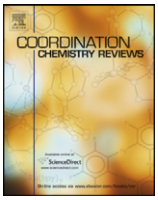
Coordination Chemistry Reviews 255 (2011) 1360–1386

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

The unusual coordination chemistry of phosphorus-rich linear and cyclic oligophosphanide anions

Santiago Gómez-Ruiz[a], Evamarie Hey-Hawkins[b,*]

[a] Departamento de Química Inorgánica y Analítica, E.S.C.E.T. Universidad Rey Juan Carlos, Calle Tulipán s/n, 28933, Móstoles, Spain
[b] Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany

Contents

ARTICLE INFO

Article history:
Received 31 August 2010
Accepted 9 November 2010
Available online 19 November 2010

The authors wish to dedicate this work to the memory of Prof. Dr. H.C. Hans-Georg von Schnering, an outstanding scientist and distinguished colleague.

Keywords:
Oligophosphanides
P ligands
Phosphorus-rich anions
Phosphorus
Metal phosphides

ABSTRACT

In this review, the synthesis, reactivity and properties of linear and cyclic oligophosphanides are described. Specifically the structures and versatile reactivity of the anionic ligands $(P_4R_4)^{2-}$ (R = Bu^t, Ph, Mes), $(P_4HR_4)^-$ (R = Ph and Mes) and *cyclo*-$(P_5Bu^t{}_4)^-$ towards main group and transition metal complexes is elucidated. In addition, potential application of metal oligophosphanides as precursors for the preparation of metal phosphides is also briefly discussed.

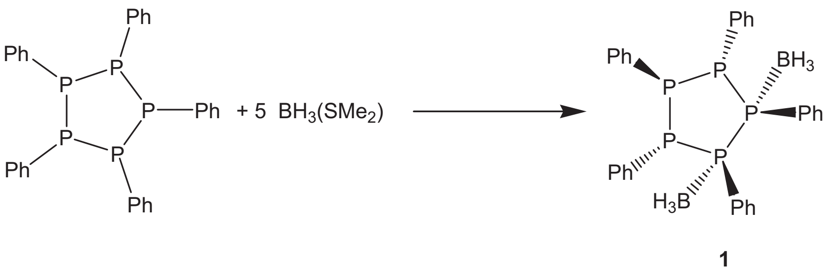
1. Introduction

The reports by Baudler and some other authors on their extensive investigations on cyclooligophosphanes *cyclo*-$(PR)_n$ [1] and catenated polyphosphanes (with hydrogen, organic or even organometallic substituents) [2] have shown that the chemistry of these compounds is analogous to that of related carbon com-

---

* Corresponding author. Tel.: +49 341 9736151; fax: +49 341 9739319.
E-mail addresses: santiago.gomez@urjc.es (S. Gómez-Ruiz), hey@uni-leipzig.de (E. Hey-Hawkins).

0010-8545/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2010.11.020

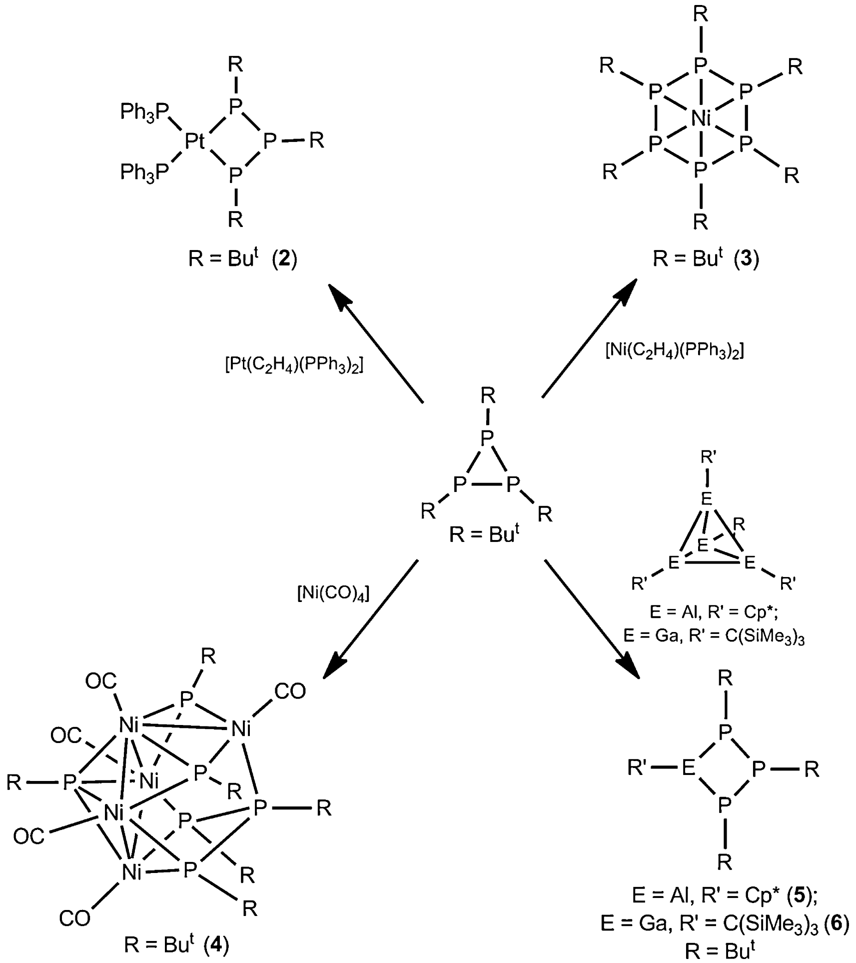


Scheme 1. Reaction of *cyclo*-P_5Ph_5 with BH_3.

pounds [3]. Among other things, this analogy is due to the existence of constitutional and configurational isomerism and valence tautomerism, as well as the existence of mixed P–C ring systems, and is rationalized by the isolobality of the fragments P/CR, PR/CR_2 and PR_2/CR_3 [1–3]. Like carbon, phosphorus shows a notable propensity to form a wide variety of P_n frameworks due to the comparatively high bond energy of P–P single bonds (ca. 200 kJ/mol, the highest value within group 15) [4].

While the chemistry of catena and cyclic polyphosphanes has been studied in depth, especially with the help of ^{31}P NMR spectroscopy and X-ray crystallography, less is known about metal complexes of these species. Only a few examples have been described, and all of them have shown that cyclic [5] and catenated oligophosphanide anions [6] exhibit a rich coordination chemistry, because each P atom may be involved in coordination *via* its free electron pair.

On the other hand, the coordination chemistry of oligophosphanide anions has hardly been explored until recently, as selective and facile syntheses were mostly unknown for the corresponding oligophosphanide anions. Besides the academic challenge, metal complexes with anionic polyphosphorus ligands are of interest as potential precursors for the development of rational syntheses of binary metal phosphides (M_xP_y), which are compounds with rare structures and interesting properties for materials science [7], such as corrosion resistance [8], catalysts for hydrodesulfurization and hydrodenitrogenation of petroleum fuels [9], oxygen barriers in capacitors [10], and magnetic properties [11]. Even today, the number of accessible metal complexes with linear and cyclic oligophosphanide ligands is still relatively small. Thus, this article will review the synthetic methods and reactivity for the preparation of metal complexes with anionic polyphosphorus rings and chains, as well as their structural and spectroscopic properties.



Scheme 2. Synthesis of metal oligophosphanide complexes using *cyclo*-$P_3Bu^t_3$ as starting material.

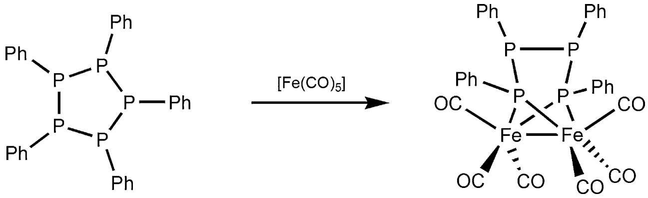
2. General synthetic methods for the preparation of metal oligophosphanides

The preparation and purification of metal complexes with oligophosphanide ligands has always been a highly challenging task. Several complexes have been reported in the literature which in many cases have been obtained serendipitously or as inseparable mixtures and were characterized only by ^{31}P NMR spectroscopy or X-ray crystallography.

Additionally, some procedures reported for the rational preparation of this kind of complexes have led to mixtures of compounds from which some target products could be isolated and fully characterized. In general, five different synthetic methods have been developed for the preparation of metal complexes with (P_nR_n) units:

Method 1: Formation of single Lewis acid–base adducts of the type *cyclo*-(P_nR_n)(ML_m)$_x$ from cyclooligophosphanes and metal complex fragments.
Method 2: The reaction of cyclooligophosphanes of the type *cyclo*-(P_nR_n) (R = alkyl, aryl; n = 3–6) with complexes of valence electron-rich metals with P–P bond cleavage.
Method 3: Dehalogenation reaction of halophosphanes with phosphane or phosphanido complexes.
Method 4: Oligomerization of phosphanes or phosphanides to form metal complexes with oligophosphanediide ligands.
Method 5: Reduction of cyclooligophosphanes with alkali metals and subsequent transmetallation of the formed alkali metal oligophosphanides with metal halides.

Classic examples of synthetic *Method 1* are the reactions of cyclooligophosphanes with metal carbonyls [$M(CO)_n$] which lead to substitution of one or more CO ligands by a phosphorus atom of the cyclooligophosphane [12,13]. In these reactions, the ring size is usually retained, but some ring expansions have also been observed.



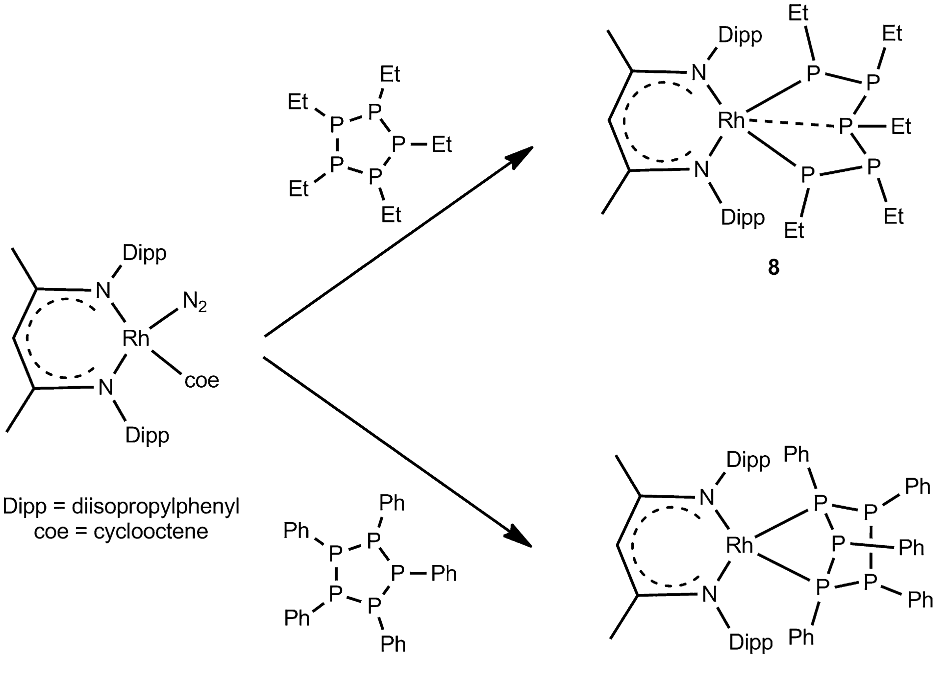
Scheme 3. Synthesis of [Fe_2(μ-P_4Ph_4)$(CO)_6$] (**7**).

Analogously, compounds such as *cyclo*-1,2-$(BH_3)_2(P_5Ph_5)$ (**1**) have been also synthesized by this method (Scheme 1) [14].

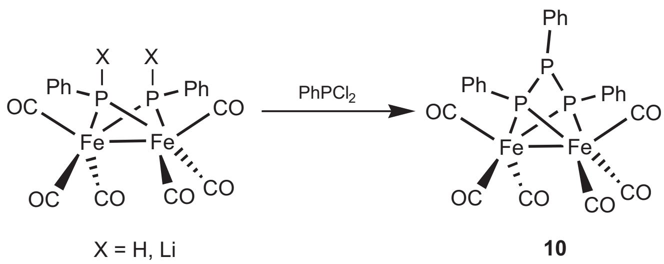
Using *Method 2*, Fenske and co-workers isolated a platinum(II) complex with a $(P_3Bu^t{}_3)^{2-}$ ligand from the reaction of *cyclo*-($P_3Bu^t{}_3$) and platinum(0) complexes (Scheme 2). With nickel(0) complexes, either ring expansion to give a nickel complex with the *cyclo*-$P_6Bu^t{}_6$ ligand, or ring opening combined with ring degradation (to PBu^t fragments) to give a pentanuclear cluster (Scheme 2) was observed, depending on the starting material [15]. Analogously, Schnöckel et al. and Uhl et al. prepared cyclic main group triphosphanediide complexes *cyclo*-($ER'PBu^t{}_3$) (E = Al, R′ = Cp*; E = Ga, R′ = $C(SiMe_3)_3$) by reaction of alkyl gallium(I) or cyclopentadienyl aluminium(I) compounds with *cyclo*-($P_3Bu^t{}_3$) (Scheme 2) [16,17].

Also using *Method 2*, West and Rheingold prepared the dinuclear iron complex [Fe_2(μ-P_4Ph_4)$(CO)_6$] (**7**) and other related compounds by reaction of *cyclo*-(P_5R_5) (R = Me, Et, Ph) with [$Fe(CO)_5$] (Scheme 3) [18].

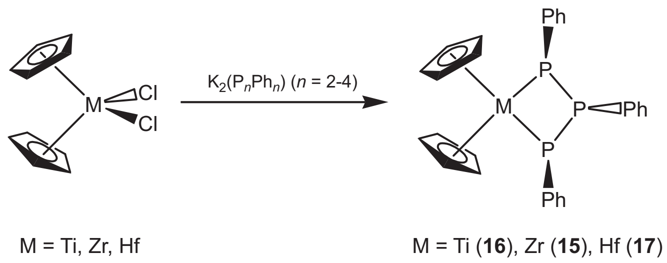
A similar method has recently been used by Stephan and co-workers for the formation of other transition metal complexes [19] such as the rhodium(III) compound [Rh(NacNac)(P_5Et_5)] (**8**) and the rhodium(I) complex [Rh(NacNac)(*cyclo*-P_5Ph_5)] (**9**) which have been obtained by the reaction of [Rh(NacNac)(coe)(N_2)] (coe = cyclooctene) with *cyclo*-(P_5R_5) (R = Et, Ph), respectively (Scheme 4). The differing nature of the products of the reactions of *cyclo*-P_5R_5 (R = Ph, Et) was probably due to the higher donor ability and lesser steric requirements of ethyl substituents in compari-



Scheme 4. Synthesis of rhodium complexes.



Scheme 5. Synthesis of $[Fe_2(\mu\text{-}P_3Ph_3)(CO)_6]$ (**10**).



Scheme 7. Synthesis of $[M(\eta^5\text{-}C_5H_5)_2(P_3Ph_3)]$ [M = Ti (**16**), Zr (**15**), Hf (**17**)].

son to phenyl groups. Thus, oxidative addition of *cyclo*-P_5Et_5 gives the more stable rhodium(III) product (**8**) while the less electron-rich *cyclo*-P_5Ph_5 favors formation of a rhodium(I) product such as **9** [19a].

Other related compounds were prepared by *Method 3* through reaction of $PhPCl_2$ with dinuclear phosphanido- or lithium phosphanido-bridged iron complexes (Scheme 5) [20,21].

In addition, we obtained the complexes $[Cp^{\circ}MoCl_2(\eta^3\text{-}P_4HCy_4)]$ (**11**) and $[Cp^{\circ}{}_2Mo_2(\mu\text{-}Cl)_2(\mu\text{-}P_4Ph_4)]$ (**12**) in very low yield by reaction of the paramagnetic molybdenum phosphane complexes $[Cp^{\circ}MoCl_4(PH_2R)]$ ($Cp^{\circ} = \eta^5\text{-}C_5EtMe_4$, R = Cy or Ph) with two equivalents of NEt_3; the mechanism of this reaction was unclear, but could involve an intermediate molybdenum phosphinidene complex (*Method 4*) [22].

Using *Method 4*, Wright and co-workers obtained $[\{Na(tmeda)(NHMe_2)\}\{cyclo\text{-}Sb(P_4Cy_4)\}]_2$ (**13**) (Cy = cyclohexane, tmeda = $Me_2NCH_2CH_2NMe_2$) by the (1:1:1) reaction of $Sb(NMe_2)_3$, PH_2Cy and NaPHCy and also the lithium salt $[Li(tmeda)(thf)\{cyclo\text{-}As(P_3Bu^t{}_3)\}]$ (**14**) by the (1:3) reaction of $As(NMe_2)_3$ and $LiPHBu^t$ [23].

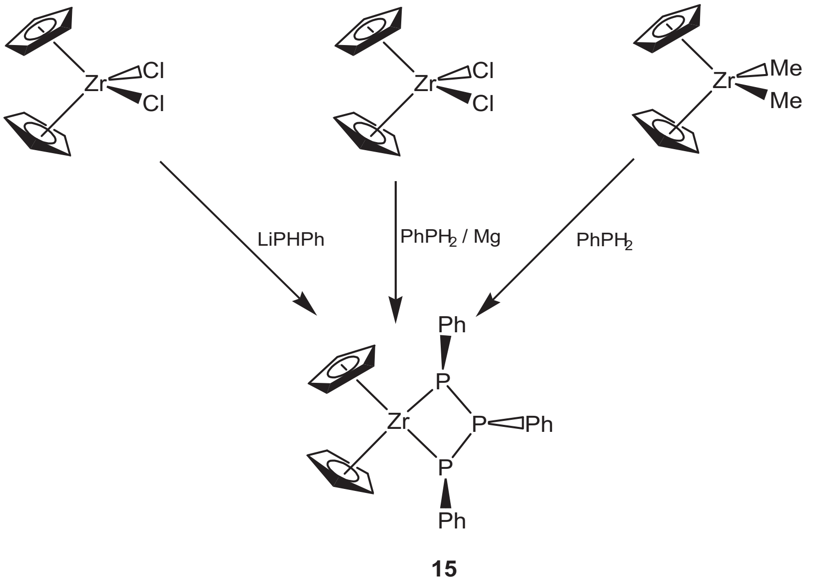
In addition, *Method 4* was employed in the synthesis of metallocene derivatives and specifically resulted in the formation of triphosphanediide ligands only. Thus, the reaction of LiPHPh or a mixture of PH_2Ph/Mg with $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ gave $[Zr(\eta^5\text{-}C_5H_5)_2(P_3Ph_3)]$ (**15**) (Scheme 6). The same zirconocene triphosphanediide (**15**) was also obtained by reaction of $[Zr(\eta^5\text{-}C_5H_5)_2Me_2]$ with PH_2Ph (Scheme 6) [24].

It seems that group 4 metallocene derivatives tend to form complexes with triphosphanediide ligands, because the chain length is not retained in the reaction of $M_2(P_nPh_n)$ (n = 2–4) with $[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (M = Ti, Zr, Hf) (*Method 5*), which always gave exclusively $[M(\eta^5\text{-}C_5H_5)_2(P_3Ph_3)]$ [M = Ti (**16**), Zr (**15**), Hf (**17**)], as was observed by Köpf and Voigtländer (Scheme 7) [25].

Another example of *Method 5* in which chain length variation occurred is the reaction of the potassium salt $K_2(P_2Bu^t{}_2)$ with $[NiCl_2(PMe_3)_2]$ to give the complex $[Ni(\eta^2\text{-}P_2Bu^t{}_2)(P_4Bu^t{}_4)]$ (**18**), in which coupling of two $(P_2Bu^t{}_2)^{2-}$ units resulted in formation of the tetraphosphanediide ligand $(P_4Bu^t{}_4)^{2-}$ (Scheme 8) [26].

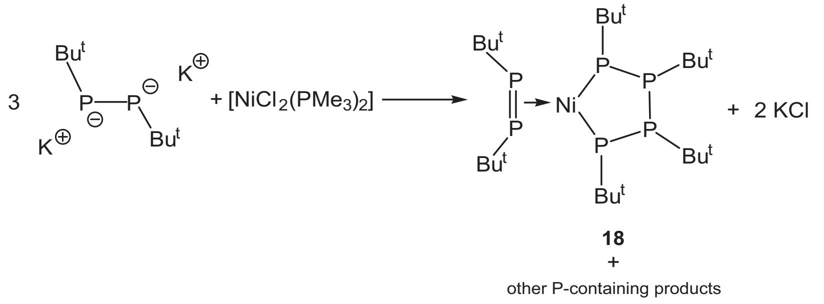
However, usually *Method 5* allows the chain length of the oligophosphanediide ligand bound to the metal to be controlled. For example, transmetallation reactions of alkali metal oligophosphanides of the type $M_2(P_nR_n)$ (n = 2–4) with some metal halides [27] as well as the reaction of $K_2(P_4Bu^t{}_4)$ with R_2ECl_2 to give *cyclo*-$(P_4Bu^t{}_4ER_2)$ [R = Me, E = Si (**19**), Ge (**20**), Sn (**21**); R = Cl, E = Si (**22**), Ge (**23**), Sn (**24**)] are clear examples of products in which the P_n chain remains intact (Scheme 9) [28].

It seems that *Method 5*, which normally retains the P_n ligand, is one of the most efficient routes for the preparation of metal oligophosphanides. However, selective preparation of highly reactive alkali metal oligophosphanides is a prerequisite. The synthesis of such compounds, $M_2(P_nR_n)$ (n = 2–4), was described more than 40 years ago by reductive cleavage of the corresponding cyclooligophosphanes with Li, Na or K [27], and other alkali metal compounds, such as $K[cyclo\text{-}(P_3Bu^t{}_2)]$ (**25**) [29], $K[cyclo\text{-}(P_5Ph_4)]$ (**26**) [30], and $Li[cyclo\text{-}(P_nBu^t{}_{n-1})]$ (n = 3 (**27**), 4 (**28**), 5 (**29**)) [31,32], were also reported, but these compounds were only obtained as inseparable mixtures.

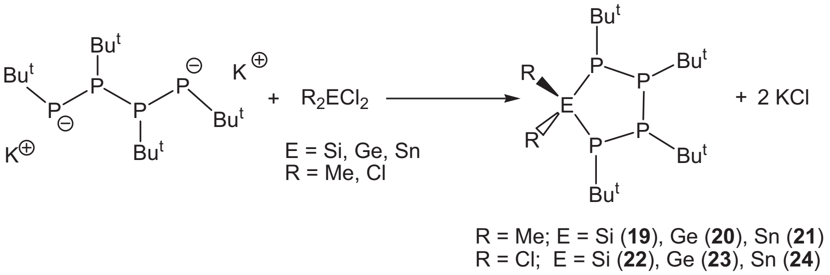


15

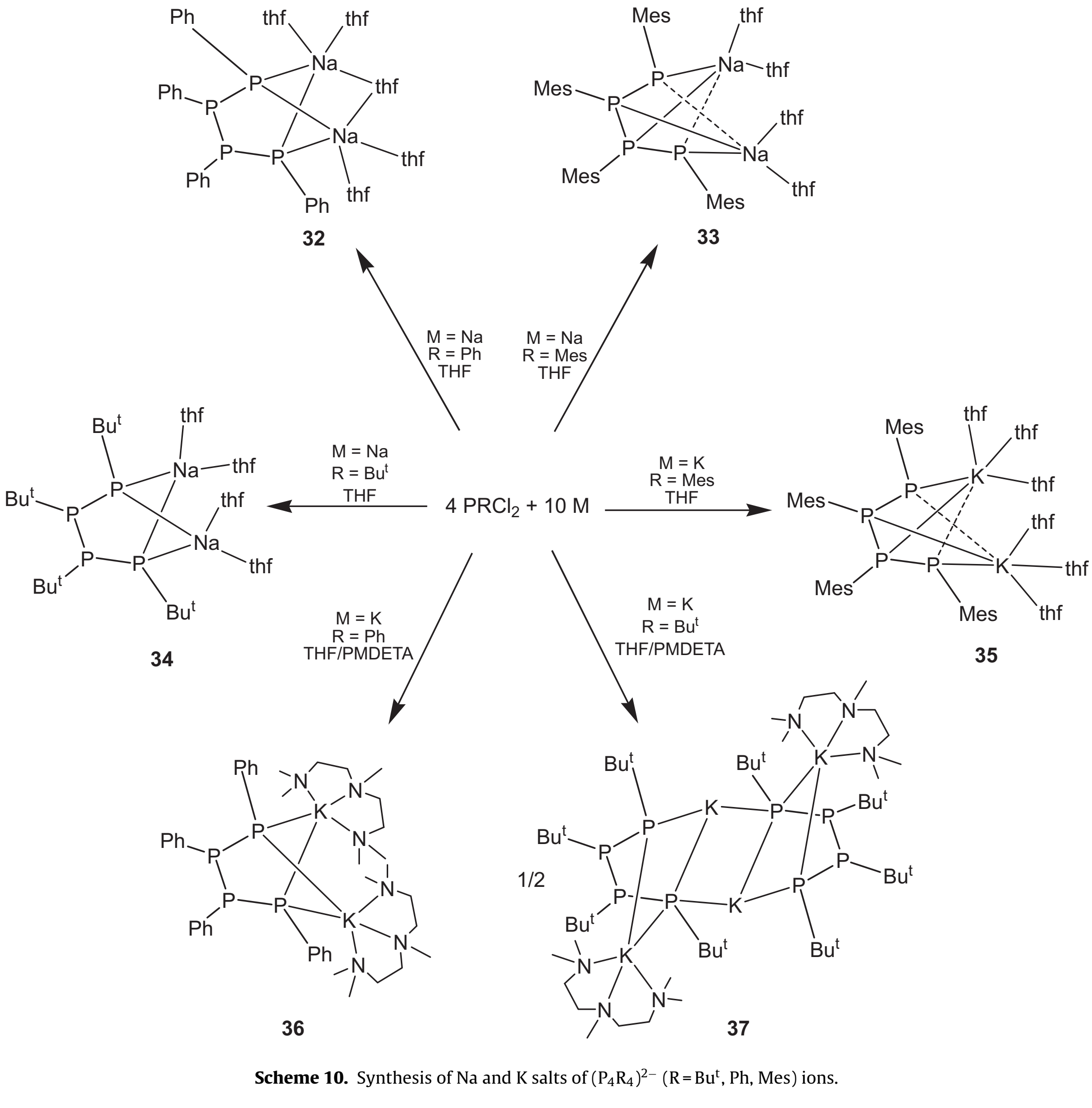
Scheme 6. Different routes for the synthesis of $[Zr(\eta^5\text{-}C_5H_5)_2(P_3Ph_3)]$ (**15**).



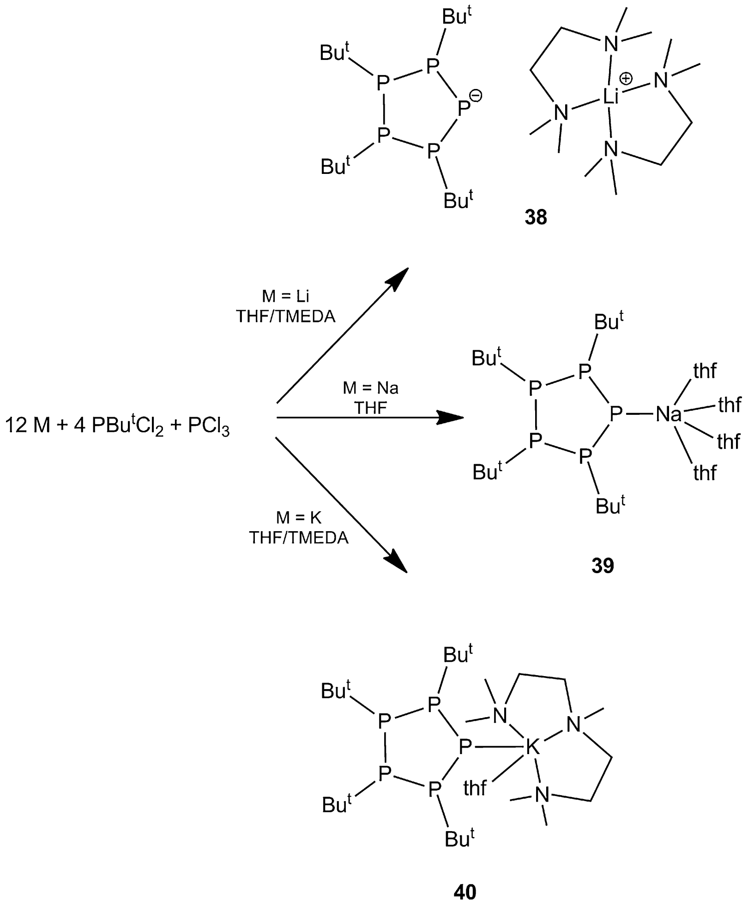
Scheme 8. Synthesis of $[\mathrm{Ni}(\eta^2\text{-}\mathrm{P_2Bu^t{}_2})(\mathrm{P_4Bu^t{}_4})]$ (**18**).



Scheme 9. Synthesis of phosphorus-rich group 14 compounds.



Scheme 10. Synthesis of Na and K salts of $(\mathrm{P_4R_4})^{2-}$ (R = Bu^t, Ph, Mes) ions.



Scheme 11. Preparation of alkali metal compounds with the *cyclo*-$(P_5Bu^t{}_4)^-$ ion.

Since 2003, the rational preparation and purification of a wide variety of alkali metal oligophosphanediides such as $[Na_2(tmeda)_3(P_3Ph_3)]$ (**30**) and $[Na_2(tmeda)_2(P_4Ph_4)]$ (**31**) (tmeda = $Me_2NCH_2CH_2NMe_2$) by Grützmacher and co-workers [33], and $[Na_2(thf)_5(P_4Ph_4)]$ (**32**), $[Na_2(thf)_4(P_4Mes_4)]$ (**33**), $[Na_2(thf)_4(P_4Bu^t{}_4)]$ (**34**), $[K_2(thf)_6(P_4Mes_4)]$ (**35**) (Mes = 2,4,6-$Me_3C_6H_2$) [34],$K_2(pmdeta)_2(P_4Ph_4)]$ (**36**) and $[K_2(pmdeta)(P_4Bu^t{}_4)]_2$ (**37**) (pmdeta = $Me_2NCH_2CH_2NMeCH_2CH_2NMe_2$) [35] by us (Scheme 10), starting from the appropriate stoichiometric ratio of $RPCl_2$ and Na (3:8 for the triphosphanediides, 4:10 for the tetraphosphanediides), were reported.

Similarly, the targeted preparation of alkali metal cyclooligophosphanides, such as $[Li(tmeda)_2]$[*cyclo*-$(P_5Bu^t{}_4)$] (**38**) [36], $Na(thf)_4$[*cyclo*-$(P_5Bu^t{}_4)$] (**39**) [37] and [K(pmedta)(thf)][*cyclo*-$(P_5Bu^t{}_4)$] (**40**) [35] (Scheme 11), was developed. Thus, suitable starting materials for the preparation of metal complexes with linear and cyclic phosphorus-rich anions were made available.

3. Alkali metal *catena*-oligophosphanediides

3.1. Dianionic phosphorus-rich chains

As mentioned above, the selective preparation of compounds of the type $[M_2(L)_x(P_nPh_n)]$ (M = Na or K, $n = 3$ or 4, L = donor molecule) was achieved only during the past decade by judicious choice of the correct stoichiometric ratio of $RPCl_2$ and alkali metal (Scheme 10). In the solid state, these compounds form isolated ion-contact complexes, in which the P_4 chain of the $(P_4R_4)^{2-}$ dianion has a *syn* arrangement and is coordinated to two alkali metal cations [33–35].

The coordination spheres of the alkali metal cations are completed by one, two or three solvent molecules. The $M_2P_4R_4$ moieties have different arrangements. The phosphorus–alkali metal distances for both the internal and terminal phosphorus atoms of the mesityl-substituted P_4 chain (complexes **33** and **35**, Table 1) are in the typical range for related sodium and potassium phosphanides. In contrast, in the phenyl- or alkyl-substituted tetraphosphanediides the alkali metal cations are exclusively coordinated by the terminal phosphorus atoms (Fig. 1).

Thus, in **33** and **35**, the phosphorus atoms in 1- and 3-position coordinate, and four-membered MP_3 chelate rings are formed. Additionally, longer contacts can be observed between the alkali metal and the second terminal phosphorus atom (Fig. 2).

The AA′BB′ coupling patterns in the ^{31}P NMR spectra of the alkali metal tetraphosphanediides **31**–**37** were analyzed. The observed

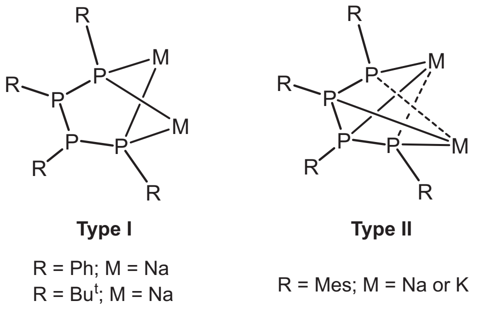


Fig. 1. Different coordination modes for $[M_2(P_4R_4)]$ (M = Na or K, R = Ph, Mes, Bu^t).

Table 1
P–P and M–P bond lengths (determined by single-crystal X-ray diffraction studies) and observed spin systems (determined by $^{31}P\{^1H\}$ NMR) in complexes with linear oligophosphanide anions.

Compound	P–P	M–P[a]	Spin system in $^{31}P\{^1H\}$ NMR	Ref.
$[Ni(\eta^2\text{-}P_2Bu^t{}_2)(P_4Bu^t{}_4)]$ (**18**)	211.0(5) 219.6(4) 223.7(5)	214.9(4) 225.7(4)	AA′BB′CC′	[26]
$[Na_2(tmeda)_2(P_4Ph_4)]$ (**30**)	216.7(4) 216.8(4) 219.0(4)	289.4(6) 291.6(6) 293.3(6) 296.0(6)	AA′BB′	[33a]
$[Na_2(thf)_5(P_4Ph_4)]$ (**32**)	216.6(1) 220.7(2)	289.2(2) 290.1(2)	AA′BB′	[34]
$[Na_2(thf)_4(P_4Mes_4)]$ (**33**)	217.7(1) 218.3(1) 225.1(1)	289.6(1) 296.1(1) 305.3(1) 316.6(1) 317.3(1) 331.6(2)	AA′BB′	[34]
$[Na_2(thf)_4(P_4Bu^t{}_4)]$ (**34**)	215.8(1) 217.0(2) 222.2(2)	281.9(1) 284.0(1) 290.1(2) 291.1(2)	AA′BB′	[34]
$[K_2(thf)_6(P_4Mes_4)]$ (**35**)	215.0(2) 215.9(2) 225.2(2)	331.4(3) 341.1(2) 343.2(3) 359.8(2) 382.3(3) 385.1(2)	AA′BB′	[34]
$[K_2(pmdeta)_2(P_4Ph_4)]$ (**36**)	217.2(1) 217.2(2) 220.7(2)	324.5(2) 327.9(2) 330.1(2) 337.2(2) 376.7(2) 381.5(2)	AA′BB′	[35]
$[K_2(pmdeta)(P_4Bu^t{}_4)]_2$ (**37**)	217.4(1) 219.0(2) 224.8(3)	308.0(2) 313.3(2) 323.1(2) 341.7(2) 342.2(2)	AA′BB′	[35]
$[Li_2(tmeda)_2(P_4Ph_4)]$ (**42**)	216.7(1) 219.0(1)	261.8(4) 265.2(4)	AA′BB′	[39]
$[K(18\text{-}crown[6])(thf)_2][P_4HMes_4]$ (**44**)	216.9(2) 219.8(2) 228.5(2)	[b]	AA′BB′X[c]	[40]
$[K(18\text{-}crown[6])(P_4HMes_4)]$ (**45**)	215.2(2) 220.2(4) 227.6(2)	336.4(2)	AA′BB′X[c]	[40]
$[K(tmeda)\{Ga(P_4Ph_4)(DAB)\}]$ (**46**)	219.4(2) 220.1(2) 223.3(3)	238.2(2)[d] 242.3(2)[d] 359.0(2)[e] 331.4(2)[e]	AA′BB′	[45]
$[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$ (**47**)	218.0(2) 220.0(3) 220.6(3) 221.3(2) 222.1(2) 224.2(3)	225.8(2) 227.1(2) 228.1(2) 229.0(2) 229.9(2) 231.5(2) 232.0(2) 239.8(2) 240.0(2) 240.3(2)	[f]	[46]
$[Cu_4(P_4Ph_4)_2(PH_2Ph)_2(PCyp_3)_2]$ (**48**)	218.6(1) 218.6(1) 220.5(1)	222.6(2) 222.7(1) 227.6(2) 228.5(2) 230.1(1) 233.4(1)	[f]	[47]
$[Rh(P_4HMes_4)(cod)]$ (**49**)	219.9(1) 221.2(1) 222.3(1)	225.7(2) 229.9(1)	ABCDX[c]	[47]

Table 1 (*Continued*)

Compound	P–P	M–P[a]	Spin system in $^{31}P\{^{1}H\}$ NMR	Ref.
$[Ni(\eta^2\text{-}P_2Mes_2)(PEt_3)_2]$ (**51**)	213.6(2)	226.1(1) 226.3(1)	AA′XX′	[48]
$[Ni(\eta^2\text{-}P_2Mes_2)(PMe_2Ph)_2]$ (**52**)	213.7(1)	224.9(1) 226.0(1)	AA′XX′	[48]
$[Pd(\eta^2\text{-}P_2Mes_2)(PBu^n{}_3)_2]$ (**53**)	214.2(2)	237.7(1) 238.2(1)	AA′XX′	[48]
$[Pd(\eta^2\text{-}P_2Mes_2)(PMe_2Ph)_2]$ (**54**)	214.1(1)	236.9(1) 238.1(1)	AA′XX′	[48]
$[Pt(P_4Mes_4)(cod)]$ (**55**)	221.4(2) 222.4(2)	232.8(2)	AA′XX′	[50]
$[Pt(P_4Mes_4)(dppe)]$ (**56**)	219.5(3) 221.4(3) 223.6(3)	233.8(2) 234.7(2)	AA′BCXX′	[50]
$[Pt(P_4Mes_4)(C{\equiv}NBu^t)_2]$ (**57**)	221.3(2) 221.3(2) 222.1(2)	231.9(1) 233.9(1)	[g]	[50]
$[Pt(P_4Mes_4)(C{\equiv}NCy)_2]$ (**58**)	221.1(2) 221.2(2) 221.5(2)	233.1(2) 233.1(2)	[g]	[50]
$[Na(thf)_3][Rh(P_3Mes_3)(cod)]$ (**59**)	221.4(2) 222.0(2)	299.9(2)[h] 315.7(2)[h] 231.5(1)[i] 232.9(2)[i]	AXX′	[51]
$[Ag_4(P_6Mes_6)_2]$ (**60**)	215.3(2) 221.3(4) 225.7(3)	248.0(2) 250.1(2) 256.3(2)	AA′BB′XX′	[51]
$[Ta(\eta^5\text{-}C_5Me_5)(Ph)(P_6Ph_5)]$ (**61**)	209.6(3) 213.3(3) 218.5(3) 221.1(3) 221.3(3)	241.6(2) 252.8(2) 256.1(2) 265.9(2)	ABCDEX	[52]
$[Na(Et_2O)_3][Na_3(Et_2O)_2Ni_3(\mu\text{-}P_2Ph_2)_2(\eta^2\text{-}P_2Ph_2)_3]$ (**62**)	211.5(3) 213.4(4) 213.5(3) 218.5(3) 219.2(3)	219.4(2)[j] 219.5(2)[j] 219.9(3)[j] 220.9(2)[j] 221.0(3)[j] 221.5(2)[j] 221.5(3)[j] 222.2(3)[j] 222.5(3)[j] 223.1(3)[j] 225.0(3)[j] 226.1(3)[j] 290.5(5)[h] 298.6(4)[h] 298.7(4)[h] 299.6(4)[h] 300.1(4)[h]	[f]	[53]
$[K(pmdeta)]_2[Ni(P_4Ph_4)(P_2Ph_2)]$ (**63**)	211.2(2) 218.9(2) 220.7(2) 221.0(2)	218.7(2)[j] 219.7(2)[j] 223.1(2)[j] 224.1(2)[j] 354.5(2)[e] 362.0(3)[e]	AA′BB′XX′[k]	[53]

---

[a] Refers to M–P bond of the P_n chain.

[b] No K–P bond, separated ions.

[c] Refers to spin system in ^{31}P NMR.

[d] Ga–P bond.

[e] K–P bond.

[f] Severe line broadening precluded numerical analysis of the coupling patterns.

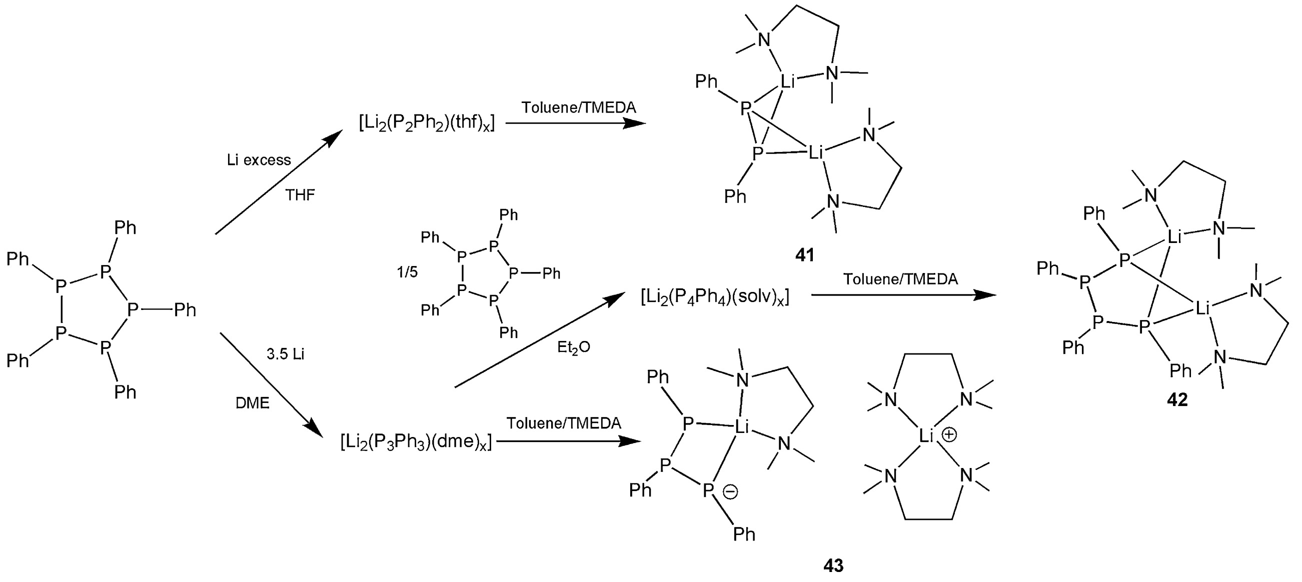
[g] Severe overlap of the signals precluded numerical analysis of the coupling patterns.

[h] Na–P bond.

[i] Rh–P bond.

[j] Ni–P bond.

[k] Due to the presence of more than one isomer in solution, the reported signals are those corresponding to the major isomer, presumably the all-*trans* isomer.



Scheme 12. Synthesis of lithium oligophosphanediides.

coupling constants indicated that the basic structural features which are observed in the solid state for these species are retained in solution.

When lithium sand was used in the reaction with $MesPCl_2$ (4:10), the formation of the corresponding $(P_4Mes_4)^{2-}$ anion was observed by ^{31}P NMR spectroscopy; however, the product could not be isolated [38].

A different synthetic approach was successfully employed for the corresponding lithium oligophosphanediides $[Li_2(tmeda)_x(P_nPh_n)]$ ($n=2, 3, 4$) by Grützmacher et al. starting from different stoichiometric amounts of pentaphenylcyclopentaphosphane and lithium (Scheme 12).

X-ray diffraction studies of some of these compounds showed that $[Li_2(tmeda)_2(P_2Ph_2)]$ (**41**) and $[Li_2(tmeda)_2(P_4Ph_4)]$ (**42**) (Fig. 3) are ion triples, while an ion pair was observed in $[Li(tmeda)_2][Li(tmeda)(P_3Ph_3)]$ (**43**). ^{31}P NMR studies supported the assumption that these structures are retained in solution [39].

3.2. Monoprotonated anionic phosphorus-rich chains

Monoprotonated tetraphosphanide anions $(P_4HMes_4)^-$ were obtained as potassium salts $[K(18\text{-crown}[6])(thf)_2][P_4HMes_4]$ (**44**) and $[K(18\text{-crown}[6])(P_4HMes_4)]$ (**45**) from the reaction of $K_2(P_4Mes_4)$ with one equivalent of HCl (dissolved in Et_2O) and subsequent addition of 18-crown[6] (Scheme 13).

Compound **44** displays an ion-separated structure in which the potassium cation is coordinated by 18-crown[6] and two THF

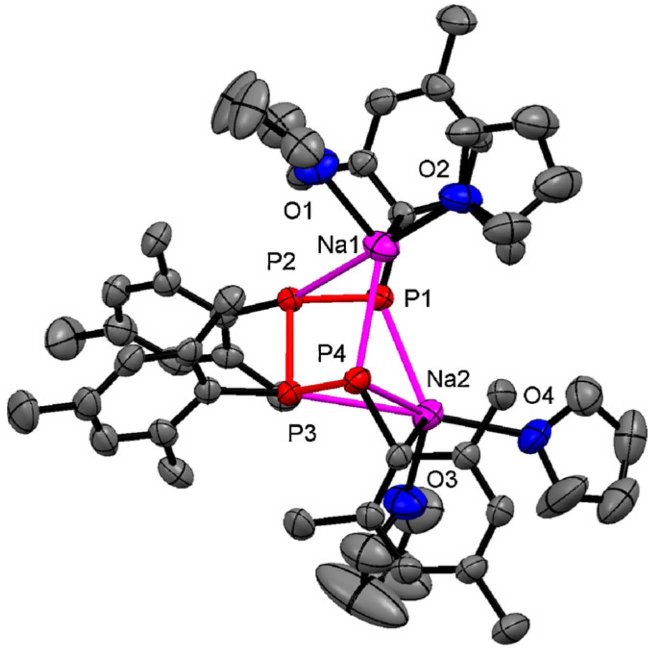


Fig. 2. Molecular structure of $[Na_2(thf)_4(P_4Mes_4)]$ (**33**) (hydrogen atoms have been omitted for clarity).

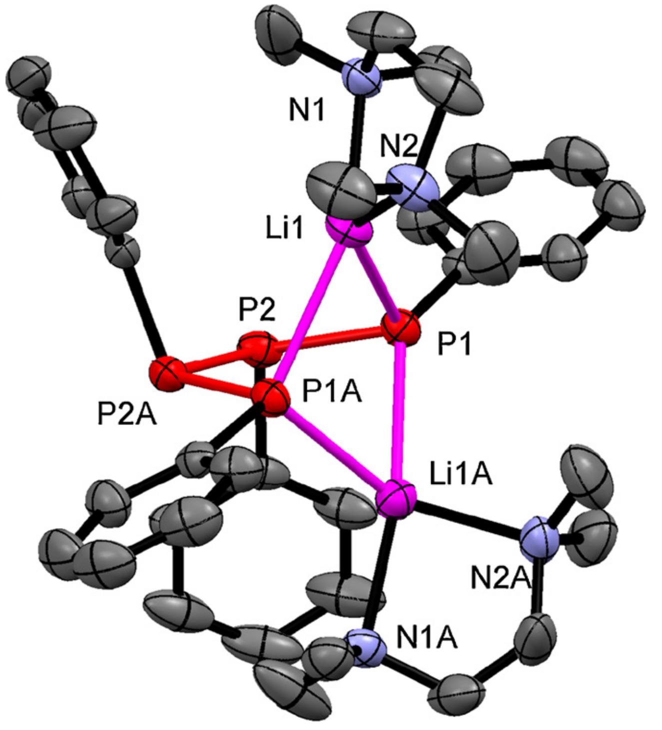
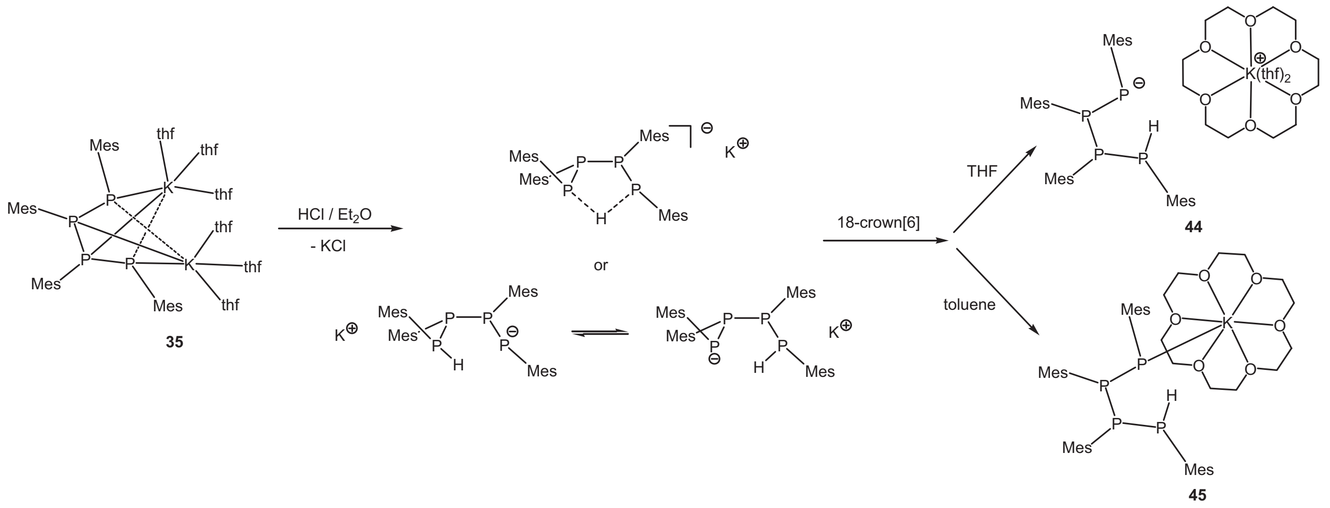


Fig. 3. Molecular structure of $[Li_2(tmeda)_2(P_4Ph_4)]$ (**42**) (hydrogen atoms have been omitted for clarity).



Scheme 13. Preparation of [K(18-crown[6])(thf)$_2$][P_4HMes_4] (**44**) and [K(18-crown[6])(P_4HMes_4)] (**45**).

molecules (Fig. 4). On the other hand, the molecular structure of the analogous compound **45** reveals an ion-contact complex in which the potassium cation is surrounded by 18-crown[6] and one terminal phosphorus atom of the $(P_4HMes_4)^-$ anion of **45**. ^{31}P NMR spectroscopic studies on **44** and **45** indicated that the $(P_4HMes_4)^-$ ion displays a number of remarkable features, including its lability in solution and the fluxional behavior of its P–H hydrogen atom with different proposed alternative structures [40].

The reactivity of the sodium and potassium compounds **32**, **33**, **35** and **36** and the *in situ* generated $(P_4HR_4)^-$ anion towards several transition metal complexes has been studied and will be described in Section 5.

4. Alkali metal *cyclo*-oligophosphanides

The targeted synthesis of anionic ring systems such as M[*cyclo*-(P_5R_4)] (M = Li, Na or K; R = Pr^i, Bu^t, Ph) has been reported [36,37,41]. These compounds have been synthesized by the reaction of lithium, sodium or potassium with the corresponding $RPCl_2$ and PCl_3 in the ratio 12:4:1 in THF (Scheme 11). A product mixture is obtained usually comprising M[*cyclo*-(P_3R_2)], M[*cyclo*-(P_4R_3)], *cyclo*-(P_4R_4), $M_2(P_4R_4)$ and M[*cyclo*-(P_5R_4)]. Systematic variation of the reaction conditions led to optimization of the synthesis of M[*cyclo*-(P_5R_4)], which was obtained with only small amounts of the other alkali metal salts and *cyclo*-(P_4R_4). Only M[*cyclo*-(P_5R_4)] and *cyclo*-(P_4R_4) are soluble in *n*-pentane and could thus be separated from the other by-products. Subsequent separation of *cyclo*-(P_4R_4) from M[*cyclo*-(P_5R_4)] is possible by sublimation of the former. Additionally, M[*cyclo*-(P_5R_4)] can also be separated from the impurities by crystallization. In the solid state, an all-*trans* arrangement of the *tert*-butyl groups of the P_5 ring in [Li(tmeda)$_2$][*cyclo*-($P_5Bu^t{}_4$)] (**38**) [36], [Na(thf)$_4$][*cyclo*-($P_5Bu^t{}_4$)] (**39**) [37], and [K(pmedta)(thf)][*cyclo*-($P_5Bu^t{}_4$)] (**40**) [35] is observed. The chiral P_5 ring has an envelope conformation in which the neutral phosphorus atoms are almost coplanar, while the anionic phosphorus atom lies about 80 pm above this plane (Fig. 5).

The envelope conformation of the ring with the Bu^t groups in all-*trans* conformation seems to be retained in solution, as the $^{31}P\{^1H\}$ NMR spectrum of these compounds showed an ABB′CC′ spin system indicating that only one conformational isomer is present. The observed coupling constants suggest that the all-*trans* isomer is preferred.

In all alkali metal complexes, the P(1)–P(5) bond length of ca. 212 pm is about 8–10 pm shorter than the other P–P bonds of the

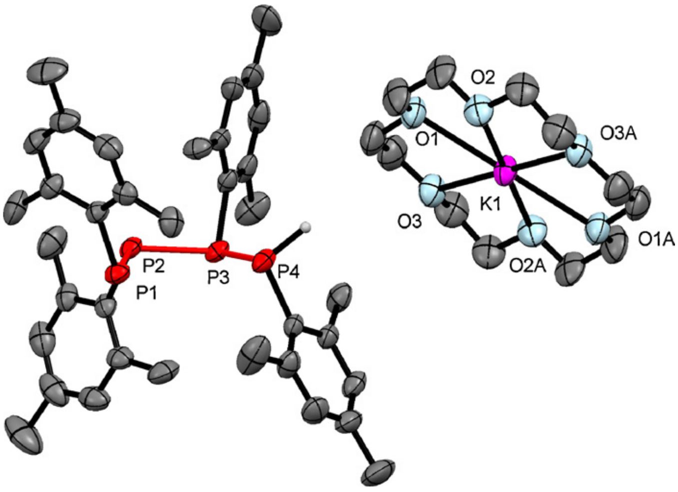


Fig. 4. Molecular structure of [K(18-crown[6])(thf)$_2$][P_4HMes_4] (**44**) (hydrogen atoms other than P–H and coordinated THF molecules at potassium have been omitted for clarity).

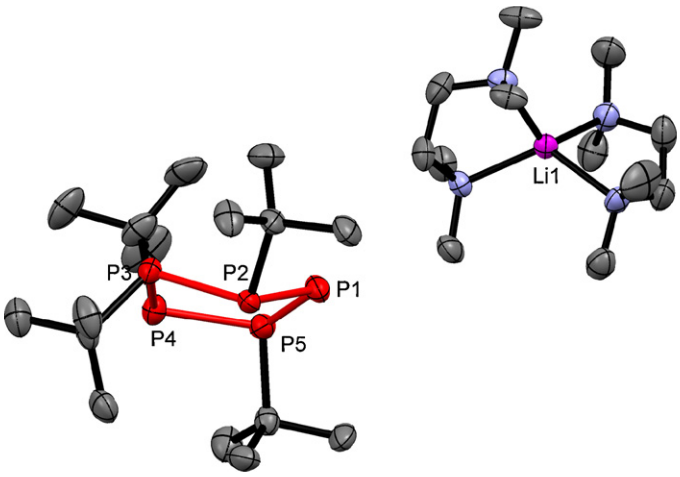


Fig. 5. Molecular structure of [Li(tmeda)$_2$][*cyclo*-($P_5Bu^t{}_4$)] (**38**) (hydrogen atoms have been omitted for clarity).

Table 2
P–P and M–P bond lengths (determined by single crystal X-ray diffraction studies) and observed spin systems (determined by $^{31}P\{^1H\}$ NMR spectroscopy) in complexes with cyclic oligophosphanide anions.

Compound	P–P[a]	P–P[b]	M–P (of P_5)	Spin system in $^{31}P\{^1H\}$ NMR	Ref.
$[Li(tmeda)_2][\textit{cyclo}\text{-}(P_5Bu^t{}_4)]$ (**38**)	220.7(2) 221.5(2) 221.6(2) 222.6(2)	212.5(2)	490.4(6)[c]	ABB′CC′	[36]
$[Na(thf)_4][\textit{cyclo}\text{-}(P_5Bu^t{}_4)]$ (**39**)	220.4(2) 220.8(1) 221.1(2) 222.9(1)	213.2(2)	293.8(2)	ABB′CC′	[37]
$[K(pmedta)(thf)\{\textit{cyclo}\text{-}(P_5Bu^t{}_4)\}]$ (**40**)	219.5(4) 220.8(6) 221.4(3) 222.6(5)	212.9(3)	325.3(3)	ABB′CC′	[35]
$[Rh\{\textit{cyclo}\text{-}(P_5Bu^t{}_4)\}(PPh_3)_2]$ (**66**)	220.6(2) 220.8(2) 223.8(2) 224.1(3)	212.9(2)	231.3(2) 238.5(2)	ABCDEFG	[56]
$[Ni\{\textit{cyclo}\text{-}(P_5Bu^t{}_3)\}(PEt_3)_2]$ (**67**)	219.9(1) 220.1(2) 220.2(2) 221.1(2)	211.8(2)[d]	223.2(1) 223.9(1)	ABB′CC′DD′	[37]
$[Ni\{\textit{cyclo}\text{-}(P_5Bu^t{}_4)\}_2]$ (**68**)	220.1(1) 220.3(1) 220.7(1) 222.6(1)	212.2(1)	217.5(2) 229.4(2)	AA′BB′CC′DD′EE′	[57]
$[Pd\{\textit{cyclo}\text{-}(P_5Bu^t{}_4)\}_2]$ (**72**)	219.6(2) 219.9(2) 220.2(2) 222.5(2)	212.3(2)	229.2(1) 243.4(1)	AA′BB′CC′DD′EE′	[57]
$[Pd\{\textit{cyclo}\text{-}(P_5Bu^t{}_3)\}(PPh_3)_2]$ (**73**)	219.7(5) 219.7(5) 219.7(5) 220.1(5)	213.7(5)	235.4(3) 239.5(3)	[e]	[57]
$[PtCl\{\textit{cyclo}\text{-}(P_4Bu^t{}_3)PBu^t\}(PMe_2Ph)]$ (**74**)	219.8(2) 221.2(2) 221.9(2) 222.7(2) 225.0(2)		230.1(2) 232.7(2)	ABCDEF	[57]
$[Cu\{\textit{cyclo}\text{-}(P_5Bu^t{}_4)\}(PPh_3)_2]$ (**76**)	221.0(2) 221.1(2) 221.9(2) 222.2(2)	214.6(2)	228.6(2)	[f]	[58]
$[Cu_2(\mu\text{-}Cl)\{\textit{cyclo}\text{-}(P_5Bu^t{}_4)\}(PCyp_3)_2]$ (**77**)	220.0(2) 220.5(2) 221.5(2) 221.8(2)	214.6(2)	225.6(1) 221.0(1) 227.3(1) 223.3(1)	[f]	[58]
$[Cu_4\{\textit{cyclo}\text{-}(P_4Bu^t{}_3)PBu^t\}_4]$ (**78**)	219.3(2) 221.4(2) 221.7(2) 222.2(1) 222.5(2)		221.4(1) 222.7(2)	[g]	[58]
$[Ag_4\{\textit{cyclo}\text{-}(P_4Bu^t{}_3)PBu^t\}_4]$ (**79**)	218.7(1) 221.9(1) 222.0(1) 222.4(2) 222.7(1)		238.3(1) 240.2(1)	[g]	[58]
$[Au\{\textit{cyclo}\text{-}(P_5Bu^t{}_4)\}(PCyp_3)]$ (**80**)	217.3(2) 220.7(2) 221.6(2) 222.5(2) 223.0(2)		233.3(2)	ABCDEX	[58]
$[Au_4\{\textit{cyclo}\text{-}(P_4Bu^t{}_3)PBu^t\}_4]$ (**82**)	219.7(5) 221.2(5) 221.3(5) 222.8(6) 222.9(7)		232.1(3)	[g]	[58]

[a] Regular P–P bonds of the P_5 ligand.

[b] Short P–P bond of the $P_5Bu^t{}_4$ ligand due to interaction of the lone pair of electrons at the anionic phosphorus atom with unoccupied orbitals (with σ*- and d-orbital contributions) at the adjacent phosphorus atom. In case of $P_5Bu^t{}_3$ ligands this refers to the P=P bond length.

[c] No Li–P bond, separated ions.

[d] P=P double bond.

[e] This complex was only characterized by single-crystal X-ray diffraction studies.

[f] Severe line broadening precluded numerical analysis of the coupling patterns.

[g] Poor solubility of this complex prevented $^{31}P\{^1H\}$ NMR analysis.

five-membered ring (Table 2), which have values ranging from 220 to 222 pm, validating the larger coupling constant $^1J(P_A, P_B) = {}^1J(P_A, P_{B'})$ of ca. 390 Hz observed in the $^{31}P\{^1H\}$ NMR spectra.

Interestingly, compound **38** consists of separated $[Li(tmeda)_2]^+$ cations and $[cyclo\text{-}(P_5Bu^t{}_4)]^-$ anions (Fig. 5). The lithium cation is coordinated in a usual distorted tetrahedral fashion by four nitrogen atoms of two TMEDA molecules, which prevents interaction of the cation with the anion and thus results in a "naked" $[cyclo\text{-}(P_5Bu^t{}_4)]^-$ anion (Li(1)···P(1) 494.0(6) pm) [36]. This type of anionic two-coordinate phosphorus atom is typical in metal complexes of white phosphorus [42], but rare for linear or cyclic oligophosphanides [43].

The reactivity of the sodium salt **39** towards several main group and transition metal complexes has been studied and will be described in Section 6.

5. Reactivity of $(P_4R_4)^{2-}$ ions

5.1. Main group metal complexes with the $(P_4R_4)^{2-}$ ion

The highly reducing nature of $(P_4R_4)^{2-}$ dianions limits their use as transmetallation reagents for metal salts in high oxidation states [28]. Thus, reactions of the $(P_4R_4)^{2-}$ anion with p-block main group metal salts such as $SnCl_2$, $AlEt_2Cl$, $AlCyCl_2$, $Ga(DAB)I_2$, GaI, $InCyBr_2$ or $GaCl_3$ (Cy = cyclohexyl, DAB = *N*,*N*′-bis(2,6-diisopropyl)phenyldiazabutadiene) did not lead to the desired transmetallation products; instead, either elemental metal, cyclooligophosphanes or unidentified products where obtained [44].

In this context, the only known example of a group 13 metal with a $(P_4R_4)^{2-}$ ion is the complex $[K(tmeda)\{Ga(P_4Ph_4)(DAB)\}]$ (**46**) [45], which was obtained by reaction of $[K(tmeda)\{Ga(DAB)\}]$ and *cyclo*-P_5Ph_5 (5:1) (Scheme 14). The synthetic method used for the preparation of **46** is analogous to that carried out for the preparation of $[Ga\{C(SiMe_3)_3\}(P_3Bu^t{}_3)]$ (**6**) (Scheme 2) by Uhl and Benter [17].

The molecular structure of **46** shows that the potassium ion is coordinated by two phosphorus atoms of the GaP_4 ring of the spirocyclic system and a TMEDA molecule. Additionally, η^6-arene interaction by one of the *N* substituents of the GaN_2C_2 fragment is observed (Fig. 6). It is noteworthy that the phenyl substituents at phosphorus are *syn* (P(1), P(2)), *anti* (P(2), P(3)), *anti* (P(3), P(4)) to each other. Thus, all phosphorus atoms are chemically inequivalent in the solid state. This is, however, not observed by $^{31}P\{^1H\}$NMR spectroscopy in solution, where an AA′BB′ system (Table 1) with two broad signals at −80.2 and −6.1 ppm was observed, that is, either the structure is not retained in solution or a fluxional process takes place which may involve cleavage and reformation of Ga–P and/or P–P bonds [45].

5.2. Reactivity of the $(P_4R_4)^{2-}$ ion towards transition metals

In contrast to reactions with p-block metals, $(P_4R_4)^{2-}$ anions exhibit diverse reactivity towards a wide variety of transition metal compounds. One of the first interesting results was obtained with copper(I) compounds [46]. While the reaction of CuCl with $[Na_2(thf)_5(P_4Ph_4)]$ (**32**) or $K_2(P_4Bu^t{}_4)$ led only to a black precipitate consisting of elemental copper, NaCl and the cyclophosphanes *cyclo*-(P_nPh_n) (*n* = 4–6) or *cyclo*-$(P_4Bu^t{}_4)$, respectively, the reaction of $[CuCl(PCyp_3)_2]$ (Cyp = *cyclo*-C_5H_9) with $[Na_2(thf)_5(P_4Ph_4)]$ (**32**) yielded the tetranuclear copper(I) complex $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$ (**47**) (Fig. 7, Scheme 15), avoiding reduction of the metal cation and leading to the transmetallation product.

The X-ray structure determination of **47** revealed that it consists of a tetranuclear aggregate of four Cu^+ cations with two bridging $(P_4Ph_4)^{2-}$ anions (Fig. 7). Three of the four copper atoms are additionally coordinated by tricyclopentylphosphane ligands, giving rise to a Cu_4P_{11} core with fused five- and six-membered rings. In this core, three of the copper(I) atoms have a distorted trigonal-planar geometry (Cu(1), Cu(3) and Cu(4)) while one copper(I) atom (Cu(2)) has a distorted tetrahedral environment.

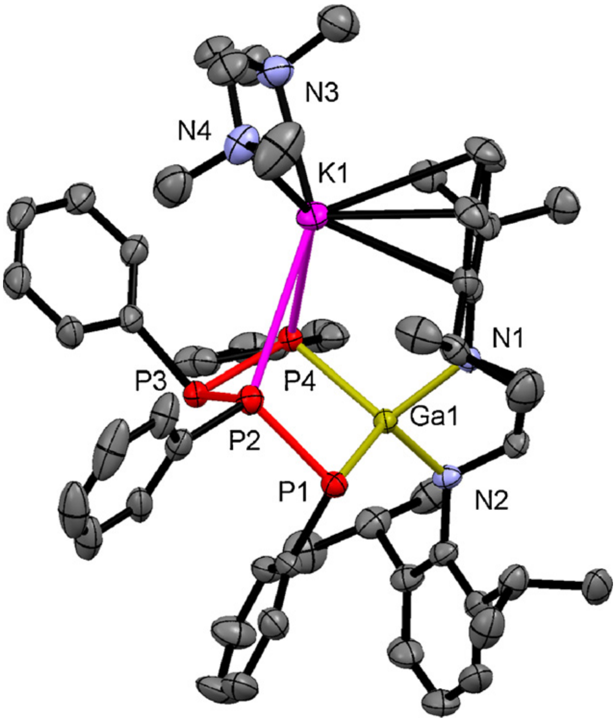


Fig. 6. Molecular structure of $[K(tmeda)\{Ga(P_4Ph_4)(DAB)\}]$ (**46**) (hydrogen atoms have been omitted for clarity).

The P–P bond lengths of the chains are in the range for single bonds (Table 1), and the P_4 chains are in a *syn* arrangement with large torsion angles (ca. 62° and 67°) compared to the structure of $[Na_2(thf)_5(P_4Ph_4)]$ (**32**) (ca. 32°). This is a phenomenon caused by the coordination of an internal phosphorus atom of the chain to copper in each of the $(P_4Ph_4)^{2-}$ ligands, which restricts the flexibility of the latter to adapt to the coordination requirements of the copper cations.

47 shows a complex $^{31}P\{^1H\}$ NMR spectrum at room temperature with several broad peaks of different intensity, as was expected for an unsymmetrical spin system of 11 different phosphorus nuclei if its solid-state structure were retained in solution. This spectrum is even more complicated at lower temperatures (down to −80 °C)

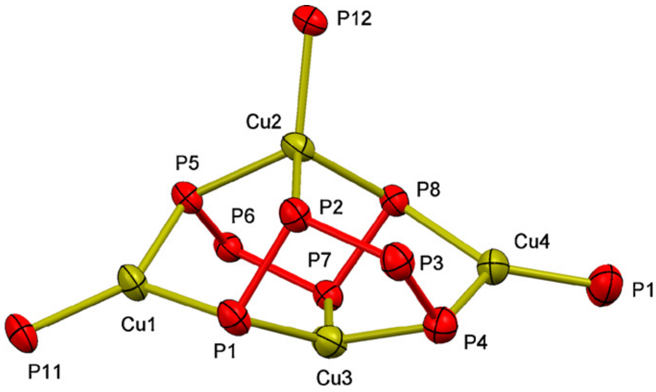
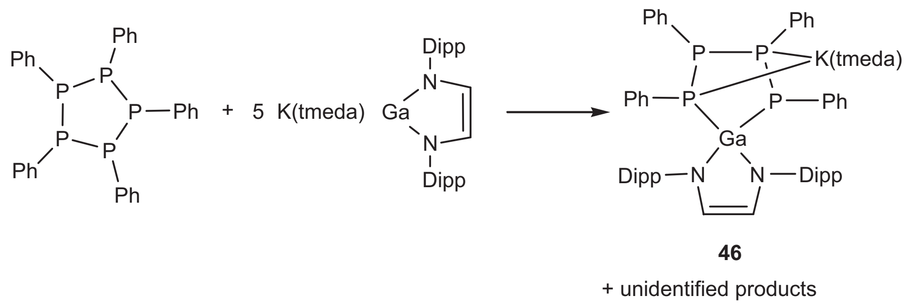


Fig. 7. Section of the molecular structure of $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$ (**47**) (only copper and phosphorus atoms are shown).



Scheme 14. Synthesis of [K(tmeda){Ga(P_4Ph_4)(DAB)}] (**46**).

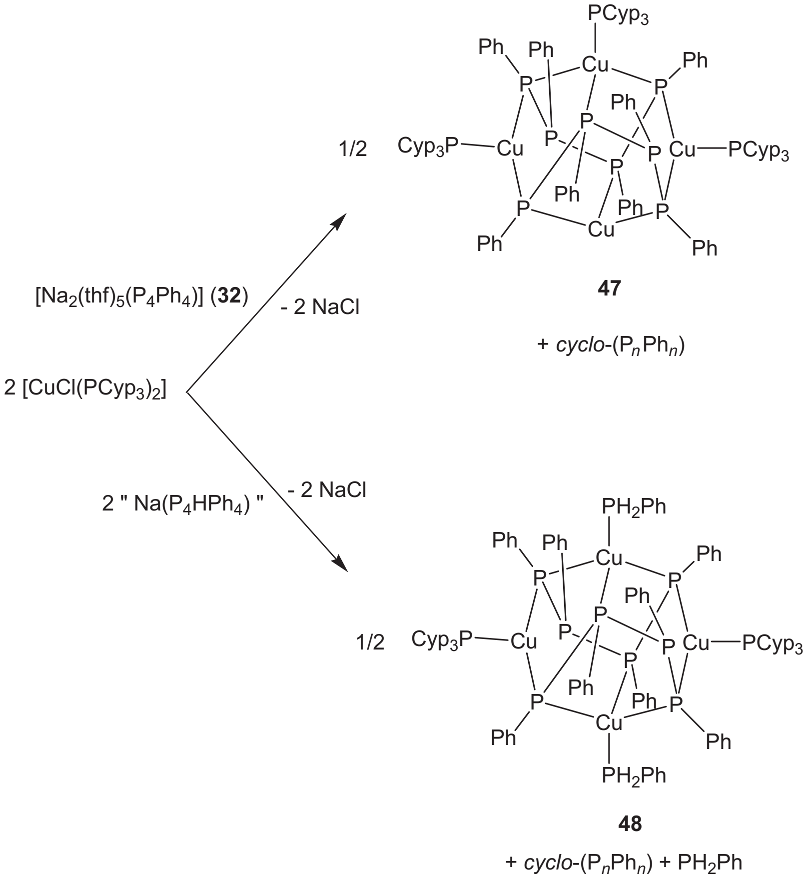
with broader multiplets indicating that line broadening at room temperature may not exclusively be caused by coupling between phosphorus and the quadrupolar ^{63}Cu/^{65}Cu nuclei, but also by an unresolved fluxional process.

The analogous compound [$Cu_4(P_4Ph_4)_2(PH_2Ph)_2(PCyp_3)_2$] (**48**) [47] was obtained by reaction of one equivalent of [$Na_2(thf)_5(P_4Ph_4)$] (**32**) or $K_2(P_4Ph_4)$ with one equivalent of HCl [40], followed by subsequent reaction with one equivalent of [$CuCl(PCyp_3)_2$]. The reaction mechanism includes the rearrangement of two equivalents of "*in situ*" generated $(P_4HPh_4)^-$ to one equivalent of $(P_4Ph_4)^{2-}$ and one equivalent of $P_4H_2Ph_4$. The neutral tetraphosphane is very unstable in solution and decomposes rapidly to give a mixture of phosphanes, of which PH_2Ph is coordinated to two copper atoms. **48** has similar structural features to **47** (Table 1); however, in this case a centrosymmetric arrangement of the Cu_4P_{12} cluster with a tetranuclear aggregate of four Cu^+ ions with two bridging $(P_4Ph_4)^{2-}$ dianions is observed (Fig. 8). In this case, two copper(I) centers have tetrahedral geometry and the other two exhibit trigonal-planar coordination.

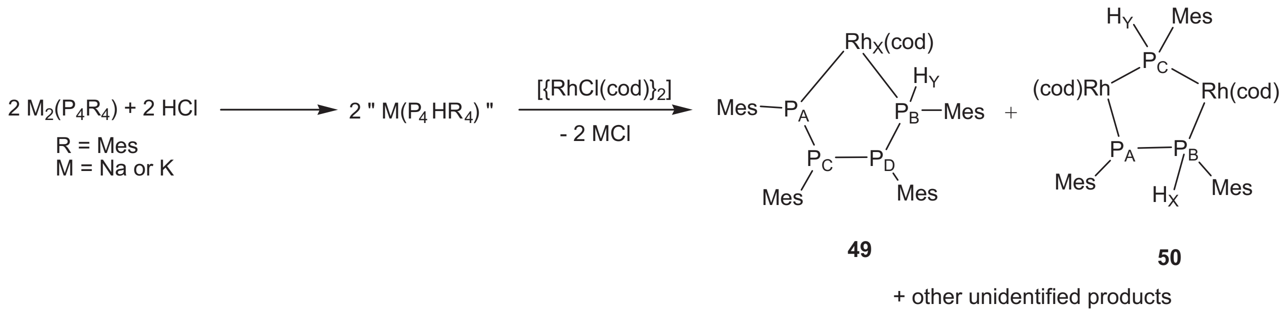
Furthermore, reactions of the *in situ* generated analogous $(P_4HMes_4)^-$ anion with rhodium(I) salts allowed for the first time the rational synthesis of a transition metal tetraphosphanido complex with a $(P_4HMes_4)^-$ ligand, namely [Rh(P_4HMes_4)(cod)] (**49**) (Scheme 16) [47], while [Cp°$MoCl_2(\eta^3$-$P_4HCy_4)$] (**11**) was only obtained in very low yield *via* the reaction of [Cp°$MoCl_4(PH_2Cy)$] with two equivalents of NEt_3 [22]. The formation of **49** was always accompanied by [{Rh(cod)}$_2$(μ-P_2HMes_2)(μ-PHMes)] (**50**); successive recrystallizations allowed both complexes to be separated.

In **49**, the $(P_4HR_4)^-$ ligand chelates the rhodium atom by coordination through terminal phosphorus atoms P(1) and P(4) of the chain (Fig. 9).

The proton-coupled ^{31}P NMR spectrum of **49** shows an ABCDXY spin system in which a highly complex signal with a very large ^1J(P_B, H) coupling constant of 335.2 Hz was observed. In addition, the ter-



Scheme 15. Synthesis of copper(I) complexes [$Cu_4(P_4Ph_4)_2(PCyp_3)_3$] (**47**) and [$Cu_4(P_4Ph_4)_2(PH_2Ph)_2(PCyp_3)_2$] (**48**).



Scheme 16. Synthesis of rhodium(I) oligophosphanido complexes.

minal phosphorus atoms of the P_4 chain exhibit ^{31}P–^{103}Rh coupling (^{1}J(P, Rh) 167.6 and 85.3 Hz). This spectrum clearly indicates that the structure of **49** is retained in solution.

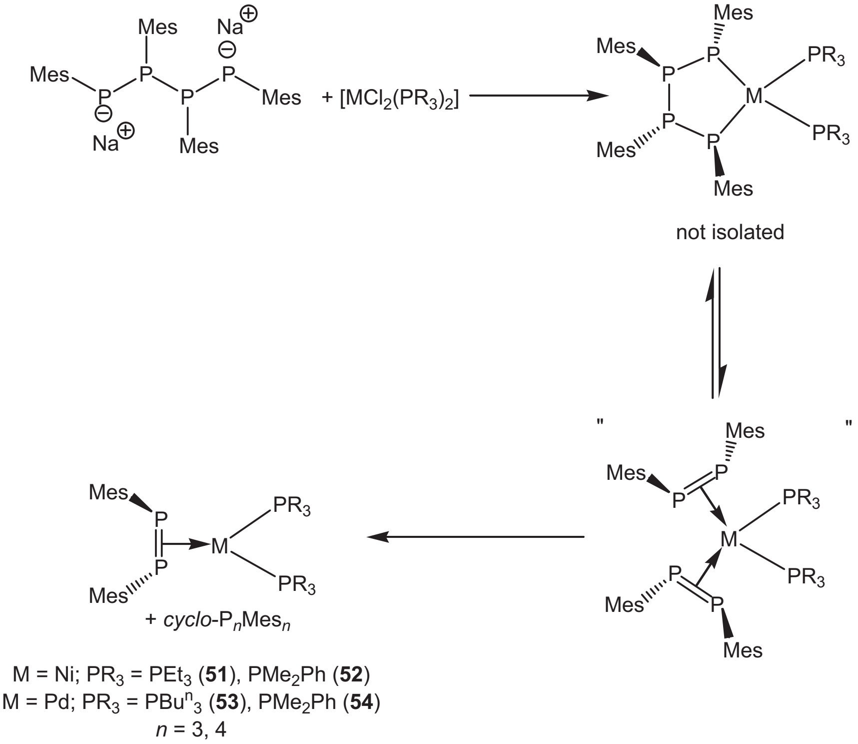
Coming back to the reactivity of the $(P_4R_4)^{2-}$ ions, the dimesityldiphosphene complexes $[Ni(\eta^2\text{-}P_2Mes_2)(PEt_3)_2]$ (**51**), $[Ni(\eta^2\text{-}P_2Mes_2)(PMe_2Ph)_2]$ (**52**), $[Pd(\eta^2\text{-}P_2Mes_2)(PBu^n{}_3)_2]$ (**53**) and $[Pd(\eta^2\text{-}P_2Mes_2)(PMe_2Ph)_2]$ (**54**) were obtained in the reaction of $[Na_2(P_4Mes_4)]$ with the corresponding nickel or palladium complexes $[NiCl_2(PEt_3)_2]$, $[NiCl_2(PMe_2Ph)_2]$, $[PdCl_2(PBu^n{}_3)_2]$ and $[PdCl_2(PMe_2Ph)_2]$, respectively (Scheme 17) [48].

The first step in this reaction is assumed to include the formation of the nickel(II) or palladium(II) tetraphosphanediide species, which undergo an intramolecular redox reaction to give the corresponding nickel(0) or palladium(0) bis(dimesityldiphosphene) complexes. The latter are unstable and eliminate a diphosphene ligand to give the isolated products **51**–**54** and *cyclo*-P_nMes_n ($n = 3$ and 4).

An AA′XX′ spin system with $^{2}J(P, P_{cis})$ coupling constants close to zero was observed in the $^{31}P\{^{1}H\}$ NMR spectra of **51**–**54**, as was previously reported for analogous group 10 complexes by Pidcock and co-workers, who observed slow rotation (on the NMR timescale) of the diphosphene ligand around the C_2 axis [49].

The molecular structures of compounds **51**–**54**, determined by single-crystal X-ray diffraction studies, revealed similar structural parameters to those described in previously reported nickel, palladium and platinum diphosphene complexes [49], with short P–P bonds of ca. 211 pm (Table 1).

A different behavior was observed in transmetallation reactions of $(P_4R_4)^{2-}$ with platinum(II) complexes, which led to the corresponding platinum(II) tetraphosphanediides, due to the higher stability of platinum(II) in comparison to nickel(II) and palladium(II). Thus, the reaction of $[Na_2(thf)_4(P_4Mes_4)]$ (**33**) with one equivalent of $[PtCl_2(cod)]$ or $[PtCl_2(dppe)]$ (dppe = bis(diphenylphosphino)ethane) gave $[Pt(P_4Mes_4)(cod)]$ (**55**) and $[Pt(P_4Mes_4)(dppe)]$ (**56**), respectively (Scheme 18) [50], which were the first platinum complexes containing a tetramesityltetraphosphane-1,4-diide ligand. The Pt–P bonds of these complexes are very stable, and no evidence of insertion of CO, CS_2, white phosphorus or ethyl diazoacetate into the Pt–P bonds or reaction with MeI was observed. Analogous reactions of **55** and **56** with *tert*-butyl isocyanide and cyclohexyl isocyanide yielded only the complexes $[Pt(P_4Mes_4)(C{\equiv}NBu^t)_2]$ (**57**) and $[Pt(P_4Mes_4)(C{\equiv}NCy)_2]$ (**58**), respectively, in which ligand transfer had occurred instead of the targeted insertion reactions. Insertion



Scheme 17. Proposed reaction mechanism for the formation of Ni and Pd dimesityldiphosphene complexes.

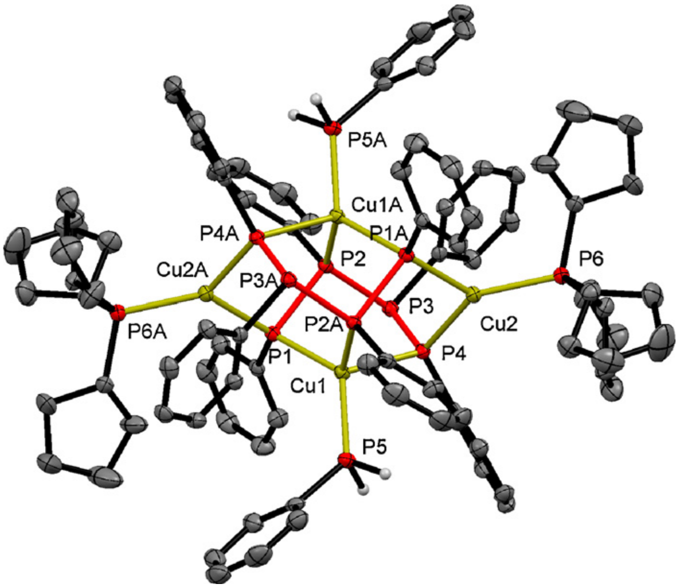


Fig. 8. Molecular structure of [$Cu_4(P_4Ph_4)_2(PH_2Ph)_2(PCyp_3)_2$] (**48**) (hydrogen atoms other than P–H have been omitted for clarity).

of isocyanides into the Pt–P bonds did not take place even when performing the reactions at higher temperatures (up to 110 °C) or after prolonged reaction times (2–150 h; Scheme 18).

In the molecular structure of **55**–**58**, the P_4 chain has a *syn* arrangement, as was observed for the alkali metal compounds, forming a five-membered ring with platinum in an envelope conformation (Fig. 10). The Pt–P bond lengths of ca. 233 pm (Table 1) are in the range for platinum(II) phosphanido complexes such as [$Pt(P_3Bu^t{}_3)(PPh_3)_2$] (**2**) (Scheme 2) [15d].

While the $^{31}P\{^{1}H\}$ NMR spectra of **55** and **56** showed higher order AA′XX′ (Fig. 11) and AA′BCXX′ spin systems with platinum satellites $^{1}J(^{31}P,^{195}Pt)$ of 1146 Hz for **55** and 2261 and 780 Hz for **56**, indicating that the structure observed in the solid state is retained in solution, the $^{31}P\{^{1}H\}$ NMR spectra of **57** and **58** gave only one multiplet at ca. −40 ppm, due to severe overlap of signals, which showed no changes with varying temperature and precluded full analysis of chemical shifts and coupling constants.

Of the group 9 metals, mainly rhodium complexes were studied. The reaction of [$\{RhCl(cod)\}_2$] with $(P_4Mes_4)^{2-}$ gave a mixture of compounds, of which [$Na(thf)_3$][$Rh(P_3Mes_3)(cod)$] (**59**) with a trimesityltriphosphane-1,3-diide ligand was structurally charac-

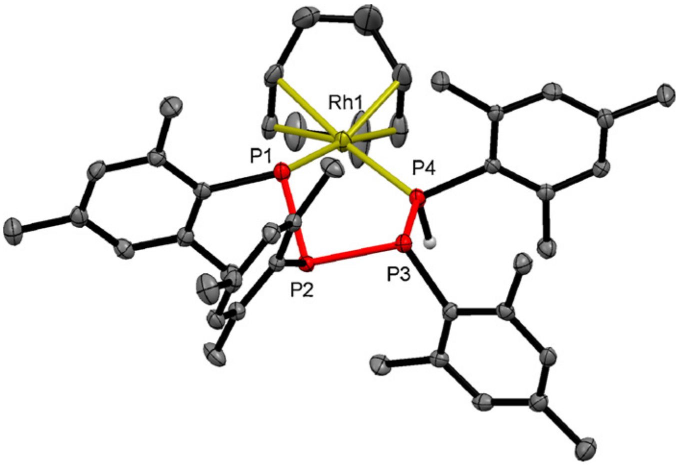
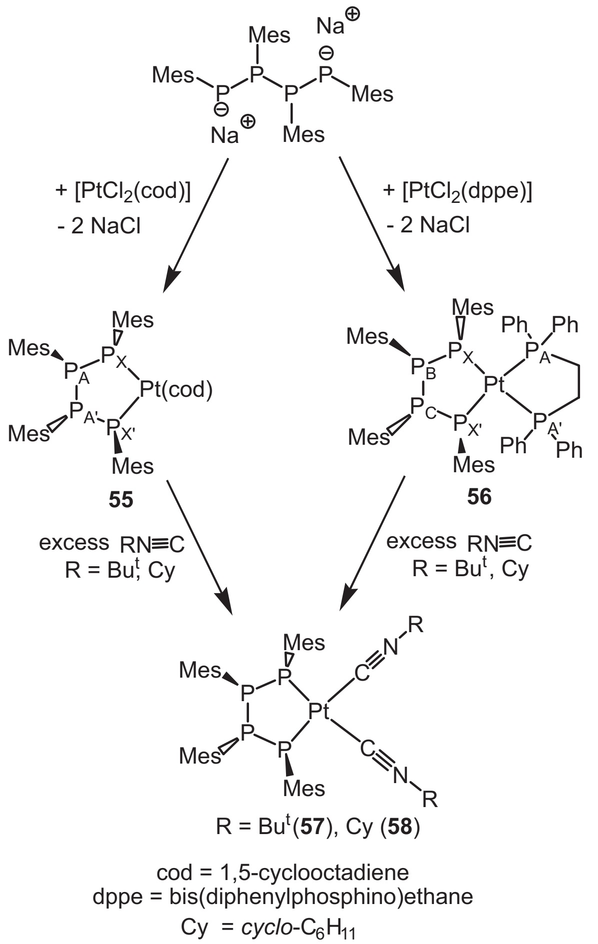


Fig. 9. Molecular structure of [$Rh(P_4HMes_4)(cod)$] (**49**) (hydrogen atoms other than P–H have been omitted for clarity).



Scheme 18. Synthesis and reactivity of platinum(II) tetramesityltetraphosphane-1,4-diide complexes.

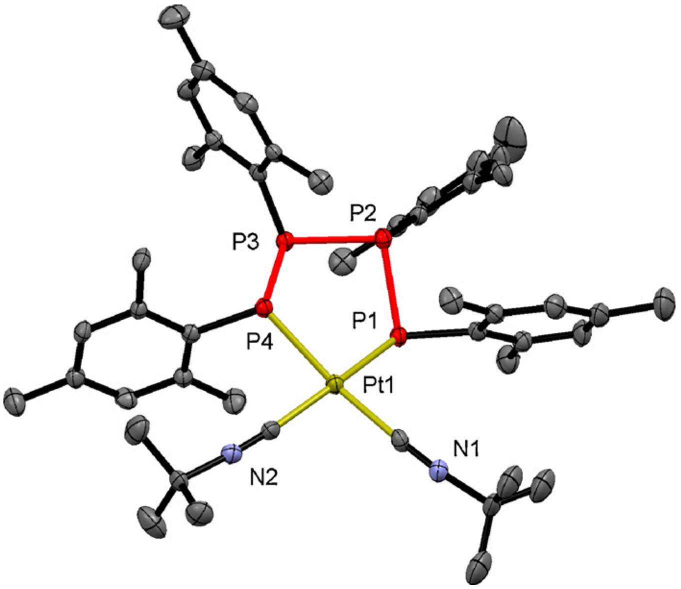
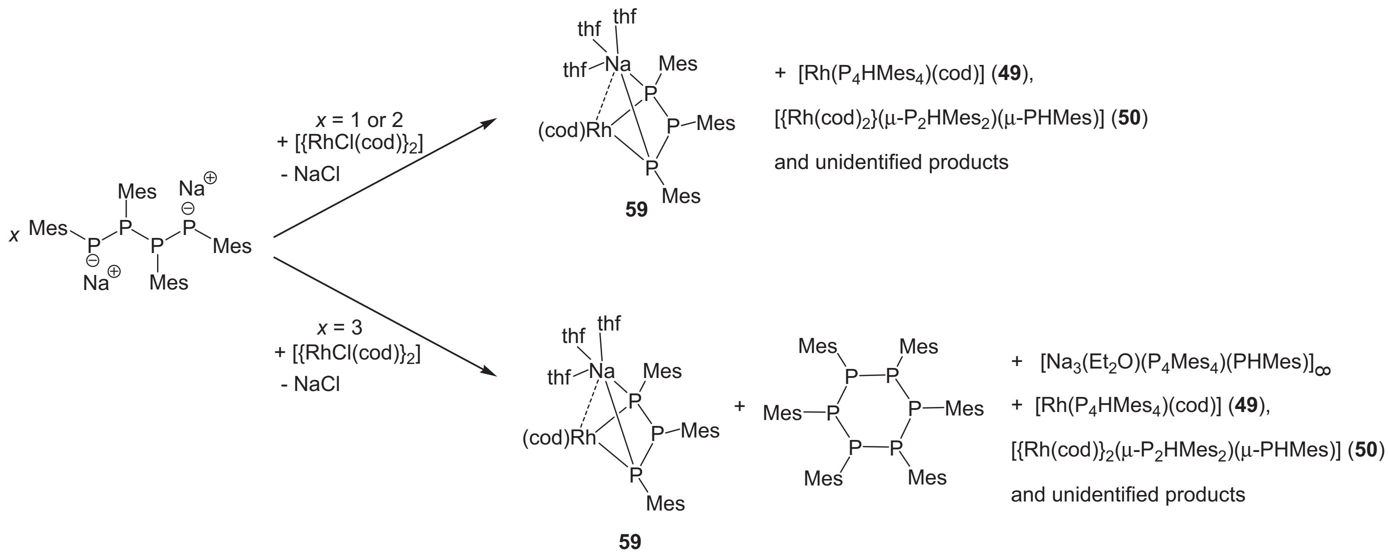


Fig. 10. Molecular structure of [$Pt(P_4Mes_4)(C{\equiv}NBu^t)_2$] (**57**) (hydrogen atoms have been omitted for clarity).



Scheme 19. Synthesis of $[Na(thf)_3][Rh(P_3Mes_3)(cod)]$ (**59**).

terized (Scheme 19) [51]. Several attempts to get insight into the mechanism of this reaction by changing the reaction conditions and stoichiometry resulted in the isolation of the side products *cyclo*-P_6Mes_6 and $[Na_3(Et_2O)(P_4Mes_4)(PHMes)]$, which indicated that this reaction may occur *via* P–P bond cleavage to give $(P_3Mes_3)^{2-}$ and PH_2Mes although the reaction mechanism is still not clear.

The $^{31}P\{^1H\}$ NMR spectrum of **59** exhibits two broad signals at −30 and −46 ppm at room and low temperature (−80 °C). The molecular structure of **59** (Fig. 12) determined by single-crystal X-ray diffraction studies shows that the $(P_3Mes_3)^{2-}$ ligand chelates the rhodium atom *via* its two terminal phosphorus atoms (P(1) and P(3)), leading to a similar coordination to that observed in $[Pt(P_3Bu^t{}_3)(PPh_3)_2]$ (**2**) [15d] and $[Ga\{C(SiMe_3)_3\}(P_3Bu^t{}_3)]$ (**6**) [17] (Scheme 2). One of the two negative charges of the trimesityltriphosphane-1,3-diide ligand is counterbalanced by sodium cation Na(1), which interacts with the terminal phosphorus atoms of the P_3 chain and presumably with the rhodium atom (Na(1)–Rh(1) 310.5(2) pm). This Na–Rh interaction was studied by shared electron number (SEN) and natural bond orbital (NBO) analysis, which showed that the Na–Rh contact is stronger than the interactions between Na and P, and thus indicates some covalent character [51].

Oxidative coupling to give a P_6 chain was also found in the reaction of $[Na_2(thf)_4(P_4Mes_4)]$ (**33**) with two equivalents of $[AgCl(PPh_3)_2]$, which gave $[Ag_4(P_6Mes_6)_2]$ (**60**), a tetranuclear complex with two hexamesitylhexaphosphane-1,6-diide ligands, as the main product of the reaction, albeit in modest yield (Scheme 20) [51].

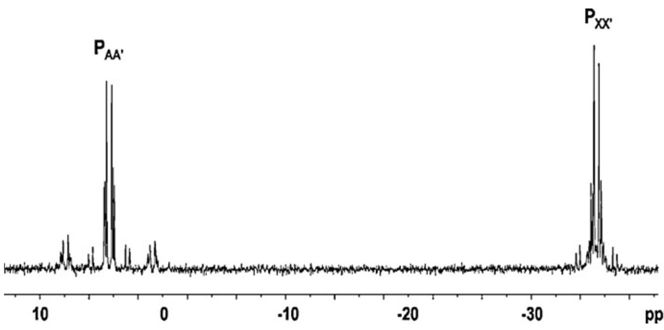


Fig. 11. $^{31}P\{^1H\}$ NMR spectrum (161.97 MHz) of $[Pt(P_4Mes_4)(cod)]$ (**55**) at room temperature.

The formation of this complex may occur by a simple redox reaction (Eq. (1)) that involves the formation of elemental silver, which was detected in the black solid which precipitates when the reaction is carried out.

$$6Ag^+ + 3(P_4Mes_4)^{2-} \rightleftarrows 4Ag^+ + 2(P_6Mes_6)^{2-} + 2Ag^0 \qquad (1)$$

The molecular structure of **60** reveals the formation of two linear $(P_6Mes_6)^{2-}$ ligands, bound by four phosphorus atoms (the terminal ones P(3), and P(1)) to four silver(I) atoms with distorted trigonal-planar geometry (Fig. 13). As was observed for the copper complexes **47** and **48**, this complex shows five and six-membered rings in its structure. In addition, the four Ag atoms of this complex are related by a crystallographic S_4 axis and are thus located on the vertices of an imaginary tetrahedron with Ag···Ag distances of 327.9(2) and 334.6(2) pm indicating intramolecular argentophilic contacts [51].

Characterization of this complex was very difficult due to its poor solubility in polar or non-polar solvents once the crystals were

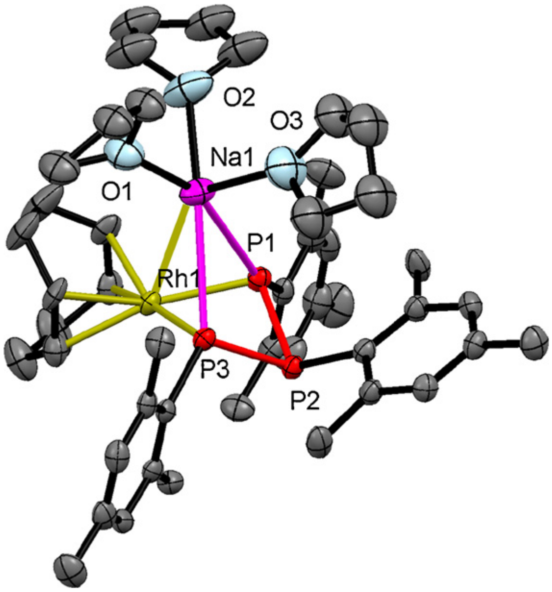
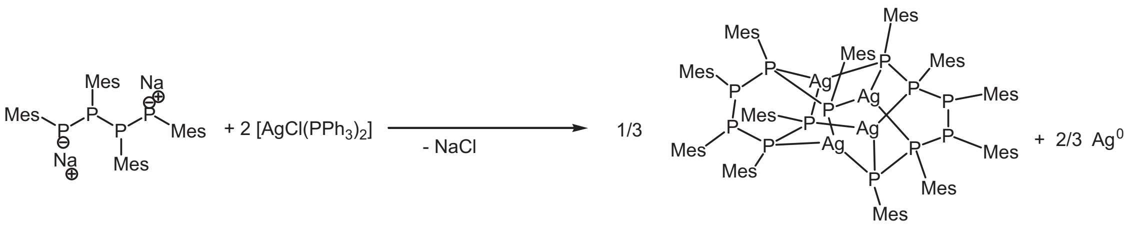
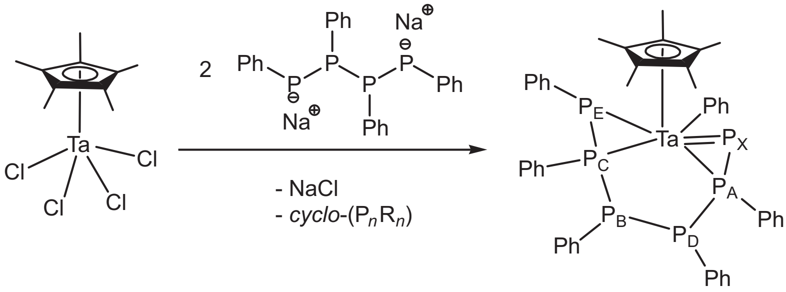


Fig. 12. Molecular structure of $[Na(thf)_3][Rh(P_3Mes_3)(cod)]$ (**59**) (hydrogen atoms have been omitted for clarity).



60

Scheme 20. Synthesis of [$Ag_4(P_6Mes_6)_2$] (**60**).



61

Scheme 21. Synthesis of [Ta(η^5-C_5Me_5)(Ph)(P_6Ph_5)] (**61**).

isolated. The $^{31}P\{^1H\}$ NMR spectrum of **60** showed three broad multiplets at −100.6, −14.3 and 0.7 ppm at room temperature, suggesting an AA′BB′XX′ system. These signals are in agreement with the symmetry of the structure in the solid state, and suggest that the linear structure of the novel dianionic P_6 chain may also be retained in solution.

A related linear P_6-based trianion was observed in the complex [Ta(η^5-C_5Me_5)(Ph)(P_6Ph_5)] (**61**), which was obtained in the reaction of the sodium salt of $(P_4Ph_4)^{2-}$ with [Ta(η^5-C_5Me_5)Cl_4] [52] and contains an unprecedented oligophosphanide trianion $(P_6Ph_5)^{3-}$, acting as a terminal phosphanyl phosphinidene ligand (Scheme 21).

The ^{31}P NMR spectrum of the reaction mixture showed formation of a variety of cyclooligophosphanes and the phosphinidene-bridged complex [{Ta(η^5-C_5Me_5)Cl(μ-PPh)}$_2$] as well as numerous low-intensity multiplets which could not be assigned. Further reactions under different reaction conditions and with other stoichiometric ratios did not help to gain insight into the reaction mechanism. However, complex **61** was fully characterized by spectroscopic methods and by X-ray diffraction studies. The molecular structure of **61** consists of a mononuclear, highly distorted pentagonal-pyramidal tantalum complex with coordination of a tetradentate trianionic $(P_6Ph_5)^{3-}$ ligand (P(1), P(2), P(5) and P(6); Fig. 14) and a phenyl group. The apical position is occupied by an η^5-coordinating pentamethylcyclopentadienyl ligand.

The $^{31}P\{^1H\}$ NMR spectrum of **61** showed a first-order ABCDEX spin system, with the signal of the phosphorus atom of the terminal phosphinidene group observed at ca. 370 ppm (Fig. 15).

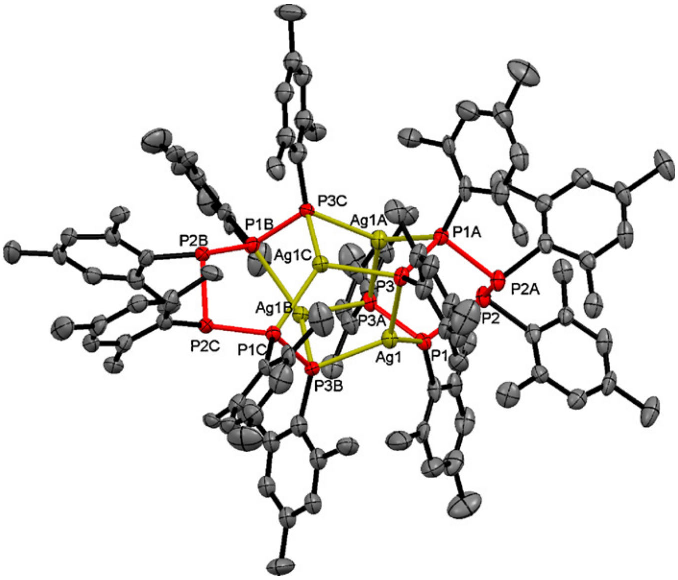


Fig. 13. Molecular structure of [$Ag_4(P_6Mes_6)_2$] (**60**) (hydrogen atoms have been omitted for clarity).

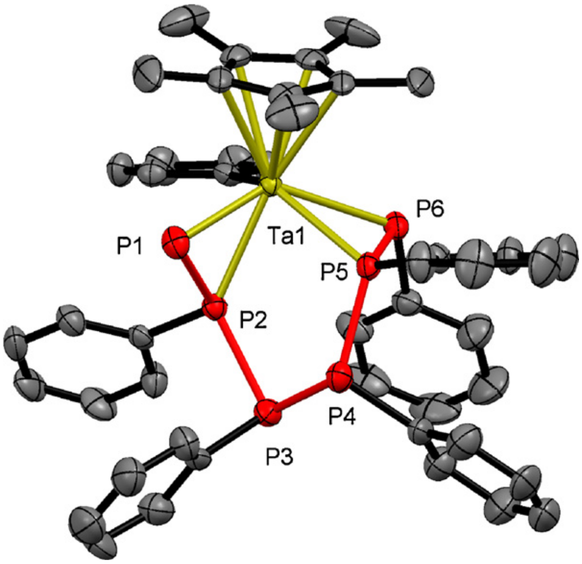
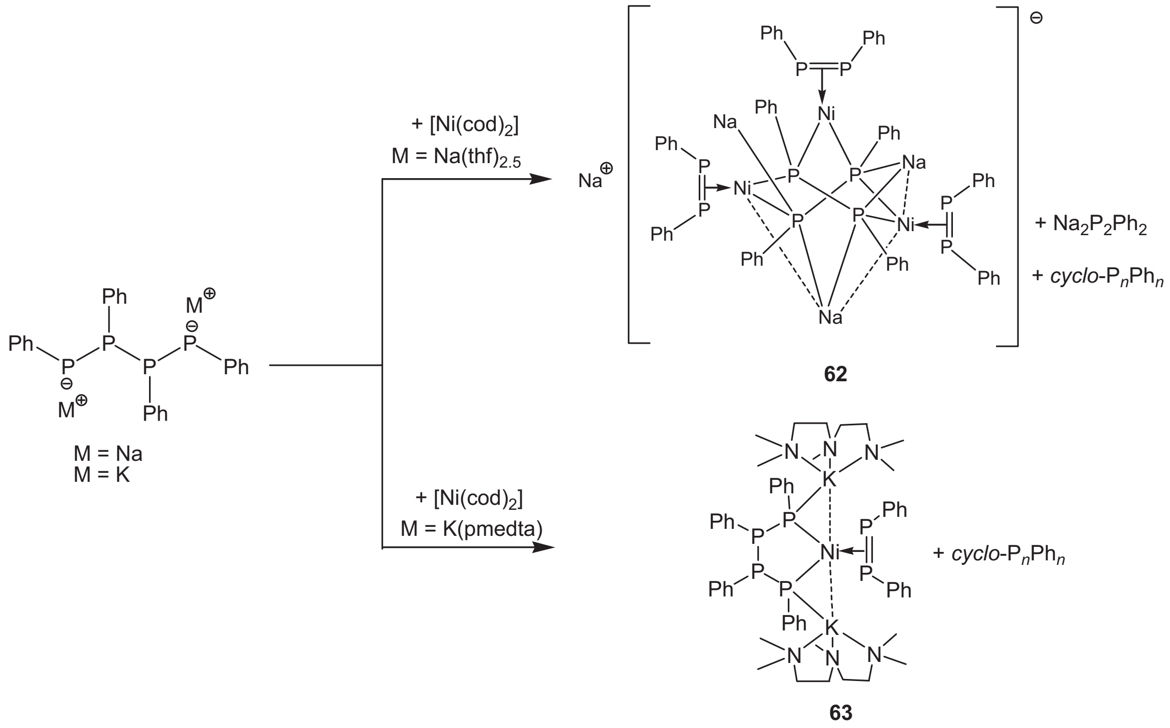


Fig. 14. Molecular structure of [Ta(η^5-C_5Me_5)(Ph)(P_6Ph_5)] (**61**) (hydrogen atoms have been omitted for clarity).



Scheme 22. Reactivity of Na and K salts of $(P_4Ph_4)^{2-}$ towards $[Ni(cod)_2]$.

To avoid oxidative coupling of oligophosphanide anions, a metal(0) complex, namely $[Ni(cod)_2]$, was employed in reactions with the sodium and potassium salts of the $(P_4Ph_4)^{2-}$ ion. However, P–P bond cleavage of tetraphenyltetraphosphane-1,4-diide was observed in the reaction of $[Na_2(thf)_5(P_4Ph_4)]$ (**28**) with one equivalent of $[Ni(cod)_2]$, leading to formation of $[Na(Et_2O)_3][Na_3(Et_2O)_2Ni_3(\mu\text{-}P_2Ph_2)_2(\eta^2\text{-}P_2Ph_2)_3]$ (**62**), presumably *via* reductive cleavage of the $(P_4Ph_4)^{2-}$ ion by nickel(0) to give two $(P_2Ph_2)^{2-}$ ions and oxidation of $(P_4Ph_4)^{2-}$ by nickel(II) (see also Scheme 17) to give two diphenyldiphosphene ligands (Scheme 22) [53]. In addition, this reaction generated a mixture of oligophosphanes and oligophosphanides from which $Na_2P_2Ph_2$ and *cyclo*-P_4Ph_4 were identified.

An analogous reaction between the less reactive $[K_2(pmdeta)_2(P_4Ph_4)]$ (**36**) and $[Ni(cod)_2]$ (ratio 1:1 or 2:1) gave as a major product the complex $[K(pmdeta)]_2[Ni(P_4Ph_4)(\eta^2\text{-}P_2Ph_2)]$ (**63**) (Scheme 22), and provided some insight into the mechanism of formation of **62** (Scheme 23). Complex **63** can be considered to be the potassium analogue of the intermediate species in the formation of **62**; however, in the case of potassium, the K–Ni and K–P interactions stabilize the NiP_4 framework and prevent further reaction to give the corresponding potassium analogue of $[Na(Et_2O)_3][Na_3(Et_2O)_2Ni_3(\mu\text{-}P_2Ph_2)_2(\eta^2\text{-}P_2Ph_2)_3]$ (**62**).

Both complexes were characterized by single-crystal X-ray diffraction studies. The molecular structure of **62** shows an ionic complex with an $Na_3Ni_3P_{10}$ anionic core in which two diphenyldiphosphanediide ligands bridge three nickel(0) atoms. Each nickel atom is additionally coordinated in an η^2-fashion by a *trans*-diphenyldiphosphene ligand. The three sodium cations interact with the phosphorus atoms of the diphenyldiphosphanediide ligands as well as the nickel atoms (short Na···Ni contacts of 302.6(3), 316.2(4) and 326.8(3) pm) (Fig. 16). This anionic moiety is counterbalanced by a separated sodium cation which is additionally coordinated by three diethyl ether molecules.

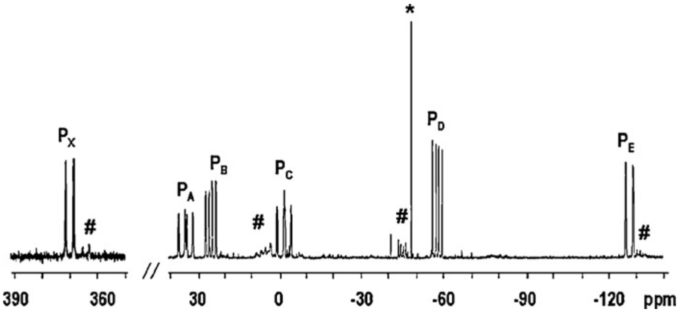


Fig. 15. $^{31}P\{^1H\}$ NMR spectrum (161.97 MHz) of $[Ta(\eta^5\text{-}C_5Me_5)(Ph)(P_6Ph_5)]$ (**61**) (# minor diastereoisomer of **61**, * *cyclo*-P_4Ph_4).

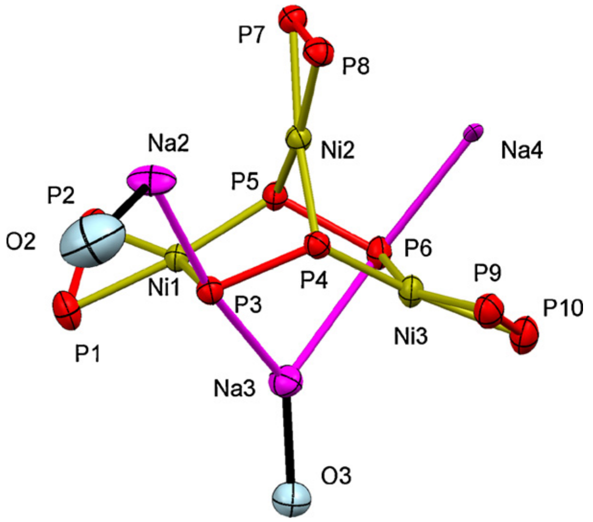
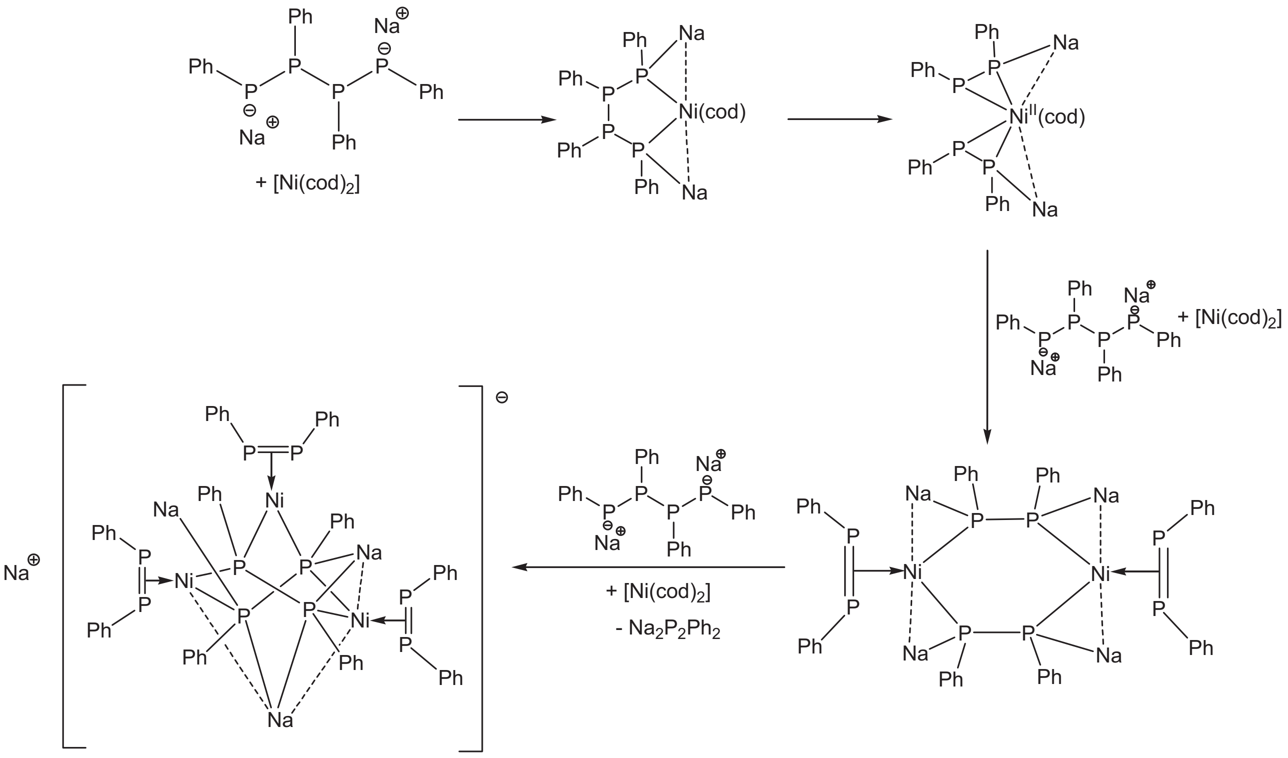


Fig. 16. Anionic part of the molecular structure of $[Na(Et_2O)_3][Na_3(Et_2O)_2Ni_3(\mu\text{-}P_2Ph_2)_2(\eta^2\text{-}P_2Ph_2)_3]$ (**62**). Hydrogen and carbon atoms have been omitted for clarity.



62

Scheme 23. Proposed mechanism for the formation of $[Na(Et_2O)_3][Na_3(Et_2O)_2Ni_3(\mu\text{-}P_2Ph_2)_2(\eta^2\text{-}P_2Ph_2)_3]$ (**62**) (Et_2O donor molecules omitted).

The molecular structure of **63** shows that the nickel atom and the four phosphorus atoms of the dianionic P_4 chain form a puckered five-membered ring. The nickel atom is coordinated by both phosphorus atoms of the diphosphene ligand (P(5) and P(6)) and the terminal phosphorus atoms of the $(P_4Ph_4)^{2-}$ ligand (P(1) and P(4)) in the equatorial positions, and the potassium atoms (K(1) and K(2)) in the axial positions (Table 1), giving rise to pseudo-octahedral coordination of the metal atom. This structure shows short K···Ni distances of 318.5(2) pm for K1 and 310.7(2) pm for K(2), which are the shortest distances reported for an Ni···K interaction in a complex (Fig. 17).

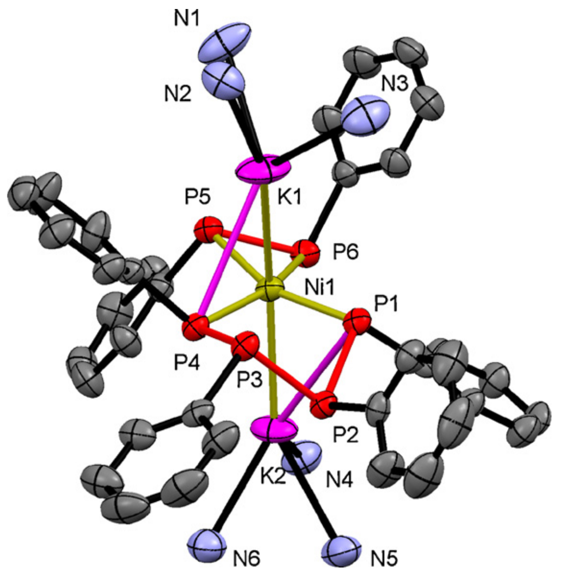


Fig. 17. Molecular structure of $[K(pmdeta)]_2[Ni(P_4Ph_4)(\eta^2\text{-}P_2Ph_2)]$ (**63**) (all hydrogen atoms and carbon atoms of the pmdeta molecules have been omitted for clarity).

The $^{31}P\{^1H\}$ NMR spectra of **62** and **63** showed notable differences. While the spectrum of **62** exhibited very broad signals at room and low temperature (down to −80 °C) which were very similar to those found in its solid-state $^{31}P\{^1H\}$ CP MAS NMR spectrum, the spectrum of **63** consisted of a set of three signals corresponding to an AA′BB′XX′ spin system, which indicates that the dianionic P_4 chain with all-*trans* conformation, observed in the solid state, is retained in solution.

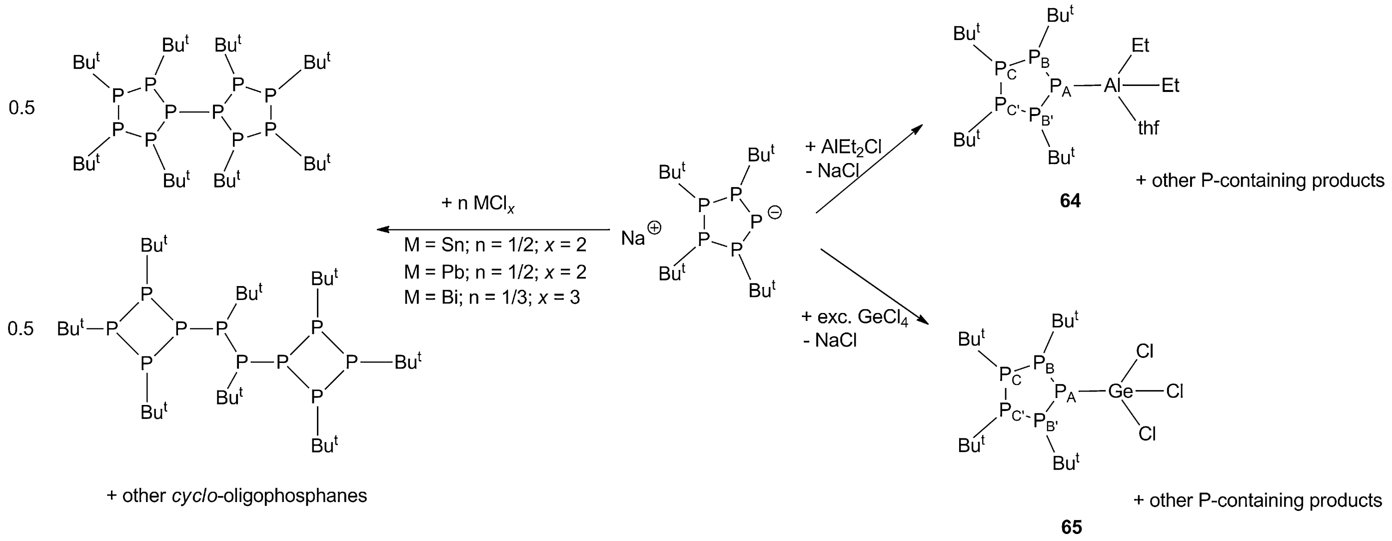
Finally, several other reactions of the sodium and potassium salts of the $(P_4R_4)^{2-}$ ions with transition metal complexes, such as $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$, $[CoCl_2(PPh_3)_2]$, $NiCl_2$, $[Mo(\eta^5\text{-}C_5H_5)Cl_2]_2$, $[Mo(\eta^5\text{-}C_5EtMe_4)Cl_2]_2$, $[MoBr_2(CO)_2(PPh_3)_2]$, Cp_3Yb and $Yb(OSO_2CF_3)_3$, in our hands did not (yet) result in isolable compounds which could be fully characterized. However, $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures with $[ZnCl_2(py)_2]$ (py = pyridine) or $[ZnCl_2(tmeda)]$, showed AA′BB′ spin systems which were presumably due to the formation of the corresponding $[Zn(P_4R_4)(L)_n]$ (L = py, $n = 2$; L = tmeda, $n = 1$) complexes [54].

6. Reactivity of the *cyclo*-$(P_5Bu^t{}_4)^-$ ion

6.1. Reactivity of the cyclo-$(P_5Bu^t{}_4)^-$ ion towards main group metals

As was already observed for the $(P_4R_4)^{2-}$ ions, the highly reducing nature of the *cyclo*-$(P_5Bu^t{}_4)^-$ ion complicates its use as transmetallation reagent for metals in high oxidation states.

In the case of p-block main group metals, such as aluminium, germanium, tin, lead and bismuth, differences in reactivity were observed. While the 1:1 reaction of the sodium salt $[Na(thf)_4][$*cyclo*-$(P_5Bu^t{}_4)]$ (**39**) with $AlEt_2Cl$ and $GeCl_4$ gave a mixture of products



Scheme 24. Reactivity of the sodium salt of *cyclo*-(P$_5$Bu^t$_4$)$^-$ towards main group metals.

including the expected complexes [AlEt$_2${*cyclo*-(P$_5$Bu^t$_4$)}(thf)] (**64**) and [GeCl$_3${*cyclo*-(P$_5$Bu^t$_4$)}] (**65**) (Scheme 24) [55], the reaction of **39** with SnCl$_2$ (2:1), PbCl$_2$ (2:1) or BiCl$_3$ (1:1) resulted in the formation of the phosphorus-rich compounds {*cyclo*-(P$_5$Bu^t$_4$)}$_2$ and {*cyclo*-(P$_4$Bu^t$_3$)PBu^t}$_2$ among other cyclooligophosphanes and elemental metal (Sn, Pb or Bi, respectively), presumably *via* initial formation of the corresponding unstable metal phosphanides [M{*cyclo*-(P$_5$Bu^t$_4$)}$_x$] (Scheme 24) [55].

The phosphanide complexes **64** and **65** were isolated and characterized by ^{31}P{^{1}H} NMR spectroscopy and other analytical techniques. The ^{31}P{^{1}H} NMR spectra showed ABB′CC′ spin systems (ratio 1:2:2), indicating that in solution the P$_5$ ring is bound to the metal atom only by the anionic phosphorus atom.

Reactions with other p-block main group metal compounds such as GaCl$_3$ or SnPh$_3$Cl were also unsuccessful, and in spite of the observation of signals of phosphorus-rich metal compounds in the ^{31}P{^{1}H} NMR spectra, no compounds could be isolated [38].

6.2. Reactivity of the cyclo-(P$_5$Bu^t$_4$)$^-$ ion towards transition metals

Transmetallation reactions of the sodium salt [Na(thf)$_4$][*cyclo*-(P$_5$Bu^t$_4$)] (**39**) with transition metal complexes were more successful. Thus, the 1:1 reaction with [RhCl(PPh$_3$)$_3$] gave the rhodium(I) complex [Rh{*cyclo*-(P$_5$Bu^t$_4$)}(PPh$_3$)$_2$] (**66**; Scheme 25), in which the tetra-*tert*-butylcyclopentaphosphanide ligand, is bound to rhodium via the anionic phosphorus atom and one of the adjacent phosphorus atoms of the ring (Fig. 18) [56].

As was observed for the alkali metal compounds with the *cyclo*-(P$_5$Bu^t$_4$)$^-$ ion, the P$_5$ ring in **66** has an envelope conformation with an all-*trans* conformation of the Bu^t groups (Table 2). This conformation is retained in solution, as indicated by the ^{31}P{^{1}H} NMR spectrum, which showed six multiplets (ratio 1:1:1:2:1:1, ABCDEFG spin system, in which the spins D and E overlap).

Reactions of [Na(thf)$_4$][*cyclo*-(P$_5$Bu^t$_4$)] (**39**) with group 10 complexes are clearly influenced by the nature of the co-ligand of the metal complex, the metal, the reaction conditions and the stoichiometric ratio. Thus, the reaction of **39** with [NiCl$_2$(PEt$_3$)$_2$] (2:1) in polar or nonpolar solvents gave the unusual nickel(0) η^2-3,4,5-tri-*tert*-butylcyclopentaphosphene complex [Ni{*cyclo*-(P$_5$Bu^t$_3$)}(PEt$_3$)$_2$] (**67**) [37], *via* cleavage of a P–C(Bu^t) bond of the anionic *cyclo*-(P$_5$Bu^t$_4$) ring and elimination as Bu^{t}Cl (Scheme 26). Formation of Bu^{t}Cl was indirectly proved by the detection of *cyclo*-(P$_5$Bu^t$_4$H) and isobutene, which are the products of the subsequent reaction of Bu^{t}Cl and [Na(thf)$_4$][*cyclo*-(P$_5$Bu^t$_4$)] (**39**).

However, the transmetallation reaction (2:1) of [Na(thf)$_4$][*cyclo*-(P$_5$Bu^t$_4$)] (**39**) with [NiCl$_2$(bipy)], which contains the more labile bipyridine ligand, gave the expected product, [Ni{*cyclo*-(P$_5$Bu^t$_4$)}$_2$] (**68**) (Scheme 26) [57]. **68** is relatively unstable on heating in solution and rearranges to [Ni{*cyclo*-(P$_5$Bu^t$_4$)PBu^t}{*cyclo*-(P$_4$Bu^t$_3$)}] (**69**). Presumably, the intermediate [Ni{*cyclo*-(P$_5$Bu^t$_4$)}{*cyclo*-(P$_4$Bu^t$_3$)PBu^t}] is formed first, and subsequent migration of the exocyclic PBu^t group of *cyclo*-(P$_4$Bu^t$_3$)PBu^t to the *cyclo*-(P$_5$Bu^t$_4$) ligand gives the novel *cyclo*-{(P$_5$Bu^t$_4$)PBu^t}$^-$ ligand.

Furthermore, reaction of **39** with the nickel dichloride complex with triphenylphosphane ligands (which are weaker ligands than PEt$_3$, but stronger than bipy), [NiCl$_2$(PPh$_3$)$_2$] (1:2), gave the unexpected product [NiCl{*cyclo*-(P$_5$Bu^t$_4$)}(PPh$_3$)] (**70**) (Scheme 26) instead of the expected compound **68**.

Similar behavior was found for palladium(II) complexes. Thus, the major product in the reaction of **39** with [PdCl$_2$(PMe$_2$Ph)$_2$] (2:1) was the palladium(0) η^2-3,4,5-tri-*tert*-butylcyclopentaphosphene complex [Pd{*cyclo*-(P$_5$Bu^t$_3$)}(PMe$_2$Ph)$_2$] (**71**), and only traces of the

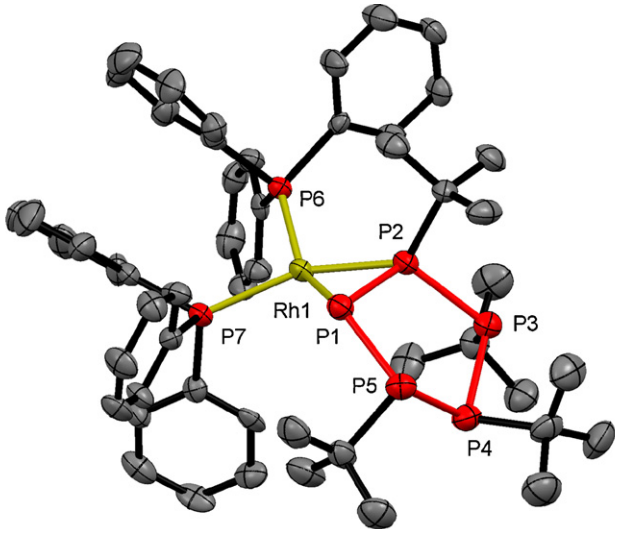
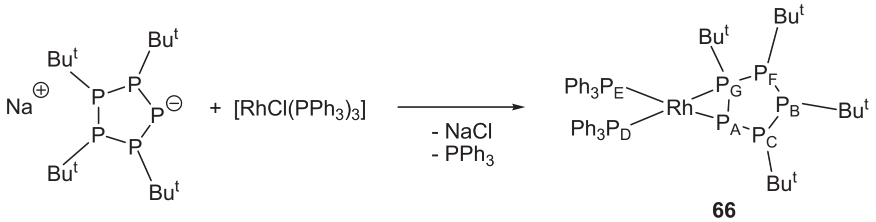
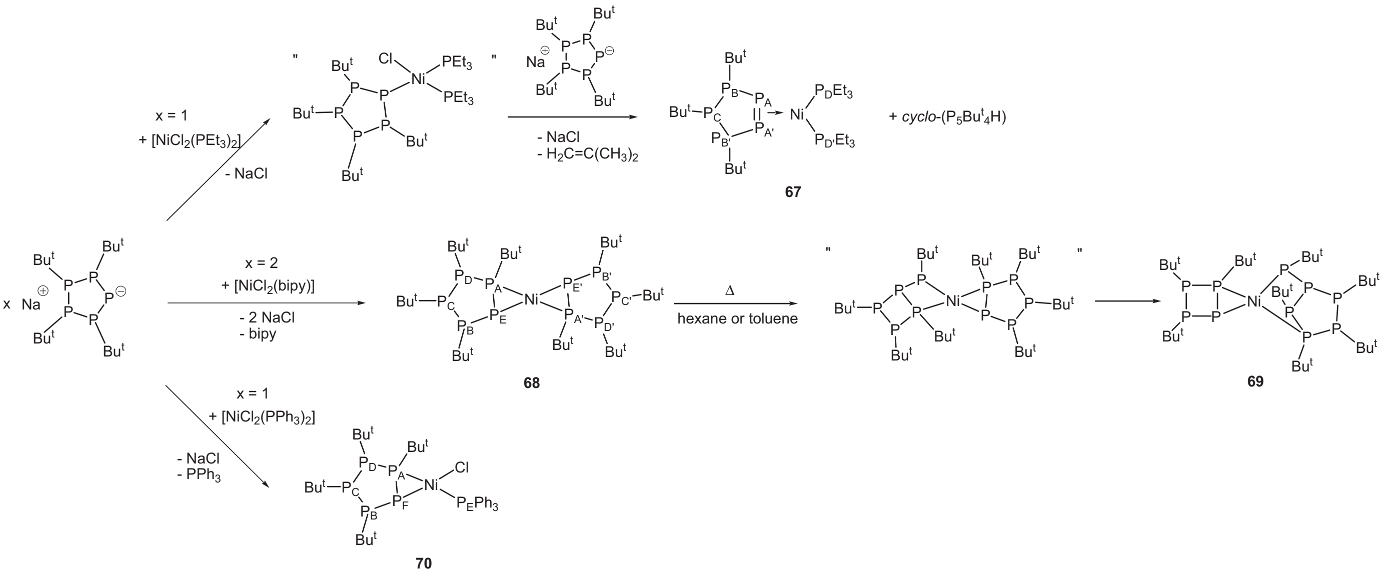


Fig. 18. Molecular structure of [Rh{*cyclo*-(P$_5$Bu^t$_4$)}(PPh$_3$)$_2$] (**66**) (hydrogen atoms have been omitted for clarity).



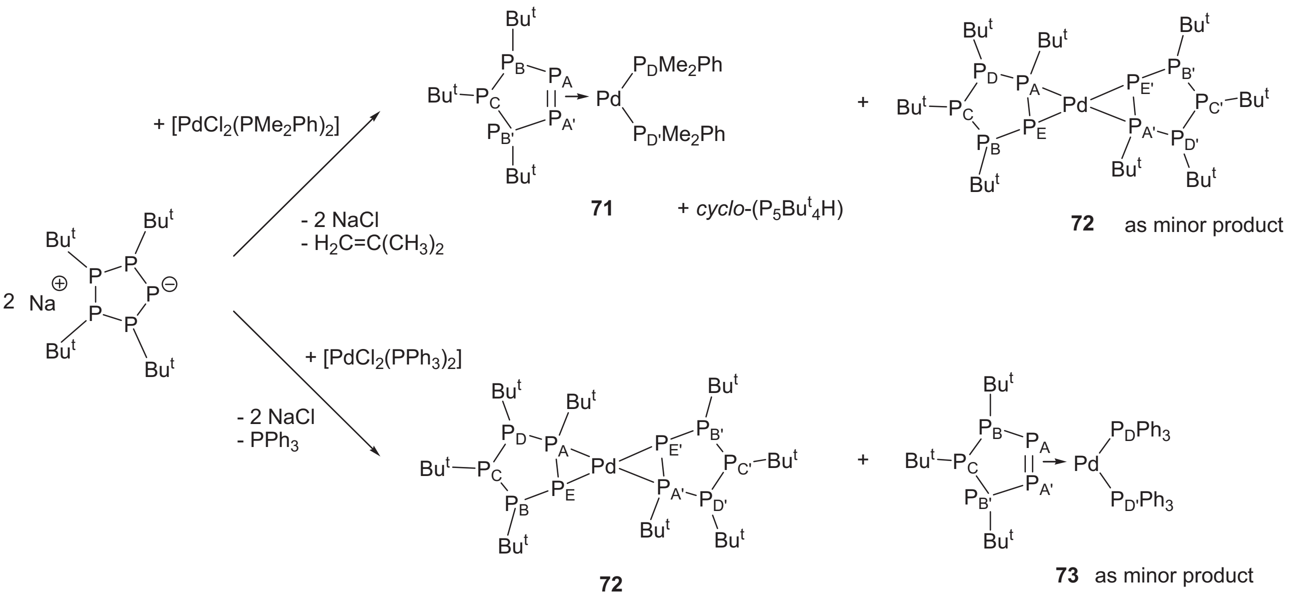
Scheme 25. Synthesis of the rhodium complex [Rh{*cyclo*-($P_5Bu^t{}_4$)}(PPh_3)$_2$] (**66**).



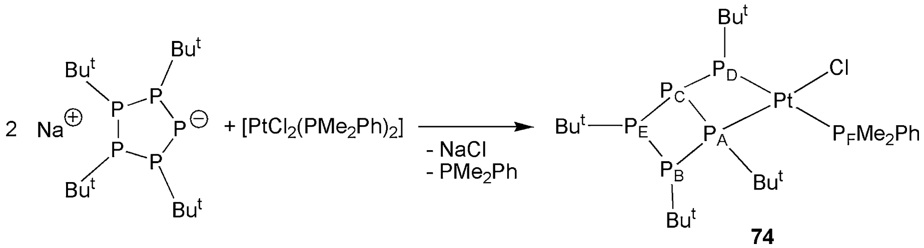
Scheme 26. Reactivity of the *cyclo*-($P_5Bu^t{}_4$)$^-$ ion towards nickel(II) complexes.

transmetallation product [Pd{*cyclo*-($P_5Bu^t{}_4$)}$_2$] (**72**) were obtained (Scheme 27). In addition, in the reaction of **39** with [$PdCl_2(PPh_3)_2$] (2:1), which contains the more labile PPh_3, the expected product [Pd{*cyclo*-($P_5Bu^t{}_4$)}$_2$] (**72**) was isolated, but a small amount of the complex [Pd{*cyclo*-($P_5Bu^t{}_3$)}(PPh_3)$_2$] (**73**) was also formed (Scheme 27) [57].

In the case of platinum(II) complexes, the reaction of **39** with [$PtCl_2(PPh_3)_2$] gave [PtCl{*cyclo*-($P_4Bu^t{}_3$)PBu^t}(PMe_2Ph)] (**74**) (Scheme 28), in which ring contraction had occurred to give the {*cyclo*-($P_4Bu^t{}_3$)PBu^t}$^-$ ion, which was proposed as intermediate in the formation of the nickel complex [Ni{*cyclo*-($P_5Bu^t{}_4$)PBu^t}{*cyclo*-($P_4Bu^t{}_3$)}] (**69**) [57].



Scheme 27. Reactivity of the *cyclo*-($P_5Bu^t{}_4$)$^-$ ion towards palladium(II) complexes.



74

Scheme 28. Synthesis of [PtCl{*cyclo*-($P_4Bu^t_3$)PBu^t}(PMe_2Ph)] (**74**).

The group 10 metal complexes **67**–**74** were characterized by $^{31}P\{^1H\}$ NMR spectroscopy. Most compounds showed first- or higher-order spin systems in accordance with their structures (Table 2). Thus, complexes with the *cyclo*-($P_5Bu^t_3$) ligand and two coordinated phosphanes (**67**, **71** and **73**) show an AA′BB′CDD′ spin system with a large (absolute) coupling constant $^1J(P_A, P_{A'})$ of ca. 470 Hz, which indicates multiple-bond character between P_A and $P_{A'}$ [57]. On the other hand, the $^{31}P\{^1H\}$ NMR spectra of the homoleptic complexes **68** and **72** exhibit five multiplets for an AA′BB′CC′DD′EE′ spin system. These spectra showed the presence of more than one isomer in solution (*cis* and *trans*, due to the chirality of P_A and $P_{A'}$), however, the signals for the *trans* isomer were clearly predominant. An ABCDEF spin system (ratio 1:1:2:1:1) was observed in the $^{31}P\{^1H\}$ NMR spectrum of **70**, while the spectrum of **74** showed a typical first-order ABCDEF spin system with 132 lines in which phosphorus atom A appeared at ca. −125 ppm, due to the "small-ring effect" which shifts all signals to higher field [57].

X-ray diffraction studies on these group 10 metal complexes gave more information about their solid-state structures (Table 2). The molecular structure of homoleptic complexes with two *cyclo*-($P_5Bu^t_4$) ligands (**68** and **72**) showed the typical all-*trans* arrangement of the Bu^t groups, an envelope conformation of the P_5 ring (Fig. 19) and binding of the anionic phosphorus atom and one of its adjacent phosphorus to the metal center. In addition, the P–P bond lengths of the P_5 rings showed a short P–P bond of ca. 215 pm due to interaction of the lone pair of electrons at the anionic phosphorus atom with unoccupied orbitals (with σ*- and d-orbital contributions) at the adjacent phosphorus atom (Table 2) [37].

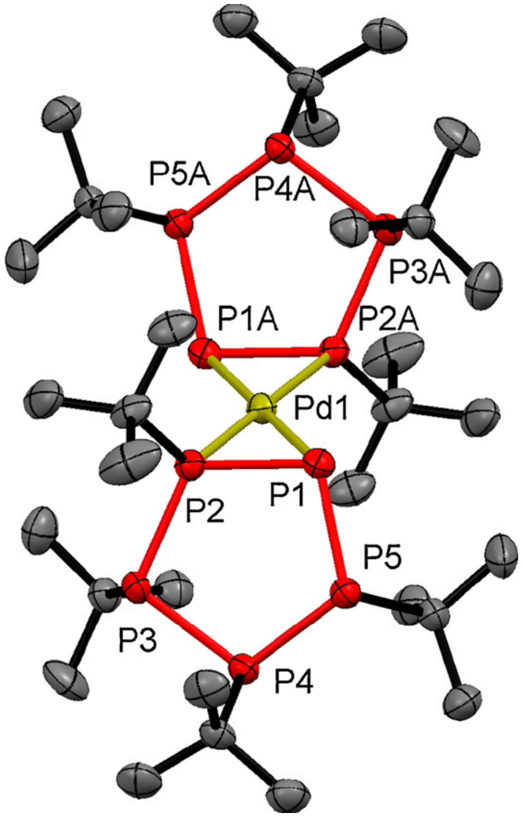


Fig. 19. Molecular structure of [Pd{*cyclo*-($P_5Bu^t_4$)}$_2$] (**72**) (hydrogen atoms have been omitted for clarity).

The "all-*trans*" conformation of the Bu^t groups of the P_5 ligand in an envelope conformation was also observed for the P_5 ring of the *cyclo*-($P_5Bu^t_3$) ligand of the complexes **67**, **71** and **73**; this ligand is coordinated to the metal center *via* both phosphorus atoms of the P═P bond (Fig. 20). Furthermore, the P═P bond length of the P_5 ligand of about 213 pm indicates its multiple bond character.

Both [Ni{*cyclo*-($P_5Bu^t_4$)PBu^t}{*cyclo*-($P_4Bu^t_3$)}] (**69**) (Fig. 21) and [PtCl{*cyclo*-($P_4Bu^t_3$)PBu^t}(PMe_2Ph)] (**74**) (Fig. 22) have a P_4 ring in a butterfly conformation. Furthermore, **69** shows also a very rare seven-membered norbornene-like metallabicycle for the Ni{*cyclo*-($P_5Bu^t_4$)PBu^t} moiety (Fig. 21).

In view of the results obtained in the reactions of [Na(thf)$_4$][*cyclo*-($P_5Bu^t_4$)] (**39**) with complexes of the nickel triad, the coordination chemistry of the *cyclo*-$(P_5Bu^t_4)^-$ ion towards group 11 complexes was explored. Here, it was also observed that the reactivity of the cyclic anion is notably dependent on the metal, its co-ligands and the reaction conditions [58].

Thus, the reaction of [Na(thf)$_4$][*cyclo*-($P_5Bu^t_4$)] (**39**) with [CuCl(PCyp$_3$)$_2$] (1:1) or [CuCl(PPh$_3$)$_3$] (1:1) gave the transmetallation products [Cu{*cyclo*-($P_5Bu^t_4$)}(PCyp$_3$)$_2$] (**75**) and [Cu{*cyclo*-($P_5Bu^t_4$)}(PPh$_3$)$_2$] (**76**), in which the *cyclo*-$(P_5Bu^t_4)^-$ ligand remained intact (Scheme 29). However, formation of [Cu$_2$(μ-Cl){*cyclo*-($P_5Bu^t_4$)}(PCyp$_3$)$_2$] (**77**) was observed when starting from

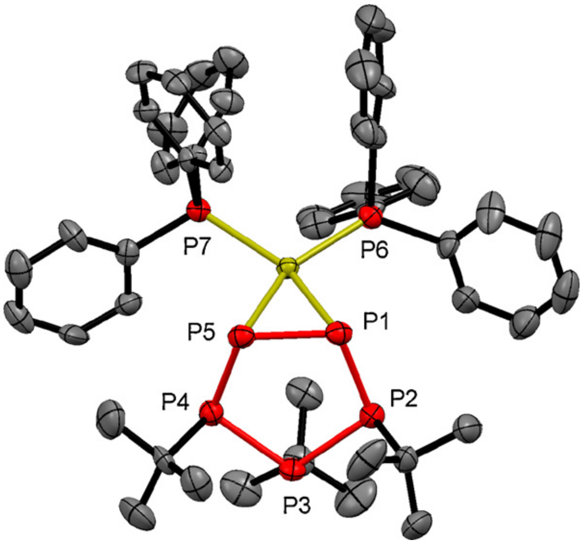
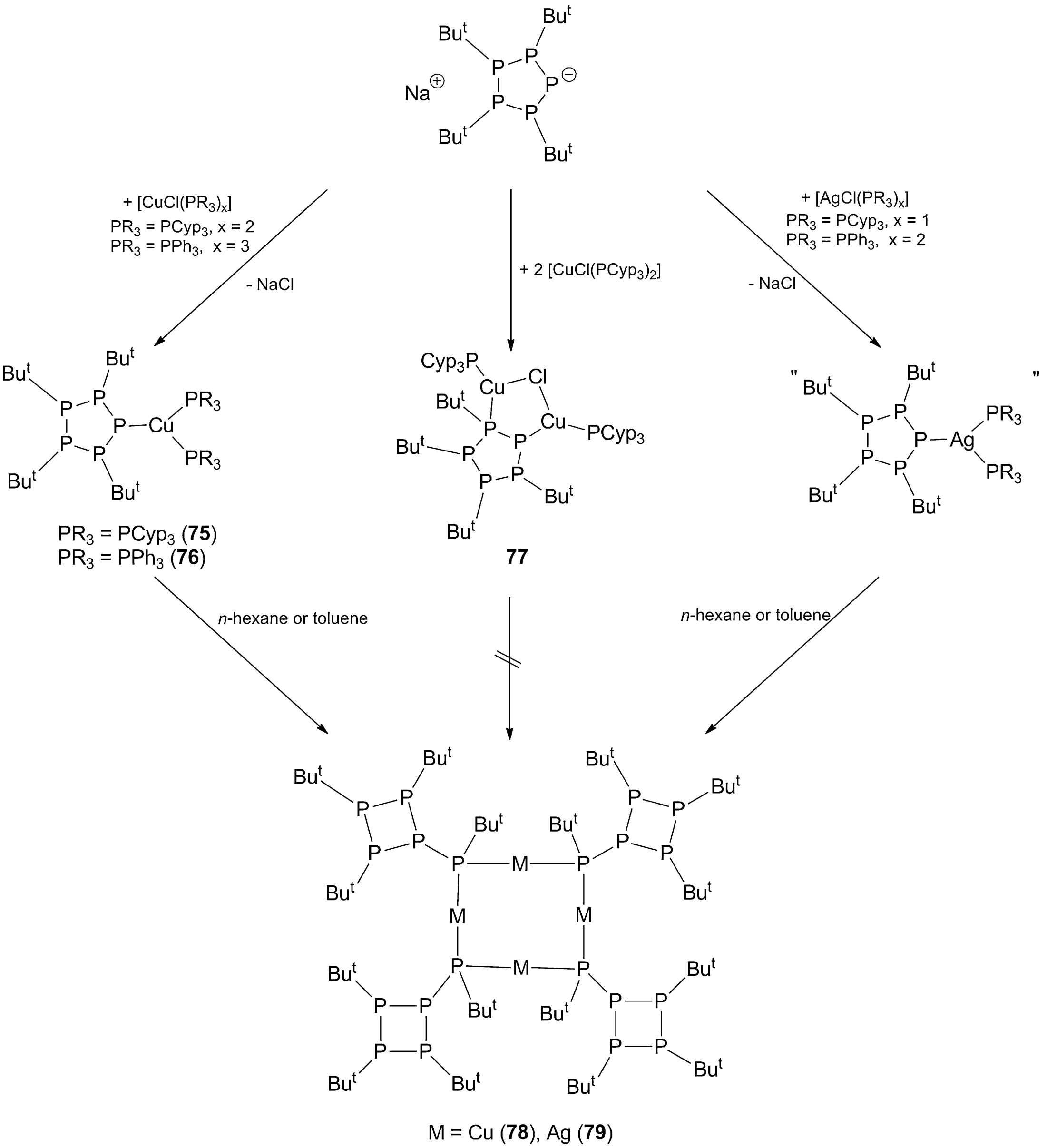


Fig. 20. [Pd{*cyclo*-($P_5Bu^t_3$)}(PPh$_3$)$_2$] (**73**) (hydrogen atoms have been omitted for clarity).



Scheme 29. Reactivity of the *cyclo*-($P_5Bu^t{}_4$)$^-$ ion towards copper(I) and silver(I) complexes.

[CuCl(PCyp$_3$)$_2$] and [Na(thf)$_4$][*cyclo*-($P_5Bu^t{}_4$)] (**39**) in 2:1 molar ratio (Scheme 29).

Complexes **75** and **76** rearranged in non-polar solvents over several weeks to give the tetrameric compound [Cu$_4${*cyclo*-($P_4Bu^t{}_3$)PBu^t}$_4$] (**78**) (Scheme 29), in which the P$_5$ ring is contracted to a four-membered ring. The resulting *cyclo*-($P_4Bu^t{}_3$)PBu^t ligand bridges two metal atoms by coordination of the exocyclic phosphorus atom of the ligand. This rearrangement was not observed for **77**.

An analogous compound [Ag$_4${*cyclo*-($P_4Bu^t{}_3$)PBu^t}$_4$] (**79**) was isolated in the reaction of [Na(thf)$_4$][*cyclo*-($P_5Bu^t{}_4$)] (**39**) with [AgCl(PCyp$_3$)]$_4$ (4:1) or [AgCl(PPh$_3$)$_2$] (1:1) (Scheme 29). It seems that the mononuclear species were formed first (detected in the reaction mixtures by ^{31}P NMR spectroscopy, but not isolated) but were relatively unstable and rearranged rapidly to give the tetranuclear complex **79** (Scheme 29) [58].

In the case of gold(I) complexes, the reaction of **39** with [AuCl(PCyp$_3$)] (1:1) led to formation of the monomeric compound [Au{*cyclo*-($P_5Bu^t{}_4$)}(PCyp$_3$)] (**80**), which also rearranged in non-

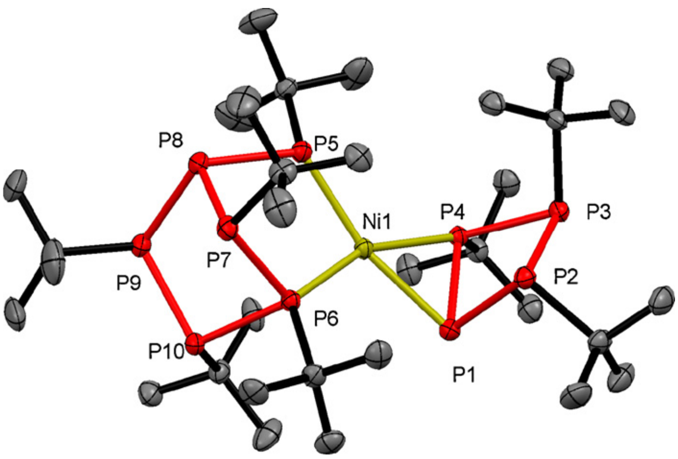
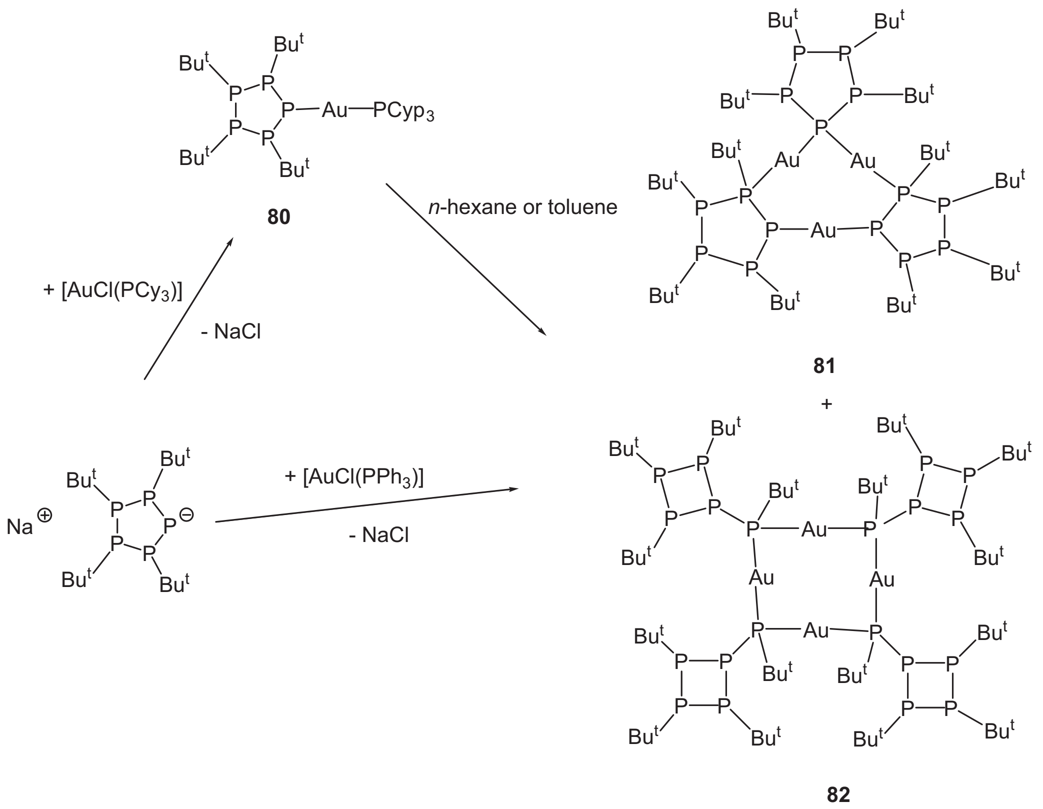


Fig. 21. [Ni{*cyclo*-($P_5Bu^t{}_4$)PBu^t}{*cyclo*-($P_4Bu^t{}_3$)}] (**69**) (hydrogen atoms have been omitted for clarity).



Scheme 30. Reactivity of the *cyclo*-$(P_5Bu^t{}_4)^-$ ion towards gold(I) complexes.

polar solvents to give a mixture of oligomeric compounds, of which $[Au_3\{cyclo\text{-}(P_5Bu^t{}_4)\}_3]$ (**81**) and $[Au_4\{cyclo\text{-}(P_4Bu^t{}_3)PBu^t\}_4]$ (**82**) were characterized (Scheme 30). No monomeric species were detected in the reaction of **39** with $[AuCl(PPh_3)]$, which also resulted in a mixture of oligomeric compounds in which **81** and **82** were detected (Scheme 30) [58].

The group 11 complexes were studied by $^{31}P\{^1H\}$ NMR spectroscopy. Severe line broadening caused by the quadrupole moment of the metal atoms (^{63}Cu, ^{65}Cu) was observed. In addition, dynamic processes involving the phosphorus-rich ligands in the silver and gold compounds and poor solubility of the polynuclear complexes **78**, **79**, **81** and **82** limited the numerical analysis of the chemical shifts and coupling constants of the spectra. Full analysis was only possible for $[Au\{cyclo\text{-}(P_5Bu^t{}_4)\}(PCyp_3)]$ (**80**), which at −80 °C showed six multiplets corresponding to an ABCDEX spin system (Fig. 23).

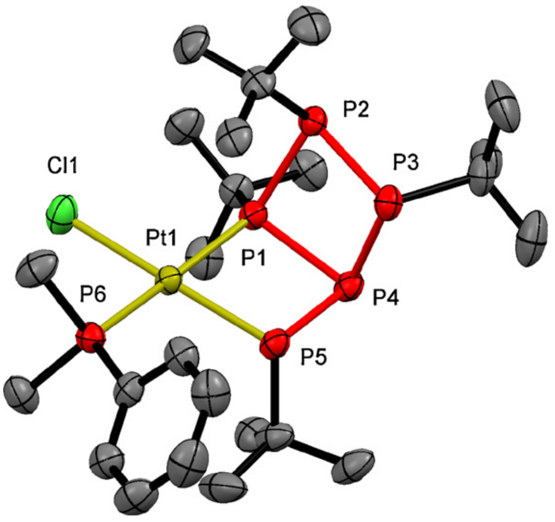


Fig. 22. $[PtCl\{cyclo\text{-}(P_4Bu^t{}_3)PBu^t\}(PMe_2Ph)]$ (**74**) (hydrogen atoms have been omitted for clarity).

The large difference in chemical shifts of the atoms P_A and P_E indicates that one of these phosphorus atoms may be involved in coordination to gold, leading to a coordination number of three at the metal center. At room temperature, this tricoordinate gold complex (A, Scheme 31) may be in rapid equilibrium with an identical structure involving coordination of the other adjacent phosphorus atom (B, Scheme 31, windscreen-wiper mechanism) and/or with the structure in which only the anionic phosphorus atom is bound to gold (C, Scheme 31).

X-ray diffraction studies on the group 11 complexes gave more information about the solid-state structures (Table 2). The molecular structure of complexes with the *cyclo*-$(P_5Bu^t{}_4)$ ligand (**75**, **76**, **77** and **80**) showed the typical all-*trans* arrangement of the Bu^t groups and an envelope conformation of the P_5 ring (Fig. 24). In **75**, **76** and **80** only the anionic phosphorus atom of the P_5 ring is bound to

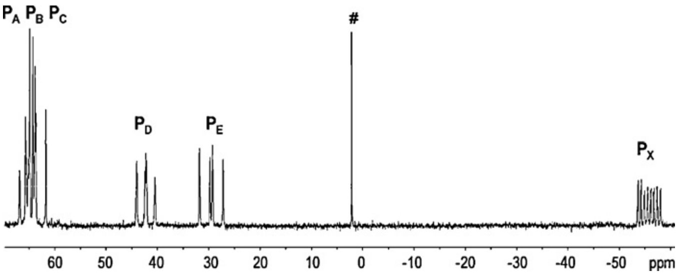
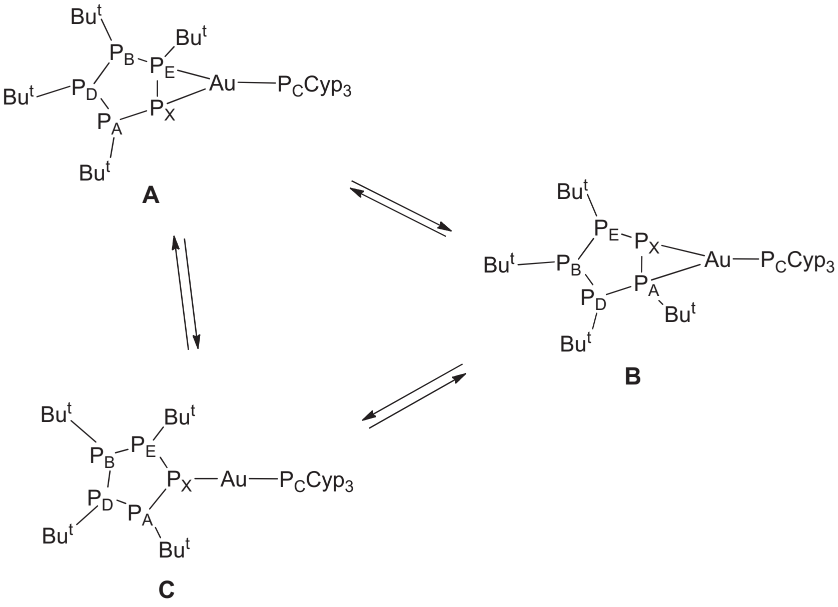


Fig. 23. Low-temperature $^{31}P\{^1H\}$ NMR spectrum (161.97 MHz) of $[Au\{cyclo\text{-}(P_5Bu^t{}_4)\}(PCyp_3)]$ (**80**) (at −80 °C, impurity: # $PCyp_3$).



Scheme 31. Proposed equilibrium for the different species of the gold complex [Au{*cyclo*-($P_5Bu^t{}_4$)}($PCyp_3$)] (**80**) at room temperature.

the metal, resulting in trigonal-planar copper complexes **75** and **76** and linear gold complex **80** (Fig. 24) [58]. In **77**, the P_5 ring bridges a Cu_2Cl fragment via the anionic and an adjacent phosphorus atom. The two copper atoms have a trigonal-planar environment (Fig. 25) [58].

Both copper atoms are nearly coplanar with the two phosphorus atoms of the $PCyp_3$ ligands (P(6) and P(7)). The two copper atoms, P(1) and P(2) of the P_5 ligand and Cl(1) form a five-membered ring with an envelope conformation (Fig. 25).

Finally, in the tetrameric complexes **78**, **79** and **82**, the four-membered *cyclo*-($P_4Bu^t{}_3$) groups are in a butterfly conformation with an all-*trans* arrangement of the Bu^t substituents with only coordination of the exocyclic phosphorus atom of the {*cyclo*-($P_4Bu^t{}_3$)PBu^t}$^-$ ligand, bridging two metal centers. Each metal atom is coordinated in a distorted linear fashion (Fig. 26).

Further reactions of the sodium salt **39** with other transition metal complexes, such as [Ti(η^5-C_5H_5)$_2$Cl$_2$], [Zr(η^5-C_5H_5)$_2$Cl$_2$], [CoCl$_2$(PPh$_3$)$_2$], Cp$_3$Yb, Yb(OSO$_2$CF$_3$)$_3$ and [Ta(η^5-C_5Me_5)Cl$_4$], were performed but did not lead to isolable products. However, ^{31}P{^{1}H} NMR spectra of the reaction mixtures with zinc(II) complexes, [{RhCl(cod)}$_2$] and [MnBr(CO)$_5$] showed complex signals which indicate the formation of (possibly rearranged) phosphorus-rich metal complexes, but further investigations must be carried out for their full characterization [59].

7. Future applications of phosphorus-rich metal oligophosphanides

Phosphorus-rich metal oligophosphanides could be suitable candidates for the development of alternative routes for the preparation of metal phosphides (M_xP_y, with $y > x$) under mild conditions. One of the key steps in this process is the removal of the R groups at phosphorus, which should be facilitated by thermal decomposition. Organyl-free M_xP_y species have already been observed in the mass spectra of several of the studied complexes, e.g., [Rh_2P_3]$^+$ and [Rh_2P_2]$^+$ in [Rh(P_4HMes_4)(cod)] (**49**), [PtP_4]$^+$

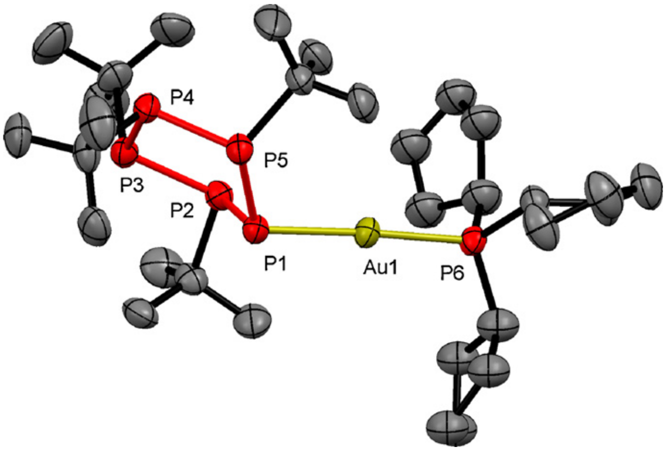


Fig. 24. Molecular structure of [Au{*cyclo*-($P_5Bu^t{}_4$)}($PCyp_3$)] (**80**) (hydrogen atoms have been omitted for clarity).

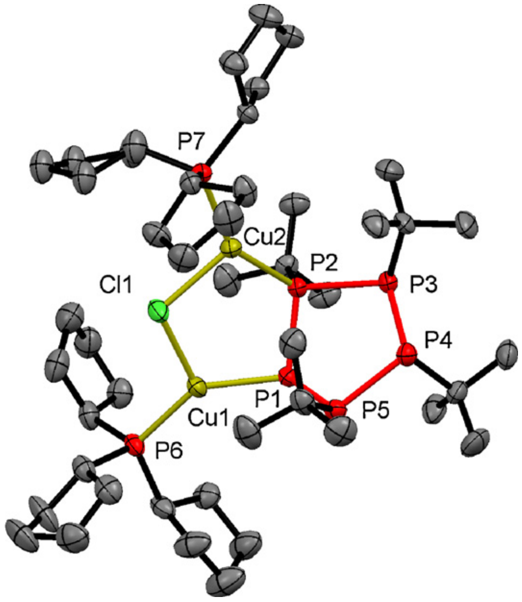


Fig. 25. Molecular structure of [Cu_2(μ-Cl){*cyclo*-($P_5Bu^t{}_4$)}($PCyp_3$)$_2$] (**77**) (hydrogen atoms have been omitted for clarity).

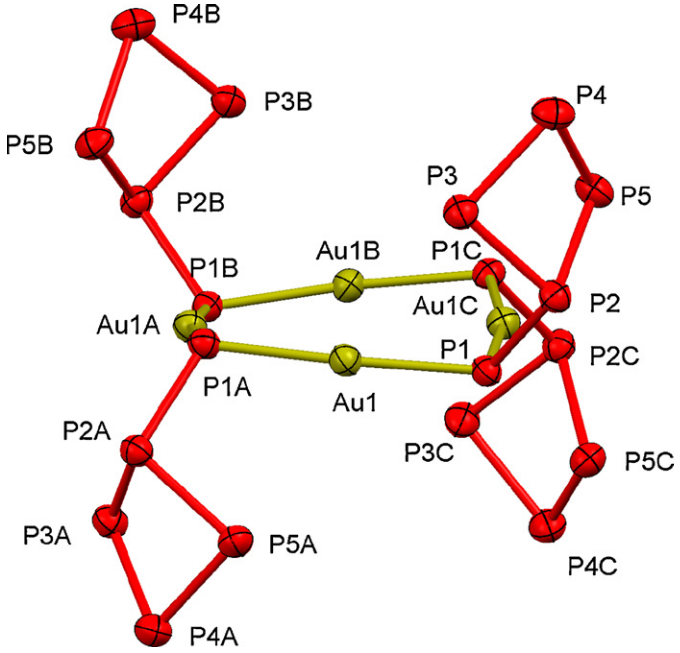


Fig. 26. Section of the molecular structure of $[Au_4\{cyclo\text{-}(P_4Bu^t_3)PBu^t\}_4]$ (**82**) (carbon and hydrogen atoms have been omitted for clarity).

in $[Pt(P_4Mes_4)(cod)]$ (**55**), $[RhP_5]^+$ in $[Rh\{cyclo\text{-}(P_5Bu^t_4)\}(PPh_3)_2]$ (**66**), $[NiP_5]^+$ and $[NiP_6]^+$ in $[Ni\{cyclo\text{-}(P_5Bu^t_4)\}_2]$ (**68**), $[NiClP_6]^+$ and $[NiP_5]^+$ in $[NiCl\{cyclo\text{-}(P_5Bu^t_4)\}(PPh_3)]$ (**70**), $[PdP_5]^+$ and $[PdP_4]^+$ in $[Pd\{cyclo\text{-}(P_5Bu^t_3)\}(PMe_2Ph)_2]$ (**71**) and $[Pd\{cyclo\text{-}(P_5Bu^t_4)\}_2]$ (**72**), $[PdP_6]^+$, $[PdP_5]^+$ and $[PdP_4]^+$ in $[Pd\{cyclo\text{-}(P_5Bu^t_3)\}(PPh_3)_2]$ (**73**), and $[PtP_5]^+$ in $[PtCl\{cyclo\text{-}(P_4Bu^t_3)PBu^t\}(PMe_2Ph)]$ (**74**). While it may be difficult to control the morphology of the resulting materials, the development of future applications of phosphorus-rich metal oligophosphanides is feasible now that procedures for their targeted synthesis have been developed.

8. Conclusions

The targeted synthesis of ions such as $(P_4R_4)^{2-}$, $(P_4HR_4)^-$ (R = Ph, Mes) and $cyclo\text{-}(P_5Bu^t_4)^-$ and their versatile reactivity towards main group and transition metal complexes allowed the preparation of a large variety of phosphorus-rich metal oligophosphanides. In reactions with the anions $(P_4R_4)^{2-}$ or $(P_4HR_4)^-$ (R = Ph, Mes), complexes with intact $(P_4R_4)^{2-}$ or $(P_4HR_4)^-$ ligands are formed or degradation or oxidative coupling was observed resulting in complexes with $(P_3R_3)^{2-}$, $(P_2R_2)^{2-}$, and diphosphene (P_2R_2) or even $(P_6R_6)^{2-}$ ligands. On the other hand, in reactions with metal complexes the $cyclo\text{-}(P_5Bu^t_4)^-$ ion was observed to either stay intact or rearrange to $cyclo\text{-}(P_5Bu^t_3)$, $cyclo\text{-}(P_4Bu^t_3)^-$, $\{cyclo\text{-}(P_4Bu^t_3)PBu^t\}^-$ or $\{cyclo\text{-}(P_5Bu_4{}^t)PBu^t\}^-$, depending on the starting materials. These phosphorus-rich metal complexes may be suitable precursors for phosphorus-rich binary metal phosphides (M_xP_y, with $y > x$), which are expected to exhibit interesting properties for materials science.

Acknowledgements

E.H.-H. would like to thank her co-workers who have worked or are still working in this research area (P. Lönnecke, S. Blaurock, R. Felsberg, A. Schisler, R. Wolf, C. Limburg, S. Bauer, H. Bittig, B. Gallego, R. Herrero, I. Jevtovikj, and A. Kircali). We are also grateful to BASF SE, Chemetall and Umicore AG for their generous donations of chemicals. Financial support from the Alexander von Humboldt-Stiftung (Humboldt-Fellowship for S.G.-R.), the Deutsche Forschungsgemeinschaft (He 1376/22-1, 22-2 and within the Graduate School of Excellence *BuildMoNa*) and the EU-COST Action CM0802 *PhoSciNet* is gratefully acknowledged.

References

[1] (a) M. Baudler, K. Glinka, Chem. Rev. 93 (1993) 1623;
(b) N. Etkin, M.C. Fermin, D.W. Stephan, J. Am. Chem. Soc. 119 (1997) 2954–2955.
[2] See for example:
(a) M. Baudler, Pure Appl. Chem. 52 (1980) 755;
(b) M. Baudler, Angew. Chem. 94 (1982) 520;
M. Baudler, Angew. Chem. Int. Ed. Engl. 21 (1982) 492;
(c) M. Baudler, Z. Chem. 24 (1984) 352;
(d) M. Baudler, Angew. Chem. 99 (1987) 429;
M. Baudler, Angew. Chem. Int. Ed. Engl. 26 (1987) 419;
(e) C. Moser, F. Belaj, R. Pietschnig, Chem. Eur. J. 15 (2009) 12589.
[3] K.B. Dillon, F. Mathey, J.F Nixon, Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-organic Chemistry, Wiley, Chichester, 1998.
[4] Y.R. Luo, Comprehensive Handbook of Chemical Bond Energies, CRC Press, Boca Raton, 2007.
[5] S. Gómez-Ruiz, E. Hey-Hawkins, New J. Chem. 34 (2010) 1525.
[6] S. Gómez-Ruiz, E. Hey-Hawkins, Metal complexes with anionic polyphosphorus chains as potential precursors for the synthesis of metal phosphides, in: M. Peruzzini, L. Gonsalvi (Eds.), Phosphorus Compounds: Advanced Tools in Catalysis and Material Sciences, Catalysis and Material Science Applications Series, Catalysis by Metal Complexes, Vol.36, first ed., Springer, London UK, 2011, March, ISBN: 978-90-481-3816-6.
[7] (a) R. Hoffmann, Angew. Chem. 94 (1982) 725;
(b) H.-G. von Schnering, W. Hönle, Chem. Rev. 88 (1988) 243.
[8] J. Liu, X. Chen, M. Shao, C. An, W. Yu, Y. Qian, J. Cryst. Growth 252 (2003) 297.
[9] (a) I.I. Abu, K.J. Smith, Appl. Catal. A: Gen. 328 (2007) 58;
(b) K. Senevirathne, A.W. Burns, M.E. Bussell, S.L. Brock, Adv. Funct. Mater. 17 (2007) 3933;
(c) Y. Shu, S.T. Oyama, Carbon 43 (2005) 1517;
(d) R. Prins, G. Pirngruber, T. Weber, Chimia 55 (2001) 791;
(e) V. Zuzaniuk, R. Prins, J. Catal. 219 (2003) 85;
(f) J.A. Rodriguez, J.-Y. Kim, J.C. Hanson, S.J. Sawhill, M.E. Bussell, J. Phys. Chem. B 107 (2003) 6276.
[10] C. Stinner, R. Prins, T. Weber, J. Catal. 202 (2001) 187.
[11] (a) H. Chiriac, A.-E. Moga, M. Urse, I. Paduraru, N. Lupu, J. Magn. Magn. Mater. 272–276 (2004) 1678;
(b) J. Park, B. Koo, K.Y. Yoon, Y. Hwang, M. Kang, J.G. Park, T. Hyeon, J. Am. Chem. Soc. 127 (2005) 8433;
(c) S. Boyanov, J. Bernardi, F. Gillot, L. Dupont, M. Womes, J.M. Tarascon, L. Monconduit, M.L. Doublet, Chem. Mater. 18 (2006) 3531;
(d) Z. Gu, M. Parans Paranthaman, Z. Pan, Cryst. Growth Des. 9 (2009) 525.
[12] See for example:
(a) A.B. Burg, W. Mahler, J. Am. Chem. Soc. 80 (1958) 415;
(b) K. Issleib, M. Keil, Z. Anorg. Allg. Chem. 333 (1964) 10;
(c) H.G. Ang, J.S. Shannon, B.O. West, Chem. Commun. (1965) 10;
(d) G.W.A. Fowles, D.K. Jenkins, Chem. Commun. (1965) 61;
(e) A. Forster, C.S. Cundy, M. Green, F.G.A. Stone, Inorg. Nucl. Chem. Lett. 2 (1966) 233;
(f) M. Baudler, F. Salzer, J. Hahn, Z. Naturforsch. 37B (1982) 1529;
(g) M. Baudler, F. Salzer, J. Hahn, E. Därr, Angew. Chem. 97 (1985) 410;
M. Baudler, F. Salzer, J. Hahn, E. Därr, Angew. Chem. Int. Ed. 14 (1985) 415.
[13] A.-M. Caminade, J.-P. Majoral, R. Mathieu, Chem. Rev. 91 (1991) 575.
[14] R. Wolf, M. Finger, C. Limburg, A.C. Willis, S.B. Wild, E. Hey-Hawkins, Dalton Trans. (2006) 831.
[15] (a) R. Ahlrichs, D. Fenske, H. Oesen, U. Schneider, Angew. Chem. 104 (1992) 312;
(b) J. Queisser, D. Fenske, Z. Anorg. Allg. Chem. 620 (1994) 58;
(c) J. Queisser, H. Oesen, D. Fenske, B. Lehari, Z. Anorg. Allg. Chem. 620 (1994) 1821;
(d) D. Fenske, J. Queisser, H. Schottmüller, Z. Anorg. Allg. Chem. 624 (1998) 443;
(e) D. Fenske, J. Queisser, H. Schottmüller, Z. Anorg. Allg. Chem. 622 (1996) 1731.
[16] C. Üffing, C. von Hänisch, H. Schnöckel, Z. Anorg. Allg. Chem. 626 (2000) 1557.
[17] W. Uhl, M. Benter, J. Chem. Soc. Dalton Trans. (2000) 3133.
[18] B.O. West, in: A.K. Rheingold (Ed.), Homoatomic Rings, Chains and Macromolecules of Main-Group Elements, Elsevier, Amsterdam, 1977, p. 409.
[19] (a) S.J. Geier, D.W. Stephan, Chem. Commun. (2008) 2779;
(b) S.J. Geier, D.W. Stephan, Chem. Commun. (2008) 99;
(c) G. Bai, P. Wei, A.K. Das, D.W. Stephan, Dalton Trans. 1141 (2006).
[20] R. Bartsch, S. Hietkamp, S. Morton, O. Stelzer, J. Organomet. Chem. 222 (1981) 263.
[21] (a) L. Weber, D. Bungardt, K. Reizig, R. Boese, R. Benn, Chem. Ber. 120 (1987) 451;
(b) L. Weber, U. Sonnenberg, Chem. Ber. 124 (1991) 725.
[22] R. Felsberg, S. Blaurock, P. Junk, R. Kirmse, A. Voigt, E. Hey-Hawkins, Z. Anorg. Allg. Chem. 630 (2004) 806.

[23] M.A. Beswick, N. Choi, A.D. Hopkins, M. McPartlin, M.E.G. Mosquera, P.R. Raithby, A. Rothenberger, D. Stalke, A.J. Wheatley, D.S. Wright, Chem. Commun. (1998) 2485.

[24] (a) E. Hey, S.G. Bott, J.L. Atwood, Chem. Ber. 121 (1988) 561;
(b) E. Hey, Z. Naturforsch. 43B (1988) 1271.

[25] H. Köpf, R. Voigtländer, Chem. Ber. 114 (1981) 2731.

[26] R.A. Jones, M.H. Seeberger, B.R. Whittlesey, J. Am. Chem. Soc. 107 (1985) 6424.

[27] (a) K. Issleib, K. Krech, Chem. Ber. 98 (1965) 2545;
(b) E. Fluck, K. Issleib, Z. Anorg. Allg. Chem. 339 (1965) 274;
(c) K. Issleib, K. Krech, Chem. Ber. 99 (1966) 1310;
(d) K. Issleib, M. Hoffmann, Chem. Ber. 99 (1966) 1320;
(e) K. Issleib, Ch. Rockstroh, I. Duchek, E. Fluck, Z. Anorg. Allg. Chem. 360 (1968) 77;
(f) K. Issleib, K. Krech, J. Prakt. Chem. 311 (1969) 463.

[28] (a) B. Riegel, A. Pfitzner, G. Heckmann, E. Fluck, H. Binder, Phosphorus Sulfur Silicon 93–94 (1994) 173;
(b) B. Riegel, A. Pfitzner, G. Heckmann, H. Binder, E. Fluck, Z. Anorg. Allg. Chem. 620 (1994) 8;
(c) B. Riegel, A. Pfitzner, G. Heckmann, H. Binder, E. Fluck, Z. Anorg. Allg. Chem. 621 (1995) 1989;
(d) D. Bongert, G. Heckmann, W. Schwarz, H.D. Hausen, H. Binder, Z. Anorg. Allg. Chem. 621 (1995) 1358–1364;
(e) D. Bongert, G. Heckmann, W. Schwarz, H.D. Hausen, H. Binder, Z. Anorg. Allg. Chem. 622 (1996) 1167;
(f) D. Bongert, G. Heckmann, H.D. Hausen, W. Schwarz, H. Binder, Z. Anorg. Allg. Chem. 622 (1996) 1793–1798;
(g) H. Binder, B. Schuster, W. Schwarz, K.W. Klinkhammer, Z. Anorg. Allg. Chem. 625 (1999) 699.

[29] M. Baudler, C. Gruner, G. Fürstenberg, B. Kloth, F. Saykowski, U. Özer, Z. Anorg. Allg. Chem. 446 (1978) 169.

[30] A. Schmidpeter, G. Burget, Phosphorus Sulfur 22 (1985) 323.

[31] G. Fritz, K. Stoll, Z. Anorg. Allg. Chem. 538 (1986) 78.

[32] G. Fritz, R. Biastoch, K. Stoll, T. Vaahs, D. Hanke, H.W. Schneider, Phosphorus Sulfur 30 (1987) 385.

[33] (a) J. Geier, H. Rüegger, M. Wörle, H. Grützmacher, Angew. Chem. 115 (2003) 4081;
J. Geier, H. Rüegger, M. Wörle, H. Grützmacher, Angew. Chem. Int. Ed. 42 (2003) 3951;
(b) J. Geier, J. Harmer, H. Grützmacher, Angew. Chem. 116 (2004) 4185;
J. Geier, J. Harmer, H. Grützmacher, Angew. Chem. Int. Ed. 43 (2004) 4093.

[34] R. Wolf, A. Schisler, P. Lönnecke, C. Jones, E. Hey-Hawkins, Eur. J. Inorg. Chem. (2004) 3277.

[35] R. Wolf, E. Hey-Hawkins, Z. Anorg. Allg. Chem. 632 (2006) 727.

[36] R. Herrero, S. Gómez-Ruiz, J.Z. Dávalos, E. Hey-Hawkins, C. R. Chimie 13 (2010) 1185.

[37] A. Schisler, P. Lönnecke, U. Huniar, R. Ahlrich, E. Hey-Hawkins, Angew. Chem. 113 (2001) 4345;
A. Schisler, P. Lönnecke, U. Huniar, R. Ahlrich, E. Hey-Hawkins, Angew. Chem. Int. Ed. Engl. 40 (2001) 4216.

[38] S. Gómez-Ruiz, R. Herrero, E. Hey-Hawkins, unpublished results.

[39] D. Stein, A. Dransfeld, M. Flock, H. Rüegger, H. Grützmacher, Eur. J. Inorg. Chem. (2006) 4157.

[40] R. Wolf, S. Gómez-Ruiz, J. Reinhold, W. Böhlmann, E. Hey-Hawkins, Inorg. Chem. 45 (2006) 9107.

[41] A. Schisler, Dissertation, Universität Leipzig, 2003.

[42] See for example:
(a) M. Peruzzini, I. de los Ríos, A. Romerosa, F. Vizza, Eur. J. Inorg. Chem. (2001) 593;
(b) M. Scheer, Coord. Chem. Rev. 163 (1997) 271, and references therein.

[43] (a) R.A. Bartlett, M.M. Olmstead, P.P. Power, Inorg. Chem. 25 (1986) 1243;
(b) R.A. Bartlett, H.V.R. Dias, H. Hope, B.D. Murray, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 108 (1986) 6921;
(c) P.P. Power, Acc. Chem. Res. 21 (1988) 147.

[44] (a) R. Wolf, Dissertation, Universität Leipzig, 2005;
(b) R. Wolf, S. Gómez-Ruiz, E-Hey-Hawkins, unpublished results.

[45] R.J. Baker, C. Jones, D.P. Mills, D.M. Murphy, E. Hey-Hawkins, R. Wolf, Dalton Trans. (2006) 64.

[46] R. Wolf, E. Hey-Hawkins, Angew. Chem. 117 (2005) 6398;
R. Wolf, E. Hey-Hawkins, Angew. Chem. Int. Ed. 44 (2005) 6241.

[47] S. Gómez-Ruiz, R. Wolf, E. Hey-Hawkins, Dalton Trans. (2008) 1982.

[48] S. Gómez-Ruiz, E. Hey-Hawkins, Dalton Trans. (2007) 5678.

[49] (a) J. Chatt, P.B. Hitchcock, A. Pidcock, C.P. Warrens, K.R. Dixon, J. Chem. Soc. Chem. Commun. (1982) 932;
(b) J. Chatt, P.B. Hitchcock, A. Pidcock, C.P. Warrens, K.R. Dixon, J. Chem. Soc. Dalton Trans. (1984) 2237.

[50] S. Gómez-Ruiz, B. Gallego, E. Hey-Hawkins, Dalton Trans. (2009) 2915.

[51] S. Gómez-Ruiz, R. Frank, B. Gallego, S. Zahn, B. Kirchner, E. Hey-Hawkins, Eur. J. Inorg. Chem (2010), doi:10.1002/ejic.201001137 (in press).

[52] R. Wolf, E. Hey-Hawkins, Eur. J. Inorg. Chem. (2006) 1348.

[53] S. Gómez-Ruiz, S. Zahn, B. Kirchner, W. Böhlmann, E. Hey-Hawkins, Chem. Eur. J. 14 (2008) 8980.

[54] R. Wolf, S. Gómez-Ruiz, A. Kircali, E. Hey-Hawkins, unpublished results.

[55] A. Schisler, P. Lönnecke, T. Gelbrich, E. Hey-Hawkins, Dalton Trans. (2004) 2895.

[56] A. Schisler, P. Lönnecke, E. Hey-Hawkins, Inorg. Chem. 44 (2005) 461.

[57] S. Gómez-Ruiz, A. Schisler, P. Lönnecke, E. Hey-Hawkins, Chem. Eur. J. 13 (2007) 7974.

[58] S. Gómez-Ruiz, R. Wolf, S. Bauer, H. Bittig, A. Schisler, P. Lönnecke, E. Hey-Hawkins, Chem. Eur. J. 14 (2008) 4511.

[59] A. Kircali, A. Schisler, R. Wolf, R. Herrero, S. Gómez-Ruiz, E. Hey-Hawkins, unpublished results.