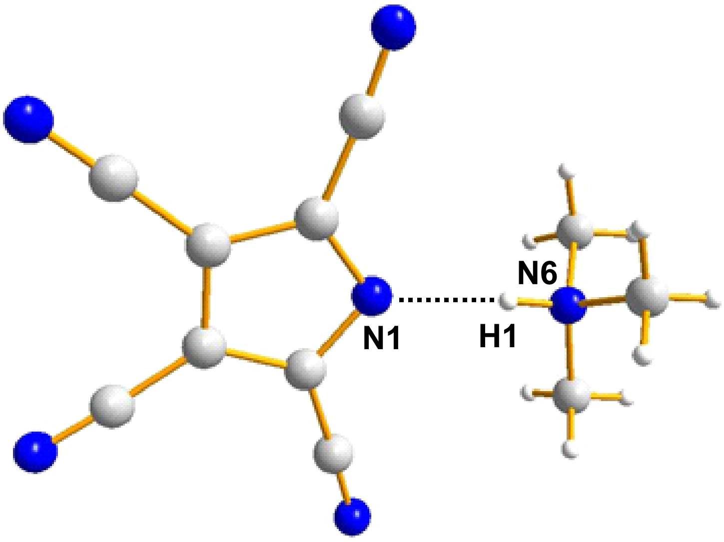


Figure 21: Ball and stick representation of **16** with the color code: blue –Nitrogen, gray – Carbon, white – Hydrogen.

There are coordinative interactions between cation and anion are observed. However, as illustrated in Figure 22, anion••••anion π–π stacking [131, 132] is observed between the TCP layers (3.5–3.6 Å).

The "π stacking" describes an interaction of the π-electrons of a compound with other π-electrons. For example, the phenyl rings of a compound can interact with the solvent (benzene, toluene), therefore, the removal of the solvent is difficult.[83] The TCP rings show strong intermolecular interactions, as shown here.

As can be seen in Figure 22, the TCP rings are in two orientations (A, B), which then alternately layers one above the other. The red, dashed lines represent the interactions of the π-electron pairs are to each other.

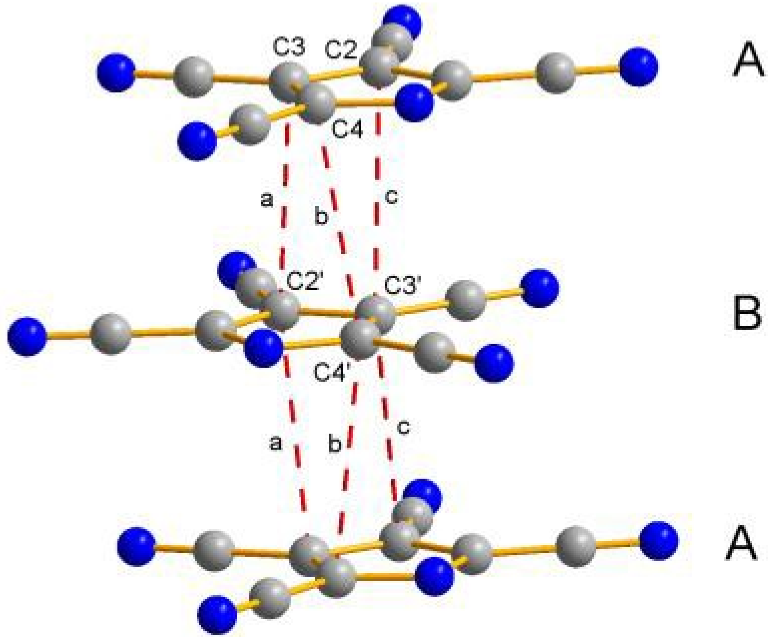


Figure 22: Ball and stick representation, wherein the dashed red lines show interaction between of the π-electrons (π stacking) of various levels. Distances [Å]: ***a*** = 3.63, ***b*** = 3.58, ***c*** = 3.5.

3.5.15 Synthesis of tripropylammoniumtetracyanopyrrolide [^{n}Pr$_3$NH]TCP (17)

The synthesis of this reaction was carried out according to the following procedure. A solution of tripropylammoniumchloride in water was added to a solution of tetracyanopyrrole in water at room temperature. After stirring overnight, the resulting was filtrated.

For purification, the yellow filtrate was evaporated to dryness to yield a yellow precipitate, washed two times with dichloromethane and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution in acetonitrile at room temperature for three days resulted colorless crystals of [^{n}Pr$_3$NH]TCP (Scheme 39).

$$\text{HTCP} + [^n\text{Pr}_3\text{N}]\text{HCl} \xrightarrow{H_2O} [^n\text{Pr}_3\text{NH}]\text{TCP} + \text{HCl}$$

Yield: 63%

Scheme 39: Synthesis of tripropylammoniumtetracyanopyrrolide.

The synthesized compound **17** crystallizes in the triclinic unit cell space group *P*-1. The crystal structure gave tripropylammoniumtetracyanopyrrolide (Figure 23). The carbon-nitrogen bond length in the C≡N groups is on average 1.145 (2) Å.[120] The distances C1−C2 1.398 (2), C2−C3 1.409 (2) and C3−C4 1.397 (2) Å are also here between the values for a C−C single and double bond (Σr_{cov} C=C 1.34 and C−C 1.54 Å),[115] the distances N1−C1 1.353 (2), N1−C4 1.350 (2) Å and the exocyclic C−C bond lengths (1.414−1.430 Å), are in good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.[36]

The distance between N32−H32 was 1.000 (13) Å[32] and the distance between N1….H32 was 2.100 (13) Å and the solid state structure of [^{n}Pr$_3$NH]TCP consists of ion pairs of the monomer units, which are associated by H-bonding between the H atom of [^{n}Pr$_3$NH]$^+$ ion and one of the N atoms of the TCP ion where was the distance between N1…..H32−N32 is 2.97 (18) Å (Figure 23).[36]

The C_2v symmetry of the TCP anion is confirmed by the interatomic distances in the same molecule (for example, N1−C1 equal to N1−C4). It shows that the π-electrons thus all the atoms are highly delocalized and connected formal in five-membered ring by a double bond with each other, as in other aromatic systems.

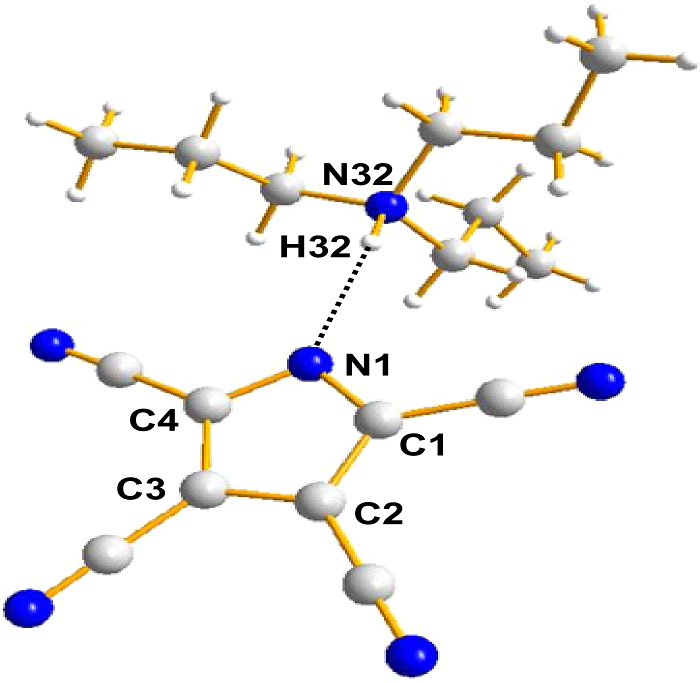


Figure 23: Ball and stick representation of **17** with the color code: blue –Nitrogen, gray – Carbon, white – Hydrogen.

There are coordinative interactions between cation and anion are observed. However, as illustrated in Figure 24, anion••••anion π–π stacking [131, 132] is observed between the TCP layers (3.3–3.6 Å).

As can be seen in Figure 24, the TCP rings are in two orientations (A, B), which then alternately layers one above the other. The red, dashed lines represent the interactions of the π-electron pairs are to each other.

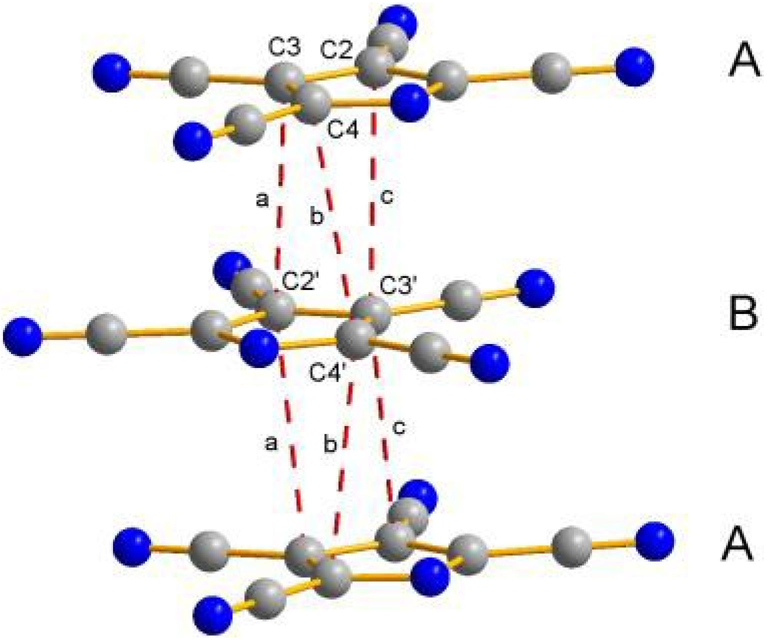


Figure 24: Ball and stick representation, wherein the dashed red lines show interaction between of the π-electrons (π stacking) of various levels. Distances [Å]: ***a*** =3.65, ***b*** = 3.35, ***c*** = 3.61.

The C≡N group can be detected on the vibration in the **Raman** spectrum, the band appears as a very sharp at 2234 cm^{-1}. In the **IR-ATR** spectrum, the band appears as very strong at 2220 cm^{-1}.

Characteristic of the TCP anion are the four **^{13}C NMR** signals occurring at a shift of 119.4, 114.3, 112.2 and 102.4 ppm. It involves singlet signals as where the methyl and ethyl group of the cation, which can be found at 11.36, 17.20 and 53.95 ppm respectively.

A **^{1}H NMR** spectrum appears signals at 1.05, 1.74 and 2.96 ppm, which are attributed to the methyl group and two ethyl groups respectively, and a singlet signal at 9.50 ppm, which is attributed to the NH group in CD_2Cl_2.

By **DSC** measurement the melting point at 65 °C and decompose temperature at 320 °C, at a heating rate of 10 K / min were determined.

The aim of the syntheses of these trialkylammoniumtetracyanopyrrolides $[R_3NH]$TCP (16: R= Me, 17: R= ^{n}Pr) was reactions planed with metal hydroxides $M(OH)_x$ and metal hydrides M_xH_y to form new coordination polymers. But there was no more time to carry out these reactions.

4. Summary

The aim of this study was to examine the coordination chemistry of novel donor-acceptor complexes (with new CN linkers) containing neutral phosphorus(III)cyanide and anions such as tetracyanopyrrolide (TCP).

In this work the possibility of the reaction $P(CN)_3$ with weakly coordinating anions $(WCA)^-$ such as $Ag(OOCCF_3)$, $Ag[Al(OCH(CF_3)_2)_4]$, $AgBF_4$ and $Ag[B(C_6F_5)_4]\bullet Et_2O$ was investigated as CN super carrier in a metathesis reaction.

In all reactions except the reaction with $Ag[B(C_6F_5)_4]$ the presence of a distinct CN band at 2164 cm^{-1} in the IR-ATR spectrum of the white precipitate was observed. This agrees well with comparative data of $(AgCN)_\infty$ from the literature.[92] Nevertheless it could not be isolated any product which could result from AgCN elimination.

In the reaction of $P(CN)_3$ with $Ag(OOCCF_3)$ and $AgBF_4$, no changes in **^{31}P NMR** and **IR-ATR** spectra compared to the spectra from the starting materials were observed.

With $P(CN)_3$ and $Ag[Al(OCH(CF_3)_2)_4]$, changes in **^{13}P NMR** and **IR-ATR** spectra compared to the spectra from the starting materials were observed.

About the reaction of $P(CN)_3$ with $Ag[B(C_6F_5)_4]\bullet Et_2O$ at room temperature or low temperature (−70 °C), no reaction has occurred. After heating the solution for two hours the **^{19}F NMR** spectrum gave more signals compared to ^{19}F NMR spectrum of starting material and led to decomposition of the anion because the use of heating.

The resulting residue from the mixture after removal of the solvent for all of these reactions is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as CH_3CN or THF, but it shows a solubility in DMSO, and this confirms to the formation of the polymer.

Generally, in all reactions, there are no isolated products, only a mixture from products and starting materials. The crystals obtained from the reaction solutions were characterized always as $P(CN)_3$.

Reactions from $P(CN)_3$ as Lewis acid with different Lewis bases were tested. In the reaction of $P(CN)_3$ with Et_3N and TMEDA, there is observed a change in ^{13}P NMR and IR-ATR spectra compared to the starting solution.

With $P(CN)_3$ and $B(C_6F_5)_3$, there is observed a change in **^{11}B NMR** spectrum compared to ^{11}B NMR spectrum of $B(C_6F_5)_3$

In the reaction of $P(CN)_3$ with 2,2'-bipyridine and sulfur at room temperature or low temperature (−70 °C), no reaction has occurred, where in **^{31}P NMR** and **IR-ATR** spectra show the same signal for $P(CN)_3$ and the same vibration for CN group at $P(CN)_3$.

About the reaction of $P(CN)_3$ with DMAP (DMAP = 4-dimethylaminopyridine) and 1,8-DAN (DAN = diaminonaphthalene), changes in **^{31}P NMR** and **IR-ATR** spectra at room temperature or low temperature compared to the spectra from the starting materials were observed.

In the **^{31}P NMR** spectrum for the reaction of $P(CN)_3$ with $LiN(SiMe_3)_2$, a major signal at −197.50 ppm was observed and confirmed the formation of $[P(CN)_2]^-$anion[17].

In the reaction of $P(CN)_3$ with trimethylamine and sodium tetraphenylborate the isolated crystals from this reaction were only triethylammoniumsalt of the tetraphenylborate, where the proton could come from the solvent.

About the reaction of $P(CN)_3$ with Et_3N and $AgBF_4$, there is observed a change in **^{31}P NMR** spectrum, as well as, in the **IR-ATR** spectrum shows a vibration for CN group at 2164 cm^{-1} was confirmed the formation of AgCN. Additionally, in the reaction of $P(CN)_3$ with PPh_3 and $Na[B(Ph)_4]$, there is also observed a change in **^{31}P NMR** spectrum compared to the spectra from the starting materials

The resulting residue from the mixture after removal of the solvent in all reactions is almost insoluble in non-polar or slightly polar organic solvents such as hexane or toluene and also insoluble in common polar organic solvents such as CH_3CN or THF, except the resulting residue from the reaction with $B(C_6F_5)_3$ and 1,8-diaminonaphthalene shows a good solubility in polar solvents such as CH_2Cl_2, CH_3CN and THF.

Although the presence of more changes in **NMR** (**^{31}P**, **^{19}F** and **^{11}B**) and **IR-ATR** spectra compared to the spectra from the starting materials were observed, but in all reactions, there are no isolated products, only a mixture from products and starting materials.

The product for the reaction of PPh_3 with $P(CN)_3$ in a dichloromethane solution was unexpected and was obtained as colorless crystals of the product $[Ph_3P{=}N{-}C(CN)_2{-}C(CN)_2{-}N{=}PPh_3]{\bullet}2CH_2Cl_2$ **(5)**. That means an oxidation from P(III) to P(V) has occurred.

The using $P(CN)_3$ as a ligand in transition metal chemistry was investigated. In all reactions of $P(CN)_3$ with transition metal complexes the formation of a new product were observed except the reaction with $[Mo(CO)_3(EtCN)_3]$ was referred always to the presence of $P(CN)_3$.

The product for the reaction of $P(CN)_3$ with dichloro(*p*-cymene)ruthenium(II)dimer was insoluble in most of solvents, just in DMSO, so it may be that it is a polymer. The product for the reaction of $P(CN)_3$ with palladium and nickel complexes was $Pd(CN)_2{\bullet}(PPh_3)_2$ and $Ni(CN)_2{\bullet}$(triphos), respectively and was characterized by mean of X-ray crystallography, that means an oxidation from Pd(0) to Pd(II) in the case Pd complex and an oxidation from Ni(0) to Ni(II) in the case Ni complex has occurred, as well as, there was no coodination of phosphorus atom to metal ion in both reactions, but the product in both reactions was not a polymer because it was soluble in CH_2Cl_2. About the reaction of $P(CN)_3$ with tungsten complex, the resulting residue was not a polymer also because it was soluble in CH_2Cl_2 but that it was not possible to isolate any crystals.

Finally, reactions from $P(CN)_3$ with room temperature ionic liquids (RT-ILs) in CH_2Cl_2 and THF solvents were investigated. New signals in **^{31}P NMR** and **IR-ATR** spectra from the reaction of $P(CN)_3$ with $EMim[N(CN)_2]$ in two different solvents were observed, but the residue for these reactions was almost insoluble in nonpolar or slightly polar organic solvents such as hexane or toluene, but showed a very poor solubility in common polar organic solvents such as MeCN and THF. But that it was not possible to isolate any product.

At the same time, the resulting residue from the reaction of $P(CN)_3$ with $EMim[N(CN)_2]$ was unstable in water and a hydrolyzation took place, because ^{31}P NMR spectrum in D_2O was gave new signals and referred to form phosphoroxide or phosphonic acid $[DPO(OD)_2]$.

About the reaction of $P(CN)_3$ with silver dicyanoamide-tris-(pentafluorophenyl)borane•diether, all results were referred the formation of a new product with a good solubility in MeCN, that means it was not a polymer. But that it was not possible to isolate any product.

In the second part of this thesis, the possibility of using the tetracyanopyrrolide anion as a ligand in transition metal chemistry was investigated. New transition metal complexes containing the tetracyanopyrrolide anion $[C_4(CN)_4N]^-$ (TCP) were synthesized from tetracyanpyrrole (HTCP) and characterized by mean of X-ray crystallography. The complexes showed that, the TCP anion acts as a monodentate ligand towards transition metal ions. Only the η^1- N-σ coordination mode via the electron pair of the N atom of the pyrrole ring was found.

The other possible coordination mode, via the N atoms of the nitrile substituents, which was published before from our group for the structure of NaTCP,[36] was observed for the product of reaction HTCP with $Mn(acac)_3$ in acetonitrile and characterized by mean of X-ray crystallography.

In the reaction of $[Me_4N]$TCP with $Cu(NO_3)_2 \bullet 3H_2O$ in acetonitrile/water, the tetracyanopyrrolide anion underwent hydrolysis of one cyano sustituent to a carboxamide group, transforming TCP into tricyano-2-pyrrole(carboxamide).

AgTCP was prepared in high yield after isolating from reaction $[Me_4N]$TCP with $AgNO_3$ in acetone/water and could characterized completely for the first time. Additionally, a new procedure was found for the preparation of tetracyanopyrrole (HTCP) in high yield (71%) from reaction AgTCP with excess HCl in water and HTCP obtained could also be fully characterized.

However, a sandwich structure with η^5-pyrrolide ligands as characteristic for prepared complexes was not observed, which is obviously caused by the low electron density in the central C_4N ring due to the strong electron-withdrawing effect of the nitrile substituents.

New salts bearing the TCP anion were synthesized from reaction $[R_3NH]Cl$ (R= Me or ^{n}Pr) with HTCP in water and were characterized by mean of X-ray crystallography. The aim of the syntheses of these trialkylammoniumtetracyanopyrrolides $[R_3NH]$TCP were the following reactions planed with metal hydroxides $M(OH)_x$ and metal hydrides M_xH_y to form new coordination polymers. But there was no more time to carry out these reactions.

5. Appendix

5.1 Experimental part

5.1.1 Working technique

Unless otherwise indicated, all experiments where absolute solvents were used and carried out under argon atmosphere using Schlenk technique. All glassware was baked out for three times with a hot air blower in a high vacuum and cooled under argon atmosphere. The filling and transfer to hydrolysis substances was carried out under an inert atmosphere in a drybox. Solvents were distilled under argon atmosphere and transferred for the experiments with disposable syringes. The disposable syringes have been previously purged three times with argon.

The solvents used were obtained through the chemical trade and if necessary cleaned and dried by literature methods.[133] Dichloromethane CH_2Cl_2 was purified analogously to a literature method[134] and only about P_4O_{10}, then dried over CaH_2 and freshly distilled. Tetrahydrofuran (THF), benzene (C_6H_6) and toluene (C_7H_8) were dried over Na / benzophenone and freshly distilled. Fluorobenzene (Ar.F) and acetonitrile (CH_3CN) were dried over CaH_2 and freshly distilled. Magnesium hydroxide $Mg(OH)_2$ was freshly precipitated from an aqueous solution of $MgCl_2$ (Merck 99%) with an aqueous solution of sodium hydroxide NaOH (VWR, 98.8%). The solid hydroxide was filtered off and washed three times with water and dried under reduced pressure. Starting materials were either obtained the chemicals trade or produced by known methods from the literature.

Literature synthesis known: $Ag(OOCCF_3)$,[135] $Ag[Al(OCH(CF_3)_2)_4]$,[136] $AgBF_4$,[137] $Ag[B(C_6F_5)_4]{\cdot}Et_2O$,[138] $B(C_6F_5)_3$,[138] Et_3N (Merck, 99%), TMEDA (Aldrich, 99%), 2,2'-bipyridine (Fluka, 99%), PPh_3 (Fluka, 97%), Sulfur (Riedel-de Haën, 99%), $Na[B(Ph)_4]$ (Fluka, 98%), $LiN(SiMe_3)_2$,[139] 1,8-diamino naphthalene (Alfa Aesar, 97%), dichloro-(*P*-cymene)ruthenium(II)dimer,[140] $Pd(PPh_3)_4$,[141] 1,1,1-tris[(diphenylphosphino)methyl)ethane,[142] $Fe(Cp)_2PF_6$,[143] [hydridotris(3,5-dimethylpyrazolyl)borate tricarbonyl tungsten(II)],[144] $[Mo(CO)_3(EtCN)_3]$,[145] $Ag[N\{CN{\cdot}B(C_6F_5)_3\}_2]{\cdot}Et_2O$,[111] $Ni(COD)_2$,[146] $EMim{\cdot}N(CN)_2$,[147] $BMim{\cdot}N(CN)_2$,[147] NaCN (Alfa Aesar, 98%), CS_2 (Aldrich, 99%), DMF (Grüssing, 99%), NaN_3 (Acros Organics, 99%), $[Me_4N]Cl$ (Roth, 98%), $(NH_4)_2S_2O_8$ (Roth, 99%), $C_2H_4Cl_2$ (Roth, 99%), $AgNO_3$ (Fluka, 99%), $Cu(NO_3)_2{\bullet}3H_2O$ (Merck, 99%), zinc powder (Riedel-de

Haën, 99%), iron powder (FerakBerlin, 99.5%), ethanol (Roth, 99%), isopropyl alcohol (Roth, 99%), silver tetracyanopyrrolide AgTCP,[36] tetracyano-1,4-dithiin$C_8N_4S_2$,[36, 56] Tetracyanopyrrole HTCP,[36] $[Me_4N]$TCP,[36] trimethylammoniumchloride (Aldrich,98%), $Cu(acac)_2$,[148] $Mn(acac)_3$,[149] $Cr(acac)_3$,[150] tripropylammoniumchloride.[151]

5.1.2 Analytical methods

Single-crystal

Crystals for X-ray crystal were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) k during measement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer using graghite monochromated Mo Kα radition (λ= 0.71073 A°). The structures were solved by direct methods (***SHELXS-97***)[152] and refined by full-matrix least squares procedures (***SHELXL-97***).[153] Semi-empirical absorption corrections were applied (**SADABS**).[154] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were added arithmetically, with two exception found in compounds **16** and **17** where the bridging N6─H1·····N1 in **16** and the bridging N32─ H32·····N1 in **17** hydrogen atom are located and refined without constraint.

NMR spectroscopy

NMR: ^1H-, ^{11}B-, ^{13}C-, ^{19}F-, ^{31}P- and ^{29}Si-INEPT-NMR spectra were obtained on a Bruker *AVANCE 250* (250 MHz) and *AVANCE 300* (300 MHz) or *AVANCE 500* (500 MHz) spectrometers and were referenced internally to the deuterated solvent (^{13}C NMR, CD_3CN: δ_{Ref} = 1.3 and 118.2 ppm, d6-DMSO: δ_{Ref} = 39.5 ppm, CD_2Cl_2: δ_{Ref} = 54.0 ppm) or to protic impurities in the deuterated solvent (^1H, CD_2HCN: δ_{Ref} = 1.93 ppm, d6-DMSO: δ_{Ref} = 2.49 ppm, $CHDCl_2$: δ_{Ref} = 5.31 ppm). $[D_3]CD_3CN$, $[D_6]$DMSO and $[D_2]CD_2Cl_2$ were dried with molecular sieves (3A°). Extra (^{11}B, $B(OH)_3$: δ_{Ref} = 0 ppm, ^{19}F, $CFCl_3$: δ_{Ref} = 0 ppm, ^{31}P: 85% H_3PO_4, δ_{Ref} = 0 ppm and ^{29}Si: $SiMe_4$, δ_{Ref} = 0 ppm).

IR spectroscopy

For the recording of spectra a Nicolet 380 FT-IR spectrometer with a Smart Orbit ATR unit was used.

Raman spectroscopy

For recording the spectra was either a) Bruker VERTEX 70 FT-IR with RAM II FT-Raman module equipped with a Nd: YAG laser (1064 nm) or a b) Lab RAM HR 800 Horiba Jobin Yvon equipped with a BX40 microscope (focus 1 microns) or an olympus MPLAN 50xNA 0.70 lens. To stimulate an infrared laser (785 nm, 100 mW, air cooled, diode laser), a red laser (633 nm, 17 mW, HeNe-laser); or a blue laser (532 nm, 50 mW, air-cooled, frequency-doubled Nd: YAG solid-state laser) was used.

Elemental Analysis

Analysator Flash EA 1112 from Thermo Quest, or C/H/N/S-Mikroanlysator TruSpec-932 from Leco was used.

DSC

DSC 823e from Mettler-Toledo (heating rate 10K/min) was used.

TGA measurements

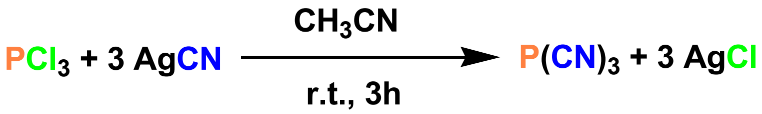
TGA measurements were performed on a Setaram TGA-DSC LapSys 1600 under argon with a heating rate of 5K/min carried out. Mass losses were about the derivation of TG-curve evaluated (DTG curve). The temperatures of the mass losses were on the determined integration of DTG curve. The temperatures indicated correspond to the interpolated intersection of the tangent at the inflection point of the DTG curve with the interpolated baseline of DTG curve. All data were analyzed using the setsoft received 2000 software.

Mass spectroscopy

Finnigan MAT 95-XP from Thermo Electron (ESI-TOF) was used.

5.1.3 Synthesis of starting materials

5.1.3.1 Synthesis of tricyanophosphine

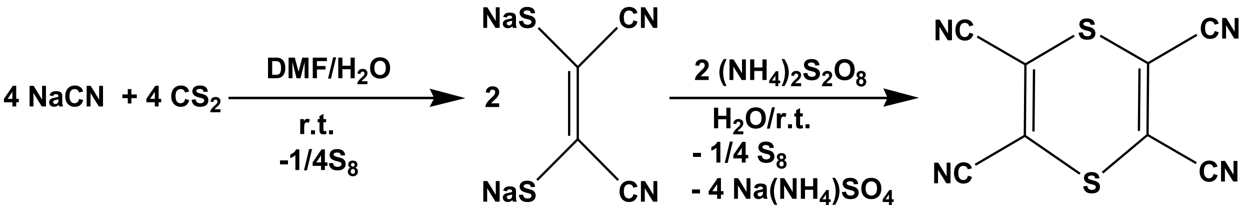


$$PCl_3 + 3\ AgCN \xrightarrow[\text{r.t., 3h}]{CH_3CN} P(CN)_3 + 3\ AgCl$$

The synthesis is carried out following a literature method.[4] To a suspension solution of AgCN (41.00 g, 306.2 mmol) in acetonitrile (150 mL), a trichlorophosphine (11.5 g, 83.74 mmol) was added with stirring at ambient temperature. The suspension obtained was stirred for 3 hours as the exclusion of light and then filtered off the excess AgCN through a G4 frit. The filter residue was washed twice with CH_3CN and the filtrate carefully was dried in a vacuum. It should be ensured that $P(CN)_3$ already sublimated under high vacuum at room temperature; it should be also ensured by additional cooling that only the solvent was evaporated. The white-yellowish solid obtained was purified by sublimation at 1×10^{-3} mbar and possibly gentle heating to 60 °C. This gave 8.08 g $P(CN)_3$ (74.11 mmol) in colorless needles, yield 88%

EA% calc. (found) C 33.05 (32.39); N 38.54 (37.76). **^{13}C NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): $\delta = 110.74$ (d, 3C, *C*N). **^{31}P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): $\delta = -125.2$ (s, $P(CN)_3$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2204 (m), 1241 (w), 622 (s), 593 (vs), 570 (vs). **Raman** (25 °C, 65 mW, 24 scans, cm^{-1}): 2209 (5), 2204 (8), 627 (1), 599 (1), 571 (2), 465 (3), 145 (4), 117 (10).

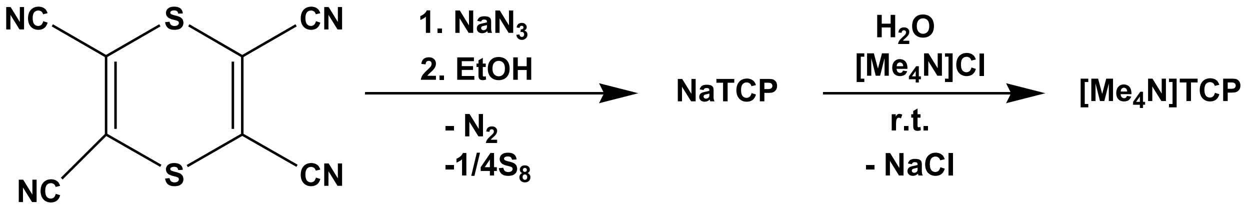
5.1.3.2 Synthesis of tetracyano-1,4-dithiin ($C_8N_4S_2$)



A suspension of NaCN (30.0 g, 612 mmol) and DMF (185mL) was stirred vigorously and CS_2 (46.6 g, 612 mmol) was added dropwise over 40min. H_2O (dest. 1.5 L) was added and the mixture was stirred overnight at ambient temperature. The precipitate (sulfur) was removed by filtration. A solution of H_2O (dest. 305mL) and $(NH_4)_2S_2O_8$ (139.7 g, 216 mmol) was added to the filtrate dropwise over an hour, the mixture was stirred over 40min, and the raw product was collected by filtration. Several recrystallisations from a saturated dichloroethane solution of tetracyano-1,4-dithiin resulted yellow crystals. Yield 22 g (67 %, 102 mmol) tetracyano-1,4-dithiin.

C/H/N/S analysis % calc. (found): C 44.43 (44.21); H 0.0 (0.0); N 25.91 (25.35); S 29.66 (29.61). **^{13}C NMR** (300 K, d_6-DMSO, 250.13 MHz): δ = 125.4 (s, 4C, *C*N), 112.4 (s, 4C, C_{quat}). **IR** (25 °C, ATR, 32 scans cm^{-1}): 2242 (w), 2229 (w), 2218 (w), 1558 (w), 1519 (vs), 1176 (m), 1157 (m), 1054 (w), 1011 (s), 972 (s), 933 (m), 873 (m), 811 (w), 645 (m), 619 (w). **Raman** (25 °C, 65 mW, 3 scans, cm^{-1}): 2243 (5), 2229 (10), 2220 (10), 1562 (7), 1522 (1), 1158 (1), 1130 (1), 646 (2), 621 (2), 524 (2), 516 (1), 506 (3), 472 (4), 351 (2), 341 (2), 312 (1).

5.1.3.3 Synthesis of tetramethylammoniumtetracyanopyrrolide [Me$_4$N]TCP



Tetracyano-1,4-dithiin (10.8 g, 50 mmol), sodium azide (3.25 g, 50 mmol), and (200 mL) of ethanol was mixed and stirred overnight, and nitrogen slowly evolved. The dark red reaction mixture was filtered to remove elemental sulfur, and the filtrate was evaporated to dryness under reduced pressure. Water (dest. 200mL) was added, and a brown solid that contained appreciable amounts of elemental sulfur was removed by filtration. The aqueous filtrate was decolorized with (Darco) and stirred at 0 °C, tetramethylammoniumchloride (11g, 100 mmol) was added as a saturated aqueous solution. Reddish brown tetramethylammoniumtetracyanopyrrolide 8.4 g (70 %, 35 mmol) was removed by filtration, washed with water, and dried under reduced pressure.

Several recrystallisations from a saturated isopropylalcohol solution of tetramethylammonium tetracyanopyrrolide resulted colorless crystals.

DSC: m.p. 272 °C, $\boldsymbol{T}_{\mathrm{dec}}$ = 324 °C**.** **C/H/N analysis** % calc. (found): C 59.99 (59.14); H 5.03 (5.56); N 34.98 (33.86). **^{1}H NMR** (300 K, d_6-DMSO, 250.13 MHz): δ= 3.09 (s, 12H, CH_3). **^{13}C NMR** (300 K, d_6-DMSO, 250.13 MHz): δ = 119.7 (s, 2C, C_{quat}), 114.5 (s, 2C, C_{quat}), 112.4 (s, 2C, C_{quat}), 102.0 (s, 2C, C_{quat}), 54.4 (s, 4C, $C\mathrm{H}_3$). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3041 (w), 2982 (w), 2759 (w), 2720 (w), 2221 (vs), 1543 (w), 1485 (vs), 1475 (s), 1450 (s), 1383 (m), 1330 (m), 1290 (m), 1271 (m), 1204 (w), 1183 (w), 1133 (w), 1074 (m), 948 (vs), 788 (w), 676 (w), 557 (w). **Raman** (25 °C, 65 mW, 30 scans, cm^{-1}): 2233 (6), 1474 (3), 1415 (4), 1308 (2), 751 (4), 540 (3). **MS (ESI-TOF):** calcu.(found): cation 74.0964 (74.0971), anion 166.0159 (166.0160).

5.1.3.4 Synthesis of Silver tetracyanopyrrolide AgTCP

$$\mathbf{[Me_4N]TCP + AgNO_3 \xrightarrow[acetone]{H_2O} AgTCP + [Me_4N]NO_3}$$

To a stirred solution of tetramethylammoniumtetracyanopyrrolide (2.4 g, 10 mmol) in water (dest. / acetone 10 mL: 100 mL), a solution of silver nitrate $AgNO_3$ (2.2 g, 13 mmol) in water (dest., 30 mL) was added at ambient temperature. After stirring for 3h as the exclusion of light, the tan silver salt was collected by filtration, washed three times with ethanol (20 mL), and dried under reduced pressure; Yield 2.05 g (75% , 7.48 mmol).

DSC: m.p. 270 °C, $\boldsymbol{T}_{\mathrm{dec}}$ = 313 °C. **C/H/N analysis** % calc. (found) for **$AgTCP\cdot 0.5H_2O$**: C 33.95 (33.40); H 0.36 (0.09); N 24.75 (23.34). **^{13}C NMR** (298.2 K, d_6-DMSO, 300.13 MHz): δ =119.8 (s, 2C, C_{quat}), 114.3 (s, 2C, C_{quat}), 112.3 (s, 2C, C_{quat}), 102.1 (s, 2C, C_{quat}). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3560 (w), 2973 (w), 2935 (w), 2899 (w), 2798 (w), 2741 (w), 2650 (w), 2260 (m), 2233 (vs), 2031 (w), 1981 (w), 1614 (w), 1481 (s), 1420 (s), 1325 (m), 1240 (w), 1092 (m), 1036(w), 951 (w), 903 (w), 876 (w), 844 (w), 810 (w), 714 (w), 696 (m), 683 (m), 611 (w), 557 (w), 534 (w). **MS (ESI-TOF):** calcu. (found) cation 106.9045 (106.9047), anion 166.0159 (166.0160).

5.1.3.5 Synthesis of tetracyanopyrrole HTCP

Procedure 1

$$[Me_4N]TCP \xrightarrow[CH_3CN]{10\%\ HCl} HTCP + [Me_4N]Cl$$

A column containing Amberlyst 15 ion-exchange resin (200g) was thoroughly washed with 10 mol 10% HCl, deionized water, acetone, and acetonitrile. A solution of tetramethylammoniumtetracyanopyrrolide (2.4g, 10 mmol) in acetonitrile (30 mL) was slowly added to the top of the column. The free pyrrole was eluted with acetonitrile and the eluent evaporated to dryness under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel column. The column was eluted with ethylacetate/*n*-heptane (v:v = 3:1). The resulting purified fractions were combined and evaporated under reduced pressure. The precipitate was washed two times with dichloromethane (15 mL) under heating, and dried *in vacuo* at room temperature; Yield 0.75 g (45 %, 4.5 mmol).

C/H/N analysis % calc. (found): C 57.49 (57.04); H 0.60 (0.47); N 41.90 (41.28). **^{1}H NMR** (300 K, CD_3CN, 250.13 MHz): δ= 11.03 (s, 1H, N*H*). **^{13}C NMR** (298 K, CD_3CN, 250.13 MHz): δ = 112.1 (s, 2C, C_{quat}), 108.8 (s, 2C, C_{quat}), 107.6 (s, 2C, C_{quat}), 105.7 (s, 2C, C_{quat}). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3543 (vw), 3168 (s), 3101 (s), 3001 (m), 2902 (w), 2819 (w), 2708 (w), 2291 (vw), 2260 (m), 2243 (vs), 1596 (w), 1494 (m), 1452 (s), 1347 (w), 1256 (s), 1224 (m), 1190 (m), 1018 (w), 962 (w), 936 (vw), 837 (w), 745 (vs), 685 (vs), 673 (s).

Procedure 2

$$AgTCP \xrightarrow[H_2O]{excess\ HCl} HTCP + AgCl$$

To a stirred suspension of silver tetracyanopyrrolide (1.5 g, 5.47 mmol) in water (dest., 65 mL), hydrochloric acid (0.39 g, 10.68 mmol) was added at ambient temperature. The resulting suspension was allowed to stir overnight. The resulting suspension was filtered, and the resulting yellow filtrate was evaporated to dryness to yield a yellow precipitate. The precipitate was washed two times with dichloromethane (15 mL) under heating, and dried *in vacuo* at room temperature for 6 h. Sublimation of the yellow residue at (150 °C) for 6 h gave 0.65 g (71%, 3.89 mmol) of tetracyanopyrrole as a white crystalline solid.

DSC: m.p. 207 °C, T_{dec} = 237 °C. **C/H/N analysis** % calc. (found): C 57.49 (57.24); H 0.60 (0.41); N 41.90 (41.28). **^{1}H NMR** (298 K, CD_3CN, 300.13 MHz): δ= 11.09 (s, 1H, N*H*). **^{13}C NMR** (298 K, CD_3CN, 300.13 MHz): δ = 112.1 (s, 2C, C_{quat}), 108.7 (s, 2C, C_{quat}), 107.6 (s, 2C, C_{quat}), 105.8 (s, 2C, C_{quat}). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3170(m), 3100 (m), 2999 (m), 2962 (m), 2902 (w), 2818 (w), 2706 (w), 2291 (vw), 2260 (m), 2244 (s), 2198 (w), 1678 (w), 1602 (w), 1566 (w), 1493 (m), 1452 (m), 1348(w), 1258 (vs), 1224 (m), 1204(w), 1190 (w), 1087 (s), 1017 (s), 937 (w), 865 (w), 837 (m), 796 (vs), 744 (vs), 685 (vs), 673 (s). **Raman** (25 °C, 12 mW, 8 scans, cm^{-1}): 3048 (1), 2252 (10), 1597 (0.3), 1496 (3), 1446 (5), 1348 (1), 1086 (1), 685 (1), 518 (2), 138 (2). **MS** *m/z* (%) = 167 (100) [M]. **HRMS (ESI):** calcu. for $C_8N_5^-$ 166.01592; found 166.01578

5.1.4 Synthesis of compounds

5.1.4.1 Reactions of tricyanophosphine

5.1.4.1.1 Reaction of $P(CN)_3$ with $Ag(OOCCF_3)$

To a stirred solution of $P(CN)_3$ (0.028 g, 0.26 mmol) in tetrahydrofuran (6 mL), a solution of silver trifluoroacetate (0.055 g, 0.25 mmol) in tetrahydrofuran (6 mL) was added dropwise at ambient temperature. The white suspension solution was allowed to stir overnight as the exclusion of light, resulting in precipitation of white precipitate. The white precipitate was removed by filtration and was washed with tetrahydrofuran, the solvent was removed *in vacuo*. The resulting residue was washed two times with tetrahydrofuran and was dried *in vacuo*.

***Analytical data for white precipitate*:**

C/H/N analysis % found C 9.88; H 0.89; N 9.37; F 1.99; P 3.63. **^{19}F NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ= −76.15 to −76.17 (m, 1.0), −76.85 (s, 0.2). **^{31}P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 3.46 (s). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2943 (w), 2860 (w), 2162 (vs), 1238 (m), 1182 (m), 1122 (m), 999 (s), 984 (s), 744 (m), 621 (m).

***Analytical data for resulting residue*:**

C/H/N analysis % found C 29.42; H 1.28; N 21.91; F 11.21. **^{13}C NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 106.80 (d, 3C, *C*N). **^{19}F NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ= −76.80 (s, 1.0), −76.34 (s, 0.3). **^{31}P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ= −142.14 (s, $P(CN)_3$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2958 (vw), 2929 (vw), 2873 (vw), 2204 (m), 1783 (w), 1267 (w), 1223 (w), 1165 (w), 1039 (w), 926 (w), 829 (w), 775 (w), 621 (s), 594 (vs), 575 (vs). **MS (ESI-TOF):** cation 241.813 (8), 282.839 (2), 415.747 (3), 591.681 (2), 724.589 (2), anion 119.986 (5), 158.912 (10) $Ag(CN)_2$, 293.820 (4), 426.729 (2).

5.1.4.1.2 Reaction of $P(CN)_3$ with $Ag[Al(OCH(CF_3)_2)_4]$

To a stirred solution of $P(CN)_3$ (0.028 g, 0.26 mmol) in dichloromethane (10 mL), a solution of $Ag[Al(OCH(CF_3)_2)_4]$ (0.20 g, 0.25 mmol) in dichloromethane (5 mL) was added dropwise at ambient temperature. The white suspension solution was allowed to stir two days as the exclusion of light, resulting in precipitation of white precipitate. The white precipitate was removed by filtration and was washed with dichloromethane, the solvent was removed *in vacuo*. The resulting residue was washed two times with dichloromethane and was dried *in vacuo*.

***Analytical data for white precipitate*:**

C/H/N analysis % found C 9.25; H 0.57; N 9.59; F 6.30; P 1.72. **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2166 (m), 1373 (w), 1300 (m), 1229 (vs), 1200 (vs), 1105 (vs), 982 (vs), 897 (m), 806 (m), 744 (m), 687 (s), 665 (m), 638 (s), 627 (s), 554 (m).

***Analytical data for resulting residue*:**

C/H/N analysis % found C 20.67; H 0.62; N 9.81; F 16.06; P 10.79. **^{1}H NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 4.40 (m, 4H, C*H*). **^{19}F NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ= −77.35 (s, 1.0), −76.06 (s, 2.5), −74.48 (t, 3.0,), −73.33 (s, 1.2). **^{31}P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 29.65 (s, 1.0), 129.35 (s, 0.2), 139.77 (s, 0.2). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2958 (w), 2928 (w), 2858 (vw), 2193 (vw), 2168 (vw), 1371 (m), 1292 (m), 1192 (vs), 1095 (vs), 987 (m), 874 (s), 858 (s), 733 (m), 687 (vs). **Raman** (25 °C, 65 mW, 4 scans, cm^{-1}): 3015 (0.8), 2970 (1), 2953 (1), 2921 (1), 2898 (0.8), 2210 (0.2), 1496 (0.3), 1460 (0.6), 1382 (1), 1299 (0.7), 1260 (0.5), 1207 (1), 1101 (1), 1084 (0.5), 999 (0.3), 928 (3), 858 (10), 776 (2), 719 (2), 702 (2), 690 (1), 576 (2), 539 (1), 526 (1), 335 (5), 302 (2), 203 (2).

5.1.4.1.3 Reaction of $P(CN)_3$ with $AgBF_4$

To a stirred solution of $P(CN)_3$ (0.028 g, 0.26 mmol) in dichloromethane (10 mL), a solution of silver tetraflouridoborate (0.048 g, 0.25 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The white suspension solution was allowed to stir two days as the exclusion of light, resulting in precipitation of white precipitate. The white precipitate was removed by filtration and was washed with dichloromethane, the solvent was removed *in vacuo*. The resulting residue was washed two times with dichloromethane and was dried *in vacuo*.

***Analytical data for white precipitate*:**

C/H/N analysis % found C 8.75; H 0.11; N 10.44; F 0.0; P 1.47. **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2918 (w), 2850 (w), 2164 (vs), 1124 (m), 1059 (m), 849 (m), 822 (m), 623 (w), 542 (w).

***Analytical data for resulting residue*:**

C/H/N analysis % found C 30.05; H 0.66; N 29.88; P 17.97.^{19}**F NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): $\delta = -156.09$ (s, 1.0), -149.60 (s, 0.4), -35.90 (s, 0.05), -30.95 (s, 0.05). ^{11}**B NMR** (298.2 K, CD_2Cl_2, 96.3 MHz): $\delta = -0.03$ (s). ^{31}**P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): $\delta = -125.1$ (s, $P(CN)_3$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3213 (w), 2924 (w), 2852 (w), 2658 (w), 2488 (w), 2370 (w), 2281 (w), 2204 (m), 2094 (m), 1614 (m), 1466 (m), 1014 (s), 845 (vs), 621 (s), 573 (vs).

5.1.4.1.4 Reaction of $P(CN)_3$ with $Ag[B(C_6F_5)_4]\cdot Et_2O$

Procedure 1

To a stirred solution of $P(CN)_3$ (0.028 g, 0.26 mmol) in dichloromethane (10 mL), a suspension solution of $Ag[B(C_6F_5)_4]\cdot Et_2O$ (0.22 g, 0.25 mmol) in dichloromethane (10 mL) was added dropwise at –70 °C over a period of five minutes. The resulting suspension solution was allowed to warm up to ambient temperature and was stirred three days as the exclusion of light and then filtrated. The solvent was removed *in vacuo*, and the residue was washed two times with dichloromethane and was dried *in vacuo*.

^{31}**P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): $\delta = -125.2$ (s, $P(CN)_3$). ^{19}**F NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): $\delta = -133.13$ (s, *o*-F), -163.64 (t, *p*-F), -167.56 (s, *m*-F). ^{11}**B NMR** (298.2 K, CD_2Cl_2, 96.3 MHz): $\delta = -16.65$ (s).

Procedure 2

To a stirred solution of $P(CN)_3$ (0.055 g, 0.50 mmol) in toluene (10 mL), a solution of $Ag[B(C_6F_5)_4]\cdot Et_2O$ (0.43 g, 0.50 mmol) in toluene (10 mL) was added dropwise at ambient temperature. The colorless solution was allowed to stir overnight as the exclusion of light and then filtered. The resulting solution was heated for four hours at 50 °C with stirring. The solvent was removed *in vacuo*, and the oil residue was dissolved in dichloromethane and concentrated, the solvent was removed *in vacuo* and the oil residue was dried *in vacuo*.

Analytical data for colorless solution after stirring overnight:

^{31}P NMR (298.2 K, Toluene-d$_8$, 300.13 MHz): δ = −131.72 (s, P(CN)$_3$). **^{19}F NMR** (298.2 K, Toluene-d$_8$, 300.13 MHz): δ = −132.22 (s, *o*-F), −163.11 (d, *p*-F), −167.09 (d, *m*-F). **^{11}B NMR** (298.2 K, Toluene-d$_8$, 96.3 MHz): *δ* = − 16.23 (s).

Analytical data for colorless solution after heating:

^{31}P NMR (298.2 K, Toluene-d$_8$, 300.13 MHz): δ = −131.70 (s, 1.0, P(CN)$_3$), − 99.62 (s, 0.3). **^{19}F NMR** (298.2 K, Toluene-d$_8$, 300.13 MHz): δ = − 131.85 to− 133.67 (m), − 139.08 to −139.16 (m), −157.99 to −158.18 (m), −162.33 to −162.51 (m), −164.50 to −164.99 (m), − 166.40 (s).**^{11}B NMR** (298.2 K, Toluene-d$_8$, 96.3 MHz): *δ* = − 15.98 (s).

Analytical data for solution after dissolving in CH$_2$Cl$_2$ and concentrated:

^{31}P NMR (298.2 K, CD$_2$Cl$_2$, 300.13 MHz): δ = 36.68 to 37.73 (m, 1.0), 41.61 (s, 0.1). **^{19}F NMR** (298.2 K, CD$_2$Cl$_2$, 300.13 MHz): δ = −132.99 to −133.42 (m), −139.16 (s) , −159.10 to −159.41 (m), −165.53 to −165.97 (m). **^{11}B NMR** (298.2 K, CD$_2$Cl$_2$, 96.3 MHz): *δ* = − 12.00 (s), −16.62 (s), −21.85 (s).

5.1.4.1.5 Reaction of P(CN)$_3$ with triethylamine

To a stirred colorless solution of P(CN)$_3$ (0.055 g, 0.50 mmol) in dichloromethane (10 mL), triethylamine (0.051 g, 0.50 mmol) was added dropwise at –70 °C over a period of five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight, resulting in an orange brown solution. The solvent was removed in *vacuo*, and the brown oil residue was washed two times with dichloromethane and was dried in *vacuo*.

^{31}P NMR (298.2 K, CD$_2$Cl$_2$, 300.13 MHz, integration normalized to [P(CN)$_2$]$^-$) for a yellow solution: δ = − 9.15 (s, 0.2), −35.55 (s, 0.3), −195.52 (s, 1.0, [P(CN)$_2$]$^-$). **^{31}P NMR** (298.2 K,

CD_2Cl_2, 300.13 MHz, integration normalized to $[P(CN)_2]^-$) for an orange-brown solution: $\delta = -8.98$ (s, 4.0), -33.69 (s, 2.2), -35.27 (s, 3.8), -194.87 (s, 1.0, $[P(CN)_2]^-$).

***Analytical data for resulting residue after drying*:**

C/H/N analysis % found C 37.26; H 6.22; N 13.26. **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3369 (m), 2987 (m), 2951 (m), 2885 (w), 2685 (m), 2497 (m), 2361 (w), 2200 (w), 2128 (w), 1651 (m), 1475 (m), 1454 (m), 1396 (m), 1362 (m), 1282 (s), 1223 (s), 1159 (s), 1132 (s), 1093 (vs), 1063 (s), 1038 (s), 1012 (s), 951 (s), 837 (s), 804 (s), 714 (s), 608 (vs).

5.1.4.1.6 Reaction of $P(CN)_3$ with tetramethylethylenediamine

To a stirred colorless solution of $P(CN)_3$ (0.055 g, 0.50 mmol) in dichloromethane (10 mL), tetramethylethylene diamine (0.058 g, 0.50 mmol) was added dropwise at –70 °C over a period of five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight, resulting in an orange brown solution. The solvent was removed *in vacuo*, and the brown oil residue was washed two times with dichloromethane and was dried *in vacuo*.

^{31}P NMR (296 K, CD_2Cl_2, 300.13 MHz, integration normalized to $[P(CN)_2]^-$) for a yellow solution: $\delta = -22.5$ (s, 0.8), -162.81 (s, 5.0), -194.73 (s, 1.0, $[P(CN)_2]^-$). **^{31}P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz integration normalized to $[P(CN)_2]^-$) for an orange-brown solution: $\delta = -22.31$ (s, 1.4), -34.37 (s, 1.1), -45.05 (s, 0.5), -50.53 (s, 0.9), -168.68 (s, 4.4), -194.34 (s, 1.0, $[P(CN)_2]^-$).

***Analytical data for resulting residue after drying*:**

C/H/N analysis % found C 34.97; H 7.73; N 15.64. **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3375 (vw), 3018 (m), 2958 (m), 2920 (m), 2781 (w), 2569 (s), 2526 (m), 2455 (s), 2428 (s), 2220 (w), 2197 (w), 2106 (w), 2077 (m), 1470 (s), 1412 (m), 1288 (vs), 1240 (s), 1155 (m), 1095 (s), 1022 (s), 1003 (vs), 984 (vs), 943 (vs), 903 (vs), 797 (m), 743 (m), 650 (m), 608 (s).

5.1.4.1.7 Reaction of $P(CN)_3$ with 2, 2' –bipyridine

Procedure 1

To a stirred colorless solution of $P(CN)_3$ (0.028 g, 0.25 mmol) in tetrahydrofuran (10 mL), a solution of 2, 2'-bipyridine (0.039 g, 0.25 mmol) in tetrahydrofuran (10 mL) was added dropwise at –70 °C over a period of five minutes. The resulting colorless solution was allowed to warm up to ambient temperature and was stirred overnight. The solvent was removed in *vacuo*, and the yellow oil residue was washed two times with tetrahydrofuran and was dried in *vacuo*.

^{31}P NMR (296 K, CD_2Cl_2, 300.13 MHz, integration normalized to $P(CN)_3$) for colorless solution: $\delta = -21.10$ (s, 0.01), −35.14 (s, 0.01), −50.86 (s, 0.1), −99.76 (s, 0.01), −142.19 (s, 1.0, $P(CN)_3$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3055 (w), 2924 (w), 2852 (w), 2200 (w), 2164 (vw), 2077 (w), 1618 (w), 1583 (m), 1529 (m), 1473 (w), 1458 (m), 1421 (m), 1300 (m), 1277 (m), 1221 (m), 1173 (w), 1148 (m), 1090 (m), 1074 (m), 1038 (m), 991 (s), 941 (m), 893 (m), 808 (m), 758 vs), 725 (m), 619 (s), 588 (s).

Procedure 2

To a stirred colorless solution of $P(CN)_3$ (0.028 g, 0.25 mmol) in dichloromethane (10 mL), a solution of 2,2'-bipyridine (0.039 g, 0.25 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The resulting colorless solution was allowed to stir overnight at ambient temperature, resulting a yellow solution. The solvent was removed in vacuo, and the pale yellow residue was washed two times with dichloromethane and was dried in *vacuo*.

C/H/N analysis % found C 58.94; H 3.92; N 21.22; P 11.35. **^{31}P NMR** (296 K, CD_2Cl_2, 300.13 MHz, integration normalized to $P(CN)_3$) for a yellow solution: $\delta = 14.48$ (s, 0.2), −126.56 (s, 1.0, $P(CN)_3$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3076 (w), 3055 (w), 3016 (w), 2200 (w), 2079 (w), 2004 (vw), 1963 (vw), 1927 (vw), 1898 (vw), 1859 (vw), 1616 (w), 1583 (m), 1556 (m), 1529 (m), 1458 (m), 1421 (m), 1300 (m), 1277 (m), 1250 (m), 1173 (w), 1148 (m), 1094 (m), 1074 (m), 1038 (m), 991 (s), 962 (m), 808 (m), 758 (vs), 725 (m), 654 (w), 619 (s), 557 (s).

5.1.4.1.8 Reaction of $P(CN)_3$ with sulfur

To a stirred colorless solution of $P(CN)_3$ (0.11 g, 1.1 mmol) in tetrahydrofuran (10 mL), a solution of sulfur (0.032 g, 1 mmol) in tetrahydrofuran (10 mL) was added dropwise at –70 °C over a period of five minutes. The resulting colorless solution was allowed to warm up to ambient temperature and was stirred overnight. The solvent was removed in *vacuo*, and the pale yellow residue was dried in *vacuo*.

^{31}P NMR (296 K, CD_2Cl_2, 300.13 MHz, integration normalized to $P(CN)_3$) for colorless solution: $\delta = -63.7$ (s,0.04), -142.2 (s, 1.0, $P(CN)_3$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2926 (vw), 2858 (vw), 2204 (w), 1256 (w), 1014 (w), 914 (w), 748 (w), 579 (vs)

5.1.4.1.9 Reaction of $P(CN)_3$ with 4-dimethylaminopyridine

Procedure 1

To a stirred colorless solution of $P(CN)_3$ (0.055 g, 0.50 mmol) in tetrahydrofuran (10 mL), a solution of 4-dimethylaminopyridine (0.061 g, 0.50 mmol) in tetrahydrofuran (10 mL) was added dropwise at –70 °C over a period of five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight, resulting a yellow solution. The solvent was removed in *vacuo*, and the brown oil residue was washed two times with tetrahydrofuran and was dried in *vacuo*.

C/H/N analysis % found C 48.35; H 5.41; N 23.14; P 29.25. **^{31}P NMR** (296 K, CD_2Cl_2, 300.13 MHz, integration normalized to $P(CN)_3$) for a yellow solution: $\delta = -33.27$ (s, 0.03), -150.6 (s, 1.0, $P(CN)_3$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3078 (w), 2930 (w), 2202 (w), 2081 (w), 1643 (vs), 1560 (s), 1441 (m),1400 (s), 1317 (m), 1211 (s), 1121 (s), 1059 (vs), 1028 (s), 941 (s), 814 (s), 743 (s), 604 (s).

Procedure 2

To a stirred colorless solution of $P(CN)_3$ (0.055 g, 0.50 mmol) in dichloromethane (10 mL), a solution of 4-dimethylaminopyridine (0.061 g, 0.50 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The resulting yellow solution was allowed to stir overnight, resulting a brown solution. The solvent was removed in *vacuo*, and the brown oil residue was washed two times with dichloromethane and was dried in *vacuo*.

C/H/N analysis % found C 46.73; H 4.76; N 22.67; P 14.62. **^{31}P NMR** (296 K, CD_2Cl_2, 300.13 MHz) for a brown solution: δ= −16.08 (s, 0.01),− 32.02 (s, 0.02), − 170.66 (s, 1.0). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3390 (w), 3225 (w), 3072 (w), 2924 (m), 2852 (m), 2677 (w), 2355 (w), 2206 (w), 2104 (w), 2081 (w), 1963 (w), 1641 (vs), 1603 (m), 1556 (s), 1443 (m), 1400 (m), 1259 (m), 1209 (s), 1063 (vs), 1028 (s), 978 (vs), 939 (vs), 806 (vs), 771 (s), 743 (s), 602 (s). **HRMS (EI):** calcu. for DMAP 122.08; found 121 (10)

5.1.4.1.10 Reaction of $P(CN)_3$ with 1,8-diaminonaphthalene

To a stirred solution of $P(CN)_3$ (0.050 g, 0.45 mmol) in dichloromethane (10 mL), a solution of 1,8-diaminonaphthalene (0.071 g, 0.45 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The resulting yellow solution was allowed to stir overnight. The solvent was removed in *vacuo*, and the yellow residue was dried in *vacuo*.

C/H/N analysis % found C 53.59; H 4.12; N 12.67; P 14.67. **^{1}H NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 7.31 (m, 4H, *m*-C*H*), 6.68 (d, 2H, *o*-C*H*), 3.66 (s, 2H, N*H*). **^{13}C NMR** (300 K, CD_2Cl_2, 250.13 MHz): δ = 136.46 to 136.09 (m, 1C, *C*=*C*), 126.94 (s, 2C, *C*H), 122.23 (s, 2C, *C*H), 111.69 (s, 2C, *C*H). **^{31}P NMR** (298.4 K, CD_2Cl_2, 300.13 MHz): δ = 18.77 (s, 1.0), −12.37 (s, 0.2). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3361 (m), 3306 (m), 3055 (m), 2162 (w), 1909 (w), 1738 (w), 1620 (vw), 1595 (s), 1487 (w), 1462 (m), 1410 (w), 1358 (m), 1300 (m), 1257 (m), 1182 (m), 1161 (m), 1119 (w), 1057 (m), 1034 (m), 970 (m), 912 (m), 878 (m), 814 (s), 789 (m), 752 (vs), 679 (m), 635 (m), 619 (m), 555 (m). **MS (ESI-TOF):** cation 159.09222 (10), anion 112.98591 (2), 339.23369 (10).

5.1.4.1.11 Reaction of $P(CN)_3$ with $B(C_6F_5)_3$

To a stirred solution of $P(CN)_3$ (0.055 g, 0.50 mmol) in dichloromethane (10 mL), a solution of $B(C_6F_5)_3$ (0.26 g, 0.50 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The colorless solution was allowed to stir overnight. The solvent was removed in *vacuo*, and the pale yellow residue was dried in *vacuo*.

C/H/N analysis % found C 38.26; H 0.34; N 5.46; P 5.25; F 45.89. **^{19}F NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = −133.71 (d, *o*-F), −154.99 (s, *p*-F), −163.39 to −163.57 (m, *m*-F). **^{11}B NMR** (298.2 k, CD_2Cl_2, 96.3 MHz): *δ* = − 4.18 (s, 1.0), − 21.7 (s, 0.2). **^{31}P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz, integration normalized to $P(CN)_3$): δ = 11.14 (s, 0.08), −125.64 (s, 1.0, $P(CN)_3$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3566 (vw), 3246 (w), 2200 (w), 1647 (m), 1518 (s), 1460 (vs), 1385 (m), 1288 (m), 1182 (w), 1101 (s), 972 (vs), 860 (m), 795 (m), 773 (s), 739 (s), 681 (s), 617 (m), 577 (m). **Raman** (25 °C, 65 mW, 6 scans, cm^{-1}): 2276 (0.1), 2204 (0.3), 1649 (1), 1393 (1), 859 (0.5), 796 (1), 685 (0.6), 624 (0.6), 583 (10), 493 (9), 447 (10), 391 (7), 357 (0.3), 285 (0.6), 232 (2), 158 (1).

5.1.4.1.12 Reaction of $P(CN)_3$ with $3B(C_6F_5)_3$

To a stirred solution of $P(CN)_3$ (0.028 g, 0.25 mmol) in dichloromethane (10 mL), a solution of $B(C_6F_5)_3$ (0.42 g, 0.82 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The colorless solution was allowed to stir two days. The solvent was removed in *vacuo*, and the pale yellow residue was dried in *vacuo*.

C/H/N analysis % found C 40.10; H 0.23; N 1.91; P 1.81; F 43.41. **^{13}C NMR (**298.2 K, CD_2Cl_2, 300.13 MHz): δ = 150.20 (s), 146.95 to 146.79 (m, o-*C*), 139.59 to 139.32 (m, p-*C*), 136.46 to 136.03 (m, m-*C*). **^{19}F NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = −130.64 (s, *o*-F), −148.65 (s, *p*-F), − 161.94 to −162.05 (m, *m*-F). **^{11}B NMR** (298.2 k, CD_2Cl_2, 96.3 MHz): *δ* = 31.03 (br, 1.0),−21.80 (s, 0.4). **^{31}P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz, integration normalized to $P(CN)_3$): δ = 5.40 (s, 0.3), − 25.99 (s, 0.05), − 52.10 (s, 0.08), −129.18 (s, 1.0, $P(CN)_3$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3689 (vw), 3562 (vw), 3495 (vw), 3246 (vw), 2200 (vw), 1647 (m), 1608 (w), 1518 (s), 1458 (vs), 1379 (s), 1319 (w), 1288 (m), 1159 (w), 1101 (s), 1016 (m),966 (vs), 860 (m), 796 (m), 773 (s), 739 (m), 681 (s), 621 (m), 575 (m). **Raman** (25 °C, 65 mW, 8 scans, cm^{-1}): 2279 (0.3), 2199 (0.2), 1645 (4), 1392 (3), 1382 (3), 1310 (0.5), 1299 (0.6), 852 (5), 791 (0.5), 728 (0.6), 654 (1), 580 (8), 494 (9), 469 (3), 440 (10), 390 (7), 380 (7), 279 (1), 233 (2), 155 (2).

5.1.4.1.13 Reaction of $P(CN)_3$ with Lithium bis(trimethylsilyl)amide

To a stirred colorless solution of $P(CN)_3$ (0.028 g, 0.26 mmol) in tetrahydrofuran (5 mL), a solution of $LiN(SiMe_3)_2$ (0.043 g, 0.26 mmol) in tetrahydrofuran (5 mL) was added dropwise at –70 °C over a period of five minutes. The colorless solution was stirred at this temperature for 30 min. The resulting colorless solution was allowed to warm up to ambient temperature and was stirred for three hours, resulting in a yellow solution. The solvent was removed in *vacuo*, and the yellow residue was washed two times with tetrahydrofuran and was dried in *vacuo*.

***Analytical data for yellow solution*:**

^{1}H NMR (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 0.30 (s, 9H, $Si(CH_3)_3$). **^{31}P NMR** (298.4 K, CD_2Cl_2, 300.13 MHz): δ = −197.50 (s, $[P(CN)_2]^-$). **^{29}Si-INEPT-NMR** (298.7 K, CD_2Cl_2, 59.6 MHz): *δ* = –11.71 (s, $(CH_3)_3Si$).

***Analytical data for resulting residue after drying*:**

C/H/N analysis % found C 30.63; H 4.18; N 19.92. **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3223 (m), 2957 (w), 2926 (w), 2845 (w), 2370 (w), 2193 (w), 2039 (vw), 1633 (w), 1456 (vw), 1134 (s), 1080 (s), 933 (m), 841 (s), 754 (m).

5.1.4.1.14 Reaction of $P(CN)_3$ with triethylamine and silver tetraflourido borate

To a stirred colorless solution of $P(CN)_3$ (0.055 g, 0.50 mmol) in dichloromethane (10 mL), a triethylamine (0.051 g, 0.50 mmol) was added dropwise at –70 °C over a period of five minutes. The resulting yellow solution was stirred at this temperature for one hour. To this a yellow solution, a solution of silver tetraflouridoborate (0.098 g, 0.50 mmol) in dichloromethane (10 mL) was added dropwise at –70 °C over a period of five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight as the exclusion of light, resulting in precipitation of silver cyanide. The precipitate was removed by filtration and the solvent was removed in *vacuo*. The resulting yellow residue was dried in *vacuo*.

C/H/N analysis % calc. (found) for **AgCN**: C 8.97 (8.56); H 0.0 (0.0); N 10.46 (9.52). **IR** (ATR, 25 °C, 32 scans, cm^{-1}) for **AgCN**: 2164 (vs), 1306 (vw), 1237 (m), 1126 (s), 1059 (s), 820 (m), 805 (m). ^{31}**P NMR** (299.1 K, CD_2Cl_2, 300.13 MHz) for a yellow solution: $\delta = -35.92$ (s, 0.5), -51.64 (s, 1.0). ^{31}**P NMR** (299.2 K, CD_2Cl_2, 300.13 MHz, after drying): $\delta = -35.67$ (s). ^{19}**F NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): $\delta = -151.47$ (s). ^{11}**B NMR** (298.2 K, CD_2Cl_2, 96.3 MHz): $\delta = -1.11$ (s)

5.1.4.1.15 Reaction of $P(CN)_3$ with trimethylamine and sodium tetraphenyl borate

To a stirred colorless solution of $P(CN)_3$ (0.028 g, 0.25 mmol) in tetrahydrofuran (10 mL), triethylamine (0.025 g, 0.25 mmol) was added dropwise at –70 °C over a period of five minutes. The resulting yellow solution was stirred at this temperature for 30 min. To this a yellow solution, a solution of $Na[B(Ph)_4]$ (0.085 g, 0.25 mmol) in tetrahydrofuran (10 mL) was added dropwise at –70 °C over a period five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight. This solution was concentrated and stored at –30 °C for four days, which results in the deposition of colorless crystals.

^{11}**B NMR** (298.3 K, CD_2Cl_2, 96.3 MHz): $\delta = -6.61$ (s). ^{31}**P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz, integration normalized to $P(CN)_3$) for a yellow solution: $\delta = -75.48$ (s, 0.06), -142.80 (s, 1.0, $P(CN)_3$), -195.74 (s,0.08, $[P(CN)_2]^-$).

5.1.4.1.16 Reaction of $P(CN)_3$ with triphenylphosphine and sodium phenyl borate

To a stirred colorless solution of $P(CN)_3$ (0.028 g, 0.25 mmol) in tetrahydrofuran (5 mL), a solution of PPh_3 (0.65 g, 0.25 mmol) in tetrahydrofuran (5 mL) was added dropwise at –70 °C over a period of five minutes. The resulting yellow solution was stirred at this temperature for 30 min. To this a yellow solution, a solution of $Na[B(Ph)_4]$ (0.085 g, 0.25 mmol) in tetrahydrofuran (10 mL) was added dropwise at –70 °C over a period of five minutes. The resulting pale yellow solution was allowed to warm up to ambient temperature and was stirred for three days. The solvent was removed *in vacuo*, and the pale yellow residue was dried *in vacuo*.

^{11}**B NMR** (298.4 K, CD_2Cl_2, 96.3 MHz): $\delta = -12.16$ (s). ^{31}**P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz, integration normalized to $P(CN)_3$): δ = 26.23 (s), − 5.57 (s, , PPh_3), − 142.26 (s, $P(CN)_3$).

5.1.4.1.17 Reaction of $P(CN)_3$ with triphenylphosphine (5)

To a stirred colorless solution of $P(CN)_3$ (0.055 g, 0.50 mmol) in dichloromethane (10 mL), a solution of PPh_3 (0.13 g, 0.50 mmol) in dichloromethane (10 mL) was added dropwise at – 40 °C over a period of five minutes. The resulting yellow solution was allowed to warm up to ambient temperature and was stirred overnight, resulting in an orange brown solution. This solution was concentrated and stored at –30 °C for three days, which results in the deposition of colorless crystals.

^{31}**P NMR** (296 K, CD_2Cl_2, 300.13 MHz) for a yellow solution: δ = 62.46 (m, 0.1), 27.39 (s, 1.0), −44.71 (m, 0.1), −50.89 (s, 0.01), −190.47 (s, 0.01, $[P(CN)_2]^-$). ^{31}**P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz) for an orange-brown solution: δ = 62.57 (s, 0.02), 41.16 (s, 0.2), 37.49 (s, 0.3), 30.50 (s, 1.0), −5.47 (s, 0.4, PPh_3), −137.75 (s, 0.1), −186.63 (s, 0.2), −190.30 (s, 0.3, $[P(CN)_2]^-$).

***Analytical data for colorless crystals*:**

C/H/N analysis % calc. (found) for $[Ph_3P{=}N-C(CN)_2-C(CN)_2-N{=}PPh_3]\bullet 2CH_2Cl_2$ C 62.13 (64.75); H 4.03 (4.77); N 9.88 (6.69). ^{1}**H NMR** (298.8 K, CD_2Cl_2, 300.13 MHz): δ = 7.58 to 7.23 (m, 30 H, Ph). ^{13}**C NMR** (300.3 K, CD_2Cl_2, 300.13 MHz): δ = 137 .64 (d, 2C, $N-C(CN)_2-C(CN)_2$), 134.07 to 133.93 (d, 3C, $C-P$), 132.70 to 132.20 (m, 6C, CH), 129.11 to 128.79 (m, 9C, CH). ^{31}**P NMR** (296 K, CD_2Cl_2, 300.13 MHz): δ = 27.65 (s). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3055 (w), 2351 (w), 2187 (w), 1981 (w), 1700 (vw), 1817 (vw), 1578 (m), 1556 (m), 1481 (m), 1435 (s), 1310 (m), 1178 (m), 1157 (m), 1115 (s), 1068 (m), 1026 (m), 995 (s), 928 (s), 851 (m), 743 (s), 719 (vs), 689 (vs), 617 (m). **HRMS (EI):** calcu. for $PPh_3P{=}N$ 276.29; found 277.0 (10)

5.1.4.1.18 Reaction of $P(CN)_3$ with dichloro (*p*-cymene)ruthenium(II) dimer

To a stirred solution of $P(CN)_3$ (0.028 g, 0.26 mmol) in dichloromethane (10 mL), a solution of dichloro-(*p*-cymene)ruthenium(II)dimer (0.16 g, 0.26 mmol) in dichloromethane (10 mL) was added dropwise at ambient temperature. The resulting red solution was allowed to stir overnight. The solvent was reduced to about 3 ml, and addition of excess diethyl ether (10 mL) with vigorous stirring gave the yellow precipitate. The solvent was removed in *vacuo*, and the yellow residue was washed two times with dichloromethane and was dried *in vacuo*.

C/H/N analysis % calc. (found) for *[(p-cymene)$RuCl_2$•$P(CN)_3$•CH_2Cl_2]* C 33.62 (35.23); H 3.22 (3.94); N 8.40 (7.57). **^{1}H NMR** (300 K, d_6-DMSO, 250.13 MHz): δ = 1.16 (d, 6H. $HC(CH_3)_2$), 2.23 (s, 3H, CH_3), 7.10 to 7.05 (m, 5H, Ph). **^{13}C NMR** (300 K, d_6-DMSO, 500.13 MHz): δ = 20.53 (s, HC−CH_3), 23.95 (s, HC−$(CH_3)_2$), 32.95 (s, HC−$(CH_3)_2$), 126.05 (s, CH−Ph), 128.77 (s, CH), 134.52 (s, CH), 145.28 (s, CH). **^{31}P NMR** (300 K, d_6-DMSO, 250.13 MHz): δ = −11.33 (s). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3063 (w), 2964 (m), 2930 (m), 2872 (m), 2143 (s), 1504 (m), 1466 (m), 1387 (m), 1279 (m), 1198 (m), 1161 (m), 1088 (m), 1057 (m), 1034 (m), 926 (m), 862 (s), 802 (m), 594 (s). **HRMS (EI):** calcu. for *p*-cymene 134.21; found 134 (9)

5.1.4.1.19 Reaction of $P(CN)_3$ with tetrakis(triphenylphosphine) palladium(0) (6)

To a stirred solution of excess $P(CN)_3$ (0.065 g, 0.6 mmol) in tetrahydrofuran (10 mL), a solution of $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol) in tetrahydrofuran (10 mL) was added directly at –70 °C. The resulting yellow solution was stirred at this temperature for 30 min. The resulting yellow solution after stirring for 3h was changed to a pale yellow solution at ambient temperature. This pale yellow solution was allowed to stir overnight. The yellow precipitate was removed by filtration and dissolved in dichloromethane. This solution was concentrated and stored at –30 °C for one day, which results in the deposition of colorless crystals.

C/H/N analysis % calc. (found) for *[$Pd(PPh_3)_2(CN)_2$]•$2CH_2Cl_2$•5THF* C 59.39 (60.81); H 6.15 (6.61); N 2.31 (2.40). **^{1}H NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 7.59 to 7.38 (m, 30H, Ph). **^{31}P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 23.06 (s). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3047 (w), 2943 (w), 2864 (w), 2804 (w), 2131 (w), 1479 (m), 1433 (m), 1371 (w), 1331 (w), 1310 (w), 1279 (w), 1180 (w), 1159 (w), 1094 (s), 1072 (w), 1026 (m), 997 (m), 845 (w), 748 (s), 727 (m), 708 (m), 689 (vs), 617 (w). **Raman** (25 °C, 12 mW, 6 scans, cm^{-1}): 3169 (0.2), 3144 (0.2), 3056 (2), 2957 (0.1), 2144 (3), 1584 (7), 1480 (0.3), 1436 (0.3), 1329 (0.2), 1309 (0.2), 1182 (0.8), 1157 (0.6), 1091 (4), 1023(4), 996 (10), 915 (0.2), 846 (0.2), 750 (0.3), 705 (1), 685 (0.8), 613 (1), 530 (5), 500 (0.2), 492 (0.2), 439 (2), 411 (2), 358 (0.7), 283 (0.6), 251 (2), 220 (0.7), 196 (2).

5.1.4.1.20 Reaction of $P(CN)_3$ with 1, 1, 1- tris(diphenylphosphinomethyl) ethane nickel(0) (7)

To a stirred yellow solution of $Ni(COD)_2$ (0.054 g, 0.20 mmol) in tetrahydrofuran (10 mL), a solution of 1,1,1-tris(diphenylphosphinomethyl)ethane (0.124 g, 0.20 mmol) in tetrahydrofuran (10 mL) was added directly. The resulting red solution was stirred at ambient temperature for 4h. To this a red solution, a solution of $P(CN)_3$ (0.021 g, 0.20 mmol) in tetrahydrofuran (10 mL) was added dropwise at ambient temperature over a period of five minutes. The resulting deep brown solution was allowed to stir overnight. The brown precipitate was removed by filtration, resulting in a deep brown solution. The solvent was removed *in vacuo*, and a brown residue was dissolved in dichloromethane and concentrated, diethyl ether was added dropwise to this solution and stored at ambient temperature for two days, which results in the deposition of red crystals.

^{1}H NMR (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 7.37 to 7.00 (m, 30H, Ph – H), 2.45 (br, 6H, *triphos* – CH_2), 1.07 (t, 3H, *triphos*– CH_3). **^{31}P NMR** (299 K, CD_2Cl_2, 300.13 MHz): δ = 26.40 (s, 0.05), 8.18 (m, 0.1), −1.05 (d, 1.0), −3.74 (s, 3.3), −57.46 (s, 0.5). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3053 (w), 2922 (w), 2852 (w), 2116 (w), 1666 (w), 1587 (w), 1483 (w), 1435 (m), 1308 (w), 1236 (m), 1180 (s), 1155 (s), 1117 (s), 1095 (s), 984 (s), 802 (m), 739 (s), 714 (s), 690 (vs), 617 (m), 565 (s). **Raman** (25 °C, 65 mW, 6 scans, cm^{-1}): 3055 (0.2), 2123 (0.1), 1585 (2), 1572 (0.6), 1482 (0.2), 1434 (0.2), 1186 (0.7), 1158 (0.8), 1096 (1), 1027 (3), 998 (10), 840 (0.1), 688 (1), 615 (2), 574 (0.1), 425 (0.3), 323 (0.3), 254 (0.6).

5.1.4.1.21 Reaction of $P(CN)_3$ with [hydrido tris(3,5-dimethylpyrazolyl) borate tricarbonyltungsten(II)] and ferroceniumhexafluoro hexafluorophosphate

To a stirred yellow solution of [hydrido tris(3,5-dimethylpyrazolyl)boratetricarbonyltungsten] (0.21g, 0.36 mmol) in dichloromethane (15 mL), a powder of ferroceniumhexafluorophosphate (0.12 g, 0.36 mmol) was added directly. The resulting deep green solution was stirred at ambient temperature for 30 min. To this a deep green solution, a solution of $P(CN)_3$ (0.04 g, 0.36 mmol) in dichloromethane (15 mL) was added dropwise at ambient temperature. The resulting deep brown solution was allowed to stir overnight, resulting in a deep brown solution. The solvent was removed *in vacuo*, and the deep brown residue was washed two times with diethyl ether and was dried in *vacuo*.

C/H/N analysis % found C 37.45; H 3.63; N 13.68; P 5.41. **^{1}H NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 6.0 (s, 3H, Tp − C*H*), 4.14 (s, 9H, Tp − C*H*$_3$), 2.40 (m, 9H, Tp − C*H*$_3$). **^{19}F NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = −73.3 (d, 6F, $PF_6{}^-$). **^{31}P NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = − 65.68 (s), −144.51 (spilet, $[PF_6]^-$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3394 (vw), 2962 (vw), 2933 (w), 2875 (w), 2553 (vw), 2231 (vw), 2183 (vw), 2098 (w), 2081 (vw), 1932 (m), 1815 (m), 1543 (m), 1448 (m), 1416 (m), 1365 (m), 1257 (w), 1202 (m), 1107 (m), 1067 (m), 951 (m), 876 (m), 837 (vs), 822 (s), 741 (m), 692 (m), 642 (m), 586 (m). **MS (ESI-TOF):** calcu. (found): cation 566.167 (566.143) $(TpW(CO)_3H)^+$, 542.167 (2), anion 144.96473 (144.96467). **HRMS (EI):** calcu. for $Fe(Cp)_2$ 186.04; found 186 (10)

5.1.4.1.22 Reaction of $P(CN)_3$ with tris(propionitrile)tricarbonylmolybdenum(0)

To a stirred colorless solution of $P(CN)_3$ (0.044 g, 0.4 mmol) in dichloromethane (10 mL), a solution of $[Mo(CO)_3(EtCN)_3]$ (0.035 g, 0.1 mmol) in dichloromethane (10 mL) was added directly. The resulting brown suspension solution was allowed to stir overnight. The dark brown precipitate was removed by filtration, resulting in a yellow solution. The solvent was removed in *vacuo*, and the brown residue was dried in *vacuo*.

Analytical data for yellow solution:

^{1}H NMR (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 1.22 (m, 9H, C*H*$_3$), 2.24 (m, 9H, C*H*$_2$). **^{13}C NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 92.06 (s), 16.35 (s, 3C, *C*H$_2$), 10.72 (s, 3C, *C*H$_3$). **^{31}P NMR** (298.5 K, CD_2Cl_2, 300.13 MHz): δ = −125.36 (s, 1.0, $P(CN)_3$).

Analytical data for brown residue:

IR (ATR, 25 °C, 32 scans, cm^{-1}): 2959 (w), 2928 (w), 2858 (w), 2205 (w), 2183 (vw), 2070 (w), 1949 (m), 1724 (w), 1599 (w), 1580 (w), 1489 (w), 1462 (w), 1380 (w), 1270 (m), 1124 (m), 1073 (m), 1039 (w), 978 (w), 742 (w), 621 (s), 594 (vs), 575 (vs).

5.1.4.1.23 Reaction of $P(CN)_3$ with 1-ethyl-3 methylimidazolium dicyanamide in dichloromethane

To a stirred solution of $P(CN)_3$ (0.3 g, 2.75 mmol) in dichloromethane (20 mL), a solution of 1-ethyl-3-methylimidazolium dicyanamide (0.5 g, 2.82 mmol) was added dropwise at 0 °C over a period of five minutes. The resulting yellow solution was stirred at this temperature for 2 h. The resulting yellow solution after stirring for 4 h was changed to a brown solution at ambient temperature. This brown solution was allowed to stir overnight. The solvent was removed in *vacuo*, and the brown residue was washed two times with acetonitrile and was dried in *vacuo*.

DSC: T_{dec} = 305 °C. **C/H/N analysis %** found C 41.39; H 4.33; N 36.32; P 11.61. **^{1}H NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 9.05 (s, 1H, NC*H*N), 7.40 (m, 1H, MeNC*H*), 7.36 (m, 1H, EtNC*H*), 4.32 (q, 2H, NC*H*$_2$), 4.00 (s, 3H, NC*H*$_3$), 1.56 (t, 3H, -C*H*$_3$). **^{13}C NMR** (273 K, CD_2Cl_2, 500.13 MHz): δ = 135.3 (s, 1C, N*C*HN), 123.0 (s, 1C, MeN*C*H), 121.4 (s, 1C, EtN*C*H), 118.8 (s, 1C, *C*N), 44.8 (s, 2C, N*C*H$_2$), 35.9 (s, 1C, N*C*H$_3$), 14.5 (s, 1C, NCH$_2$-*C*H$_3$). **^{31}P NMR** (272.9 K, CD_2Cl_2, 500.13 MHz) for a yellow solution: δ = −25 (s. 0.05), −154.2 (s,1.0), −165.2 (s, 0.002). **^{31}P NMR** (298.2 K, CD_3CN, 300.13 MHz) for a brown precipitate: δ = −194.38 (s, $[P(CN)_2]^-$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3146 (w), 3093 (m), 2981 (w), 2165 (m), 2133 (m), 2081 (w), 1445 (s), 1381, (s), 1308 (s), 1163 (vs), 1058 (s), 1021 (s), 977 (s), 831 (s),742 (s), 700 (s), 645 (s), 619 (vs), 593 (vs).

5.1.4.1.24 Reaction of $P(CN)_3$ with 1-ethyl-3-methylimidazolium dicyanamide in tetrahydrofuran

To a stirred solution of $P(CN)_3$ (0.3 g, 2.75 mmol) in tetrahydrofuran (10 mL), a solution of 1-ethyl-3-methylimidazolium dicyanamide (0.5 g, 2.82 mmol) was added dropwise at 0 °C over a period of five minutes. The resulting yellow solution was stirred at this temperature for 2h. The resulting yellow solution was allowed at ambient temperature to stir overnight, resulting a deep brown oil solution. The solvent was removed in *vacuo*, and the resulting deep brown oil precipitate was washed six times with acetonitrile. The resulting brown precipitate was removed by filtration and was dried for 12 h in *vacuo*. The resulting deep brown solution, the solvent was removed in *vacuo*, and the deep brown residue was washed two times with tetrahydrofuran and was dried in *vacuo*.

Analytical data for deep brown oil precipitate after stirring overnight:

C/H/N analysis % found C 44.72; H 5.03; N 34.82; P 11.28. **^{1}H NMR** (298.2 K, CD_3CN, 300.13 MHz): δ = 8.61 (s, 1H, NC*H*N), 7.33 (m, 1H, MeNC*H*), 7.29 (m, 1H, EtNC*H*), 4.11 (q, 2H, NCH_2), 3.77 (s, 3H, NCH_3), 1.35 (t, 3H, -CH_3). **^{13}C NMR** (298.2 K, CD_3CN, 300.13 MHz): δ = 135.71 (s, 1C, N*C*HN), 123.37 (s, 1C, MeN*C*H), 121.62 (s, 1C, EtN*C*H), 118.8 (s, 1C, *C*N), 44.60 (s, 2C, NCH_2), 35.80 (s, 1C, NCH_3), 14.38 (s, 1C, NCH_2-CH_3). **^{31}P NMR** (298.2 K, CD_3CN, 300.13 MHz) for a deep brown oil precipitate: δ = −194.43 (s, $[P(CN)_2]^-$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3147 (m), 3095 (m), 2982 (m), 2873 (m), 2173 (s), 2133 (m), 1520 (s), 1447 (s), 1383 (s), 1333 (s), 1224 (vs), 1163 (vs), 1058 (s), 1021 (s), 958 (s), 875 (s), 833 (s), 742 (vs), 700 (s), 645 (s), 619 (vs).

Analytical data for brown precipitate after washing with acetonitrile:

TGA/DSC: $T_{dec} =$ 333 °C. **C/H/N analysis %** found C 42.95; H 4.81; N 34.97; P 12.86. **^{1}H NMR** (298.2 K, CD_3CN, 300.13 MHz): δ = 8.59 (s, 1H, NC*H*N), 7.36 (m, 1H, MeNC*H*), 7.32 (m, 1H, EtNC*H*), 4.20 (q, 2H, NCH_2), 3.85 (s, 3H, NCH_3), 1.48 (m, 3H,-CH_3). **^{13}C NMR** (298.2 K, CD_3CN, 300.13 MHz): δ = 135.49 (s, 1C, N*C*HN), 122.79 (s, 1C, MeN*C*H), 121.08 (s, 1C, EtN*C*H), 118.8 (s, 1C, *C*N), 44.03 (s, 2C, NCH_2), 35.09 (s, 1C, NCH_3), 13.82 (s, 1C, NCH_2-CH_3). **^{31}P NMR** (298.2 K, CD_3CN, 300.13 MHz) for a brown precipitate: δ = −194.38 (s, $[P(CN)_2]^-$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3149 (m), 3102 (m), 2984 (m), 2172 (m), 1495 (s), 1464 (s), 1446 (s), 1382 (s), 1219 (s), 1164 (vs), 1058 (s), 1030 (s), 958 (s), 834 (s), 742 (s), 700 (s), 645 (s), 619 (vs). **MS (ESI-TOF):** calcu. (found): cation 111.0916 (111.0918), anion 110.9759(9), 234.8954 (5), 293.1779 (2).

Analytical data for deep brown precipitate after removal the solvent:

C/H/N analysis % found C 40.64; H 5.21; N 25.35; P 9.79. **^{1}H NMR** (298.2 K, CD_3CN, 300.13 MHz): δ = 8.78 (s, 1H, NC*H*N), 7.40 (m, 1H, MeNC*H*), 7.35 (m, 1H, EtNC*H*), 4.22 (q, 2H, NC*H*$_2$), 3.87 (s, 3H, NC*H*$_3$), 1.47 (t, 3H, -C*H*$_3$). **^{13}C NMR** (298.2 K, CD_3CN, 300.13 MHz): δ = 135.49 (s, 1C, N*C*HN), 122.79 (s, 1C, MeN*C*H), 121.08 (s, 1C, EtN*C*H), 118.8 (s, 1C, *C*N), 44.03 (s, 2C, N*C*H$_2$), 35.09 (s, 1C, N*C*H$_3$), 13.82 (s, 1C, N*C*H$_2$-CH$_3$). **^{31}P NMR** (298.2 K, CD_3CN, 300.13 MHz) for a brown solution: δ = −194.30 (s, $[P(CN)_2]^-$). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 3357 (w), 3147 (m), 3094 (m), 2984 (m), 2170 (m), 2136 (m), 1563 (s), 1504 (s), 1465 (s), 1448 (s), 1382 (s), 1333 (s), 1222 (s), 1165 (vs), 1060 (s), 1031 (s), 958 (s), 838 (s), 745 (s), 700 (s), 646 (s), 620 (vs), 593 (vs).

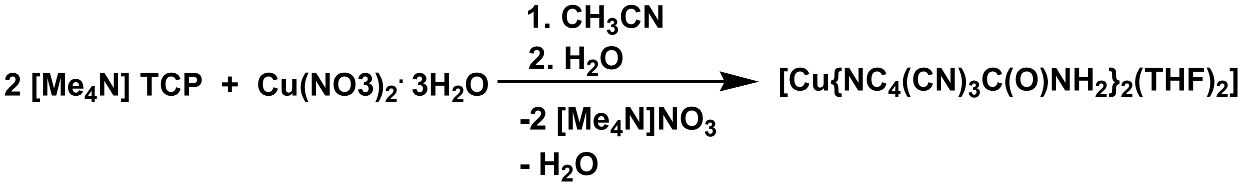
5.1.4.1.25 Reaction of $P(CN)_3$ with silver dicyanoamide–tris-(pentafluor phenyl)borane·diether

To a stirred colorless solution of $P(CN)_3$ (0.015 g, 0.14 mmol) in fluorobenzene (10 mL), a solution of $Ag[N\{CN.B(C_6F_5)_3\}_2]\cdot 2Et_2O$ (0.19 g, 0.14 mmol) in fluorobenzene (10 mL) was added dropwise at ambient temperature. The resulting yellow solution after stirring 40 min was allowed to stir overnight, resulting a yellow solution. The solvent was removed in *vacuo*, and the yellow residue was dried in *vacuo*.

C/H/N analysis % found C 40.06; H 2.35; N 6.35; P 3.44. **^{19}F NMR** (298.2 K, CD_3CN, 300.13 MHz): δ= −113.72 (s, Ph.F), −133.75 (m, 10F, *o*-F), −159.54 (t, 10F, *p*-F), −165.73 (m, 10F, *m*-F). **^{11}B NMR** (298.2 K, CD_3CN, 96.3 MHz): δ = −13.35 (s). **^{31}P NMR** (298.2 K, CD_3CN, 300.13 MHz): δ = 142.88 (s, 1.0), 49.67 (s, 0.28), 17.39 (s, 0.22). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2997 (w), 2222 (w), 2160 (vw), 1533 (m), 1516 (s), 1462 (vs), 1379 (m), 1283 (m), 1178 (m), 1144 (m), 1095 (s), 1070 (m), 1022 (m), 974 (vs), 893 (s), 843 (m), 804 (s), 773 (m), 731 (m), 717 (m), 683 (s), 609 (m).

5.1.4.2 Reactions of tetracyanopyrrolide

5.1.4.2.1 Synthesis of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis(tetrahydrofuran)copper(II) $[Cu\{NC_4(CN)_3C(O)NH_2\}_2(THF)_2]$ (8)

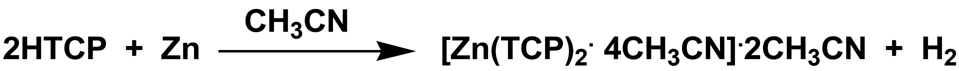


$$2\,[Me_4N]\,TCP + Cu(NO3)_2\cdot 3H_2O \xrightarrow[\substack{-2\,[Me_4N]NO_3 \\ -\,H_2O}]{\substack{1.\ CH_3CN \\ 2.\ H_2O}} [Cu\{NC_4(CN)_3C(O)NH_2\}_2(THF)_2]$$

To a stirred solution of tetramethyltetracyanopyrrolide (0.048 g, 0.2 mmol) in acetonitrile (10 mL), a solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.029 g, o.1 mmol) in water (dest., 10 mL) was added at ambient temperature. The acetonitrile was evaporated, and the solution was filtered. The filtrate was evaporated to dryness to yield 6 mg (10%, 0.010 mmol) as a greenish yellow precipitate of **8**. Crystals suitable for x-ray crystal structure determination were obtained by vapor diffusion of diethyl ether into a tetrahydrofuran solution of **8**

C/H/N analysis % calc. (found): C 50.04 (48.93); H 3.50 (4.41); N 24.32 (22.65). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3393 (m), 3342 (m), 3250 (w), 3170 (m), 2985 (m), 2879 (m), 2723 (w), 2644 (w), 2233 (s), 1981 (vw), 1664 (vs), 1578 (s), 1529 (s), 1477 (m), 1450 (vs), 1387 (m), 1364 (m), 1325 (m), 1246 (m), 1213 (m), 1192 (m), 1128 (w), 1099 (s), 1069 (m), 1034 (s), 948 (w), 937(w), 889 (s), 829 (m), 778 (m), 743 (s), 729 (s), 699 (m), 660 (s), 604 (s).

5.1.4.2.2 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II) acetonitrile solvate $[Zn(TCP)_2\cdot 4CH_3CN]\cdot 2CH_3CN$ (9)



$$2HTCP + Zn \xrightarrow{CH_3CN} [Zn(TCP)_2\cdot 4CH_3CN]\cdot 2CH_3CN + H_2$$

To a stirred solution of tetracyanopyrrole (0.3 g, 1.79 mmol) in acetonitrile (10 mL), a powder of zinc (0.078 g, 1.19 mmol) was added in one portion at ambient temperature. The resulting suspension was allowed to stir overnight. The unconsumed powder of zinc was removed by filtration, and the resulting solution was concentrated *in vacuo* to a volume of approximately 4 mL. Storage at 8 °C for one day resulted colorless crystals, which rapidly lost included solvent when taken out of the solution. By removal of the supernatant by syringe and dried *in vacuo* at room temperature 0.25 g (44 %, 0.39 mmol) of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II)acetonitrile solvate (**9**) as a white crystalline solid were obtained.

TGA/DSC (5 K/min): 475 °C loss of one equivalent of acetonitrile, 497 °C start of decomposition. **C/H/N analysis** % calc. (found) for [Zn(TCP)$_2$·4CH$_3$CN]: C 51.31 (47.05); H 2.15 (2.56); N 34.90 (32.50). **^{13}C NMR** (300 K, CD$_3$CN, 500.13 MHz): δ =112.8 (s, 2C, C$_{quat}$), 108.9 (s, 2C, C$_{quat}$), 108.2 (s, 2C, C$_{quat}$), 104.8 (s, 2C, C$_{quat}$). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3381 (m), 3007 (w), 2938 (w), 2749 (w), 2351 (vw), 2316 (w), 2232 (s), 1632 (m), 1484 (m), 1425 (m), 1308 (m), 1231 (vs), 1203 (s), 1149 (vs), 1102 (vs), 982 (s), 806 (m), 744 (m), 702 (s), 690 (s), 639 (s), 554 (s). **Raman** (25 °C, 23 mW, 6 scans, cm^{-1}): 2937 (1), 2926 (1), 2231 (10), 1476 (2), 1416 (2), 1313 (1), 1091 (0.3).

5.1.4.2.3 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II) acetonitrile solvate [Fe(TCP)$_2$·4CH$_3$CN]·2CH$_3$CN (10)

$$\mathbf{2HTCP + Fe \xrightarrow{CH_3CN} [Fe(TCP)_2{\cdot}4CH_3CN]{\cdot}2CH_3CN + H_2}$$

To a stirred solution of tetracyanopyrrole (0.26 g, 1.55 mmol) in acetonitrile (10 mL), a powder of iron (0.054 g, 0.96 mmol) was added in one portion at ambient temperature. The resulting suspension was allowed to stir overnight. The uncosumed powder of iron was removed by filtration, and the resulting solution was concentrated *in vacuo* to a volume of approximately 4 mL. Storage at 8 °C for one day resulted colorless crystals, which rapidly lost included solvent when taken out of the solution. By removal of the supernatant by syringe and dried *in vacuo* at room temperature 0.22 g (45 %, 0.35 mmol) of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II)acetonitrile solvate (**10**) as a white crystalline solid were obtained.

TGA/DSC (5 K/min): 110-130 °C loss of two equivalents of acetonitrile, 360 °C start of decomposition. **C/H/N analysis** % calc. (found) for [$Fe(TCP)_2 \cdot 4CH_3CN$]: C 52.19 (50.27); H 2.19 (2.73); N 35.51 (33.56). **^{13}C NMR** (298.2 K, CD_3CN, 300.13 MHz): δ = 112.8 (s, 2C, C_{quat}), 108.9 (s, 2C, C_{quat}), 108.2 (s, 2C, C_{quat}), 104.7 (s, 2C, C_{quat}). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3366 (m), 3247 (w), 3200 (w), 2934 (w), 2795 (w), 2739 (w), 2310 (w), 2281 (m), 2227(vs), 2167 (w), 1639 (m), 1481 (s), 1422 (m), 1367 (m), 1334 (m), 1239 (w), 1201 (w), 1096 (m), 1033 (m), 977 (w), 939 (m), 902 (w), 837 (w), 785 (w), 692 (s), 665 (m), 654 (m), 624 (m), 600 (m), 564 (m). **Raman** (25 °C, 23 mW, 6 scans, cm^{-1}): 2934 (1), 2237 (10), 1483 (3), 1423 (3), 1317 (2).

5.1.4.2.4 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium (II) acetonitrile solvate [$Mg(TCP)_2 \cdot 4CH_3CN$]$\cdot 2CH_3CN$ (11)

$$2HTCP + Mg(OH)_2 \xrightarrow{CH_3CN} [Mg(TCP)_2 \cdot 4CH_3CN] \cdot 2CH_3CN + 2H_2O$$

To a stirred solution of tetracyanopyrrole (0.36 g, 2.2 mmol) in acetonitrile (10 mL), a solution of magnesium hydroxide $Mg(OH)_2$ (0.07 g, 1.20 mmol) in acetonitrile (10 mL) was added at ambient temperature. The resulting solution was allowed to stir overnight. The resulting was filtered, and the filtrate was concentrated *in vacuo* to a volume of approximately 5 mL. Storage at 8 °C for one week resulted colorless crystals, which rapidly lost included solvent when taken out of the solution. By removal of the supernatant by syringe and dried *in vacuo* at room temperature 0.41 g (64 %, 0.68 mmol) of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II)acetonitrile solvate (**11**) as a white crystalline solid were obtained.

TGA/DSC (5 K/min): 73-120 °C loss of three equivalents of acetonitrile, 248 °C start of decomposition. **C/H/N analysis** % calc. (found) for [$Mg(TCP)_2 \cdot 4CH_3CN$]: C 55.35 (52.67); H 2.32 (1.94); N 37.66 (36.84). **^{13}C NMR** (298.4 K, CD_3CN, 300.13 MHz): δ = 118.1 (s, 2C, C_{quat}), 112.7 (s, 2C, C_{quat}), 111.4 (s, 2C, C_{quat}), 103.2 (s, 2C, C_{quat}). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3406 (m), 3182 (m), 3104 (m), 3003 (m), 2941 (w), 2732 (w), 2313 (w), 2285 (m), 2227(vs), 1650 (m), 1479 (m), 1454 (m), 1417 (m), 1369 (m), 1336 (m), 1259 (w), 1095 (m), 1085 (m), 1033 (m), 941 (w), 837 (w), 694 (s), 686 (s). **Raman** (25 °C, 65 mW, 20 scans, cm^{-1}): 2937 (0.3), 2235 (7), 1571 (1), 1483 (5), 1421 (10), 1311 (10), 883 (2), 530 (3), 109 (3).

5.1.4.2.5 Synthesis of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II) acetonitrile solvate $[Cu(TCP)_2 \cdot 4CH_3CN] \cdot 2CH_3CN$ (12)

$$2\,HTCP + Cu(acac)_2 \xrightarrow{CH_3CN} [Cu(TCP)_2 \cdot 4CH_3CN] \cdot 2CH_3CN + 2H(acac)$$

To a suspension solution of di(acetylacetonate)copper(II) $Cu(acac)_2$ (0.195 g, 0.74 mmol) in acetonitrile (10 mL), a solution of tetracyanopyrrole (0.25 g, 1.49 mmol) in acetonitrile (10 mL) was added at ambient temperature. The resulting dark green solution was allowed to stir overnight, was filtered, and the resulting filtrate was concentrated *in vacuo* to a volume of approximately 5 mL. Storage at 8 °C for one day resulted green crystals, which rapidly lost included solvent when taken out of the solution. By removal of the supernatant by syringe and dried *in vacuo* at room temperature 0.31 g (65 %, 0.48 mmol) of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II)acetonitrile solvate (**12**) as a green crystalline solid were obtained.

TGA/DSC (5 K/min): 59-168 °C loss of three equivalents of acetonitrile, 452 °C start of decomposition. **C/H/N analysis** % calc. (found) for $[Cu(TCP)_2 \cdot 4CH_3CN]$: C 51.48 (47.59); H 2.16 (1.56); N 35.02 (32.55). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3000 (w), 2937 (w), 2815 (vw), 2757 (w), 2659 (w), 2323 (m), 2268 (m), 2267(m), 2231 (vs), 1581 (w), 1519 (w), 1479 (s), 1425 (s), 1367 (s), 1348 (s), 1108 (m), 1029 (m), 946 (m), 931 (m), 715 (m), 692 (m), 597 (w), 528 (w). **Raman** (25 °C, 12 mW, 5 scans, cm^{-1}): 2933 (1), 2239 (10), 1484 (3), 1426 (2), 1327 (2), 805 (3), 743 (2), 528 (1), 308 (2).

5.1.4.2.6 Synthesis of di(acetylacetonate)-1,5-N-μ-tetracyanopyrrolido manganese (III) [Mn(acac)$_2$TCP] (13)

$$\mathrm{HTCP} + \mathrm{Mn(acac)_3} \xrightarrow{\mathrm{CH_3CN}} [\mathrm{Mn(acac)_2TCP}] + \mathrm{H(acac)}$$

To a stirred solution of tetracyanopyrrole (0.2 g, 1.19 mmol) in acetonitrile (10 mL), a solution of tri(acetylacetonate)manganese(III) Mn(acac)$_3$ (0.419 g, 1.19 mmol) in acetonitrile (10 mL) was added at ambient temperature. The resulting yellow-black solution was allowed to stir overnight, was filtered, and the resulting yellow-black filtrate was evaporated to dryness to yield a yellow precipitate of **13**, washed two times with benzene (10 mL) and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by vapor diffusion of benzene into acetonitrile solution of **13**. Yield 0.36 g (72%, 0.86 mmol) of di(acetylacetonate)-1,5-N-μ-tetracyanopyrrolido manganese(III) as a yellow crystalline solid were obtained.

DSC: m.p. 56-57 ^{o}C. $\boldsymbol{T}_{\mathrm{dec}}$ = 210 ^{o}C. **C/H/N analysis** % calc. (found): C 51.56 (51.73); H 3.37 (3.70); N 16.70 (15.09). **IR** (25 ^{o}C, ATR, 32 scans cm^{-1}): 3108 (w), 3005(w), 2925 (w), 2740 (w), 2655 (vw), 2248(w), 2232 (m), 1512 (vs), 1476(s), 1420 (s), 1361 (m),1334 (vs), 1285 (s), 1185 (m), 1095 (m), 1032(s), 1019 (s), 938 (s), 836(w), 801 (s), 689(s), 659 (m), 636 (s), 533 (w). **Raman** (25 ^{o}C, 12 mW, 20 scans, cm^{-1}): 2923 (0.5), 2232 (6), 1565 (2), 1477 (2), 1421 (1), 1322 (2), 1032 (2), 991 (9), 686 (2), 456 (10), 217 (10). **MS (ESI-TOF):** calcu. (found): cation 253.0267 (253.0265), anion 166.01592 (166.01595).

5.1.4.2.7 Synthesis of acetonitrile-di(acetylacetonate)tetracyanopyrrolido Chromium (III) [Cr(acac)$_2$TCP·CH$_3$CN]•0.67CH$_3$CN (14)

$$\mathrm{HTCP} + \mathrm{Cr(acac)_3} \xrightarrow{\mathrm{CH_3CN}} [\mathrm{Cr(acac)_2TCP{\cdot}CH_3CN}] + \mathrm{H(acac)}$$

To a stirred solution of tetracyanopyrrole (0.2 g, 1.19 mmol) in acetonitrile (10 mL), a solution of tri(acetylacetonate)chromium(III) Cr(acac)$_3$ (0.42 g, 1.19 mmol) in acetonitrile (10 mL) was added at ambient temperature. The red solution was allowed to stir overnight, was filtered, and the resulting red filtrate was concentrated *in vacuo* to a volume of approximately

5 mL. Storage at 8 °C for one week resulted brown crystals. By removal of the supernatant by syringe and dried *in vacuo* at room temperature 0.22 g (38 %, 0.45 mmol) of acetonitrile-di(acetylacetonate)tetracyanopyrrolidochromium(III) (**14**) as a brown crystalline solid were obtained.

TGA/DSC (5 K/min): 153 °C loss of two equivalents of acetonitrile, 247 °C start of decomposition. **C/H/N analysis** % calc. (found) for **14**$^\bullet$$CH_3CN$: C 53.29 (53.14); H 4.22 (3.26); N 20.43 (21.17). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3000 (w), 2937 (w), 2326 (w), 2300 (w), 2232 (m), 1616 (w), 1542 (s), 1519 (vs), 1481 (s), 1423 (s), 1349 (vs), 1282 (s), 1187 (m), 1108 (m), 1025 (s), 935 (m), 777 (m), 717 (m), 684 (s), 657 (m), 618 (m). **Raman** (25 °C, 12 mW, 10 scans, cm^{-1}): 2926 (1), 2240 (10), 1483 (2), 1425 (2), 1365 (1), 1333 (1), 1284 (1), 1189 (0.3), 1111 (0.3), 947 (1), 686 (0.5), 524 (0.5), 457 (3). **MS (ESI-TOF):** calcu. (found): cation 250.02918 (250.02905), anion 166.01592 (166.01593).

5.1.4.2.8 Reaction of HTCP with tri(acetylacetonate)manganese(III)

To a stirred solution of tetracyanopyrrole (0.25 g, 1.50 mmol) in acetonitrile (10 mL), a solution of tri(acetylacetonate)manganese(III) $Mn(acac)_3$ (0.1 g, 0.28 mmol) in acetonitrile (10 mL) was added at ambient temperature. The resulting yellow-black solution was allowed to stir overnight, was filtered, and the resulting yellow-black filtrate was evaporated to dryness to yield a yellow precipitate, washed two times with benzene (10 mL) and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by vapor diffusion of benzene into acetonitrile solution of 1% di(acetylacetonate)-1,5-N-μ-tetracyanopyrrolido manganese(III) as a yellow crystalline solid (**13**) and 99% tetraacetonitrile-bis(tetracyanopyrrolido)manganese(II)acetonitrile solvate (**15**) as a colorless crystalline solid were obtained.

***Analytical data for colorless crystals 15*:**

TGA/DSC (5 K/min): 50-65 °C loss of two equivalents of acetonitrile, 218 °C start of decomposition. **C/H/N analysis** % calc. (found) for $[Mn(TCP)_2{\cdot}4CH_3CN]$: C 52.28 (52.99); H 2.19 (1.80); N 35.56 (33.70). **IR** (25 °C, ATR, 32 scans cm^{-1}): 3559 (m), 3498 (m), 3232 (w), 3051(w), 2942 (w), 2792 (w), 2701 (w), 2559 (w), 2325 (w), 2232 (vs), 2166 (vw), 1651 (vw), 1644 (vw), 1537 (m), 1516 (m), 1470 (m), 1421 (m), 1337 (s), 1285 (s), 1192 (w), 1094 (m), 1032(m), 1020 (m), 899 (m), 837 (m), 801 (w), 691 (s), 674 (s), 636 (s). **Raman** (25 °C, 12 mW, 20 scans, cm^{-1}): 2935 (0.2), 2236 (8), 1483 (3), 1422 (3), 1316 (3), 1095 (1), 939 (0.3), 699 (0.7), 533 (1) 467 (0.6), 396 (0.7), 214 (0.5), 117 (8).

5.1.4.2.9 Synthesis of trimethylammoniumtetracyanopyrrolide [Me$_3$NH]TCP (16)

$$\mathrm{HTCP} + [\mathrm{Me_3N}]\mathrm{HCl} \xrightarrow{\mathrm{H_2O}} [\mathrm{Me_3NH}]\mathrm{TCP} + \mathrm{HCl}$$

To a stirred solution of tetracyanopyrrole (0.2 g, 1.19 mmol) in water (dest., 10 mL), a solution of trimethylammoniumchloride [Me$_3$NH]Cl (0.114 g, 1.19 mmol) in water (dest. 10 mL) was added at ambient temperature. The mixture was allowed to stir overnight. The resulting solution was filtered, and the filtrate was evaporated to dryness to yield a yellow precipitate of **16**, washed two times with dichloromethane (10 mL), and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution of **16** in acetonitrile. Yield 0.21 g (77%, 0.92 mmol) of trimethylammoniumtetracyanopyrrolide as a colorless crystalline solid were obtained.

TGA/ DSC: m.p. 184-185 ^{o}C, 298 ^{o}C start of decomposition. **C/H/N analysis** % calc. (found) for **16**$^{\cdot}$CH$_3$CN: C 58.42 (56.57); H 4.90 (4.33); N 36.68 (35.74). **^{1}H NMR** (298 K, CD$_3$CN, 300.13 MHz): δ= 4.41 (s, 9H, C*H$_3$*), 7.38 (br, 1H, N*H*). **^{13}C NMR** (298 K, CD$_3$CN, 300.13 MHz): δ = 119.4 (s, 2C, C_{quat}), 114.3 (s, 2C, C_{quat}), 112.1 (s, 2C, C_{quat}), 102.4 (s, 2C, C_{quat}), 44.6 (s, 3C, *C*H$_3$). **IR** (25 ^{o}C, ATR, 32 scans cm^{-1}): 3381 (vw), 3051(m), 3028 (m), 2982 (w), 2730 (s), 2558(w), 2528 (m), 2480 (m), 2253(w), 2234 (m), 2224 (vs), 1682 (w), 1633 (w), 1475 (vs), 1452(s), 1420 (m), 1371 (w), 1329 (m), 1246 (m), 1088 (m), 1059 (w), 979 (s), 940 (w), 811 (w), 683 (m). **Raman** (25 ^{o}C, 12 mW, 20 scans, cm^{-1}): 2972 (0.4), 2235 (10), 1476 (2), 1418 (1), 1317 (1), 1088 (0.2), 529 (0.3), 513 (0.3), 121 (1). **MS (ESI-TOF):** calcu. (found): cation 60.08078 (60.08103), anion 166.01592 (166.01629).

5.1.4.2.10 Synthesis of tripropylammoniumtetracyanopyrrolide $[^n\mathrm{Pr_3NH}]\mathrm{TCP}$ (17)

$$\mathrm{HTCP} + [^n\mathrm{Pr_3N}]\mathrm{HCl} \xrightarrow{\mathrm{H_2O}} [^n\mathrm{Pr_3NH}]\mathrm{TCP} + \mathrm{HCl}$$

To a stirred solution of tetracyanopyrrole (0.22 g, 1.32 mmol) in water (dest. 10 mL), a solution of tripropylammoniumchloride $[^n\mathrm{Pr_3NH}]\mathrm{Cl}$ (0.24 g, 1.33 mmol) in water (dest., 10 mL) was added at ambient temperature. The mixture was allowed to stir overnight. The resulting solution was filtered, and the filtrate was evaporated to dryness to yield a yellow precipitate of **17**, washed two times with dichloromethane (10 mL), and dried *in vacuo* at room temperature. Crystals suitable for x-ray crystal structure determination were obtained by slowly evaporating a saturated solution of **17** in acetonitrile. Yield 0.26 g (63%, 0.84 mmol) of tripropylammoniumtetracyanopyrrolide as a colorless crystalline solid were obtained.

DSC: m.p. 65 °C. $T_{\mathrm{dec}} = 320$ °C. **C/H/N analysis** % calc. (found) for **17**: C 65.78 (64.85); H 7.14 (7.19); N 27.08 (26.40). **^{1}H NMR** (298 K, $\mathrm{CD_2Cl_2}$, 300.13 MHz): δ= 1.05 (m, 9H, $\mathrm{C}H_3$), 1.74 (m, 6H, $\mathrm{C}H_2$), 2.96 (m, 6H, $\mathrm{C}H_2$), 9.5 (s, 1H, NH). **^{13}C NMR** (298 K, $\mathrm{CD_2Cl_2}$, 300.13 MHz): δ = 119.4 (s, 2C, C_{quat}), 114.3 (s, 2C, C_{quat}), 112.1 (s, 2C, C_{quat}), 102.4 (s, 2C, C_{quat}), 11.36 (s, 3C, $C\mathrm{H_3}$), 17.20 (s, 3C, $C\mathrm{H_2}$), 53.95 (s, 3C, $C\mathrm{H_2}$). **IR** (25 °C, ATR, 32 scans $\mathrm{cm^{-1}}$): 3537 (vw), 3112 (m), 3036 (w), 2974 (m), 2942 (m), 2883 (m), 2790 (w), 2718 (w), 2675 (w), 2535 (w), 2220 (vs), 1471 (s), 1459 (m), 1414 (m), 1381 (m), 1327 (m), 1263 (w), 1238 (w), 1075 (m), 1042 (w), 983 (m), 943 (w), 916 (w), 900 (w), 756 (m), 682 (m), 585 (vw), 556(vw). **Raman** (25 °C, 12 mW, 20 scans, $\mathrm{cm^{-1}}$): 2973 (0.5), 2946 (1.0), 2882 (0.8), 2234 (10), 1476 (4.0), 1415 (2.0), 1311 (2.0), 1074 (0.7), 1037 (0.3), 678 (0.5), 514 (0.3), 485 (0.4), 308 (0.2), 123 (1.0).

5.2 Data on the X-ray structure analysis

Table S1. Crystallographic details of **5, 6** and **7**

	5	**6**	**7**
Chem. Formula	$C_{42}H_{30}N_6P_2{\cdot}2(CH_2Cl_2)$	$C_{38}H_{30}N_2PdP_2{\cdot}2(CH_2Cl_2)$	$C_{43}H_{39}N_2NiP_3{\cdot}2(CH_2Cl_2)$
Form. Wght.[g mol $^{-1}$]	850.51	852.83	905.23
Color	block, colorless	block, colorless	Block, red
Cryst. System	monoclinic	orthorhombic	monoclinic
Space Group	$P2_1/n$	*Pbca*	$P2_1/c$
a [Å]	9.5445(3)	20.5853(19)	15.0113(5)
b [Å]	15.0102(5)	7.8698(7)	15.3108(5)
c [Å]	15.1053(5)	23.149(2)	19.2747(6)
α [°]	90	90	90
β [°]	91.891(2)	90	99.602(2)
γ [°]	90	90	90
V [Å^3]	2162.9(12)	3750.1(6)	4367.9(2)
Z	2	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.306	1.509	1.377
μ [mm^{-1}]	0.39	0.90	0.83
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured reflections	5835	46647	77740
Independent reflections	30921	5454	15706
Reflections with $I > 2\sigma(I)$	4327	2682	11493
$R_{int.}$	0.096	0.164	0.043
$F(000)$	876	1728	1872
R1 (R [$F^2 > 2\sigma(F^2)$])	0.043	0.056	0.043
wR_2 (F^2)	0.113	0.126	0.114
GooF	1.01	1.01	1.01
Parameter	286	223	556
CCDC #	–	–	–

Table S2. Crystallographic details of **8, 9** and **10**

	8	**9**	**10**
Chem. Formula	$C_{24}H_{20}CuN_{10}O_4$	$C_{24}H_{12}N_{14}Zn\cdot 2(C_2H_3N)$	$C_{24}H_{12}N_{14}Fe\cdot 2(C_2H_3N)$
Form. Wght.[g mol $^{-1}$]	576.04	643.95	634.43
Color	colorless	colorless	colorless
Cryst. System	monoclinic	triclinic	triclinic
Space Group	$P2_1/c$	P-1	P-1
a [Å]	6.5689(6)	7.8924 (2)	7.9176 (3)
b [Å]	18.9107(16)	9.9655 (2)	10.0034 (4)
c [Å]	10.2306(8)	10.5178 (3)	10.5107 (4)
α [°]	90	96.241 (1)	83.719 (2)
β [°]	99.729(5)	102.190 (1)	77.806 (2)
γ [°]	90	90.050 (1)	89.997 (2)
V [Å^3]	1252.59(18)	803.56 (3)	808.58 (5)
Z	2	1	1
$\rho_{calc.}$ [g cm^{-3}]	1.527	1.331	1.303
μ [mm^{-1}]	0.93	0.81	0.51
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured reflections	11421	26442	26868
Independent reflections	2449	5770	5805
Reflections with $I > 2\sigma(I)$	1551	4270	4967
$R_{int.}$	0.083	0.052	0.046
$F(000)$	590	328	324
R1 (R [$F^2 > 2\sigma(F^2)$])	0.051	0.041	0.033
wR_2 (F^2)	0.142	0.092	0.085
GooF	1.04	1.02	1.05
Parameter	178	208	209
CCDC #	–	–	–

Table S3. Crystallographic details of **11, 12** and **13**

	11	**12**	**13**
Chem. Formula	$C_{24}H_{12}N_{14}Mg.2(C_2H_3N)$	$C_{24}H_{12}N_{14}Cu.\ 2(C_2H_3N)$	$C_{18}H_{14}MnN_5O_4$
Form. Wght.[g mol $^{-1}$]	602.89	642.28	419.28
Color	colorless	block, green	block, yellow
Cryst. System	triclinic	triclinic	triclinic
Space Group	*P*-1	*P*-1	*P*-1
a [Å]	7.9203(3)	7.9992(5)	9.0254 (4)
b [Å]	10.0077(4)	9.8401(5)	10.4561 (4)
c [Å]	10.4993(4)	10.4333(6)	11.3113 (5)
α [°]	83.738(2)	95.531(3)	105.321 (2)
β [°]	77.828(2)	103.644(3)	102.991 (2)
γ [°]	89.900(2)	90.829(3)	101.330 (2)
V [Å^3]	808.46(5)	793.76(8)	965.27 (7)
Z	1	1	2
$\rho_{calc.}$ [g cm^{-3}]	1.238	1.343	1.443
μ [mm^{-1}]	0.10	0.73	0.72
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	123	173
Measured reflections	26901	25680	14755
Independent reflections	5806	5717	5553
Reflections with $I > 2\sigma(I)$	4392	4641	4444
$R_{int.}$	0.042	0.032	0.032
F(000)	310	327	428
R1 (R [$F^2 > 2\sigma(F^2)$])	0.043	0.038	0.037
wR_2 (F^2)	0.121	0.083	0.101
GooF	1.04	1.03	1.02
Parameter	208	208	260
CCDC #	–	–	–

Table S4. Crystallographic details of **14** and **15**

	14	**15**
Chem. Formula	$C_{20}H_{17}CrN_6O_4{}^{\cdot}0.67(C_2H_3N)$	$C_{24}H_{12}N_{14}Mn.\ 2(C_2H_3N)$
Form. Wght.[g mol $^{-1}$]	484.76	633.52
Color	block, brown	block, colorless
Cryst. System	monoclinic	triclinic
Space Group	*C2/c*	*P*-1
a [Å]	28.3609 (13)	7.9176(3)
b [Å]	17.2005 (7)	10.0167(4)
c [Å]	15.1665 (6)	10.4982(4)
α [°]	90	96.522(2)
β [°]	101.244(2)	102.882(2)
γ [°]	90	90.642(2)
V [Å^3]	7256.5(5)	805.81(5)
Z	12	1
ρ_{calc}. [g cm^{-3}]	1.331	1.306
μ [mm^{-1}]	0.51	0.45
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073
T [K]	123	123
Measured reflections	51374	26410
Independent reflections	10541	5583
Reflections with $I > 2\sigma(I)$	5642	4641
R_{int}.	0.105	0.033
F(000)	2996	323
R1 (R [$F^2 > 2\sigma(F^2)$])	0.054	0.038
wR$_2$ (F^2)	0.127	0.083
GooF	1.01	1.04
Parameter	458	208
CCDC #	–	–

Table S5. Crystallographic details of **16** and **17**

	16	**17**
Chem. Formula	$C_3H_{10}N^+ \cdot C_8N_5^-$	$C_9H_{22}N^{+ \cdot} C_8N_5^-$
Form. Wght.[g mol $^{-1}$]	226.25	310.40
Color	block, colorless	block, colorless
Cryst. System	orthorhombic	triclinic
Space Group	*pnma*	*P*-1
a [Å]	18.6039(5)	14.0557(3)
b [Å]	6.6761(2)	15.0423(3)
c [Å]	9.7709(3)	27.4242(6)
α [°]	90	78.144(10)
β [°]	90	79.978(10)
γ [°]	90	75.436(10)
V [Å ^{3}]	1213.56(6)	5446.2(2)
Z	4	12
$\rho_{calc.}$ [g cm $^{-3}$]	1.238	1.136
μ [mm $^{-1}$]	0.08	0.07
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073
T [K]	123	173
Measured reflections	20462	128321
Independent reflections	2351	26266
Reflections with $I > 2\sigma(I)$	1866	15918
$R_{int.}$	0.032	0.034
F(000)	472	1992
R1 (R [$F^2 > 2\sigma(F^2)$])	0.040	0.058
wR_2 (F^2)	0.110	0.164
GooF	1.05	1.02
Parameter	105	1381
CCDC #	–	–

5.3 Selected interatomic distances and angles in the structures

Scheme S1. Numbering scheme of tetracyanodiiminophosphorane [Ph$_3$P=N− C(CN)$_2$− C(CN)$_2$ − N=PPh$_3$] (**5**)

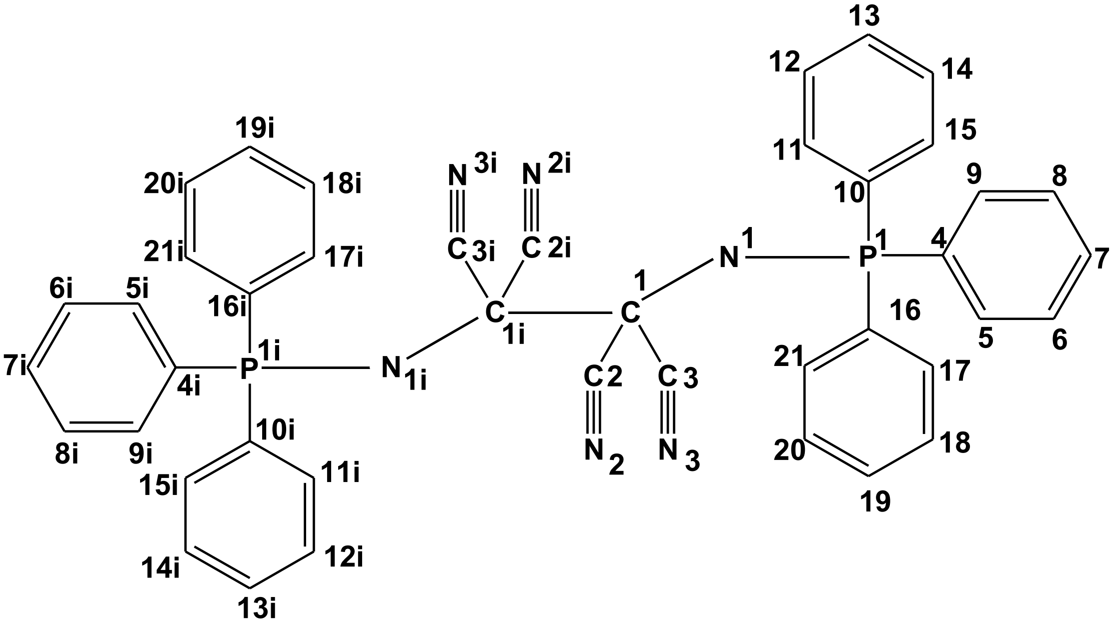


Table S6. Selected bond lengths (Å) angles (°) and torsion angles (°) of **5**.

P1—N1	1.5765(13)	**C9 —C4—P1**	118.09(13)
P1 — C10	1.7987(15)	**C6 —C5—C4**	119.99(18)
P1 — C16	1.8018(16)	**C13 —C14—C15**	120.18(17)
P1 — C4	1.8026(16)	**C10 —C15—C14**	119.88(16)
N1—C1	1.4090(19)	**C21 —C16—C17**	119.09(15)
N2—C2	1.140(2)	**C21 —C16—P1**	120.42(12)
N3—C3	1.138(2)	**C17 —C16—P1**	120.18(12)
C1 —C2	1.498(2)	**C18 —C17—C16**	120.19(17)
C1 —C3	1.499(2)	**C19 —C18—C17**	120.14(18)
C1 —C1 ^{i}	1.596(2)	**C20 —C19—C18**	119.94(17)
C4 —C5	1.392(2)	**C10 —P1—N1—C1**	160.52(13)
C4 —C9	1.393(2)	**C16 —P1—N1—C1**	41.83(16)
C5 —C6	1.386(3)	**C4 —P1—N1—C1**	−81.55(15)
C6 —C7	1.376(3)	**P1 —N1—C1—C2**	54.76(19)
C7 —C8	1.377(3)	**P1 —N1—C1—C3**	−70.45(17)

C14 —C15	1.391(2)	**P1 —N1—C1—C1^{i}**	172.51(12)
C16 —C17	1.394(2)	**N1 —C1—C2—N2**	14(3)
C17—C18	1.384(3)	**C3 —C1—C2—N2**	142(3)
C18—C19	1.381(3)	**C16 —P1—C10—C15**	−76.42(14)
C19—C20	1.374(3)	**C4 —P1—C10—C15**	37.99(15)
C20—C21	1.383(2)	**N1 —P1—C10—C11**	−21.80(15)
C8—C9	1.390(2)	**C16 —P1—C10—C11**	102.05(14)
C10 —C15	1.390(2)	**C4 —P1—C10—C11**	−143.54(14)
C16 —C21	1.390(2)	**C15 —C10—C11—C12**	0.3(3)
C10 —C11	1.391(2)	**P1 —C10—C11—C12**	−178.15(14)
C11 —C12	1.389(2)	**C10 —C11—C12—C13**	− 0.8(3)
C12 —C13	1.374(3)	**N1 —P1—C4—C9**	−16.54(15)
C13 —C14	1.379(3)	**C10 —P1—C4—C9**	99.53(13)
N1 —P1—C10	104.88(7)	**C16 —P1—C4—C9**	−144.95(13)
N1 —P1—C16	115.69(7)	**C1^{i}—C1—C2—N2**	−106(3)
C10 —P1—C16	107.86(7)	**N1 —C1—C3—N3**	−14(2)
N1 —P1—C4	113.80(8)	**C2 —C1—C3—N3**	−144(2)
C10 —P1—C4	108.10(7)	**C1^{i}—C1—C3—N3**	104(2)
C16 —P1—C4	106.18(7)	**N1 —P1—C4—C5**	166.29(13)
C1 —N1—P1	129.29(10)	**P1 —C10—C15—C14**	178.70(13)
N1 —C1—C2	116.62(13)	**N1 —P1—C16—C21**	93.45(15)
N1 —C1—C3	113.83(12)	**C4 —P1—C16—C21**	−139.26(14)
C2 —C1—C3	106.89(12)	**N1 —P1—C16—C17**	−80.15(16)
N1 —C1—C1^{i}	107.81(14)	**C4 —P1—C16—C17**	47.13(16)
C2 —C1—C1^{i}	105.03(14)	**P1 —C16—C17—C18**	173.85(16)
C3 —C1—C1^{i}	105.81(14)	**P1 —C16—C21—C20**	−174.02(14)
C5 —C4—P1	122.41(13)		

Symmetry code: (i) −*x*+1,−*y*+2,−*z*.

Scheme S2. Numbering scheme of bis(triphenylphosphine) dicyanopalladium (II) $[(Ph_3P)_2Pd(CN)_2]$ (**6**)

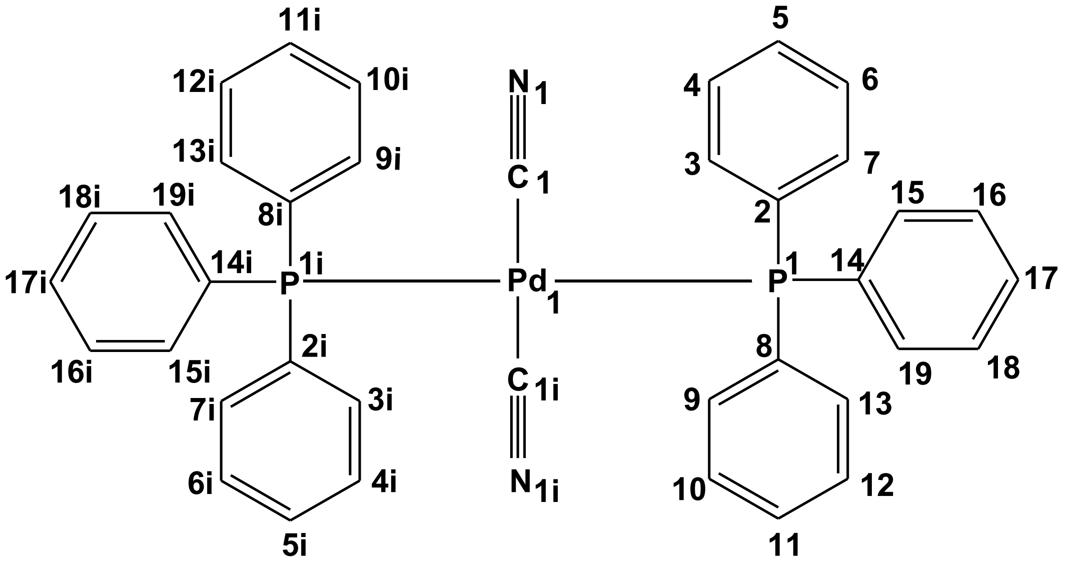


Table S7. Selected bond lengths (Å) angles (°) and torsion angles (°) of **6**.

Pd1—C1	1.994(5)	**P1 ^{i}—Pd1—P1—C14**	96(100)
Pd1—C1 ^{i}	1.994(5)	**C1—Pd1—P1—C8**	108.36(19)
Pd1—P1 ^{i}	2.3140(11)	**C1 ^{i}—Pd1—P1—C8**	−71.64(19)
Pd1—P1	2.3140(11)	**P1 ^{i}—Pd1—P1—C8**	−24(100)
P1—C14	1.804(4)	**C1—Pd1—P1—C2**	−12.7(2)
P1—C8	1.810(4)	**C1 ^{i}—Pd1—P1—C2**	167.3(2)
P1—C2	1.813(4)	**P1 ^{i}—Pd1—P1—C2**	−145(100)
C11—C20	1.755(6)	**C14—P1—C8—C9**	−100.2(4)
C12—C20	1.736(6)	**C2—P1—C8—C9**	149.2(4)
C8—C9	1.386(6)	**Pd1—P1—C8—C9**	20.0(4)
C8—C13	1.395(6)	**C14—P1—C8—C13**	79.6(4)
N1—C1	1.133(6)	**Pd1—P1—C8—C13**	−160.2(3)
C3—C4	1.386(6)	**C14—P1—C2—C7**	2.9(4)
C3—C2	1.389(6)	**C12—C20—C11**	112.6(3)
C2—C7	1.385(6)	**C2—P1—C14—C15**	−80.1(4)
C15—C16	1.373(6)	**Pd1—P1—C14—C15**	47.8(4)
C17—C18	1.377(7)	**P1—C14—C19—C18**	178.3(3)
C11—C12	1.368(7)	**P1—C14—C15—C16**	179.9(4)

C4—C5	1.377(7)	**P1—C8—C13—C12**	179.6(4)
C5—C6	1.368(7)	**C1^{i}—Pd1—C1—N1**	−167(12)
C14—C19	1.370(6)	**P1^{i}—Pd1—C1—N1**	−14(9)
C19—C18	1.389(6)	**P1—Pd1—C1—N1**	166(9)
C1—Pd1—C1^{i}	180.0(3)	**C14—C19—C18—C17**	1.7(7)
C1—Pd1—P1^{i}	86.37(12)	**C2—C3—C4—C5**	0.3(7)
C1^{i}—Pd1—P1^{i}	93.63(12)	**Pd1—P1—C2—C7**	−119.1(4)
C1—Pd1—P1	93.63(12)	**Pd1—P1—C2—C3**	−177.0(4)
C1^{i}—Pd1—P1	86.37(12)	**C8—P1—C14—C19**	61.0(4)
P1^{i}—Pd1—P1	180.00(8)	**Pd1—P1—C14—C19**	−8.5(4)
C14—P1—C8	107.7(2)	**C2—C3—C7—C6**	−130.4(4)
C14—P1—C2	104.7(2)	**Pd1—P1—C14—C15**	0.7(7)
C8—P1—C2	103.85(19)	**C4—C5—C6—C7**	0.1(8)
C14—P1—Pd1	109.25(14)	**C2—C7—C6—C5**	− 0.4(8)
C8—P1—Pd1	112.09(15)		
C2—P1—Pd1	118.59(15)		
C9—C8—P1	121.1(3)		
C4—C3—C2	120.4(4)		
C7—C2—P1	122.5(4)		
N1—C1—Pd1	177.3(4)		
C17—C18—C19	120.2(5)		
C6—C7—C2	121.3(5)		
C15—C14—P1	117.7(3)		
C1—Pd1—P1—C14	−132.37(19)		
C1^{i}—Pd1—P1—C14	47.63(19)		

Symmetry code: (i) −*x*,−*y*,−*z*.

Scheme S3. Numbering scheme of 1, 1, 1-tris(diphenylphosphinomethyl)ethanedicyano Nickel(II) 1,1,1-tris($(Ph_3)_2PCH_2$)CCH_3•$Ni(CN)_2$ (**7**)

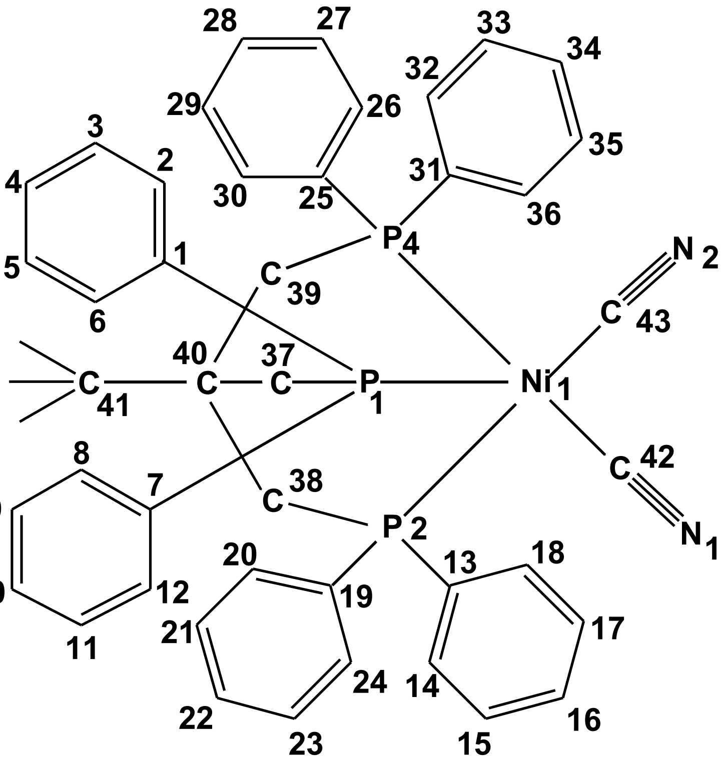


Table S8. Selected bond lengths (Å) angles (°) and torsion angles (°) of **7**.

Ni1—C43	1.8757(17)	**C42—Ni1—P2**	109.61(5)
Ni1—C42	1.8828(16)	**P4—Ni1—P2**	94.199(16)
Ni1—P4	2.1963(4)	**P1—Ni1—P2**	90.609(17)
Ni1—P1	2.2016(4)	**C1—P1—C7**	100.49(8)
Ni1—P2	2.3656(5)	**C1—P1—C37**	104.58(7)
P1—C1	1.8167(17)	**C7—P1—C37**	104.40(8)
P1—C7	1.8322(18)	**C1—P1—Ni1**	115.63(5)
P1—C37	1.8529(16)	**C7—P1—Ni1**	117.46(6)
P2—C19	1.8364(17)	**C37—P1—Ni1**	112.63(5)
P2—C13	1.8367(18)	**C19—P2—C13**	99.21(8)
P2—C38	1.8603(17)	**C19—P2—C38**	105.56(8)

P4—C31	1.8177(16)	**C13—P2—C38**	102.53(8)
P4—C25	1.8312(15)	**C19—P2—Ni1**	118.14(6)
P4—C39	1.8350(16)	**C13—P2—Ni1**	120.13(6)
N1—C42	1.147(2)	**C38—P2—Ni1**	109.31(6)
N2—C43	1.148(2)	**C31—P4—C25**	101.94(7)
C1—C6	1.387(2)	**C31—P4—C39**	108.19(8)
C1—C2	1.398(2)	**C25—P4—C39**	100.64(7)
C2—C3	1.385(3)	**C31—P4—Ni1**	111.87(5)
C3—C4	1.382(3)	**C25—P4—Ni1**	121.08(5)
C4—C5	1.384(3)	**C39—P4—Ni1**	111.85(6)
C5—C6	1.392(2)	**C2—C1—P1**	119.43(13)
C7—C8	1.395(3)	**C27—C28—C29**	120.40(16)
C7—C12	1.400(3)	**C36—C31—P4**	116.15(13)
C8—C9	1.394(3)	**C12—C7—P1**	118.54(16)
C25—C30	1.392(2)	**C40—C37—P1**	117.44(11)
C25—C26	1.399(2)	**C40—C38—P2**	118.12(11)
C26—C27	1.394(2)	**C39—C40—C38**	111.52(14)
C28—C29	1.386(2)	**C14—C13—P2**	121.57(14)
C31—C36	1.397(2)	**C24—C19—P2**	115.53(13)
C35—C36	1.392(2)	**N1—C42—Ni1**	177.87(16)
C37—C40	1.544(2)	**N2—C43—Ni1**	177.21(15)
C38—C40	1.553(2)	**C43—Ni1—P1—C1**	7.02(16)
C39—C40	1.540(2)	**C42—Ni1—P1—C1**	76.30(8)
C9—C10	1.387(4)	**P4—Ni1—P1—C1**	− 79.90(6)
C14—C15	1.392(3)	**P2—Ni1—P1—C1**	− 174.10(6)
C19—C24	1.400(3)	**C43—Ni1—P1—C7**	− 111.47(16)
C23—C24	1.387(3)	**C42—Ni1—P1—C7**	− 42.19(9)
C42—Ni1—P4	156.03(5)	**P4—Ni1—P1—C7**	161.61(8)
C43—Ni1—P1	158.73(5)	**P2—Ni1—P1—C7**	67.42(8)
C42—Ni1—P1	87.50(5)	**P1—Ni1—P2—C19**	161.85(7)
P4—Ni1—P1	89.571(16)	**P4—Ni1—P2—C13**	− 166.40(7)
C43—Ni1—P2	110.66(5)	**C42—Ni1—P2—C38**	128.77(8)
P1—Ni1—P2—C38	41.20(7)	**Ni1—P1—C1—C2**	162.30(12)
C16—C17—C18—C13	− 0.2(3)	**C27—C28—C29—C30**	1.5(3)
Ni1—P2—C19—C20	− 124.66(16)	**C25—P4—C31—C32**	114.55(15)
Ni1—P2—C19—C24	57.10(15)	**Ni1—P1—C37—C40**	14.96(14)
C31—P4—C25—C30	154.62(13)	**P1—C7—C12—C11**	178.66(18)
C39—P4—C25—C26	80.84(14)	**Ni1—P2—C13—C18**	− 19.02(18)
C42—Ni1—P4—C31	− 19.22(14)	**Ni1—P4—C39—C40**	22.56(14)
P2—Ni1—P4—C31	154.23(6)	**C43—Ni1—C42—N1**	17(4)
P1—Ni1—P4—C25	− 176.19(6)	**C42—Ni1—C43—N2**	− 36(3)
C43—Ni1—P4—C39	143.34(8)	**P2—Ni1—C43—N2**	− 145(3)
P2—Ni1—P4—C39	32.67(6)		

Scheme S4. Numbering scheme of bis(1,2,3-tricyanopyrrole-4-carboxamide)-bis (tetrahydrofuran)copper(II) $[Cu\{NC_4(CN)_3C(O)NH_2\}_2(THF)_2]$ (**8**)

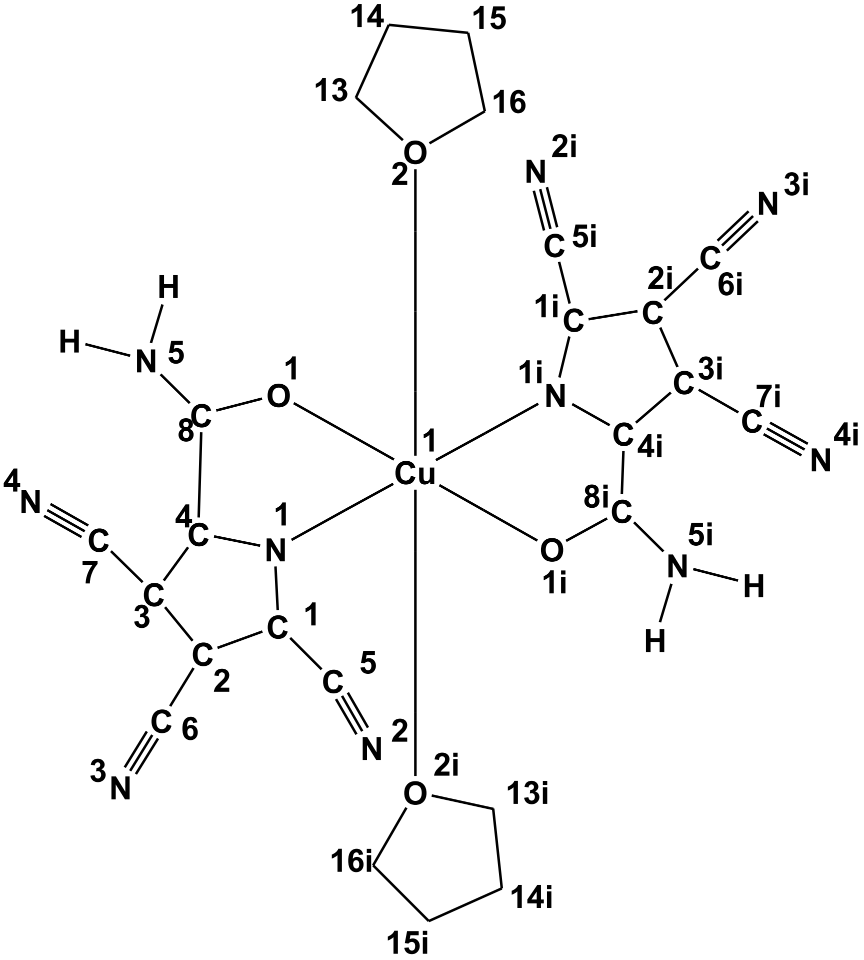


Table S9. Selected bond lengths (Å) angles (°) and torsion angles (°) of **8**.

Cu1 − N1^{i}	1.975 (3)	**N1—C1—C2**	110.7 (4)
Cu1 − N1	1.975 (3)	**N1—C1—C5**	124.7 (3)
Cu1 − O1^{i}	1.998 (3)	**C2—C1—C5**	124.5 (4)
Cu1 − O1	1.998 (3)	**N2—C5—C1**	177.0 (5)
Cu1 − O2	2.476 (27)	**N3—C6—C2**	177.7 (6)
Cu1 − O2^{i}	2.476 (27)	**N4—C7—C3**	177.8 (5)
O1 − C8	1.263 (4)	**O1—C8—N5**	121.7 (4)
N4 − C7	1.133 (5)	**O1—C8—C4**	116.6 (3)
C4 − N1	1.356 (5)	**N5—C8—C4**	121.5 (3)

C4 − C3	1.403 (5)	**C13—O2—C16**	101.6 (3)
C4 − C8	1.460 (6)	**O2—C13—C14**	107.0 (4)
N1 − C1	1.342 (5)	**C13—C14—C15**	103.7 (4)
N3 − C6	1.136 (6)	**C16—C15—C14**	104.2 (4)
C3 − C2	1.403 (6)	**O2—C16—C15**	104.6 (4)
C3 − C7	1.445 (5)	**N1 ^{i}—Cu1—O1—C8**	– 174.7 (3)
N5 − C8	1.319 (5)	**N1—Cu1—O1—C8**	5.3 (3)
N2 − C5	1.129 (5)	**O1 ^{i}—Cu1—O1—C8**	– 14.0 (100)
C2 − C1	1.405 (5)	**C3—C4—N1—C1**	– 0.2 (5)
C2 − C6	1.433 (6)	**C8—C4—N1—C1**	– 175.3 (3)
C1 − C5	1.431 (6)	**C3—C4—N1—Cu1**	– 176.3 (3)
O2 − C13	1.431 (4)	**C8—C4—N1—Cu1**	1.2 (4)
O2 − C16	1.461 (5)	**N1 ^{i}—Cu1—N1—C1**	– 127.0 (100)
C13 − C14	1.481 (6)	**O1 ^{i}—Cu1—N1—C1**	– 8.5 (4)
C14 − C15	1.522 (6)	**O1—Cu1—N1—C1**	171 5 (4)
C15 − C16	1.484 (7)	**N1^{i}—Cu1—N1—C4**	59.0 (100)
N1 ^{i}—Cu1—N1	180.00 (17)	**O1^{i}—Cu1—N1—C4**	176.7 (3)
N1 ^{i}—Cu1—O1 ^{i}	81.95 (12)	**O1—Cu1—N1—C4**	– 3.3 (3)
N1—Cu1—O1 ^{i}	98.05 (12)	**N1—C4—C3—C2**	0.3 (5)
N1 ^{i}—Cu1—O1	98.05 (12)	**C8—C4—C3—C2**	174.0 (4)
N1—Cu1—O1	81.95 (12)	**N1—C4—C3—C7**	– 177.4 (4)
O1 ^{i}—Cu1—O1	180.00 (2)	**C8—C4—C3—C7**	– 3.7 (8)
C8—O1—Cu1	113.9 (3)	**C4—C3—C2—C1**	– 0.2 (5)
N1—C4—C3	109.5 (4)	**C7—C3—C2—C1**	177.6 (4)
N1—C4—C8	115.0 (3)	**C4—C3—C2—C6**	180.0 (4)
C3—C4—C8	135.2 (4)	**C7—C3—C2—C6**	– 2.3 (7)
C1—N1—C4	107.7 (3)	**C4—N1—C1—C2**	0.1 (5)
C1—N1—Cu1	140.1 (2)	**Cu1—N1—C1—C2**	– 174.9 (3)
C4—N1—Cu1	112.1 (3)	**C4—C3—C7—N4**	153.0 (12)
C2—C3—C4	106.7 (3)	**Cu1—O1—C8—N5**	174.6 (3)
C2—C3—C7	124.8 (4)	**Cu1—O1—C8—C4**	– 6.1 (5)
C4—C3—C7	128.5 (4)	**N1—C4—C8—O1**	3.4 (6)
C3—C2—C1	105.4 (4)	**C3—C4—C8—O1**	– 170.1 (4)
C3—C2—C6	127.0 (3)	**C13—C14—C15—C16**	4.2 (6)
C1—C2—C6	127.6 (4)	**C13—O2—C16—C15**	42.8 (6)
N1—C4—C8—N5	– 177.3 (4)	**C14—C15—C16—O2**	– 28.8 (7)
C3—C4—C8—N5	9.2 (7)		
C16—O2—C13—C14	– 40.6 (5)		
O2—C13—C14—C15	22.6 (6)		

Symmetry code: (i) 1-*x*, 1-*y*, -*z*.

Scheme S5. Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)zinc(II) acetonitrile solvate $[Zn(TCP)_2{}^{\bullet}4CH_3CN]^{\bullet}2CH_3CN$ (**9**)

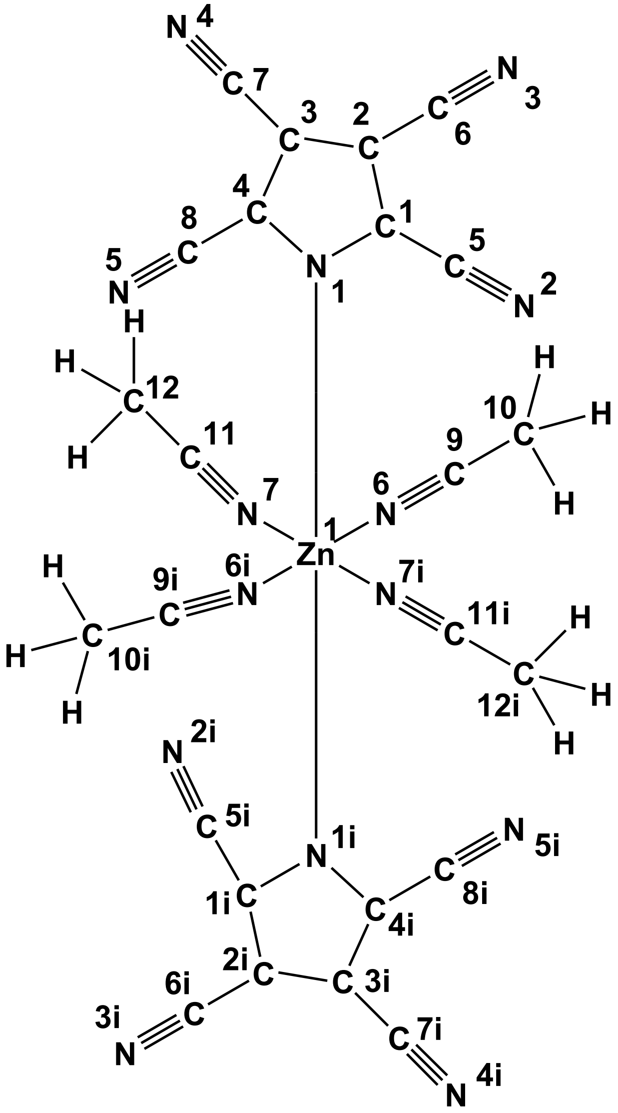


Table S10. Selected bond lengths (Å) angles (°) and torsion angles (°) of **9**.

C1 − N1	1.3615 (17)	**N4—C7—C3**	178.44 (18)
C1 − C2	1.3926 (18)	**N5—C8—C4**	175.96 (15)
C1 − C5	1.432 (2)	**N6—C9—C10**	177.62 (16)
C2 − C3	1.409 (2)	**N7—C11—C12**	178.87 (17)
C2 − C6	1.421 (2)	**N8—C13—C14**	178.6 (2)
C3 − C4	1.3973 (19)	**C1—N1—C4**	105.17 (11)

C3 − C7	1.423 (2)	**C1—N1—Zn1**	127.68 (9)
C4 − N1	1.3624 (17)	**C4—N1—Zn1**	127.10 (9)
C4 − C8	1.427 (2)	**C9—N6—Zn1**	163.84 (12)
C5 − N2	1.146 (2)	**C11—N7—Zn1**	174.52 (12)
C6 − N3	1.1456 (19)	**N6—Zn1—N6^{i}**	180.00
C7 − N4	1.140 (2)	**N6—Zn1—N1^{i}**	90.22 (4)
C8 − N5	1.1438 (19)	**N6^{i}—Zn1—N1^{i}**	89.78 (4)
C9 − N6	1.1380 (18)	**N6—Zn1—N1**	89.78 (4)
C9 − C10	1.455 (2)	**N6^{i}—Zn1—N1**	90.22 (4)
C11 − N7	1.1376 (19)	**N1^{i}—Zn1—N1**	180.00
C11 − C12	1.449 (2)	**N6—Zn1—N7**	89.32 (5)
C13 − N8	1.127 (2)	**N6^{i}—Zn1—N7**	90.68 (5)
C13 − C14	1.454 (3)	**N1^{i}—Zn1—N7**	90.36 (4)
N1 − Zn1	2.1528 (11)	**N1—Zn1—N7**	89.64 (4)
N6 − Zn1	2.1513 (12)	**N6—Zn1—N7^{i}**	90.68 (5)
N7 − Zn1	2.1567 (13)	**N6^{i}—Zn1—N7^{i}**	89.32 (5)
Zn1 − N6^{i}	2.1513 (12)	**N1^{i}—Zn1—N7^{i}**	89.64 (4)
Zn1 − N1^{i}	2.1528 (11)	**N1—Zn1—N7^{i}**	90.36 (4)
Zn1 − N7^{i}	2.1567 (13)	**N7—Zn1—N7^{i}**	180.00 (3)
N1—C1—C2	111.93 (12)	**N1—C1—C2—C3**	– 0.25 (16)
N1—C1—C5	123.70 (12)	**C5—C1—C2—C3**	178.39 (14)
C2—C1—C5	124.35 (13)	**N1—C1—C2—C6**	178.04 (13)
C1—C2—C3	105.59 (12)	**C5—C1—C2—C6**	– 3.3 (2)
C1—C2—C6	127.37 (13)	**C1—C2—C3—C4**	0.24 (15)
C3—C2—C6	127.01 (13)	**C6—C2—C3—C4**	– 178.05 (14)
C4—C3—C2	105.77 (12)	**C1—C2—C3—C7**	178.89 (14)
C4—C3—C7	126.52 (14)	**C6—C2—C3—C7**	0.6 (2)
C2—C3—C7	127.69 (13)	**C2—C3—C4—N1**	– 0.17 (16)
N1—C4—C3	111.54 (12)	**C7—C3—C4—N1**	– 178.84 (13)
N1—C4—C8	124.67 (12)	**C2—C3—C4—C8**	179.21 (13)
C3—C4—C8	123.78 (12)	**C7—C3—C4—C8**	0.5 (2)
N2—C5—C1	176.63 (17)	**C2—C1—N1—C4**	0.14 (16)
N3—C6—C2	178.98 (16)	**C5—C1—N1—C4**	– 178.50 (13)
C2—C1—N1—Zn1	– 177.34 (9)		
C5—C1—N1—Zn1	4.0 (2)		
C3—C4—N1—C1	0.02 (16)		
C8—C4—N1—C1	– 179.36 (13)		
C3—C4—N1—Zn1	177.52 (9)		
C8—C4—N1—Zn1	– 1.86 (19)		

Symmetry code: (i) 1-*x*, 1-*y*, -*z*.

Scheme S6. Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)iron(II) acetonitrile solvate $[Fe(TCP)_2{}^{\bullet}4CH_3CN]^{\bullet}2CH_3CN$ (**10**)

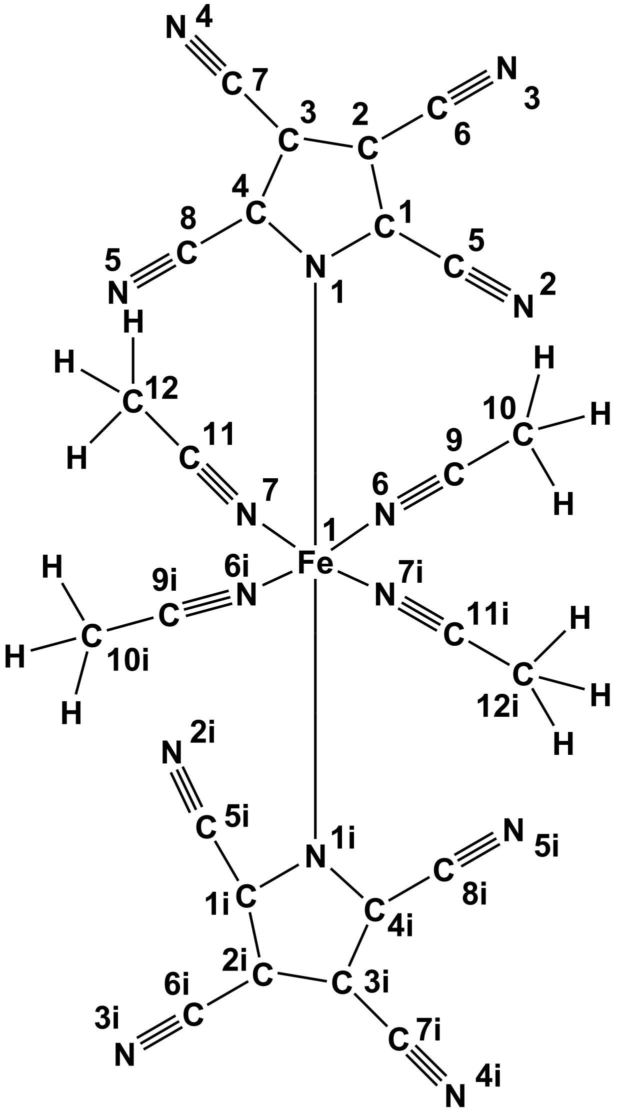


Table S11. Selected bond lengths (Å) angles (°) and torsion angles (°) of **10**.

C1 — N1	1.3632 (12)	**N7—Fe1—N7 ^{i}**	180.00
C1 — C2	1.3971 (13)	**N6—Fe1—N1**	89.78 (3)
C1 — C5	1.4314 (14)	**N6 ^{i}—Fe1—N1**	90.22 (3)
C2 — C3	1.4082 (14)	**N7—Fe1—N1**	89.54 (3)
C2 — C6	1.4218 (14)	**N7 ^{i}—Fe1—N1**	90.46 (3)

C3 — C4	1.3980 (13)	**N6—Fe1—N1^{i}**	90.22 (3)
C3 — C7	1.4213 (14)	**N6^{i}—Fe1—N1^{i}**	89.78 (3)
C4 — N1	1.3635 (12)	**N7—Fe1—N1^{i}**	90.46 (3)
C4 — C8	1.4275 (14)	**N7^{i}—Fe1—N1^{i}**	89.54 (3)
C5 — N2	1.1447 (15)	**N1—Fe1—N1^{i}**	180.00
C6 — N3	1.1466 (14)	**N1—C1—C2—C3**	– 0.27 (11)
C7 — N4	1.1452 (15)	**C5—C1—C2—C3**	178.27 (10)
C8 — N5	1.1480 (14)	**N1—C1—C2—C6**	177.89 (9)
C9 — N6	1.1406 (13)	**C5—C1—C2—C6**	– 3.57 (17)
C11 —N7	1.1385 (13)	**C1—C2—C3—C4**	0.19 (11)
C11 — C12	1.4529 (15)	**C6—C2—C3—C4**	–177.97 (10)
C13 —N8	1.1283 (18)	**C1—C2—C3—C7**	178.64 (10)
C13 —C14	1.4481 (19)	**C6—C2—C3—C7**	0.47 (18)
N1 — Fe1	2.1920 (8)	**C2—C3—C4—N1**	– 0.05 (11)
N6 — Fe1	2.1588 (9)	**C7—C3—C4—N1**	– 178.53 (10)
C9 — C10	1.4519 (14)	**C2—C3—C4—C8**	179.30 (9)
N1 — Fe1	2.1659 (9)	**C7—C3—C4—C8**	0.83 (17)
Fe1 — N6^{i}	2.1589 (9)	**C2—C1—N1—C4**	0.24 (11)
Fe1 — N7^{i}	2.1659 (9)	**C5—C1—N1—C4**	– 178.32 (10)
Fe1 — N1^{i}	2.1920 (8)	**C2—C1—N1—Fe1**	– 177.37 (6)
N1—C1—C2	111.77 (9)	**C3—C1—N1—Fe1**	4.07 (14)
N1—C1—C5	123.49 (9)	**C3—C4—N1—C1**	– 0.11 (11)
C2—C1—C5	124.73 (9)	**C8—C4—N1—C1**	– 179.46 (9)
C1—C2—C3	105.62 (8)	**C3—C4—N1—Fe1**	177.51 (6)
C1—C2—C6	127.21 (10)	**C8—C4—N1—Fe1**	– 1.84 (14)
C3—C2—C6	127.14 (9)		
C4—C3—C2	105.84 (8)		
C4—C3—C7	126.44 (10)		
C2—C3—C7	127.69 (9)		
N1—C4—C3	111.56 (8)		
N1—C4—C8	124.21 (9)		
C3—C4—C8	124.23 (9)		
N2—C5—C1	176.97 (12)		
N3—C6—C2	179.24 (12)		
N4—C7—C3	178.93 (14)		
N5—C8—C4	176.12 (11)		
N6—C9—C10	177.47 (11)		
N7—C11—C12	178.83 (13)		
N8—C13—C14	178.67 (17)		
C1—N1—C4	105.20 (8)		
C1—N1—Fe1	127.60 (6)		
C4—N1—Fe1	127.15 (6)		
C9—N6—Fe1	164.01 (8)		
C11—N7—Fe1	173.84 (9)		
N6—Fe1—N6^{i}	180.00		

N6—Fe1—N7	89.01 (3)		
N6 ^{i}—Fe1—N7	90.99 (3)		
N6—Fe1—N7 ^{i}	90.99 (3)		
N6 ^{i}—Fe1—N7 ^{i}	89.01 (3)		

Symmetry code: (i) *–x*, *–y*, *-z*.

Scheme S7. Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)magnesium(II) acetonitrile solvate $[Mg(TCP)_2{}^{\bullet}4CH_3CN]^{\bullet}2CH_3CN$ (**11**)

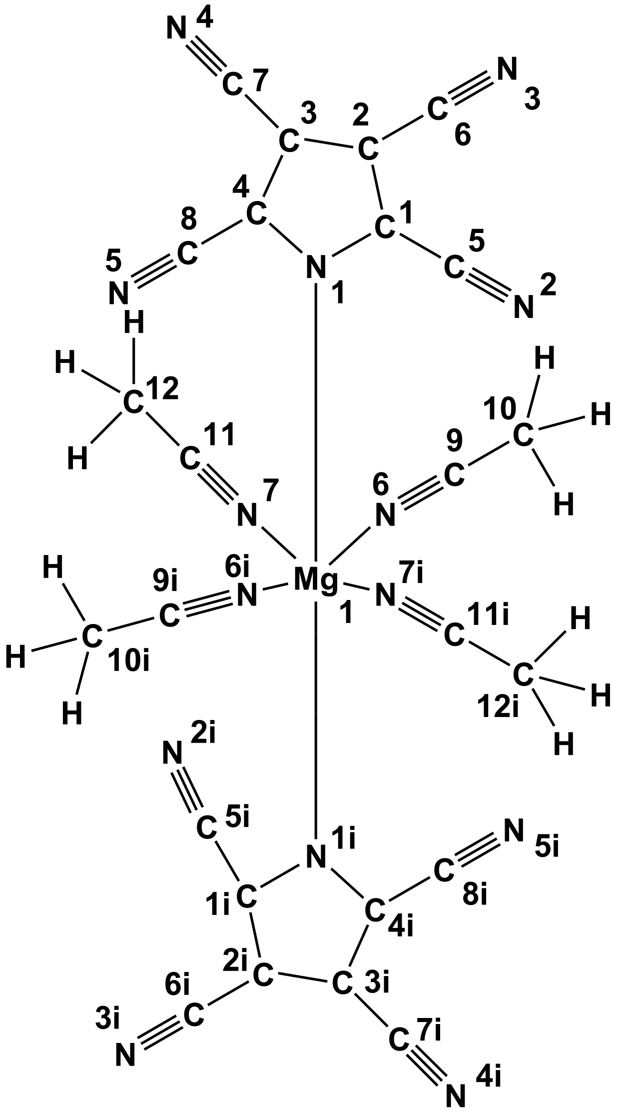


Table S12. Selected bond lengths (Å) angles (°) and torsion angles (°) of **11**.

Mg1 — N6	2.1488 (9)	**N7—C11—C12**	178.82 (13)
Mg1 — N6^{i}	2.1488 (9)	**N8—C13—C14**	178.78 (16)
Mg1 — N7^{i}	2.1561 (9)	**C1—N1—C4**	104.83 (8)
Mg1 — N7	2.1562 (9)	**C1—N1—Mg1**	127.50 (6)
Mg1 — N1^{i}	2.2031 (8)	**C4—N1—Mg1**	127.62 (6)
Mg1 — N1	2.2031 (8)	**C9—N6—Mg1**	165.02 (8)
N1 — C1	1.3616 (12)	**C11—N7—Mg1**	174.48 (9)
N1 — C4	1.3658 (12)	**N6—Mg1—N6^{i}**	180.00 (4)
N2 — C5	1.1458 (13)	**N6—Mg1—N7**	89.83 (3)
N3 — C6	1.1411 (15)	**N6^{i}—Mg1—N7**	90.17 (3)
N4 — C7	1.1453 (14)	**N6—Mg1—N7^{i}**	90.17 (3)
N5 — C8	1.1471 (14)	**N6^{i}—Mg1—N7^{i}**	89.83 (3)
N6 — C9	1.1419 (13)	**N7^{i}—Mg1—N7**	180.00
N7 — C11	1.1394 (13)	**N6—Mg1—N1**	89.91 (3)
C1 — C2	1.3933 (13)	**N6^{i}—Mg1—N1**	90.09 (3)
C1 — C5	1.4320 (13)	**N7—Mg1—N1**	89.52 (3)
C2 — C3	1.4022 (14)	**N7^{i}—Mg1—N1**	90.48 (3)
C2 — C6	1.4263 (14)	**N6—Mg1—N1^{i}**	90.09 (3)
C3 — C4	1.3968 (13)	**N6^{i}—Mg1—N1^{i}**	89.91 (3)
C3 — C7	1.4225 (13)	**N7—Mg1—N1^{i}**	90.48 (3)
C4 — C8	1.4290 (14)	**N7^{i}—Mg1—N1^{i}**	89.52 (3)
C9 — C10	1.4465 (15)	**N1^{i}—Mg1—N1**	180.00
C11 — C12	1.4513 (15)	**N1—C1—C2—C3**	0.05 (11)
N8 — C13	1.1279 (18)	**C5—C1—C2—C3**	– 179.16 (9)
C13 — C14	1.448 (2)	**N1—C1—C2—C6**	178.48 (9)
N1—C1—C2	111.88 (8)	**C5—C1—C2—C6**	– 0.73 (16)
N1—C1—C5	123.95 (8)	**C1—C2—C3—C4**	– 0.30 (11)
C2—C1—C5	124.17 (9)	**C6—C2—C3—C4**	–178.7 (1)
C1—C2—C3	105.90 (8)	**C1—C2—C3—C7**	178.15 (10)
C1—C2—C6	126.34 (9)	**C6—C2—C3—C7**	– 0.25 (17)
C3—C2—C6	127.74 (9)	**C2—C3—C4—N1**	0.47 (11)
C4—C3—C2	105.67 (8)	**C7—C3—C4—N1**	– 177.99 (9)
C4—C3—C7	127.04 (9)	**C2—C3—C4—C8**	178.35 (10)
C2—C3—C7	127.26 (9)	**C7—C3—C4—C8**	3.19 (17)
N1—C4—C3	111.71 (9)	**C1—N1—C4—C3**	– 0.43 (11)
N1—C4—C8	123.49 (9)	**C1—N1—C4—C8**	178.41 (9)
C3—C4—C8	124.79 (9)	**Mg1—N1—C1—C2**	– 177.36 (6)
N2—C5—C1	176.17 (10)	**Mg1—N1—C1—C5**	1.85 (14)
N3—C6—C2	179.04 (13)	**C4—N1—C1—C2**	0.23 (11)
N4—C7—C3	179.14 (12)	**C4—N1—C1—C5**	179.44 (9)
N5—C8—C4	177.14 (12)	**Mg1—N1—C4—C3**	177.15 (6)
N6—C9—C10	177.47 (11)	**Mg1—N1—C4—C8**	– 4.01 (14)

Symmetry code: (i) 1–*x*, 1–*y*, 1–*z*.

Scheme S8. Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)copper(II) acetonitrile solvate $[Cu(TCP)_2{}^{\cdot}4CH_3CN]^{\cdot}2CH_3CN$ (**12**)

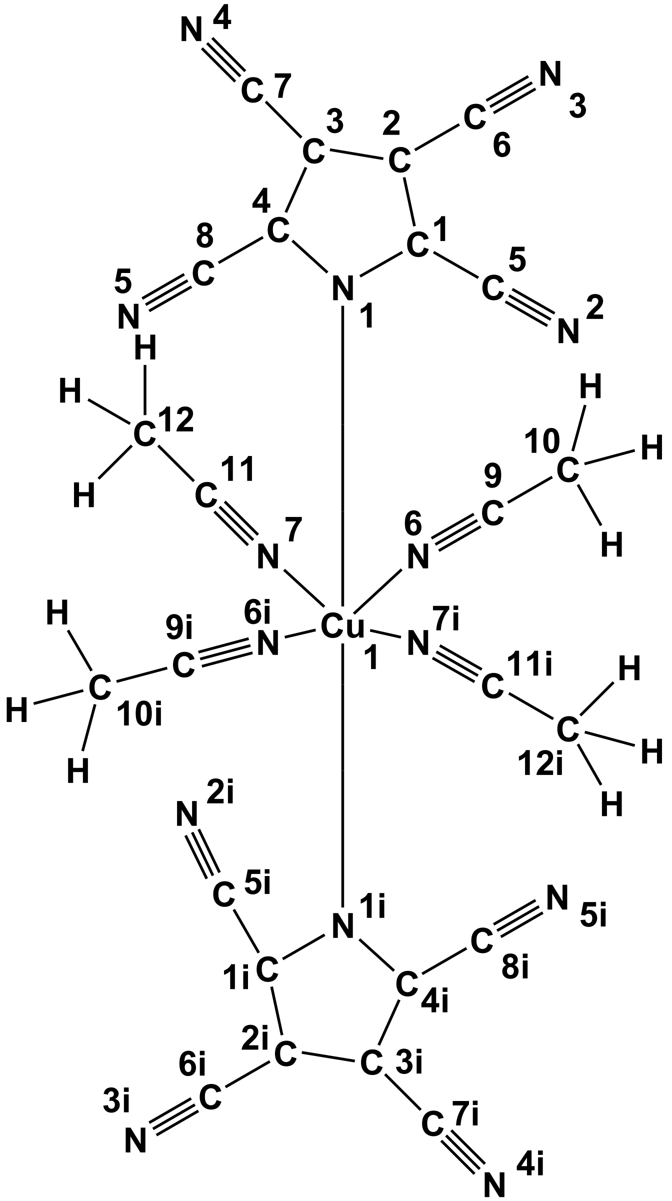


Table S13. Selected bond lengths (Å) angles (°) and torsion angles (°) of **12**.

Cu1 — N1 ^{i}	2.0258 (10)	**N7—Cu1—N7 ^{i}**	180.000
Cu1 — N1	2.0258 (10)	**C4—N1—C1**	105.41 (10)
Cu1 — N6	2.0251 (11)	**C4—N1—Cu1**	127.35 (8)
Cu1 — N6 ^{i}	2.0251 (11)	**C1—N1—Cu1**	127.21 (9)
Cu1 — N7	2.3451 (12)	**C9—N6—Cu1**	176.94 (11)

Cu1 — N7^{i}	2.3451 (12)	**C11—N7—Cu1**	156.50 (11)
N1 — C4	1.3639 (16)	**N1—C1—C2**	111.39 (11)
N1 — C1	1.3659 (16)	**N1—C1—C5**	124.63 (12)
N2 — C5	1.1484 (18)	**C2—C1—C5**	123.98 (12)
N3 — C6	1.1463 (18)	**C1—C2—C3**	105.87 (11)
N4 — C7	1.1447 (19)	**C2—C1—C5**	123.98 (12)
N5 — C8	1.1447 (18)	**C1—C2—C6**	126.73 (12)
N6 — C9	1.1397 (18)	**C3—C2—C6**	127.37 (12)
N7 — C11	1.1399 (18)	**C4—C3—C2**	105.88 (11)
C1 — C2	1.3949 (18)	**C4—C3—C7**	126.50 (12)
C1 — C5	1.4303 (19)	**C2—C3—C7**	127.59 (12)
C2 — C3	1.4086 (18)	**N1—C4—C3**	111.45 (11)
C2 — C6	1.4219 (18)	**N1—C4—C8**	125.12 (11)
C3 — C4	1.3949 (17)	**C3—C4—C8**	123.43 (12)
C3 — C7	1.4228 (19)	**N2—C5—C1**	175.52 (14)
C4 — C8	1.4332 (18)	**N3—C6—C2**	179.04 (15)
C9 — C10	1.450 (2)	**N4—C7—C3**	178.75 (16)
C11 — C12	1.4507 (19)	**N5—C8—C4**	174.73 (14)
C13 —N8	1.134 (2)	**N6—C9—C10**	178.24 (15)
C13 — C14	1.454 (2)	**N7—C11—C12**	177.54 (15)
N1^{i}—Cu1—N1	180.00 (6)	**N8—C13—C14**	178.9 (2)
N1^{i}—Cu1—N6	89.80 (4)	**C4—N1—C1—C2**	– 0.20 (14)
N1 —Cu1—N6	90.20 (4)	**Cu1—N1—C1—C2**	178.30 (9)
N1^{i}—Cu1—N6^{i}	90.20 (4)	**C4—N1—C1—C5**	179.29 (12)
N1 — Cu1— N6^{i}	89.80 (4)	**Cu1—N1—C1—C5**	– 2.21 (19)
N6—Cu1—N6^{i}	180.000	**N1—C1—C2—C3**	0.24 (15)
N1^{i}—Cu1—N7	89.62 (4)	**C5—C1—C2—C3**	– 179.26 (12)
N1—Cu1—N7	90.38 (4)	**N1—C1—C2—C6**	– 177.90 (12)
N6—Cu1—N7	87.24 (4)	**C5—C1—C2—C6**	2.6 (2)
N6^{i}—Cu1—N7	92.76 (4)	**C1—C2—C3—C4**	– 0.18 (14)
N1^{i}—Cu1—N7^{i}	90.38 (4)	**C6—C2—C3—C4**	177.95 (13)
N1 —Cu1—N7^{i}	89.62 (4)	**C1—C2—C3—C7**	178.36 (13)
N6—Cu1—N7^{i}	92.76 (4)	**C6—C2—C3—C7**	– 0.2 (2)
N6^{i}—Cu1—N7^{i}	87.24 (4)	**C1—N1—C4—C3**	0.08 (14)
Cu1—N1—C4—C3	– 178.42 (8)	**C7—C3—C4—N1**	178.27 (12)
C1—N1—C4—C8	179.94 (12)	**C2—C3—C4—C8**	– 179.80 (12)
Cu1—N1—C4—C8	1.44 (18)	**C7—C3—C4—C8**	– 1.6 (2)
C2—C3—C4—N1	0.06 (15)		

Symmetry code: (i) –*x*, –*y*, 1–*z*.

Scheme S9. Numbering scheme of di(acetylacetonate)-1,5-N-μ-tetracyanopyrrolido manganese (III) [Mn(acac)$_2$TCP] (**13**)

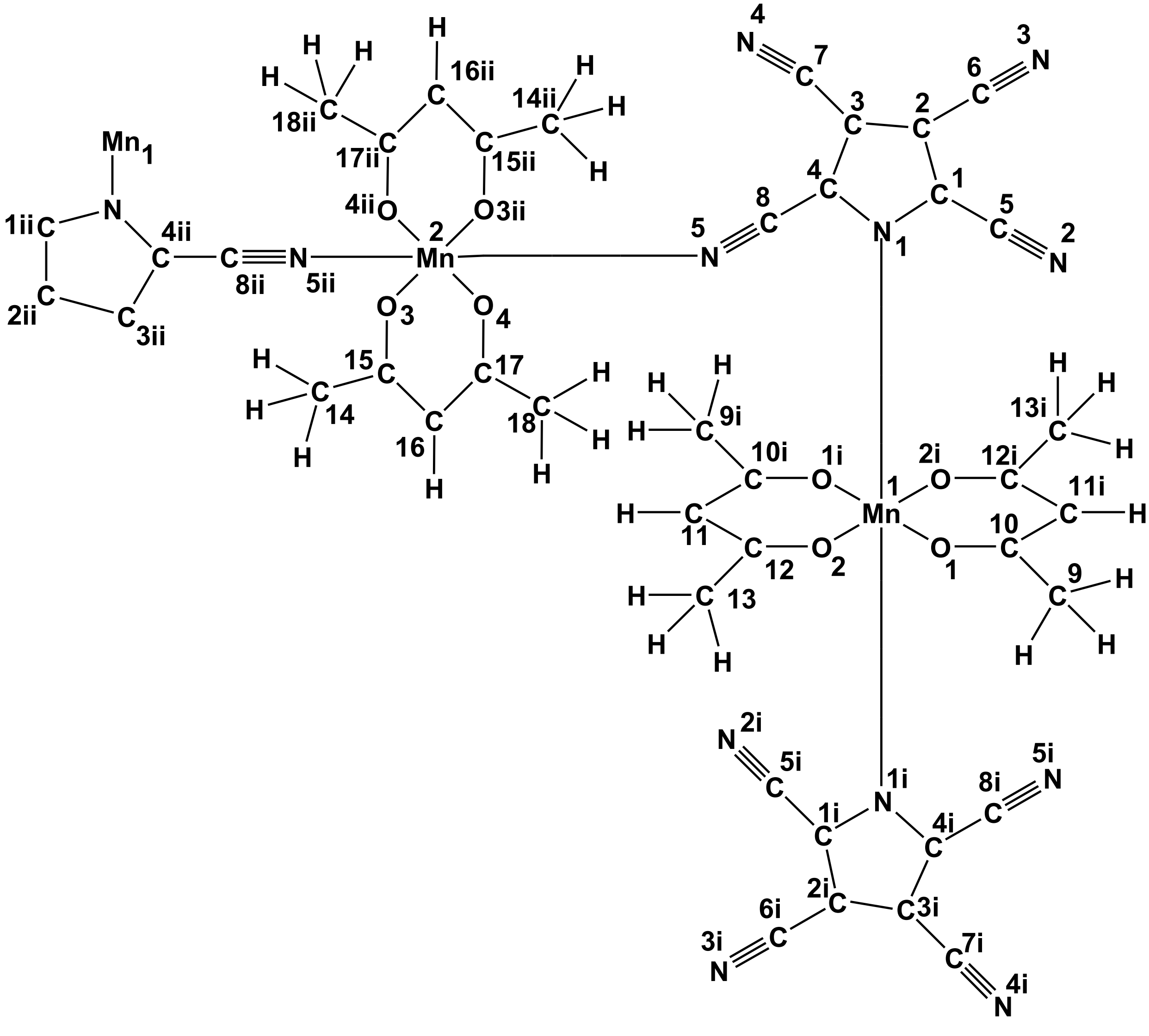


Table S14. Selected bond lengths (Å) angles (^{o}) and torsion angles (^{o}) of **13**.

Mn1 — O1	1.890 (1)	**C11 — C10 — C9**	121.79 (15)
Mn1 — O1 ^{i}	1.8901 (10)	**O4 ^{ii} — Mn2 — O3 ^{ii}**	91.70 (5)
Mn1 — O2	1.9092 (11)	**O4 — Mn2 — O3 ^{ii}**	88.30 (5)
Mn1 — O2 ^{i}	1.9092 (11)	**O3 — Mn2 — O3 ^{ii}**	180.000
Mn1 — N1 ^{i}	2.2994 (13)	**O4 ^{ii} — Mn2 — N5 ^{ii}**	94.76 (5)
Mn1 — N1	2.2994 (13)	**O4 — Mn2 — N5 ^{ii}**	85.24 (5)
C1 — N1	1.356 (2)	**O3 — Mn2 — N5 ^{ii}**	90.35 (5)
C1 — C2	1.395 (2)	**O3 ^{ii} — Mn2 — N5 ^{ii}**	89.65 (5)
C1 — C5	1.430 (2)	**O4 ^{ii} — Mn2 — N5**	85.24 (5)
N1 — C4	1.3604 (19)	**O4 — Mn2 — N5**	94.76 (5)
O1 — C10	1.2821 (19)	**O3 — Mn2 — N5**	89.65 (5)
Mn2 — O4 ^{ii}	1.8993 (11)	**O3 ^{ii} — Mn2 — N5**	90.35 (5)
Mn2 — O4	1.8993 (11)	**N5 ^{ii} — Mn2 — N5**	180.000
Mn2 — O3	1.9024 (11)	**C1 — C2 — C3**	105.53 (14)
Mn2 — O3 ^{ii}	1.9024 (11)	**C1 — C2 — C6**	126.91 (14)
Mn2 — N5 ^{ii}	2.3618 (14)	**C3 — C2 — C6**	127.50 (15)
Mn2 — N5	2.3619 (13)	**C12 — O2 — Mn1**	127.24 (10)
C2 — C3	1.405 (2)	**C4 — C3 — C2**	105.70 (13)
C2 — C6	1.421 (2)	**C4 — C3 — C7**	128.57 (15)
N2 — C5	1.142 (2)	**C2 — C3 — C7**	125.73 (16)
O2 — C12	1.277 (2)	**C15 — O3 — Mn2**	127.04 (11)
C3 — C4	1.397 (2)	**N1 — C4 — C3**	111.67 (13)
C3 — C7	1.426 (2)	**N1 — C4 — C8**	123.14 (14)
N3 — C6	1.144 (2)	**C3 — C4 — C8**	125.19 (14)
O3 — C15	1.2897 (19)	**N5 — C8 — C4**	174.80 (17)
C4 — C8	1.433 (2)	**O4 — C17 — C16**	124.29 (16)
N4 — C7	1.141 (2)	**O4 — C17 — C18**	114.66 (15)
O4 — C17	1.286 (2)	**C16 — C17 — C18**	121.06 (16)
N5 — C8	1.141 (2)	**C15 — C16 — C17**	123.65 (16)
C13 — C12	1.500 (2)	**O3 — C15 — C16**	124.48 (16)
C12 — C11	1.391 (2)	**O3 — C15 — C14**	114.44 (15)
C11 — C10	1.387 (3)	**C16 — C15 — C14**	121.08 (16)
C10 — C9	1.494 (2)	**C2 — C1 — N1— C4**	0.12 (19)
C18 — C17	1.494 (2)	**C5 — C1 — N1— C4**	− 179.40 (15)
C17 — C16	1.390 (2)	**C2 —C1 — N1— Mn1**	179.89 (10)
C16 — C15	1.386 (2)	**C5 —C1 — N1— Mn1**	0.4 (2)
C15 — C14	1.499 (2)	**O2—Mn1—O1—C10**	− 4.91 (14)
O1 — Mn1 — O1 ^{i}	180.00 (7)	**O2—Mn1—O1—C10**	175.09 (14)
O1 — Mn1 — O2	91.77 (5)	**N1—Mn1—O1—C10**	− 96.59 (13)
O1 ^{i} — Mn1 — O2	88.23 (5)	**N1—Mn1—O1—C10**	83.41 (13)
O1 — Mn1 — O2 ^{i}	88.23 (5)	**N1 — C1 — C2 — C3**	− 0.33 (19)
O1 ^{i} — Mn1 — O2 ^{i}	91.77 (5)	**C5 — C1 — C2 — C3**	179.18 (16)
O2 — Mn1 — O2 ^{i}	180.000	**N1 — C1 — C2 — C6**	− 177.49 (16)

O1 — Mn1 — N1^{i}	88.70 (5)	**C5 — C1 — C2 — C6**	2.0 (3)
O1^{i} — Mn1 — N1^{i}	91.30 (5)	**C1 — C2 — C3 — C4**	0.39 (17)
O2 — Mn1 — N1^{i}	91.71 (5)	**C6 — C2 — C3 — C4**	177.54 (16)
O2^{i} — Mn1 — N1^{i}	88.29 (5)	**C1— C2 — C3 — C7**	179.69 (16)
O1 — Mn1 — N1	91.30 (5)	**C6— C2 — C3 — C7**	− 3.2 (3)
O1^{i}— Mn1 — N1	88.70 (5)	**C1— N1 —C4 — C3**	0.15 (18)
O2 — Mn1 — N1	88.29 (5)	**Mn1 —N1 — C4— C3**	− 179.62 (10)
O2^{i} — Mn1 — N1	91.71 (5)	**C1— N1 —C4 — C8**	179.96 (15)
O1 — Mn1 — N1^{i}	180.000	**Mn1 —N1 — C4— C8**	0.2 (2)
N1 — C1 — C2	112.00 (13)	**C2 — C3 — C4 — N1**	− 0.35 (18)
N1 — C1 — C5	123.21 (15)	**C7 — C3 — C4 — N1**	− 179.62 (16)
C2 — C1 — C5	124.79 (15)	**O3—Mn2—O4—C17**	13.67 (13)
C1 — N1 — C4	105.11 (13)	**O3—Mn2—O4—C17**	− 166.33 (13)
C1 — N1 — Mn1	125.71 (10)	**N5—Mn2—O4—C17**	− 76.54 (13)
C4 — N1 — Mn1	129.18 (10)	**N5—Mn2—O4—C17**	103.46 (13)
C10 — O1 — Mn1	128.2 (1)	**Mn1—O2—C12—C11**	− 3.4 (3)
O4^{ii} — Mn2 — O4	180.000	**Mn1—O2—C12—C13**	176.58 (12)
O4^{ii} — Mn2 — O3	88.30 (5)	**O2—C12 —C11—C10**	− 3.0 (3)
O4 — Mn2 — O3	91.70 (5)	**C13—C12—C11—C10**	177.04 (18)
C1 7 — O4 — Mn2	127.17 (11)	**Mn1—O1—C10—C11**	0.8 (2)
N2 — C5 — C1	175.1 (2)	**Mn1—O1—C10—C9**	− 179.72 (11)
C8 — N5 — Mn2	167.56 (14)	**C12—C11—C10—O1**	4.4 (3)
N3 — C6 — C2	178.75 (19)	**C12—C11—C10—C9**	− 175.02 (17)
N4 — C7 — C3	177.9 (2)	**Mn2—O4—C17—C16**	− 9.2 (2)
O2 — C12 — C11	124.61 (16)	**Mn2—O4—C17—C18**	170.96 (10)
O2 — C12 — C13	114.21 (15)	**O4—C17 —C16—C15**	− 2.7 (3)
C11 — C12 — C13	121.17 (16)	**C18—C17—C16—C15**	177.12 (15)
C10 — C11 — C12	123.72 (16)	**Mn2—O3—C15—C16**	4.6 (2)
O1 — C10 — C11	124. 05 (14)	**Mn2—O3—C15—C14**	− 175.86 (11)

Symmetry codes: (i) –*x*, –*y*, –*z*; (ii) -1-*x*, -*y*, -1-*z*.

Scheme S10. Numbering scheme of acetonitrile-di(acetylacetonate)tetracyanopyrrolido chromium(III) $[Cr(acac)_2TCP^{\cdot}CH_3CN]\cdot0.67CH_3CN$ (**14**)

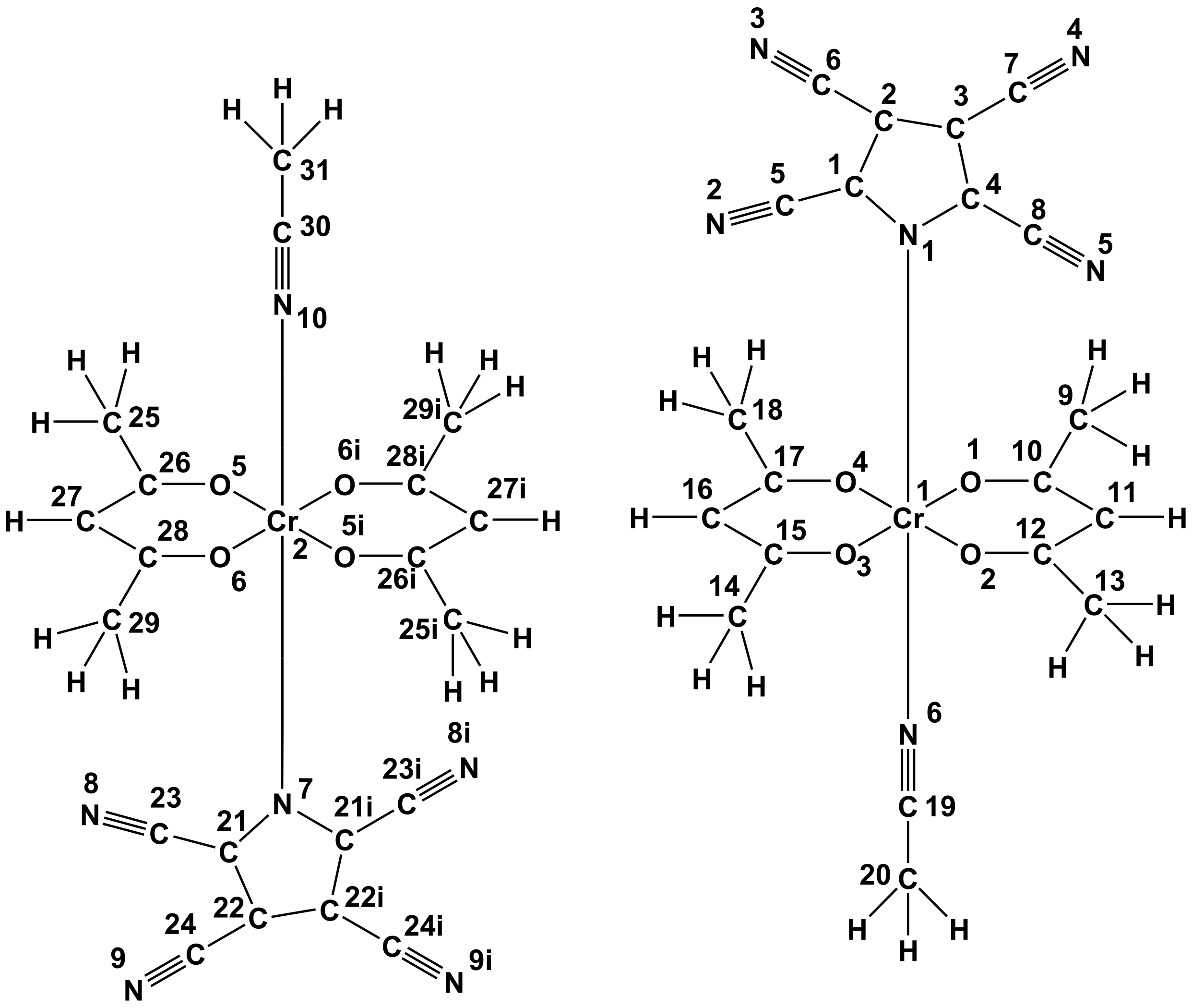


Table S15. Selected bond lengths (Å) angles (°) and torsion angles (°) of **14**.

Cr1 − O3	1.9297 (18)	**N6 − C19 − C20**	179.5 (4)
Cr1 − O2	1.9328 (16)	**O6 − Cr2 − O6 ^{i}**	177.58 (11)
Cr1 − O4	1.9364 (16)	**O6 − Cr2 − O5**	90.76 (7)
Cr1 − O1	1.9420 (18)	**O6 ^{i} − Cr2 − O5**	89.26 (7)
Cr1 − N6	2.049 (2)	**O6 − Cr2 − O5 ^{i}**	89.26 (7)
Cr1 − N1	2.066 (2)	**O6 ^{i} − Cr2 − O5 ^{i}**	90.76 (7)
N1 − C4	1.364 (3)	**O5 − Cr2 − O5 ^{i}**	179.34 (11)

N1 − C1	1.365 (3)	**O6 − Cr2 − N10**	91.21 (6)
C1 − C2	1.382 (4)	**O6^{i} − Cr2 − N10**	91.21 (6)
C1 − C5	1.436 (3)	**O5 − Cr2 − N10**	89.67 (6)
C2 − C3	1.415 (3)	**O5^{i} − Cr2 − N10**	89.67 (6)
C2 − C6	1.428 (4)	**O6 − Cr2 − N7**	88.79 (6)
C3 − C4	1.383 (4)	**O6^{i} − Cr2 − N7**	88.79 (6)
C3 − C7	1.430 (4)	**O5 − Cr2 − N7**	90.33 (6)
C4 − C8	1.435 (3)	**O5^{i} − Cr2 − N7**	90.33 (6)
C5 − N2	1.142 (3)	**C2 − C3 − C7**	126.6 (2)
C6 − N3	1.142 (3)	**N1 − C4 − C3**	111.4 (2)
C7 − N4	1.133 (3)	**N1 − C4 − C8**	123.9 (2)
C8 − N5	1.140 (3)	**C3 − C4 − C8**	124.5 (2)
O1 − C10	1.280 (3)	**N2 − C5 − C1**	173.6 (3)
O2 − C12	1.285 (3)	**N3 − C6 − C2**	178.6 (3)
C9 − C10	1.496 (4)	**N4 − C7 − C3**	178.6 (3)
C10 − C11	1.394 (3)	**N5 − C8 − C4**	173.8 (3)
C11 − C12	1.389 (4)	**C10 − O1 − Cr1**	126.54 (16)
C12 − C13	1.498 (3)	**C12 − O2 − Cr1**	126.50 (16)
N6 − C19	1.135 (3)	**O1 − C10 − C11**	123.9 (2)
C19 − C20	1.450 (4)	**O1 − C10 − C9**	115.2 (2)
Cr2 − O6	1.9379 (17)	**C11 − C10 − C9**	121.0 (3)
Cr2 − O6^{i}	1.9379 (17)	**C12 − C11 − C10**	125.1 (3)
Cr2 − O5	1.9389 (16)	**O2 − C12 − C11**	123.8 (2)
Cr2 − O5^{i}	1.9389 (16)	**O2 − C12 − C13**	115.3 (3)
Cr2 − N10	2.040 (3)	**C11 − C12 − C13**	120.9 (3)
Cr2 − N7	2.067 (3)	**N10 − Cr2 − N7**	180.000
N7 − C21	1.370 (3)	**C21 − N7 − C21^{i}**	105.3 (3)
N7 − C21^{i}	1.370 (3)	**C21 − N7 − Cr2**	127.34 (15)
C21 − C22	1.386 (4)	**C21^{i} − N7 − Cr2**	127.34 (15)
C21 − C23	1.430 (3)	**N7 − C21 − C22**	111.3 (2)
C22 − C22^{i}	1.412 (5)	**N7 − C21 − C23**	124.3 (3)
C22 − C24	1.424 (4)	**C22 − C21 − C23**	124.3 (3)
C23 − N8	1.142 (3)	**C21 − C22 − C21^{i}**	106.04 (13)
C24 − N9	1.136 (3)	**C21 − C22 − C24**	126.7 (2)
O5 − C26	1.278 (3)	**C22^{i} − C22 − C24**	127.12 (15)
O6 − C28	1.279 (3)	**N8 − C23 − C21**	172.4 (3)
C25 − C26	1.505 (3)	**N9 − C24 − C22**	178.4 (3)
C26 − C27	1.396 (3)	**C26 − O5 − Cr2**	127.86 (15)
C27 − C28	1.391 (4)	**C28 − O6 − Cr2**	127.86 (15)
C28 − C29	1.501 (3)	**O5 − C26 − C27**	124.4 (2)
O3 − C15	1.277 (3)	**O5 − C26 − C25**	115.2 (2)
O4 − C17	1.279 (3)	**C27 − C26 − C25**	120.4 (3)
C14 − C15	1.500 (4)	**C28 − C27 − C26**	124.4 (3)
C15 − C16	1.392 (3)	**O6 − C28 − C27**	124.4 (2)
C16 − C17	1.391 (4)	**C15 − O3 − Cr1**	127.55 (16)

C17 − C18	1.498 (3)	**C17 − O4 − Cr1**	126.85 (15)
C30 − N10	1.137 (5)	**N10 − C30 − C31**	180.000
C30 − C31	1.453 (6)	**C30 − N10 − Cr2**	180.000
N11 − C32	1.126 (5)	**N11 − C32 − C33**	178.6 (5)
C32 − C33	1.454 (5)	**C4 − N1 − C1 − C2**	0.4 (3)
O3 − Cr1 − O2	88.27 (7)	**Cr1 − N1 − C1 − C2**	− 172.81 (17)
O3 − Cr1 − O4	91.65 (7)	**Cr1 − N1 − C1 − C5**	7.7 (4)
O2 − Cr1 − O4	177.12 (8)	**N1 − C1 − C2 − C3**	0.1 (3)
O3 − Cr1 − O1	178.06 (8)	**C5 − C1 − C2 − C3**	179.5 (3)
O2 − Cr1 − O1	90.72 (7)	**C1 − C2 − C3 − C4**	− 0.5 (3)
O4 − Cr1 − O1	89.46 (7)	**C6 − C2 − C3 − C4**	176.5 (3)
O3 − Cr1 − N6	87.75 (8)	**C1 − N1 − C4 − C3**	− 0.8 (3)
O2 − Cr1 − N6	92.58 (8)	**Cr1 − N1 − C4 − C3**	172.49 (17)
O4 − Cr1 − N6	90.29 (8)	**C1 − N1 − C4 − C8**	174.1 (2)
O1 − Cr1 − N6	90.66 (8)	**Cr1 − N1 − C4 − C8**	− 12.6 (4)
O3 − Cr1 − N1	91.74 (8)	**C2 − C3 − C4 − N1**	0.9 (3)
O2 − Cr1 − N1	87.88 (8)	**C7 − C3 − C4 − C8**	6.4 (4)
O4 − Cr1 − N1	89.24 (7)	**Cr1 − O1 − C10 −C11**	9.4 (4)
O1 − Cr1 − N1	89.86 (8)	**Cr1 − O1 − C10 − C9**	− 170.84 (17)
N6 − Cr1 − N1	179.30 (9)	**Cr1 − O2 − C12 −C11**	− 12.6 (4)
C4 − N1 − C1	105.5 (2)	**Cr1 − O2 − C12 −C13**	168.80 (18)
C4 − N1 − Cr1	126.80 (16)	**Cr1 − O3 − C15 −C16**	− 2.3 (4)
C1 − N1 − Cr1	127.31 (17)	**Cr1 − O3 − C15 −C14**	177.89 (19)
N1 − C1 − C2	111.3 (2)	**Cr1 − O4 − C17 −C16**	− 7.5 (4)
N1 − C1 − C5	124.4 (2)	**Cr1 − O4 − C17 −C18**	171.55 (17)
C2 − C1 − C5	124.3 (2)	**C21 − N7 − C21 −C22**	− 0.50 (15)
C1 − C2 − C3	106.0 (2)	**Cr2 − N7 − C21 −C22**	179.50 (15)
C1 − C2 − C6	127.4 (4)	**C21 − N7 − C21 −C23**	176.9 (3)
C3 − C2 − C6	126.5 (2)	**Cr2 − N7 − C21 −C23**	−3.1 (3)
C4 − C3 − C2	105.8 (2)	**N7 − C21 − C22 − C22^{i}**	1.3 (4)
C4 − C3 − C7	127.6 (2)	**N7 − C21 − C22 − C24**	− 175.1 (2)
C19 − N6 − Cr1	174.9 (2)	**Cr2 − O5 − C26 −C27**	− 1.6 (4)
Cr2 − O5 − C26 −C25	178.05 (17)	**Cr2 − O6 − C28 −C29**	171.71 (18)
Cr2 − O6 − C28 −C27	−7.4 (4)	**C26 − C27 − C28 -C29**	− 178.3 (3)

Symmetry code: (i) *–x*, *–y*, 0.5-*z* .

Scheme S11. Numbering scheme of tetraacetonitrile-bis(tetracyanopyrrolido)manganese(II) acetonitrile solvate $[Mn(TCP)_2{\cdot}4CH_3CN]{\cdot}2CH_3CN$ (**15**)

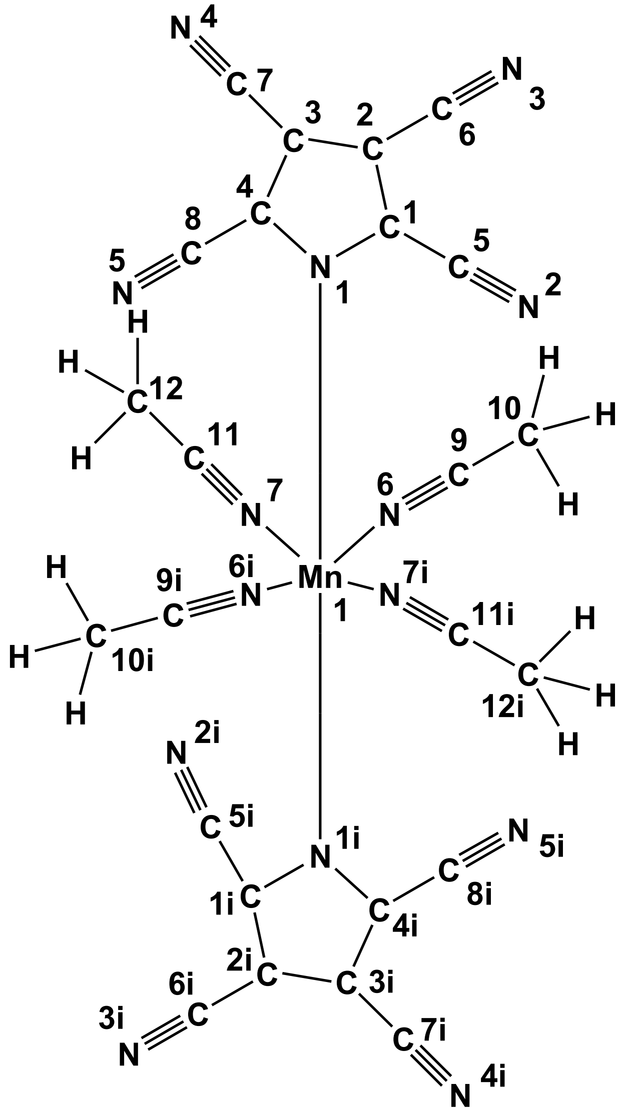


Table S16. Selected bond lengths (Å) angles (°) and torsion angles (°) of **15**.

Mn1—N7 ^{i}	2.2249(8)	**C9—N6—Mn1**	174.48(7)
Mn1—N7	2.2250(8)	**C11—N7—Mn1**	161.51(7)
Mn1—N6	2.2299(8)	**N1—C1—C2**	111.68(7)
Mn1—N6 ^{i}	2.2300(8)	**N1—C1—C5**	123.94(7)
Mn1—N1 ^{i}	2.2600(7)	**C2—C1—C5**	124.37(7)

Mn1—N1	2.2600(7)	**C1—C2—C3**	105.78(7)
N1—C1	1.361(1)	**C1—C2—C6**	126.20(8)
N1—C4	1.3635(10)	**C3—C2—C6**	128.00(8)
N2—C5	1.1499(12)	**C4—C3—C2**	105.57(7)
N3—C6	1.1451(13)	**C4—C3—C7**	127.06(8)
N4—C7	1.1466(12)	**C2—C3—C7**	127.35(8)
N5—C8	1.1500(13)	**N1—C4—C3**	111.78(7)
N6—C9	1.1416(12)	**N1—C4—C8**	123.25(7)
N7—C11	1.1420(11)	**C3—C4—C8**	124.96(8)
C1—C2	1.3987(11)	**N2—C5—C1**	176.49(9)
C1—C5	1.4292(12)	**N3—C6—C2**	178.64(11)
C2—C3	1.4087(12)	**N4—C7—C3**	179.23(10)
C2—C6	1.4215(12)	**N5—C8—C4**	177.57(10)
C3—C4	1.3979(11)	**N6—C9—C10**	179.23(10)
C3—C7	1.4228(12)	**N7—C11—C12**	177.85(10)
C4—C8	1.4299(12)	**N8—C13—C14**	178.86(13)
C9—C10	1.4524(13)	**C4—N1—C1—C2**	− 0.19(9)
C11—C12	1.4511(12)	**Mn1—N1—C1—C2**	177.39(5)
N8—C13	1.1359(15)	**C4—N1—C1—C5**	−179.45(8)
C13—C14	1.4526(16)	**Mn1—N1—C1—C5**	−1.87(12)
N7^{i}—Mn1—N7	180.000	**N1—C1—C2—C3**	0.01(10)
N7^{i}—Mn1—N6	90.32(3)	**C5—C1—C2—C3**	179.27(8)
N7—Mn1—N6	89.68(3)	**N1—C1—C2—C6**	−178.54(8)
N7^{i}—Mn1—N6^{i}	89.68(3)	**C5—C1—C2—C6**	0.71(14)
N7—Mn1—N6^{i}	90.32(3)	**C1—C2—C3—C4**	0.17(9)
N6—Mn1—N6^{i}	180.000	**C6—C2—C3—C4**	178.69(9)
N7^{i}—Mn1—N1^{i}	89.60(3)	**C1—C2—C3—C7**	−178.32(8)
N7—Mn1—N1^{i}	90.40(3)	**C6—C2—C3—C7**	0.20(15)
N6—Mn1—N1^{i}	90.59(3)	**C1—N1—C4—C3**	0.31(9)
N6^{i}—Mn1—N1^{i}	89.41(3)	**Mn1—N1—C4—C3**	−177.26(5)
N7^{i}—Mn1—N1	90.39(3)	**C1—N1—C4—C8**	−178.35(8)
N7—Mn1—N1	89.60(3)	**Mn1—N1—C4—C8**	4.09(12)
N6—Mn1—N1	89.41(3)	**C2—C3—C4—N1**	− 0.3(1)
N6^{i}—Mn1—N1	90.59(3)	**C7—C3—C4—N1**	178.19(8)
N1^{i}—Mn1—N1	180.000	**C2—C3—C4—C8**	178.33(8)
C1—N1—C4	105.19(7)	**C7—C3—C4—C8**	−3.18(14)
C1—N1—Mn1	127.10(5)		
C4—N1—Mn1	127.66(6)		

Symmetry code: (i) 1-*x*, 1-*y*, 2-*z*.

Scheme S12. Numbering scheme of trimethylammoniumtetracyanopyrrolide

[Me_3NH]TCP (**16**)

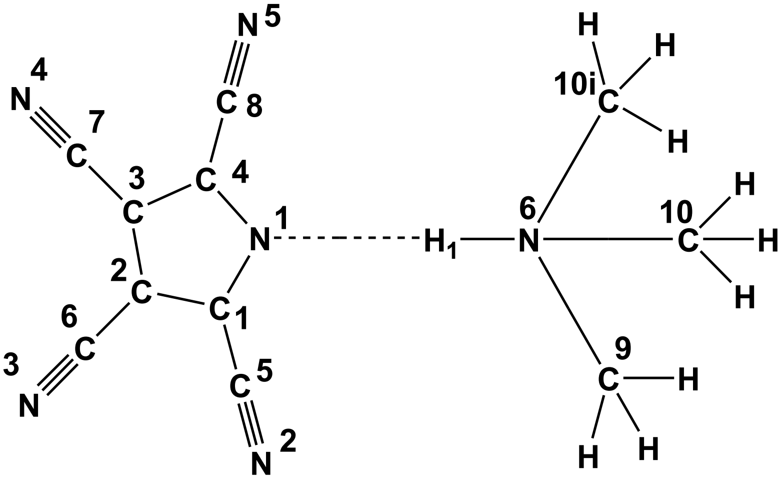


Table S17. Selected bond lengths (Å) angles (°) and torsion angles (°) of **16**.

N1 − C1	1.3567 (15)	**N1− C1 − C5**	122.25 (10)
N1 − C4	1.3574 (13)	**C2 − C1 − C5**	125.51 (11)
N2 − C5	1.1470 (16)	**C1 − C2 − C3**	105.19 (10)
N3 − C6	1.1485 (17)	**C1 − C2 − C6**	128.81 (10)
N4 − C7	1.1495 (14)	**C3 − C2 − C6**	125.99 (10)
N5 − C8	1.1488 (17)	**C4 − C3 − C2**	105.63 (9)
C1 − C2	1.3996 (15)	**C4 − C3 − C7**	127.93 (10)
C1 − C5	1.4299 (15)	**C2 − C3 − C7**	126.44 (10)
C2 − C3	1.4094 (15)	**N1 − C4 − C3**	111.93(10)
C2 − C6	1.4171 (17)	**N1 − C4 − C8**	123.37 (10)
C3 − C4	1.3995 (15)	**C3 − C4 − C8**	124.69 (9)
C3 − C7	1.4184 (15)	**N2 − C5 − C1**	178.32 (14)
C4 − C8	1.4305 (16)	**N3 − C6 − C2**	177.88 (12)
N6 − H1	**0.915 (18)**	**N4 − C7 − C3**	179.31 (13)
N1 − H1	**1.955(180)**	**N5 − C8 − C4**	175.51 (12)
N6 − C10^{i}	1.4876 (11)	**C10**^{i} **− N6 − C10**	111.17 (10)
N6 − C10	1.4877 (11)	**C10**^{i} **− N6 − C9**	111.46 (6)

N6 − C9	1.4879 (15)	**C10 − N6 − C9**	111.46 (6)
C1− N1 − C4	105.00 (9)	**C1 − C2 − C3 − C7**	180.000
N1− C1 − C2	112.24 (9)	**C6 − C2 − C3 − C7**	0.000
C4 − N1 − C1 − C2	0.000	**C1 − N1 − C4 − C3**	0.000
C4 − N1 − C1 − C5	180.000	**C1 − N1 − C4 − C8**	180.000
N1 − C1 − C2 − C3	0.000	**C2 − C3 − C4 − N1**	0.000
C5 − C1 − C2 − C3	180.000	**C7 − C3 − C4 − N1**	180.000
N1 − C1 − C2 − C6	180.000	**C2 − C3 − C4 − C8**	180.000
C5 − C1 − C2 − C6	0.000	**C7 − C3 − C4 − C8**	0.000
C1 − C2 − C3 − C4	0.000		
C6 − C2 − C3 − C4	180.000		

Symmetry code: (i) *x*, 0.5–*y*, *z*.

Scheme S13. Numbering scheme of tripropylammoniumtetracyanopyrrolide

[^{n}Pr$_3$NH]TCP (**17**)

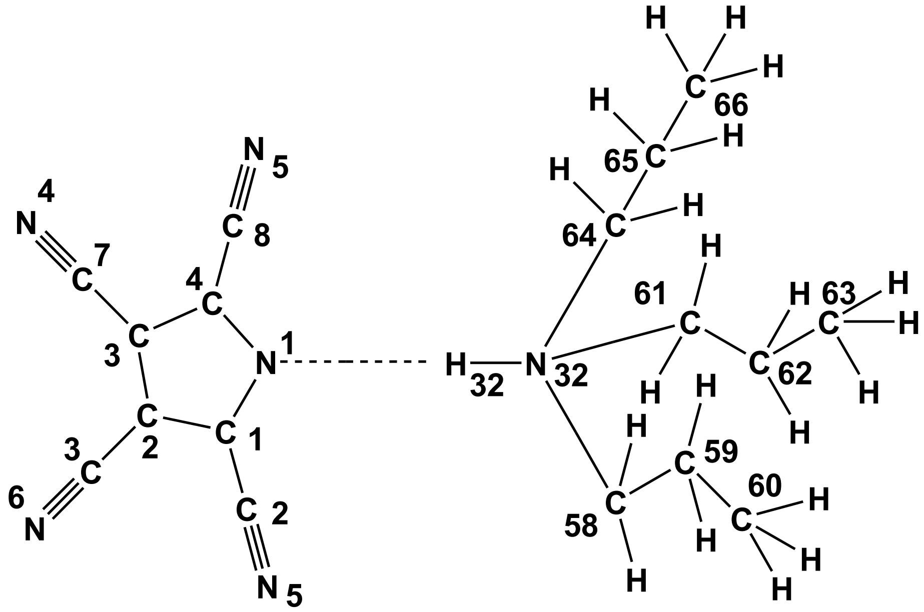


Table S18. Selected bond lengths (Å) angles (°) and torsion angles (°) of **17**.

N1 − C4	1.349 (2)	**N32 − C61 − C62**	112.93 (14)
N1 − C1	1.353 (2)	**C64 − C65 − C66**	110.01 (17)
N2 − C5	1.147 (3)	**N32 − C64 − C65**	114.67 (14)
N3 − C6	1.149 (2)	**C61 − C62 − C63**	110.12 (17)
N4 − C7	1.141 (2)	**C4 − N1 − C1 − C2**	− 0.1 (2)
N5 − C8	1.145 (2)	**C4 − N1 − C1 − C5**	177.74 (18)
C1 − C2	1.398 (2)	**N1 − C1 − C2 − C3**	0.5 (2)
C1 − C5	1.430 (3)	**C5 − C1 − C2 − C3**	−177.21 (18)
C2 − C3	1.409 (2)	**N1 − C1 − C2 − C6**	179.99 (18)
C2 − C6	1.418 (2)	**C5 − C1 − C2 − C6**	2.3 (3)
C3 − C4	1.397 (2)	**C1 − C2 − C3 − C4**	− 0.70 (19)
C3 − C7	1.414 (3)	**C6 − C2 − C3 − C4**	179.82 (17)
C4 − C8	1.429 (2)	**C1 − C2 − C3 − C7**	179.49 (18)
N32 − H32	**1.0000 (13)**	**C6 − C2 − C3 − C7**	0.0 (3)
N1 − H32	**2.1005 (13)**	**C1 − N1 − C4 − C3**	− 0.4 (2)

N32 − C58	1.501 (2)	**C1 − N1 − C4 − C8**	− 179.50 (16)
N32 − C64	1.505 (2)	**C2 − C3 − C4 − N1**	0.7 (2)
N32 − C61	1.507 (2)	**C7 − C3 − C4 − N1**	−179.48 (17)
C58 − C59	1.508 (3)	**C2 − C3 − C4 − C8**	179.79 (16)
C59 − C60	1.514 (3)	**C7 − C3 − C4 − C8**	− 0.4 (3)
C61 − C62	1.512 (3)	**C64− N32− C58− C59**	− 50.99 (19)
C62 − C63	1.516 (3)	**C61− N32− C58− C59**	− 178.34 (14)
C64 − C65	1.509 (3)	**N32− C58− C59− C60**	−169.92 (15)
C65 − C66	1.520 (3)	**C58− N32− C61− C62**	− 63.47 (18)
C4 − N1 − C1	104.27 (14)	**C64− N32− C61− C62**	168.14 (14)
N1 − C1 − C2	112.67 (15)	**N32− C61− C62− C63**	− 176.46 (15)
N1 − C1 − C5	121.72 (17)	**C58− N32− C64− C65**	− 59.4 (2)
C2 − C1 − C5	125.56 (16)	**C61− N32− C64− C65**	68.0 (2)
C1 − C2 − C3	105.11 (15)	**N32− C64− C65− C66**	− 177.15 (17)
C1 − C2 − C6	127.98 (16)		
C3 − C2 − C6	126.91 (16)		
C4 − C3 − C2	104.94 (15)		
C4 − C3 − C7	127.22 (16)		
C2 − C3 − C7	127.84 (16)		
N1 − C4 − C3	113.00 (15)		
N1 − C4 − C8	121.97 (16)		
N2 − C5 − C1	177.7 (2)		
N3 − C6 − C2	179.9 (2)		
N4 − C7 − C4	179.4 (2)		
N5 − C8 − C4	177.3 (2)		
C58 − N32 − C64	113.59 (13)		
C58 − N32 − C61	111.70 (13)		
C64 − N32 − C61	111.63 (13)		
N32 − C58 − C59	114.67 (14)		

5.4 List of figures

5.5 List of schemes

5.6 List of tables

6. References

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Curriculum vitae

Personal Data:

Full name: Omar Mowafaq Younis AL-Ramadhani

Gender: Male

Date of birth: 03 August 1976

Place of birth: Mosul, Iraq

Nationality: Iraqi

Family status: Married

Languages: Arabic (native)
English (professional proficiency)
German (working proficiency)

Email: omar.younis2@uni-rostock.de
omar76a@yahoo.com

Education:

1991 – 1994: AL-Garbia secondary school, Mosul, Iraq

1994 – 1998: B.Sc., General Chemistry, University of Mosul, College of Science
Department of Chemistry, Iraq

1998 – 2000: M.Sc., Inorganic Chemistry, University of Mosul, College of Science
Department of Chemistry, Iraq

2012 – : Beginning of doctoral studies, University of Rostock , Institute of Chemistry
Department of Inorganic Chemistry, Germany

Major Research: Synthesis and characterization of new CN-based transition metal complexes

Scholarships awarded:

1. Scholarship Awarded by DAAD as doctoral researcher for the year 2011 to 2012 at Friedrich-Schiller-University Jena, Germany.

2. Scholarship Awarded by DAAD as doctoral researcher for the year 2012 to 2015 at University of Rostock, Germany.

Employment Record:

2001 − 2006: Assist. Lecturer of Inorganic Chemistry

2007 – present: Lecturer of Inorganic Chemistry, University of Mosul, College of Science
Department of Chemistry, Iraq

Teaching Tasks:

- Practical Inorganic Chemistry (*Synthesis of Inorganic Compounds, including techniques and characterization*). Laboratories **2nd** grade, University of Mosul, College of Science, Department of Chemistry, Iraq

- Practical Inorganic Chemistry (*Coordination Chemistry, Preparation and characterization of Coordination Compounds).* Laboratories **3rd** grade, University of Mosul, College of Science, Department of Chemistry, Iraq

Publications:

1. Synthesis and Characterization of Dinuclear Metal Complexes Stabilized by Tetradentate Schiff Base Ligands, Eid A. Abdalrazaq, Omar M. AL-Ramadane, Khansa S. AL-Numa, *American Journal of Applied Sciences* **2010**, *7*, 628-633.

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Research Interests:

- Organometallic Chemistry
- Bioinorganic Chemistry
- Coordination Chemistry

Rostock, 21 April 2016

Omar Mowafaq Younis