Reactivity Studies of Methylzirconocene Phosphide Complexes

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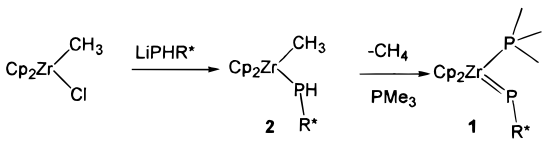
The reaction of $Cp_2ZrMe(PHR)$ with benzophenone, cyclohexanone, acetone, benzaldehyde, and benzophenone results in the insertion of the organic substrate into the Zr−P bond. In this way, the complexes $Cp_2ZrMe(OCPh_2PH(C_6H_2$-2,4,6-*t*-$Bu_3))$ (**3**), $Cp_2ZrMe(OC_6H_{10}PH(C_6H_2$-2,4,6-*t*-$Bu_3))$ (**4**), $Cp_2ZrMe(OCMe_2PHR)$ (R = (C_6H_2-2,4,6-*t*-Bu_3) (**5**), R = (C_6H_2-2,4,6-Me_3) (**8**), and $Cp_2ZrMe(NC(Ph)PH(C_6H_2$-2,4,6-*t*-$Bu_3))$ (**6**) were prepared. The species $Cp_2ZrMe(PH$-(C_6H_2-2,4,6-Me_3)) (**7**) was also formed in the reaction of Cp_2ZrMe_2 with $H_2P(C_6H_2$-2,4,6-Me_3); however, **7** reacted further with Cp_2ZrMe_2 to give the bimetallic species $(Cp_2ZrMe)_2(\mu$-$P(C_6H_2$-2,4,6-$Me_3)$ (**9**). In the analogous reaction of Cp_2ZrMe_2 with 1 equiv of $H_2P(C_6H_2$-2,4,6-Me_3), the species $(Cp_2Zr)(Cp_2ZrPH(C_6H_2$-2,4,6-$Me_3))(\mu$-P_6H_2-2,4,6-$Me_3))(\mu$-η^1-η^5-$C_5H_4)$ (**11**) was obtained. Compound **11**, which results from cyclopentadienyl C−H bond activation, was also formed directly from degradation of the unstable terminal phosphinidene species $Cp_2Zr(P(C_6H_2$-2,4,6-$Me_3))(PMe_3)$ (**12**). The implications of this chemistry are considered and discussed. Compound **3**, **9**, and **11** have been characterized crystallographically.

Introduction

The intense study of early metal−ligand multiple bonds is motivated not only by questions of structure and bonding but also by issues of stability and reactivity.[1] These systems offer both new reactivity patterns and new reagents for the synthesis of compounds incorporating heteroatoms. While landmark contributions in this area have dealt with early metal oxide, sulfide, and imide derivatives,[2] we and others[3] have focused on early metal phosphinidene species (M=PR). Several years ago, we explored a variety of approaches employing P−H bond activation for the synthesis of Zr-phosphides and dimeric phosphinidene derivatives.[4] These studies suggested that the stabilization of a monometallic terminal Zr−phosphinidene complex required a sterically demanding substituent on P. This view was subsequently validated by the isolation of the first mononuclear Zr−phosphinidene complex Cp_2Zr-(PR*)(PMe_3) (R* = C_6H_2-2,4,6-*t*-Bu_3) (**1**).[5] The most expedious path to this species involves loss of methane from the intermediate $Cp_2ZrMe(PH(C_6H_2$-2,4,6-*t*-$Bu_3))$ (**2**) in the presence of PMe_3 (eq 1).[6] A wide range of



(1)

reactions in which **1** effects both intra- and intermolecular phosphinidene group transfer reactions have been examined.[6]

More recently, we have shown that **1** also provides access to phosphametallacyclobutenes via [2 + 2] cycloaddition reactions with alkynes.[7] The resulting metallacycles are reactive in their own right and have been shown to be useful synthons for a variety of cyclic organophosphorus derivatives.[8] In this paper, we examine reactions of intermediate methylzirconocene phosphide complexes such as **2** as well as related species with less sterically demanding substituents. The Zr−P bonds of these species undergo insertion reactions with

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organic substrates in preference to methane elimination. Furthermore, when methane elimination is allowed to proceed, diminished steric demands of the substituent on P results in a highly reactive phosphinidene species which effects cyclopentadienyl C−H bond activation.

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. 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. All organic reagents were purified by conventional methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-300 operating at 300 and 75 MHz, respectively. ^{31}P and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AC-200 operating at 81 MHz. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$ and 85% H_3PO_4, respectively. Yields obtained by ^{1}H NMR were determined in reference to a CH_2Cl_2 internal standard which was introduced by employing a concentric NMR tube insert. Low- and high-resolution EI mass spectral data were obtained employing a Kratos Profile mass spectrometer outfitted with a N_2 glovebag enclosure for the inlet port. Combustion analyses were performed by Galbraith Laboratories Inc. Knoxville, TN, or Schwarzkopf Laboratories, Woodside, NY. Glass reaction vessels fitted with ground glass joints and Teflon stopcocks are referred to as "bombs". $PH_2(C_6H_2$-2,4,6-*t*-$Bu_3)$ and $PH_2(C_6H_2$-2,4,6-$Me_3)$ were purchased from the Quantum Design Chemical Co. All other reagents were purchased from the Aldrich Chemical Co. Cp_2ZrMe_2,[9] $Cp_2ZrMeCl$[10], $Cp_2Zr(P(C_6H_2$-2,4,6-*t*-$Bu_3))(PMe_3)$ (**1**),[5,6] $Cp_2ZrMe(PH(C_6H_2$-2,4,6-*t*-$Bu_3))$ (**2**),[6] $(Cp_2ZrCl)_2(\mu$-$P(C_6H_2$-2,4,6-$Me_3))$ (**10**),[4] and $LiHP(C_6H_2$-2,4,6-*t*-$Bu_3)\cdot 3THF$[11] were prepared by literature methods. The procedure of Power et al.[12] was employed to prepare $Li_2P(C_6H_2$-2,4,6-$Me_3)$. In all instances, Ar refers to the $(C_6H_2$-2,4,6-*t*-$Bu_3)$ group and Mes refers to the $(C_6H_2$-2,4,6-$Me_3)$ group.

Synthesis of $Cp_2ZrMe(OCPh_2PH(C_6H_2$-2,4,6-*t*-$Bu_3))$ (3), $Cp_2ZrMe(OC_6H_{10}PH(C_6H_2$-2,4,6-*t*-$Bu_3))$ (4), $Cp_2ZrMe(OCMe_2PH(C_6H_2$-2,4,6-*t*-$Bu_3))$ (5), $Cp_2ZrMe(NC(Ph)PH(C_6H_2$-2,4,6-*t*-$Bu_3))$ (6), and $Cp_2ZrMe(OCMe_2PH(C_6H_2$-2,4,6-$Me_3))$ (8). Compounds **3**−**6** and **8** were prepared through similar routes with the appropriate substitutions of phosphide and organic substrate; thus only one representative procedure is given. To a benzene solution of $Cp_2ZrMeCl$ (136 mg, 0.5 mmol) and benzophenone (91 mg, 0.5 mmol) was added a benzene solution of $LiHP(C_6H_2$-2,4,6-*t*-$Bu_3)\cdot$THF (250 mg, 0.5 mmol). The resulting solution turned orange and then immediately turned a very pale yellow. After standing for 2 h, the solvent was removed in vacuo and the product was extracted into pentane. Filtration was followed by a reduction in the volume of the solution under reduced pressure. Colorless crystals formed over 12 h at room temperature and were isolated by filtration. (**3**) Yield: 289 mg (83%). ^{1}H NMR (25 °C, C_6D_6): δ 7.49 (m, 2H, Ph*H*), 7.33 (m, 1H, Ph*H*), 7.18 (m, 1H, Ph*H*), 7.00 (m, 6H, Ph*H*), 6.72 (m, 2H, Ph*H*), 5.86 (s, 5H, Cp), 5.71 (s, 5H, Cp), 5.67 (d, $|J_{P-H}| = 244.6$ Hz, 1H, P*H*), 1.42 (s, 9H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu), 1.25 (s, 9H, ^{t}Bu), 0.66 (s, 3H, Me). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 157.0 (s, quat), 156.6 (d, $|J| = 17.1$ Hz, quat), 149.4 (s, quat), 147.0 (d, $|J| = 21.5$ Hz, quat), 143.9 (s, quat), 130.9 (d, $|J| = 44.6$ Hz, quat), 129.0 (d, $|J| = 8.3$ Hz, arom *C*H), 127.3 (s, arom *C*H), 126.8 (s, arom *C*H), 126.7 (s, arom *C*H), 126.3 (s, arom *C*H), 125.4 (s, arom *C*H), 122.3 (s, arom *C*H), 111.2 (s, Cp), 110.9 (s, Cp), 94.1 (d, $|J| = 18.9$ Hz, O*C*), 38.6 (s, $C(CH_3)_3$), 37.9 (s, $C(CH_3)_3$), 34.6 (s, $C(CH_3)_3$), 34.3 (d, $|J| = 10.7$ Hz, $C(CH_3)_3$), 33.8 (s, $C(CH_3)_3$), 31.5 (s, $C(CH_3)_3$), 22.5 (s, Me). ^{31}P NMR (25 °C, C_6D_6): δ −8.6 (d, $|J_{P-H}| = 244.1$ Hz). Anal. Calcd for $C_{42}H_{53}OPZr$: C, 72.47; H, 7.67. Found: C, 72.30; H, 7.45. (**4**) Yield: 72% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 7.39 (m, 2H, Ar*H*), 5.93 (s, 5H, Cp), 5.91 (s, 5H, Cp), 4.79 (d, $|J_{P-H}| = 222.5$ Hz, 1H, P*H*), 2.2−1.1 (m, 10H, Cy*H*), 1.67 (s, 9H, ^{t}Bu), 1.54 (s, 9H, ^{t}Bu), 1.28 (s, 9H, ^{t}Bu), 0.42 (s, 3H, Me). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 157.2 (br s, quat), 148.6 (s, quat), 132.2 (d, $|J| = 38.9$ Hz, quat), 122.0 (s, arom *C*H), 110.8 (s, Cp), 110.5 (s, Cp), 87.0 (d, $|J| = 9.5$ Hz, O*C*), 39.6 (d, $|J| = 19.0$ Hz, *C*H$_2$), 38.1 (d, 35.4 (d, $|J| = 11.8$ Hz, $C(CH_3)_3$), 34.7 (s, $C(CH_3)_3$), 34.3 (s, $C(CH_3)_3$), 31.2 (s, $C(CH_3)_3$), 25.6 (s, *C*H$_2$), 22.6 (s, *C*H$_2$), 21.9 (d, $|J| = 9.7$ Hz, *C*H$_2$), 20.7 (s, Me). ^{31}P NMR (25 °C, C_6D_6): δ −24.9 (d, $|J_{P-H}| = 222.3$ Hz). HRMS (EI) *m/e*: calcd for $C_{35}H_{53}OPZr$ 595.2642; found 595.2630 ($M^+ - CH_3$). (**5**) Yield: 73% (by ^{1}H NMR) ^{1}H NMR (25 °C, C_6D_6): δ 7.44 (s, 2H, Ar*H*), 5.87 (s, 5H, Cp), 5.82 (s, 5H, Cp), 5.01 (d, $|J_{P-H}| = 228.7$ Hz, 1H, P*H*), 1.69 (s, 9H, ^{t}Bu), 1.53 (s, 9H, ^{t}Bu), 1.29 (s, 9H, ^{t}Bu), 1.04 (d, $|^3J_{P-H}| = 10.9$ Hz, 3H, Me), 0.82 (d, $|^3J_{P-H}| = 3.8$ Hz, 3H, Me), 0.36 (s, 3H, ZrMe). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 156.6 (s, quat), 154.3 (s, quat), 148.8 (s, quat), 132.9 (d, $|J| = 38.3$ Hz, quat), 121.9 (s, arom *C*H), 121.8 (s, arom *C*H), 110.5 (s, Cp), 110.4 (s, Cp), 84.7 (d, $|J| = 12.2$ Hz, O*C*), 38.2 (s, $C(CH_3)_3$), 38.1 (s, $C(CH_3)_3$), 35.0 (d, $|J| = 11.9$ Hz, $C(CH_3)_3$), 33.9 (s, $C(CH_3)_3$), 31.3 (s, $C(CH_3)_3$), 19.9 (s, Me). ^{31}P NMR (25 °C, C_6D_6): δ −30.1 (d, $|J_{P-H}| = 229.1$ Hz). HRMS (EI) *m/e*: calcd for $C_{32}H_{49}OPZr$ 555.2329, found: 555.2334 ($M^+ - CH_3$). (**6**) Yield: 56% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 7.62 (d, $|^4J_{P-H}| = 2.1$ Hz, 1H, Ar*H*), 7.51 (br, 1H, Ar*H*), 7.17−7.09 (m, 5H, Ph*H*), 6.17 (d, $|J_{P-H}| = 234.3$ Hz, 1H, P*H*), 5.60 (s, 5H, Cp), 5.58 (s, 5H, Cp), 1.73−1.49 (br, 18H, *o*-^{t}Bu), 1.44 (s, 9H, *p*-^{t}Bu), −0.25 (br s, 3H, Me). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 177.9 (d, $|J| = 30.5$ Hz, N=*C*), 150.1 (s, quat), 142.2 (d, $|J| = 34.1$ Hz, quat), 129.3 (s, arom *C*H), 128.1 (s, arom *C*H), 125.8 (s, arom *C*H), 122.3 (br s, arom *C*H), 108.0 (s, Cp), 107.8 (s, Cp), 38.1 (br s, *o*-$C(CH_3)_3$), 35.1 (s, *p*-$C(CH_3)_3$), 33.5 (br s, *o*-$C(CH_3)_3$), 33.4 (br s, *o*-$C(CH_3)_3$), 31.5 (s, p-$C(CH_3)_3$), 17.2 (br s, Me). ^{31}P NMR (25 °C, C_6D_6): δ −44.8 (d, $|J_{P-H}| = 233.9$ Hz). HMRS (EI) *m/e*: calcd for $C_{36}H_{48}NPZr$ 615.2567, *m/e* found 615.2582. (**8**) Yield: 73% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 6.80 (s, 2H, Mes-*H*), 5.83 (s, 5H, Cp), 5.82 (s, 5H, Cp), 4.42 (d, $|J_{P-H}| = 216.5$ Hz, 1H, P*H*), 2.50 (s, 6H, *o*-Me), 2.07 (s, 3H, *p*-Me), 1.29 (d, $|^3J_{P-H}| = 5.5$ Hz, 3H, Me), 1.24 (d, $|^3J_{P-H}| = 11.8$ Hz, 3H, Me), 0.38 (s, 3H, ZrMe). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 142.4 (d, $|J| = 10.4$ Hz, quat), 137.8 (s, quat), 130.6 (d, $|J| = 24.1$ Hz, quat), 129.3 (s, arom *C*H), 110.5 (s, Cp), 83.2 (d, $|J| = 7.6$ Hz, O*C*), 33.1 (d, $|J| = 4.1$ Hz, Me)), 31.8 (s, Me), 24.1 (d, $|J| = 11.7$ Hz, Me), 20.8 (s, Me), 19.2 (s, Me). ^{31}P NMR (25 °C, C_6D_6): δ −48.9 (d, $|J_{P-H}| = 217.7$ Hz).

Synthesis of $(Cp_2ZrMe)_2(\mu$-$P(C_6H_2$-2,4,6-$Me_3))$ (9). To a toluene solution of Cp_2ZrMe_2 (503 mg, 2.0 mmol) was added a toluene solution of $H_2P(C_6H_2$-2,4,6-$Me_3)$ (152 mg, 1.0 mmol). The colorless solution was placed in a bomb and heated at 110 °C for 5 h, during which time it became a deep indigo. After cooling to room temperature, the volume was reduced and the solution allowed to stand for 3 days. Large, extremely air-sensitive dark blue crystals formed and were isolated by filtration. Yield: 511 mg (82%). ^{1}H NMR (25 °C, C_6D_6): δ 7.08 (s, 2H, Ar*H*), 5.66 (s, 20H, Cp), 2.35 (s, 6H, *o*-Me), 2.27 (s, 3H, *p*-Me), 0.24 (d, $|^3J_{P-H}| = 3.1$ Hz, 6H, ZrMe). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 138.1 (s, quat), 134.4 (s, quat), 128.3 (s, arom *C*H), 109.8 (s, Cp), 27.9 (s, Me), 26.6 (d, $|J| = 9.0$ Hz, Me), 20.9 (s, Me). ^{31}P NMR (25 °C, C_6D_6): δ 303.2 (s). Anal. Calcd for $C_{31}H_{37}PZr$: C, 59.76; H, 5.99. Found: C, 59.67; H, 5.88.

Synthesis of $(Cp_2Zr)(Cp_2ZrPH(C_6H_2$-2,4,6-$Me_3))(\mu$-$P(C_6H_2$-2,4,6-$Me_3))(\mu$-η^1:η^5-$C_5H_4)$ (11). (i) To a toluene solution of Cp_2ZrMe_2 (503 mg, 2.0 mmol) was added a toluene

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Table 1. Crystallographic Data

	3	**9**	**11**
formula	$C_{42}H_{53}OPZr$	$C_{31}H_{37}PZr_2$	$C_{38}H_{42}P_2Zr_2$
formula weight	696.07	623.05	743.14
crystal size (mm)	0.26 × 0.31 × 0.43	0.23 × 0.25 × 0.26	0.35 × 0.27 × 0.33
a, Å	11.062(2)	19.253(6)	13.310(6)
b, Å	18.456(2)	7.761(2)	20.958(9)
c, Å	18.629(2)	20.197(6)	13.299(3)
β, deg	97.37(1)	107.88(2)	93.22(3)
vol, Å^3	3771.8(8)	2872(1)	2704(3)
crystal system	monoclinic	monoclinic	monoclinic
space group	*Cc*	$P2_1/n$	$P2_1/n$
Z	4	4	4
μ (cm^{-1})	3.63	7.98	6.72
d(calc) (g/cm^3)	1.23	1.44	1.33
temp (°C)	24	24	24
λ (Å)	0.71069 Mo Kα	0.71069 Mo Kα	0.71069 Mo Kα
scan speed (deg/min)	8	8	8
scan range (deg)	1.0 above Kα_1 1.0 below Kα_1	1.0 above Kα_1 1.0 below Kα_1	1.0 above Kα_1 1.0 below Kα_1
bkgd/scan time ratio	0.5	0.5	0.5
2θ, index range	4.5−50, $hk\pm l$	4.5−50, $hk\pm l$	4.5−50, $hk\pm l$
data collected	3445	5063	6728
unique data $F_o^2 > 3\sigma(F_o^2)$	1378	2422	1907
variables	194	297	289
transmission factors	0.889−1.000	0.916−1.000	0.659−1.000
R^a (%)^a	3.50	4.65	8.10
$R_w{}^a$ (%)	5.22	5.63	8.02
goodness of fit	1.51	1.81	2.04

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

solution of $H_2P(C_6H_2$-2,4,6-$Me_3)$ (304 mg, 2.0 mmol). The colorless solution was placed in a bomb and heated at 110 °C for 5 h, during which time it became dark brown. After cooling to room temperature, the toluene was removed under reduced pressure and the product was then dissolved in diethyl ether. Upon standing overnight, dark brown crystals formed which were isolated by filtration. Yield: 520 mg (70%). (ii) To a benzene suspension of $(Cp_2ZrCl)_2(\mu$-$P(C_6H_2$-2,4,6-$Me_3))$ (**10**) (322 mg, 0.5 mmol) was added excess PMe_3 and a benzene suspension of $Li_2P(C_6H_2$-2,4,6-$Me_3)$ (90 mg, 0.55 mmol). The mixture was stirred vigorously for 12 h, after which time it was filtered. ^{31}P NMR of the reaction mixture showed the clean formation of $Cp_2Zr(P(C_6H_2$-2,4,6-$Me_3))(PMe_3)$ (**12**). After filtration, the solvent was removed in vacuo and the product dissolved in diethyl ether. Upon standing overnight, dark brown crystals formed and were isolated by filtration. Yield: 238 mg (64%). ^{1}H NMR (25 °C, C_6D_6): δ 7.03 (s, 1H, Ar*H*), 6.95 (s, 1H, Ar*H*), 6.92 (s, 2H, Mes-*H*), 6.50 (br d, $|^3J_{P-H}| = 7.1$ Hz, 1H, C*H*), 6.29 (s, 5H, Cp), 5.98 (br s, 1H, C*H*), 5.66 (s, 5H, Cp), 5.25 (s, 5H, Cp), 5.12 (br, 1H, C*H*), 4.65 (br, 1H, C*H*), 3.27 (dd, $|^1J_{P-H}| = 203.5$ Hz, $|^3J_{P-H}| = 10.8$ Hz, 1H, P*H*), 2.69 (s, 3H, Me), 2.49 (s, 6H, *o*-Me), 2.40 (s, 3H, Me), 2.25 (s, 3H, Me), 2.23 (s, 3H, Me). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 175.1 (s, quat), 148.1 (d, $|J| = 11.9$ Hz, quat), 145.3 (d, $|J| = 32.4$ Hz, quat), 141.1 (d, $|J| = 9.2$ Hz, quat), 138.5 (d, $|J| = 7.8$ Hz, quat), 138.0 (s, quat), 135.8 (s, quat), 132.7 (s, quat), 128.8 (s, arom *C*H), 128.6 (s, arom *C*H), 128.1 (s, arom *C*H), 111.2 (s, arom *C*H), 110.2 (d, $|J| = 4.5$ Hz, Cp), 109.8 (s, Cp), 108.8 (s, arom *C*H), 106.3 (s, Cp), 106.1 (s, arom *C*H), 106.0 (s, arom *C*H), 25.2 (s, Me), 25.1 (s, Me), 24.1 (br s, Me), 20.9 (s, Me), 20.8 (s, Me). ^{31}P NMR (25 °C, C_6D_6): δ 395.4 (d, $|J_{P-P}| = 29.1$ Hz), −84.2 (dd, $|^1J_{P-H}| = 203.0$ Hz, $|J_{P-P}| = 29.0$ Hz. Anal. Calcd for $C_{38}H_{42}P_2Zr_2$: C, 61.42; H, 5.70; Found: C, 61.34; H, 5.67.

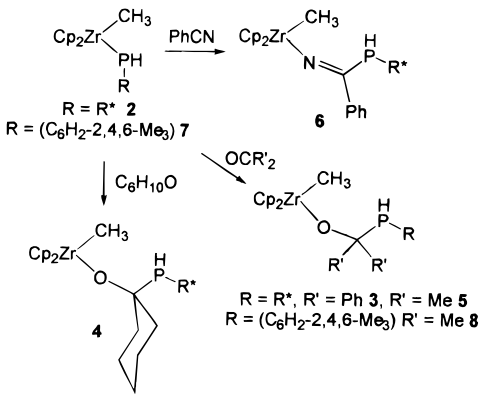
X-ray Data Collection and Reduction. X-ray-quality crystals of **3**, **9**, and **11** were obtained directly from the preparation as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC5 diffractometer equipped with graphite-monochromatized Mo Kα radiation. The initial orientation matrix was 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 system. Ultimately, 25 reflections ($20° < 2\theta < 25°$) were used to obtain the final lattice parameters and the orientation matrices. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups. The data sets were collected in three shells ($4.5° < 2\theta < 50.0°$), and three standard reflections were recorded every 197 reflections. Fixed scan rates were employed. Up to four repetitive scans of each reflection at the respective scan rates were averaged to ensure meaningful 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 collections. The data were processed using the TEXSAN crystal solution package operating on a SGI Challenger mainframe with remote X-terminals. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[13,14] The Zr atom positions were determined using direct methods employing 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 $\omega(|F_o| - |F_c|)^2$, where the weight ω 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 each refinement, the number of non-hydrogen atoms that were assigned anisotropic temperature factors was limited so as to maintain a reasonable data:variable ratio. Empirical absorption corrections were applied to the data sets based on ψ-scan data. 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. The hydrogen atom contributions were calculated but

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

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

Scheme 1



not refined. In the case of **3**, the hydrogen atom on P was located and included in the final cycle of refinement and the correct enantiomorph was determined by refinement of the enantiomorphs of the model. The decay of the crystal of **9** was significant (~20%) but approximately linear during data collection. Although a decay correction was applied to the data, the inferior quality of the data is reflected in the poor agreement of chemically similar Zr−C distances of the Zr−methyl groups as well as the thermal parameters of C(31). Nonetheless, the connectivity of **9**, is affirmed by the solution. In the case of **11**, the phosphide hydrogen atom could not be located. The final values of R, R_w, and the maximum Δ/σ on any of the parameters in the final cycles of the refinements are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as supporting information.

Results and Discussion

Previous work has shown that the reaction of $Cp_2ZrMeCl$ with $LiPH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)$ yields $Cp_2ZrMe(PH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3))$ (**2**),[5,6] which undergoes loss of methane over a 3-day period and yields **1** in the presence of PMe_3. In the present study, **2** was generated in the presence of benzophenone via addition of the phosphide to a solution of $Cp_2ZrMeCl$ and benzophenone. The resulting solution turned orange, presumably a result of the formation of **2**, and then immediately became very pale yellow. After workup, colorless crystals of the product **3** were isolated in 83% yield. The ^{31}P NMR spectrum of **3** showed a single resonance at −8.6 ppm which exhibited P−H coupling of 244.1 Hz, indicative of the phosphide moiety. The observation of a ^1H NMR singlet at 0.66 ppm suggested the presence of a Zr−Me fragment. Furthermore, two resonances in both the ^1H and ^{13}C NMR spectra may be attributed to diastereotopic cyclopentadienyl groups which result from the presence of the chiral P center. Collectively, these data support the formulation of **3** as $Cp_2ZrMe(OCPh_2PH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3))$. In a similar fashion, generation of **2** in the presence of cyclohexanone or acetone afforded the related complexes $Cp_2ZrMe(OC_6H_{10}PH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3))$ (**4**) and $Cp_2ZrMe(OCMe_2PH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3))$ (**5**), respectively, while the presence of benzonitrile yielded the product **6** (Scheme 1). The ^{31}P NMR spectrum of **6** showed a single resonance at −44.8 with a P−H coupling constant of 233.9 Hz, in agreement with the presence of a secondary phosphide moiety. The ^{13}C doublet at 177.9 ppm is attributed to the N=C, while the P−C coupling constant of 30.5 Hz confirmed the formation a P−C bond. These data verify the formulation of **6** as $Cp_2ZrMe(NC(Ph)PH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3))$.

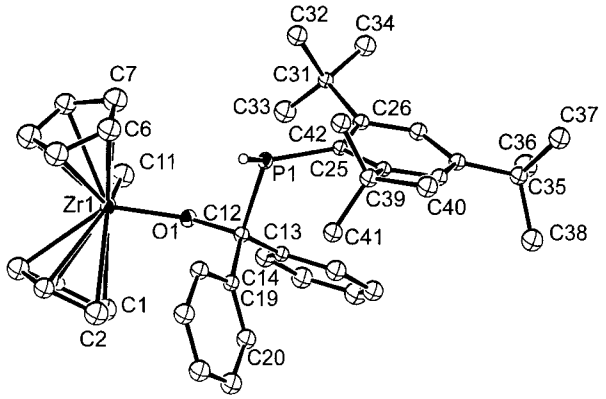


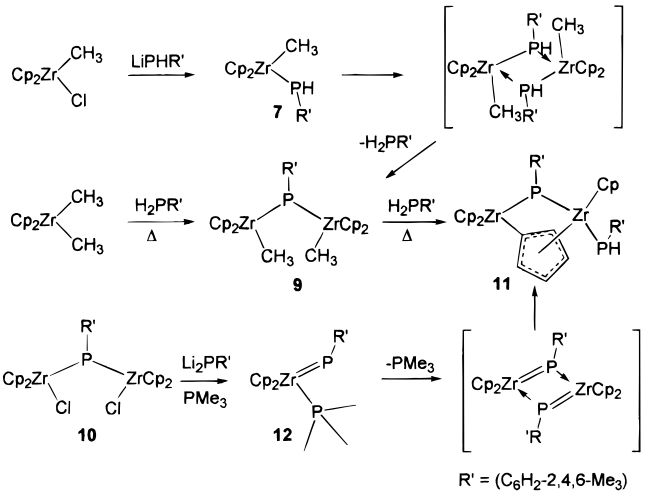
Figure 1. ORTEP drawing of **3**: 30% thermal ellipsoids are shown. Zr(1)−O(1), 1.926(9) Å; Zr(1)−C(11), 2.27(2) Å; P(1)−C(12), 1.99(1) Å; P(1)−C(25), 1.83(1) Å. O(1)−Zr(1)−C(11), 95.9(5)°; C(12)−P(1)−C(25), 109.7(6)°; Zr(1)−O(1)−C(12), 167.7(9)°.

The formulation of the above insertion products was confirmed crystallographically for compound **3** (Figure 1). The geometry about Zr is typical of zirconocene derivatives. The Zr−methyl carbon distance is 2.27(2) Å, while the Zr−O bond is 1.926(9) Å. The O−Zr−C angle of 95.9(5)° is slightly less than the O−Zr−O angle seen in the dialkoxide complex $Cp_2Zr(\mu\text{-}OCH_2CMe_2\text{-}CH_2O)_2ZrCp_2$.[15] The Zr−O−C angle of 167.7(9)° is similar to that seen in related Zr−alkoxide derivatives, suggesting some degree of Zr−O π-bonding. Mechanistically, it is noteworthy that independent generation of **2** and subsequent addition of ketone afforded the identical products described above. As well, mixture of $LiPH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)$ with ketone resulted in no reaction, thus precluding formation of **3**−**5** from a reagent of the form $LiOCR_2PH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)$. These data as well as the structural studies confirm that the above species are formed via insertion of benzophenone into the Zr−P bond. The result is a secondary phosphorus center which exhibits a typical pseudopyramidal geometry.

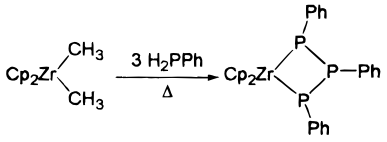
The analogous methylzirconocene phosphide complex $Cp_2ZrMe(PH(C_6H_2\text{-}2,4,6\text{-}Me_3))$ (**7**) was generated from the reaction of $Cp_2ZrMeCl$ with $LiPH(C_6H_2\text{-}2,4,6\text{-}Me_3)$, as evidenced by the ^{31}P NMR resonance at −6.0 ppm ($|J_{P-H}| = 228.5$ Hz). Although this species is unstable it too undergoes insertion of acetone yielding the mesityl analogue of **5** (i.e., $Cp_2ZrMe(OCMe_2PH(C_6H_2\text{-}2,4,6\text{-}Me_3))$ (**8**)) (Scheme 1). The instability of **7** was demonstrated by monitoring the reaction of $Cp_2ZrMeCl$ with $LiPH(C_6H_2\text{-}2,4,6\text{-}Me_3)$ by ^{31}P NMR spectroscopy. After 30 min at 25 °C the resonance attributable to **7** began to diminish, and a resonance at 303 ppm along with the resonance attributable to the free phosphine $H_2P(C_6H_2\text{-}2,4,6\text{-}Me_3)$ appeared concurrently. These data suggested the possibility that **7** underwent a bimolecular reaction to afford a phosphinidene bridged complex by elimination of an equivalent of phosphine (Scheme 2). Attempts to confirm this scenario via isolation of this new complex were unsuccessful, as NMR data confirmed

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

Scheme 2



further reactions had produced a complex mixture of unidentified products. In an effort to further explore and clarify the effect of less sterically demanding substituents, alternative synthetic pathways were sought. Earlier reports by Hey et al.[16] described the synthesis of $Cp_2Zr(PPh)_3$ from the reaction of Cp_2ZrMe_2 with H_2PPh (eq 2). In a similar fashion, heating a colorless



(2)

mixture of 2 equiv of Cp_2ZrMe_2 with $H_2P(C_6H_2$-2,4,6-$Me_3)$ at 110 °C for 5 h resulted in a color change to deep indigo. After cooling and standing for 3 days, large dark blue crystals of **9** were isolated in 82% yield. The ^{31}P NMR spectrum of **9** showed a single resonance at 303 ppm. This chemical shift together with the absence of P−H coupling suggested a phosphinidene bridged complex, while the ^1H and ^{13}C NMR data were consistent with the presence of two Zr-bound methyl groups. Compound **9** was thus formulated as $(Cp_2ZrMe)_2(\mu$-$P(C_6H_2$-2,4,6-$Me_3)$ (Scheme 2). Despite the extreme air-sensitivity of **9**, as well as a problem of crystal decay during data collection, X-ray crystallographic data did confirm the proposed connectivity (Figure 2). Two Cp_2ZrMe units are bridged by the mesitylphosphinidene unit with Zr−P distances of 2.606(3) and 2.646(3) Å. The Zr−P−Zr angle is 136.6(1)°, while the sum of the angles about P indicate its planar geometry, similar to that observed for the closely related species $(Cp_2ZrCl)_2(\mu$-$P(C_6H_2$-2,4,6-$Me_3)$ (**10**).[4]

The corresponding reaction of Cp_2ZrMe_2 with 1 equiv of $H_2P(C_6H_2$-2,4,6-$Me_3)$ at 110 °C for 5 h resulted in the formation of a dark brown product **11** which was isolated in 70% yield. This compound exhibited ^{31}P NMR resonances at 395.4 and −84.2 ppm with a P−P coupling constant of 29.0 Hz. The latter resonance also exhibited a J_{P-H} of 203.0 Hz. The ^1H NMR spectrum of **11** showed the resonances attributable to three cyclopentadienyl groups at 6.29, 5.66, and 5.25 ppm. In addition, resonances of 5.98 and 5.12 ppm were assigned to an η^1:η^5-C_5H_4 fragment. These data, in addition to

(16) Hey, E.; Bott, S. G.; Atwood, J. L. *Chem. Ber.* **1988**, *121*, 561.

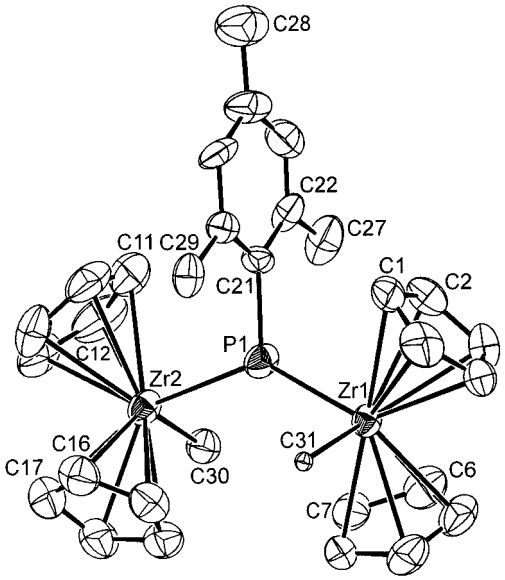


Figure 2. ORTEP drawing of **9**: 30% thermal ellipsoids are shown. Zr(1)−P(1), 2.606(3) Å; Zr(2)−P(1), 2.646(3) Å; P(1)−C(21), 1.84(1) Å. Zr(1)−P(1)−Zr(2), 136.6(1)°; P(1)−Zr(1)−C(31), 99.4(2)°; P(1)−Zr(2)−C(30), 98.1(3)°.

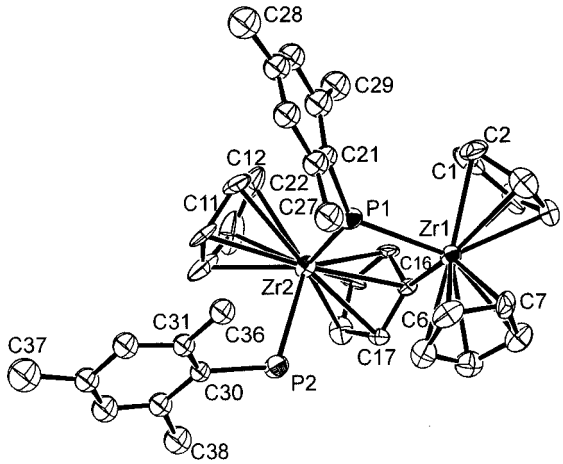


Figure 3. ORTEP drawing of **11**: 30% thermal ellipsoids are shown. Zr(1)−P(1), 2.586(7) Å; Zr(1)−C(6), 2.49(3) Å; Zr(2)−P(1), 2.576(7) Å; Zr(2)−P(2) 2.718(7) Å. P(1)−Zr(1)−C(6), 88.9(7)°; P(1)−Zr(2)−P(2), 96.5(2)°; Zr(1)−P(1)−Zr(2), 93.3(2)°.

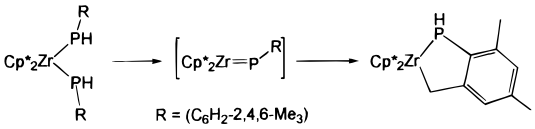
the ^{13}C NMR data, were in accord with the formulation of **11** as $(Cp_2Zr)(Cp_2ZrPH(C_6H_2$-2,4,6-$Me_3))(\mu$-$P(C_6H_2$-2,4,6-$Me_3))(\mu$-η^1:η^5-$C_5H_4)$ (Scheme 2).

The formulation of **11** was confirmed crystallographically (Figure 3). The two Zr centers are bridged by a phosphinidene moiety as well as an η^1:η^5-cyclopentadienyl ring. The bridging Zr−P distances at 2.586(7) and 2.576(7) Å are slightly shorter than those seen in **9** while the Zr−P−Zr angle of 93.3(2)° is significantly smaller than the corresponding angle in **9**, consistent with the presence of the second bridging fragment. These parameters compare well with those previously reported for $(Cp_2Zr)(Cp_2ZrCl)(\mu$-$PSiPh_3)(\mu$-η^1:η^5-$C_5H_4)$ (Zr−P 2.549(6), 2.559(6) Å; Zr−P−Zr 95.2(2)°).[4] The small difference in the bridging Zr−P distances is consistent with a π-component of the Zr(2)−P(1) bond as described for the structurally related species (Cp_2Zr)-$(Cp_2ZrCl)(\mu$-$PSiPh_3)(\mu$-η^1:η^5-$C_5H_4)$.[4] The terminal phosphide ligand of **11** manifests in a dramatically longer Zr−P distance of 2.718(7) Å, which compares well with

the longer Zr−P distance in $(C_5H_4SiMe_3)_2Zr(PPh_2)_2$ (2.694(3) Å).[17] The P−Zr−P and P−Zr−C angles in **11** are 96.5(2)° and 88.9(7)°, respectively, comparable to the corresponding angles in $(Cp_2Zr)(Cp_2ZrCl)(\mu\text{-}PSiPh_3)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)$.[4]

An alternative synthesis of **11** has been achieved from the unstable terminal phosphinidene species $Cp_2Zr(P(C_6H_2\text{-}2,4,6\text{-}Me_3))(PMe_3)$ (**12**) (Scheme 2). **12** was cleanly generated by the reaction of $Li_2P(C_6H_2\text{-}2,4,6\text{-}Me_3)$ with **10** in the presence of PMe_3, as evidenced by ^{31}P NMR resonances consistent with data previously reported for **12**.[18] This reaction is thought to proceed through initial formation of a bis-phosphinidene bridged dimer followed by subsequent reaction with PMe_3. However, **12** was not isolable; upon standing overnight at 25 °C or when the solvent is removed in vacuo, **12** degraded to produce free PMe_3 and **11**. A plausible mechanism involves dissociation of PMe_3 from **12**, dimerization, and subsequent irreversible intramolecular cyclopentadienyl C−H bond activation (Scheme 2). Thus, while **12** appears to be the kinetic product from this mixture, **11** is the thermodynamic product.

We have previously described similar intramolecular C−H bond activation in the terminal phosphinidene species $Cp^*_2Zr{=}P(C_6H_2\text{-}2,4,6\text{-}Me_3)$ to produce $Cp^*_2ZrPH(C_6H_2\text{-}(2\text{-}CH_2)\text{-}4,6\text{-}Me_2)$ (eq 3).[19] Presumably the greater steric demands of the Cp* ligands prevent dimerization, consequently favoring intramolecular C−H activation of the mesityl ligand. In a similar way, the lack of cyclopentadienyl C−H bond activation in terminal phosphinidene **1** may be attributed to the greater steric demands of the supermesityl group, which preclude dimerization. Owing to the fact that **11** does not possess any sterically demanding substituents, dimerization and subsequent cyclopentadienyl C−H bond activation transpire.



(3)

In summary, mononuclear methylzirconocene phosphide complexes are reactive species. The chemistry herein demonstrates the ease with which organic unsaturates can insert into the Zr−P bond. Alternatively, methylzirconocene phosphide complexes can react via loss of methane to provide convenient access to Zr−phosphinidene species. These compounds can be observed and isolated only when steric demands preclude further reaction. In the absence of such bulk, dimerization and subsequent intramolecular C−H bond activation have been observed. The potential for intermolecular C−H bond activation by early metal phosphinidenes is the subject of ongoing study.

Acknowledgment. Support of this research from the NSERC of Canada is acknowledged. T.L.B. is grateful for the award of an NSERC postgraduate scholarship.

Supporting Information Available: Tables of crystallographic parameters, hydrogen atom parameters, and thermal parameters for **3**, **9**, and **11** (30 pages). Ordering information is given on any current masthead page.

OM960412+

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(18) Ho, J.; Rousseau, R.; Stephan, D. W. *Organometallics* **1994**, *13*, 1918.
(19) Hou, Z.; Stephan, D. W. *J. Am. Chem. Soc.* **1992**, *114*, 10088.