

# Synthesis, Structure, and Bonding in Zirconocene Primary Phosphido (PHR<sup>-</sup>), Phosphinidene (PR<sup>2-</sup>), and Phosphide (P<sup>3-</sup>) Derivatives

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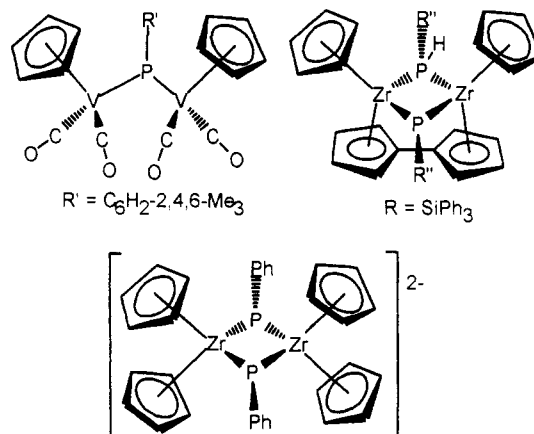
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The syntheses of the Zr primary phosphido complexes Cp<sub>2</sub>Zr(PH(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>))Cl (1) and Cp<sub>2</sub>Zr(PH(C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>))Cl (2) from the appropriate LiPHR and 1 equiv of Cp<sub>2</sub>ZrCl<sub>2</sub> are described. In reactions of PH<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>) or PH<sub>2</sub>SiMe<sub>3</sub> with Cp<sub>2</sub>ZrHCl, the respective bridging-phosphinidene derivatives (Cp<sub>2</sub>ZrCl)<sub>2</sub>(μ<sub>2</sub>-PC<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>) (3) and Cp<sub>2</sub>Zr(μ<sub>2</sub>-PSiPh<sub>3</sub>)(μ<sub>2</sub>-η<sup>1</sup>:η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)ZrCpCl (4) are obtained. These products are planar at phosphorus, indicative of Zr–P π-bonding. Reaction of PH(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>) with excess Cp<sub>2</sub>ZrHCl results in the formation of the planar, trinuclear phosphide complex (Cp<sub>2</sub>Zr)<sub>2</sub>(μ<sub>2</sub>-Cl)(μ<sub>3</sub>-P)(ZrCp<sub>2</sub>Cl) (5). This species 5 is also generated from the addition of PH(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>) to a mixture of Cp<sub>2</sub>ZrCl<sub>2</sub> and Mg. The mixed-valent product 5 is paramagnetic, exhibiting an EPR spectrum typical of Zr(III)–P species. Under similar reaction conditions, but with prolonged exposure to Mg, the diamagnetic phosphide derivative (CpZr(μ<sub>2</sub>-η<sup>1</sup>:η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>))<sub>3</sub>(μ<sub>3</sub>-P) (6) is obtained. In contrast to 5, the geometry at phosphorus in 6 is pyramidal. The terminal phosphinidene complexes Cp<sub>2</sub>Zr(P(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>))(PMe<sub>3</sub>) (7) and Cp<sub>2</sub>Zr(P(C<sub>6</sub>H<sub>2</sub>-Me<sub>3</sub>))(PMe<sub>3</sub>) (8) are generated via the reaction of 1 or 2 with KH and PMe<sub>3</sub>. The reaction mechanisms operative in the formation of these phosphinidene or phosphide complexes are discussed. MO calculations were performed on models of the terminal and bridging phosphinidene complexes as well as the planar and pyramidal trinuclear phosphide complexes. These studies provide insights regarding the structure and bonding in these compounds. Cumulatively, this work implies that phosphinidene species are generally highly reactive, exhibiting the ability to induce C–H and P–C activation. Crystallographic data are reported herein for compounds 1, 4, and 5. Compound 1: space group P2<sub>1</sub>/a with *a* = 16.179(15) Å, *b* = 10.167(4) Å, *c* = 17.515(6) Å, β = 105.88(5)°, *V* = 2771(5) Å<sup>3</sup>, and *Z* = 4. Compound 4: space group P1̄ with *a* = 11.159(8) Å, *b* = 16.434(13) Å, *c* = 10.490(8) Å, α = 95.49(7)°, β = 111.63(6)°, γ = 71.73°, *V* = 2771(5) Å<sup>3</sup>, and *Z* = 2. Compound 5: space group P2<sub>1</sub>/a with *a* = 15.683(6) Å, *b* = 10.379(4) Å, *c* = 17.250(6) Å, β = 93.28(4)°, *V* = 2802(2) Å<sup>3</sup>, and *Z* = 4.

## Introduction

Transition-metal–ligand multiple bonded systems have been a subject of interest over the past 20 years.<sup>1</sup> More recently this interest has focused on related early-metal compounds. Several groups have studied early-metal–oxide (M=O),<sup>2</sup> –sulfide (M=S),<sup>3</sup> and –imide (M=NR)<sup>4</sup> systems, all of which have proved highly reactive. In some instances, such compounds evoke C–H activation, while others act as synthons to a variety of organic derivatives via reaction with organic substrates. Related early-metal phosphinidenes (i.e. M=PR) have also been the subject of recent efforts. The first fully characterized terminal phosphinidene complex, Cp<sub>2</sub>Mo(PC<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>), was

reported by Lappert and co-workers.<sup>5</sup> The related bridged complex (CpV(CO)<sub>2</sub>)<sub>2</sub>(PR), described by Cowley et al.,<sup>6</sup>



was the first phosphinidene derivative of the group V metals. We subsequently described the synthesis of the related group IV metal species (Cp<sub>2</sub>ZrCl)<sub>2</sub>(PR') (R' = C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>) prepared by oxidative addition of P–H bonds

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to Zr(II).<sup>7</sup> Via a related synthesis, the neutral mixed-valent Zr(IV)/Zr(III) species [(CpZr)<sub>2</sub>(PSiPh<sub>3</sub>)(PHSiPh<sub>3</sub>)-(C<sub>10</sub>H<sub>8</sub>)] has been prepared,<sup>8</sup> while metathetical reactions have been used to prepare the dimeric Zr(III) phosphinidene anions [Cp<sub>2</sub>Zr(PPh)]<sub>2</sub><sup>2-</sup> and [(Cp<sub>2</sub>Zr)<sub>2</sub>(PPh)(PPh)]<sup>-</sup>.<sup>8,9</sup> Mononuclear early-metal phosphinidenes have proved more difficult to access, although transient mononuclear Zr-phosphinidene species, Cp\*<sub>2</sub>Zr(PR') (R' = C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>), are generated from Zr(IV) diphosphido derivatives.<sup>10</sup> The Zr=P double bond in this transient phosphinidene is reactive, undergoing reactions with both P-H and internal C-H bonds as well as cycloaddition and insertion of acetonitrile.<sup>10</sup> In a related system, intervention by PMe<sub>3</sub> results in the trapping of the terminal phosphinidene complex Cp<sub>2</sub>Zr(PR\*)(PMe<sub>3</sub>) (R\* = C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>).<sup>11</sup> In this paper, we examine synthetic routes to mononuclear and bridging phosphinidenes employing sterically demanding phosphines. In some instances, the use of such bulky reagents induces P-C bond cleavage, yielding trinuclear Zr-phosphide (P<sup>3-</sup>) derivatives.<sup>12</sup> Some of the mechanistic aspects of this chemistry are considered. Molecular orbital (MO) calculations are also described, as they provide some insight regarding the structure of mononuclear and bridging phosphinidene (PR<sup>2-</sup>) complexes as well as the phosphide (P<sup>3-</sup>) species.

## Experimental Section

**General Data.** All preparations were done under an atmosphere of dry, O<sub>2</sub>-free N<sub>2</sub>, employing either Schlenk-line techniques or a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N<sub>2</sub> and degassed by the freeze-thaw method at least three times prior to use. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker AC-300 operating at 300, 75, and 81 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to SiMe<sub>4</sub> and 85% H<sub>3</sub>PO<sub>4</sub>, respectively. X-Band EPR spectra were recorded on a Bruker EPS-300e 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<sub>2</sub>ZrHCl and Cp<sub>2</sub>ZrCl<sub>2</sub> were purchased from the Aldrich Chemical Co. The primary phosphines PH<sub>2</sub>SiPh<sub>3</sub>, PH<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>), and PH<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>) were purchased from Quantum Design Inc.

**Synthesis of Cp<sub>2</sub>Zr(PH(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>))Cl (1) and Cp<sub>2</sub>Zr(PH(C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>))Cl (2).** These compounds were prepared in a similar manner; thus, one representative preparation is described. To a 5-mL THF solution of PH<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>) (278 mg, 1.00 mmol) was added 1 equiv of *n*-BuLi in hexane. The solution was stirred for several hours at 25 °C and subsequently filtered. Cp<sub>2</sub>ZrCl<sub>2</sub> (292 mg, 1.00 mmol) was added, and the solution became red-brown immediately. The mixture was stirred for 30 min and allowed to stand overnight. The solution was filtered, the volume was reduced, and pentane was allowed to diffuse slowly into the mixture. Orange-brown crystals of 1 were deposited in 90% yield. 1: <sup>31</sup>P{<sup>1</sup>H} NMR (THF, 25 °C, δ) 83.2 (d, |J<sub>P-H</sub>| = 269 Hz); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, δ) 7.53 (br s, 2H, Ph), 5.65 (s, 10H, Cp), 4.08 (d, 1H, PH, |J<sub>P-H</sub>| = 269 Hz), 1.55 (s, 9H, Me), 1.31 (s, 18H, Me); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, δ) 130.5, 129.6, 127.1, 111.5, 109.2, 32.0, 31.9, 30.4. Anal. Calcd for C<sub>28</sub>H<sub>40</sub>-CIPZr: C, 62.95; H, 7.55. Found: C, 62.65; H, 7.45. 2: yield

90%; <sup>31</sup>P{<sup>1</sup>H} NMR (THF, 25 °C, δ) 43.0 (d, |J<sub>P-H</sub>| = 292 Hz); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, δ) 6.90 (s, 2H, Ph), 5.68 (d, 10H, Cp, |J<sub>P-H</sub>| = 12.0 Hz), 4.55 (d, 1H, PH, |J<sub>P-H</sub>| = 292 Hz), 2.44 (s, 6H, Me), 2.20 (s, 3H, Me); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, δ) 129.7, 129.6, 129.1, 113.1, 110.8, 23.4, 21.7. Anal. Calcd for C<sub>19</sub>H<sub>22</sub>CIPZr: C, 55.93; H, 5.43. Found: C, 55.80; H, 5.35.

**Synthesis of (Cp<sub>2</sub>ZrCl)<sub>2</sub>(μ<sub>2</sub>-PC<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>) (3).** (i) Cp<sub>2</sub>ZrCl<sub>2</sub> (292 mg, 1.00 mmol) was dissolved in 4 mL of THF and excess Mg turnings were added. After it was stirred for 1 h, the solution was filtered and PH<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>) (76 mg, 0.50 mmol) was added. The solution became dark green gradually. The mixture was stirred for 1 h and the volume reduced by half. When this mixture stood overnight, dark green crystals of 3 were deposited in 85% yield.

(ii) To a THF (1 mL) solution of 2 (102 mg, 0.25 mmol) was added Cp<sub>2</sub>ZrHCl (65 mg, 0.25 mmol) at 25 °C. After the mixture stood for 30 min, monitoring the reaction by <sup>31</sup>P{<sup>1</sup>H} NMR revealed the quantitative formation of 3: <sup>31</sup>P{<sup>1</sup>H} NMR (THF, 25 °C, δ) 325.5 (s); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, δ) 6.70 (s, 2H, Ph), 6.01 (s, 20H, Cp), 2.20 (s, 6H, CH<sub>3</sub>), 2.08 (s, 3H, CH<sub>3</sub>). Anal. Calcd for C<sub>29</sub>H<sub>31</sub>Cl<sub>2</sub>PZr<sub>2</sub>: C, 52.47; H, 4.71. Found: C, 52.20; H, 4.60.

**Synthesis of Cp<sub>2</sub>Zr(μ<sub>2</sub>-PSiPh<sub>3</sub>)(μ<sub>2</sub>-η<sup>1</sup>:η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)/ZrCpCl (4).** To a suspension of Cp<sub>2</sub>ZrHCl (258 mg, 1.00 mmol) in toluene was added PH<sub>2</sub>SiPh<sub>3</sub> (146 mg, 0.50 mmol). The mixture was stirred overnight, during which time the solution became blue-black. The solution was filtered and allowed to stand overnight. Blue-black crystals of 4 were deposited: yield 45%; <sup>31</sup>P{<sup>1</sup>H} NMR (THF, 25 °C, δ) 243.5 (s); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, δ) 7.95-7.93 (m, 5H, Ph), 7.29-7.23 (m, 10H, Ph), 6.57 (m, 1H, Cp), 6.05 (m, 1H, Cp), 6.00 (s, 5H, Cp), 5.75 (s, 5H, Cp), 5.70 (s, 5H, Cp), 5.38 (m, 1H), 4.52 (m, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, δ) 136.63, 135.03, 129.28, 127.91, 111.49, 110.74, 110.57, 110.18, 108.67, 107.60. Anal. Calcd for C<sub>38</sub>H<sub>34</sub>CIPZr<sub>2</sub>: C, 61.72; H, 4.63. Found: C, 61.50; H, 4.50.

**Synthesis of (Cp<sub>2</sub>Zr)<sub>2</sub>(μ<sub>2</sub>-Cl)(μ<sub>3</sub>-P)(ZrCp<sub>2</sub>Cl) (5).** (i) To a 2-mL THF solution of PH<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>) (140 mg, 0.50 mmol) was added Cp<sub>2</sub>ZrHCl (258 mg, 1.00 mmol) at 25 °C. The solution became red-brown immediately. The mixture was stirred for 30 min and allowed to stand overnight. The solution was filtered, the volume was reduced, and pentane was allowed to diffuse slowly into the mixture. Dark purple crystals of 5 were deposited in 35% yield.

(ii) Cp<sub>2</sub>ZrCl<sub>2</sub> (292 mg, 1.00 mmol) was dissolved in THF (3 mL), and excess Mg turnings were added. The resulting dark brown solution was stirred for 1 h and then filtered. PH<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>) (140 mg, 0.50 mmol) was added. Stirring was continued for a further 1 h and the solution allowed to stand overnight. Green crystalline needles were deposited. This material was recrystallized from benzene/pentane to give dark purple crystals of 5: yield 40%; EPR (THF, 25 °C) *g* = 2.001, ⟨*a*<sub>P</sub>⟩ = 22.8 G; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, δ) 5.96 (s). Anal. Calcd for C<sub>30</sub>H<sub>30</sub>Cl<sub>2</sub>PZr<sub>3</sub>: C, 47.03; H, 3.95. Found: C, 46.89; H, 3.50.

**Synthesis of (CpZr(μ<sub>2</sub>-η<sup>1</sup>:η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>))<sub>3</sub>(μ<sub>3</sub>-P) (6).** (i) To a 2-mL THF solution of Cp<sub>2</sub>ZrCl<sub>2</sub> (146 mg, 0.50 mmol) was added excess Mg turnings. The solution was stirred for 1 h, and then PH<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>) (140 mg, 0.50 mmol) was added. The mixture was allowed to stand overnight. Excess Mg turnings were then removed by filtration, the solvent was removed, and the residue was extracted into benzene. Slow diffusion of hexane into the solution yielded 6 in 10% yield.

(ii) To a THF solution of 1 (267 mg, 0.50 mmol) was added Cp<sub>2</sub>ZrCl<sub>2</sub> (292 mg, 1.00 mmol) and excess Mg turnings. The mixture was stirred vigorously for 2 h and then allowed to stand overnight. The solution was filtered, the solvent was removed, and the residue was extracted into benzene. Slow diffusion of hexane into the solution yielded 6 in 20% yield: <sup>31</sup>P{<sup>1</sup>H} NMR (THF, 25 °C, δ) 782.6 (s); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, δ) 6.21 (s, 5H, Cp), 6.15 (m, 1H, Cp), 5.62 (m, 1H, Cp), 5.19 (m, 1H, Cp), 4.80 (m, 1H, Cp). Anal. Calcd for C<sub>30</sub>H<sub>27</sub>PZr<sub>3</sub>: C, 52.06; H, 3.93. Found: C, 51.90; H, 3.80.

**Generation of Cp<sub>2</sub>Zr(P(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>))(PMe<sub>3</sub>) (7) and Cp<sub>2</sub>Zr(P(C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>))(PMe<sub>3</sub>) (8).** To a THF solution (4 mL) of 1 (267 mg, 0.50 mmol) was added excess KH and PMe<sub>3</sub>.

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Table 1. Crystallographic Parameters

	1	4	5
formula	C <sub>28</sub> H <sub>40</sub> ClPZr	C <sub>38</sub> H <sub>35</sub> ClPSiZr <sub>2</sub>	C <sub>30</sub> H <sub>30</sub> Cl <sub>2</sub> PZr <sub>3</sub>
fw	534.27	768.65	766.11
cryst color, form	red-black blocks	black blocks	black blocks
cryst size	0.32 × 0.30 × 0.28	0.30 × 0.32 × 0.22	0.25 × 0.37 × 0.40
a (Å)	16.179(15)	11.159(8)	15.683(6)
b (Å)	10.167(4)	16.434(13)	10.379(4)
c (Å)	17.515(6)	10.490(8)	17.250(9)
α (deg)		95.49(7)	
β (deg)	105.88(5)	111.63(6)	93.28(4)
γ (deg)		71.73(6)	
cryst syst	monoclinic	triclinic	monoclinic
space group	P2 <sub>1</sub> /a (No. 14)	P $\bar{1}$ (No. 2)	P2 <sub>1</sub> /a (No. 14)
V (Å <sup>3</sup> )	2771(5)	1698(2)	2804(2)
D <sub>calcd</sub> (g cm <sup>-3</sup> )	1.28	1.50	1.81
Z	4	2	4
abs coeff, μ (cm <sup>-1</sup> )	5.63	8.00	13.60
radiation (λ (Å))	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
temp (°C)	24	24	-40
scan speed (deg min <sup>-1</sup> )	8.0 (θ/2θ) (1-3 scans)	8.0 (θ/2θ) (1-3 scans)	8.0 (θ/2θ) (1-3 scans)
scan range (deg)	1.0 below Kα <sub>1</sub> to 1.0 above Kα <sub>2</sub>	1.0 below Kα <sub>1</sub> to 1.0 above Kα <sub>2</sub>	1.0 below Kα <sub>1</sub> to 1.0 above Kα <sub>2</sub>
bkgd/scan ratio	0.5	0.5	0.5
no. of data collected	5174	3652	5255
2θ range (deg)	4.5-50.0	4.5-45.0	4.5-50.0
index range	h,k,±l	±h,±k,l	h,k,±l
no. of data F <sub>o</sub> <sup>2</sup> > 3σ(F <sub>o</sub> <sup>2</sup> )	1966	1963	2342
no. of variables	280	198	175
transmissn factors	0.940-1.000	0.751-1.000	0.454-1.000
R (%) <sup>a</sup>	5.10	8.21	8.22
R <sub>w</sub> (%) <sup>a</sup>	3.07	6.98	5.74
largest Δ/σ	0.001	0.002	0.001
goodness of fit	1.42	2.98	2.63

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|; R_w = [\sum (|F_o| - |F_c|)^2 / \sum |F_o|^2]^{0.5}$$

The solution was stirred for 1 h. Monitoring of the reaction by <sup>31</sup>P{<sup>1</sup>H} NMR revealed the formation of 7 in 40% yield. 7: <sup>31</sup>P{<sup>1</sup>H} NMR (THF, 25 °C, δ) 792.7 (d, |J<sub>P-P</sub>| = 21 Hz), -10.9 (d, |J<sub>P-P</sub>| = 21 Hz). 8: yield >90%; <sup>31</sup>P{<sup>1</sup>H} NMR (THF, 25 °C, δ) 766.1 (d, |J<sub>P-P</sub>| = 24 Hz), -2.3 (d, |J<sub>P-P</sub>| = 24 Hz).

**X-ray Data Collection and Reduction.** X-ray quality crystals of 1, 4, and 5 were obtained directly from the preparations as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O<sub>2</sub>-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC6 diffractometer equipped with graphite-monochromated 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. Ultimately, 25 reflections (20° < 2θ < 25°) were used to obtain the final lattice parameters and the orientation matrices. Crystal data are summarized in Table 1. The data sets were collected in three shells (4.5° < 2θ < 50.0°), and 3 standard reflections were recorded every 197 reflections. Fixed scan rates were employed. Up to 4 repetitive scans of each reflections at the respective scan rates were averaged to ensure meaningful 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 an SGI mainframe computer with remote X terminals. The reflections with F<sub>o</sub><sup>2</sup> > 3σF<sub>o</sub><sup>2</sup> were used in the refinements.

**Structure Solution and Refinement.** Non-hydrogen atomic scattering factors were taken from the literature tabulations.<sup>13,14</sup> The Zr atom positions were determined using direct methods employing either of the SHELX-86 direct-methods routines. 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(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup>, where the weight w is defined as 4F<sub>o</sub><sup>2</sup>/2σ(F<sub>o</sub><sup>2</sup>) and F<sub>o</sub> and F<sub>c</sub> are the observed and calculated structure factor amplitudes. In the final cycles of refinement the heavy atoms were assigned anisotropic temperature factors for each structure. In the case of 1, the carbon atoms were also refined anisotropically, whereas for 4 and 5 the carbon atoms were assigned isotropic thermal parameters so as to maintain a reasonable data to variable ratio. Empirical absorption corrections were applied to each of the data sets on the basis of ψ-scan data and by employing the software resident in the TEXSAN package. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C-H bond length of 0.95 Å. In the case of 1, the hydrogen atom on P was located in a difference Fourier map. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the atom to which they are bonded. The hydrogen atom contributions were calculated but not refined. The final values of R and R<sub>w</sub> are given in Table 1. The maximum Δ/σ values on any of the parameters in the final cycles of the refinement are also given in Table 1. The residual electron density was of no chemical significance. The following data are tabulated: positional parameters (Table 2) and selected bond distances and angles (Table 3). Hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as supplementary material.

**Molecular Orbital Calculations.** Extended Huckel (EH) and Fenske-Hall (FH) molecular orbital (MO) calculations were performed on a VAX 3520 workstation. EHMO calculations were performed by employing the implementation of FORTICON8 resident in the TRIBBL program package.<sup>15</sup> A detailed description of the FH nonempirical MO method has been described elsewhere.<sup>16</sup> Models were constructed on the basis of idealized geometries derived from the crystallographic data presented herein and elsewhere.

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(14) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

Table 2. Positional Parameters

atom	x	y	z	atom	x	y	z
Compound 1							
Zr(1)	0.88947(5)	0.23203(8)	0.90562(5)	C(14)	0.6404(7)	0.523(1)	0.4350(5)
Cl(1)	1.0476(1)	0.1963(2)	0.9355(1)	C(15)	0.9763(5)	0.4455(9)	0.6845(5)
P(1)	0.8791(2)	0.4448(2)	0.8272(1)	C(16)	1.0155(5)	0.316(1)	0.7201(6)
C(1)	0.8278(5)	0.4725(7)	0.7207(4)	C(17)	1.0163(6)	0.557(1)	0.7407(7)
C(2)	0.8758(5)	0.4465(7)	0.6651(4)	C(18)	1.0059(5)	0.470(1)	0.6104(6)
C(3)	0.8312(6)	0.4217(8)	0.5862(5)	C(19)	0.798(1)	0.250(4)	0.996(1)
C(4)	0.7445(5)	0.4350(8)	0.5586(4)	C(20)	0.826(2)	0.377(2)	0.9903(8)
C(5)	0.7009(5)	0.4809(8)	0.6103(5)	C(21)	0.909(2)	0.382(2)	1.024(1)
C(6)	0.7385(5)	0.5033(7)	0.6915(4)	C(22)	0.935(1)	0.265(3)	1.0523(6)
C(7)	0.6827(5)	0.5695(8)	0.7390(5)	C(23)	0.868(2)	0.183(2)	1.035(1)
C(8)	0.7256(5)	0.6956(8)	0.7791(5)	C(24)	0.847(1)	0.131(1)	0.7712(7)
C(9)	0.6641(5)	0.4720(9)	0.7997(5)	C(25)	0.775(1)	0.151(1)	0.788(1)
C(10)	0.5937(5)	0.609(1)	0.6859(5)	C(26)	0.774(1)	0.072(2)	0.849(1)
C(11)	0.6957(6)	0.404(1)	0.4713(5)	C(27)	0.848(2)	0.004(2)	0.871(1)
C(12)	0.6328(8)	0.293(1)	0.4726(6)	C(28)	0.891(1)	0.041(2)	0.817(1)
C(13)	0.7519(7)	0.365(1)	0.4214(6)				
Compound 4							
Zr(1)	0.6221(2)	0.8036(1)	0.2929(2)	C(18)	0.474(3)	0.603(2)	-0.182(3)
Zr(2)	0.5499(2)	0.7268(1)	-0.0706(2)	C(19)	0.609(3)	0.575(2)	-0.161(3)
Cl(1)	0.6897(7)	0.6652(4)	0.4169(6)	C(20)	0.685(3)	0.570(2)	-0.021(3)
P(1)	0.7492(6)	0.7555(4)	0.1275(6)	C(21)	0.987(2)	0.859(1)	0.206(2)
Si(1)	0.9567(6)	0.7506(4)	0.1532(6)	C(22)	0.922(2)	0.925(1)	0.111(2)
C(1)	0.644(2)	0.897(1)	0.497(2)	C(23)	0.931(2)	1.009(2)	0.140(2)
C(2)	0.635(2)	0.947(1)	0.389(2)	C(24)	1.023(2)	1.019(2)	0.275(2)
C(3)	0.759(2)	0.908(1)	0.367(2)	C(25)	1.088(2)	0.954(2)	0.368(2)
C(4)	0.837(2)	0.841(1)	0.453(2)	C(26)	1.072(2)	0.871(1)	0.332(2)
C(5)	0.761(2)	0.835(1)	0.537(2)	C(27)	1.078(2)	0.674(1)	0.298(2)
C(6)	0.433(2)	0.793(1)	0.069(2)	C(28)	1.221(2)	0.653(1)	0.318(2)
C(7)	0.406(2)	0.883(1)	0.101(2)	C(29)	1.318(2)	0.592(2)	0.410(2)
C(8)	0.377(2)	0.895(1)	0.222(2)	C(30)	1.285(2)	0.540(1)	0.478(2)
C(9)	0.386(2)	0.816(1)	0.268(2)	C(31)	1.146(2)	0.553(1)	0.450(2)
C(10)	0.417(2)	0.753(1)	0.179(2)	C(32)	1.053(2)	0.618(1)	0.362(2)
C(11)	0.508(3)	0.877(2)	-0.166(2)	C(33)	0.991(2)	0.719(1)	-0.011(2)
C(12)	0.381(3)	0.858(2)	-0.226(3)	C(34)	1.071(2)	0.758(1)	-0.052(2)
C(13)	0.406(3)	0.791(2)	-0.308(2)	C(35)	1.098(2)	0.730(2)	-0.173(2)
C(14)	0.538(3)	0.760(2)	-0.304(3)	C(36)	1.063(3)	0.667(2)	-0.241(3)
C(15)	0.597(3)	0.817(2)	-0.217(3)	C(37)	0.984(3)	0.626(2)	-0.210(3)
C(16)	0.596(3)	0.586(2)	0.050(2)	C(38)	0.952(2)	0.654(2)	-0.089(2)
C(17)	0.463(3)	0.607(2)	-0.052(3)				
Compound 5							
Zr(1)	0.6805(1)	0.2172(2)	0.1369(1)	C(13)	0.536(1)	-0.202(2)	0.124(1)
Zr(2)	0.5494(1)	-0.1321(2)	0.2635(1)	C(14)	0.503(1)	-0.075(2)	0.126(1)
Zr(3)	0.7492(1)	0.1840(2)	0.3375(1)	C(15)	0.430(1)	-0.079(2)	0.166(1)
Cl(1)	0.7956(3)	0.3274(5)	0.2252(3)	C(16)	0.468(2)	-0.224(2)	0.374(2)
Cl(2)	0.6769(3)	-0.2817(5)	0.2611(4)	C(17)	0.430(2)	-0.108(3)	0.357(2)
P(1)	0.6301(3)	0.0750(5)	0.2499(3)	C(18)	0.499(1)	-0.026(2)	0.386(1)
C(1)	0.545(1)	0.292(2)	0.066(1)	C(19)	0.571(1)	-0.097(2)	0.406(1)
C(2)	0.612(1)	0.384(2)	0.052(1)	C(20)	0.558(1)	-0.232(2)	0.400(1)
C(3)	0.632(1)	0.447(2)	0.120(2)	C(21)	0.693(1)	0.407(2)	0.374(1)
C(4)	0.577(1)	0.386(2)	0.178(1)	C(22)	0.626(1)	0.323(2)	0.385(1)
C(5)	0.531(1)	0.290(2)	0.144(1)	C(23)	0.656(1)	0.239(2)	0.447(1)
C(6)	0.739(1)	0.003(2)	0.091(1)	C(24)	0.737(1)	0.271(2)	0.474(1)
C(7)	0.807(1)	0.086(2)	0.100(1)	C(25)	0.760(1)	0.372(2)	0.427(1)
C(8)	0.799(1)	0.183(2)	0.048(1)	C(26)	0.838(1)	-0.004(2)	0.295(1)
C(9)	0.721(1)	0.163(2)	0.000(1)	C(27)	0.802(1)	-0.039(2)	0.365(1)
C(10)	0.683(1)	0.052(2)	0.029(1)	C(28)	0.835(1)	0.033(2)	0.426(1)
C(11)	0.415(1)	-0.205(2)	0.187(1)	C(29)	0.892(1)	0.117(2)	0.393(1)
C(12)	0.484(1)	-0.280(2)	0.163(1)	C(30)	0.892(1)	0.095(2)	0.316(1)

## Results and Discussion

**Synthesis.** The reaction of the bulky phosphides with  $\text{Cp}_2\text{ZrCl}_2$  affords the species  $\text{Cp}_2\text{Zr}(\text{PHR})\text{Cl}$  ( $\text{R} = \text{C}_6\text{H}_2\text{-}2,4,6\text{-}t\text{-Bu}_3$ , **1**;  $\text{R} = \text{C}_6\text{H}_2\text{-}2,4,6\text{-Me}_3$ , **2**). These compounds exhibit singlets in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 83.2 and 43.0 ppm, respectively, as well as the anticipated resonances in the  $^1\text{H}$  NMR spectra. Coupling of a single proton to P in the  $^{31}\text{P}$  NMR spectrum confirms the formulation as primary phosphide derivatives. These compounds are found to be quite stable in solution and in the solid state in the absence of air or moisture. This is in contrast to related phosphide derivatives in which the substituents are less sterically demanding. In those cases, species such as  $\text{Cp}_2\text{Zr}(\text{PR}_2)\text{Cl}$  are prone to ligand redistribution reac-

tions, affording  $\text{Cp}_2\text{ZrCl}_2$  and  $\text{Cp}_2\text{Zr}(\text{PR}_2)_2$ .<sup>17</sup> The absence of such redistribution in the present systems is presumably attributable to the unfavorable steric crowding associated with the diphosphide species  $\text{Cp}_2\text{Zr}(\text{PHR})_2$ . This is also consistent with the recently demonstrated reactivity of  $\text{Cp}_2\text{Zr}(\text{PHR})_2$ , in which such species readily eliminate  $\text{PH}_2\text{R}$ , affording access to mononuclear phosphinidene derivatives.<sup>10</sup> The species **1** is also generated by the elimination of  $\text{H}_2$  in the reaction of equal molar amounts of  $\text{PH}_2\text{R}$  and  $\text{Cp}_2\text{ZrHCl}$ , although this synthetic route is not clean, affording additional products (vide infra).

The compound  $(\text{Cp}_2\text{ZrCl})_2(\text{PC}_6\text{H}_2\text{-}2,4,6\text{-Me}_3)$  (**3**) was

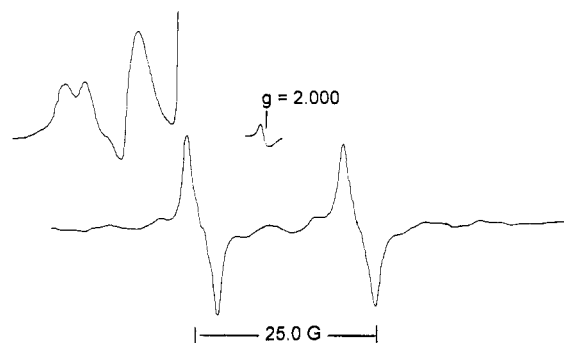
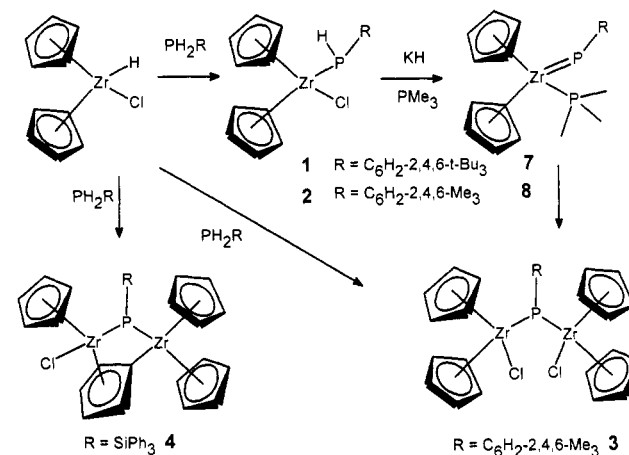
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**Table 3. Selected Bond Distances (Å) and Angles (deg)**

Compound 1			
Zr(1)–Cl(1)	2.494(3)	Zr(1)–P(1)	2.543(3)
Zr(1)–C(19)	2.45(2)	Zr(1)–C(20)	2.51(2)
Zr(1)–C(21)	2.52(2)	Zr(1)–C(22)	2.49(1)
Zr(1)–C(23)	2.43(2)	Zr(1)–C(24)	2.49(1)
Zr(1)–C(25)	2.50(1)	Zr(1)–C(26)	2.46(2)
Zr(1)–C(27)	2.44(2)	Zr(1)–C(28)	2.50(2)
P(1)–C(1)	1.844(7)		
Cl(1)–Zr(1)–P(1)	98.61(9)	Zr(1)–P(1)–C(1)	128.4(2)
Compound 4			
Zr(1)–Cl(1)	2.490(6)	Zr(1)–P(1)	2.549(6)
Zr(1)–C(1)	2.49(2)	Zr(1)–C(2)	2.50(2)
Zr(1)–C(3)	2.54(2)	Zr(1)–C(4)	2.59(2)
Zr(1)–C(5)	2.55(2)	Zr(1)–C(6)	2.55(2)
Zr(1)–C(7)	2.55(2)	Zr(1)–C(8)	2.54(2)
Zr(1)–C(9)	2.49(2)	Zr(1)–C(10)	2.51(2)
Zr(2)–P(1)	2.559(6)	Zr(2)–C(6)	2.29(2)
Zr(2)–C(11)	2.59(2)	Zr(2)–C(12)	2.59(3)
Zr(2)–C(13)	2.53(2)	Zr(2)–C(14)	2.51(3)
Zr(2)–C(15)	2.53(3)	Zr(2)–C(16)	2.56(2)
Zr(2)–C(17)	2.50(3)	Zr(2)–C(18)	2.47(3)
Zr(2)–C(19)	2.55(3)	Zr(2)–C(20)	2.53(2)
P(1)–Si(1)	2.206(8)	Si(1)–C(21)	1.91(2)
Si(1)–C(27)	1.87(2)	Si(1)–C(33)	1.88(2)
Cl(1)–Zr(1)–P(1)	99.7(2)	P(1)–Zr(2)–C(6)	82.8(6)
Zr(1)–P(1)–Zr(2)	95.2(2)	Zr(1)–P(1)–Si(1)	130.0(3)
Zr(2)–P(1)–Si(1)	134.6(3)	P(1)–Si(1)–C(21)	111.2(7)
P(1)–Si(1)–C(27)	108.6(7)	P(1)–Si(1)–C(33)	111.2(7)
Compound 5			
Zr(1)–Cl(1)	2.563(5)	Zr(1)–P(1)	2.605(5)
Zr(2)–Cl(2)	2.534(5)	Zr(2)–P(1)	2.512(5)
Zr(3)–Cl(1)	2.581(5)	Zr(3)–P(1)	2.594(6)
Zr(1)–C(1)	2.51(2)	Zr(1)–C(2)	2.47(2)
Zr(1)–C(3)	2.52(2)	Zr(1)–C(4)	2.51(2)
Zr(1)–C(5)	2.48(2)	Zr(1)–C(6)	2.55(2)
Zr(1)–C(7)	2.52(2)	Zr(1)–C(8)	2.49(2)
Zr(1)–C(9)	2.53(2)	Zr(1)–C(10)	2.53(2)
Zr(2)–C(11)	2.54(2)	Zr(2)–C(12)	2.49(2)
Zr(2)–C(13)	2.51(2)	Zr(2)–C(14)	2.52(2)
Zr(2)–C(15)	2.50(2)	Zr(2)–C(16)	2.54(3)
Zr(2)–C(17)	2.54(3)	Zr(2)–C(18)	2.55(2)
Zr(2)–C(19)	2.49(2)	Zr(2)–C(20)	2.57(2)
Zr(3)–C(21)	2.56(2)	Zr(3)–C(22)	2.59(2)
Zr(3)–C(23)	2.53(2)	Zr(3)–C(24)	2.54(2)
Zr(3)–C(25)	2.49(2)	Zr(3)–C(26)	2.52(2)
Zr(3)–C(27)	2.49(2)	Zr(3)–C(28)	2.52(2)
Zr(3)–C(29)	2.49(2)	Zr(3)–C(30)	2.47(2)
Cl(1)–Zr(1)–P(1)	92.4(2)	Cl(2)–Zr(2)–P(1)	96.9(2)
Cl(1)–Zr(3)–P(1)	92.2(2)	Zr(1)–Cl(1)–Zr(3)	88.3(2)
Zr(1)–P(1)–Zr(2)	137.0(2)	Zr(1)–P(1)–Zr(3)	87.1(2)
Zr(2)–P(1)–Zr(3)	132.0(2)		

prepared in one of several ways. In our original communication involving P–H activation,<sup>7</sup> we described the reaction of  $\text{Cp}_2\text{ZrCl}_2$ , Mg, and  $\text{PH}_2\text{C}_6\text{H}_2\text{-2,4,6-Me}_3$  as a synthetic route to **3** in 85% yield. This species **3** exhibits a downfield singlet  $^{31}\text{P}$  resonance at 325.5 ppm, which is consistent with the bridging nature of the phosphinidene moiety. As previously described, the X-ray crystallographic data confirm the planarity of the coordination sphere about P and establish that the Zr–P distances are 2.597(6) and 2.637(6) Å and that the  $\text{PZrCl}$  planes are canted by  $54.92^\circ$  with respect to each other. Subsequently, it was found that the reaction of **2** with excess  $\text{Cp}_2\text{ZrHCl}$  also yields **3** quantitatively.

In a similar reaction of  $\text{PH}_2\text{SiPh}_3$  with excess  $\text{Cp}_2\text{ZrHCl}$  in toluene, the compound **4** was isolated.  $^1\text{H}$  NMR data were consistent with the presence of a bridging  $\eta^1:\eta^5$ -cyclopentadienyl ring as well as three other  $\eta^5$ -cyclopentadienyl ring environments. A singlet  $^{31}\text{P}$  resonance at 243.5 ppm suggested the presence of a bridging phosphinidene moiety. The fact that **4** exhibits a  $^{31}\text{P}$  resonance upfield of **3** is consistent with the presence of the  $\text{SiPh}_3$

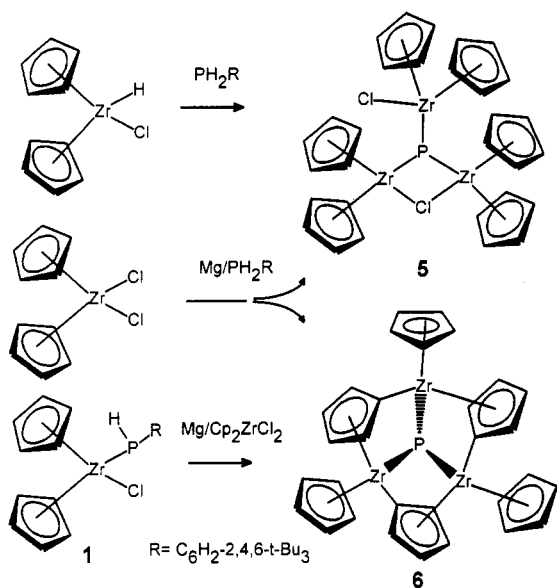
**Figure 1.** EPR spectrum of **7** in THF at 25 °C.**Scheme 1. Synthetic Routes to 1–4, 7, and 8**

substituent. X-ray data (vide infra) provided the unambiguous characterization of **4** as  $\text{Cp}_2\text{Zr}(\mu_2\text{-PSiPh}_3)(\mu_2\text{-}\eta^1\text{-}\eta^5\text{-C}_5\text{H}_4)\text{ZrCpCl}$  (Scheme 1).

In a similar reaction employing the more sterically demanding phosphine  $\text{PH}_2(\text{C}_6\text{H}_2\text{-2,4,6-}t\text{-Bu}_3)$  and excess  $\text{Cp}_2\text{ZrHCl}$ , the paramagnetic species **5** is isolated in 35% yield. Compound **5** exhibits a simple doublet resonance in the EPR spectrum at  $g = 2.001$  with a hyperfine coupling constant of 22.8 G, consistent with the presence of a Zr(III)–P moiety (Figure 1). The formulation of **5** was determined via an X-ray crystallographic study to be  $(\text{Cp}_2\text{-Zr})_2(\mu_2\text{-Cl})(\mu_3\text{-P})(\text{ZrCp}_2\text{Cl})$  (vide infra). In addition to **5**, **1** is also identified in this reaction mixture. An alternate route to **5** involves the reaction of  $\text{Cp}_2\text{ZrCl}_2$  with excess Mg and  $\text{PH}_2(\text{C}_6\text{H}_2\text{-2,4,6-}t\text{-Bu}_3)$ . In this latter synthesis, the paramagnetic product **5** is isolated in 40% yield when  $\text{Cp}_2\text{ZrCl}_2$  and Mg are stirred initially for 1 h and the excess Mg is removed by filtration prior to the addition of phosphine. Prolonged exposure of the mixture to Mg in THF affords the diamagnetic product **6**, albeit in low yield (10%) (Scheme 2). This species **6** exhibits a  $^{31}\text{P}$  NMR resonance at 782.6 ppm, and the  $^1\text{H}$  NMR data imply P–C bond cleavage has also occurred in this case, as no resonances attributable to the phosphine substituent were observed. The  $^1\text{H}$  NMR data indicated the presence of both  $\eta^5$ - and  $\eta^1:\eta^5$ -cyclopentadienyl rings. The downfield nature of the  $^{31}\text{P}$  resonance is suggestive of a bare pyramidal P atom bound to three metal atoms.<sup>18</sup> We have previously communicated the characterization of **6** as  $(\text{CpZr}(\mu_2\text{-}\eta^1:\eta^5\text{-C}_5\text{H}_4))_3(\mu_3\text{-P})$  by X-ray methods. The data showed that **6** has 3-fold symmetry through a pyramidal P atom which caps a triangle of Zr atoms, each of which

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Scheme 2. Synthetic Routes to 5 and 6

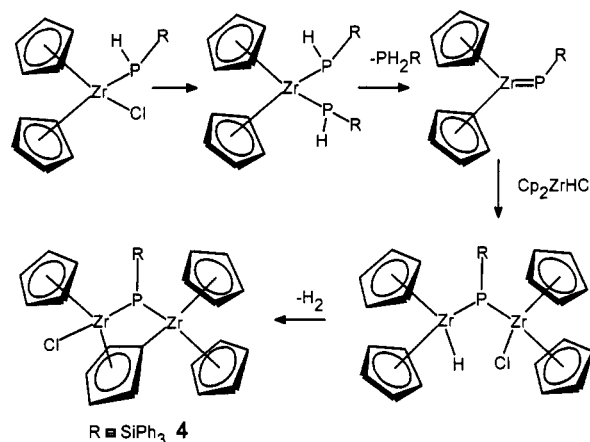


are bound to two  $\eta^5$ - and one  $\eta^1$ -cyclopentadienyl ring. Compound 6 is also isolable in slightly better yield (20%) from the reaction of 1, Mg, and excess  $Cp_2ZrCl_2$ .

As indicated above, mononuclear phosphinidene complexes are rare. It has been previously shown that such Zr species can be generated from the zirconocene diphosphides, and the structural characterization of  $Cp_2Zr(PC_6H_2-2,4,6-t-Bu_3)(PMe_3)$  (7) has been described. An alternative method of generation of 7 involves the reaction of 1 with KH in the presence of  $PMe_3$ . In a similar manner, the species  $Cp_2Zr(P(C_6H_2-2,4,6-Me_3))(PMe_3)$  (8) (Scheme 1) is generated from 2, as indicated by the  $^{31}P$  NMR resonances at 766.1 and  $-2.3$  ppm with a P—P coupling constant of 24 Hz. The downfield resonance is attributable to the  $sp^2$  P of the phosphinidene fragment. Although 8 could be generated and spectroscopically characterized in this manner, attempts to isolate this compound were unsuccessful. The apparent instability of 8 may reflect the greater accessibility of the Zr=P double bond in 8. The generation of 7 and 8 via reaction of 1 and 2 with KH is foreshadowed in the literature, as Vaughan and Hillhouse<sup>19</sup> described reactions of the related hafnium phosphides  $Cp_2Hf(PHR)Cl$  with  $NaN(SiMe_3)_2$ . In those cases, NMR data suggested the formation of hafnium phosphinidene complexes but these phosphinidene products were neither trapped or isolated.

**Mechanistic Considerations.** We previously suggested that formation of 3 from reaction of  $Cp_2ZrCl_2$ , Mg, and  $PH_2R$  involves a transient terminal phosphinidene species generated by the oxidative addition of P—H bonds to *in situ* generated Zr(II) and subsequent loss of  $H_2$ .<sup>7</sup> This mechanism is supported herein, as addition of  $Cp_2ZrCl_2$  to a solution of 8 results in the quantitative generation of 3. Isolation of 3 from reaction of  $Cp_2ZrHCl$  and phosphine suggests an alternate route to 3 involving the intermediacy of the phosphide complex 2. This is further supported by the direct acidolysis of the P—H bond of 2 by  $Cp_2ZrHCl$ . Given this view, one might expect the parallel reaction of  $PH_2SiPh_3$  with  $Cp_2ZrHCl$  to yield a  $SiPh_3$  analog of 3; however, the species 4 is derived. In a consideration of 4 from a retro-synthetic perspective, the final steps are suggested to involve addition of  $Cp_2ZrHCl$  to the transient phosphinidene  $Cp_2ZrPSiPh_3$ , followed by

Scheme 3. Proposed Mechanism of Formation of 4



activation of a cyclopentadienyl C—H bond. This view leads one to query the manner of generation of such transient phosphinidene. Initial acidolysis affords the phosphide complex  $Cp_2ZrCl(PSiPh_3)$ . This species may be unstable with respect to ligand redistribution, thus providing an avenue to  $Cp_2Zr(PSiPh_3)_2$  and  $Cp_2ZrCl_2$ . Such diphosphides are known to lose phosphine and generate transient terminal phosphinidenes. This mechanism (Scheme 3) for the formation of 4 is supported by the observation of  $^1H$  NMR resonances attributable to  $Cp_2ZrCl_2$  in the reaction mixture. Moreover, this postulate is consistent with the demonstrated reactivity of complexes containing terminal phosphinidene moieties.<sup>8</sup>

Reactions involving the more sterically demanding (*tert*-butylphenyl)phosphine afford the trizirconium phosphide derivatives 5 and 6. The mechanisms of formation of these species clearly involve P—C bond cleavage but are otherwise unknown. Carty and co-workers<sup>20</sup> have shown that a weak interaction of the P—C bond with an electron-deficient Ru center in  $Ru_3(CO)_9(\mu-PPh_2)(\mu-H)$  foreshadows the P—C bond cleavage which occurs on heating to give  $Ru_5(CO)_{16}(\mu-PPh_2)(\mu-P)$ . While the Lewis acidity of the Zr center may facilitate P—C bond activation in a similar fashion, it is not precisely clear how P—C bond activation occurs in the present systems. It is tempting to propose a role for phosphinidene intermediates in the course of these reactions. Monitoring of the reactions leading to 5 by  $^{31}P$  NMR provided no information as to the nature of the intermediates; however, a  $^{31}P$  NMR resonance at 630 ppm suggests a phosphinidene intermediate was present in the reaction mixtures, yielding 6. The natures of this and other intermediates in these and other P—C bond activation reactions remain unclear and are the subject of ongoing study.<sup>21</sup>

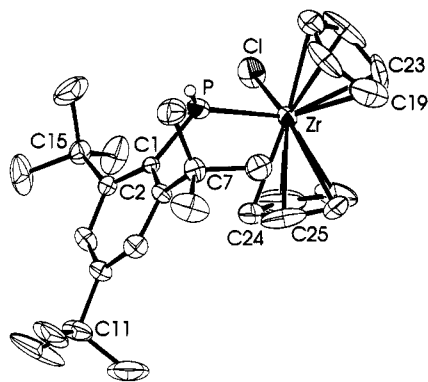
**Structural Studies.** An X-ray crystallographic study of 1 showed that the Zr center adopts a pseudo-tetrahedral coordination sphere with two  $\eta^5$ -cyclopentadienyl rings, a chloride and the primary phosphide ligands (Figure 2). The Zr—P bond distance in 1 is 2.543(3) Å, which is comparable to the Zr—P distances found in  $Cp_2ZrCl(P(C_6H_2-2,4,6-t-Bu_3)SiMe_3)$  (2.541(4) Å)<sup>22</sup> and  $Cp_2ZrCl(P(SiMe_3)_2)$  (2.547(6) Å) and shorter than the Zr—P distances found in  $(C_5H_4SiMe_3)_2Zr(PPh_2)_2$  (2.694(3),

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**Figure 2.** ORTEP drawing of **1** (30% thermal ellipsoids are shown). All hydrogen atoms except for those on P are omitted for clarity.

2.536(3) Å<sup>23</sup> and Cp<sub>2</sub>ZrMe(P(SiMe<sub>3</sub>)<sub>2</sub>) (2.629(3) Å).<sup>24</sup> The Zr—P—C angle of 128.4(2)° and the location of the hydrogen atom suggest a planar geometry about P consistent with Zr—P multiple bonding. This view is also consistent with the fact that the Zr—P bond distance in **1** is significantly shorter than those reported for other Zr(IV) phosphide species where the geometry about P is known to be pyramidal (Table 4).<sup>11,23–26</sup> The phenyl ring is oriented away from the cyclopentadienyl rings, as expected, and the Zr—Cl distance of 2.494(3) Å and the P—Zr—Cl angle of 98.61(9)° are similar to those reported for the related species Cp<sub>2</sub>ZrCl(P(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>-SiMe<sub>3</sub>)).<sup>22</sup>

The solid-state structure of **4** was determined crystallographically. In this complex two pseudotetrahedral Zr centers are bridged by a phosphinidene moiety and an η<sup>1</sup>:η<sup>5</sup>-cyclopentadienyl ring (Figure 3). The coordination sphere of the Zr center bonded to the bridging cyclopentadienyl ring in an η<sup>1</sup> fashion is completed by two η<sup>5</sup>-cyclopentadienyl rings. A chloride and an η<sup>5</sup>-cyclopentadienyl ring complete the coordination sphere of the other Zr center. The Zr—P bond distances in **4** are Zr(1)—P = 2.549(6) Å and Zr(2)—P = 2.559(6) Å. These are shorter than the analogous distances in **3**, suggesting a slightly higher degree of π-interaction between the P and Zr atoms in **4**. The geometry about the P atom in **4** is planar, as the angles give a sum of 359.8° with a Zr—P—Zr angle of 95.2(2)°. Participation by the SiPh<sub>3</sub> in P—Si dπ—pπ bonding may augment and thus enhance the Zr—P π-interaction. The Zr(2)—C(6), Zr(1)—Cl, and P—Si distances of 2.29(2), 2.490(6), and 2.206(8) Å, respectively, are typical. The Zr...Zr separation in **4** is 3.773(3) Å. As expected, this is greater than the Zr...Zr distances seen in Zr(III) phosphide dimers, where some degree of metal-metal interaction has been implied.<sup>8</sup>

The molecular structure of **5** was confirmed crystallographically. An ORTEP drawing of **5** is shown in Figure 4. The central atom of the molecule is a planar P atom which is bonded to three Zr atoms, each of which is also bonded to two η<sup>5</sup>-cyclopentadienyl rings. Two of the Zr atoms are also bridged by a chloride ion, while the third

Zr center is bonded to a terminal chlorine atom. Thus, the geometry of the coordination spheres of each of the Zr centers is best described as pseudotetrahedral. The Zr—P distances with the doubly bridged portion of the molecule are 2.605(5) and 2.594(6) Å while the bridging Zr—Cl(1) distances are 2.563(5) and 2.581(5) Å. In addition, the Zr—P—Zr and Zr—Cl—Zr angles within this four-membered ring are 87.1(2) and 88.3(2)°, respectively, while the P—Zr—Cl angles are 92.4(2) and 92.2(2)°. This Zr<sub>2</sub>PCl core geometry is similar to that seen in the structurally related Zr(III) dimer (Cp<sub>2</sub>Zr)<sub>2</sub>(μ-PMe<sub>2</sub>)(μ-Cl).<sup>27</sup> In contrast, the Zr(2)—P distance is 2.512(5) Å. This bond length is shorter than the Zr—P distances seen in the phosphinidene bridged species **3** and **4**. It is also noteworthy that the Zr(2)—P distance in **5** is the shortest Zr—P bond observed for Zr phosphide derivatives, with the exception of the mononuclear phosphinidene species **7** (2.505(4) Å; Table 4).<sup>11</sup> This distance together with the planarity of the P atom suggests a significant degree of π-bonding between Zr(2) and P. The exocyclic P—Zr—Cl angle of 96.9(2)° is slightly less while the Zr(2)—Cl(2) distance of 2.534(5) Å is slightly greater than the analogous parameters in **1**. These structural data confirm the mixed-valent nature of **5**, formally containing one Zr(III) and two Zr(IV) centers. While structural data imply that the exocyclic Zr is best described as Zr(IV), a facile exchange mechanism may result in rapid exchange of the Zr environments in solution (Scheme 4). The proposition of fluxionality in **5** is consistent with the observation of a single <sup>1</sup>H NMR resonance attributable to cyclopentadienyl rings at 25 °C. The paramagnetic nature of **5** precludes further characterization of this fluxional process by NMR methods.

**Molecular Orbital Calculations.** EH and FHMO calculations were performed on models for mononuclear and bridging phosphinidene complexes as well as pyramidal and planar phosphide compounds constructed on the basis of crystallographic data for **3–7**. In several of these models the R groups on P were replaced by H, employing a P—H distance of 1.42 Å. No symmetry constraints were considered for these models.

**Mononuclear Phosphinidenes.** MO calculations for the model Cp<sub>2</sub>MPH were performed initially for M = Zr in which a bent geometry of the M—P—H angle was incorporated. The molecular orbital scheme is similar to that seen for typical Cp<sub>2</sub>ML<sub>2</sub> complexes (Figure 5). Mixing of the 2a<sub>1</sub> and b<sub>2</sub> frontier orbitals of the Cp<sub>2</sub>M fragment with orbitals on P results in the σ and π components of the metal-phosphorus double bond. The LUMO is essentially the 1a<sub>1</sub> orbital of the Cp<sub>2</sub>M fragment first described by Hoffmann and Lauher.<sup>28</sup>

Perturbations of the geometry at P were considered. If the Zr—P—R fragment was made linear, some small degree of mixing of the higher energy b<sub>1</sub> Cp<sub>2</sub>Zr fragment orbital with the P p orbital occurs, providing a small degree of stabilization. However, concurrent with this is a diminished σ-overlap of the P sp orbital and the Cp<sub>2</sub>Zr 2a<sub>1</sub> orbital, resulting in a net increase in total energy. This increase in energy is illustrated in the plot of the Zr—P—R angle as a function of the total energy of the system (Figure 6). The M—P—H angle was varied from 100° toward linearity and the total energy calculated. In the case of Cp<sub>2</sub>ZrPH, the lowest total energy was derived from the geometry in

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Table 4. Zr(IV)-P Structural Data

compd	Zr-P (Å)	$\delta(^{31}\text{P})^a$	ref	compd	Zr-P (Å)	$\delta(^{31}\text{P})^a$	ref
Zr(IV) Phosphido (PR <sub>2</sub> <sup>-</sup> ) Derivatives							
Cp* <sub>2</sub> Zr(PH(C <sub>6</sub> H <sub>2</sub> -2,4,6-Me <sub>3</sub> )) <sub>2</sub>	2.63(2)	39.0	10	(C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>2</sub> Zr(PPh <sub>2</sub> ) <sub>2</sub>	2.694(3), 2.536(3)	144.1	23
Cp* <sub>2</sub> Zr[(PC <sub>6</sub> H <sub>2</sub> -2,4,6-Me <sub>3</sub> ) <sub>2</sub> ]	2.650(3), 2.659(3)	131.0	10	(C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>2</sub> Zr((PPh) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )	2.560(4), 2.647(6)	-3.9, 211.5 <sup>b</sup>	26
Cp* <sub>2</sub> ZrCH <sub>2</sub> (PH(C <sub>6</sub> H <sub>2</sub> -2,4,6-Me <sub>2</sub> ))	2.648(2)	-42.6	10	Cp <sub>2</sub> ZrCl(P(C <sub>6</sub> H <sub>2</sub> -2,4,6- <i>t</i> -Bu <sub>3</sub> )-SiMe <sub>3</sub> )	2.541(4)	156	22
Cp* <sub>2</sub> Zr(CPh)(PR'PHR')	2.60(1)	92.3, 74.5	10	Cp <sub>2</sub> ZrCl(P(SiMe <sub>3</sub> ) <sub>2</sub> )	2.547(6)	-108.9	24
Cp*Zr[NCMe(PPh) <sub>3</sub> ]	2.744(3)	11.8, -5.1, -53.5	10	Cp <sub>2</sub> ZrMe(P(SiMe <sub>3</sub> ) <sub>2</sub> )	2.629(3)	-119.1	24
Cp* <sub>2</sub> Zr[(PCy) <sub>3</sub> ]	2.623(4), 2.623(4)	106.0, -146.2	25	Cp <sub>2</sub> Zr[(PPh) <sub>3</sub> ]	2.631(5), 2.622(5)	89.1, -187.3	25
Cp <sub>2</sub> ZrCl(PH(C <sub>6</sub> H <sub>2</sub> -2,4,6- <i>t</i> -Bu <sub>3</sub> )) (1)	2.543(3)	83.2	<i>c</i>	Cp <sub>2</sub> Zr[(PCy) <sub>3</sub> ]	2.621(6), 2.620(6)	126.0, -182.5	25
				[Cp <sub>2</sub> ZrBr((PPh) <sub>2</sub> ) <sup>-</sup> ]	2.745(5), 2.677(4)	-48.5, -75.0	25
Zr(IV) Phosphinidene (PR) Derivatives							
Cp <sub>2</sub> Zr(PC <sub>6</sub> H <sub>2</sub> -2,4,6- <i>t</i> -Bu <sub>3</sub> )- (PMe <sub>3</sub> )	2.505(4), 2.741(5)	792.4, -12.0	10	Cp <sub>2</sub> Zr(μ-PSiPh <sub>3</sub> )(μ-C <sub>5</sub> H <sub>4</sub> )ZrCpCl (4)	2.549(6), 2.559(6)	243.5	<i>c</i>
(Cp <sub>2</sub> ZrCl) <sub>2</sub> (μ-PC <sub>6</sub> H <sub>2</sub> -2,4,6-Me <sub>3</sub> ) (3)	2.597(6), 2.637(6)	325.5	6	[(CpZr) <sub>2</sub> (PH(SiPh <sub>3</sub> ))(PSiPh <sub>3</sub> )- (μ-C <sub>10</sub> H <sub>8</sub> )]	2.619(5), 2.617(5), 2.582(5), 2.678(5)	NA <sup>d</sup>	7
Zr Phosphide (P <sup>3-</sup> ) Derivatives							
(Cp <sub>2</sub> Zr) <sub>2</sub> (μ-PZrCp <sub>2</sub> Cl)(μ-Cl) (5)	2.605(5), 2.512(5), 2.594(6)	NA <sup>d</sup>	<i>c</i>	(CpZr(μ-C <sub>5</sub> H <sub>4</sub> )) <sub>3</sub> P (6)	2.575(1)	782.6	11

<sup>a</sup> All NMR data recorded at 25 °C unless noted otherwise. <sup>b</sup> Recorded at -70 °C. <sup>c</sup> This work. <sup>d</sup> Not applicable.

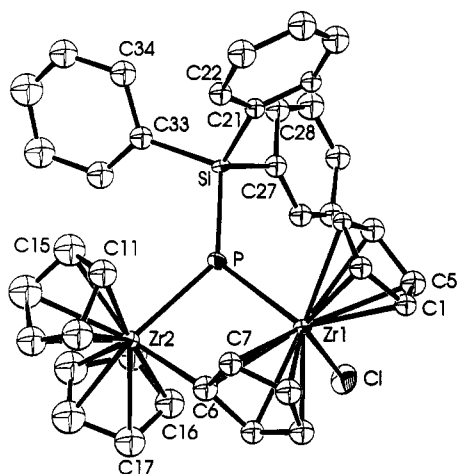


Figure 3. ORTEP drawing of 4 (30% thermal ellipsoids are shown). All hydrogen atoms are omitted for clarity.

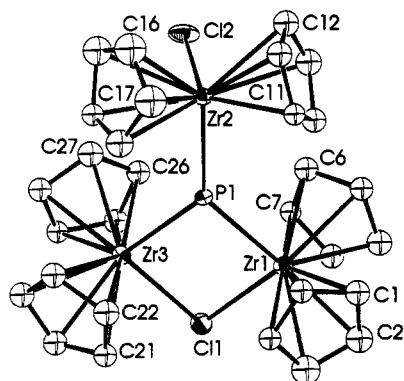


Figure 4. ORTEP drawing of 5 (30% thermal ellipsoids are shown). All hydrogen atoms are omitted for clarity.

which the Zr-P-H angle was 109.3°. In a similar manner, calculations for the model Cp<sub>2</sub>ZrPPh showed a minimum energy when the Zr-P-C angle was 120.9°. As a point of comparison, similar geometry optimization calculations were also performed for the related 18-electron species Cp<sub>2</sub>Mo=PH and Cp<sub>2</sub>Mo=PPh, where the Cp<sub>2</sub>Mo fragment 1a<sub>1</sub> orbital is fully occupied. In these cases, the lowest energy geometry corresponded to angles at P of 106.3 and 122.3°, respectively. This is consistent with the expected

Scheme 4. Proposed Mechanism for Fluxional Behavior of 5

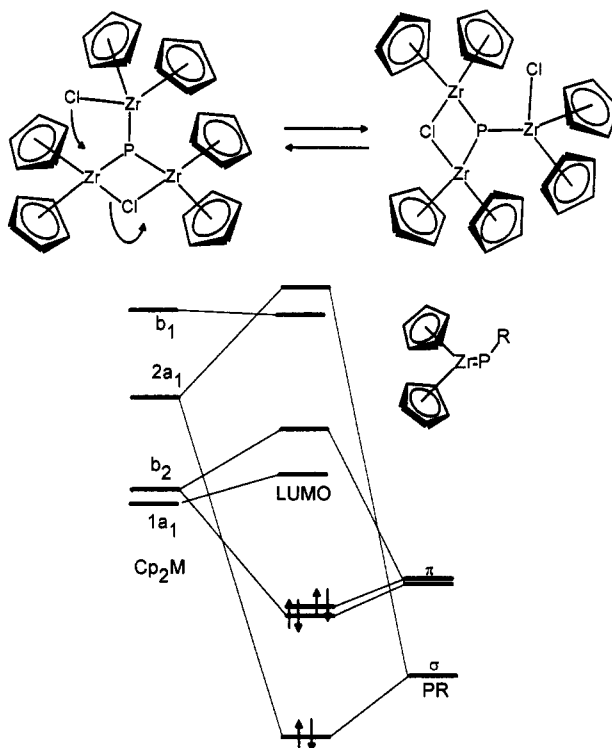
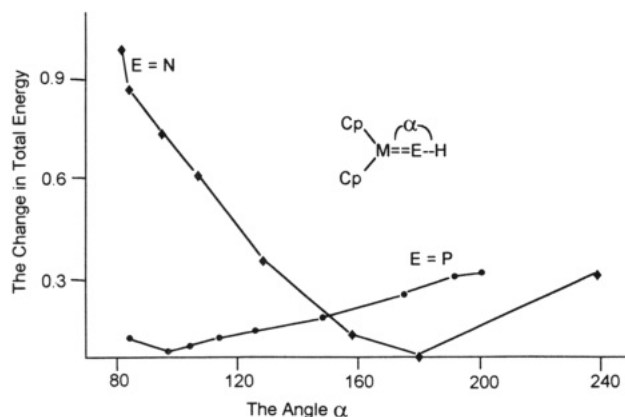


Figure 5. EMO scheme for Cp<sub>2</sub>ZrPR.

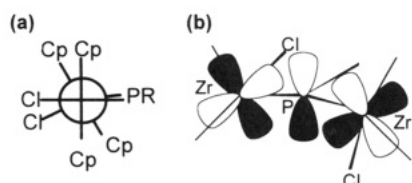
higher energy of a formally 20-electron configuration. These compare with the experimentally observed Mo-P-C angle of 115.8(2)° in Cp<sub>2</sub>MoP(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>).<sup>5</sup> A similar calculation for the related model compound Cp<sub>2</sub>MoNH showed a minimum energy geometry corresponding to an M-N-H angle of 180°, despite the expected destabilizing effect of a 19-electron count at the metal center. The present calculations are consistent with the crystallographic results for complexes of the form Cp<sub>2</sub>VNR.<sup>29</sup> It has been previously recognized on the basis of ab initio calculations that the strong π-bonding resulting

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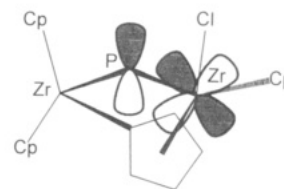
**Figure 6.** Plot of the EHMO total energy as a function of the Zr—P—H angle.



**Figure 7.** (a) Newman projection of **3** down the Zr—Zr vector. (b)  $\pi$ -Interaction between the P and Zr atoms in **3**.

in the linearity of these imido complexes is attributable to the availability of the  $b_1$  orbital of the  $Cp_2M$  fragment for metal–ligand  $\pi$ -bonding.<sup>29</sup> In the case of the phosphinidene model  $Cp_2ZrPH$ , preliminary results of ab initio calculations by Cundari predict a Zr—P—H angle of  $104^\circ$ .<sup>30</sup> The apparent preference for a bent geometry by mononuclear phosphinidenes suggests a poor overlap of the  $b_1$  frontier orbital of the  $Cp_2M$  fragment with the P  $p$  orbital in the plane containing the two Cp centroids. Clearly, the energy and the degree of  $\pi$ -overlap are determined to some extent by the strength and the length of the  $\sigma$ -bond. The absence of an  $M\equiv P$  triple bond in terminal phosphinidenes may provide both the Lewis basicity at P and acidity at the metal center that results in their reactive nature.

**Bridging Phosphinidenes.** MO calculations were performed on models constructed on the basis of the X-ray data for **3** and **4**. In the case of **3**, the planar nature of the P atom is attributed to the canted orientation of the two ClZrP planes, as depicted in the Newman projection of Figure 7a. This orientation permits partial overlap of the filled P  $p$  orbital with the  $1a_1$  frontier orbitals on each of the two  $Cp_2Zr$  fragments (Figure 7b). In **4**, as in **3**, the P coordination sphere is planar. The filled P  $p$  orbital is, of course, orthogonal to the  $Zr_2P$  plane as well as the  $PZr(2)C(6)$  plane. Thus, the filled P  $p$  orbital is not oriented for overlap with the LUMO on the Zr(2) fragment. However, as a result of the bridging  $\eta^1:\eta^5$ -cyclopentadienyl ring, the  $1a_1$  frontier orbital associated with the Zr(1) fragment is favorably oriented for a canted overlap with



**Figure 8.**  $\pi$ -Interaction between the P and Zr atoms in **4**. the P  $p$  orbital (Figure 8). This bonding description is also consistent with the differing Zr—P distances in **4**.

**Phosphide Complexes.** The MO description of **5** is similar to that presented above for **4**, in that the vacant orbitals associated with Zr(1) and Zr(3) are not geometrically disposed for overlap with the filled P orbital. However, as the  $PZr(2)Cl(2)$  plane is almost orthogonal to the  $Zr(1)PZr(2)$  plane, the  $1a_1$  orbital associated with the Zr(2) fragment is suitably oriented for a  $\pi$ -bond. This bonding dissymmetry is reflected in the relatively short Zr(2)—P distance.

In contrast to the phosphinidene complexes and the phosphide complex **5**, compound **6** exhibits a pyramidal geometry at P. The geometric constraints presented by the three  $\eta^1:\eta^5$ -cyclopentadienyl rings preclude any of the metal centers from being suitably positioned for a  $\pi$ -interaction with the P atom. Complex **6** may be viewed electronically as one would view a phosphine ( $PR_3$ ), and thus it should be possible to employ **6** as a “ligand” for mixed-metal aggregates. Synthetic studies to that end are in progress.

## Conclusions

The chemistry described above offers synthetic methods for the progressive replacement of P substituents with Zr, thus providing routes to Zr–phosphido, –phosphinidene, and –phosphide derivatives. The nature of the products obtained is clearly dependent on the steric demands of the reagents. In addition, MO considerations imply that Zr—P  $\pi$ -bonding plays a major role in determining the structural nature of the Zr—P complexes. A further implication of the present work is that phosphinidene intermediates are highly reactive and may induce C—H and P—C activation. In fact, stabilization of mononuclear phosphinidene complexes has only been achieved via a judicious choice (after the fact) of metal and phosphine substituents.

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**Supplementary Material Available:** Tables of thermal parameters, hydrogen atom positional parameters, and selected bond distances and angles for **1**, **4**, and **5** (31 pages). Ordering information is given on any current masthead page.

(30) Cundari, T. Personal communication.