The versatile reactivity of tetra-*tert*-butyl-cyclopentaphosphanide monoanions†‡§

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Received (in Montpellier, France) 6th March 2010, Accepted 20th April 2010
DOI: 10.1039/c0nj00181c

The synthesis, reactivity and properties of organic cyclic oligophosphanes have been intensively studied; however, the number of metal complexes of their related anionic species described in the literature is still small. This article reviews the different synthetic methods for the preparation of metal complexes of cyclic oligophosphanide monoanions, such as *cyclo*-$(P_nR_{n-1})^-$ (n = 3–5) (with special attention to the *cyclo*-$(P_5{}^tBu_4)^-$ ion), which may be suitable precursors for phosphorus-rich binary metal phosphides (M_xP_y, with $y > x$).

Introduction

Cyclooligophosphanes, *cyclo*-$(PR)_n$,[1] which are isolobal to cycloalkanes, have attracted the interest of chemists for a long time. While the first example of this class of compounds, *cyclo*-$(PPh)_5$, was synthesised as early as 1877,[2] the first cyclooligophosphanide anions, *cyclo*-$(P_nR_{n-1})^-$, were reported only about 100 years later by Baudler and co-workers.[3,4] Even today, the number of readily accessible pure compounds is still small. The alkali metal compounds K[*cyclo*-$(P_3{}^tBu_2)$],[3] K[*cyclo*-(P_5Ph_4)][5] and Li[*cyclo*-$(P_n{}^tBu_{n-1})$] (n = 3–5)[6,7] have only been obtained as inseparable mixtures and characterised by ^{31}P NMR spectroscopy. In spite of their potential as transmetallation agents, no further studies on their coordination chemistry were subsequently carried out.

Only more recently have we reported the targeted high yield synthesis of Na[*cyclo*-$(P_5{}^tBu_4)$], which exhibits a rich coordination chemistry due to the possibility that each P atom may be involved in coordination *via* its lone pair of electrons.[8] Additionally, metal complexes with anionic polyphosphorus ligands may be an alternative for the development of rational syntheses for binary metal phosphides (M_xP_y), which are a fascinating class of compounds with unusual structures and interesting properties for materials science.[9]

Synthesis and properties of cyclic oligophosphanides

We have reported the targeted synthesis of anionic ring systems such as M[*cyclo*-(P_5R_4)] (M = Na, K; R = ^{i}Pr, ^{t}Bu, Ph),[8,10–12] and recently also the preparation of Li[*cyclo*-$(P_5{}^tBu_4)$].[13]

Santiago Gómez-Ruiz

Santiago Gómez-Ruiz (born in Toledo in 1978) graduated in chemistry at the University of Castilla-La Mancha (Spain) in 2001 and then moved to Rey Juan Carlos University (Madrid, Spain), where he was appointed as an Assistant Professor and earned his PhD degree in 2004. In 2006, as an Alexander von Humboldt Research Fellow, he joined Professor Hey-Hawkins' group at the Universität Leipzig (Germany), where he worked for two years on metal complexes with phosphorus-rich anions. In 2009, he was appointed as a Professor at Rey Juan Carlos University where he currently works on the synthesis of biocompatible materials functionalized with metal complexes with anticancer properties.

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Evamarie Hey-Hawkins (1957) has been a Full Professor of Inorganic Chemistry at Universität Leipzig, Germany, since 1993. She received her diploma (1982) and doctoral degree (1983) at the University of Marburg, Germany. After stays in the UK (University of Sussex, 1984–85) and Australia (Western Australia and ANU, 1985–87), she completed her habilitation at Marburg (1988). From 1988–90 she worked at the MPI for Solid State Research, Stuttgart, and was awarded a Heisenberg Grant (1990–94). Her scientific interests are in organophosphorus and transition metal chemistry. Since 2007 she has been the Speaker of the Excellence Graduate School "BuildMoNa".

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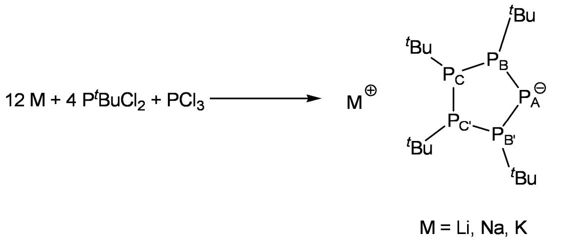
† Dedicated to Professor Pascal Le Floch. The scientific community has lost a great scientist and a marvellous person.

‡ This article is part of a themed issue on Main Group chemistry.

§ Electronic supplementary information (ESI) available: ^{31}P NMR data summary. See DOI: 10.1039/c0nj00181c



Scheme 1 Synthesis of M[*cyclo*-($P_5{}^tBu_4$)] (M = Li, Na, K).

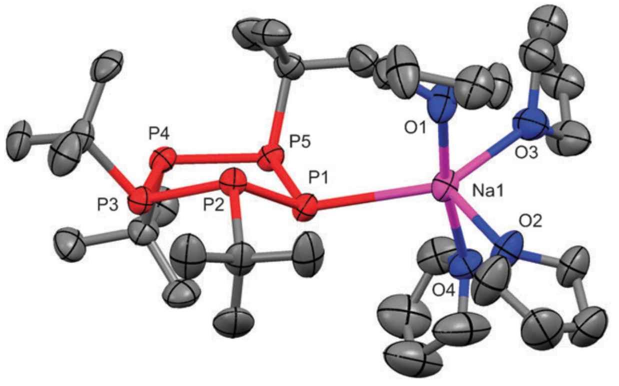


Fig. 1 The molecular structure of [Na(thf)$_4$][*cyclo*-($P_5{}^tBu_4$)] (**2**).[8] The hydrogen atoms are omitted for clarity.

These compounds were synthesised by the reaction of the alkali metal with the corresponding dichlorophosphane, $RPCl_2$, and PCl_3 in the ratio 12 : 4 : 1 in THF to give a product mixture, 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)] (Scheme 1).

The synthesis of M[*cyclo*-($P_5{}^tBu_4$)] was optimised by systematic variation of the reaction conditions. Only M[*cyclo*-($P_5{}^tBu_4$)] and *cyclo*-($P_4{}^tBu_4$) are soluble in n-pentane and could be subsequently separated by sublimation of *cyclo*-($P_4{}^tBu_4$) from M[*cyclo*-($P_5{}^tBu_4$)]. Additionally, M[*cyclo*-($P_5{}^tBu_4$)] can be also purified by crystallisation.

In the solid state, [Li(tmeda)$_2$][*cyclo*-($P_5{}^tBu_4$)] (**1**)[13] (TMEDA = $Me_2NCH_2CH_2NMe_2$), [Na(thf)$_4$][*cyclo*-($P_5{}^tBu_4$)] (**2**)[8] and [K(pmedta)(thf)][*cyclo*-($P_5{}^tBu_4$)] (**3**)[12] (PMEDTA = $Me_2NCH_2CH_2NMeCH_2CH_2NMe_2$) show an all-*trans* arrangement of the *tert*-butyl groups with an envelope conformation of the chiral P_5 ring (Fig. 1).

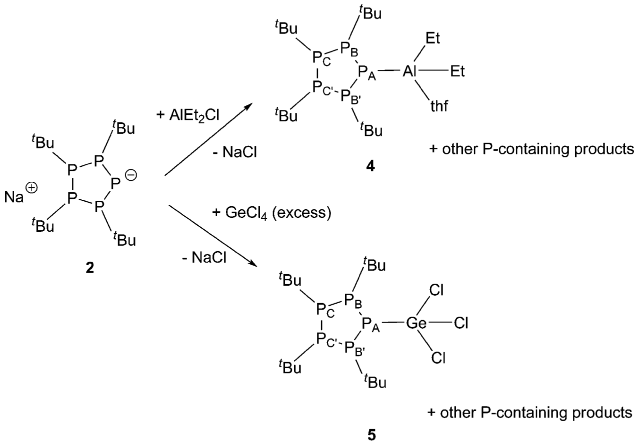
This ring conformation is retained in solution, as indicated by an ABB′CC′ spin system in the $^{31}P\{^1H\}$ NMR spectrum of these compounds and the observed coupling constants (see the ESI§), suggesting that the all-*trans* isomer is also preferred in solution.

Reactivity of [Na(thf)$_4$][*cyclo*-($P_5{}^tBu_4$)]

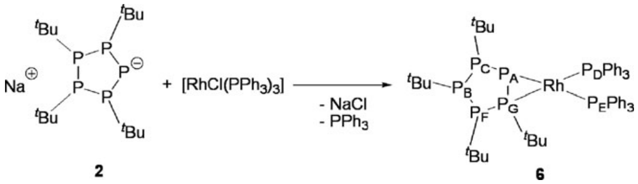
Main group metal chemistry

The optimised synthesis of alkali metal cyclooligophosphanides opened up the possibility of studying the reactivity of these anions.

Compounds of aluminium, germanium, tin, lead and bismuth showed different reactivities. The reaction of **2** with $AlEt_2Cl$ and $GeCl_4$ gave a mixture of products, including the expected transmetallation products [AlEt$_2${*cyclo*-($P_5{}^tBu_4$)}(thf)] (**4**) and [GeCl$_3${*cyclo*-($P_5{}^tBu_4$)}] (**5**), which were isolated and characterised by $^{31}P\{^1H\}$ NMR spectroscopy and mass spectrometry. These two complexes showed an ABB′CC′ spin system (ratio 1 : 2 : 2, see the ESI§) in the $^{31}P\{^1H\}$ NMR spectrum,



Scheme 2 The reaction of [Na(thf)$_4$][*cyclo*-($P_5Bu^t{}_4$)] (**2**) with $AlEt_2Cl$ and $GeCl_4$.



Scheme 3 The synthesis of [Rh{*cyclo*-($P_5{}^tBu_4$)}(PPh$_3$)$_2$] (**6**).

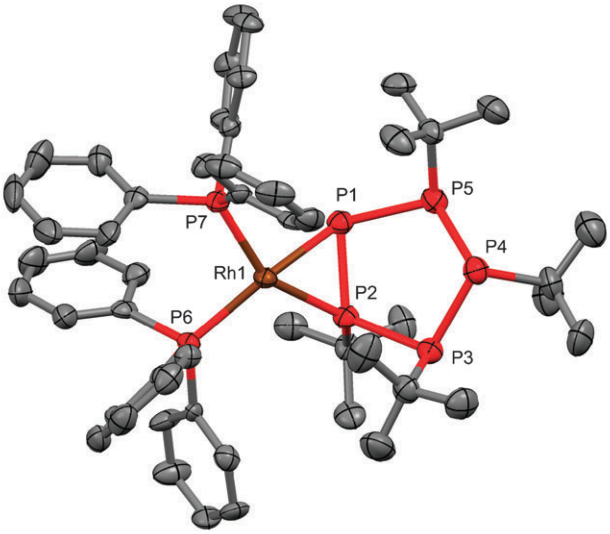


Fig. 2 The molecular structure of [Rh{*cyclo*-($P_5{}^tBu_4$)}(PPh$_3$)$_2$] (**6**).[15] The hydrogen atoms are omitted for clarity.

which indicates that, in solution, the P$_5$ ring is bound to the metal atom only *via* the anionic phosphorus atom (Scheme 2).[14]

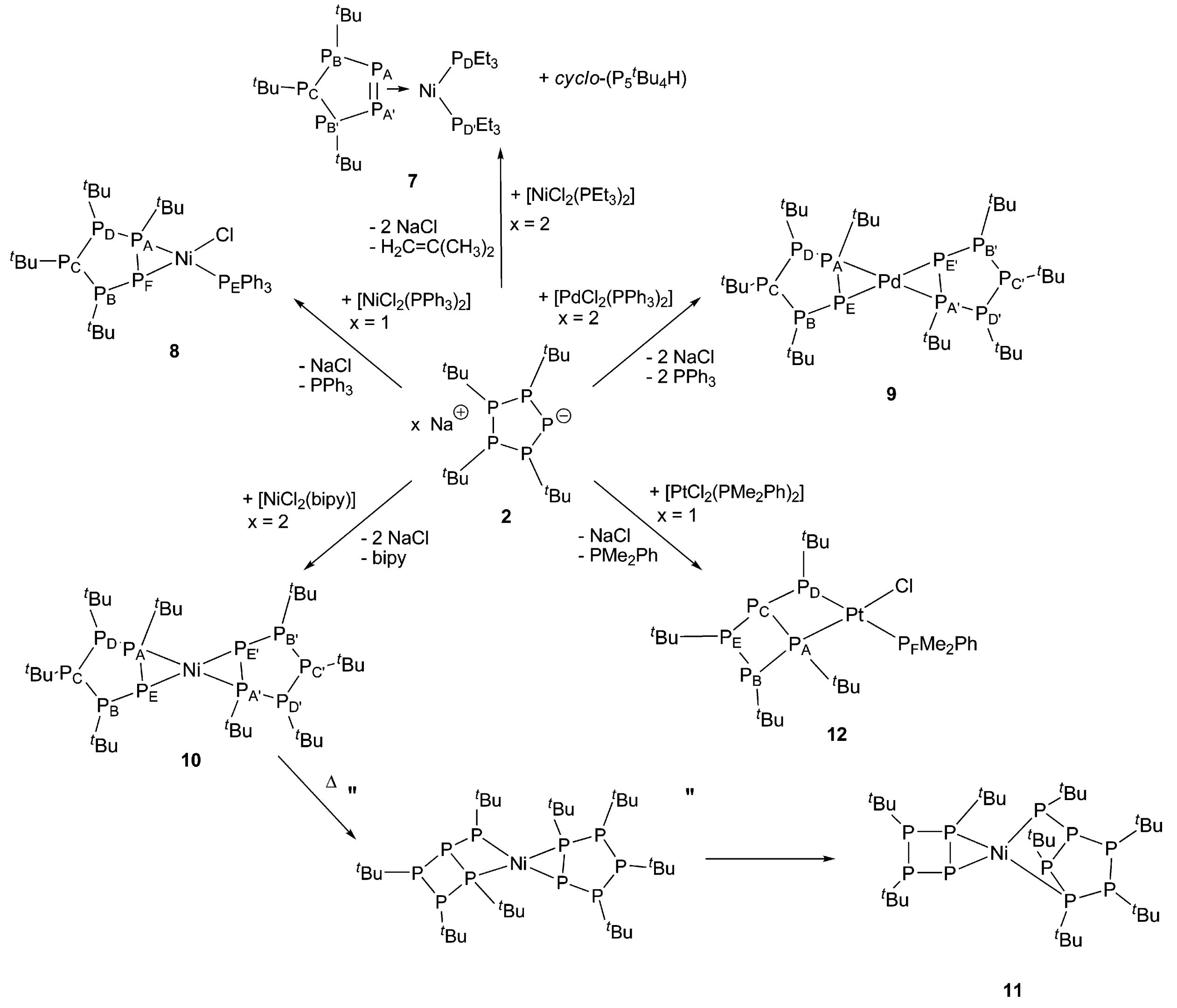
However, the analogous reaction of **2** with SnCl$_2$, PbCl$_2$ or BiCl$_3$ resulted in the formation of the phosphorus-rich compounds {*cyclo*-(P$_5{}^t$Bu$_4$)}$_2$ and {*cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu}$_2$, and elemental metal, presumably *via* initial formation of the corresponding unstable metal phosphanides [M{*cyclo*-(P$_5{}^t$Bu$_4$)}$_x$].[14]

Transition metal chemistry

More exciting results were obtained with transition metal complexes. One of our first studies was the transmetallation reaction of **2** with [RhCl(PPh$_3$)$_3$] (1 : 1) to give a rhodium(I) complex with a tetra-*tert*-butylcyclopentaphosphanide ligand, namely [Rh{*cyclo*-(P$_5{}^t$Bu$_4$)}(PPh$_3$)$_2$] (**6**; Scheme 3).[15]

The molecular structure of **6** revealed the first example of a chelating tetra-*tert*-butylcyclopentaphosphanide ligand, in which the metal is coordinated by the anionic phosphorus atom and one of the adjacent phosphorus atoms of the ring (Fig. 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, see the ESI§). Interestingly, organyl-free fragment [RhP$_5$]$^+$ was observed in the mass spectrum, indicating that complex **6** could be a suitable precursor for the formation of binary rhodium phosphides under appropriate conditions.

Transmetallation reactions of [Na(thf)$_4$][*cyclo*-(P$_5{}^t$Bu$_4$)] (**2**) with complexes of the nickel triad showed a marked dependence on the nature of the co-ligand and the transition metal employed. Thus, **2** reacted with [NiCl$_2$(PEt$_3$)$_2$] in polar or non-polar solvents to give the unexpected nickel(0) η^2-3,4,5-tri-*tert*-butylcyclopentaphosphene complex [Ni{*cyclo*-(P$_5{}^t$Bu$_3$)}-(PEt$_3$)$_2$] (**7**) *via* cleavage of a ^{t}Bu group of the anionic *cyclo*-(P$_5{}^t$Bu$_4$) ring as ^{t}BuCl to give the previously unknown cyclopentaphosphene ring (Scheme 4).[8] The formation of ^{t}BuCl was indirectly proved by the detection of *cyclo*-(P$_5{}^t$Bu$_4$H) and isobutene, which are the products of the subsequent reaction of ^{t}BuCl and [Na(thf)$_4$][*cyclo*-(P$_5{}^t$Bu$_4$)] (**2**). The short P–P bond of the P$_5$ ring of this novel cyclopentaphosphene (211.8(2) pm) clearly indicates a multiple



Scheme 4 The reaction of [Na(thf)$_4$][*cyclo*-(P$_5{}^t$Bu$_4$)] (**2**) with complexes of the nickel triad.

Table 1 P–P and M–P bond lengths in complexes with *cyclo*-(P$_5{}^t$Bu$_4$)$^-$, *cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu$^-$ or *cyclo*-(P$_5{}^t$Bu$_3$) ligands (determined by single crystal X-ray diffraction studies)

Compound	P–P[a]	P–P[b]	M–P (of P$_5$)	Reference
[Li(tmeda)$_2$][*cyclo*-(P$_5{}^t$Bu$_4$)] (**1**)	220.7(2) 221.5(2) 221.6(2) 222.6(2)	212.5(2)	490.4(6)[c]	Ref. 13
[Na(thf)$_4$][*cyclo*-(P$_5{}^t$Bu$_4$)] (**2**)	220.4(2) 220.8(1) 221.1(2) 222.9(1)	213.2(2)	293.8(2)	Ref. 8
[K(pmedta)(thf)][*cyclo*-(P$_5{}^t$Bu$_4$)] (**3**)	219.5(4) 220.8(6) 221.4(3) 222.6(5)	212.9(3)	325.3(3)	Ref. 12
[Rh{*cyclo*-(P$_5{}^t$Bu$_4$)}-(PPh$_3$)$_2$] (**6**)	220.6(2) 220.8(2) 223.8(2) 224.1(3)	212.9(2)	231.3(2) 238.5(2)	Ref. 15
[Ni{*cyclo*-(P$_5{}^t$Bu$_3$)}-(PEt$_3$)$_2$] (**7**)	219.9(1) 220.1(2) 220.2(2) 221.1(2)	211.8(2)[d]	223.2(1) 223.9(1)	Ref. 8
[Pd{*cyclo*-(P$_5{}^t$Bu$_4$)}$_2$] (**9**)	219.6(2) 219.9(2) 220.2(2) 222.5(2)	212.3(2)	229.2(1) 243.4(1)	Ref. 16
[Ni{*cyclo*-(P$_5{}^t$Bu$_4$)}$_2$] (**10**)	220.1(1) 220.3(1) 220.7(1) 222.6(1)	212.2(1)	217.5(2) 229.4(2)	Ref. 16
[PtCl{*cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu}-(PMe$_2$Ph)] (**12**)	219.8(2) 221.2(2) 221.9(2) 222.7(2) 225.0(2)		230.1(2) 232.7(2)	Ref. 16
[Cu{*cyclo*-(P$_5{}^t$Bu$_4$)}-(PPh$_3$)$_2$] (**14**)	221.0(2) 221.1(2) 221.9(2) 222.2(2)	214.6(2)	228.6(2)	Ref. 18
[Cu$_4${*cyclo*-(P$_4{}^t$Bu$_3$)-P^{t}Bu}$_4$] (**15**)	219.3(2) 221.4(2) 221.7(2) 222.2(1) 222.5(2)		221.4(1) 222.7(2)	Ref. 18
[Ag$_4${*cyclo*-(P$_4{}^t$Bu$_3$)-P^{t}Bu}$_4$] (**16**)	218.7(1) 221.9(1) 222.0(1) 222.4(2) 222.7(1)		238.3(1) 240.2(1)	Ref. 18
[Au{*cyclo*-(P$_5{}^t$Bu$_4$)}-(PCyp$_3$)] (**17**)	217.3(2) 220.7(2) 221.6(2) 222.5(2) 223.0(2)		233.3(2)	Ref. 18
[Au$_4${*cyclo*-(P$_4{}^t$Bu$_3$)-P^{t}Bu}$_4$] (**19**)	219.7(5) 221.2(5) 221.3(5) 222.8(6) 222.9(7)		232.1(3)	Ref. 18
[Cu$_2$(μ-Cl){*cyclo*-(P$_5{}^t$Bu$_4$)}-(PCyp$_3$)$_2$] (**20**)	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)	Ref. 18

[a] Regular P–P bonds of the P$_5$ ligand. [b] Short P–P bond of the P$_5$ ligand due to delocalization of the lone pair at the anionic phosphorus into lower unoccupied orbitals (with σ*- and d-orbital contributions) at the adjacent phosphorus atom.[8] [c] No Li–P bond; separated ions. [d] P═P double bond.

bond (for a comparison of the P–P and M–P bond lengths, see Table 1).

Complexes with labile triphenylphosphane ligands, such as [MCl$_2$(PPh$_3$)$_2$] (M = Ni, Pd), react with **2** (1 : 2), forming [NiCl{*cyclo*-(P$_5{}^t$Bu$_4$)}(PPh$_3$)] (**8**) and [Pd{*cyclo*-(P$_5{}^t$Bu$_4$)}$_2$] (**9**), respectively, in which the *cyclo*-(P$_5{}^t$Bu$_4$) ligand is intact.[16] However, the analogous Ni(II) complex, [Ni{*cyclo*-(P$_5{}^t$Bu$_4$)}$_2$] (**10**), was only obtained when the Ni(II) bipyridine complex [NiCl$_2$(bipy)], with a more labile bipy ligand, was employed in the reaction with **2** (Scheme 4).

Interestingly, [Ni{*cyclo*-(P$_5{}^t$Bu$_4$)}$_2$] (**10**) rearranges to [Ni{*cyclo*-(P$_5{}^t$Bu$_4$)P^{t}Bu}{*cyclo*-(P$_4{}^t$Bu$_3$)}] (**11**) on mild heating *via* the intermediate [Ni{*cyclo*-(P$_5{}^t$Bu$_4$)}{*cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu}] and the subsequent migration of the exocyclic phosphanediide group of the rearranged *cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu to give the *cyclo*-(P$_5{}^t$Bu$_4$)P^{t}Bu ligand.[16] This mechanism was proposed on the basis of the reaction of **2** with [PtCl$_2$(PPh$_3$)$_2$], in which ring

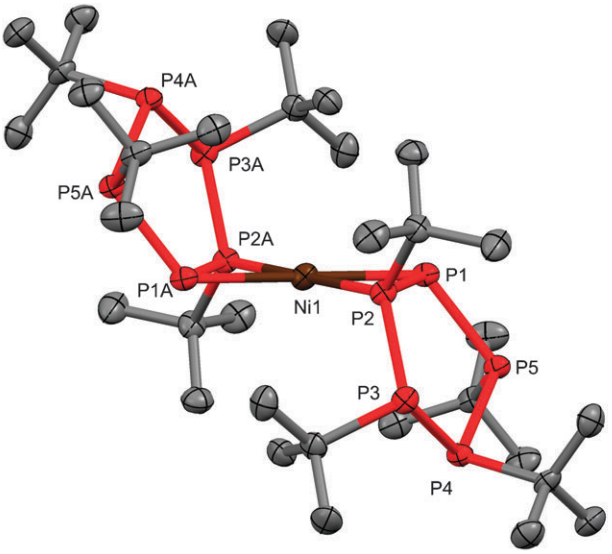


Fig. 3 The molecular structure of [Ni{*cyclo*-(P$_5{}^t$Bu$_4$)$_2$] (**10**).[16] The hydrogen atoms are omitted for clarity.

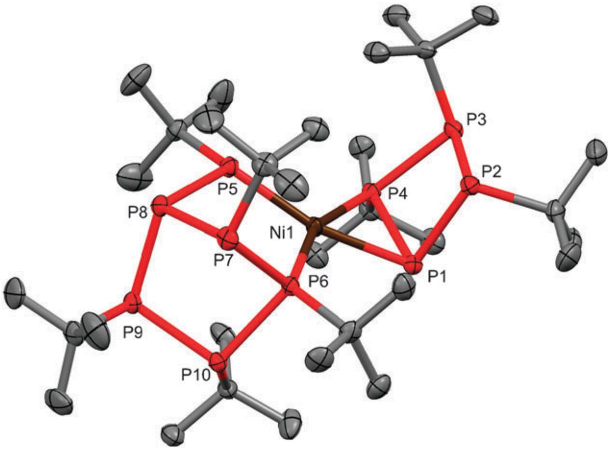


Fig. 4 The molecular structure of [Ni{*cyclo*-(P$_5{}^t$Bu$_4$)P^{t}Bu}{*cyclo*-(P$_4{}^t$Bu$_3$)}] (**11**).[16] The hydrogen atoms are omitted for clarity.

contraction occurs, giving [PtCl{*cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu}(PMe$_2$Ph)] (**12**), which contains the {*cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu}$^-$ ligand proposed as the intermediate species in the formation of **11** (Scheme 4).[16]

These phosphorus-rich group 10 metal complexes have been characterised by various spectroscopic methods, but the most useful tool for characterising this kind of compound in solution is ^{31}P{^{1}H} NMR spectroscopy. Most of the studied complexes show different first- or higher-order spin systems, according to their structures. Chemical shifts and coupling constants were calculated by using the simulation program SpinWorks[17] (for the assigning of the spin systems and further information, see the ESI§).

X-Ray diffraction studies have given more information about these compounds' solid-state structures. The X-ray structures of **9** and **10** (Fig. 3) show an all-*trans* arrangement of the ^{t}Bu groups and an envelope conformation of the P$_5$ ring,[16] as was also observed in M[*cyclo*-(P$_5{}^t$Bu$_4$)] [M = Li (**1**), Na (**2**), K (**3**)] and [Rh{*cyclo*-(P$_5{}^t$Bu$_4$)}(PPh$_3$)$_2$] (**6**) (for a comparison of the P–P and M–P bond lengths, see Table 1).

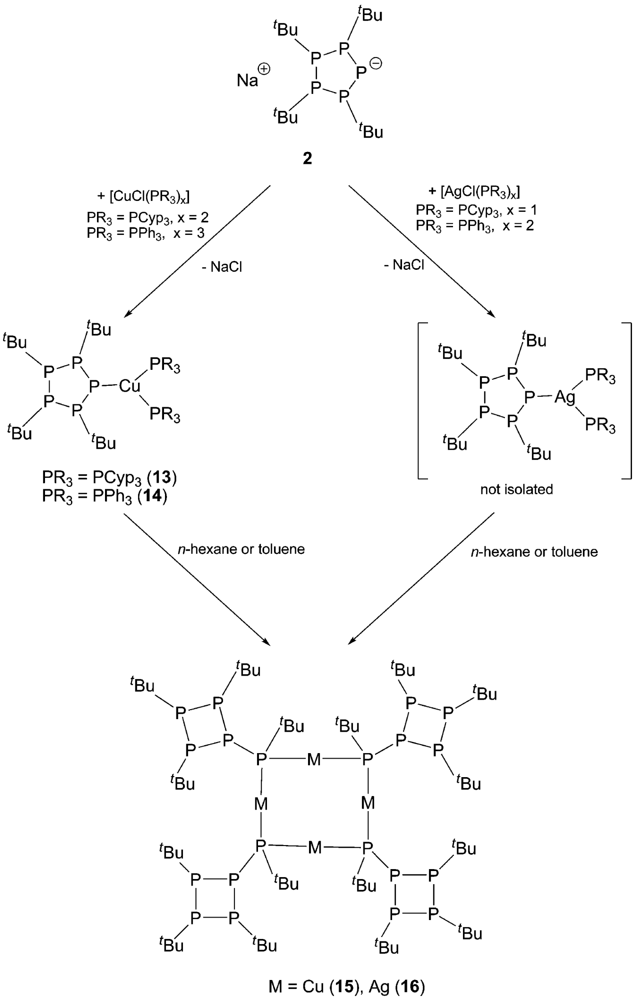
Interestingly, [Ni{*cyclo*-(P$_5{}^t$Bu$_4$)P^{t}Bu}{*cyclo*-(P$_4{}^t$Bu$_3$)}] (**11**) places the *cyclo*-(P$_4{}^t$Bu$_3$) ligand in a butterfly conformation and, in addition, a seven-membered norbornene-like metallabicycle is observed for the Ni{*cyclo*-(P$_5{}^t$Bu$_4$)P^{t}Bu} moiety (Fig. 4).[16]

Similarly, as observed for the reactions with complexes of the nickel triad, the reactivity of **2** with group 11 metal salts is also dependent on the metal and on the reaction conditions.[18] Thus, the reaction with [CuCl(PCyp$_3$)$_2$] (Cyp = *cyclo*-C$_5$H$_9$) or [CuCl(PPh$_3$)$_3$] gave the monomeric complexes [Cu{*cyclo*-(P$_5{}^t$Bu$_4$)}(PCyp$_3$)$_2$] (**13**) and [Cu{*cyclo*-(P$_5{}^t$Bu$_4$)}(PPh$_3$)$_2$] (**14**), in which the *cyclo*-(P$_5{}^t$Bu$_4$)$^-$ ligand remained intact. However, over several weeks, these complexes rearranged in solution in non-polar solvents to give the tetrameric compound [Cu$_4${*cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu}$_4$] (**15**), in which the P$_5$ ring has contracted to a *cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu ligand that bridges two metal centres through coordination of the exocyclic phosphorus atom of the ligand (Scheme 5).

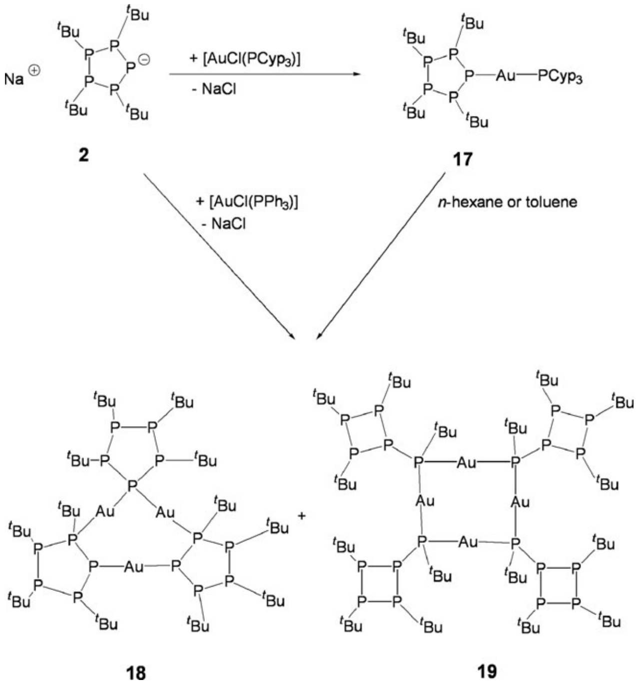
Similar behaviours were observed in the reaction of the *cyclo*-(P$_5{}^t$Bu$_4$)$^-$ ion with [AgCl(PCyp$_3$)]$_4$ (4 : 1) or [AgCl(PPh$_3$)$_2$] (1 : 1), which gave the tetrameric compound [Ag$_4${*cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu}$_4$] (**16**, isomorphous to **15**); in this case, monomeric Ag(I) species could not be isolated but were detected in the reaction mixtures.[18]

The reaction of **2** with [AuCl(PCyp$_3$)] (1 : 1) gave the monomeric compound [Au{*cyclo*-(P$_5{}^t$Bu$_4$)}(PCyp$_3$)] (**17**), with an intact *cyclo*-(P$_5{}^t$Bu$_4$)$^-$ ligand, in high yield, while the reaction with [AuCl(PPh$_3$)] gave a mixture of oligomeric compounds, from which only [Au$_3${*cyclo*-(P$_5{}^t$Bu$_4$)}$_3$] (**18**) and [Au$_4${*cyclo*-(P$_4{}^t$Bu$_3$)P^{t}Bu}$_4$] (**19**) were obtained by crystallisation.[18] Both compounds **18** and **19** were also obtained by the decomposition of **17** in non-polar solvents (Scheme 6).

In the case of group 11 compounds, ^{31}P{^{1}H} NMR spectroscopy was not as useful as for other metal complexes, because



Scheme 5 Reactions of [Na(thf)$_4$][*cyclo*-(P$_5{}^t$Bu$_4$)] (**2**) with Cu(I) and Ag(I) salts.



Scheme 6 Reactions of [Na(thf)$_4$][*cyclo*-(P$_5{}^t$Bu$_4$)] (**2**) with Au(I) complexes.

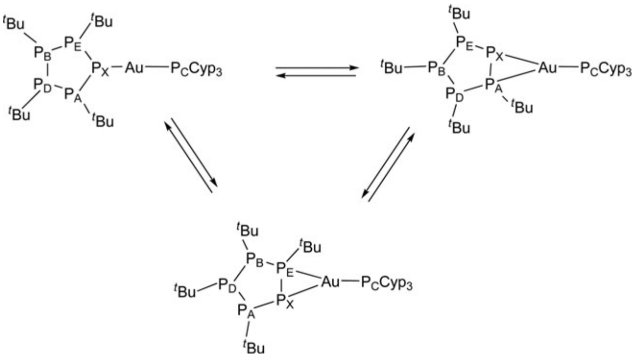
of severe line broadening caused by the quadrupole moment of the metal atoms (^{63}Cu, ^{65}Cu). Unidentified dynamic processes involving the phosphorus-rich ligands in silver and gold compounds, and the poor solubility of polynuclear compounds **15**, **16**, **18** and **19**, prevented numerical analyses of the coupling patterns by simulation of their $^{31}P\{^1H\}$ NMR spectra (for further details, see the ESI§). However, full analysis of the ^{31}P NMR spectroscopic data was possible for [Au{*cyclo*-($P_5{}^t Bu_4$)}($PCyp_3$)] (**17**).[18] At −80 °C, **17** showed six different multiplets at 65.4, 64.6, 63.7, 42.3, 29.6 and −55.8 ppm (Fig. 5), with large differences in the chemical shifts of the P_A and P_E atoms, indicating that one of these phosphorus atoms may be involved in coordination to gold, leading to a coordination number of three at the metal centre.

At room temperature, this structure may be in rapid equilibrium with an identical structure involving the coordination of the other adjacent phosphorus atom (a windscreen wiper mechanism, Scheme 7) and/or with the linear structure observed for **17** in the solid state (Fig. 6).

Some of the group 11 complexes were characterised by X-ray diffraction studies (for comparison of the P–P and M–P bond lengths, see Table 1). The molecular structures of complexes **14** (Fig. 7) and **17** (Fig. 6) are the first in which the *cyclo*-($P_5{}^t Bu_4$)$^-$ is bound to a transition metal *via* only the anionic phosphorus atom.[18]

In the tetrameric complexes **15**, **16** and **19**, the four-membered *cyclo*-($P_4{}^t Bu_3$) rings are in a butterfly conformation with an all-*trans* arrangement of the ^{t}Bu substituents, and the exocyclic phosphorus atom of the *cyclo*-($P_4{}^t Bu_3$)P^tBu ligand bridges two metal centres (Fig. 8).

The formation of [Cu_2(μ-Cl){*cyclo*-($P_5{}^t Bu_4$)}($PCyp_3$)$_2$] (**20**) was achieved when starting from [CuCl($PCyp_3$)$_2$] and **2** in a 1 : 2 molar ratio (Scheme 8).



Scheme 7 The proposed rapid equilibrium of complex [Au{*cyclo*-($P_5{}^t Bu_4$)}($PCyp_3$)] (**17**) at room temperature.

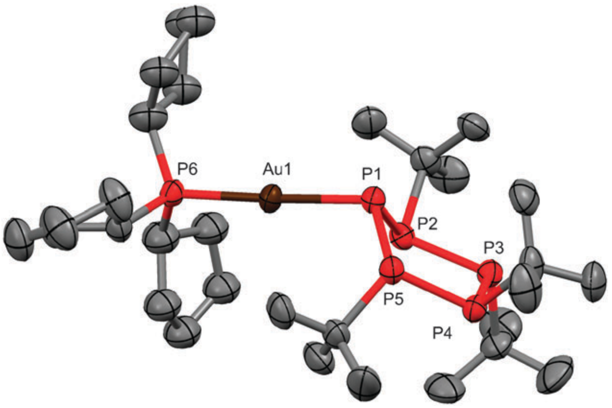


Fig. 6 The molecular structure of [Au{*cyclo*-($P_5{}^t Bu_4$)}($PCyp_3$)] (**17**).[18] The hydrogen atoms are omitted for clarity.

The structure of **20** can be viewed as a 1 : 1 adduct of **13** and CuCl, in which two phosphorus atoms of the P_5 ring are chelating two crystallographically-independent copper atoms that have a trigonal-planar environment. These two copper atoms are nearly coplanar with the two phosphorus atoms of the $PCyp_3$ ligands (P6 and P7).[18] The two copper atoms, P1

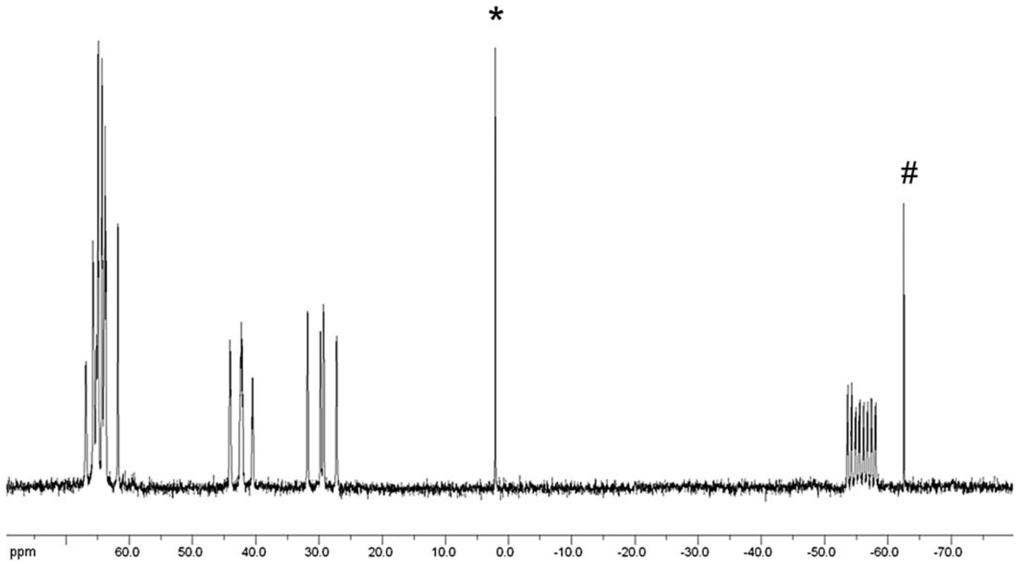


Fig. 5 The low-temperature $^{31}P\{^1H\}$ NMR spectrum of [Au{*cyclo*-($P_5{}^t Bu_4$)}($PCyp_3$)] (**17**)[18] (at −80 °C, impurities: * = $PCyp_3$ and # = *cyclo*-$P_4{}^t Bu_4$).

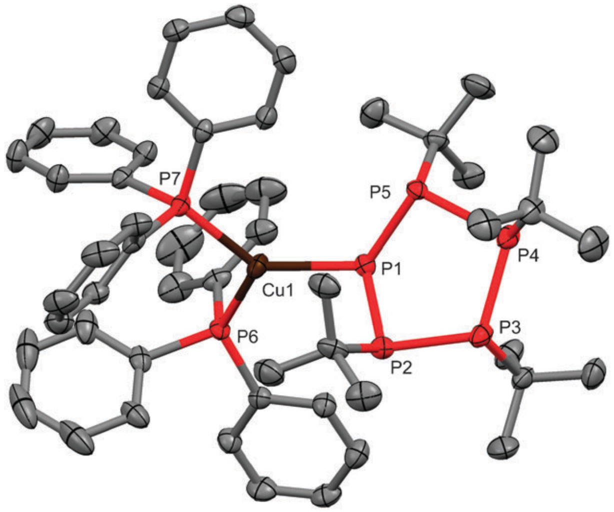


Fig. 7 The molecular structure of [Cu{*cyclo*-($P_5{}^tBu_4$)}(PPh_3)$_2$] (**14**).[18] The hydrogen atoms are omitted for clarity.

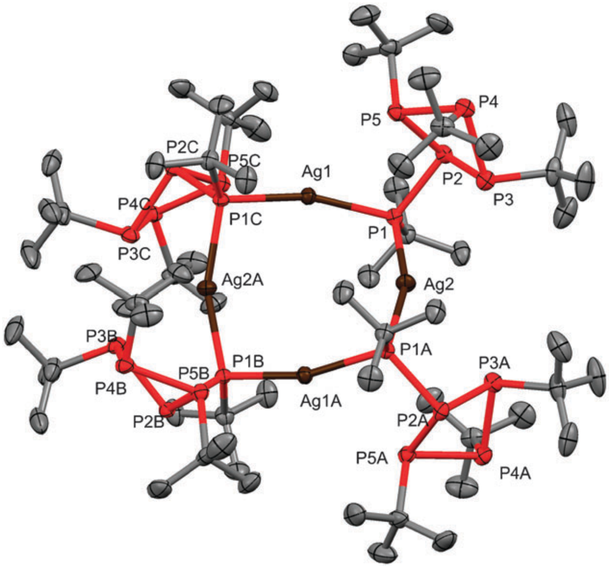
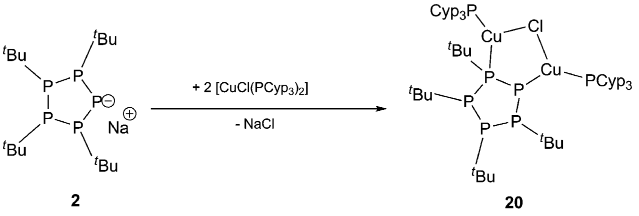


Fig. 8 The molecular structure of [Ag_4{*cyclo*-($P_4{}^tBu_3$)P^tBu}$_4$] (**16**). [Cu_4{*cyclo*-($P_4{}^tBu_3$)P^tBu}$_4$] (**15**) and [Au_4{*cyclo*-($P_4{}^tBu_3$)P^tBu}$_4$] (**19**) are isomorphous.[18] The hydrogen atoms are omitted for clarity.



Scheme 8 The reaction of [$Na(thf)_4$][*cyclo*-($P_5{}^tBu_4$)] (**2**) with two equivalents of [$CuCl(PCyp_3)_2$].

and P2, of the P_5 ligand and Cl1 form a five-membered ring with an envelope conformation (Fig. 9) (for a comparison of the P–P and M–P bond lengths, see Table 1).

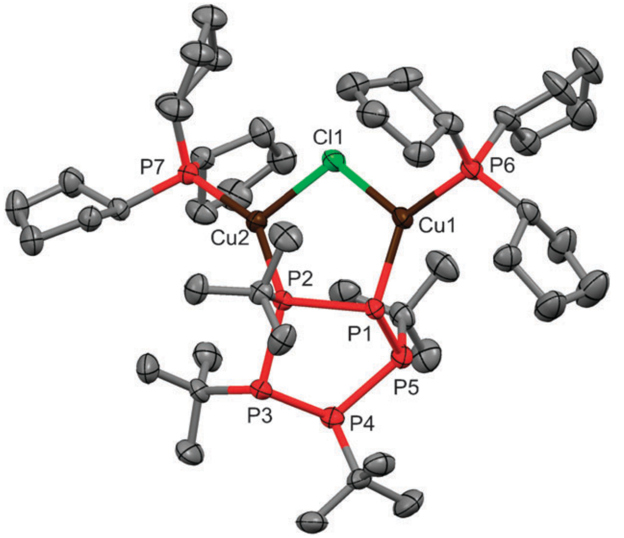


Fig. 9 The molecular structure of [Cu_2(μ-Cl){*cyclo*-($P_5{}^tBu_4$)}($PCyp_3$)$_2$] (**20**).[18] The hydrogen atoms are omitted for clarity.

Summary

We have shown the versatility of *cyclo*-($P_5{}^tBu_4$)$^-$ ligands in reactions with main group and transition metal complexes. Thus, the *cyclo*-($P_5{}^tBu_4$)$^-$ ligand can rearrange to *cyclo*-($P_5{}^tBu_3$), *cyclo*-($P_4{}^tBu_3$)$^-$, {*cyclo*-($P_4{}^tBu_3$)P^tBu}$^-$, {*cyclo*-($P_5{}^tBu_4$)P^tBu}$^-$, or stay intact, 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

We are grateful to BASF SE, Chemetall and Umicore AG ($RhCl_3$ and $H[AuCl_4]$) 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.

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