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Substituent-Free P_1, P_2, and P_3 Complexes of Zirconium

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The chemistry of early metal imide (M=NR),[1] oxide (M=O), and sulfide (M=S)[2] systems has been developed with a view to generating new reagents for the incorporation of heteroatoms in organic compounds.[3] Our recent studies of Zr phosphinidenes (M=PR) offer extensions of this approach to organophosphorus compounds.[4] In general, these early metal–heteroatom multiple bonds are stabilized employing sterically demanding ancillary groups, as is the case for $Cp_2Zr{=}PC_6H_2\text{-}t\text{-}Bu_3(PMe_3)$.[5] However, severe steric demands may facilitate P–C bond cleavage, as previously seen in the formation of $(CpZr(\mu\text{-}C_5H_4))_3P$.[6] This latter observation suggests that it may be possible to employ such P–C bond cleavages as a synthetic route to substituent-free phosphorus complexes. While such early metal–P_x derivatives are rare, they are generally synthesized via reactions of elemental phosphorus.[7] Employing an E–C bond cleavage approach, Evans and co-workers have achieved Sm-mediated formation of the substituent-free Bi–Bi bond in $(Cp^*_2Sm)_2(\mu\text{-}Bi_2)$ via the reaction of Cp^*_2Sm and $BiPh_3$.[8] In this report, we describe sterically congested Zr–P systems which induce P–C bond activation, affording access to Zr complexes which incorporate one, two, or three substituent-free phosphorus atoms.

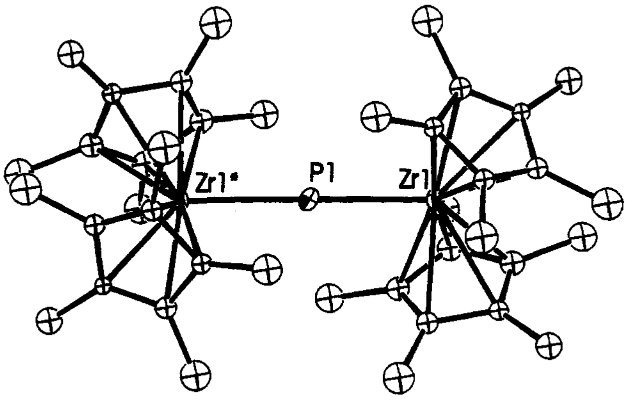

Figure 1. ORTEP drawing of $(Cp^*_2Zr)_2(\mu\text{-}P)$ (3). 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.

The complex $Cp^*_2Zr(PH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3))Cl$ (**1**) is derived from the reaction of $Cp^*_2ZrCl_2$ with $KPH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)$.[9] The sterically demanding nature of the substituents in **1** results in no further substitution, even in the presence of excess phosphide, unlike the analogous species $Cp^*_2Zr(PH(C_6H_2\text{-}2,4,6\text{-}Me_3))_2$.[5] However, the generation of **1** via the reaction of $Cp^*_2ZrCl_2$ with excess KH and phosphine in THF at 25 °C resulted in further reaction. On being stirred for several hours, the $^{31}P\{^1H\}$ resonance attributable to **1** is replaced by two low-field resonances. One of these products, compound **2**, is isolated in 15–20% yield by removal of the solvent and extraction of the residue with pentane. This compound **2** exhibits a singlet $^{31}P\{^1H\}$ resonance at 959 ppm and a ^1H NMR signal attributable only to the Cp* rings. Repeated attempts to obtain X-ray quality crystals of **2** were unsuccessful; however, elemental analysis, FAB-MS, and additional chemical data (*vide infra*) led to the formulation of **2** as $(Cp^*_2Zr)_2(\mu\text{-}P_2)$.[9] Although unconfirmed by X-ray methods, **2** is thought to be a structural analog of the species $(Cp^*_2Sm)_2(\mu\text{-}Bi_2)$.[8] In addition to **2**, a second species **3** was isolated in 10% yield from the pentane washings. This compound is paramagnetic, exhibiting a doublet EPR resonance at $g = 1.989$, with a P hyperfine coupling constant of 26 G. An X-ray crystallographic study of **3** revealed the formulation as $(Cp^*_2Zr)_2(\mu\text{-}P)$ (Figure 1).[10] This formally mixed-valent Zr(IV)/Zr(III) species sits on a crystallographically imposed $2/m$ axis of symmetry with a geometry at P approaching linearity. The Zr′–P–Zr angle of 166.6(4)° is comparable to that reported in the "linear" phosphinidene complex $WCl_2(PMePh_2)_2(CO)(PC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)$ (W–P–C 168.2(2)°).[11] The Zr–P bond length is 2.545(3) Å, a distance consistent with Zr–P multiple bond character.[5,12] The imposed symmetry dictates that the Cp* centroid–centroid vectors on the two Zr atoms are perpendicular. This geometry permits π-interactions between P and each of the Zr centers, forming a dimetallaphosphacumulene.[13] Compound **3** represents the first such species to be structurally characterized, although the related arsina- and stibacumulenes $(Cp^*Mn(CO)_2)_2(\mu\text{-}E)$ (E = As, Sb) have been reported.[14]

While complexes **2** and **3** are clearly derived from intriguing P–C bond cleavage reactions, this "one-pot synthesis" provides only moderate to poor yields and precludes significant mechanistic insight. As an alternative, the reaction of 2 equiv of $PH_2(C_6H_2\text{-}$

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(9) All spectral data were recorded in C_6D_6 unless otherwise noted. (i) ^1H NMR. **1**: δ 7.59 (s), 7.49 (s), 6.17 (d), 1.79 (d), 1.56 (s) 1.35 (s). **2**: δ 2.09 (s). **4**: δ 1.70 (s), 4.68 (d of d). **5**: δ 1.66 (s). **6**: δ 1.87 (s). (ii) $^{31}P\{^1H\}$ NMR. **1**: δ 117.0. **2**: δ 959.5. **4**: δ 134.3. **5**: δ 450.4. **6**: δ 490.4 (d), 245.6 (t), $|J_{P-P}| = 598$ Hz. (iii) EPR (THF). **3**: $g = 1.989$, $\langle a_P \rangle = 26$ G. Satisfactory elemental analyses were obtained for compounds **1**, **2**, **4**, and **6**.

(10) Mo Kα radiation ($\lambda = 0.710\,69$ Å) and a Rigaku AFC6-S diffractometer were used to collect the data ($4.5° < 2\theta < 50°$) for each compound. **3**: $C_{40}H_{60}PZr_2$ Monoclinic space group $P2/c$ (No. 13), $a = 15.205(4)$ Å, $b = 13.302(4)$ Å, $c = 15.481(5)$ Å, $\beta = 104.39(2)°$. **6**: $C_{40}H_{60}PZr_2$, tetragonal space group $P\bar{4}2_1c$ (No. 114), $a = 14.720(9)$ Å, $c = 19.464(13)$ Å. The solution was obtained and refined employing the TEXSAN software from MSC. Refinements (data $I > 3\sigma(I)$, variables R, R_w). **3**: 1189, 116, 0.0823, 0.0948. **6**: 857, 95, 0.0656, 0.0732.

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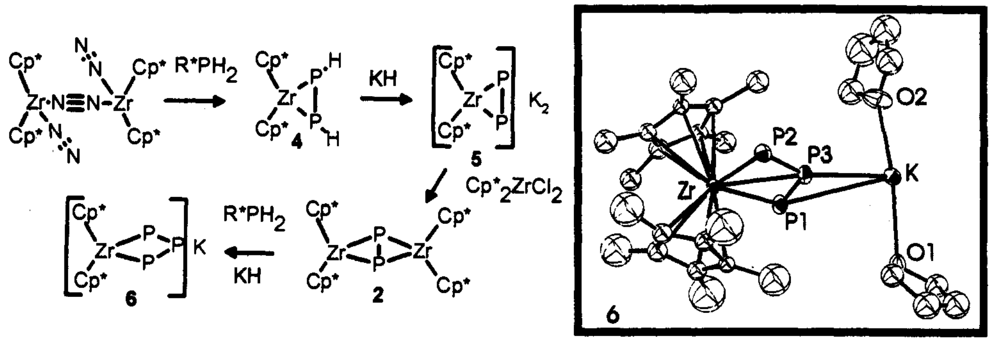
Scheme 1



2,4,6-*t*-Bu$_3$) with (Cp*$_2$Zr(N$_2$))$_2$(μ-N$_2$)[15] in benzene at 25 °C was investigated. This reaction proceeds smoothly to give on subsequent workup species **4** in 75–90% isolated yield. ^{1}H NMR showed resonances attributable to the methyl and PH protons; no resonances due to the supermesityl substituents were observed. Two P–H coupling constants were observed, 310.0 and 21.3 Hz.[9] Together, these data are consistent with the formulation of **4** as Cp*$_2$Zr((PH)$_2$). ^{1}H NMR data from the mother liquor also confirmed the formation of C$_6$H$_3$-2,4,6-*t*-Bu$_3$ en route to **4**. Reaction of **4** with KH at 25 °C in THF leads to the generation of species **5**, which exhibited a ^{31}P{^{1}H} resonance at 449.5 ppm.[8] The ^{1}H NMR spectrum of **5** shows only resonances attributable to methyl and THF protons, consistent with the formulation of **5** as [Cp*$_2$Zr(P$_2$)][K(THF)$_x$]$_2$ (Scheme 1). Subsequent addition of 1 equiv of Cp*$_2$ZrCl$_2$ to the solution of **5** yields **2** quantitatively.

Compound **2** undergoes a slow reaction with excess PH$_2$(C$_6$H$_2$-2,4,6-*t*-Bu$_3$) in the presence of KH in THF at 25 °C. After about 1 week, the ^{31}P NMR resonance attributable to **2** was replaced by a doublet at 490.4 ppm and a triplet at 245.6 ppm. Direct P–P bonds are implied by the $|J_{P-P}|$ value of 598 Hz.[8] Red crystals of this new species **6** were isolated in 30% yield. An X-ray crystallographic study of **6**[9] revealed that the asymmetric unit contains Cp*$_2$ZrP$_3$K(THF)$_{1.5}$ (Scheme 1). Three phosphorus atoms in a plane are bonded to Zr such that the Zr–P distances are 2.550(8), 2.55(1), and 2.853(9) Å, the latter being the central Zr–P distance. This geometry is in contrast to that typically seen for metal complexes of P$_3$ rings, where a triangle of P atoms bonds symmetrically to the metal.[16] The P–P distances of 2.09(1) and 2.10(1) Å are significantly shorter than the single P–P bonds seen in Cp$_2$M(PR)$_3$ complexes[17] and yet longer than the P=P double bond of (P(C$_6$H$_2$-2,4,6-*t*-Bu$_3$))$_2$ (2.034(2) Å),[18] suggestingsome degree of P–P multiple bonding. Electrostatic interactions between P and K atoms at distances ranging from 3.37(1) to 3.61(1) Å result in the infinite lattice in the solid state. Two Cp*$_2$ZrP$_3$ units are bridged by two K atoms, yielding a "dimeric unit" which becomes the extended array as these units interact with the adjacent units through K. One of the THF molecules bridges symmetry-related K atoms.

Monitoring the initial "one-pot synthesis" of **2** and **3** by ^{31}P{^{1}H} NMR spectroscopy was informative in retrospect. The initial formation of **1** was confirmed by the appearance of the resonance at 117.0 ppm. After about 0.5 h, this resonance diminished and was replaced with a singlet at 134.3 ppm, attributed to species **4**. This signal was subsequently replaced by resonances attributable to two products: the minor component **5** and the major product **2**. These observations are consistent with the stoichiometric reaction sequence observed above (Scheme 1), suggesting that **4** and **5** are intermediates en route to the P$_2$ product **2**. Furthermore, the isolation of **3** from the "one-pot" mixture, albeit in low yield, may be viewed as the trapping of a short-lived P$_1$ intermediate, although the mixed-valent nature of **3** points to a complex and as yet unknown reaction sequence involving reduction.

The above chemistry demonstrates that a sterically demanding environment may induce P–C bond cleavage and thus provide access to substituent-free P derivatives. The generality of this approach and the utility of the derived products in the construction of main group polyatomic anion complexes is currently being explored.

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Supplementary Material Available: Spectral and analytical data for **1**–**6**, table of crystallographic data, structures, and tables of thermal and hydrogen atom parameters and bond distances and angles for **3** and **6** (20 pages); listing of observed and calculated structure factors for **3** and **6** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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