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A Selective Synthesis of the 1,3,4-Triphospholide Anion

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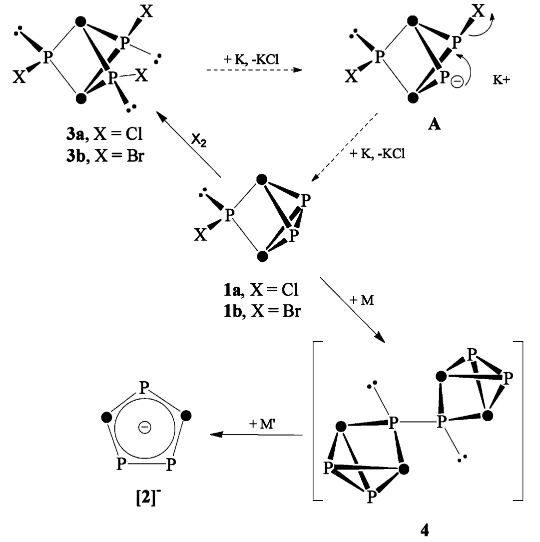
Summary: [$Mg_2(\mu$-$Cl)_3(THF)_6$][2,5-($C^tBu)_2$-1,3,4-P_3] *and* K[2,5-($C^tBu)_2$-1,3,4-P_3] *are formed quantitatively from reduction of the tricyclic-triphosphorus compound* $ClP_3(C^tBu)_2$ *with Mg or K; the mechanistic insights gained from these studies lead to a new and "economic" synthesis of the* [2,5-($C^tBu)_2$-1,3,4-$P_3]^-$ *anion from the phosphalkyne* $^tBuC{\equiv}P$.

There has been considerable interest in the chemistry of transition metal complexes carrying the η^5-2,5-($C^tBu)_2$-1,3,4-P_3 ligand.[1] Until recently, the apparent parallels between the ligating properties of the η^5-C_5H_5 and η^5-2,5-($C^tBu)_2$-1,3,4-P_3 ligands have been interpreted in terms of the diagonal relationship between C and P and the isolobal relationship between CR and P.[2,3] However, recent experimental and theoretical studies have suggested that there is a delicate balance between the η^5-2,5-($C^tBu)_2$-1,3,4-P_3 ligand behaving as a surrogate η^5-C_5H_5 ligand and as a ligand where the order of the frontier orbitals of the η^5-P_3C_2 system is reversed, with interesting consequences for bonding and reactivity.[4−6] It can be argued that in order to capitalize on this interesting behavior it is important to develop more efficient and selective pathways to the 2,5-($C^tBu)_2$-1,3,4-P_3 anion, for which the most practical reported synthesis is from the reaction of the phosphaalkyne $^tBuC{\equiv}P$ and alkali metals in a nonselective reaction requiring repeated recrystallization of moisture-sensitive alkali metal salts in order to separate the 1,3,4-triphospholide anion (42% yield) from the 1,3-diphospholide anion (37% yield).[7] In a new approach, we have focused on the reduction of the tricyclic $ClP_3(C^tBu)_2$ compound **1a** (Scheme 1)[8] and have found that reaction with either Li or Na metal in thf leads to the selective and quantitative formation of the lithium and sodium salts of the aromatic anion [**2**]$^-$,[9] which corresponds to an overall yield from $^tBuC{\equiv}P$ of 53%. In this paper we show that (i) our new synthetic pathway can be expanded to provide quantitative and regioselective access to both K and Mg salts of the triphospholide anion and (ii) the mechanistic insights gained from these studies lead to a new and "economic" synthesis of the [2,5-($C^tBu)_2$-1,3,4-$P_3]^-$ anion from the phosphalkyne $^tBuC{\equiv}P$.

Scheme 1[a]



[a] ● = C^tBu; M = Li, Na, K, Mg, Eu, Sm; M′ = Li, Na, K, Mg. Note that the structure of complex **4** has not been unequivocally assigned.

Reaction (room temperature, 1 h) of **1a** with an excess of magnesium metal (turnings or powder) in THF led to a change in color of the reaction mixture from pale yellow to red/brown; examination of the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed only the characteristic doublet and triplet resonances of the 2,5-($C^tBu)_2$-1,3,4-P_3 anion.[10] Extraction of the reaction

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[10] Synthesis of $[Mg_2(\mu$-$Cl)_3(THF)_6]^+$[**2**]$^-$: In a typical experiment, compound **1a** (267 mg, 1 mmol) was dissolved in THF (10 mL) and added to an excess of Mg powder/activated magnesium turnings (ca. 0.42 g, 17 mmol). The resulting mixture was stirred for 1 h, during which time it turned a dark red/brown color. A ^{31}P NMR spectrum recorded after 15 min indicated mainly $[Mg_2(\mu$-$Cl)_3(THF)_6]^+$[**2**]$^-$ but with some **4**; after 1 h, conversion into $[Mg_2(\mu$-$Cl)_3(THF)_6]^+$[**2**]$^-$ was quantitative. The solution was filtered (porosity 3 sinter with Celite) and washed with THF (3 × 5 mL). The solvent was removed in vacuo and the resultant brown solid dissolved in toluene. Colorless crystals were obtained following storage at 25 °C for 48 h. $^{31}P\{^1H\}$ NMR (121.42 MHz, +25 °C, C_4H_8O): δ 247.5 (t, $^2J_{P-P}$ 47 Hz), 240.5 (d, $^2J_{P-P}$ 47 Hz) ppm. No satisfactory elemental analysis could be obtained owing to loss of THF from the crystals upon attempted isolation of the solid, which was placed under vacuum (10^{-2} Torr, 30 min) prior to transfer to the glovebox.

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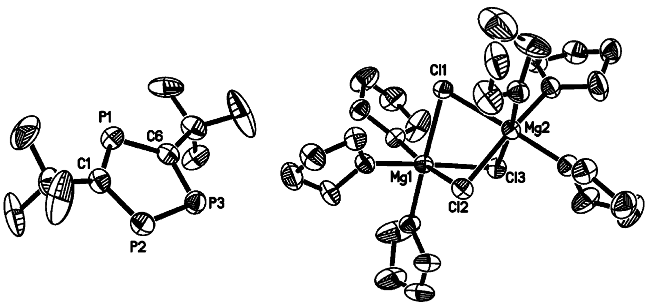

Figure 1. Molecular structure of $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+[\mathbf{2}]^-$. Thermal ellipsoids are shown at the 40% probability level.

mixture with toluene and cooling of the solution afforded colorless crystals of $[Mg_2(\mu\text{-}Cl)_3(THF)_6][2,5\text{-}(C^tBu)_2\text{-}1,3,4\text{-}P_3]$ $\{[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+[\mathbf{2}]^-\}$, which were shown by single-crystal X-ray crystallography to have the structure depicted in Figure 1.[11] This is, to our knowledge, the first example of an alkaline earth metal salt of the 1,3,4-triphospholide anion.

The $[2,5\text{-}(C^tBu)_2\text{-}1,3,4\text{-}P_3]^-$ anion does not show any close contacts with its cation partner, $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$; the closest magnesium center is more than 6 Å from the centroid of the P_3C_2 ring, and the nearest ring atom to magnesium is P(2), at a distance of 5.767 Å. It is therefore reasonable to conclude that this solid-state structure contains a "naked" $[2,5\text{-}(C^tBu)_2\text{-}1,3,4\text{-}P_3]^-$ anion.[12] The ring has dimensions comparable to ligated triphospholide anions, being planar with four P−C bonds of similar length {1.735(3), 1.748(3), 1.731(4), and 1.746(3) Å; mean 1.740 Å}: the P−P bond is short {2.091(1) Å; cf. P=P 2.00−2.05 Å, P−P ca. 2.22 Å}.[13] It is interesting to compare this system with the "naked" $C_5H_5^-$ prepared by Mews and co-workers utilizing the noncoordinating TAS^+ $\{S(NMe_2)_3{}^+\}$ cation.[14] Here the closest anion−sulfur contact is 5.129 Å and the C−C bond lengths within the $[C_5H_5]^-$ anion are shorter than in the corresponding lithium and transition metal compounds. The unusual dimagnesium cation has a confacial bioctahedral geometry: this cation has been previously observed in reductions of niobium complexes with magnesium,[15] and it has also been proposed to play an important role in the Schlenk equilibrium.[16] It has been suggested that $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$ arises from the combination of $[MgCl]^+$ and $MgCl_2$.[17]

Reaction (rt, 2 h) of a THF solution of **1a** with a potassium mirror led to quantitative ($^{31}P\{^1H\}$ NMR) formation of $K[2,5\text{-}(C^tBu)_2\text{-}1,3,4\text{-}P_3]$ $(K^+[\mathbf{2}]^-)$, a compound previously described by Cloke and co-workers in <50% yield.[18] An insight into the pathways followed when **1a** reacts with reducing agents came from a study of the reaction of **1a** in THF with the lanthanide Sm (powder or chips) or Eu (chips). These are, of course, weaker reducing agents ($E°$ Sm^{3+}/Sm −2.30 V, Eu^{3+}/Eu −1.99 V) than the alkali metals but similar to magnesium (Mg^{2+}/Mg −2.356 V); here there is the interesting possibility that $\eta^5\text{-}P_3C_2$-ligated Ln complexes might be formed. In the event this did not occur, instead the product, **4**, was formed, which exhibited three resonances (δ 207.9, −113.4, and −268.9 ppm) in the $^{31}P\{^1H\}$ NMR spectrum and a major peak at $m/z = 462$ in the mass spectrum. Although the structure has not been unequivocally assigned, the data are consistent with a symmetric dimer of formula $P_6(C^tBu)_4$ where two P_3C_2 units are linked by a P−P bond (Scheme 1).[19] It was therefore plausible to propose that **4** is an intermediate in the formation of the anion $[\mathbf{2}]^-$ on reduction of **1**. This was confirmed on observing the $^{31}P\{^1H\}$ NMR spectrum of a D_8-THF solution of **1a** on addition of either lithium or magnesium metal. In both cases resonances corresponding to the presence of the P−P bonded compound **4** were observed; however, as the reduction reaction proceeded, they decreased in intensity to be replaced by the resonances corresponding to either $Li^+[\mathbf{2}]^-$ or $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+[\mathbf{2}]^-$.

In considering the conclusions summarized in the "southern" part of Scheme 1 we realized that it should be possible to access the sequence of reactions $\mathbf{1} \rightarrow \mathbf{4} \rightarrow [\mathbf{2}]^-$ from the "north" by reacting the trichloro compound **3a**, which can be obtained by chlorination of **1a**,[20] with an alkali metal. Indeed reaction of **3a** with 2 equiv of K gives a mixture of **1a**, $K^+[\mathbf{2}]^-$, and **3a** in a 10:1:15 ratio, which can be rationalized by the initial formation of the monoanion **A**, which then collapses to regenerate **1a**, further addition of potassium completing the sequence $\mathbf{1a} \rightarrow \mathbf{4} \rightarrow [\mathbf{2}]^-$. This successful linking of the "northern" and "southern" parts of Scheme 1 then reminded us that, in G. Becker's original paper describing the synthesis of the triphospholide anion, it was also reported that treatment (C_6H_6, 60 °C) of $^tBuC{\equiv}P$ with 1 equiv of PBr_3 afforded an isolated 73% yield of the tribromo compound **3b**, whose structure was confirmed by single-crystal X-ray crystallography.[21] This implied that the sequence of reactions $^tBuC{\equiv}P \rightarrow \mathbf{3b} \rightarrow M[\mathbf{2}]$ would provide an efficient two-step synthesis of the anion $[2,5\text{-}(C^tBu)_2\text{-}1,3,4\text{-}P_3]^-$ from the phosphaalkyne $^tBuC{\equiv}P$. Having confirmed the efficacy of the $PBr_3/{}^tBuC{\equiv}P$ reaction, we found that reduction of *crude* **3b** with an excess of either lithium or magnesium resulted in quantitative conversion to the corresponding anions [M]**2**. The reaction proceeded most smoothly by employ-

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[11] Single crystals were grown from toluene, mounted in an inert oil, and transferred to the cold gas stream of the diffractometer. Crystal data: $C_{34}H_{66}Cl_3Mg_2O_6P_3$, $M = 818.75$, monoclinic space group Cc, $a = 13.1649(5)$ Å, $b = 15.4416(6)$ Å, $c = 21.9499(8)$ Å, $U = 4400.4(3)$ Å^3, $T = 173$ K, $Z = 4$, $\mu(\text{Mo K}\alpha) = 0.384$ mm^{-1}, 23 190 reflections measured, 9855 unique ($R_{\text{int}} = 0.0405$), which were used in all calculations. The final R_1 $[I > 2\sigma(I)]$ was 0.0413.

[12] We know of two further references to "naked" triphospholide anions, neither of which are currently reported on the Cambridge Crystallographic Database: the $[Li(dme)_3]^+$ salt of $[\mathbf{2}]^-$ in ref 10 and the $[Li(tmeda)_2]^+$ salt of $[\mathbf{2}]^-$ in the 1996 University of Sussex Ph.D. Thesis of V. Caliman.

[13] See, for example: Pestana D.C.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 528, and references therein.

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[19] Synthesis of $(CBu^t)_2P_2P\text{-}PP_2(CBu^t)_2$ (**4**): To a THF (2 mL) solution of **1** (30 mg, 0.113 mmol) was added an excess Eu pieces/Sm powder. The mixture was stirred at room temperature for 3 days. The solution was filtered and the solvent removed under vacuum to give a white solid, from which the following data were obtained: $^{31}P\{^1H\}$ NMR (121.49 MHz, +25 °C, C_6D_6) δ 207.9 (m), −113.4 (m), −268.9 (m) ppm; EI-MS, m/z 462 (65%, M), 232 (93%, M − $(CBu^t)_2P_3$).

[20] Compound **3a** may also be prepared from the reaction of $Zr(\eta^5\text{-}C_5H_5)_2\{P_2(CBu^t)_2\}$ with PCl_5; see ref 8.

[21] Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Weeber, U.; Westerhausen, M. *Nova Acta Leopold.* **1985**, *59*, 55.

ing magnesium as the reducing agent, and this process was monitored in situ by NMR spectroscopy. Over the course of several hours it was possible to observe the singlet resonance for **3b** decrease in intensity to be replaced by resonances that were assigned to $BrP_3(C^tBu)_2$, **1b**, on the basis of their similarity to those of **1a**. Subsequently the resonances for **1b** bleached to be replaced by those for the dimer **4** and, after 24 h, quantitative conversion to $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+[\mathbf{2}]^-$. This corresponds to a conversion of $^tBuC{\equiv}P$ to $[\mathbf{2}]^-$ of 73%.

In summary, we have demonstrated that the triphosphorus cage compounds **1** and **3** are both excellent precursors for the 1,3,4-triphospholide anion. Furthermore, as **3b** may be easily prepared from $^tBuC{\equiv}P$ and PBr_3 and reduction of the resulting crude product proceeds quantitatively to give $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+[\mathbf{2}]^-$, we suggest that this synthetic route provides facile and selective access to the 1,3,4-triphospholide anion.

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Supporting Information Available: Synthesis and reduction of **3b**. This material is available free of charge via the Internet at http://pubs.acs.org. Also see: http://www.rsc.org/suppdata/xx/b0/b000000x/.

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