Zirconium Chlorides with Multidentate Dialkylphosphido Ligands

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The multidentate phosphido ligand $[^-P(CH_2CH_2PMe_2)_2]$ enables the isolation of new classes of zirconium phosphides; preliminary studies, including details of new complexes prepared and the crystal structure of a unique Zr^{III} binuclear complex with three phosphido ligands, each exhibiting different coordination behaviour, are reported.

Dialkylphosphides of electropositive transition metals are rare; for the group 4 metals in oxidation state (IV) they are limited to cyclopentadienyl derivatives of the types $[Cp_2M(PR_2)_2]$,[1] $[Cp_2M(PR_2)X]$,[2] $[CpM(PR_2)_nX_{3-n}]$ (n = 1, 2)[3] and homoleptic phosphides of the type $[M(PR_2)_5]^-$ and $[M(PR_2)_4]$[4] stabilised by bulky $^-PR_2$ ligands (R = cyclohexyl). Thus far, there are no well characterised examples of phosphido complexes of these metals containing only halide and phosphide ligands although there is a report of a zirconium(IV) halide complex with the bridging spirocyclic tetraphosphido ligand, $[C(CH_2PPh^-)_4]$.[5] More general access to ternary phosphides with halide ligands would be desirable since this would greatly broaden the scope of studies of phosphido complexes.

Recently, it has been shown that potentially chelating terdentate amido ligands of the type $[^-N(CH_2CH_2ER_2)_2]$ (R = alkyl, E = N, P, As) are capable of stabilising new classes of dialkylamido metal halides[6] for which analogues with simple

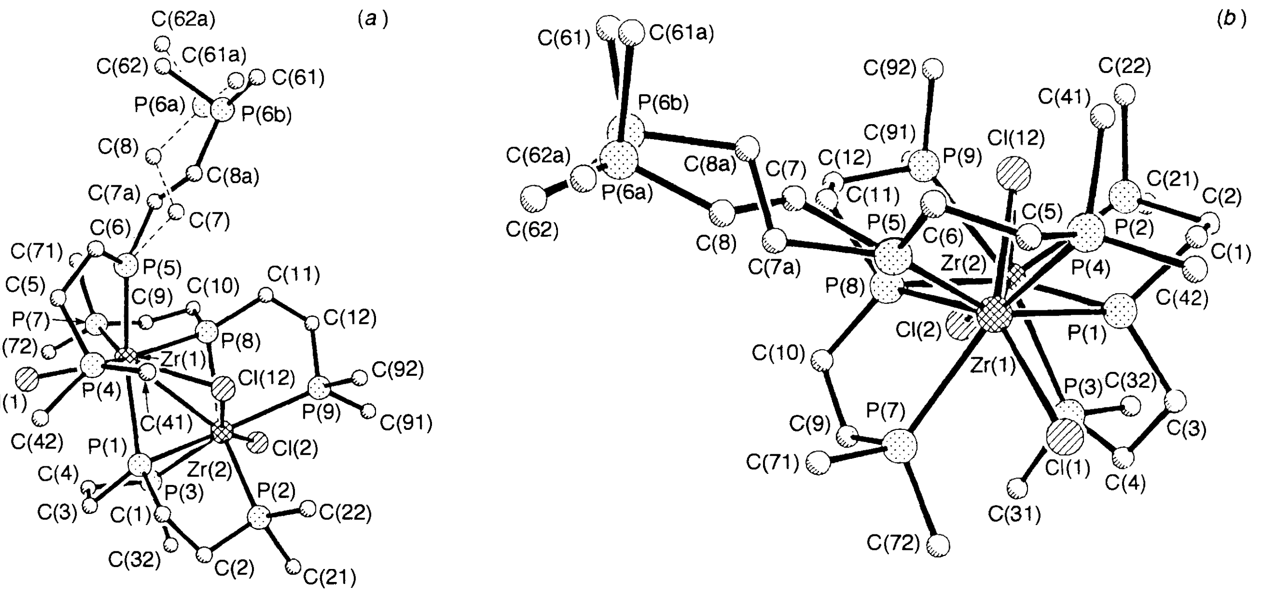

Fig. 1 Two alternative views of the structure of [$Zr_2Cl_3(PPP)_3$] to show the complex coordination of (PPP) around the Zr atoms. Selected bond lengths (Å) for $Zr_2Cl_3(PPP)_3$: Zr(1)–Zr(2), 3.361(2); Zr(1)–P(4), 2.703(3); Zr(1)–P(5), 2.514(4); Zr(1)–P(7), 2.778(3); Zr(1)–Cl(1), 2.566(3); Zr(1)–P(8), 2.673(3); Zr(1)–P(1), 2.665(3); Zr(1)–Cl(12), 2.712(3); Zr(2)–P(8), 2.629(3); Zr(2)–P(1), 2.672(3); Zr(2)–Cl(12), 2.674(3); Zr(2)–P(9), 2.782(3); Zr(2)–P(2), 2.744(3); Zr(2)–P(3), 2.748(3); Zr(2)–Cl(2), 2.508(5).

dialkylamido ligands are unstable with respect to disproportionations or proportionations. We have applied this approach to the stabilisation of ternary phosphido complexes of electropositive transition metals with the new ligand [$^-P(CH_2CH_2PMe_2)_2$] (PPP^-).

Previously[7] we described reactions of $ZrCl_4$ with one and two mole equivalents of LiPPP per Zr, leading to complexes characterised as [$(PPPZrCl_3)_2$] and [PPP_2ZrCl_2], respectively. In the latter reaction, supernatant solutions remaining after crystallisation of the product were shown to contain the oxidation product [$(Me_2PCH_2CH_2)_2P\text{–}P(CH_2CH_2PMe_2)_2$-($PPP)_2$] as well as an ESR active and as yet unidentified zirconium compound. The use of 3 mol equiv. of LiPPP maximises the formation of $(PPP)_2$ and enables the isolation of a dark, red-brown, crystalline material. This compound is diamagnetic in solution and in the solid state and conforms to the stoichiometry [$Zr_2Cl_3(PPP)_3$]. Both $^{31}P[^1H]$† and ^1H NMR‡ spectra are complex. The former indicates the presence of coordinated [δ 14.5(t), 10.9(m), 0.6(m), −0.3(m)] and uncoordinated tertiary phosphine [δ −51.8(d)] assigned on the basis of chemical shift, as well as at least three distinct phosphide functions [δ 139.8(m), 130.4(m), 126.6(m)]. The chemical shifts of the peaks assigned to phosphido phosphorus atoms are similar to those for previously observed bridging phosphides.[1b] Terminal π-bonded dialkylphosphides have been reported to resonate at lower fields (*e.g.* δ 261.3 in a $Hf^{IV}PBu^t{}_2$ complex[4]) however chemical shifts may be significantly influenced by σ–π (*i.e.* pyramidal-planar) phosphide interconversions[1a] and commonly appear in a similar region to those of bridging phosphides. Further investigations of the spectroscopic and chemical properties of this compound are being undertaken and will be reported elsewhere. The complex spectra and lack of diagnostic data prompted us to obtain the X-ray structure of the compound.§

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† It is clear that the ^{31}P NMR spectrum is more complex than would be expected (based on the solid state structure) and a complete explanation of it is not available. Although the compound may be recrystallised in reasonably good yield (*ca.* 70%) it appears that the solution structure may not be identical to the solid state structure and/or dissolution accompanies rearrangements to a mixture of compounds. Further studies are in progress in order to understand better this solution behaviour.

‡ NMR spectra were collected on a Bruker WM360 spectrometer in perdeuteriotoluene at 360 MHz (^1H) and 145 MHz (^{31}P) and were referenced to residual protons of solvent (^1H) or externally to H_3PO_4 (85%).

§ *Cell data and X-ray data collection*: Crystals of the title compound grew as large, dark red–brown blocks from petroleum ether (b.p. 40–60 °C) and were cut to an appropriate size. That used for cell and X-ray data collection was irregular but had approximate dimensions 0.25 × 0.25 × 0.3 mm, and was sealed into a Lindemann glass capillary under oxygen-free dry argon in a dry box.

Crystal data: $C_{24}H_{60}P_9Cl_3Zr_2$, $M = 916.28$, monoclinic, space group *Cc* (No. 9), $a = 16.725(7)$, $b = 27.074(10)$, $c = 11.834(6)$ Å, $\beta = 114.91(3)°$, $V = 4860(4)$ Å^3, $Z = 4$, $D_c = 1.26$ g cm^{-3}, $F(000) = 1880$.

Data were recorded at room temperature (293 K) in the range $3° < 2\theta < 60°$ on the Siemens P3m/v, automated four-circle diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) and $\omega:2\theta$ scans with variable scan speed for $0 \leq h \leq 19$, $0 \leq k \leq 38$ and $-16 \leq l \leq 15$. During collection, two standard reflections were remeasured every 200 reflections and no significant fluctuations in these intensities were observed. Of 7344 independent reflections, 6769 unique data were used to solve the structure by a combination of heavy atom and Fourier difference syntheses. 3847 data with $F > 6\sigma(F)$ were used in the final stages of refinements. The intensity data were corrected for Lorentz, polarisation and X-ray absorption effects [μ_{calc}(Mo-Kα) = 8.9 cm^{-1}]. The latter by an empirical method, using 366 measured ψ scans. A weighting scheme of the form $w^{-1} = [\sigma^2(F) + gF^2]$, with $g = 0.0011$, gave a satisfactory analysis.

All non-hydrogen atoms, except in the disordered chain, were refined using anisotropic displacement parameters and this reached convergence at $R(R')$ 0.042 (0.052), the maximum shift : error ratio in the final 6 cycles of full-matrix least-squares refinement was 0.12, mean 0.007, and goodness of fit 1.07. The data : parameter ratio was 11 : 1 and the largest positive residual peak in the difference map +0.5 eÅ^{-3}.

All calculations were carried out on a DEC μ-vaxII computer using the SHELXTL PLUS system of programs.[9]

In the early difference maps and in subsequent refinement it was obvious that the terminal [$C(7)H_2C(8)H_2P(6a)Me_2$] arm attached to P(5) exhibited a positional disorder. The most appropriate model to fit the observed intensities is a 50 : 50 occupation of the two alternative atomic sites for the terminal [$CH_2CH_2PMe_2$] atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

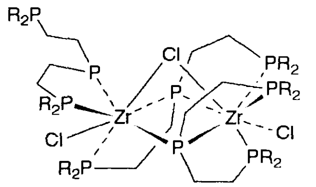

Fig. 2 A representation of the structure of $Zr_2Cl_3(PPP)_3$

The structure (Fig. 1) shows a unique coordination environment for zirconium. The molecule is binuclear with a Zr–Zr distance of 3.361(2) Å.¶ Each Zr atom supports a terminal chloride, and they are bridged by two phosphides and a third chloride. Each bridging phosphide is different however, with one spanning the Zr–Zr axis and each of its terminal tertiary phosphines coordinated to different zirconium atoms; whilst the other has its tertiary phosphines coordinated to only Zr(2). The coordination sphere of Zr(1) is then made up by the third phosphide [P(5)]. This ligand is chelating with a pendant tertiary phosphine [P(6a/b)]. The pendant arm is disordered, no doubt due to rotational freedom, and the disorder is adequately modelled with just two conformations for the P and C atoms of the pendant arm. The phosphide [P(5)] is π-bonded to the zirconium atom [Zr(1)], in one conformation it is quite planar [Σ bond angles = 359.9(23)°] and in the other conformation it is tending toward planar [Σ bond angles = 352.5(24)°]. The complex coordination environment around the zirconium atoms is more clearly represented in Fig. 2.

A number of features of this structure are surprising. The coordination behaviour of the phosphido ligands is difficult to rationalise but the compound demonstrates the versatility of this potentially tridentate phosphido ligand system since it can clearly coordinate zirconium in a number of manners including both bridging and terminal environments. Presumably, it has then an ability to satisfy coordination constraints dictated by the metal; a feature that may be of considerable value in stabilising unusual new classes of complexes.

The compound is diamagnetic in the solid state and contains Zr^{III} atoms, hence unpaired electrons must be interacting although the Zr–Zr distance [3.361(2) Å] is long for a bonding interaction.‖ There is a report of a diamagnetic Zr^{III} dimer $[Cp_4Zr_2(\mu\text{-}PMe_2)_2]$[8] containing bridging dialkylphosphide ligands and for which metal–metal bonding is absent, Zr–Zr = 3.653 Å, and for which spin pairing is presumed to occur *via* the phosphide bridges. It is possible that any metal–metal bonding is not significant in the present compound and its diamagnetism arises from a similar mechanism. It is also noteworthy that the bridging atoms are not symmetrically disposed around the Zr–Zr axis in so far as they fall into a T-shaped arrangement rather than approximately regular trigonal. The two bridging phosphides and the two zirconium atoms are approximately coplanar this plane being orthogonal to the Zr(1)–Zr(2)–Cl(12) plane. This arrangement can be seen in Fig. 1(*b*).

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¶ Selected bond lengths are collected in Fig. 1 caption.

‖ In comparison to (for example) $Zr_2Cl_4(\mu\text{-}Cl)_2(PBu_3)_4$ [Zr–Zr = 3.182(1) Å] where the authors propose a metal–metal bond, J. H. Wengrovius, R. R. Schrock and C. S. Day, *Inorg. Chem.*, 1981, **20**, 1844.