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P–H and Cyclopentadienyl C–H Activation en Route to Homo- and Heterobinuclear Zirconocene Phosphide and Phosphinidene Complexes

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Oxidative additions of P–H bonds to "zirconocene" have been studied. The resulting zirconocene–phosphide–hydrides are not stable and react further to give a variety of products the nature of which depends on the electronic and steric properties of the phosphide moiety. In the case of the $PhPH_2$ derivative, cyclopentadienyl C–H activation occurs affording the fulvalenide–phosphide dimer $[CpZr(\mu\text{-}PHPh)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (1) in the similar reaction of $CyPH_2$, the isolated product is $[Cp_2Zr(\mu\text{-}PHCy)]_2$ (2). The isolated derivative of $(2,4,6\text{-}Me_3C_6H_2)\text{-}PH_2$ resembles 1 and was confirmed crystallographically to be $[CpZr(\mu\text{-}PH(2,4,6\text{-}Me_3C_6H_2)]_2\text{-}(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (3). The compound 3 crystallizes in the space group $P\bar{1}$ with $a = 12.037(8)$ Å, $b = 14.699(8)$ Å, $c = 10.514(5)$ Å, $\alpha = 103.79(5)°$, $\beta = 108.87(5)°$, $\gamma = 101.89(6)°$, $Z = 2$, and $V = 1626(2)$ Å^3. In the case of Ph_3SiPH_2 three products were obtained. $[Cp_2Zr(\mu\text{-}PH(SiPh_3)]_2$ (4) and $[CpZr(\mu\text{-}PH(SiPh_3))]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (5) are the major products, while $[CpZr]_2(\mu\text{-}PH\text{-}(SiPh_3)(\mu\text{-}PSiPh_3)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (6) is also formed in low yield. The compound 4·THF crystallizes in the space group $P2_1/n$ with $a = 11.653(15)$ Å, $b = 14.355(6)$ Å, $c = 16.958(9)$ Å, $\beta = 93.74(8)°$, $Z = 4$, and $V = 2830(6)$ Å^3, while 5 crystallizes in the space group $C2/c$ with $a = 15.155(6)$ Å, $b = 17.304(8)$ Å, $c = 17.822(7)$ Å, $\beta = 93.79(3)°$, $Z = 4$, and $V = 4663(3)$ Å^3. The phosphide–phosphinidene-bridged, mixed-valent Zr(IV)/Zr(III) compound 6·$[(THF)_2Li(\mu\text{-}Cl)]_2$·THF crystallizes in the space group $P\bar{1}$ with $a = 11.063(7)$ Å, $b = 30.112(24)$ Å, $c = 10.874(8)$ Å, $\alpha = 96.21(7)°$, $\beta = 119.10(5)°$, $\gamma = 84.21(7)°$, $Z = 2$, and $V = 3142(9)$ Å^3. The course of these reactions is discussed in terms of the electronic and steric properties of the phosphines. The mechanism for cyclopentadienyl C–H activation is considered, and a dimeric Zr(IV) intermediate $[CpZr\text{-}(\mu\text{-}\eta^5\text{-}\eta^1\text{-}C_5H_4)(PHR)]_2$ is proposed on the basis of spectroscopic data derived from monitoring these reactions. Alternative synthetic routes to these dimers were explored. The dimers 2 and 4 were obtained from the reactions of zirconocene dichloride with Mg in the presence of the respective phosphine. These dimers 2 and 4 were also isolated from the reaction of the primary phosphine with zirconocene–hydride chloride. The compound $[Cp_2Zr(\mu\text{-}PHPh)]_2$ (7) was isolated in a similar reaction. The species 7 crystallizes in the space group $C2/c$ with $a = 30.083(13)$ Å, $b = 9.175(6)$ Å, $c = 21.292(9)$ Å, $\beta = 111.35(3)°$, $Z = 8$ and $V = 5473(9)$ Å^3. Direct reaction of Li_2PPh and Cp_2ZrCl_2 or deprotonation of 2 generates the bis(phosphinidene)-bridged homobimetallics $[Cp_2Zr(\mu\text{-}PR)]_2^{2-}$ (R = Ph, 8a, R = Cy, 8b). Reaction of 8a with a proton source and TMEDA affords the mono(phosphinidene)-bridged complex $[(Cp_2Zr)_2(\mu\text{-}PHPh)(\mu\text{-}PPh)]$-$[(THF)_2Li(TMEDA)]$ (9). The compound 9·THF crystallizes in the space group $P\bar{1}$ with $a = 13.520(5)$ Å, $b = 18.313(7)$ Å, $c = 11.411(4)$ Å, $\alpha = 99.27(3)°$, $\beta = 105.43(3)°$, $\gamma = 98.89(3)°$, $Z = 2$, and $V = 2630(2)$ Å^3. Similarly, reaction of 8a with Me_3O^+ generates the species $[(Cp_2Zr)_2(\mu\text{-}PMePh)(\mu\text{-}PPh)]Li$ (10). The heterobimetallic complex $Cp_2Zr(\mu\text{-}PHCy)(\mu\text{-}\eta^1\text{-}\eta^2\text{-}OC)\text{-}Mo(CO)Cp$ (11) is derived from the reaction of 2 with $[CpMo(CO)_3]_2$. This product crystallizes in the space group $P\bar{1}$ with $a = 14.425(4)$ Å, $b = 16.871(4)$ Å, $c = 10.411(4)$ Å, $\alpha = 102.24(4)°$, $\beta = 104.14(2)°$, $\gamma = 65.44(2)°$, $Z = 2$, and $V = 2217(1)$ Å^3. Deprotonation of 11 affords the phosphinidene-bridged heterobimetallic $[Cp_2Zr(\mu\text{-}PCy)(\mu\text{-}\eta^1\text{-}\eta^2\text{-}OC)Mo(CO)Cp]^-$ (12). This process is reversible. The chemistry and structural data for these phosphide and phosphinidene species are presented and discussed. In particular, the structural data for the Zr(III) species are considered in light of recent postulates of "super-long" metal–metal bonding in related zirconocene dimers. Some of the discussion is supported by the results of Fenske–Hall and extended Huckel molecular orbital calculations.

Introduction

The wide spread application of metal–carbon, –oxygen, –sulfur, and –nitrogen multiple bonds throughout organometallic chemistry[1] has spurred recent interest in transition metal phosphinidenes. Generally the most common routes to such compounds have been either the metathesis of halide ions from dihalophosphines by metal carbonylate anions or the thermolysis or photolysis of specifically desiged phosphinidene precursors.[2] These synthetic strategies are not applicable to group 4 metals, and thus few Ti, Zr, or Hf phosphinidene complexes, or for that matter phosphides, are known. It was in 1966

(1) *Metal-Ligand Multiple Bonds*; Nugent, W. A., Mayer, J. M., Eds.; J. Wiley and Sons: New York, 1988.

(2) For recent review see: Huttner, G. *Pure Appl. Chem.* 1986, *58*, 585.

and 1967 when the first reports[3] of early metal phosphide derivatives appeared; however, it was not until 1983 that Baker et al.[4] synthesized and structurally characterized a series of Zr and Hf species of the form $Cp_2M(PR_2)_2$. Later that same year, Baker et al.[5] also described homoleptic phosphide species such as $[Li(DME)]Hf(PCy_2)_5]$. Since then, related phosphide complexes of the forms Cp_2M-$(PRR')_2$,[6] $Cp_2M(PPh)_2$,[7] and $Cp_2M(PR)_2$[8,9] have been prepared and characterized.[10] The chemistry of the related compounds $Cp^*HfCl_2(P(CMe_3)_2)$ and $Cp^*HfCl(P(CMe_3)_2)_2$ has been examined by Bercaw et al.,[11] while Hillhouse et al. have studied the chemistry of $Cp^*_2HfH(PHPh)$.[12] Gambarotta et al.[13] as well as ourselves[14] have studied the chemical, structural, magnetic, and theoretical aspects of dimeric Ti(III) and Zr(III) phosphides of the form $[Cp_2M$-$(\mu\text{-}PR_2)]_2$, while more recently the mononuclear intermediates in the formation of the Ti(III) dimers have drawn attention.[15,16] Related systems that contain the phosphinidene moiety (PR) are rare. Cowley et al. have described the compound $(CpV(CO)_2)_2(\mu\text{-}PR)$.[17] More recently we described the use of oxidative addition of P–H bonds as a synthetic route to the first Zr–phosphinidene complex $(Cp_2ZrCl)_2(\mu\text{-}PR)$.[18] In this report, this approach is expanded and the dependence of the product on the nature of the phosphine examined. The Zr(IV) phosphide–hydrides formed by initial oxidative addition of P–H to Zr(II) are unstable, either losing H_2 to give highly reactive Zr–phosphinidene intermediates or forming Zr(III) dimers. Cyclopentadienyl C–H activation by the transient Zr–phosphinidenes affords related fulvalenide–phosphide dimers. An alternative approach to Zr–phosphinidene derivatives is the deprotonation of primary phosphide complexes. Such deprotonations are reversible affording the facile interconversion of Zr phosphide and phosphinidene species. This method has been extended to a heterobimetallic Zr/Mo species. Fenske–Hall and extended Huckel molecular orbital calculations for the dimeric Zr(III) phosphide and phosphinidene complexes have been considered in the light of the structural and spectroscopic data as well as recent claims of "super-long" metal–metal bonding.[19,20] Preliminary results of some of the chemistry described herein have been previously communicated.[18,21]

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Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing either Schlenk techniques or a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2 and degassed by the freeze–thaw method at least three times prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-300 operating at 300 and 75 MHz, respectively. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-200 operating at 81 MHz. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. EPR spectra were recorded on a Varian E-12 EPR spectrometer. DPPH was used as the external reference. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. Cp_2ZrCl_2, Cp_2-ZrCHl, and n-BuLi were purchased from the Aldrich Chemical Co. $PhPH_2$, $CyPH_2$, $(2,4,6\text{-}Me_3C_6H_2)PH_2$, $(C_6H_5)_3SiPH_2$, and $[CpMo(CO)_3]_2$ were purchased from either the Strem Chemical Co. or the Pressure Chemical Co.

Synthesis of $[CpZr(\mu\text{-}PHPh)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (1). Cp_2ZrCl_2 (292 mg, 1.00 mmol) was dissolved in THF (50 mL), and n-BuLi (0.80 mL, 2.5 M, 2.00 mmol) was added at –78 °C. The mixture was warmed to room temperature and $PhPH_2$ (110 mg, 1.00 mmol) was added, and the new mixture was allowed to stand overnight during which time dark brown crystals of 1 were deposited. Yield: 30%. ^1H NMR (C_6D_6, 25 °C, δ): 7.68–7.10 (m, 10H, Ph); 5.49 (s, 10H, Cp); 4.76 (d of m, 4H, $C_{10}H_8$), 3.97 (d of m, 4H, $C_{10}H_8$) $|J_{H-H}|$ = 3.6 Hz. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, δ): 137.77, 136.74, 129.07, 125.42 (Ph); 113.97, 93.71, 87.60 ($C_{10}H_8$); 95.36 (Cp). Anal. Calc: C, 58.33; H, 4.59. Found: C, 58.10; H, 4.30.

Synthesis of $[Cp_2Zr(\mu\text{-}PHCy)]_2$ (2). Method i. Cp_2ZrCl_2 (292 mg, 1.00 mmol) was dissolved in THF (50 mL), and n-BuLi (0.80 mL, 2.5 M, 2.00 mmol) was added at –78 °C. The mixture was warmed to room temperature for 1 h and then cooled to –78 °C where $CyPH_2$ (116 mg, 1.00 mmol) was added. The mixture was allowed to stand at 25 °C overnight. During this time black crystals of 2 were deposited. Yield: 50%.

Method ii. Cp_2ZrCl_2 (292 mg, 1.00 mmol) was dissolved in THF (50 mL), and excess Mg was added. The mixture was stirred for 0.5 h. After filtering off of the excess Mg, $CyPH_2$ (116 mg, 1.00 mmol) was added and the mixture was allowed to stand overnight during which time black crystals of 2 were deposited. Yield: 90%.

Method iii. To a suspension of Cp_2ZrHCl (258 mg, 1.00 mmol) in THF (50 mL) was added $CyPH_2$ (116 mg, 1.00 mmol), and the mixture was allowed to stand overnight during which time black crystals of 2 were deposited. Yield: 45%. ^1H NMR (C_6D_6, 25 °C, δ): 6.21 (s, 10H, Cp); 1.2–2.5 (m, 11H, Cy). Anal. Calc: C, 57.10; H, 6.59. Found: C, 57.33; H, 6.87.

Synthesis of $[CpZr(\mu\text{-}PH(2,4,6\text{-}Me_3C_6H_2)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (3). Cp_2ZrCl_2 (292 mg, 1.0 mmol) was dissolved in THF (50 mL), and n-BuLi (0.80 mL, 2.5 M, 2.00 mmol) was added at –78 °C. The mixture was allowed to warm to room temperature for 1 h and then cooled to –78 °C where $(2,4,6\text{-}Me_3C_6H_2)PH_2$ (152 mg, 1.00 mmol) was added. The mixture was allowed to slowly come to 25 °C overnight. Upon the slow diffusion of hexane into the solution, brown crystals of 3 were deposited. Yield: 20%. ^1H NMR (C_6D_6, 25 °C, δ): 6.81 (s, 4H, Ph); 5.53 (s, 10H, Cp); 4.99 (m, 4H, $C_{10}H_8$), 3.64 (m, 4H, $C_{10}H_8$); 2.15 (s, 12H, CH_3); 2.05 (s, 6H, CH_3). Anal. Calc: C, 61.42; H, 5.70. Found: C, 61.20; H, 5.50.

Synthesis of $[Cp_2Zr(\mu\text{-}PHSiPh_3)]_2$ (4). Method i. Cp_2-ZrCl_2 (292 mg, 1.00 mmol) was dissolved in THF (50 mL), and n-BuLi (0.80 mL, 2.5 M, 2.00 mmol) was added at –78 °C. The mixture was allowed to warm to room temperature for 1 h and then cooled to –78 °C where Ph_3SiPH_2 (292 mg, 1.00 mmol) was added. The mixture was allowed to stand, slowly coming to 25 °C overnight. During this time blue-black crystals of 4·THF were deposited. Yield: 10%.

Method ii. Cp_2ZrCl_2 (292 mg, 1.00 mmol) was dissolved in THF (50 mL), and excess Mg was added. The mixture was

allowed to stand for 1 h. After filtering off of the excess Mg, Ph₃SiPH₂ (292 mg, 1.00 mmol) was added and the mixture was allowed to stand overnight during which time blue-black crystals of 4·THF were deposited. Yield: 50%.

Method iii. To a suspension of Cp₂ZrHCl (258 mg, 1.00 mmol) in THF (50 mL) was added Ph₃SiPH₂ (292 mg, 1.00 mmol), and the mixture was stirred for 24 h. On standing overnight, blue-black crystals of 4·THF were deposited. Yield: 45%. ¹H NMR (C₆D₆, 25 °C, δ): 7.63 (m, 3H, Ph), 7.58 (s, 6H, Ph), 7.55 (s, 6H, Ph); 6.21 (s, 10H, Cp). Anal. Calc: C, 65.58; H, 5.11. Found: C, 65.30; H, 5.10.

Synthesis of [CpZr(μ-PHSiPh₃)]₂(μ-η⁵-η⁵-C₁₀H₈) (5) and [CpZr]₂(μ-PHSiPh₃)(μ-PSiPh₃)(μ-η⁵-η⁵-C₁₀H₈)·[(THF)₂Li(μ-Cl)]₂ (6). The reaction is performed as described above for 4 (method i). After isolation of 4, slow diffusion of hexane into the mother liquor affords red-brown crystals of 5 in 35% yield. In addition a few needles of the red-brown 6 were physically separated from the product. Yield (estimated): <2%. ¹H NMR for 5 (C₆D₆, 25 °C, δ): 7.75–7.72 9m, 30H, Ph); 5.61 (s, 10H, Cp), 6.31 (m, 4H, C₁₀H₈), 5.21 (m, 4H, C₁₀H₈). Anal. Calc: C, 65.71; H, 4.92. Found: C, 65.50; H, 4.80.

Synthesis of [Cp₂Zr(μ-PHPh)]₂ (7). To a suspension of Cp₂ZrHCl (257 mg, 1.00 mmol) in toluene was added PPhH₂ (110 mg, 1.00 mmol). This mixture was stirred overnight, becoming dark brown. Purple needles were deposited. These needles were recrystallized from THF/hexane, affording dark brown crystals of 7. Yield: 10%. ¹H NMR (C₆D₆, 25 °C, δ): 7.28–7.21 (m, 3H, Ph), 7.94 (m, 2H, Ph); 6.21 (s, 10H, Cp). Anal. Calc: C, 65.58; H, 5.11. Found: C, 65.30; H, 5.10.

Generation of [Cp₂Zr(μ-PPh)]₂[Li(THF)₃]₂ (8a). To a THF solution of PhPH₂ (1.100 g, 10.0 mmol) was added 2 equiv of *n*-BuLi (8.0 mL, 2.5 M, 20.0 mmol) at -78 °C. To the resulting suspension of yellow solid in an orange solution was added Cp₂ZrCl₂ (2.920 g, 10.0 mmol). The dark red-brown mixture was stirred overnight. On storage at -30 °C overnight black extremely air sensitive crystals of 8a were deposited. EPR (THF, 25 °C): g = 2.018, ⟨aₚ⟩ = 17.7 G, ⟨a_Zr⟩ = 7.0 G. ¹H NMR (C₆D₆, 25 °C, δ): 7.60–7.53 (m, 4H, Ph), 7.39–7.31 (m, 6H, Ph); 6.02 (s, 20H, Cp), 3.55 (s, 24H, THF), 1.40 (s, 24H, THF).

Generation of [Cp₂Zr(μ-PCy)]₂K₂ (8b). To a THF solution of 2 (0.050 g, 0.074 mmol) was added excess KH. The mixture which became dark red-brown was stirred overnight. The resulting solution was filtered, stored at -30 °C for several days, and monitored by EPR spectroscopy. EPR (THF, 25 °C): g = 2.016, ⟨aₚ⟩ = 17.5 G.

Synthesis of [(Cp₂Zr)₂(μ-PHPh)(μ-PPh)][(THF)₂Li(TMEDA)] (9). To a THF solution of 8a formed as above was added 1 equiv of TMEDA·HCl. From this mixture, black crystals of 9 were deposited. ¹H NMR (C₆D₆, 25 °C, δ): 7.64–7.61 (m, 10H, Ph), 5.68 (s, 20H, Cp), 3.56 (br s, 8H, THF), 1.40 (br s, 8H, THF), 2.36 (s, 4H, TMEDA), 2.10 (s, 12H, TMEDA). EPR (THF, 25 °C): g = 2.016, ⟨aₚ⟩ = 13.6 G, ⟨a_H⟩ = 2.0 G, ⟨a_Zr⟩ = 7.0 G. Anal. Calc: C, 59.58; H, 6.85. Found: C, 59.30; H, 6.70.

Generation of [(Cp₂Zr)₂(μ-PMePh)(μ-PPh)]Li (10). To a solution of 8a was added 1 equiv of Me₃OBF₄. The mixture was stirred for 1 h and the reaction monitored by EPR. EPR (THF, 25 °C): g = 2.004, ⟨aₚ⟩ = 19.5 G, ⟨aₚ'⟩ = 14.0 G.

Synthesis of Cp₂Zr(μ-PHCy)(μ-OC)Mo(CO)Cp (11). This compound was synthesized by employing the method previously published for Cp₂Zr(μ-PR₂)(μ-OC)Mo(CO)Cp with the use of 2 as the Zr precursor. Recrystallization of 11 from benzene/acetonitrile gave orange crystals. Yield: 60%. ³¹P NMR (C₆H₆, 25 °C, δ): 136.4 (d, |J_P–H| = 298 Hz). ³¹P NMR (C₄H₈O, 25 °C, δ): 136.0 (d, |J_P–H| = 298 Hz). ¹H NMR (C₆D₆, 25 °C, δ): 5.45 (d, |J_P–H| = 0.2 Hz, 5H, Cp), 5.18 (d, |J_P–H| = 1.2 Hz, 5H, Cp), 4.98 (s, 5H, Cp), 4.51 (d of d, |J_P–H| = 298 Hz, |J_H–H| = 9.0 Hz, 1H, PH), 1.20–2.50 (m, 11H, Cy). ¹H NMR (C₄D₈O, 25 °C, δ): 5.65 (s, 5H, Cp), 5.33 (s, 5H, Cp), 5.13 (s, 5H, Cp), 4.79 (d of d, (d, |J_P–H| = 298 Hz, |J_H–H| = 8.2 Hz, 1H, PH), 1.30–2.60 (m, 11H, Cy). IR (C₄H₈O, cm⁻¹): 1855, 1564. Anal. Calcd: C, 49.90; H, 4.92. Found: C, 49.50; H, 4.80.

Generation of [Cp₂Zr(μ-PCy)(μ-OC)Mo(CO)Cp]K (12). To a THF solution of 11 was added excess KH. The mixture was stirred for 2–3 days, during which time the color changed from orange to brick-red. The mixture was filtered and the product examined by NMR and IR. Attempts to isolate the product either by addition of 18-crown-6 or by cation exchange with several ammonium salts were unsuccessful. Yield (by NMR): >95%. ³¹P{¹H} NMR (C₄D₈O, 25 °C, δ): 259.8 (s). ¹H NMR (C₄D₈O, 25 °C, δ): 5.39 (s, 5H, Cp), 5.31 (s, 5H, Cp), 4.90 (s, 5H, Cp), 1.1–2.4 (m, 11H, Cy). IR (C₄H₈O, cm⁻¹): 1795, 1531.

Deuteration of 12. To a solution of 12 was added a slight excess of ND₄Cl. The reaction resulted in a color change from brick-red to orange. The product Cp₂Zr(μ²-PDCy)(μ²-OC)Mo(CO)Cp (11b) was characterized by NMR spectroscopy. A small amount of 11 was also observed due to the incomplete deuteration of the ammonium salt. The NMR spectrum of 11b was identical to that reported for 11 except for the absence of the P–H proton resonance. ³¹P NMR for (C₄H₈O, 25 °C 11b, δ): 134.3 (t, |J_P–D| = 47 Hz).

X-ray Data Collection and Reduction.²² X-ray-quality crystals of 1–7, 9, and 11 were obtained directly from the preparations as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O₂-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC6 diffractometer equipped with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 20 machine-centered reflections selected by an automated peak search routine. These data were used to determine the crystal systems. Automated Laue system check routines around each axis were consistent with the crystal systems reported in Table I. Ultimately, 25 reflections (20 ° < 2θ < 25°) were used to obtain the final lattice parameters and the orientation matrices. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space group given in Table I. The data sets were collected in one shell (4.5° < 2θ < 50.0°), and three standard reflections were recorded every 197 reflections. Fixed scan rates were employed. Up to four repetitive scans of each reflection at the respective scan rates were averaged to ensure meaningful counting statistics. The number of scans of each reflection was determined by the intensity. The intensities of the standards showed no statistically significant change over the duration of the data collection. The data were processed using the TEXSAN crystal solution package operating on a VAX 3520 workstation. The reflections with Fₒ² > 3σFₒ² were used in the refinement.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.²³,²⁴ The Zr atom positions were determined using direct methods by employing either the SHELX-86 or MITHRIL direct-methods routines. In each case, the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function w(|Fₒ| – |Fᶜ|)², where the weight, w, is defined as 4Fₒ²/2σ(Fₒ²) and Fₒ and Fᶜ are the observed and calculated structure factor amplitudes. In the final cycles of refinement all heavy atoms were assigned anisotropic temperature factors. The number of carbon atoms assigned anisotropic thermal parameters varied and was set so as to maintain a reasonable data:variable ratio in each case. In the case of 6 the asymmetric unit also contained half of a molecule of [(THF)₂Li-(μ-Cl)]₂ as well as a molecule of THF. Similarly, in the case of 4 and 9, THF molecules of crystallization were also located and refined. Hydrogen atom positions were calculated and allowed

(22) The details of the crystallographic determinations of compounds 1 and 2 have been previously reported.¹⁸,²¹

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Table I. Crystallographic Parameters

	3	4	5	6	7	9	11
formula	$C_{38}H_{42}P_2Zr_2$	$C_{64}H_{68}O_2P_2Si_2Zr_2$	$C_{56}H_{50}P_2Si_2Zr_2$	$C_{68}H_{73}ClLiO_3P_2Si_2Zr_2$	$C_{32}H_{32}P_2Zr_2$	$C_{50}H_{71}LiN_2O_3P_2Zr_2$	$C_{23}H_{27}MoO_2PZr$
cryst. color. form	black blocks	black blocks	black blocks	black blocks	black blocks	black blocks	blocks
a (Å)	12.037(8)	11.653(15)	15.155(6)	11.063(7)	30.083(13)	13.520(5)	14.425(4)
b (Å)	14.699(8)	14.355(6)	17.304(8)	30.112(24)	9.175(6)	18.313(7)	16.871(4)
c (Å)	10.514(5)	16.958(9)	17.822(7)	10.874(8)	21.292(9)	11.411(4)	10.411(4)
α (deg)	103.79(5)			96.21(7)		99.27(3)	102.24(4)
β (deg)	108.87(5)	93.74(8)	93.79(3)	119.10(5)	111.35(3)	105.43(3)	104.14(2)
γ (deg)	101.89(6)			84.21(7)		98.89(3)	65.44(2)
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
V (Å^3)	1626(2)	2830(6)	4463(3)	3142(9)	5473(9)	2630(2)	2217(1)
density (g cm^{-3}) (calcd)	1.52	1.37	1.46	1.35	1.60	1.26	1.66
Z	2	2	4	2	8	2	2
cryst dimens (mm)	0.40 × 0.48 × 0.44	0.43 × 0.38 × 0.44	0.33 × 0.35 × 0.34	0.40 × 0.30 × 0.50	0.30 × 0.35 × 0.45	0.40 × 0.30 × 0.50	0.40 × 0.45 × 0.35
abs coeff, μ (cm^{-1})	7.524	5.004	5.939	4.994	8.840	4.864	11.013
radiation, λ (Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
temp (°C)	24	−37	24	24	24	−37	24
scan speed (deg/min)	16.0 ($\theta/2\theta$)	8.0 ($\theta/2\theta$)	8.0 ($\theta/2\theta$)	32.0 ($\theta/2\theta$)	16.0 ($\theta/2\theta$)	16.0 ($\theta/2\theta$)	16.0 ($\theta/2\theta$)
scan range (deg)	1.0 below Kα_1, 1.0 above Kα_2	1.0 below Kα_1, 1.0 above Kα_2	1.0 below Kα_1, 1.0 above Kα_2	1.0 below Kα_1, 1.0 above Kα_2	1.0 below Kα_1, 1.0 above Kα_2	1.0 below Kα_1, 1.0 above Kα_2	1.0 below Kα_1, 1.0 above Kα_2
bkgd/scan time ratio	0.5	0.5	0.5	0.5		0.5	0.5
data collcd	6047	5479	4435	11743	5193	9700	8160
2θ range (deg)	4.5–50.0	4.5–50.0	4.5–50.0	4.5–50.0	4.5–50.0	4.5–50.0	4.5–50.0
index range	$h,\pm k,\pm l$	$h,\pm k,\pm l$	$h,k,\pm l$	$h,\pm k,\pm l$	h,k,l	$h,\pm k,\pm l$	$h,\pm k,\pm l$
data $F_o^2 > 3\sigma(F_o^2)$	2290	1877	1410	1638	3355	4101	3962
variables	279	250	140	165	362	450	505
R (%)	5.67	5.82	5.98	8.91	7.20	6.06	4.42
R_w (%)	5.62	5.61	5.82	9.09	7.21	6.71	4.65
largest Δ/σ in final least-squares cycle	0.001	0.034	0.001	0.030	0.011	0.021	0.023

to ride on the carbon to which they are bonded by assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. In all cases the hydrogen atom contributions were calculated but not refined. The final values of R and R_w are given in Table I. The maximum Δ/σ values on any of the parameters in the final cycles of the refinements are given in Table I. The residual electron densities were of no chemical significance. Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and selected bond distances and angles for the various Zr dimers (Table S3) have been deposited as supplementary material.

Molecular Orbital Calculations. Extended Huckel and Fenske–Hall molecular orbital calculations were performed on a VAX 3520 workstation. EHMO calculations were performed by employing the implimentation of FORTICON8 resident in the package TRIBBL.[25] A detailed description of the Fenske–Hall nonempirical MO method has been described elsewhere.[26] Models were constructed on the basis of idealized geometries derived from the crystallographic data presented herein.

Results and Discussion

Syntheses. "Cp$_2$Zr" can be generated for in situ use by employing the method established by Negishi et al.[27,28] This is done via the reaction of Cp$_2$ZrCl$_2$ with 2 equiv of n-BuLi at −78 °C in THF.

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β-Hydrogen elimination from the intermediate dialkyl species affords the highly reactive Zr(II)–alkene intermediate which is the effective source of zirconocene. Reaction of this species with a series of primary phosphines has been investigated. In each case immediate reaction is apparent from the dramatic color change upon addition of the phosphine. The initial pale solutions become brown-black within 5 min. The isolated products of the reactions were the crystalline brown/black materials 1–3, obtained from these reactions using PhPH$_2$, CyPH$_2$, and (2,4,6-Me$_3$C$_6$H$_2$)PH$_2$, respectively, while in the case of Ph$_3$SiPH$_2$, three brown-black products 4–6 were obtained. The compounds 1–5 exhibited ^{1}H NMR resonances attributable to the cyclopentadienyl groups and the respective phosphine substituent. However, in the case of 1, 3, and 5, there were additional resonances attributable to a fulvalenide moiety. In each case, no ^{1}H NMR resonances attributable to phosphide protons or ^{31}P{^{1}H} NMR resonances were observed. These apparently conflicting results prompted crystallographic studies of these products. These investigations confirmed that 1–5 are Zr(III)–phosphide dimers, where 1, 3, and 5 are formulated as [CpZr(μ-PRH)]$_2$(μ-η^5-η^5-C$_{10}$H$_8$) while 2 and 4 are formulated as [Cp$_2$Zr(μ-PRH)]$_2$, respectively (*vide infra*). In the case of 6, the yield was extremely low. In fact only a couple of crystals were physically separated from the other products 4 and 5. Thus, this species was only characterized by crystallography, which confirmed the formulation of 6 as the most unusual Zr(IV)/Zr(III) mixed-valent compound [CpZr]$_2$(μ-PHSiPh$_3$)(μ-PSiPh$_3$)(μ-η^5-η^5-C$_{10}$H$_8$). Numer-

Table II.   Positional Parameters

atom	x	y	z	atom	x	y	z
			Molecule 3				
Zr(1)	0.1131(1)	0.3567(1)	0.1890(1)	C(18)	0.096(1)	0.041(1)	0.405(2)
Zr(2)	0.0876(1)	0.2064(1)	0.3884(1)	C(19)	0.191(1)	0.111(1)	0.530(1)
P(1)	0.2608(3)	0.3746(3)	0.4472(4)	C(20)	0.280(1)	0.158(1)	0.492(2)
P(2)	−0.0172(3)	0.1687(3)	0.1085(4)	C(21)	−0.181(1)	0.102(1)	−0.020(1)
C(1)	−0.030(1)	0.381(1)	0.309(1)	C(22)	−0.236(1)	0.132(1)	−0.138(1)
C(2)	0.058(1)	0.474(1)	0.353(1)	C(23)	−0.357(1)	0.086(1)	−0.229(1)
C(3)	0.045(1)	0.504(1)	0.233(1)	C(24)	−0.436(1)	0.014(1)	−0.205(2)
C(4)	−0.053(1)	0.432(1)	0.115(1)	C(25)	−0.380(1)	−0.017(1)	−0.092(2)
C(5)	−0.099(1)	0.357(1)	0.161(1)	C(26)	−0.257(1)	0.024(1)	−0.001(2)
C(6)	0.322(1)	0.398(1)	0.172(1)	C(27)	−0.165(1)	0.206(1)	−0.185(2)
C(7)	0.268(1)	0.298(1)	0.105(1)	C(28)	−0.568(2)	−0.036(2)	−0.308(2)
C(8)	0.167(1)	0.282(1)	−0.015(1)	C(29)	−0.207(1)	−0.019(1)	0.109(2)
C(9)	0.155(1)	0.375(1)	−0.022(1)	C(30)	0.333(1)	0.484(1)	0.611(1)
C(10)	0.251(1)	0.447(1)	0.095(2)	C(31)	0.353(1)	0.475(1)	0.748(2)
C(11)	−0.043(1)	0.317(1)	0.395(1)	C(32)	0.387(1)	0.557(1)	0.865(2)
C(12)	0.037(1)	0.336(1)	0.538(1)	C(33)	0.408(1)	0.654(1)	0.858(1)
C(13)	0.004(1)	0.251(1)	0.573(1)	C(34)	0.393(1)	0.663(1)	0.727(2)
C(14)	−0.093(1)	0.179(1)	0.457(1)	C(35)	0.357(1)	0.581(1)	0.604(1)
C(15)	−0.123(1)	0.220(1)	0.346(1)	C(36)	0.347(1)	0.378(1)	0.772(1)
C(16)	0.241(1)	0.120(1)	0.348(2)	C(37)	0.446(1)	0.738(1)	0.990(2)
C(17)	0.131(1)	0.049(1)	0.293(2)	C(38)	0.357(1)	0.606(1)	0.473(2)
			Molecule 4				
Zr(1)	0.35405(8)	0.0062(1)	0.03460(6)	C(16)	0.383(1)	0.3995(9)	−0.1270(7)
P(1)	0.4889(2)	0.1258(2)	−0.0320(2)	C(17)	0.501(1)	0.3217(8)	0.0922(6)
Si(1)	0.5029(3)	0.2802(2)	−0.0133(2)	C(18)	0.410(1)	0.3747(9)	0.1168(7)
C(1)	0.244(1)	0.044(1)	0.1513(8)	C(19)	0.407(1)	0.408(1)	0.1921(8)
C(2)	0.311(1)	0.125(1)	0.1372(7)	C(20)	0.496(1)	0.388(1)	0.2474(7)
C(3)	0.425(1)	0.098(1)	0.1574(7)	C(21)	0.586(1)	0.332(1)	0.2255(7)
C(4)	0.426(1)	0.004(1)	0.1796(6)	C(22)	0.590(1)	0.301(1)	0.1485(7)
C(5)	0.318(1)	−0.0290(9)	0.1758(7)	C(23)	0.639(1)	0.3256(8)	−0.0528(6)
C(6)	0.281(1)	−0.050(1)	−0.0993(7)	C(24)	0.696(1)	0.402(1)	−0.0213(8)
C(7)	0.234(1)	−0.112(1)	−0.0452(7)	C(25)	0.794(1)	0.438(1)	−0.052(1)
C(8)	0.159(1)	−0.060(1)	−0.0008(8)	C(26)	0.834(1)	0.397(1)	−0.118(1)
C(9)	0.157(1)	0.0311(9)	−0.0315(8)	C(27)	0.780(1)	0.324(1)	−0.1513(8)
C(10)	0.231(1)	0.036(1)	−0.0923(8)	C(28)	0.680(1)	0.288(1)	−0.1205(7)
C(11)	0.373(1)	0.3288(8)	−0.0713(6)	O(1)	1.015(2)	0.330(2)	0.112(2)
C(12)	0.264(1)	0.295(1)	−0.0608(7)	C(31)	0.933(2)	0.355(2)	0.165(2)
C(13)	0.169(1)	0.329(1)	−0.1037(8)	C(32)	0.921(2)	0.271(1)	0.213(1)
C(14)	0.181(1)	0.397(1)	−0.1592(8)	C(33)	1.001(2)	0.201(1)	0.179(1)
C(15)	0.287(1)	0.434(1)	−0.1697(7)	C(34)	1.044(2)	0.230(2)	0.113(1)
			Molecule 5				
Zr(1)	0.02606(9)	0.17869(8)	0.34957(7)	C(14)	−0.328(1)	0.071(1)	0.5104(8)
P(1)	−0.1187(2)	0.1526(2)	0.2654(2)	C(15)	−0.329(1)	0.0024(9)	0.4754(8)
Si(1)	−0.2136(2)	0.0560(2)	0.2745(2)	C(16)	−0.292(1)	−0.0026(8)	0.4052(8)
C(1)	−0.028(1)	0.0709(8)	0.4287(8)	C(17)	−0.3132(9)	0.0726(8)	0.2050(7)
C(2)	0.009(1)	0.1269(9)	0.4783(8)	C(18)	−0.382(1)	0.0205(9)	0.2021(8)
C(3)	0.099(1)	0.1282(9)	0.4695(8)	C(19)	−0.458(1)	0.030(1)	0.1579(9)
C(4)	0.119(1)	0.0765(9)	0.4156(8)	C(20)	−0.468(1)	0.095(1)	0.1152(8)
C(5)	0.041(1)	0.0398(8)	0.3887(8)	C(21)	−0.402(1)	0.1495(8)	0.1157(8)
C(6)	0.0975(9)	0.3104(9)	0.3248(7)	C(22)	−0.3239(9)	0.1386(8)	0.1635(7)
C(7)	0.093(1)	0.3027(8)	0.4037(8)	C(23)	−0.1762(8)	−0.0464(8)	0.2591(7)
C(8)	−0.0013(9)	0.3044(8)	0.4171(7)	C(24)	−0.131(1)	−0.0896(9)	0.3137(8)
C(9)	−0.0482(8)	0.3085(8)	0.3477(7)	C(25)	−0.103(1)	−0.164(1)	0.299(1)
C(10)	0.0103(8)	0.3126(8)	0.2900(6)	C(26)	−0.122(1)	−0.199(1)	0.230(1)
C(11)	−0.2577(8)	0.0614(7)	0.3708(7)	C(27)	−0.168(1)	−0.1587(9)	0.1782(8)
C(12)	−0.2622(9)	0.1330(8)	0.4098(8)	C(28)	−0.1948(9)	−0.0849(8)	0.1901(8)
C(13)	−0.297(1)	0.1370(8)	0.4795(8)				
			Molecule 6				
Zr(1)	0.4663(2)	0.25792(6)	0.8869(2)	C(37)	0.312(2)	0.3128(7)	1.260(2)
Zr(2)	0.2730(2)	0.25248(6)	1.0684(2)	C(38)	0.395(2)	0.2747(6)	1.322(2)
P(1)	0.2302(4)	0.2962(2)	0.8545(4)	C(39)	0.499(2)	0.2672(5)	1.287(2)
P(2)	0.4444(5)	0.1973(1)	1.0248(5)	C(40)	0.481(2)	0.3007(5)	1.198(2)
Si(1)	0.0393(5)	0.3017(2)	0.6493(5)	C(41)	0.590(2)	0.1036(6)	0.944(2)
Si(2)	0.4617(5)	0.1239(2)	1.0079(5)	C(42)	0.566(2)	0.0663(7)	0.853(2)
C(1)	0.365(2)	0.2564(6)	0.627(2)	C(43)	0.666(3)	0.0512(8)	0.810(2)
C(2)	0.336(2)	0.2162(6)	0.647(2)	C(44)	0.778(2)	0.0747(8)	0.856(2)
C(3)	0.463(2)	0.1922(6)	0.721(2)	C(45)	0.804(2)	0.1136(7)	0.941(2)
C(4)	0.569(2)	0.2178(6)	0.742(2)	C(46)	0.707(2)	0.1283(6)	0.987(2)
C(5)	0.508(2)	0.2590(6)	0.683(2)	C(47)	0.534(2)	0.1034(6)	1.191(2)
C(6)	0.532(2)	0.3340(5)	1.020(2)	C(48)	0.622(2)	0.0650(7)	1.219(2)
C(7)	0.625(2)	0.3206(6)	0.968(2)	C(49)	0.681(2)	0.0484(8)	1.355(2)
C(8)	0.704(2)	0.2824(6)	1.032(2)	C(50)	0.650(2)	0.0679(8)	1.450(2)
C(9)	0.668(2)	0.2721(5)	1.130(2)	C(51)	0.571(2)	0.1070(7)	1.427(2)
C(10)	0.560(1)	0.3025(5)	1.122(1)	C(52)	0.511(2)	0.1255(6)	1.293(2)
C(11)	−0.103(2)	0.3313(5)	0.680(2)	C(53)	0.300(2)	0.0953(5)	0.895(2)

Table II (Continued)

atom	x	y	z	atom	x	y	z
				Molecule 6			
C(12)	−0.080(2)	0.3545(6)	0.806(2)	C(54)	0.273(2)	0.0555(6)	0.930(2)
C(13)	−0.186(2)	0.3789(6)	0.823(2)	C(55)	0.153(2)	0.0327(7)	0.844(2)
C(14)	−0.318(2)	0.3796(6)	0.712(2)	C(56)	0.059(2)	0.0495(7)	0.724(2)
C(15)	−0.347(2)	0.3572(6)	0.587(2)	C(57)	0.077(2)	0.0871(7)	0.680(2)
C(16)	−0.239(2)	0.3325(6)	0.572(2)	C(58)	0.195(2)	0.1110(6)	0.766(2)
C(17)	0.072(2)	0.3393(5)	0.540(2)	Cl	0.5014(6)	0.4496(2)	−0.1093(6)
C(18)	−0.027(2)	0.3425(6)	0.395(2)	O(1)	0.516(2)	0.4411(5)	0.219(2)
C(19)	−0.005(2)	0.3710(7)	0.315(2)	O(2)	0.230(2)	0.4781(8)	−0.016(2)
C(20)	0.107(2)	0.3948(7)	0.374(2)	C(59)	0.502(3)	0.461(1)	0.335(3)
C(21)	0.204(2)	0.3925(7)	0.514(2)	C(60)	0.639(3)	0.472(1)	0.438(3)
C(22)	0.182(2)	0.3639(6)	0.594(2)	C(61)	0.750(3)	0.447(1)	0.412(3)
C(23)	−0.037(2)	0.2489(6)	0.535(2)	C(62)	0.652(3)	0.423(1)	0.277(3)
C(24)	−0.006(2)	0.2313(6)	0.427(2)	C(63)	0.178(4)	0.442(1)	−0.085(4)
C(25)	−0.060(2)	0.1940(7)	0.347(2)	C(64)	0.040(5)	0.454(2)	−0.222(5)
C(26)	−0.141(2)	0.1703(7)	0.376(2)	C(65)	0.072(6)	0.488(2)	−0.235(7)
C(27)	−0.176(2)	0.1853(7)	0.477(2)	C(66)	0.133(6)	0.514(2)	−0.095(6)
C(28)	−0.121(2)	0.2243(6)	0.556(2)	Li	0.435(4)	0.477(1)	0.056(4)
C(31)	0.071(2)	0.2046(6)	0.912(2)	O(3)	0.103(3)	0.051(1)	0.229(3)
C(32)	0.153(2)	0.1825(6)	1.038(2)	C(67)	0.165(3)	0.094(1)	0.264(4)
C(33)	0.148(2)	0.2112(6)	1.150(2)	C(68)	0.221(3)	0.104(1)	0.411(4)
C(34)	0.061(2)	0.2475(7)	1.090(2)	C(69)	0.268(3)	0.058(1)	0.460(3)
C(35)	0.015(2)	0.2441(6)	0.945(2)	C(70)	0.197(2)	0.0272(8)	0.352(2)
C(36)	0.367(2)	0.3284(6)	1.186(2)				
				Molecule 7			
Zr(1)	0.63856(7)	0.4183(3)	0.5223(1)	C(15)	0.5684(8)	0.567(3)	0.514(1)
Zr(2)	0.63858(7)	0.0924(3)	0.6228(1)	C(16)	0.5823(8)	0.604(3)	0.461(1)
P(1)	0.6434(2)	0.3784(7)	0.6480(3)	C(17)	0.5732(8)	0.494(3)	0.414(1)
P(2)	0.6445(2)	0.1323(6)	0.5025(3)	C(18)	0.695(1)	0.629(3)	0.527(1)
C(1)	0.6158(7)	0.497(2)	0.695(1)	C(19)	0.719(1)	0.539(3)	0.583(1)
C(2)	0.6489(8)	0.558(3)	0.756(1)	C(20)	0.726(1)	0.416(4)	0.560(1)
C(3)	0.628(1)	0.654(3)	0.792(1)	C(21)	0.7083(9)	0.415(3)	0.491(1)
C(4)	0.580(1)	0.685(3)	0.768(1)	C(22)	0.691(1)	0.549(3)	0.471(1)
C(5)	0.5497(8)	0.606(3)	0.713(1)	C(23)	0.5690(8)	−0.064(3)	0.556(1)
C(6)	0.5681(7)	0.515(3)	0.675(1)	C(24)	0.585(1)	−0.105(3)	0.626(1)
C(7)	0.6191(7)	0.011(3)	0.427(1)	C(25)	0.5750(8)	0.010(3)	0.664(1)
C(8)	0.5718(7)	−0.003(3)	0.395(1)	C(26)	0.555(1)	0.123(3)	0.617(1)
C(9)	0.5504(8)	−0.097(3)	0.339(1)	C(27)	0.5518(7)	0.078(3)	0.554(1)
C(10)	0.5840(9)	−0.175(3)	0.315(1)	C(28)	0.7274(8)	0.105(3)	0.679(1)
C(11)	0.631(1)	−0.156(3)	0.349(1)	C(29)	0.718(1)	−0.016(4)	0.644(1)
C(12)	0.651(1)	−0.055(3)	0.404(1)	C(30)	0.695(1)	−0.115(3)	0.676(1)
C(13)	0.5554(7)	0.379(2)	0.439(1)	C(31)	0.6936(9)	−0.041(3)	0.730(1)
C(14)	0.5521(7)	0.421(3)	0.498(1)	C(32)	0.7102(9)	0.100(3)	0.730(1)
				Molecule 9			
Zr(1)	0.84452(8)	0.82317(6)	1.0821(1)	C(28)	0.523(1)	0.7418(9)	1.117(2)
Zr(2)	0.67597(8)	0.67278(6)	1.1597(1)	C(29)	0.480(1)	0.666(1)	1.082(1)
P(1)	0.8281(2)	0.7856(2)	1.2868(3)	C(30)	0.495(1)	0.6334(8)	1.184(2)
P(2)	0.6922(2)	0.7112(2)	0.9560(3)	C(31)	0.548(1)	0.690(1)	1.284(1)
C(1)	0.8244(8)	0.8477(6)	1.425(1)	C(32)	0.569(1)	0.758(1)	1.248(2)
C(2)	0.784(1)	0.8196(6)	1.513(1)	O(1)	0.636(1)	0.2563(8)	0.310(1)
C(3)	0.786(1)	0.8622(9)	1.626(1)	O(2)	0.7146(8)	0.1851(6)	0.0946(8)
C(4)	0.831(1)	0.939(1)	1.650(1)	N(2)	0.876(1)	0.2117(6)	0.384(1)
C(5)	0.875(1)	0.9694(7)	1.570(1)	N(3)	0.864(1)	0.3496(7)	0.296(1)
C(6)	0.872(1)	0.9245(7)	1.460(1)	C(33)	0.590(2)	0.327(2)	0.325(2)
C(7)	0.6887(9)	0.6453(6)	0.815(1)	C(34)	0.530(2)	0.312(2)	0.419(3)
C(8)	0.747(1)	0.6647(7)	0.736(1)	C(35)	0.501(2)	0.241(2)	0.404(2)
C(9)	0.734(1)	0.6147(8)	0.625(1)	C(36A)	0.605(6)	0.218(4)	0.449(7)
C(10)	0.664(1)	0.5487(8)	0.588(1)	C(36B)	0.539(4)	0.210(3)	0.284(4)
C(11)	0.602(1)	0.5278(8)	0.664(1)	C(37)	0.734(1)	0.202(1)	−0.012(2)
C(12)	0.616(1)	0.5756(7)	0.777(1)	C(38)	0.684(2)	0.132(1)	−0.111(2)
C(13)	0.9552(9)	0.7355(7)	1.003(1)	C(39)	0.620(2)	0.083(1)	−0.061(2)
C(14)	0.969(1)	0.8019(8)	0.957(1)	C(40)	0.648(2)	0.112(1)	0.072(2)
C(15)	1.025(1)	0.8607(7)	1.058(1)	C(41)	0.905(1)	0.148(1)	0.319(2)
C(16)	1.0437(9)	0.8331(7)	1.166(1)	C(42)	0.859(2)	0.196(1)	0.492(2)
C(17)	0.997(1)	0.7548(8)	1.127(1)	C(43)	0.965(2)	0.277(1)	0.432(2)
C(18)	0.744(1)	0.9036(7)	0.950(1)	C(44)	0.957(2)	0.332(2)	0.380(3)
C(19)	0.841(1)	0.9433(8)	1.000(2)	C(45)	0.872(2)	0.377(2)	0.183(3)
C(20)	0.860(1)	0.9656(7)	1.126(2)	C(46)	0.839(1)	0.416(1)	0.361(2)
C(21)	0.770(1)	0.9354(8)	1.155(1)	Li(1)	0.760(2)	0.247(1)	0.260(2)
C(22)	0.700(1)	0.8973(7)	1.044(1)	O(3)	0.831(1)	0.3719(8)	0.673(1)
C(23)	0.816(2)	0.596(1)	1.171(3)	C(47)	0.772(2)	0.348(1)	0.751(2)
C(24)	0.732(3)	0.554(1)	1.073(2)	C(48)	0.819(2)	0.408(1)	0.868(2)
C(25)	0.657(2)	0.533(1)	1.110(2)	C(49)	0.876(2)	0.470(1)	0.842(2)
C(26)	0.682(2)	0.552(1)	1.235(2)	C(50)	0.895(2)	0.445(1)	0.721(2)
C(27)	0.783(2)	0.5927(9)	1.278(1)				

Table II (Continued)

| atom	x	y	z	atom	x	y	z
			Molecule 11				
Mo(1)	0.01966(6)	0.37577(5)	0.22162(7)	C(41)	−0.104(1)	0.4921(7)	0.106(1)
Mo(2)	0.35626(6)	−0.18468(5)	0.78721(8)	C(42)	−0.0559(9)	0.5276(7)	0.216(2)
Zr(1)	0.14249(6)	0.19876(5)	0.36349(8)	C(43)	−0.080(1)	0.5106(8)	0.327(1)
Zr(2)	0.47741(7)	−0.24060(7)	1.07806(9)	C(44)	−0.144(1)	0.4652(8)	0.281(2)
P(1)	−0.0066(2)	0.2413(1)	0.1562(2)	C(45)	−0.1578(8)	0.4544(6)	0.143(1)
P(2)	0.5305(2)	−0.2854(2)	0.8416(2)	C(51)	0.5850(6)	−0.3958(5)	0.7491(8)
O(1)	0.2044(4)	0.3076(4)	0.4526(6)	C(52)	0.6948(8)	−0.4460(7)	0.812(1)
O(2)	0.1607(6)	0.3089(5)	0.0097(7)	C(53)	0.7437(9)	−0.5365(7)	0.735(1)
O(3)	0.3081(5)	−0.1471(4)	1.0727(6)	C(54)	0.7415(8)	−0.5294(7)	0.596(1)
O(4)	0.2844(6)	−0.3398(5)	0.7178(8)	C(55)	0.633(1)	−0.4825(8)	0.529(1)
C(1)	−0.0055(6)	0.1882(5)	−0.0193(8)	C(56)	0.5835(8)	−0.3924(7)	0.605(1)
C(2)	−0.0914(8)	0.2479(6)	−0.1126(9)	C(57)	0.3181(7)	−0.1596(6)	0.957(1)
C(3)	−0.0938(9)	0.2076(7)	−0.257(1)	C(58)	0.3108(7)	−0.2794(7)	0.744(1)
C(4)	−0.099(1)	0.1185(7)	−0.278(1)	C(61)	0.6396(9)	−0.210(1)	1.143(1)
C(5)	−0.0149(9)	0.0590(7)	−0.186(1)	C(62)	0.610(1)	−0.209(1)	1.258(1)
C(6)	−0.0153(7)	0.0994(6)	−0.0415(9)	C(63)	0.517(1)	−0.138(1)	1.269(1)
C(7)	0.1350(7)	0.3405(5)	0.361(1)	C(64)	0.486(1)	−0.0919(8)	1.162(1)
C(8)	0.1105(7)	0.3331(5)	0.091(1)	C(65)	0.564(1)	−0.136(1)	1.085(1)
C(21)	0.0009(8)	0.2674(7)	0.501(1)	C(71)	0.405(1)	−0.351(1)	1.053(1)
C(22)	0.0940(9)	0.2472(7)	0.590(1)	C(72)	0.500(2)	−0.3989(9)	1.035(2)
C(23)	0.1445(8)	0.1587(7)	0.582(1)	C(73)	0.567(1)	−0.388(1)	1.159(2)
C(24)	0.084(1)	0.1213(6)	0.487(1)	C(74)	0.498(1)	−0.335(1)	1.244(1)
C(25)	−0.0043(9)	0.186(1)	0.436(1)	C(75)	0.402(1)	−0.317(1)	1.180(2)
C(31)	0.260(1)	0.128(1)	0.198(2)	C(81)	0.2346(9)	−0.085(1)	0.647(1)
C(32)	0.317(1)	0.1413(9)	0.305(3)	C(82)	0.290(1)	−0.0403(8)	0.737(1)
C(33)	0.324(1)	0.091(1)	0.388(1)	C(83)	0.390(1)	−0.0748(8)	0.720(2)
C(34)	0.268(1)	0.0443(7)	0.325(2)	C(84)	0.401(1)	−0.1421(8)	0.616(1)
C(35)	0.230(1)	0.069(1)	0.207(2)	C(85)	0.305(1)	−0.147(1)	0.566(1)
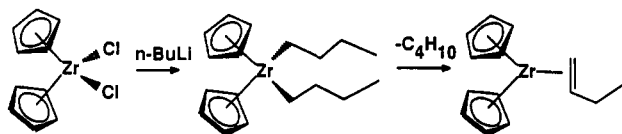
ous attempts to modify the reaction conditions to enhance the yield of **6** were unsuccessful affording instead **4** and **5**.

R = SiPh₃ **6**
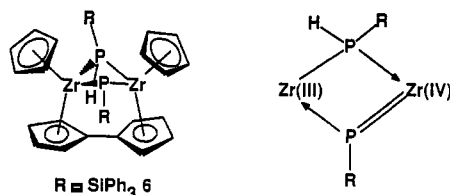
Alternative synthetic routes to these products were explored. The reaction of Cp₂ZrCl₂ with Mg is known to proceed in the presence of excess PMe₃ to give the Zr(II) species Cp₂Zr(PMe₃)₂.[29] With this precedent in mind, the reactions of Cp₂ZrCl₂, Mg, and primary phosphines were explored. A THF suspension of Cp₂ZrCl₂ with Mg was stirred at room temperature under an inert atmosphere for 0.5 h in order to initiate the heterogeneous reduction of Zr(IV). These red-brown mixtures became uniformly brown/black upon addition of the respective primary phosphines. In the case of the CyPH₂ and Ph₂SiPH₂, the crystalline products **2** and **4** could be obtained in this manner. Alternatively, compounds **2** and **4** could also be isolated from the direct reaction of Cp₂ZrHCl with the respective primary phosphines (Scheme I). A similar reaction of Cp₂ZrHCl with PPhH₂ affords the product [Cp₂Zr(μ-PHPh)]₂ (**7**), albeit in low yields. The formulation of **7** was confirmed crystallographically (*vide infra*).

Mechanistic Considerations of P–H and Cyclopentadienyl C–H Activation. The reactions of Cp₂Zr with

**Scheme I. Alternate Synthetic Route to Zr(III)–Phosphide Dimers**
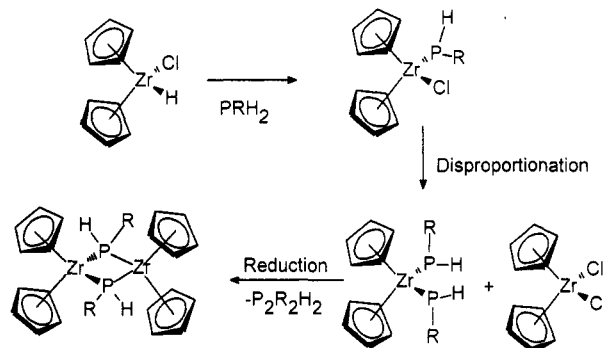
primary phosphines have been monitored by ^{31}P NMR. For the reaction of PPhH₂ a resonance is seen at 62 ppm with $|J_{P-H}| = 194$ Hz, typical of terminal phosphides. This species is transient and is attributed to the initial oxidative addition of P–H affording the reactive species Cp₂ZrH-(PPhH) (Scheme II). Such intermediates have been observed spectroscopically in related reactions of Cp*₂Zr with CyPH₂,[18] while Vaughan and Hillhouse[12] have isolated and structurally characterized the analogous hafnium complexes Cp₂HfH(PRH). Continued spectroscopic monitoring reveals the loss of the resonance attributable to Cp₂ZrH(PPhH) and the appearence of a low-field resonance at 549 ppm, which shows no coupling to protons.[30] This species is also short-lived and is thought to be the highly reactive terminal phosphinidene intermediate.[30] Subsequent reaction is evidenced by the growth of a doublet ^{31}P resonance at 77 ppm, which is attributed to the cyclopentadienyl C–H addition to th Zr=PR moiety affording a species **13** in which η^5-η^1-cyclopentadienyl

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(29) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394.

(30) Similar low-field resonances were observed in the other phosphine systems. No P–H coupling was seen. However, in all cases the species were transient and not isolable. The resonances observed for the following phosphine reactions were PH₂(C₆H₅t-Bu₃), 478 ppm; PH₂(C₆H₂Me₃), 526 ppm; PH₂SiPh₃, 262.9 ppm; and CyPH₂, 498.9 ppm.

Scheme II. Proposed Mechanism of Formation of Zr(III) Dimers

R = Cy 2; SiPh₃ 4; Ph 7

R = Ph 1; PhMe₃ 3; SiPh₃ 5
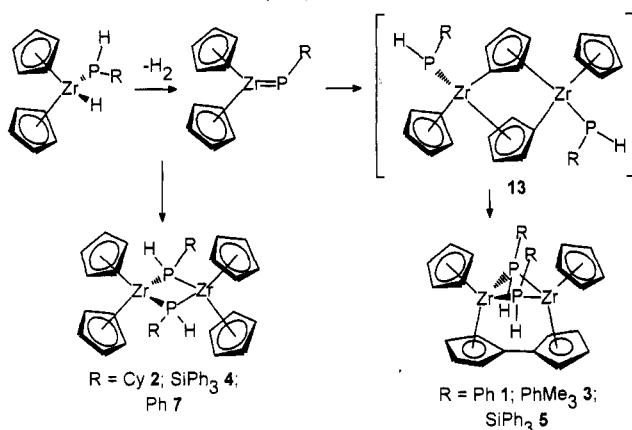
groups link two metal centers (Scheme II). Subsequent rearrangement with the formation of a C–C bond affords the fulvalenide moieties found in 1, 3, and 5, respectively. The proposal of the intermediate 13 is supported to some extent by the isolation of the phosphorus-capped species $[CpZr(\mu-\eta^5-\eta^1-C_5H_4)]_3P$ (14), as this species provides the


14
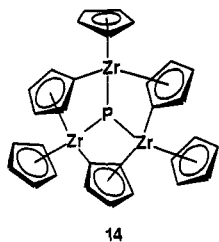
first structural precedent for such $\eta^5-\eta^1$-cyclopentadienyl groups between Zr centers.[21] In related chemistry, Choukroun et al. have recently reported the preparation of the species $[CpZrCl]_2(\mu-\eta^5-\eta^1-C_5H_4)$ via the thermolysis of Cp_2-ZrHCl to $(CpZrCl)_2(\mu-\eta^5-\eta^5-C_{10}H_8)$,[31] while Gambarotta et al.[32] have described the synthesis of $[CpZrX]_2(\mu-\eta^5-\eta^5-C_{10}H_8)$ (X = SPh, Cl, Br) from the Zr(III) species formulated as $[CpZr(PMe_3)(\mu-\eta^1-\eta^5-C_5H_4)]_2$.[33] The activation of C–H bonds by Zr(IV) centers is also supported in principle by recent reports of agostic H interactions with Cp_2Zr^{IV} centers[34] as well as by the demonstrated ability of related imido systems to effect C–H activation.[35] $\eta^1-\eta^5$-cyclopentadienyl groups have also been confirmed to be present in the related compounds $[Cp_2Th(\mu-\eta^5-\eta^1-C_5H_4)]_2$,[36] $[CpNbH(\mu-\eta^5-\eta^1-C_5H_4)]_2$,[37] and $[CpTi(PMe_3)-(\mu-\eta^5-\eta^1-C_5H_4)]_2$.[33]

In the formation of 2 and 4 C–H activation is not involved. These species may be derived from dimerization of the species $Cp_2ZrH(PHR)$ with subsequent loss of H_2. A more basic phosphide, as in $Cp_2ZrH(PHCy)$, may favor

dimerization. In the case of Ph_3SiPH_2 it appears that these two reaction pathways are competitive and thus both types of products are obtained. In addition, the formation of 6 demonstrates a third low-yield reaction pathway as 6 is viewed as the combination of a Zr(IV) phosphinidene fragment with a Zr(III) phosphide moiety.

It is more difficult to comment on the mechanism for the corresponding syntheses employing the reduction of Cp_2ZrCl_2 with Mg. As such reductions have been shown to yield Zr(II) species,[27] one might suggest a mechanism similar to that offered above involving Cp_2Zr.[38,39] However, if such a mechanism were operative, then one would expect the same products for both routes. While this is the case for the formation of 2 and 4, we have recently described the synthesis of the bridging phosphinidene complex $(Cp_2-ZrCl)_2(\mu-P(2,4,6-Me_3C_6H_2)$ (15) from the reaction of Cp_2-ZrCl_2/Mg and $(2,4,6-Me_3C_6H_2)PH_2$.[18] The fact that 15 is isolated, rather than 3, from Mg reduction points to an alternate mechanism, perhaps involving P–H activation by a Zr(III) intermediate.

15
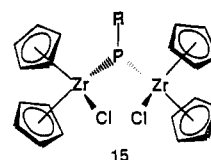
The direct reaction of the primary phosphine with Cp_2-ZrHCl also proved to be a synthetic route to 2, 4, and 7. The initial step is believed to be the acid/base reaction of the hydride and the primary phosphine affording the species $Cp_2Zr(PRH)Cl$ and H_2. Subsequent disproportionation and reduction to the observed products (Scheme II) is supported by the established chemistry of the related dialkylphosphide–chloride complexes and the known instability of zirconocene–bis(dialkylphosphides) with respect to reduction to Zr(III) at room temperature.[4,8]

Homo- and Heterobinuclear Phosphinidene-Bridged Complexes. Reaction of Cp_2ZrCl_2 with a slurry of Li_2-PPh in THF followed by filtration and cooling to –35 °C afforded the generation of an *extremely* air-sensitive and apparently thermally unstable material 8a. This product exhibited a strong triplet EPR signal. In a similar vein, treatment of the diamagnetic Zr(III) primary phosphide dimer 2 with excess KH in THF afforded a similarly strong, triplet EPR spectrum. Solid state spectra of this species exhibited a half-field transition consistent with the presence of two Zr(III) centers in the molecule. On the basis of these and subsequent reactivity data, the formulations for these products are suggested to be the salts of the dianionic, diphosphinidene species $[Cp_2Zr(\mu-PR)]_2^{2-}$ (R = Ph (8a), Cy (8b)) (Scheme III).[40] Reaction of 8a with 1 equiv of NR_3H^+ in the presence of $TMEDA\cdot HCl$ resulted in the formation of 9.[41] This species crystallized from THF/hexane. The EPR spectrum of 9 (Figure 1b) is a doublet of triplets with hyperfine coupling to two phosphorus nuclei and to the proton of the phosphide bridge. This suggested that protonation of 8a had

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(36) Baker, E. C.; Raymond, K. N.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1974**, *96*, 7586.

(37) Guggenberger, L. J. *Inorg. Chem.* **1973**, *12*, 294.

(38) The species Cp_2ZrH is proposed as an intermediate in the Mg reduction of Cp_2ZrCl_2 arising from cyclopentadienyl C–H activation by "Cp_2Zr".[37] While the role of this species in the mechanism of formation of 2 and 4 can not be eliminated, it is noted that the formation of Cp_2ZrH requires 48 h, whereas evidence of P–H activation by Cp_2Zr is observed upon addition of phosphine.

(39) Samuel, E. *Inorg. Chem.* **1983**, *22*, 2967.

(40) Crystallography data for 8a, support this formulation: Ho, J.; Drake, R. E.; Stephan, D. W. *J. Am. Chem. Soc.* **1993**, *115*, 3792.

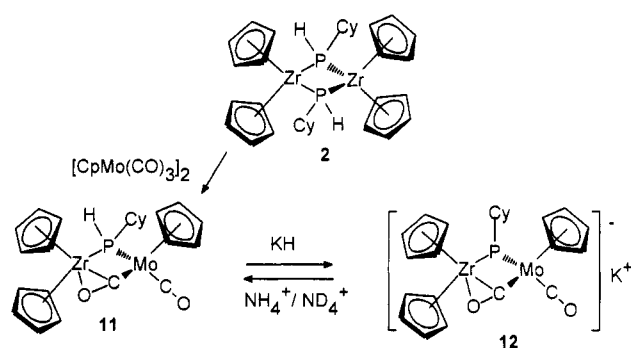**Scheme III. Generation and Protonation/Alkylation of Zr(III) Phosphinidene Dimers**

Scheme IV. Synthetic Route to Phosphide- and Phosphinidene-Bridged Heterobimetallics
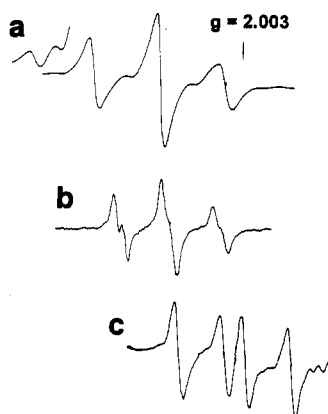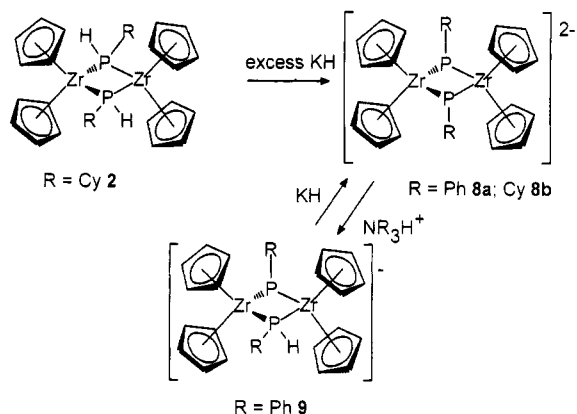
Figure 1. EPR spectra of (a) $[Cp_2Zr(\mu\text{-}PPh)]_2{}^{2-}$ (8), (b) $[(Cp_2Zr)_2(\mu\text{-}PHPh)(\mu\text{-}PPh)]^-$ (9), and (c) $[(Cp_2Zr)_2(\mu\text{-}PMePh)(\mu\text{-}PPh)]^-$ (10).

occurred. Similar to 8a, 9 also exhibited a half-field transition in the solid state spectrum indicative of two Zr(III) centers. ^{1}H NMR data for this crystalline product are consistent with the ratio of cyclopentadienyl, phenyl, TMEDA, and THF protons of 10:5:8:8. No signal attributable to a proton on phosphorus was observed, although this is not surprising given the paramagnetism of the Zr(III) centers. The formulation of 9 as the phosphinidene–phosphide-bridged complex [(Cp$_2$Zr)$_2$(μ-PPH)(μ-PHPh)]-[(TMEDA)Li(THF)$_2$] was confirmed crystallographically. Tetraalkylammonium salts of the the monoanion of 9 were isolated in a similar fashion by employing NR$_3$H$^+$ and NR$_4{}^+$.[40] The protonation of 8a to give 9 is reversible. Treatment of 9 with excess KH led to the complete loss of the EPR signal arising from 9 and the regeneration of the signal derived from 8a. Methylation of 8a using Me$_3$-OBF$_4$ afforded [(Cp$_2$Zr)$_2$(μ-PPh)(μ-PMePh)]- (10) as evidenced by the doublet of doublets signal in the EPR spectrum (Figure 1c). The inequivalence of the phosphorus atoms is evidenced by the two distinct hyperfine couplings to phosphorus. Attempts to isolate 10 have been unsuccessful to date.

A related, diamagnetic, primary phosphide-bridged heterobimetallic system is derived from the reaction of 2 with [CpMo(CO)$_3$]$_2$, a reaction that has been previously established for the analogous dialkylphosphido complexes.[42–44] The product in this case is Cp$_2$Zr(μ-PHCy)(μ-η^1-η^2-OC)Mo(CO)Cp (11) (Scheme IV). The ^{31}P-{^{1}H} NMR of 11 is a single resonance of 136.0 ppm which exhibits coupling to a single proton of 298 Hz. Although both the P and Mo centers of 11 are chiral, the NMR data are consistent with the presence of only a single pair of diastereomers. Steric arguments suggest a preference for the diastereomers in which the phosphide substituent and the cyclopentadienyl ring on Mo are on opposite sides of the ZrPMo plane. This is confirmed by a crystallographic study. The reaction of 11 with excess KH was monitored by ^{31}P NMR. As the reaction proceeds, the resonance attributable to 11 diminishes in intensity and ultimately is completely replaced by a single resonance at 259.8 ppm which exhibits no P–H coupling. The low-field shift as well as the absence of hydrogen coupling suggests that the phosphide complex 11 has been deprotonated yielding the phosphinidine-bridged complex [Cp$_2$Zr(μ-PCy)-(μ-η^1-η^2-OC)Mo(CO)Cp]- (12). In a similar manner, the differences in the cyclopentadienyl ^{1}H resonances and ν_{CO} between 11 and 12 are consistent with the generation of an anion. The deprotonation is quantitatively reversed by the addition of NH$_4$Cl resulting in the regeneration of both the ^{1}H and ^{31}P resonances arising from 11. The protonation of 12 appears to proceed regioselectively, in that only the original diastereomers of 11 are re-formed. Further, deuteration of 12 performed by treatment of 11 with ND$_4$Cl affords the deuterated complex Cp$_2$Zr(μ-PDCy)(μ-η^1-η^2-OC)Mo(CO)Cp (11b). The spectroscopic properties of 11b are identical with those of 11 with the exception of the slight shift in the ^{31}P resonance at 134.3 ppm and the P–D coupling of 47 Hz.

Structural Studies. ORTEP drawings of molecules 3–6, 9, and 11 are shown in Figures 2–7, respectively. The numbering scheme for 7 is identical to that shown for 9; thus an ORTEP of 7 is not shown.

Phosphide Dimers. In the case of 3 and 5, Zr is bonded to two phosphido groups, a π-coordinated cyclopentadienyl ring, and a π-bound C$_5$H$_4$ fragment of a fulvalene moiety. It is the presence of the fulvalene unit that distinguishes

(41) The compound [(Cp$_2$Zr)$_2$(μ-PHPh)(μ-PPh)][NPr$_4$] crystallizes in the space group $P\bar{1}$ with a = 11.308(5) Å, b = 18.430(9) Å, c = 11.267(8) Å, α = 93.86(6)°, β = 116.83(4)°, γ = 89.85(5)°, Z = 2, and V = 2090(2) Å^3. The compound [(Cp$_2$Zr)$_2$(μ-PHPh)(μ-PPh)][NBu$_4$]·THF crystallizes in the space group $C2/c$ with a = 19.424(1) Å, b = 12.294(8) Å, c = 20.901-(11) Å, β = 95.55(5)°, Z = 4, and V = 4968(5) Å^3. The compound [(Cp$_2$-Zr)$_2$(μ-PHPh)(μ-PPh)][NEt$_3$Pr] crystallizes in the space group $C2/c$ with a = 20.946(31) Å, b = 10.482(3) Å, c = 18.771(7) Å, β = 111.91(4)°, Z = 4, and V = 3824(9) Å^3.

(42) Zheng, P. Y.; Nadasdi, T. T.; Stephan, D. W. *Organometallics* **1989**, *8*, 1393.

(43) Dick, D. G.; Stephan, D. W. *Organometallics* **1990**, *9*, 1910.

(44) Dick, D. G.; Hou, Z.; Stephan, D. W. *Organometallics* **1992**, *11*, 2378.

(45) (a) Gambarotta, S.; Chiang, M. Y. *Organometallics* **1987**, *6*, 897. (b) Cuenca, T.; Herrmann, W. A.; Ashworth, T. V. *Organometallics* **1986**, *5*, 2514.
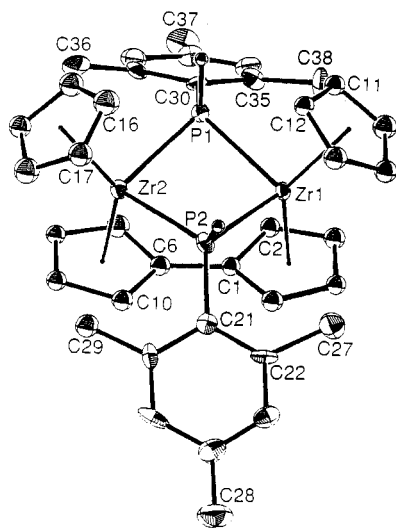
Figure 2. ORTEP drawing of molecule 3 with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity, with the exception of the hydrogen atoms on phosphorus.
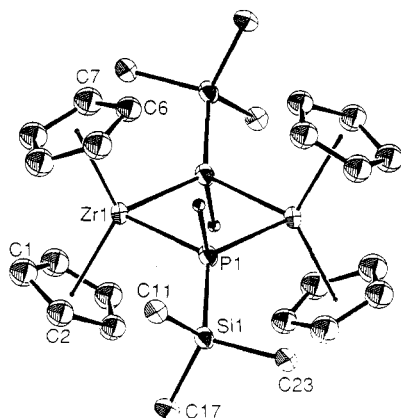
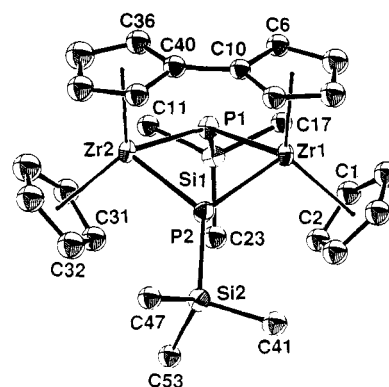**Figure 3.** ORTEP drawing of molecule of 4 with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity, with the exception of the hydrogen atoms on phosphorus.
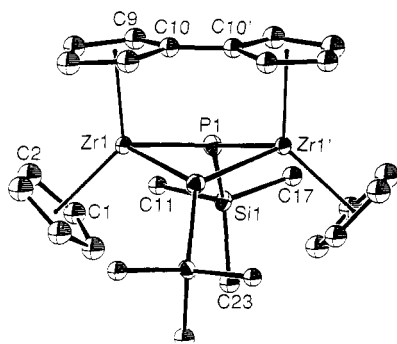

Figure 4. ORTEP drawing of molecule 5 with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

the "top" from the "bottom" of these dimers. Presumably as a result of the fulvalene fragment the phosphide substituents on phosphorus adopt a cisoid orientation. In the case of 3 the P–H bonds are oriented away from the fulvalene moiety. In contrast, in 5, the triphenylsilyl substituents are oriented away from the fulvalene unit, thereby minimizing the steric interactions between the fulvalene and Ph₃Si fragments. The fulvalene ligands are slightly bent with angles between the planes of the rings of 11.65 and 8.33° in 3 and 5, respectively. Small twists between the adjacent rings are also observed.

Figure 5. ORTEP drawing of molecule 6 with 30% thermal ellipsoids. Hydrogen atoms are omitted and only the α carbon atoms of the phenyl substituents on Si are shown for clarity.
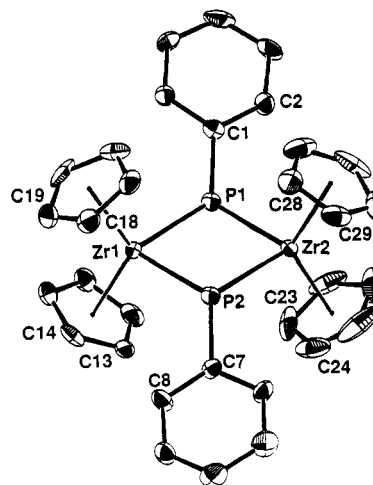
Figure 6. ORTEP drawing of the anion of 9 with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Note that the numbering scheme used here is identical to that used for the neutral species 7.
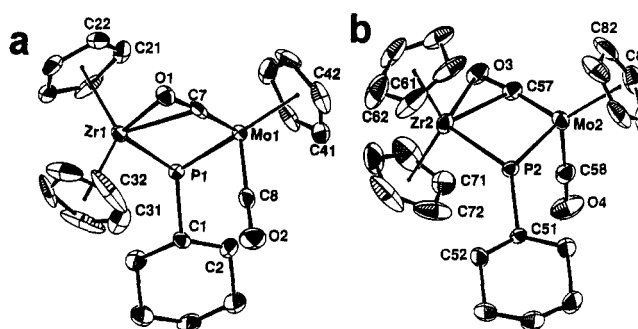
Figure 7. ORTEP drawing of the two independent molecules of 11 in the asymmetric unit with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Molecules 2, 4, and 7 are also Zr(III) phosphido-bridged dimers, although the fulvalene moiety is replaced by two cyclopentadienyl groups. In these compounds the phosphide substituents adopt a transoid orientation. This conformation presumably offers the least steric interactions between the cyclopentadienyl rings and the phosphide substituents.

In the case of compounds 3 and 5 the Zr₂P₂ cores are not planar; rather they are puckered forming angles of 23.56 and 28.24° between the ZrP₂ planes, respectively. In contrast the Zr₂P₂ cores of 2, 4, and 7 are planar. The Zr–P distances range from 2.599(4) to 2.675(5) Å. These

Table III. Selected Bond Distances (Å) and Angles (deg) for Molecule 11

Distances

Mo(1)–Zr(1)	3.230(2)	Mo(2)–Zr(2)	3.220(2)
Mo(1)–P(1)	2.385(2)	Mo(2)–P(2)	2.385(3)
Mo(1)–C(7)	1.897(9)	Mo(2)–C(57)	1.89(1)
Mo(1)–C(8)	1.94(1)	Mo(2)–C(58)	1.90(1)
Mo(1)–C(41)	2.35(1)	Mo(2)–C(81)	2.32(1)
Mo(1)–C(42)	2.34(1)	Mo(2)–C(82)	2.34(1)
Mo(1)–C(43)	2.33(1)	Mo(2)–C(83)	2.37(1)
Mo(1)–C(44)	2.36(1)	Mo(2)–C(84)	2.36(1)
Mo(1)–C(45)	2.36(1)	Mo(2)–C(85)	2.37(1)
Zr(1)–P(1)	2.627(3)	Zr(2)–P(2)	2.620(3)
Zr(1)–O(1)	2.295(6)	Zr(2)–O(3)	2.286(6)
Zr(1)–C(7)	2.353(8)	Zr(2)–C(57)	2.331(9)
Zr(1)–C(21)	2.516(9)	Zr(2)–C(61)	2.50(1)
Zr(1)–C(22)	2.495(9)	Zr(2)–C(62)	2.48(1)
Zr(1)–C(23)	2.498(9)	Zr(2)–C(63)	2.46(1)
Zr(1)–C(24)	2.50(1)	Zr(2)–C(64)	2.52(1)
Zr(1)–C(25)	2.51(1)	Zr(2)–C(65)	2.53(1)
Zr(1)–C(31)	2.48(1)	Zr(2)–C(71)	2.43(2)
Zr(1)–C(32)	2.48(1)	Zr(2)–C(72)	2.51(1)
Zr(1)–C(33)	2.48(1)	Zr(2)–C(73)	2.50(1)
Zr(1)–C(34)	2.49(1)	Zr(2)–C(74)	2.48(1)
Zr(1)–C(35)	2.50(1)	Zr(2)–C(75)	2.50(1)
P(1)–C(1)	1.857(8)	P(2)–C(51)	1.845(8)
O(1)–C(7)	1.23(1)	O(3)–C(57)	1.21(1)
O(2)–C(8)	1.15(1)	O(4)–C(58)	1.19(1)

Angles

Zr(1)–Mo(1)–P(1)	53.25(6)	Zr(2)–Mo(2)–P(2)	53.25(6)
Zr(1)–Mo(1)–C(7)	46.1(2)	Zr(2)–Mo(2)–C(57)	45.7(3)
Zr(1)–Mo(1)–C(8)	91.9(3)	Zr(2)–Mo(2)–C(58)	92.8(3)
P(1)–Mo(1)–C(7)	99.2(3)	P(2)–Mo(2)–C(57)	98.8(3)
P(1)–Mo(1)–C(8)	86.6(3)	P(2)–Mo(2)–C(58)	90.0(3)
C(7)–Mo(1)–C(8)	90.8(4)	C(57)–Mo(2)–C(58)	90.1(4)
P(1)–Zr(1)–O(1)	112.7(2)	P(2)–Zr(2)–O(3)	112.6(2)
P(1)–Zr(1)–C(7)	82.0(2)	P(2)–Zr(2)–C(57)	82.3(2)
O(1)–Zr(1)–C(7)	30.6(2)	O(3)–Zr(2)–C(57)	30.3(2)
Mo(1)–Zr(1)–P(1)	46.66(6)	Mo(2)–Zr(2)–P(2)	46.83(6)
Mo(1)–Zr(1)–O(1)	66.1(1)	Mo(2)–Zr(2)–O(3)	65.8(2)
Mo(1)–P(1)–Zr(1)	80.09(8)	Mo(2)–P(2)–Zr(2)	79.92(8)
Zr(1)–O(1)–C(7)	77.3(5)	Zr(2)–O(3)–C(57)	76.9(5)
Mo(1)–C(7)–O(1)	170.0(7)	Mo(2)–C(57)–O(3)	171.0(8)
Zr(1)–C(7)–O(1)	72.1(5)	Zr(2)–C(57)–O(3)	72.8(5)
Mo(1)–C(8)–O(2)	177.1(9)	Mo(2)–C(58)–O(4)	178.5(9)

values compare with those reported for [Cp₂Zr(μ-PMe₂)]₂ and [Cp₂Zr]₂(μ-PMe₂)(μ-Cl)[13] (Table IV) and are slightly shorter than those found for Cp₂Zr(μ-PPh₂)₂RhH(CO)-PPh₃ (Zr–P$_{av}$ = 2.680(3) Å).[46] The P–Zr–P angles in 1–5 and 7 range from 89.7(1) to 98.3(1)°, while the Zr–P–Zr' angles vary from 80.1(1) to 88.4(1)°. These values are similar to those seen in [Cp₂Zr(μ-PMe₂)]₂ and [Cp₂Zr]₂-(μ-PMe₂)(μ-Cl).[13] Zr···Zr distances in 1–5 and 7 were as short as 3.423(3) Å and as long as 3.674(5) Å. These data reflect compromise between three factors, the presence or absence of a fulvalene link, the steric and electronic properties of the phosphides, and conformation of the substituents at phosphorus. However, on examination some trends do emerge. First, the puckering of the Zr₂P₂ core dictated by the presence of fulvalenide moieties results generally in a closer approach of the metal centers than is seen in the related dicyclopentadienyl–Zr dimers. For example, comparison of the Zr···Zr distances in 4 (3.674(5) Å) and 5 (3.585(3) Å) supports this view. Second, the angles about the Zr₂P₂ cores generally fall within a small rang with the exception of compound 3. In the case of 3, the steric demands of the ortho-substituents appear to be accommodated by a substantial core distortion resulting in the comparatively small angle at P and the large angle at Zr. However, further increases in the steric demands

(46) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849.

Table IV. Structural Data for Zr Dimers

compd/ bridge	Zr···Zr	Zr–X		Zr–X–Zr'	X–Zr–X'	ref
Dicyclopentadienyl Derivatives						
I	3.669(2)	2.916(1)		77.97(3)	102.03(3)	49
S	3.530(2)	2.490(3)	2.482(3)	90.4(1)	89.6(1)	48
PMe₂	3.653(2)	2.672(5)		86.3(2)	93.8(2)	13
PMe₂, Cl	3.524(2)	2.661(2)	2.587(2)	83.2(1)	95.5(1)	13
		2.648(2)	2.595(2)	85.7(1)	95.6(1)	
2	3.607(4)	2.648(3)	2.649(5)	86.0(1)	94.0(1)	18
	3.638(4)	2.643(4)	2.647(3)	86.8(1)	93.2(1)	
4	3.674(5)	2.636(4)	2.613(4)	88.4(1)	91.6(1)	a
7	3.677(4)	2.654(7)	2.673(7)	87.3(2)	92.3(2)	a
		2.655(7)	2.672(7)	87.3(2)	92.4(2)	
9	3.672(2)	2.594(4)	2.585(3)	90.1(1)	89.8(1)	a
		2.595(3)	2.588(4)	90.4(1)	89.7(1)	
Fulvalene Derivatives						
Cl	3.233(1)	2.591(2)	2.568(2)	77.6(1)	99.5(1)	45a
		2.583(2)	2.571(2)	77.7(1)	100.5(1)	
S	3.4254(4)	2.487(1)	2.493(1)	86.60(3)	87.85(1)	32
SPh	3.420(1)	2.533(1)	2.546(1)	84.66(3)	89.78(3)	32
1	3.549(2)	2.610(4)	2.609(4)	85.4(1)	90.5(1)	21
		2.627(4)	2.620(4)	85.5(1)	90.7(1)	
3	3.423(2)	2.655(5)	2.663(4)	80.3(1)	98.3(1)	a
		2.635(4)	2.675(5)	80.1(1)	97.1(1)	
5	3.585(3)	2.599(4)	2.613(4)	86.9(1)	89.7(1)	a
6	3.570(4)	2.619(5)	2.582(5)	86.0(1)	89.5(2)	a
		2.617(5)	2.678(5)	87.5(2)	89.7(2)	

a This work.

of the phosphide substituent, as in 4 and 5, are overcome by the adoption of alternative conformations at phosphorus which result in a more typical core geometry.

Phosphinidene Complexes. The compound 6 is structurally similar to a diphosphide-bridged fulvalene dimer 5, with the replacement of one of the phosphide bridges with a phosphinidene moiety. This substitution makes 6 a rare example of a mixed-valent Zr(IV)/Zr(III) complex. The phosphide and phosphinidene fragments are distinguished in the structural data by the geometry about the respective phosphorus atoms. The geometry about P(1) is pseudopyramidal with the Zr–P–Zr' and Zr–P–C angles summing to 338.8°, whereas about P(2) the geometry is almost planar with the corresponding angles summing to 352.2°. In the only other structurally characterized Zr–phosphinidene, (Cp₂ZrCl)₂(μ-PC₆H₂Me₃),[18] the geometry about the P atom was also planar. The Zr–P distances are also consistent with this formulation as Zr–P(1) and Zr–P(2) distances averag 2.617(5) and 2.580(5) Å, respectively. The Zr–P(2) distance is significantly shorter than those seen in 4 or 5 consistent with the presence of the phosphinidene moiety in 6.

The complex 9 is a salt containing the cation [(THF)₂Li-(TMEDA)]⁺ and the anion [(Cp₂Zr)₂(μ-PHPh)(μ-PPh)]⁻. The geometry of the cation is typical and requires no further comment. The anion is geometrically similar to the diphosphide dimer 7. Despite the fact that the formulation requires inequivalent phosphorus atoms, the geometry about the two phosphorus atoms is indistinguishable. The single proton on one of the phosphorus atoms, implied by both the reaction chemistry and the formulation, was not located. Both P atoms are pseudopyramidal with Zr(1)–P–Zr(2) angles of 90.1(1) and 90.4(1)°, respectively. It is also noteworthy that while three other salts of this anion have been crystallographically characterized,[41] the anion geometry and proton disorder is identical in each case. Such a geometry at P for a bridging phosphinidene fragment while in contrast to that observed in 6 is not unexpected. In the absence of steric interactions with other ligands, the constraints of placing a phosphin-
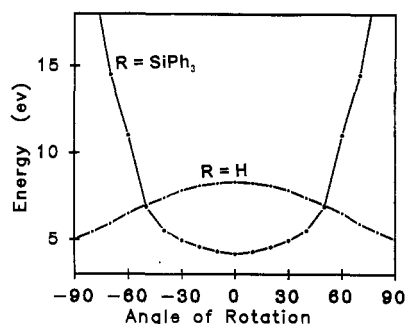
Figure 8. Plots of the total energy as a function of the orientation of the substituent on the phosphinidene P atom for $[(Cp_2Zr)_2(\mu\text{-}PH_2)(\mu\text{-}PR)]^-$ (R = H, SiPh$_3$).

idene moiety in a four-membered ring may force a pyramidal geometry at P.[47] The phenyl substituents on the P atoms of 9 adopt a transoid disposition with respect to the Zr$_2$P$_2$ plane. The P–Zr–P angles are found to be 90.5(1) and 90.7(1)°, while the Zr–P–Zr angles are 85.4(1) and 87.3(2)°. The apparent disorder of the single proton position could not be modeled. Nonetheless, the average Zr–P distance in 9 is slightly shorter than that seen in 7, consistent with the presence of the phosphinidene ligand. The angles about the Zr$_2$P$_2$ core of this paramagnetic anion are similar to that of the neutral diamagnetic dimer 7, with small perturbations resulting in a Zr···Zr separation of 3.677(4) Å.

The pyramidal nature of the phosphorus atoms in 9 is in contrast to the planar geometry about the phosphinidene phosphorus in 6. Steric effects as well as the mixed oxidation state nature of 6 may play a role in the differing geometries. However, Fenske–Hall molecular orbital calculations performed for the model compounds of the form $[(Cp_2Zr)_2(\mu\text{-}PR)(PH_2)]^-$ (R = H, SiH$_3$) reveal some relevant information. Calculation of the total energy as a function of the orientation of the substituent on the phosphinidene fragment are shown in Figure 8. For R = H, the predicted geometry is pseudopyramidal at the phosphinidene phosphorus atom, indeed that which is observed in 9. In contrast, the calculations predict a planar orientation for the model containing the silyl substituent suggesting dπ–pπ bonding between the P and Si may stabilize a planar geometry at the phosphinidene phosphorus atom in 6.

Phosphide-Bridged Heterobimetallic. The structure of 11 (Figure 7) confirms the connectivity in which a single phosphide ligand bridges the Cp$_2$Zr and Mo(CO)$_2$Cp fragments. One of the CO moieties on Mo also bridges to the Zr affording an η^1-η^2-CO fragment. The cyclohexyl substituent on P and the cyclopentadienyl ring on Mo are *transoid* with respect to the ZrPMo plane. The Zr–P distance is slightly shorter than those reported for Cp$_2$M-$(\mu\text{-}PEt_2)(\mu\text{-}\eta^1\text{-}\eta^2\text{-}OC)M'(CO)Cp$ (M = Ti, Zr; M = Mo, W) and Cp$_2$Zr(μ-PPh$_2$)(μ-η^1-η^2-OC)Mo(CO)Cp reflecting the basicity of the primary phosphide fragment in 11.[39–41]

Metal–Metal Bonding? The observed diamagnetism of zirconocene(III) or titanocene(III) diorganophosphide dimers arises as a result of antiferromagnetic coupling of the d^1 metal centers. The mechanism responsible for the diamagnetism is the subject of some interest. The spectroscopic and structural results described herein shed further light on this issue.

The structural data for the present and related Zr dimers are summarized in Table IV. The Zr···Zr distances range from 3.233(1) Å in $[CpZr(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ to 3.674-(2) Å in 4. Gambarotta et al. have previously pointed out that the Zr···Zr separation in $[CpZr(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ is comparable to those in β-Zr, β-ZrCl$_3$ and $[ZrCl_3(PBu_3)_2]_2$ thus suggesting the presence of a Zr–Zr metal–metal bond.[43] In contrast, Gambarotta et al. noted that the Zr···Zr distance of 3.653 Å in $[Cp_2Zr(\mu\text{-}PMe_2)]_2$ is well beyond the sum of the covalent radii thus arguing against the presence of a Zr–Zr bond.[13] The structural data for compounds 1–7 and 9 suggest the similar latter conclusion. Furthermore, the Zr–Zr distances in $[CpZr(\mu\text{-}S)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$[48] and $[CpZr(\mu\text{-}SPh)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$,[32] which are 3.4254(4) and 3.420(1) Å, respectively, suggest that metal–metal separation is independent of the oxidation state. Thus, if direct metal–metal interactions are present in the Zr(III) dimers, apparently they result in a minimal perturbation of the geometry. The metric parameters of the Zr$_2$P$_2$ core of 9 are within the ranges seen in the diamagnetic phosphide-bridged dimers. Yet 8 and 9 are paramagnetic, while the phosphide-bridged dimers are all diamagnetic at 25 °C. This leads to the suggestion of ligand-mediated antiferromagnetic coupling as perturbations of the electronic environments at one or both of the P atoms have a significant effect on the degree of coupling between the Zr(III) centers. Furthermore, the absence of the ^{1}H and ^{31}P signals for phosphide groups in the diamagnetic dimers suggests P participation in the mechanism of coupling between the Zr centers.

The conclusion derived from the above considerations is in conflict to the alternative explanation put forth by Benard et al.[19,20] In these detailed reports, they showed that EH and ab initio theoretical considerations for Zr-(III) phosphide dimers are consistent with the presence of direct metal–metal interactions over the range of Zr–Zr separations of 3.05–4.25 Å. Further the calculations predict a dimagnetic ground state in the absence of the bridging ligands. Thus Benard et al. concluded the bridging ligands are not involved in the attainment of a observed diamagnetic ground state and attributed the diamagnetism to the "super-long" Zr–Zr bonds. We have performed EH and Fenske–Hall MO calculations for a model of the diamagnetic dimers, i.e. $[Cp_2Zr(\mu\text{-}PH_2)]_2$. In addition, we have modeled the paramagnetic dimers 8 and 9 with the model compounds $[Cp_2Zr(\mu\text{-}PH)]_2^{2-}$ and $[(Cp_2Zr)_2(\mu\text{-}PH)(\mu\text{-}PH_2)]^-$. In each case, we have employed basis sets which both exclude and include d orbitals on P. The general bonding scheme in these dimers derived from either set of calculations is similar to that described by Benard et al.,[19,20] however, comparison among these systems reveals some important points. The net overlap populations between the Zr atoms were essentially invariant among these three models. Thus, while the presence of super-long Zr–Zr bonds seems consistent with our calculations, their strength does not parallel the magnetic properties. Also in this series of calculations when P d orbitals are included, it is observed that deprotonation of the phosphide ligands results in a significant decrease in the P(d$_z^2$) contribution to the HOMO with a corresponding increase in the P(p$_x$) and P(p$_y$) contributions. These results suggest that antifer-

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romagnetic coupling between the Zr(III) centers may be mediated by P and that perturbation of the electronic environment at P leads to a disruption in this communication and thus paramagnetism. In a previous study, we suggested that the diamagnetism of $[Cp_2Zr(\mu\text{-}PEt_2)]_2$ is mediated by the bridging ligands;[14] however, the present results are the first to suggest the participation of the P d orbitals. Further work is necessary to confirm and clarify this postulate.

Supplementary Material Available: Tables of thermal and hydrogen atom parameters and bond distances and angles (24 pages). Ordering information is given on any current masthead page.

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