Communications

Dinuclear and Diamagnetic Zirconium(III) Derivatives without Zr–Zr Bond. Synthesis and X-ray Structure of $\{Cp_2Zr[\mu\text{-}P(CH_3)_2]\}_2$ and $(Cp_2Zr)_2(\mu\text{-}Cl)[\mu\text{-}P(CH_3)_2]$

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Summary: The room-temperature reactions of Cp_2MCl_2 (M = Zr, Hf) with magnesium in the presence of $(CH_3)_2P\text{-}P(CH_3)_2$ similarly proceed with the formation of the respective poorly soluble diamagnetic M(III) dimer $\{Cp_2M[\mu\text{-}P(CH_3)_2]\}_2$ (**1**) [M = Zr (**a**), Hf (**b**)], in reasonable yield [**1a**, 45%; **1b**, 38%]. A soluble diamagnetic byproduct, $(Cp_2Zr)_2(\mu\text{-}Cl)[\mu\text{-}P(CH_3)_2]$ (**2a**), has been isolated in low yield (10%) in the case of Zr. The molecular structures of **1a** and **2a** have been determined by X-ray analyses. Crystal data for **1a**: monoclinic space group of symmetry $P2_1$; a = 8.920 (5) Å, b = 14.955 (10) Å, c = 16.952 (7) Å; β = 91.09 (4)°; Z = 4; V = 2261 (2) Å^3. Crystal data for **2a**: monoclinic $P2_1/a$; a = 15.996 (8) Å, b = 9.120 (3) Å, c = 16.172 (6) Å; β = 117.43 (4)°; V = 2094 (2) Å^3; Z = 4. In each case, a rather long intermetallic distance [3.653 (2) Å (**1a**), 3.524 (2) Å (**2a**)] excludes the presence of a M–M bond.

Dinuclear early-transition-metal complexes with a d^1 electronic configuration may provide suitable candidates for studying the occurrence of M–M single bond.[1] However, for trivalent group IVA metals, no dimeric Ti(III) complexes containing a M–M bond have been reported (except in one case[2]), while the presence of Zr–Zr bond has been postulated[3] to explain the diamagnetism observed for the corresponding dinuclear Zr(III) species. Crystallographic evidence supporting this hypothesis is limited to only two cases for zirconium ($[ZrCl_3(PBu_3)_2]_2$[4] and $(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2$[5] showing an elongated Zr–Zr separation in both cases) and none for hafnium.

Since the initial discovery by Issleib and Häcker[3a] that Cp_2ZrCl_2 undergoes halogen-reductive substitution by $LiPR_2$ (R = Et, Bu) affording the diamagnetic phosphide-bridged dimer $(Cp_2ZrPR_2)_2$, the synthesis of related phosphido-bridged derivatives has received considerable attention.[6] The nature of the alkyl substituents on the dialkylphosphide as well as the reaction temperature[7] seems to play a crucial role in the reduction reaction. Curiously, this reaction apparently does not occur for the hafnium analogue. Furthermore, the diamagnetism of the resultant species appears to depend on how the low-valent precursors are generated.[8] These reasons prompted us to reinvestigate the chemistry of the phosphido-bridged dimeric Zr(III) and Hf(III) species with the dual purpose of clarifying their structure and magnetic behavior, thereby gaining insight into the nature of the metal–metal interaction and providing Zr(III) compounds in large scale for further reactivity studies.

We report herein the synthesis of $\{Cp_2Zr[\mu\text{-}P(CH_3)_2]\}_2$ (**1a**) and $(Cp_2Zr)_2(\mu\text{-}Cl)[\mu\text{-}P(CH_3)_2]$ (**2a**) and the first structural studies of these dinuclear zirconium(III) bis(cyclopentadienyl) complexes. According to (1), the

$$2Cp_2MCl_2 + Mg + (CH_3)_2P\text{-}P(CH_3)_2 \xrightarrow[-MgCl_2]{THF} \underset{\mathbf{1a,b}}{\{Cp_2M[\mu\text{-}P(CH_3)_2]\}_2} \quad (1)$$

M = Zr (**a**), 45%; M = Hf (**b**), 38%]

room-temperature reaction of Cp_2MCl_2 (M = Zr, Hf) with magnesium turnings and dimethyldiphosphine produces a deep red slurry. After evaporation to dryness and continuous extraction with toluene, the crystalline and poorly soluble $\{Cp_2M[\mu\text{-}P(CH_3)_2]\}_2$ (**1**) [M = Zr (**a**), Hf (**b**)] is obtained in reasonable yield.

A highly soluble byproduct, $(Cp_2Zr)_2(\mu\text{-}Cl)[\mu\text{-}P(CH_3)_2]$ (**2a**), in the case of zirconium is also isolated and can be obtained in pure form (10%). The reaction apparently proceeds via the "in situ" formation of low-valent zirconium/hafnium species followed by an oxidative-addition reaction on the P–P bond. No reaction is observed between Mg and $Me_2P\text{-}PMe_2$ at room temperature even after a long time (7 days). However, the isolation of **2a** (probably an intermediate in the formation of **1a** since longer reaction periods reduce its formation) suggests that a more complicated reaction pathway occurs. Utilization of Cp'_2MCl_2 ($Cp' = CH_3C_5H_4$) led to analogous highly soluble species that can be easily isolated in pure form from toluene-pentane mixtures.[9]

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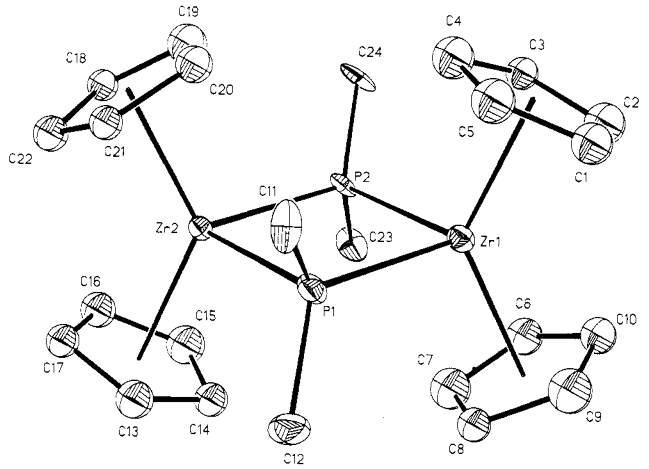

Figure 1. ORTEP drawing of molecule 1 of **1a**. Some averaged bond lengths (Å) and angles (deg) (estimated standard deviation in parentheses): Zr···Zr = 3.653 (2); Zr–P = 2.672 (5); P–Zr–P = 93.8 (2); Zr–P–Zr = 86.3 (2); Zr–cp(centroid) = 2.22 (3). Estimated standard deviations of mean value are calculated as $\sigma(\bar{x}) = [\sum_{i=1}^{n}(x - \bar{x})^2/n(n-1)]^{1/2}$ except for $n = 2$ when the larger individual esd is used.

The solid-state structures of both **1a** and **2a** have been determined by X-ray structural analysis.[10] The two complexes are both dimeric and have similar molecular arrangements. The two Cp_2Zr moieties in **1a** are linked together by two bridging phosphide groups (Figure 1) whereas in **2a** one phosphide group is replaced by a bridging chloride (Figure 2). Although there are two crystallographically independent molecules in the unit cell of **1a**, their structures do not differ significantly in any respect. The cyclopentadienyl rings in both **1a** and **2a** are bonded in the usual η^5 fashion with a normal range of Zr–cp(centroid) distances ranging from 2.20 (2) to 2.24 (2) Å. Disordered cyclopentadienyl rings is a common feature of (**1a**) and (**2a**). The disorder of the Cp rings in **1a** was severe but well-resolved. In complex **2a**, where the problem was less serious, the disorder was not resolved but indicated in the final difference Fourier map. The central core containing the Zr and bridging atoms is planar in both complexes. The values of Zr–Cl and Zr–P bond distances are as expected.[4,5,6c,f] In spite of the fact that both complexes are diamagnetic in the solid state as well as in solution,[11] the long intermetallic distances found in both complexes [3.653 (2) Å for **1a** and 3.542 (2) Å for **2a**], are inconsistent with the presence of a direct Zr–Zr bond. The corresponding hafnium analogue of **1a** can be obtained from reaction 1 and on the basis of their IR and NMR spectra possess a similar dinuclear structure. Satisfactory analytical and spectroscopic data[12] have been obtained for all the complexes. A systematic investigation of the reactivity of these species is in progress.

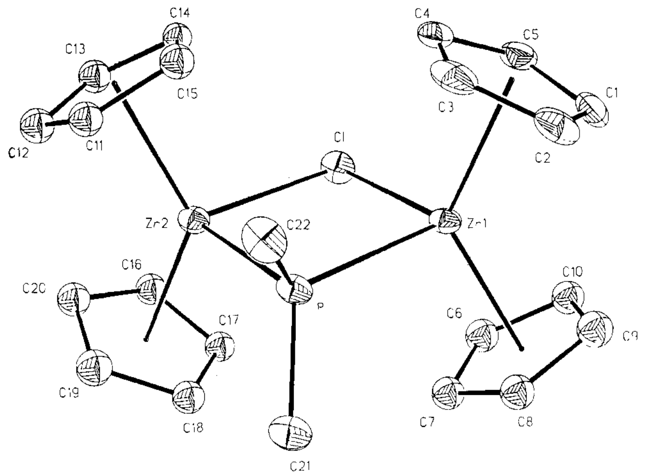

Figure 2. ORTEP drawing of **2a**. Selected bond lengths (Å) and angles (deg) (estimated standard deviation, in parentheses): Zr(1)–Zr(2) = 3.524 (2); Zr(1)–Cl = 2.587 (2); Zr(2)–Cl = 2.595 (2); Zr(1)–P = 2.661 (2); Zr(2)–P = 2.648 (2); Cl–Zr(1)–P = 95.5 (1); Cl–Zr(2)–P = 95.6 (1); Zr(1)–Cl–Zr(2) = 85.7 (1); Zr(1)–P–Zr(2) = 83.2 (1).

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Supplementary Material Available: An ORTEP drawing for **1a′** and tables of crystal data, anisotropic thermal parameters, atomic coordinates, a bond lengths and angles for both **1a** and **2a** (14 pages); listings of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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[10] X-ray diffraction data: all data sets were collected on a Nicolet R3m diffractometer using Mo radiation ($\bar{\lambda}$ = 0.71073 Å) at room temperature. Empirical absorption corrections were applied to all data sets after data processing.

1a: many attempts (including seven successive recrystallizations of analytically pure samples obtained from different preparations) to obtain good quality crystals were unsuccessful. The first X-ray data set led to an unsatisfactory refinement with negative temperature factors for the carbon atoms. Eventually the "best" crystal obtained by slow cooling of a toluene solution was chosen although significant broadening can still evident on peak scans: crystal size (mmm), 0.20 × 0.58 × 0.60; deep red prism; monoclinic, space group $P2_1$; a = 8.920 (5) Å, b = 14.955 (10) Å, c = 16.952 (7) Å; β = 91.09 (4)°; V = 2261 (2) Å^3; d(calcd) = 1.66 g/cm^{-3}; μ(Mo) = 10.5 cm^{-1} (absorption coefficient); $F(000)$ = 1144; scan mode = $\theta/2\theta$; scan speed = 5.86–19.53 deg·min^{-1}; scan width = 2.38–2.63°; measured reflections 4279, range of hkl = ($\pm h$, $+k$, $+l$); $(\sin\theta)/\lambda$ limit (Å^{-1}) = 0.595 ($2\theta_{max}$ = 50°); number of unique reflections, 4128; number of reflections used in analysis, 3387 [$I > 3\sigma(I)$]; structure solved by heavy-atom method; Zr P and methyl groups carbon atoms were refined anisotropically; the disordered carbon atoms of the cyclopentadienyl rings were refined by using rigid-body refinement; hydrogen atom positions were calculated and used in the R-value calculation but were not refined; number of variables, 232; R = 0.0922; R_w = 0.137, $\omega = 1/[\sigma^2(F_o) + 0.003(F_o)^2]$; GOF = 2.153; largest remaining peak, 4.14 e/Å^3 (the top 12 peaks were all within 1 Å to either Zr or P atoms; apart from these peaks the map is reasonably clean); largest shift/esd, final cycle, 0.046.

2a: crystal size (mm), 0.05 × 0.28 × 0.66, deep red prism; monoclinic, space group $P2_1/a$; a = 15.996 (8) Å, b = 9.120 (3) Å, c = 16.172 (6) Å; β = 117.43 (4)°; Z = 4; V = 2094 (2) Å^3; d(calcd) = 1.71 g/cm^{-3}, μ(Mo) = 11.8 cm^{-1} (absorption coefficient); $F(000)$ = 1080; ω-scan mode; scan speed = 19.53 deg·min^{-1}; scan width = 0.90°; T = 298 K; measured reflections 5291; range of hkl = ($+h$, $+k$, $\pm l$); $(\sin\theta)/\lambda$ limit (Å^{-1}) = 0.65 ($2\theta_{max}$ = 55°); number of unique reflections, 4810; number of reflections used in analysis, 2778 [$I > 3\sigma(I)$]; structure solved by direct method; P, Cl, Zr carbon atoms of the methyl groups and those on first Cp ring [C(2)–C(5)] were refined anisotropically; the other three Cp rings were disordered [% occupancy for major configuration: 74.3% for Cp(2), 53.2% for Cp(3), 51.4% for Cp(4)]; all disordered Cp rings were fixed to their ideal geometry with d_{C-C} = 1.42 Å; hydrogen atom positions were calculated and included in the R-value calculation but not refined; number of variables, 130; R = 0.044; R_w = 0.042, $\omega = 1/[\sigma^2(F_o) + 0.00015(F_o)^2]$; GOF = 1.319; largest remaining peak, 0.81 e/Å^3; largest shift/esd, final cycle, 0.006.

[11] The magnetic susceptibility of solid samples is temperature-independent in the range 4.3–280 K. Sharp NMR spectra have been obtained in solution.[12]

[12] **1a**: ^{1}H NMR (90 MHz, toluene-d_8, 80 °C) δ 4.65 (t, J_{P-H} = 1.3 Hz, 5 H, Cp), 1.45 (pseudo-t, J_{P-H} = 3.6 Hz, 3 H, Me); ^{13}C NMR (75 MHz, C_6D_6, 60 °C) δ 94.2 (Cp), 20.5 (Me). Anal. Calcd for $C_{12}H_{16}ZrP$ (Found): C, 51.06 (50.83); H, 5.67 (5.62); Zr, 32.26 (32.29), P, 10.99 (10.87). **2a**: ^{1}H NMR (90 MHz, C_6D_6, 25 °C) δ 4.94 (d, J_{P-H} = 1.3 Hz, Cp, 10 H), 1.39 (d, J_{P-H} = 7.0 Hz, Me, 3 H); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) δ 98.8 (Cp), 19.8 (Me). Anal. Calcd for $C_{22}H_{26}Zr_2ClP$ (Found): C, 49.02 (48.88); H, 4.83 (4.77); Zr, 33.80 (33.56); Cl, 6.59 (6.70). **2b**: ^{1}H NMR (90 MHz, C_6D_6, 60 °C) δ 4.63 (t, J_{P-H} = 1.3 Hz, 5 H, Cp), 1.36 (pseudo-t, J_{P-H} = 3.3 Hz, 3 H, Me); ^{13}C NMR (75 MHz, C_6D_6, 60 °C) δ 91.9 (Cp), 21.1 (Me). Anal. Calcd for $C_{12}H_{16}HfP$ (Found): C, 38.97 (39.05); H, 4.33 (4.55); Hf, 48.30 (48.29); P, 8.39 (8.73).