Making and Breaking of Phosphorus–Phosphorus Bonds

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Abstract: In contrast to their mostly unstable isolobal carbon counterparts, oligophosphanide anions, such as M($cyclo$-$P_5{}^tBu_4$) (M = Li, Na) and $M_2(P_4R_4)$ [M = Na, K; R = Ph, ^tBu, 2,4,6-$Me_3C_6H_2$ (Mes)], have unique features, depending on their composition and structure, and are highly suitable building blocks for the synthesis of phosphorus-rich metal compounds. However, alkali metal oligophosphanediides are highly reactive and highly reducing, and a major problem is their tendency for disproportionation in reactions with electrophiles. This, however, can also give rise to a fascinating chemistry of making and breaking of P–P bonds. On the other hand, neutral cyclooligophosphines, such as $cyclo$-(P_5Ph_5), are suitable stable ligands for the formation of phosphorus-rich metal complexes.

1 Introduction

The chemistry of phosphorus is, without any doubt, one of the most intriguing fields of inorganic chemistry. It comprises a vast number of classes of inorganic compounds with many elements in the periodic table and combinations thereof. A distinctive feature of phosphorus is the high dissociation energy of homonuclear bonds [1] which causes a pronounced tendency to form P–P bonds, leading to a plethora of compounds. Like carbon, phosphorus-rich molecules show constitutional, configurational and conformational isomerism as well as valence tautomerism, can exist as stable three-, four-, five- or six-membered rings and polycyclic compounds and can also contain multiple bonds – this is the main reason why phosphorus is sometimes referred to as the "carbon copy".[2] This can be rationalised with the similarity of the frontier orbitals of the fragments CH_3/PH_2, CH_2/PH and CH/P (isolobal concept [3]). Despite these striking similarities, there are some distinctive features of these compounds:
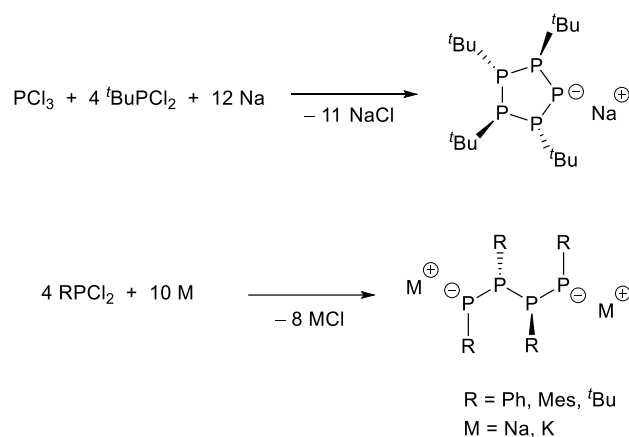
1. Every phosphorus atom has a lone pair of electrons, facilitating coordination of Lewis acids, particularly metal atoms and ions.
2. Phosphorus tends to feature smaller bond angles compared to carbon [4] which results in a different stability of the respective ring systems and polycyclic structures.[5]
3. As a result of the reduced number of bonds on phosphorus, various chiral centres are present in oligophosphines. Remarkably, the inversion barrier in some these oligophosphines is so low that this reaction already occurs at room temperature.[6,7,8] Coordination to metal ions can even further decrease the barrier.[9]
4. Disproportionation and transformation reactions of oligophosphines in general occur at much lower temperatures compared to hydrocarbons. Phosphorus hydrides, P_nH_{n+2} or $cyclo$-P_nH_n, are thus hardly isolable.[10] However, when the hydrogen atoms are replaced with bigger organic groups, such as ^tBu, the respective compounds can be significantly stabilised.[10]

The chemistry of phosphorus-rich compounds dates back to 1877 when Köhler and Michaelis investigated the reaction of $PhPCl_2$ with $PhPH_2$.[11,12] Under evolution of HCl, a product was obtained, which, based on the elemental composition (C and H), was identified as phosphobenzene, PhP=PPh. However, as was shown almost a century later, this reaction produces polymers as well as several oligomers [13] with the tetramer $cyclo$-(P_4Ph_4) as the main component.[14] Employing ^{31}P NMR spectroscopy and single crystal X-ray crystallography, all $cyclo$-oligo(phenylphosphines) with ring sizes from three to six were identified in the following years.[15–19] Even though

two of these compounds can be isolated, also the most stable one in this series, $cyclo$-(P$_5$Ph$_5$), slowly transforms to four- and six-membered rings in solution.[21] In the last four decades, the chemical library of phosphorus-rich compounds was vastly extended. One of the biggest contribution was the pioneering work of Baudler et al. who characterised a large number of catenated, cyclic and polycyclic oligophosphines with hydrogen and organic substituents.[5–12] As was shown later, phosphorus is also capable of forming unsaturated [21] and even aromatic compounds [22]. Today, many more phosphorus-rich compounds exist.

The follow-up chemistry of oligophosphines, in contrast, was considerably less investigated. One reason is their pronounced tendency to undergo transformation reactions to other phosphines even at very low temperatures making their isolation virtually impossible. This especially applies to phosphorus hydrides P$_n$H$_{n+2}$ which have mainly been characterised only by ^{31}P NMR spectroscopy in mixtures. The second reason is the rather unselective synthesis of most oligophosphines; extremely tedious methods must often be applied to obtain a pure compound.[23] However, not all oligophosphines require such complex procedures. For example, cyclooligophosphines are usually much easier to isolate, and their reactivity, particularly their coordination chemistry, have been studied, e.g. complexes with $cyclo$-(P$_n$R$_n$) (n = 3–6, R = Ph,[21,24–28] Et,[29,30] or ^{t}Bu [31–33]).

Another aspect of the reactivity of oligophosphines is the reaction with alkali metals which leads to P–P bond cleavage and formation of oligophosphanides or -phosphanediides. The linear dianionic species M$_2$(P$_4$R$_4$) (M = Li, Na, K; R = Ph, C$_2$H$_5$, $cyclo$-C$_6$H$_{11}$) were first synthesised by Issleib et al. by reduction of $cyclo$-(P$_4$R$_4$) with alkali metals.[34,35] These compounds are of special interest for coordination chemistry because of the negatively charged P atoms, which have excellent donor properties. A more facile procedure for the synthesis of linear dianionic species M$_2$(P$_4$R$_4$) (M = Na, K; R = alkyl or aryl) has been reported.[36] However, the preparation and purification of metal complexes with oligophosphanide ligands has remained a challenging task.[37–39] Hey-Hawkins et al. developed selective routes toward these oligophosphanides by one-pot reactions of PCl$_3$, chlorophosphines and alkali metals under careful control of the stoichiometry (Scheme 1).[40,41] These reactions give the desired ligands in only one, high-yielding, reaction, which, in turn, enabled the synthesis of a large variety of corresponding metal complexes.

$$PCl_3 + 4\ ^tBuPCl_2 + 12\ Na \xrightarrow[-\ 11\ NaCl]{}$$

$$4\ RPCl_2 + 10\ M \xrightarrow[-\ 8\ MCl]{}$$

R = Ph, Mes, ^{t}Bu
M = Na, K

Scheme 1: Syntheses of oligophosphanides.

Even though the chemistry of phosphorus-rich compounds and their complexes is intriguing enough to justify the corresponding research, there are also potential applications in materials science. Oligophosphine-based metal complexes can be converted to phosphorus-rich metal phosphides MP$_x$ with x > 1. Metal phosphides have numerous outstanding properties, making them highly interesting for industrial applications. This involves catalytic activity for many different reactions (hydrogen evolution,[42,43] water splitting,[44] hydrodenitrogenation and hydrodesulfuration [45–47]), ferromagnetism,[48] superconductivity,[49,50] anti-corrosive properties [51] and countless more. Despite this, their current application is limited as the synthesis of these materials is extremely challenging. Reacting the elements (metal and red phosphorus) requires very high temperatures which, however, lead to decomposition of the product due to the volatility of white phosphorus (P$_4$) under these conditions.[52] Furthermore, the extreme reaction heat can cause explosions and reactions with the material of the reaction vessel. One promising alternative method is the mild thermolysis of phosphorus-rich metal complexes. By applying relatively low temperatures, the organic groups of the molecule are cleaved off while the metal and phosphorus atoms remain in the material.[53]

The Hey-Hawkins group reported two intriguing examples of such thermolyses by using oligophosphine complexes of iron and manganese. Upon heating of [Fe{$cyclo$-(P$_5$^{t}Bu$_4$)}$_2$] to 500 °C, a new phosphorus-rich iron phosphide (formal composition FeP$_6$) was identified according to the mass loss (Scheme 2).[53] The second example is the complex [Mn$_2$(μ-Br){$cyclo$-(P$_4$^{t}Bu$_3$)P^{t}Bu}(CO)$_6$].[54] Up to 141 °C, loss of six CO molecules occurs followed by loss of four ^{t}Bu and Br (up to 315 °C) to give a compound of formal composition Mn$_2$P$_5$. Conversion to Mn$_2$P took place when thermolysed up to 1000 °C. In both cases, the elevated temperature caused elimination of the ^{t}Bu groups as isobutene.
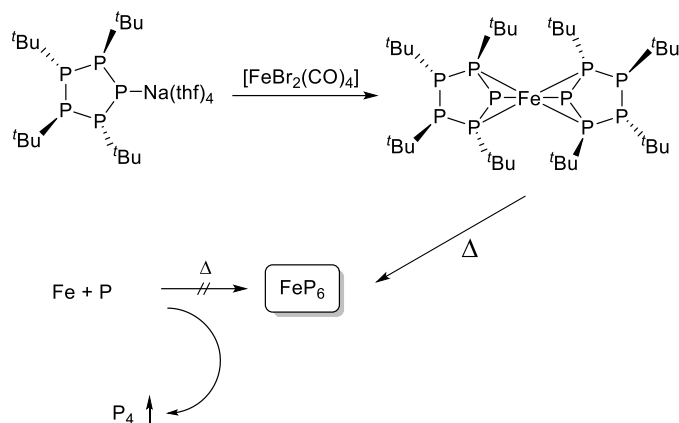
Scheme 2: Illustration of the thermolytic conversion of an oligophosphanide iron complex to a phosphorus-rich iron phosphide.

2 Results and Discussion

Over the past few years numerous phosphorus-rich transition metal complexes of linear (P$_4$R$_4$)$^{2-}$ (R = Ph, 2,4,6-Me$_3$C$_6$H$_2$ (Mes)) anions were reported by Hey-Hawkins and coworkers. Simple transmetallation reactions occur when Na$_2$(P$_4$Mes$_4$) reacts with one equivalent of the platinum(II) complexes [PtCl$_2$(L)] [L = cod (1,5-cyclooctadiene), dppe (dppe = bis(diphenylphosphino)ethane)] yielding [Pt(P$_4$Mes$_4$)(cod)] and [Pt(P$_4$Mes$_4$)(dppe)], respectively. Mere ligand exchange occurred when these products were reacted with an excess of isonitriles, RN≡C (R = $cyclo$-C$_6$H$_{11}$, ^{t}Bu), resulting in [Pt(P$_4$Mes$_4$)(C≡NR)$_2$].[55]

The first copper(I) complexes were obtained by the reaction of one equivalent of Na$_2$(P$_4$Ph$_4$) with two equivalents of [CuCl(PCyp$_3$)$_2$] (Cyp = $cyclo$-C$_5$H$_9$), which gave the tetranuclear copper(I) oligophosphanide complex [Cu$_4$(P$_4$Ph$_4$)$_2$(PCyp$_3$)$_3$] (Scheme 3).[56]
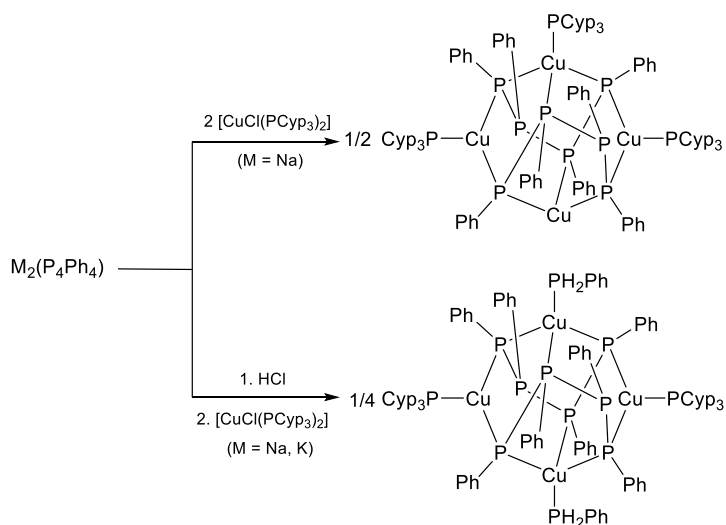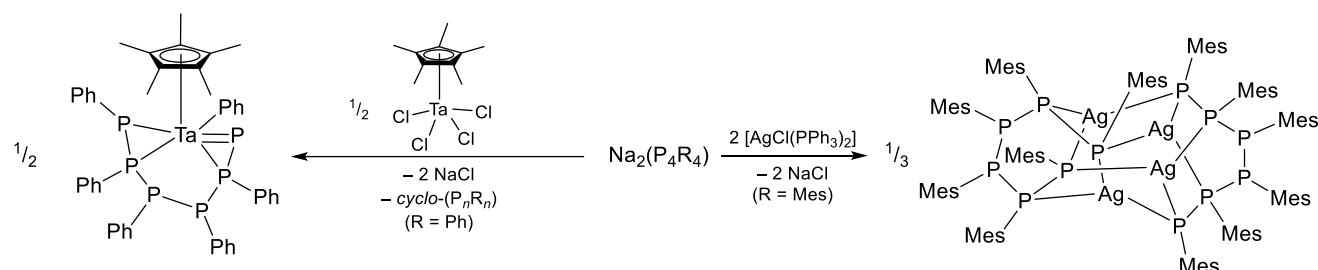

Scheme 3: Synthesis of copper(I) oligophosphanide complexes.[56,57]

The analogous tetranuclear copper(I) oligophosphanide complex [$Cu_4(P_4Ph_4)_2(PH_2Ph)_2(PCyp_3)_2$] was obtained from the reaction of $M_2(P_4Ph_4)$ (M = Na, K) with one equivalent of HCl followed by the subsequent addition of one equivalent of [$CuCl(PCyp_3)_2$] (Scheme 3).[57] Similarly, the reaction of two equivalents of *in situ* formed (P_4HMes_4)$^-$ with one equivalent of [{$RhCl(cod)$}$_2$] gave the rhodium(I) tetraphosphanido complex [$Rh(P_4HMes_4)(cod)$] with a small amount of the side product [{$Rh(cod)$}$_2(\mu$-$P_2HMes_2)(\mu$-$PHMes)$] (Scheme 4).[57]
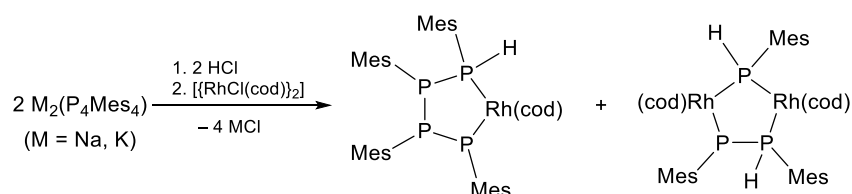
Scheme 4: Synthesis of rhodium(I) oligophosphanide complexes.[57]

The reaction of $Na_2(P_4Mes_4)$ with [$AgCl(PPh_3)_2$] gave unusual silver oligophosphanide complexes containing a di-anionic P_6 chain,[58] while the reaction with [$Ta(\eta^5$-$C_5Me_5)Cl_4$] gave an unusual product containing a P_6 trianion (Scheme 5).[59]

Scheme 5: Synthesis of unusual metal oligophosphanide complexes.[58,59]

Oxidative cleavage of the P–P bond is observed when $Na_2(P_4Mes_4)$ reacts with bis(phosphane)nickel(II) dichloride and bis(phosphane)palladium(II) dichloride to give nickel(0) and palladium(0) diphosphene complexes (Scheme 6).[60]
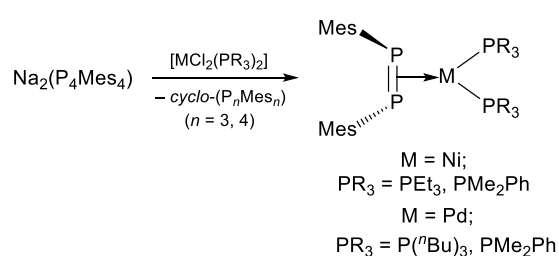
Scheme 6: Oxidative P–P bond cleavage of $Na_2(P_4Mes_4)$ by nickel(II) and palladium(II) complexes.[60]

In contrast, reductive cleavage of the P–P bond occurs in the reaction of $Na_2(P_4Ph_4)$ with one equivalent of [$Ni(cod)_2$] (Scheme 7). Similarly, the reaction of [$Ni(cod)_2$] with the less reactive potassium tetraphosphanide [$K_2(pmdeta)_2(P_4Ph_4)$] (pmdeta = *N,N,N',N'',N''*-pentamethyldiethylenetriamine) gave the complex [$K(pmdeta)$]$_2$[$Ni(P_4Ph_4)(\eta^2$-$P_2Ph_2)$], which contains both diphosphene and an intact P_4 chain of the tetraphosphanediide (Scheme 7).[61]
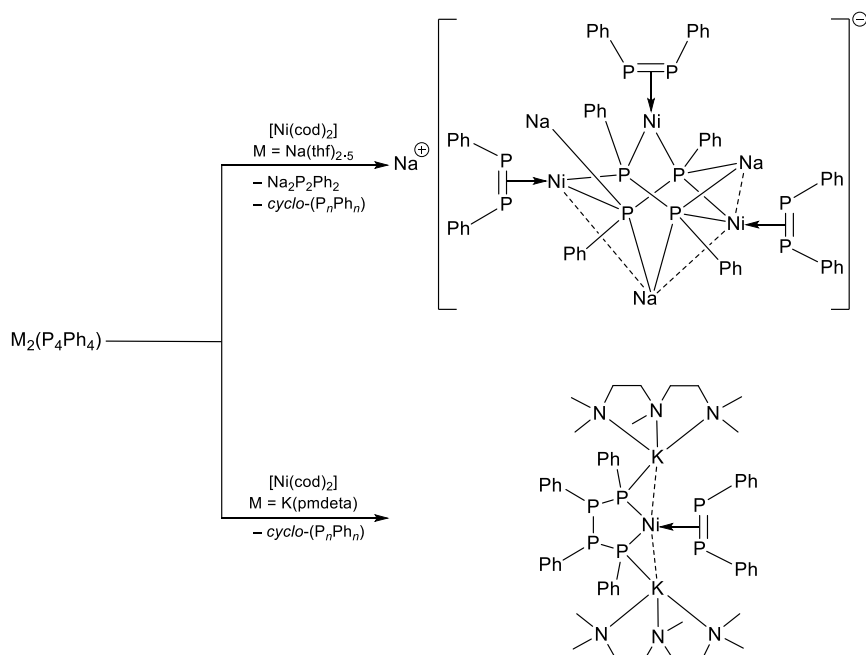
Scheme 7: Reactivity of Na and K salts of $(P_4Ph_4)^{2-}$ towards $[Ni(cod)_2]$.[61]

    Additionally, P–P bond cleavage of $Na_2(P_4Mes_4)$ occurs in the reaction with nucleophiles, such as ^nBuLi, which results in an unusual phosphorus-carbon based heterocyclic phosphaindazole anion $(P_2C_9H_9)^-$ (Scheme 8).[62]
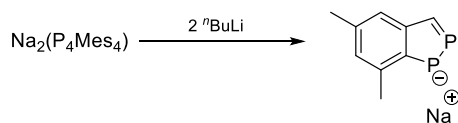

Scheme 8: Synthesis of a phosphorus-carbon based heterocyclic phosphaindazole.[62]

    Besides transition metal complexes, a few main group metal complexes of $(P_4{}^tBu_4)^{2-}$ have also been reported. A transmetallation reaction is observed when $K_2(P_4{}^tBu_4)$ reacts with one equivalent of R_2ECl_2 (E = Si, R = Me, Cl; E = Ge, R = Et; E = Sn, R = Me, ^tBu, ^nBu, Ph) to give $cyclo$-$(P_4{}^tBu_4ER_2)$ (Scheme 9).[63–67]

E = Si; R = Me, Cl
E = Ge; R = Et
E = Sn; R = Me, ^tBu, ^nBu, Ph
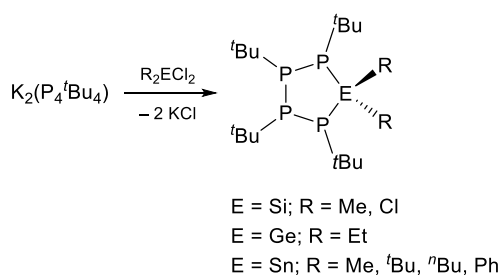
**Scheme 9**: Synthesis of group 14 metal complexes.[63–67]

    The reaction between $Na_2(P_4Mes_4)$ and two equivalents of tributyltin chloride gave the linear transmetallation product $P_4Mes_4(SnBu_3)_2$, which is surprisingly stable towards air and moisture (Scheme 10).[68]
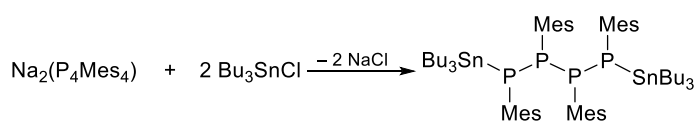

Scheme 10: Reaction of $Na_2(P_4Mes_4)$ with two equivalents of Bu_3SnCl.[68]

While oligophosphanide anions are highly reactive, neutral cyclooligophosphines are suitable ligands for the formation of stable phosphorus-rich metal complexes.[69] We have shown that the phosphorus-rich complexes [Cr(CO)$_5${$cyclo$-(P$_5$Ph$_5$)-κP^1}, [{Cr(CO)$_5$}$_2${μ-$cyclo$-(P$_5$Ph$_5$)-$\kappa P^1,P^3$}], [M(CO)$_4${$cyclo$-(P$_5$Ph$_5$)-$\kappa P^1,P^3$}] (with M = Cr, Mo, W (exo and $endo$ isomer)) are obtained in stoichiometric reactions (1:1 or 2:1) of the group 6 carbonyls with $cyclo$-(P$_5$Ph$_5$) in toluene or dichloromethane at room temperature. These complexes are air-stable at room temperature for at least one day. Single crystal structure determinations showed that the cyclopentaphosphine remains intact and acts as monodentate, bridging or bidentate ligand. Thermal decomposition of selected complexes occurs in three steps starting at ca. 220 °C and being completed at 600 °C. The decomposition products indicate that in contrast to the complexes with ^{t}Bu groups, these complexes are not suitable as precursors for the synthesis of phosphorus-rich metal phosphides.[70]
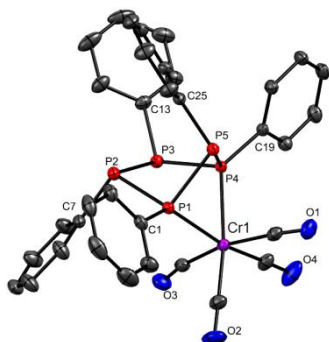
Figure 1: Molecular structures (H atoms are omitted) and atom labelling scheme for [Cr(CO)$_4${$cyclo$-(P$_5$Ph$_5$)-$\kappa P^1,P^3$}] with ellipsoids drawn at 30% probability level.
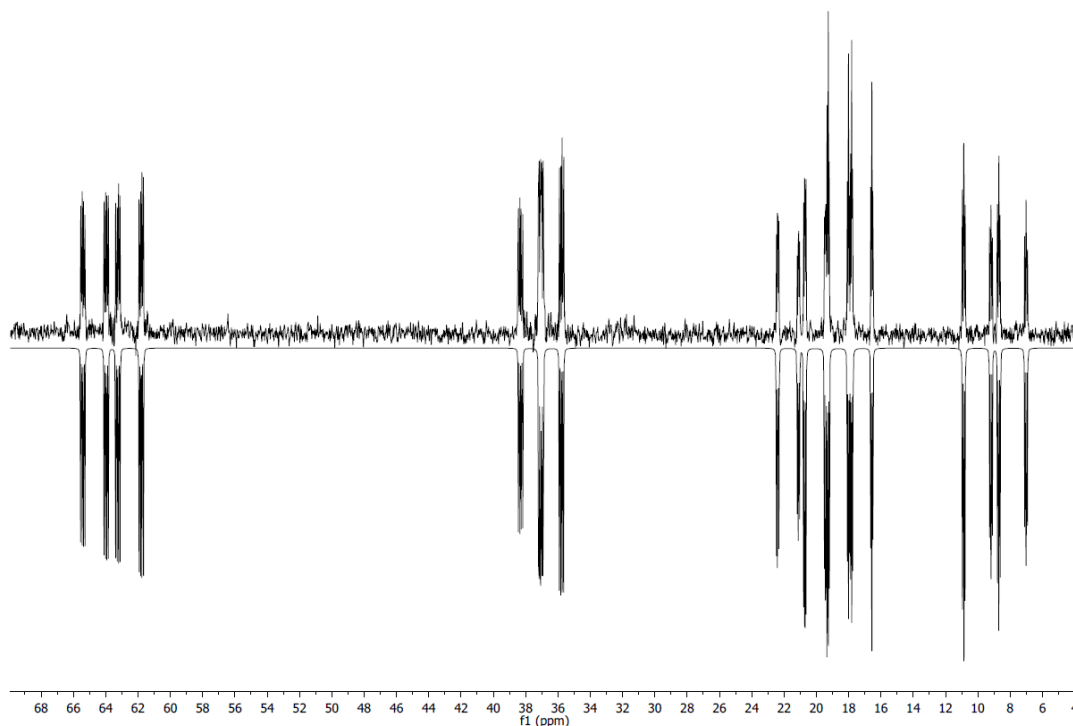
Figure 2: Experimental (top) and simulated (bottom) ^{31}P{^{1}H} NMR spectrum of complex [Cr(CO)$_4${$cyclo$-(P$_5$Ph$_5$)-$\kappa P^1,P^3$}] in C$_6$D$_6$.

Table 1: $^{31}P\{^1H\}$ NMR data (δ (ppm) and J (Hz)) of [Cr(CO)$_4${*cyclo*-(P$_5$Ph$_5$)-$\kappa P^1,P^3$}] in C$_6$D$_6$ at 25 °C.

[Cr(CO)$_4${*cyclo*-(P$_5$Ph$_5$)-$\kappa^2 P^1,P^3$}] (ABCDE spin system)	
	$\delta_A(P_A) = 63.6$ $\delta_B(P_B) = 37.0$ $\delta_C(P_C) = 20.9$ $\delta_D(P_D) = 17.9$ $\delta_E(P_E) = 9.0$

$^2J(P_C,P_E) = 29.0$	
$^1J(P_B,P_C) = -202.7$	
$^2J(P_D,P_E) = 17.2$	$^2J(P_A,P_C) = 16.4$
$^1J(P_B,P_E) = -235.0$	$^2J(P_B,P_D) = 10.3$
$^1J(P_A,P_E) = -353.6$	$^1J(P_A,P_D) = -273.7$
$^1J(P_C,P_D) = -210.2$	$^2J(P_A,P_B) = -12.0$

3 Conclusions

The targeted synthesis of ions such as (P$_4$R$_4$)$^{2-}$ (R = Ph, Mes) and *cyclo*-(P$_5$^{t}Bu$_4$)$^-$ and their versatile reactivity towards transition metal complexes allowed the preparation of a large variety of phosphorus-rich metal oligophosphanides. In reactions with these anions, complexes with intact ligands are formed, or degradation, rearrangement or oxidative coupling of the anions was observed, depending on the starting materials. In contrast, neutral cyclooligophosphines, such as *cyclo*-(P$_5$Ph$_5$), are generally much more predictable in coordination chemistry.

4 Acknowledgements

5 References

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