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Formation and Reactivity of the Early Metal Phosphides and Phosphinidenes $Cp^*_2Zr{=}PR$, $Cp^*_2Zr(PR)_2$, and $Cp^*_2Zr(PR)_3$

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The reactions of $Cp^*_2ZrCl_2$ with 2 equiv of LiPHPh led to the formation of the unstable species $Cp^*_2Zr(PHPh)_2$ (**1**), which yields $Cp^*_2Zr(PPh_2)$ (**2**) on standing for 1 h and a third product $Cp^*_2Zr(PPh)_3$ (**3**) which appears after 1 week. The compound **3** is derived cleanly from mixtures of **1** and **2** by addition of excess PH_2Ph. In the related reactions, $Cp^*_2ZrCl_2$ reacts with 2 equiv of $LiPH(C_6H_2Me_3)$ to give the wine-red diphosphido-species $Cp^*_2Zr(PH(C_6H_2Me_3))_2$ (**4**). This compound converts slowly to *ortho*-metalation product $Cp^*_2Zr(CH_2C_6H_2Me_2PH)$ (**5**) and the species $Cp^*_2Zr(PC_6H_2Me_3)_2$ (**6**). These reactions infer terminal phosphinidene intermediates. Such an intermediate can be intercepted via reaction of **4** with MeCN affording $Cp^*_2Zr(NCMe)_2P(C_6H_2Me_3)$ (**7**). Further evidence for the intermediacy of a phosphinidene complex is derived from the reaction of $Cp^*_2ZrCl_2$ and $LiPH(C_6H_2Me_3)$ in DME where the species $Cp^*_2Zr(P(C_6H_2Me_3))(Cl)Li(DME)$ (**8**) is observed. A bent terminal phosphinidene derivative $Cp_2Zr(P(C_6H_2t\text{-}Bu_3))(PMe_3)$ (**9**) (Zr=PR, 2.505(4) Å) is isolated from the reaction of Cp_2ZrCl_2 with $Li(PH(C_6H_2t\text{-}Bu_3))$ in the presence of PMe_3. While the phosphinidene intermediate affords the novel phosphametallocycle **7**, the species **5**, **6**, and **3** also act as synthons for unprecedented phospha-, diphospha-, and triphosphametallocycles. Compound **5** reacts with MeCN and benzaldehyde to effect insertion of the organic reagents into the Zr–P bonds yielding the phosphametallocycles $Cp^*_2Zr(CH_2C_6H_2Me_2PH(C(Me)N))$ (**10**) and $Cp^*_2Zr(CH_2C_6H_2Me_2PH(C(Ph)O))$ (**11**), respectively, while similar reactions of compound **6** afford the 1,2-diphosphametallocycles $Cp^*_2Zr(NC(Me)PC_6H_2Me_3)_2$ (**12**) and $Cp^*_2Zr(OCH(Ph)PC_6H_2Me_3)_2$ (**13**). Compound **12** reacts with NH_4Cl affording $Cp^*_2ZrCl(NC(Me)P(C_6H_2Me_3)PH(C_6H_2Me_3))$ (**14**). Cleavage of the Zr–P bonds in compound **6** is effected by sequential acidolysis with HCCPh affording $Cp^*_2Zr(CCPh)(P(C_6H_2Me_3)PH(C_6H_2Me_3))$ (**15**) and $Cp^*_2Zr(CCPh)_2$ (**16**), while reaction of **6** with acetone gives the dienolate complex $Cp^*_2Zr(OC(Me)CH_2)_2$ (**17**) and reaction of **6** with CH_2I_2 affords $Cp^*_2ZrI_2$ (**18**). Compound **3** acts as synthon for new 1,2,3-triphosphametallocycles as reactions of **3** with MeCN and benzaldehyde afford $Cp^*_2Zr(NC(Me))(PPh)_3$ (**19**) and $Cp^*_2Zr(OCH(Ph))(PPh)_3$ (**20**), respectively. The chemistry of these Zr–P species offers synthetic routes to a variety of unprecedented phosphametallocycles which augurs well for metal-mediated synthesis of organophosphorus compounds. The formulations of a number of these compounds have been confirmed crystallographically. These data are summarized as follows: **6**, $P2_1/n$, a = 11.464(3) Å, b = 19.140(5) Å, c = 16.165(5) Å, β = 90.93(3)°, V = 3546(3) Å^3, Z = 4; **9**, $P2_1/c$, a = 15.011(5) Å, b = 9.824(5) Å, c = 21.745(5) Å, β = 103.21(3)°, V = 3122(2) Å^3, Z = 4; **11**, $P2_1/c$, a = 19.352(6) Å, b = 10.444(8) Å, c = 19.647(12) Å, β = 109.20(3)°, V = 3750(4) Å^3, Z = 4; **13**, $P2_1/c$, a = 21.301(7) Å, b = 10.478(4) Å, c = 25.102(7) Å, β = 111.75(2)°, V = 5204(3) Å^3, Z = 4; **14**, $P2_1/n$, a = 14.731(11) Å, b = 17.401(5) Å, c = 17.143(9) Å, β = 113.83(5)°, V = 4020(4) Å^3, Z = 4; **15**, $P2_12_12_1$, a = 14.572(10) Å, b = 28.618(12) Å, c = 11.084(6) Å, V = 4622(4) Å^3, Z = 4; **19**, $P\bar{1}$, a = 12.634(4) Å, b = 17.690(4) Å, c = 10.169(4) Å, α = 103.43(2)°, β = 113.66(2)°, γ = 82.00(2)°, V = 2022(1) Å^3, Z = 2.

Introduction

The development of transition metal mediated syntheses of organic compounds is one of the primary foci of organometallic chemistry.[1] Studies in this area have contributed dramatically to the diversity of methodologies available to organic chemists while, at the same time, mechanistic and theoretical aspects of many of these processes have given rise to some of the classic axioms of inorganic chemistry. The continuing interest in such metal-mediated reactions has led to the recent studies aimed at the incorporation of heteroatoms into organometallic species and the subsequent organic products.[2-8] The robust nature of many metal–oxo and –sulfido systems have inhibited the use of such species as synthons for heteroatomic organics. However, recent results have shown that Zr and Ta species containing metal–imido

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(M=NR),[2-4] -oxo (M=O),[5-8] and -sulfido (M=S)[8] moieties have rich chemistry, suitable to applications in organic synthesis. While parallel studies of early metal phosphorus derivatives offer the potential of synthetic routes to a variety of new organophosphorus compounds, the investigations of such chemistry have received much less attention. Although early metal phosphorus derivatives were first prepared by Issleib and Hackert in 1966,[9] these species remained basically unexplored until the work of Baker et al. began in 1983.[10] Since then, the research groups of Baker,[10] Gamborotta,[11] ourselves,[12] and others[13-18] have examined early metal phosphides; however, these efforts focused primarily on the structural and theoretical aspects as well as on the chemistry of heterobimetallics derived from them.

In an effort to set the groundwork for the metal-mediated synthesis of organophosphorus compounds, several aspects of basic early metal phosphorus chemistry must be addressed. First, convenient synthetic routes must be developed which provide access to reactive early metal phosphorus derivatives. Second, such species must exhibit reactivity with organic substrates affording routes to new P–C bonds and thus new phosphametallocycles. In this paper, we address these two issues. Initially we demonstrate that the primary-phosphide complexes $Cp^*_2Zr(PHR)_2$ act as synthons for a series of reagents. A preliminary report described the generation of a zirconocene phosphinidene (i.e. $Cp^*_2Zr{=}PR$).[19] Herein, we extend this chemistry to include synthons of the form $Cp^*_2Zr(PR)_n$ (n = 1–3). These species participate in a variety of reactions, among them the activation of intramolecular sp^3 C–H bonds, the activation of P–H bonds, and as well insertion reactions involving organic substrates. Such reactivity results in a variety of new phosphazirconocycles in which one, two, or three phosphorus atoms are incorporated.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing either Schlenk line techniques or a Vacuum Atmospheres inert-atmosphere glovebox equipped with a catalyst column and an atmosphere circulation system. 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 NMR spectra were recorded on Bruker AC-300 and AC-200 spectrometers operating at 300 and 200 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. ^{31}P and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-200 operating at 81 MHz, and chemical shifts are reported relative to 85% H_3PO_4. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. $Cp^*_2ZrCl_2$ was purchased from the Strem Chemical Co., while the primary phosphines were obtained from Quantum Design.

Synthesis of LiPH(R)·nTHF. To a THF solution of primary phosphine H_2PR was added 1 equiv of BuLi in hexane at −78 °C. The mixture was then stirred at this temperature for 1 h. Evaporation of the solvent gave yellow crystalline product which was washed with hexane and dried under vacuum.

LiPH(Ph)·THF: Yield 95%; ^1H NMR (C_6D_6, 25 °C) δ 7.68 (br s, 2 H, Ph), 7.03 (br s, 2 H, Ph), 6.80 (br s, 1 H, Ph), 3.44 (br s, 4 H, THF), 3.14 (d, $|J_{P-H}|$ = 207 Hz, 1 H, PH), 1.23 (br s, 4 H, THF); ^{31}P NMR (C_6D_6, 25 °C) δ −130.4 (d, $|J_{P-H}|$ = 207 Hz).

LiPH($C_6H_2Me_3$)·2THF:[20] Yield 95%; ^1H NMR (C_6D_6, 25 °C) δ 6.92 (s, 2 H, Ph), 3.44 (br s, 8 H, THF), 2.81 (d, $|J_{P-H}|$ = 192 Hz, 1 H, PH), 2.68 (s, 6 H, Me), 2.27 (s, 3 H, Me), 1.23 (br s, 8 H, THF); ^{31}P NMR (C_6D_6, 25 °C) δ −165.7 (d, $|J_{P-H}|$ = 192 Hz); ^{31}P NMR (THF, 25 °C) δ −157.4 (d, $|J_{P-H}|$ = 167 Hz).

LiPH(C_6H_2t-Bu_3)·3THF:[20] Yield 85%; ^1H NMR (C_6D_6, 25 °C) δ 7.44 (s, 2 H, Ph), 3.46 (d, $|J_{P-H}|$ = 190 Hz, 1 H, PH), 3.45 (br s, 12 H, THF), 1.94 (s, 18 H, t-Bu), 1.35 (s, 9 H, t-Bu), 1.33 (br s, 12 H, THF); ^{31}P NMR (C_6D_6, 25 °C) δ −124.4 (d, $|J_{P-H}|$ = 190 Hz).

Generation of $Cp^*_2Zr(PHPh)_2$ (1) and $Cp^*_2Zr(PPh)_2$ (2). To a suspension of $Cp^*_2ZrCl_2$ (43 mg, 0.1 mmol) in benzene (5 mL) was added a suspension of LiPH(Ph)·THF (37 mg, 0.2 mmol) in benzene (3 mL). A red-brown solution was immediately obtained. After 1 h a ^{31}P NMR resonance attributable to $Cp^*_2Zr(PHPh)_2$ (1) was seen. A few hours later a second signal attributed to $Cp^*_2Zr(PPh)_2$ (2) appeared. After 1 week a third signal indicated the presence of $Cp^*_2Zr(PPh)_3$ (3). Attempts to separate these species from each other were unsuccessful although they could be characterized spectroscopically. Addition of H_2PPh to this mixture resulted in the immediate loss of 2 and the gradual disappearance of 1 and concomitent appearance of 3. 1: ^1H NMR (C_6D_6, 25 °C) δ 7.75 (t, $|J|$ = 7.3 Hz, 4 H, Ph), 7.17 (d, $|J|$ = 7.3 Hz, 4 H, Ph), 6.93 (t, $|J|$ = 7.3 Hz, 2 H, Ph), 4.66 (d, $|J_{P-H}|$ = 234 Hz, $|J_{P-H}|$ = 250 Hz, 2H, PH), 1.82 (s, 30 H, C_5Me_5); ^{31}P NMR (C_6D_6, 25 °C) δ: 60.0 (d, $|J_{P-H}|$ = 243 Hz). 2: ^1H NMR (C_6D_6, 25 °C) δ 7.44 (br s, 4 H, Ph), 7.01–7.17 (m, 6 H, Ph) 1.73 (s, 30 H, C_5Me_5); ^{31}P NMR (C_6D_6, 25 °C) δ 155.0 (s).

Synthesis of $Cp^*_2Zr(PPh)_3$ (3). To a suspension of $Cp^*_2ZrCl_2$ (86 mg, 0.2 mmol) in benzene (5 mL) were added 3 drops of H_2PPh by a pipet and then a benzene (5 mL) solution of LiPH(Ph)·THF (75 mg, 0.4 mmol). A red-brown solution was immediately obtained, which gradually became green overnight. The solvent was removed under vacuum, and the residue was extracted with hexane. Reduction of the volume of the solution gave green crystals of 3 (123 mg, 90% yield): ^1H NMR (C_6D_6, 25 °C) δ 8.24 (br s, 2 H, Ph), 7.86 (br s, 4 H, Ph), 6.85–7.24 (m, 9 H, Ph), 1.82 (s, 15 H, C_5Me_5), 1.48 (s, 15 H, C_5Me_5); ^{31}P NMR (C_6D_6, 25 °C) δ 62.0 (d, $|J_{P-P}|$ = 247 Hz), −135.9 (t, $|J_{P-P}|$ = 247 Hz). Anal. Calcd: C, 66.54; H, 6.61. Found: C, 66.32; H, 6.50.

Synthesis of $Cp^*_2Zr(PH(C_6H_2Me_3))_2$ (4). To a suspension of $Cp^*_2ZrCl_2$ (431 mg, 1 mmol) in benzene (5 mL) was added a benzene (5 mL) solution of LiPH($C_6H_2Me_3$)·2THF (604 mg, 2 mmol). The mixture immediately turned from pale to red and was then stirred at room temperature for 2 h. ^{31}P NMR monitoring of the reaction mixture showed only a single resonance at 39 ppm. After filtration and evaporation of the solvent, wine-red fine crystals of 4 (597 mg, 90% yield) were obtained. Reduction of the volume of a benzene solution of 4 under vacuum

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(20) In all cases, $C_6H_2Me_3$ and C_6H_2t-Bu_3 refer to the 2,4,6-trimethylphenyl and the 2,4,6-tri-*tert*-butylphenyl substituents, respectively.

gave X-ray-quality crystals in a few hours: ^{1}H NMR (C_6D_6, 25 °C) δ 6.91 (s, 4 H, Ph), 4.43 (d, $|J_{P-H}|$ = 172, $|J|$ = 172, $|J|$ = 267, $|J|$ = 330 Hz, 2 H, PH), 2.73 (br s, 6 H, Me), 2.60 (br s, 6 H, Me), 2.26 (s, 6 H, Me), 1.72 (s, 30 H, C_5Me_5); ^{31}P NMR (C_6D_6, 25 °C) δ 39.0 (d, $|J_{P-H}|$ = 172, $|J|$ = 267, $|J|$ = 330 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C) δ: 39.0 (s). Anal. Calcd: C, 68.74; H, 8.20. Found: C, 68.40; H, 8.15.

Isolation of $Cp^*_2Zr(CH_2C_6H_2Me_2PH)$ (5) and $Cp^*_2Zr(PC_6H_2Me_3)_2$ (6). From a benzene solution of 4 (332 mg, 0.5 mmol) red-brown crystals of 5 (77 mg, 30% yield) were deposited after 2–3 days. Upon further standing for the several days, dark-brown crystals of 6 (110 mg, 33% yield) were obtained from the mother liquor.[21] 5: ^{1}H NMR (C_6D_6, 25 °C) δ 6.86 (s, 1 H, Ph), 6.73 (s, 1 H, Ph), 3.54 (d, $|J_{P-H}|$ = 180 Hz, 1 H, PH), 2.75 (s, 3 H, Me), 2.26 (s, 3 H, Me), 1.72 (s, 30 H, C_5Me_5), 1.25 (s, 2 H, CH_2); ^{31}P NMR (C_6D_6, 25 °C) δ −42.6 (d, $|J_{P-H}|$ = 180 Hz). Anal. Calcd: C, 68.05; H, 8.07. Found: C, 67.82; H, 8.00. 6: ^{1}H NMR (C_6D_6, 25 °C) δ 6.93 (s, 2 H, Ph), 6.73 (s, 2 H, Ph), 3.33 (s, 6 H, Me), 2.29 (s, 6 H, Me), 1.78 (s, 30 H, C_5Me_5), 1.24 (s, 6 H, Me); ^{31}P NMR (C_6D_6, 25 °C) δ 134.9 (s); ^{31}P NMR (THF, 25 °C) δ 131.0 (s). Anal. Calcd: C, 68.95; H, 7.92. Found: C, 68.75; H, 7.80.

Synthesis of $Cp^*_2Zr(NCMe)_2P(C_6H_2Me_3)$ (7). To a benzene solution (3 mL) of 4 (66 mg, 0.1 mmol) was added MeCN (10.4 μL, 0.2 mmol) in benzene (2 mL). No apparent color change was observed. The mixture was stirred at room temperature for 2 days, and finally an orange red solution was obtained. Evaporation of the solvent gave viscous oily products, which were then dissolved in hexane. After the mixture was left standing for 2 days, needlelike orange crystals of 7 (18 mg, 30% yield) were deposited. This compound was not stable in solution and decomposed into unidentified products in 1 week as monitored in C_6D_6 by NMR: ^{1}H NMR (C_6D_6, 25 °C) δ 6.89 (s, 2 H, Ph), 2.15 (s, 3 H, Me), 1.99 (d, $|J^3_{P-H}|$ = 4.5 Hz, 6 H, MeCN), 1.89 (s, 30 H, C_5Me_5), 1.87 (br s, 6 H, Me); ^{31}P NMR (C_6D_6, 25 °C) δ 0.2 (s). Anal. Calcd: C, 66.63; H, 6.92. Found: C, 66.42; H, 6.70.

Generation of $Cp^*_2Zr(P(C_6H_2Me_3))(Cl)Li(DME)$ (8). To a dimethoxyethylene (DME) suspension of $Cp^*_2ZrCl_2$ was added 2 equiv of $LiPH(C_6H_2Me_3)\cdot 2THF$ in DME. The resulting red solution was stirred at room temperature for 1 h. Monitoring of the reaction mixture showed a singlet at 537.6 ppm with no P–H coupling in the ^{31}P NMR spectrum attributed to 8. In addition, resonance arising from the free phosphine $H_2PC_6H_2Me_3$ and 5 were observed. The species giving rise to the signal at 537.6 ppm was not stable, affording a mixture of 5 and 6 after 2 days. The addition of MeCN to the solution was monitored by ^{31}P NMR. The signal at 537.6 ppm was absent immediately, and the resonance attributable to 7 appeared. Attempts to isolate 8 were unsuccessful.

Synthesis of $Cp_2Zr(P(C_6H_2t\text{-}Bu_3)(PMe_3)$ (9). To a suspension of Cp_2ZrCl_2 (30 mg, 0.1 mmol) in benzene (3 mL) were added 3 drops of PMe_3 by a pipet and then a benzene solution (2 mL) of $LiPH(C_6H_2Bu_3)\cdot 3THF$ (100 mg, 0.2 mmol). The mixture was stirred at room temperature for 2 h, and a green-black solution was finally obtained. The solvent was removed under vacuum, and the residue was extracted with hexane. After the volume of the solution was reduced and it was left to stand at room temperature overnight, black crystals of 9 (23 mg, 40% yield) were deposited: ^{1}H NMR (C_6D_6, 25 °C) δ 7.68 (s, 2 H, Ph), 5.49 (d, $|J_{P-H}|$ = 1.7 Hz, 10 H, Cp), 1.62 (s, 18 H, *t*-Bu), 1.55 (s, 9 H, *t*-Bu), 0.66 (d, $|J^2_{P-H}|$ = 6.3 Hz, 9 H, PMe); ^{31}P NMR (C_6D_6, 25 °C) δ 792.4 (d, $|J_{P-P}|$ = 23 Hz), −12.0 (d, J_{P-P} = 23 Hz). Anal. Calcd: C, 64.88; H, 8.43. Found: C, 64.66; H, 8.28.

Generation of $Cp^*_2Zr(CH_2C_6H_2Me_2PH(C(Me)N))$ (10). Addition of an excess amount of MeCN to a red-brown C_6D_6 solution of 5 gave immediately an orange solution. ^{1}H and ^{31}P NMR spectra showed a quantitative formation of 10. This compound was not stable in the absence of excess MeCN. Placement of the solution of 10 under vacuum resulted in the re-formation of 5. 10: ^{1}H NMR (C_6D_6, 25 °C) δ 6.88 (s, 1 H, Ph), 6.58 (s, 1 H, Ph), 5.36 (d, $|J_{P-H}|$ = 225 Hz, 1 H, PH), 2.29 (s, 3 H, Me), 2.19 (s, 3 H, Me), 2.08 (d, $|J^3_{P-H}|$ = 3.6 Hz, 3 H, MeCN), 1.76 (s, 15 H, C_5Me_5), 1.54 (s, 15 H, C_5Me_5), 1.26 (s, 2 H, CH_2); ^{31}P NMR (C_6D_6, 25 °C) δ −71.9 (d, $|J_{P-H}|$ = 225 Hz).

Synthesis of $Cp^*_2Zr(CH_2C_6H_2Me_2PH(CH(Ph)O))$ (11). To a red-brown benzene solution (3 mL) of 5 (31 mg, 0.06 mmol) was added a benzene solution (2 mL) of benzaldehyde (19 μL, 0.18 mmol). The resultant orange solution was stirred at room temperature for 2 h, after which monitoring of the reaction by ^{31}P NMR showed the complete loss of 2 and the appearance of a new signal at −60.3 ppm. Reduction of the volume of the solution under reduced pressure gave orange-yellow crystals of 11 (33 mg, 89% yield): ^{1}H NMR (C_6D_6, 25 °C) δ 7.66 (d, $|J|$ = 7.7 Hz, 2H, Ph), 7.30 (t, $|J|$ = 7.7 Hz, 2 H, Ph), 7.10 (t, $|J_{P-H}|$ = 7.7 Hz, 1 H Ph), 7.07 (s, 1 H, Ph), 6.75 (s, 1H, Ph), 6.18 (d, $|J^2_{P-H}|$ = 6.3 Hz, 1 H, CH), 4.69 (d, $|J_{P-H}|$ = 218 Hz, 1 H, PH), 2.34 (s, 3 H, Me), 2.31 (s, 3 H, Me), 1.93 (s, 15 H, C_5Me_5), 1.64 (s, 15 H, C_5Me_5), 1.26 (s, 2 H, CH_2); ^{31}P NMR (C_6D_6, 25 °C) δ −60.3 (d, $|J_{P-H}|$ = 218 Hz). Anal. Calcd: C, 69.97; H, 7.67. Found: C, 69.50; H, 7.65.

Attempted Reaction of 5 with Styrene. To a C_6D_6 solution of 5 was added excess of styrene at room temperature. The reaction was monitored by ^{31}P and ^{1}H NMR, and no change was observed in a few days.

Synthesis of $Cp^*_2Zr(NC(Me)PC_6H_2Me_3)_2$ (12). To a green benzene solution (3 mL) of 6 (33 mg, 0.05 mmol) was added a benzene solution (2 mL) of MeCN (5.2 μL, 0.1 mmol) at room temperature. The color changed immediately to orange. One hour later, reduction of the volume of the solution gave orange-red crystals of 12 (35 mg, 94% yield): ^{1}H NMR (C_6D_6, 25 °C) δ 6.80 (s, 2 H, Ph), 6.49 (s, 2 H, Ph), 3.03 (s, 6 H, Me), 2.40 (s, 6 H, Me), 2.07 (t, $|J^3_{P-H}|$ = 1.5 Hz, 6 H, MeCN), 1.99 (s, 30 H, C_5Me_5), 1.94 (s, 6 H, Me); ^{31}P NMR (C_6D_6, 25 °C) δ −30.1 (s). Anal. Calcd: C, 67.79; H, 7.86. Found: C, 67.64; H, 7.49.

Synthesis of $Cp^*_2Zr(OCH(Ph)PC_6H_2Me_3)_2$ (13). To a green benzene solution (3 mL) of 6 (33 mg, 0.05 mmol) was added a benzene solution (2 mL) of PhCHO (10.2 μL, 0.1 mmol) at room temperature. The color changed immediately to wine-red and gradually to pale yellow. The mixture was stirred overnight. Reduction of the volume of the solution gave colorless crystals of 13 (42 mg, 96% yield): ^{1}H NMR (C_6D_6, 25 °C) δ 7.70 (d, $|J|$ = 7.5 Hz, 4 H, Ph), 7.11 (s, 2 H, Ph) 7.05 (t, J = 7.5 Hz, 4 H, Ph), 6.82 (t, $|J|$ = 7.5 Hz, 2 H, Ph), 6.56 (s, 2 H, Ph), 6.20 (br s, 2 H, CH), 3.35 (s, 6 H, Me), 2.52 (s, 6 H, Me), 2.14 (s, 30 H, C_5Me_5), 1.67 (s, 6 H, Me); ^{31}2P NMR (C_6D_6, 25 °C) δ −4.7 (s). Anal. Calcd: C, 71.44; H, 7.38. Found: C, 71.32; H, 7.18.

Synthesis of $Cp^*_2ZrCl(NC(Me)P(C_6H_2Me_3)PH(C_6H_2Me_3))$ (14). The mixture of 12 (37 mg, 0.05 mmol) and NH_4Cl (15 mg, 0.28 mmol) in THF was stirred at room temperature for 2 h, during which time a gradual color change from orange to pale yellow was observed. After filtration the solvent was removed and the residue dissolved into benzene. Reduction of the volume and addition of hexane gave pale yellow crystals of 14 (35 mg, 95% yield): ^{1}H NMR (C_6D_6, 25 °C) δ 6.87 (s, 1 H, Ph), 6.65 (s, 2 H, Ph), 6.57 (s, 1 H, Ph), 5.44 (d of d, $|J_{P-H}|$ = 228 Hz, $|J^2_{P-H}|$ = 10 Hz, 1 H, PH), 3.04 (s, 3 H, Me), 2.47 (s, 6H, Me), 2.15 (s, 3H, Me), 2.04 (br s, 6 H, Me), 1.99 (br s, 18 H, C_5Me_5), 1.94 (s, 15 H, C_5Me_5); ^{31}P NMR (C_6D_6, 25 °C) δ 17.9 (d, $|J_{P-P}|$ = 122 Hz), −110.7 (d of d, $|J_{P-P}|$ = 122 Hz, $|J_{P-H}|$ = 228 Hz). Anal. Calcd: C, 64.97; H, 7.63. Found: C, 64.79; H, 7.62.

Synthesis of $Cp^*_2Zr(CCPh)(P(C_6H_2Me_3)PH(C_6H_2Me_3))$ (15) and $Cp^*_2Zr(CCPh)_2$ (16). To a green benzene solution (3 mL) of 6 (33 mg, 0.05 mmol) was added a benzene solution (2 mL) of PhCCH (11.0 μL, 0.1 mmol) at room temperature. The mixture changed to red within 5 min and was stirred for 30 min. After the volume of the solution was reduced, hexane was laid on. Red crystals of 15 (34 mg, 89% yield) were obtained. When the reaction was carried out overnight, an orange-red solution was obtained which showed a complex ^{31}P NMR spectrum. After reduction of the volume and addition of hexane colorless crystals of 16 (8 mg, 28%) were obtained. 15: ^{1}H NMR (C_6D_6, 25 °C) δ 7.66 (d, $|J|$ = 7.4 Hz, 2 H, Ph), 7.20 (t, $|J|$ = 7.4 Hz, 2 H, Ph),

(21) Solutions of 6 in benzene became green upon standing at room temperature for 2 days. Nonetheless, the green crystals isolated from these solutions are 6.

Table I. Crystallographic Parameters

	6	9	11	13	14	15	19
formula	$C_{38}H_{52}P_2Zr$	$C_{31}H_{48}P_2Zr$	$C_{42}H_{53}POZr$	$C_{62}H_{64}P_2O_2Zr$	$C_{40}H_{56}ClNPZr$	$C_{46}H_{58}P_2Zr$	$C_{46}H_{51}NP_3Zr$
cryst color, form	green blocks	green-black blocks	org-yell. blocks	colorless blocks	yellow blocks	red blocks	red blocks
a (Å)	11.464(3)	15.011(7)	19.352(6)	21.301(7)	14.731(11)	14.572(10)	12.634(4)
b (Å)	19.140(5)	9.824(5)	10.444(8)	10.478(4)	17.401(5)	28.618(12)	17.690(4)
c (Å)	16.165(5)	21.745(5)	19.647(12)	25.102(7)	17.143(9)	11.084(6)	10.169(4)
α (deg)							103.43(2)
β deg	90.93(3)	103.21(3)	109.20(3)	111.75(2)	113.83(5)		113.66(2)
γ (deg)							82.00(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
V (Å^3)	3546(3)	3122(2)	3750(4)	5204(3)	4020(4)	4622(4)	2022(1)
D_{calcd} (g cm^{-3})	1.33	1.22	1.23	1.22	1.22	1.21	1.26
Z	4	4	4	4	4	4	2
cryst dimens (mm)	0.32 × 0.25 × 0.35	0.30 × 0.20 × 0.25	0.33 × 0.28 × 0.34	0.40 × 0.25 × 0.25	0.33 × 0.28 × 0.34	0.33 × 0.24 × 0.30	0.40 × 0.25 × 0.37
abs coeff, μ (cm^{-1})	4.205	4.623	3.506	3.053	4.391	3.325	4.115
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	24	24	24	24	24	24
scan speed, deg/min	16.0 ($\theta/2\theta$) (1–3 scans)	16.0 ($\theta/2\theta$) (1–3 scans)	16.0 ($\theta/2\theta$) (1–3 scans)	16.0 ($\theta/2\theta$) (1–3) scans	16.0 ($\theta/2\theta$) (1–3 scans)	8.0 ($\theta/2\theta$) (1–3 scans)	32.0 ($\theta/2\theta$) (1–4 scans)
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 ratio	0.5	0.5	0.5	0.5	0.5	0.5	0.5
data collcd	6808	6108	7235	7959	6168	4331	7459
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	$h,k,\pm l$	$h,k,\pm l$	$h,k,\pm l$	$h,k,\pm l$	$h,k,\pm l$	h,k,l	$\pm h,\pm k,l$
data $F_o^2 > 3\sigma(F_o^2)$	2411	2295	3189	1692	1994	989	3013
variables	260	257	326	268	286	140	328
R (%)	6.41	7.26	6.02	9.26	6.56	8.89	6.01
R_w (%)	6.56	7.73	6.18	8.84	6.59	8.54	6.13
largest Δ/σ	0.002	0.040	0.001	0.008	0.0001	0.06	0.02
goodness of fit	1.717	1.906	1.606	1.883	1.618	1.83	1.42

7.06 (t, $|J|$ = 7.4 Hz, 1 H, Ph), 6.79 (br s, 2 H, Ph), 6.59 (s, 2 H, Ph), 5.70 (d of d, $|J_{P-H}|$ = 209, $|J^2_{P'-H}|$ = 3.2 Hz, 1 H, PH), 2.65 (br s, 3 H, Me), 2.22 (br s, 21 H, C_5Me_5, Me), 2.11 (s, 3 H, Me), 2.05 (s, 3 H, Me), 1.80 (br s, 18 H, C_5Me_5, Me); ^{31}P NMR (C_6D_6, 25 °C) δ 92.3 (br d, $|J_{P-P}|$ = 385, Hz), −74.5 (d of d, $|J_{P-P}|$ = 385, $|J_{P-H}|$ = 209 Hz). Anal. Calcd: C, 72.30; H, 7.65. Found: C, 72.09; H, 7.38. **16**: ^{1}H NMR (C_6D_6, 25 °C) δ 7.50 (d, $|J|$ = 7.0 Hz, 4 H, Ph), 6.95–7.20 (m, 6 H, Ph), 2.07 (s, 30 H, C_5Me_5).

Synthesis of $Cp^*_2Zr(OC(Me)CH_2)_2$ (17). To a green solution of **6** (33 mg, 0.05 mmol) in benzene (3 mL) was added a benzene solution (2 mL) of MeCOMe (7.4 μL, 0.1 mmol). The mixture was stirred at room temperature overnight, and a pale solution was finally given. Reduction of the solution volume under vacuum and laying hexane resulted in the precipitation of colorless crystals of **17** (15 mg, 63% yield): ^{1}H NMR (C_6D_6, 25 °C) δ 4.08 (s, 2 H, CH_2), 4.06 (s, 2 H, CH_2), 1.93 (s, 30 H, C_5Me_5), 1.87 (s, 6 H, Me).

Synthesis of $Cp^*_2ZrI_2$ (18). To a green solution of **6** (33 mg, 0.05 mmol) in benzene (3 mL) was added a benzene solution (2 mL) of CH_2I_2 (4.0 μL, 0.05 mmol). The color of the solution changed gradually to yellow in 2 days. Reduction of the volume of the solution under reduced pressure gave yellow crystals of **18** (17 mg, 55% yield). The mother liquor showed a complex ^{31}P NMR spectrum, and no phosphorus compound was identified: ^{1}H NMR (C_6D_6, 25 °C) δ 1.96 (s).

Reaction of 6 with Phenylphosphine. The reaction of **6** with excess of H_2PPh was monitored by ^{31}P NMR at room temperature. After 3 days, the resonance attributable to **6** was lost while resonances assigned to $(PH(C_6H_2Me_3))_2$ and $Cp^*_2Zr(PH(Ph))_2$ (**1**) and $Cp^*_2Zr(PPh_2)$ (**2**) were observed. Attempts to separate and isolate these products were unsuccessful.

Attempted Reaction of 6 with Benzophenone and Diphenylacetylene. These reactions were monitored by ^{31}P NMR at room temperature, and no change was observed in a few days.

Synthesis of $Cp^*_2Zr(NC(Me))(PPh)_3$ (19). To a green benzene solution (3 mL) of **3** (34 mg, 0.05 mmol) was added 0.2 mL of MeCN. The resultant red solution was stirred at room temperature for 2 h. Evaporation of the solvent under vacuum gave red powder, which after recrystallization from benzene/hexane gave red crystals of **19** (33 mg, 91%): ^{1}H NMR (C_6D_6, 25 °C) δ 8.10–6.75 (m, 15 H, Ph), 2.07 (s, 15 H, C_5Me_5), 1.83 (s, 15 H, C_5Me_5), 1.80 (br s, 3H, Me); ^{31}P NMR (C_6D_6, 25 °C) δ 11.8 (d of d, $|J_{P-P}|$ = 148 Hz, $|J^2_{P-P}|$ = 84 Hz), −5.1 (d of d, $|J_{P-P}|$ = 208 Hz, $|J_{P-P}|$ = 148 Hz), −53.5 (d of d, $|J_{P-P}|$ = 208 Hz, $|J^2_{P-P}|$ = 84 Hz). Anal. Calcd: C, 66.09; H, 6.66. Found: C, 65.92; H, 6.42.

Synthesis of $Cp^*_2Zr(OCH(Ph))(PPh)_3$ (20). To a green benzene solution (3 mL) of **3** (34 mg, 0.05 mmol) was added 2 drops of PhCHO. The red solution was stirred at room temperature for 2 h, and the solvent was removed under vacuum to give a red powder, which was recrystallized from benzene/hexane affording red crystals of **20** (35 mg, 88% yield): ^{1}H NMR (C_6D_6, 25 °C) δ 8.10–6.50 (m, 21 H, Ph, CH), 2.07 (s, 15 H, C_5Me_5), 1.89 (s, 15 H, C_5Me_5); ^{31}P NMR (C_6D_6, 25 °C) δ 0.3 (d of d, $|J_{P-P}|$ = 140 Hz, $|J^2_{P-P}|$ = 120 Hz), −28.1 (d of d, $|J_{P-P}|$ = 197 Hz, $|J_{P-P}|$ = 140 Hz), −50.3 (d of d, $|J_{P-P}|$ = 197 Hz, $|J^2_{P-P}|$ = 120 Hz). Anal. Calcd: C, 68.24; H, 6.49. Found: C, 68.09; H, 6.37.

X-ray Data Collection and Reduction.[22] X-ray-quality crystals 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_2-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 ($20° < 2\theta < 25°$) were used

(22) Crystallographic details for compounds **4**, **5**, **7**, and **11** have been presented in part and deposited as supplementary data.[19]

to obtain the final lattice parameters and the orientation matrices. Fixed scan rates were employed. Up to four repetitive scans of each reflections at the respective scan rates were averatged to ensure meaningful statistics. The number of scans of each reflections was determined by the intensity. 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 ($4.5° < 2\theta < 50.0°$), and three standard reflections were recorded every 197 reflections. 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 workstation 3520. The reflections with $F_o^2 > 3\sigma F_o^2$ 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 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 $w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c 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 among the five structures and was set so as to maintain a reasonable data:variable ratio in each case. Hydrogen atom positions were calculated and allowed 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 on any of the parameters in the final cycles of the refinement is also given in Table I. The residual electron densities were of no chemical significance. The following data for **6**, **9**, **13–16**, **18**, and **19** have been deposited as supplementary material: positional parameters, thermal parameters, selected bond distances and angles, and hydrogen atom parameters. In the case of **16** and **18** ORTEP drawings and table of crystallographic parameters have also been deposited.

Results and Discussion

Synthesis and Reactivity of Primary Phosphide Complexes. The reaction of $Cp^*_2ZrCl_2$ with 2 equiv of LiPHPh in benzene at 25 °C was monitored by ^{31}P NMR spectroscopy. After 1 hour a resonance attributable to the species $Cp^*_2Zr(PHPh)_2$ (**1**) was seen at 60.0 ppm with a $|J_{P-H}|$ of 243 Hz. The magnitude of J_{P-H} suggests a dynamic process involving the rapid interconversion of pyramidal and planar phosphide substituents, similar to that previously observed by Baker et al.[10] A few hours later, a second new species appeared. This product exhibited a resonance at 155.0 ppm with no P–H coupling and was determined to be $Cp^*_2Zr(PPh)_2$ (**2**). On prolonged standing for 1 week the presence of a third, less abundant product was detected. This species exhibited doublet and triplet $^{31}P\{^1H\}$ NMR resonances at 62.0 and −135.9 ppm, respectively, and was formulated as the compound $Cp^*_2Zr(PPh)_3$ (**3**). Much higher yield conversion to **3** was achieved by addition of PH_2Ph to the reaction mixture containing **1** and **2**. While compound **3** could be isolated cleanly in this manner, attempts to isolate **1** and **2** independent of each other were unsuccessful. While these initial results suggested that conversions of the bis-primary diphosphide complex **1** to the diphosphide **2** and subsequently to the triphosphide **3** occurred, the course of these processes was not clear. This prompted a study of the similar reactions employing a bulkier primary phosphide.

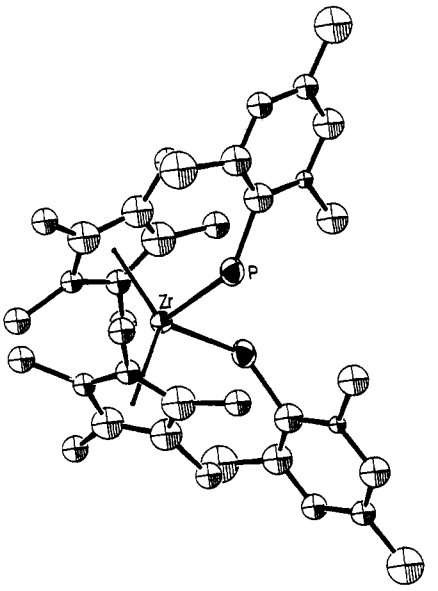
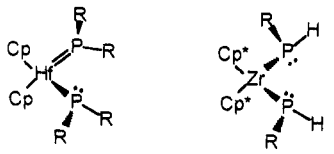


Figure 1. ORTEP drawing of **4**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–P = 2.63(2) Å and P–Zr–P′ = 96.1(7)°.

The reaction of $Cp^*_2ZrCl_2$ with 2 equiv of $LiPH(C_6H_2Me_3)$ in benzene at 25 °C gave the wine-red diphosphido-species **4** in 90% isolated yield. This species exhibited a single resonance at 39.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The coupled ^{31}P and ^1H NMR spectra of **4** are consistent with pyramidal geometry and thus the presence of diastereomers in solution. This implies that the steric demands of the trimethylphenyl substituent inhibit the interconversion of pyramidal and planar geometries at P. X-ray crystallography confirmed the formulation of **4** as $Cp^*_2Zr(PH(C_6H_2Me_3))_2$ and showed that aryl substituents adopt an orientation in the solid state so as to minimize their steric interactions (Figure 1).[22] The pseudotetrahedral zirconium center resides on a crystallography imposed 2-fold axis of symmetry with a Zr–P bond length of 2.63(2) Å, which is typical of pyramidal phosphides on Zr(IV).[10-18] The pyramidal geometry about both P atoms is in contrast to that seen for the species $Cp_2Hf(PEt_2)_2$, where one of the phosphorus atoms adopts a trigonal planar geometry, thus achieving a formal 18-electron configuration about the Hf center.[10]



It is presumably the steric demands of the $C_6H_2Me_3$ substituent and the Cp* ligands in **4** that prevents the phosphide moieties from participating in such π-bonding. The inaccessibility of a planar phosphorus geometry accounts for the observation via NMR of the diastereoisomers in solution. Despite the fact that the hydrogen

(23) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 324. (b) Cromer, D. T.; Mann, J. B. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 390.

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

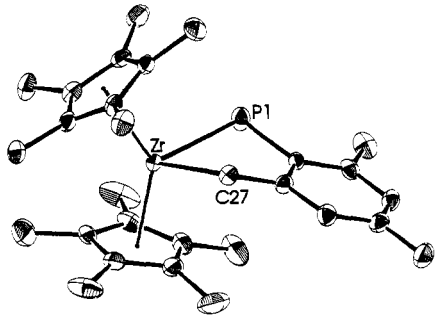


Figure 2. ORTEP drawing of **5**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–P = 2.648(2) Å, Zr–C27 = 2.329(6) Å, and P–Zr–C27 = 77.5(2)°.

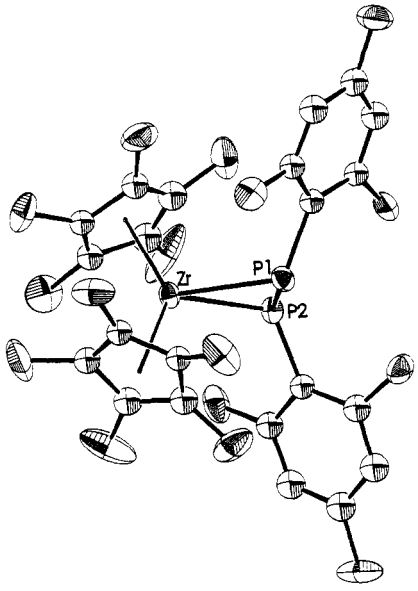
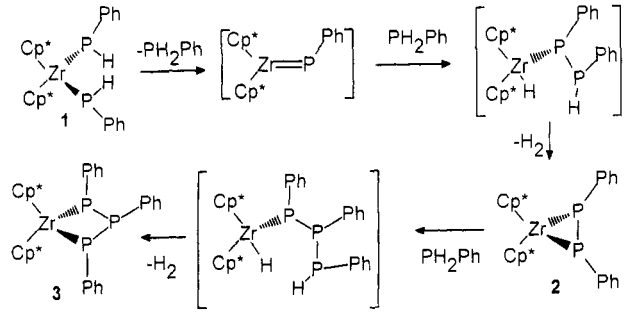


Figure 3. ORTEP drawing of **6**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–P1 = 2.650 (3) Å, Zr–P2 = 2.659 (3) Å, and P–Zr–P = 48.65(9)°.

atoms on P were not located, the crystallographically imposed symmetry requires that the handedness of the diastereomers in the solid state be *RR* and *SS* at the P atoms.

Monitoring a benzene solution of **4** by ^{31}P NMR showed a slow degradation of the compound. Loss of the resonance attributable to **4** and the growth of signals attributable to two new Zr complexes, free primary phosphine $PH_2(C_6H_2Me_3)$, and traces of $(PH(C_6H_2Me_3))_2$ occurred over a period of several days. The new Zr complexes were isolated by fractional crystallization. After 2 days, red-brown crystals of the first new product **5** were deposited. The ^{31}P NMR spectra of **5** showed a resonance at −42.6 ppm with P–H coupling of 180 Hz indicative of a direct P–H bond. In addition the ^1H NMR showed a resonance at 1.25 ppm consistent with the presence of a methylene moiety. X-ray crystallographic data confirmed the connectivity in **5** as the phosphametallocycle $Cp^*_2Zr(CH_2C_6H_2Me_2PH)$ in which the *ortho*-methyl substituent on the aryl ring was metalated (Figure 2).[22] Upon further standing for several additional days, a second new Zr derivative **6** was obtained. This compound **6** exhibited a singlet resonance in the ^{31}P NMR at 134.9 ppm, while the ^1H NMR data also suggested a formulation analogous to **2**, i.e. $Cp^*_2Zr(P(C_6H_2Me_3))_2$. This formulation of **6** was confirmed by X-ray crystallography (Figure 3). The Zr–P bonds within the three-membered ring of **6** averaged 2.654(3) Å, while the P–P bond was 2.187(4) Å. The P–Zr–P angle was found to be

Scheme I



48.65(9)°, similar to that found in other $M(PR)_2$ fragments[25] and yet much larger than the N1–Zr–N2 angle seen in $Cp_2Zr(NR)_2(py)$ (39.25(12)°).[4]

In contrast to **2**, monitoring solutions of **6** over the period of several weeks showed no further reaction, even in the presence of excess of the primary phosphine $PH_2(C_6H_2Me_3)$. It is noteworthy that addition of PH_2Ph to **6** did lead to reaction; however, it did not result in insertion to give an asymmetric P_3 species. Rather, acidolysis of the P_2R_2 fragment in **6** occurs. This yields $(PH(C_6H_2Me_3))_2$ and **1** and indicates the steric influence on the competition between insertion and acidolysis.

Phosphinidene Intermediates. The course of the reactions involving these primary phosphide derivatives supports the intermediacy of a highly reactive terminal phosphinidene intermediate of the form $Cp^*_2Zr{=}PR$. Such intermediates are formed via the loss of primary phosphine from the diphosphide precursors. In a similar vein, Bergman et al.[2] have described the generation of $Cp_2Zr{=}NR$ from $Cp_2Zr(NHR)_2$. Subsequent formation of **2** or **6** requires addition of the P–H bond of the primary phosphine to the Zr=P double bond with the regiochemistry opposite to that which permits re-formation of **1** and **4**, respectively (Scheme II). This yields a P–P bond and subsequent elimination of H_2 drives the irreversible formation of the diphosphide complexes. While the compound **2** undergoes further reaction with free phosphine to give the P_3 derivative **3** (Scheme I), the compound **6** is stable in solution, even in the presence of excess phosphine $PH_2(C_6H_2Me_3)$. This difference in reactivity is attributable to steric factors.

The formation of **5** is also indicative of a transient phosphinidene species $Cp^*_2Zr{=}P(C_6H_2Me_3)$. Intramolecular C–H bond activation of an *ortho*-methyl group of the aryl substituent by the transient phosphinidene intermediate accounts for the formation of **5** (Scheme II). Related intramolecular cyclopentadienyl C–H activation by such phosphinidene intermediates has been previously described.[12g] In the present case the reaction is sterically favored as a result of the proximity of the methyl C–H bonds to the Lewis acidic Zr center. In addition, the steric demands of the substituents inhibit the approach of primary phosphine, thus making the formation of **5** and **6** competitive.

Direct interception of the transient phosphinidene was achieved via the reaction of a solution of **4** with MeCN in benzene at 25 °C. Monitoring the solution revealed the presence of free primary phosphine PRH_2 as well as the new singlet resonance at 0.2 ppm. This new species was isolated. ^1H NMR and X-ray crystallography[22] confirmed

(25) Caminade, A. M.; Majoral, J. P.; Mathieu, R. *Chem. Rev.* **1991**, *91*, 575.

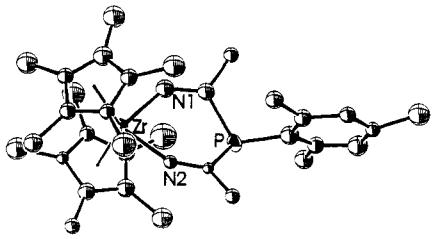
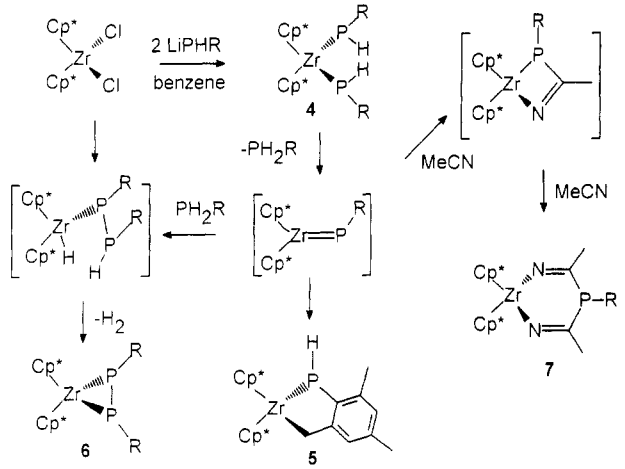


Figure 4. ORTEP drawing of **7**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–N1 = 2.02(4) Å, Zr–N2 = 2.11(3) Å, and N1–Zr–N2 = 88(1)°.

Scheme II



that the yellow-orange product was the six-membered phosphametallocycle $Cp^*_2Zr(NCMe)_2P(C_6H_2Me_3)$ (**7**) (Figure 4). The geometry about the P atom is pseudopyramidal. Compound **7** represents a rare example of a bis(imidoylphosphine) ligand. Mechanistically, this reaction is thought to involve a 2 + 2 cycloaddition of MeCN to the phosphinidene with subsequent insertion of a second equivalent of acetonitrile into the Zr–P bond (Scheme II). This view is supported in concept by the similar reaction pathway exhibited by related Zr- and Ti-imido systems in which the initial 2 + 2 addition product was observed spectroscopically.[2,3] Attempts to observe the cycloaddition product in the present case led only to the observation of **4**, **7**, and free phosphine suggesting that the ring strain in the intermediary four-membered ring results in rapid insertion of the second equivalent of nitrile into the Zr–P bond.

Attempts to isolate the phosphinidene intermediate were unsuccessful; however, direct spectroscopic evidence for a phosphinidene species is derived from the reaction of $LiPH(C_6H_2Me_3)$ and $Cp^*_2ZrCl_2$ in DME at 25 °C. In addition to a resonance attributed to **4**, a ^{31}P NMR resonance at 537 ppm with no P–H coupling is seen. The similarity of this chemical shift to that seen in other systems suggests a bridging phosphinidene group[13,26] and thus was attributed to the unstable LiCl adduct of the zirconocene phosphinidene intermediate **8**. Addition of MeCN to DME solution of **8** led to the formation of **7**, while attempts to isolate **8** or trap it employing dative donors such as PMe_3 were unsuccessful, affording instead mixtures of **5** and **6**.

A terminal phosphinidene species were isolated via alteration of the steric demands of the substituents both

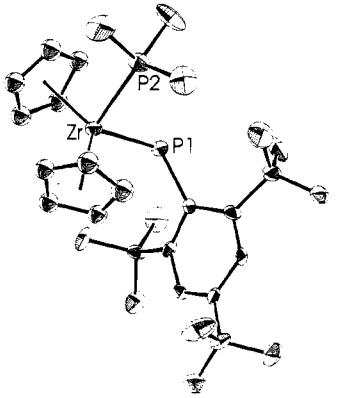
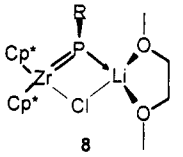
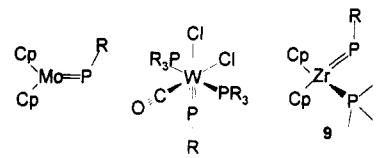


Figure 5. ORTEP drawing of **9**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–P1 = 2.505(4) Å, Zr–P2 = 2.741(5) Å, and P1–Zr–P2 = 101.4(1)°.



on the metal and on phosphorus. Reaction of Cp_2ZrCl_2 with $Li(PH(C_6H_2t\text{-}Bu_3))$ in the presence of PMe_3 affords the green-black product **9**. The compound exhibits ^{31}P NMR doublet resonances at 792 and −12 ppm, neither exhibiting direct coupling to protons. The low-field resonance in the ^{31}P NMR data[27] together with the ^1H NMR data support the formulation of **9** as phosphine adduct of the terminal phosphinidene derivative, $Cp_2Zr(P(C_6H_2t\text{-}Bu_3)(PMe_3)$. This was confirmed crystallographically (Figure 5). The formal Zr–P double bond in **9**, which is the Zr–P1 bond, is 2.505(4) Å, considerably shorter than either Zr–P2 of **9** (2.741(5) Å) or the single Zr–P bonds in **4**–**6** or the species $Cp_2ZrCl(P(C_6H_2t\text{-}Bu_3)\text{-}SiMe_3)$ (2.541(4) Å).[28] The geometry at P is bent as indicated by the Zr–P1–C1 angle of 116.1(4)° consistent with four-electron donation from P to Zr and a resulting eighteen-electron configuration about the Zr center. The characterization of **9** represents only the third example of



a terminal phosphinidene complex, $Cp_2Mo(PC_6H_2(t\text{-}Bu)_3)$[30] and $WCl_2(CO)(P(C_6H_2t\text{-}Bu_3)(PMe_2Ph)_2$[29] being previously characterized by the research groups of Lappert and Cowley, respectively. The bent phosphinidene moiety in **9** is similar to that seen for $Cp_2Mo(PR)$.[29]

Reactivity of Monophosphide Complex 5. The species **5**, which is derived from **4**, is a convenient synthon for several new phosphametallacycles. Monitoring of the reaction of **5** with MeCN by ^{31}P NMR showed a clean conversion of **5** to a new species **10**. On the basis of the ^1H NMR data, **10** was formulated as the product derived

(26) Ho, J.; Hou, Z.; Drake, R. E.; Stephan, D. W. *Organometallics* **1993**, *12*, 3145.

(27) The ^{31}P NMR chemical shifts of the "bent" terminal phosphinidene complexes[30] are as follows: $Cp_2Mo{=}P(C_6H_2(t\text{-}Bu)_3)$, 799.5 ppm; $Cp_2W{=}P\text{-}(C_6H_2(t\text{-}Bu)_3)$, 661.1 ppm.

(28) Arif, A. M.; Cowley, A. H.; Nunn, C. M.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1987**, 994.

(29) Cowley, A. H.; Pellerin, B. *J. Am. Chem. Soc.* **1990**, *112*, 6734.

(30) Hitchcock, P. B.; Lappert, M. F.; Leung, W. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282.

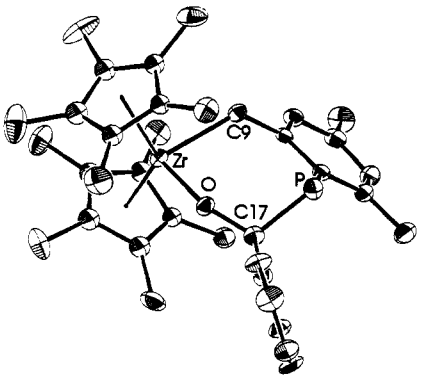
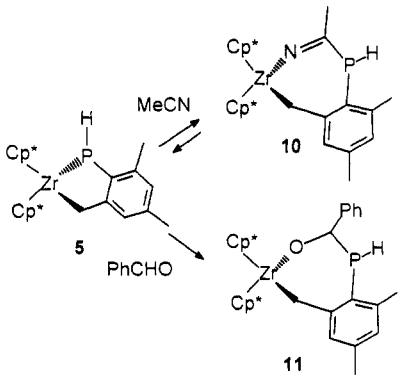


Figure 6. ORTEP drawing of 11, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–O = 1.980(5) Å, Zr–C9 = 2.336(7) Å, and O–Zr–C9 = 88.6(2)°.

Scheme III



from acetonitrile insertion into Zr–P of **5**, i.e. the phosphametallocycle $Cp^*_2Zr(CH_2C_6H_2Me_2PHC(Me)N)$ (Scheme III). This product was not stable in the absence of excess MeCN. Placement of **10** under vacuum led to the prompt reversal of this insertion with the quantitative regeneration of **5**.

In a similar reaction **5** was treated with benzaldehyde. This led to the clean production of a new species **11**. The ^{31}P NMR resonance of **11** was observed at −60.3 ppm, while the ^1H NMR data were consistent with the addition of benzaldehyde to the Zr–P bond (Scheme III). X-ray crystallography confirmed the formulation of **11** as $Cp^*_2Zr(CH_2C_6H_2Me_2PHCH(Ph)O)$ (Figure 6). The Zr–O distance of 1.980(5) Å was typical. The geometry about the P was pyramidal. The location of the H atom on P in the solid state is consistent with an opposing stereochemistry at the C and P centers. The relative stereochemistry of the chiral C and P centers was such that the aryl substituents adopted *transoid* orientation. NMR data showed no evidence of the other diastereomers in solution, thus suggesting that the insertion of benzaldehyde proceeded stereoselectively.

These insertion reactions occur into the Zr–P bond in preference to the Zr–C bond in **5**, suggesting that these reactions are mediated by the nucleophilic character of the Zr–P fragment. However, in contrast to the above organic substrates, no reaction was observed between **5** and styrene. This suggests that the insertion process is initiated by coordination of the substrate to the Lewis acidic Zr center. Thus, the basicity of acetonitrile and benzaldehyde facilitate coordination and subsequent reaction, whereas steric and electronic properties of styrene disfavor reaction. This result is also in contrast to the known reactivity of the transient terminal phosphinidene species $[PhP{=}W(CO)_5]$ with styrene.[31]

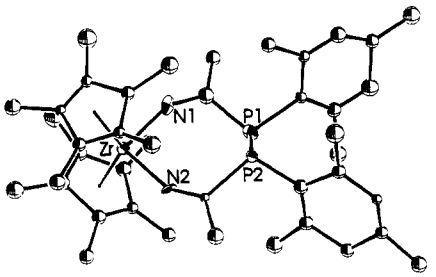
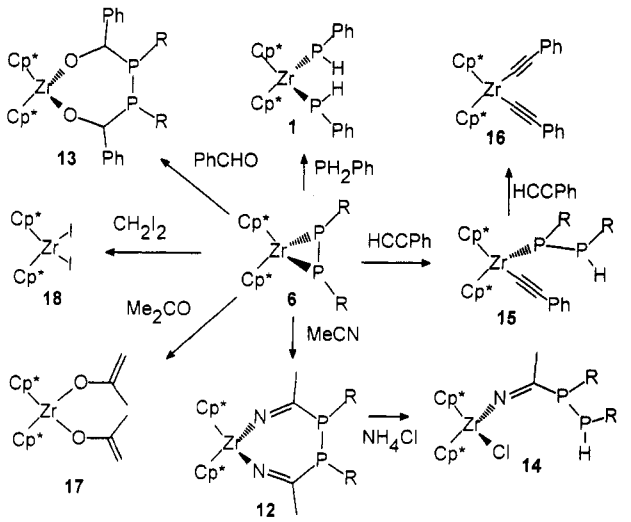


Figure 7. ORTEP drawing of **12**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–N1 = 2.07(1) Å, Zr–N2 = 2.06(1) Å, and N1–Zr–N2 = 96.1(3)°.

Scheme IV



Reactivity of Diphosphide Complex 6. The diphosphide species **6** also proved to be a reactive compound (Scheme IV). The reaction of **6** with MeCN proceeded in a manner similar to that seen for **5** as insertion occurred into the Zr–P bonds. ^{31}P NMR data for the isolated product **12** showed equivalent P atoms which gave rise to a single resonance at −30.1 ppm. ^1H NMR and X-ray crystallographic data confirmed **12** was the seven-membered 1,2-diphosphametallocycle $Cp^*_2Zr(NC(Me)P(C_6H_2Me_3))_2$ (Figure 7).[22] Attempts to observe the initial insertion product employing 1 equiv of MeCN led only to mixtures of **6** and **12**, implying that the Zr–P bond in the five-membered ring intermediate is also very reactive (Scheme IV). The metric parameters in **12** are similar to those seen in **7**, with a Zr–N distance of 2.07(1) Å and a N–Zr–N angle of 96.1(3)°. The insertion of MeCN into the Zr–P bonds affording **12** is in contrast to the reactions of $Cp_2Zr(NR)_2$ with MeCN, which yield simply the adduct $Cp_2Zr(NR)_2(NCMe)$.[4] This may be a reflection of the electrophilicity of the P centers in the ZrP_2 ring in **6**. As well, the ring strain in the three-membered ring may encourage reaction, as similar insertions have not been observed for acyclic phosphide derivatives.[10,14]

Compound **6** reacts with benzaldehyde in much the same way as **5**. Double insertion of benzaldehyde into the Zr–P bonds in **6** is supported by the observation of a single new ^{31}P NMR resonance at −4.7 ppm attributed to the product **13**. The ^1H NMR data suggested the formulation for the

(31) Lammertsma, K.; Chand, P.; Yang, S. W.; Hung, J. T. *Organometallics* **1988**, *7*, 1875.

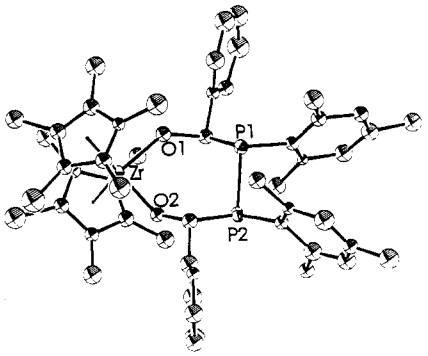


Figure 8. ORTEP drawing of **13**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–O1 = 1.98(2) Å, Zr–O2 = 2.02(2) Å, and O1–Zr–O2 = 93.9(8)°.

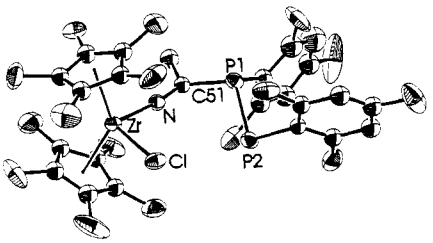


Figure 9. ORTEP drawing of **14**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–N = 2.03(1) Å, Zr–Cl = 2.491(4) Å, and N–Zr–Cl = 99.7(3)°.

product **13** as $Cp^*_2Zr(OCH(Ph)P(C_6H_2Me_3))_2$ (Scheme IV). The connectivity within this 1,2-diphosphametallocycle was confirmed by X-ray crystallographic data (Figure 8). The Zr–O distances of 1.98(2) Å as well as the O–Zr–O angle of 93.9(8)° are typical of Zr–dialkoxide derivatives.[32]

For both **12** and **13**, the relative stereochemistry of the two chiral P centers was maintained from that seen in **6**. In addition, steric demands of the substituents appear to control the relative stereochemistry of the chiral C and P centers seen in **13**. These observations supports the view that these insertion reactions proceed via initial coordination followed by a subsequent concerted insertion process. Such a reaction pathway suggests that both steric and electronic requirements may restrict the reactivity of **6**. Such is the case for benzophenone and diphenylacetylene, where neither undergo reaction with **6**.

Initial attempts to remove Zr from the 1,2-diphosphametallocycles **12** and **13** involved treatment with a weak proton source. Reaction of compound **12** with NH_4Cl proceeds cleanly to give a new species **14**. This species exhibits two coupled resonances in the ^{31}P NMR spectrum at 17.9 and −110.7 ppm with a P–P coupling constant of 122 Hz and the latter resonance also being strongly coupled to a single proton ($|J_{P-H}| = 228$ Hz). The ^1H NMR spectral data for this product **14** are consistent with the presence of one acetonitrile residue (Scheme IV). X-ray data clarified the formulation of **14** as $Cp^*_2ZrCl(NC(Me)P(C_6H_2Me_3)Ph(C_6H_2Me_3))$ (Figure 9). The Zr–N, P–P, and Zr–Cl distances in **14** were typical. The conversion of **12** to **14** is perhaps not too surprising as loss of acetonitrile via P–C bond cleavage also occurs in the re-formation of **5** from **10**. Similar treatment of **13** with NH_4Cl resulted in no reaction, reflecting the inherent stability of Zr–O bonds.

(32) Stephan, D. W. *Organometallics* **1990**, *9*, 2718.

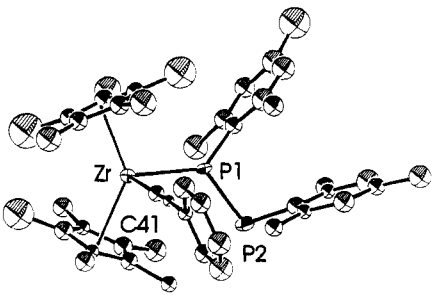


Figure 10. ORTEP drawing of **15**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–P1 = 2.60(1) Å, Zr–C41 = 2.25(4) Å, and P1–Zr–C41 = 90.2(9)°.

Compound **6** undergoes sequential acidolysis of the Zr–P bonds. The reaction with 1 equiv of HCCPh affords the product **15**. The two ^{31}P NMR resonances for **15** at 92.3 and −74.5 ppm are coupled with a J_{P-P} value of 385 Hz. The high-field resonance is also coupled to a single proton with a coupling constant of 209 Hz. These data together with the ^1H NMR data support the formulation of **15** as $Cp^*_2Zr(CCPh)(P(C_6H_2Me_3)PH(C_6H_2Me_3))$ (Scheme IV), which was confirmed crystallographically (Figure 10). In contrast to an analogous Zr–N system, $Cp_2Zr(CCR)(RNNHR)$,[4] the protonated P atom of **15**, i.e. P2, is not coordinated to Zr. The Zr–P1 distance is 2.60(1) Å similar to that observed in **6**, while the Zr–C and C–C distances in the acetylide moiety are 2.25(4) and 1.21(5) Å, respectively, and are similar to those seen in other early metal σ-acetylide derivatives such as $Cp_2Zr(CCMe)_2$[33] and $Cp_2Zr(CCR)(RNNHR)$.[4] Subsequent reaction of **15** with a second equivalent liberates $(PHR)_2$ and yields the product $Cp^*_2Zr(CCPh)_2$ **16** (Scheme IV). The identity of **16** was also confirmed crystallographically.[34] The C–C bond distances in the acetylide moieties of **16** were found to be 1.24(4) Å, similar to that seen in **15**.

Acidolysis of the Zr–P bonds of **6** is also precipitated by reaction with acetone. ^1H and ^{13}P NMR data confirm that the P-containing product is $(PHR)_2$, while the Zr product is the dienolate complex $Cp^*_2Zr(OC(Me)CH_2)_2$ (**17**) (Scheme IV). Similar acidolysis reactions have been observed for Zr–alkyls and Zr–imide derivatives.[4,35] In a related reaction, **6** was treated with CH_2I_2. The Zr-containing product was formulated by ^1H NMR as the species $Cp^*_2ZrI_2$ (**18**) (Scheme IV). This was confirmed cyrstallographically.[36] The ^{31}P NMR spectrum of the reaction mixture was consistent with Zr–P bond cleavage and the formation of several inseparable and, as yet, unidentified P-containing products.

Reactivity of Triphosphide Complexes. Although compounds of the general formulation $Cp_2Zr(PR)_3$ have been known for some time,[17,18] little is known of their reactivity. The triphosphide species **3** derived from **1**

(33) Erker, G.; Fromberg, R.; Benn, R.; Mynott, K.; Angermund, K.; Kruger, C. *Organometallics* **1989**, *8*, 911.

(34) The compound **16** crystallizes in the space group $P2_1/n$ with a = 15.148(9) Å, b = 12.534(4) Å, c = 16.182(5) Å, β = 99.80(3)°, V = 3028(2) Å^3, and Z = 4. The structure was refined (955 data, 126 variables, R = 8.13%, R_w = 9.32%). Zr–acetylide C bond distances: 2.19(3), 2.21(3) Å. C–Zr–C: 96(1)°. C–C distance in acetylide ligands: 1.23(4), 1.24(4) Å.

(35) (a) Hunter, W. E.; Hrncir, D. C.; Vann Bynum, R.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750. (b) Samuel E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263.

(36) The compound **18** crystallizes in the space group $P2_1/n$ with a = 8.592(2) Å, b = 16.240(4) Å, c = 15.781(2) Å, β = 97.27(2)°, V = 2184.2(7) Å^3, and Z = 4. The structure was refined (1721 data 201 variables, R = 4.44%, R_w = 3.24%). Zr–I distances: 2.847(2), 2.827(2) Å. I–Zr–I: 93.47-(5)°.

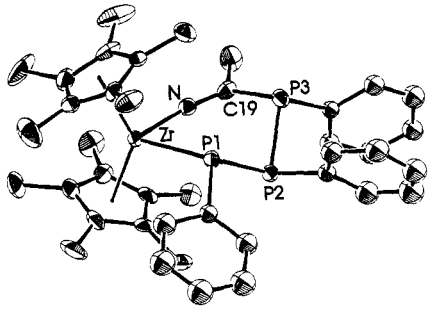
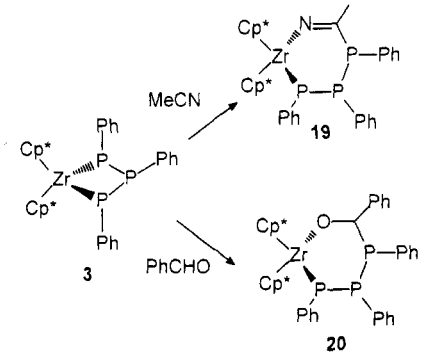


Figure 11. ORTEP drawing of **19**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Zr–N = 2.010(8) Å, Zr–P1 = 2.744(3) Å, and N–Zr–P1 = 82.4-(2)°.

Scheme V



proved to be a reactive synthon for 1,2,3-triphosphametallocycles (Scheme V). Reaction of **3** with MeCN proceeds cleanly to yield a new product **19**. ^{1}H NMR data indicates a 1:1 reaction stoichiometry, while the AMX resonance pattern observed in the ^{31}P NMR spectrum of **19** reveals the presence of three inequivalent P atoms. These data suggest the insertion of MeCN into one of the Zr–P bonds and thus a formulation of **19** as the six-membered 1,2,3-triphosphametallocyclic product $Cp^*_2Zr(NCMe)(PPh)_3$ (Scheme V). This postulate was confirmed by the crystallographic study (Figure 11). The Zr–N and Zr–P distances of 2.010(8) and 2.744(3) Å, respectively, were similar to those seen in **6** and **7**. The aryl substituents on P in **19** are on alternate sides of the metallocyclic ring. This orientation is expected in the starting material **3**, as it has been seen for related $Cp_2M(PR)_3$ compounds.[17,37]

In parallel reaction **3** was found to react with benzaldehyde. The ^{31}P NMR spectrum of the product **20** was also an AMX spectrum exhibiting coupled resonances at 0.3, −28.1, and −50.3 ppm. The ^{1}H NMR was consistent with a 1:1 addition reaction supporting the formulation of **20** as the 1,2,3-triphosphametallocycle $Cp^*_2Zr(OCH(Ph))(P(C_6H_2Me_3))_3$ (Scheme V). The isolation of **19** and **20** even in the presence of excess MeCN or PhCHO suggests that the six-membered triphosphametallocycle is quite stable in spite of the presence of the Zr–P bonds. However, it is noteworthy that on prolonged exposure to benzaldehyde the compound **20** did undergo further reaction to unidentified products.

The chemistry described herein demonstrates that the primary diphosphide derivatives $Cp^*_2Zr(PHR)_2$ are effective precursors to reactive phosphinidene intermediates. Zr–P double bonds (Zr=PR) have been shown to react with P–H bonds and intramolecular C–H bonds as well as undergo 2 + 2 cycloadditions of acetonitrile. This reactivity is reminiscent of, but distinct from, the reactivity of Zr=O, Zr=S, and Zr=NR systems. These intermediates act as synthons for phosphametallocycles as well as diphosphide and triphosphide complexes. The Zr–P single bonds of cyclic phosphide, diphosphide, and triphosphide species are also reactive. This reactivity affords synthetic routes to new mono-, 1,2-di- and 1,2,3-triphosphametallocycles, classes of compounds which are either rare or unprecedented.[38] These studies clearly demonstrate the rich reactivity of Zr–P derivatives, and such reactivity augurs well for the development of metal-mediated organophosphorus chemistry.

Acknowledgment. The financial support from the NSERC of Canada is gratefully acknowledged.

Supplementary Material Available: Tables of crystallographic data, thermal and hydrogen atom parameters, and selected bond distances and angles for all the structures and tables of crystallographic parameters and ORTEP drawings for **16** and **18** (56 pages). Ordering information is given on any current masthead page.

OM9302857

(37) Ho, J.; Stephan, D. W. Unpublished results.
(38) Hewitt, D. *Adv. Heterocycl. Chem.* **1988**, *43*, 1.