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Phosphinidene Transfer Reactions of the Terminal Phosphinidene Complex Cp$_2$Zr(PC$_6$H$_2$-2,4,6-t-Bu$_3$)(PMe$_3$)

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Abstract: The terminal zirconium phosphinidene complex Cp$_2$Zr(PR*)(PMe$_3$) (R* = C$_6$H$_2$-2,4,6-t-Bu$_3$) **2** has been synthesized in high yield, and its reactivity has been investigated. The compound Cp$_2$ZrMe(PHR*) **1** is unstable with respect to the loss of methane; in the presence of PMe$_3$ this reaction yielded **2**. Reactions of **2** with benzophenone, benzaldehyde, or isophthalaldehyde produced phosphaalkenes PhCH=PR* **3**, Ph$_2$C=PR* **4**, and 1,3-C$_6$H$_2$(CH=PR*)$_2$ **5**, respectively. PhN=C=PR* **6** resulted from the reaction of **2** with phenyl isothiocyanate while the use of cyclohexanone afforded the enolate Cp$_2$Zr(PHR*)(OC$_6$H$_9$) **7**. Phosphinidene group transfer also took place in reactions of **2** with the appropriate organic dihalide or epoxide. In this way phosphaalkenes CH$_2$=PR* **8** and CHCl=PR* **9**, phosphirane (CH$_2$CH$_2$PR*) **10**, phospholane 1,2-C$_6$H$_4$(CH$_2$PR*)$_2$ **11**, and substituted phosphiranes (CH$_2$CH)(CHCH$_2$-PR*) **12**, CH$_2$C(CCH$_2$PR*) **13**, (PhCHCH(Ph)PR*) **15**, and *trans*-(PhCHCH$_2$PR*) **16** were synthesized. The use of propylene oxide yielded the enolate Cp$_2$Zr(PHR*)(OCH$_2$CH=CH$_2$) **17**. Similar reactions of **2** with heavier group 14 dihalides and sulfides furnished Cp$_2$Zr(PR*(SiMe$_2$Cl))Cl **18**, PR*(SiMe$_2$Cl)$_2$ **19**, (Me$_2$GeCl)$_2$PR* **20**, (Me$_2$GePR*)$_2$ **21**, (t-Bu$_2$SnPR*)$_2$ **22**, and (Me$_2$SnPR*)$_2$ **23**. Intramolecular phosphinidene transfer occurred in reactions of **2** with benzonitrile and dicyclohexylcarbodiimide, giving Cp$_2$Zr(PMe$_3$)(NC(Ph)(PR*)) **25** and Cp$_2$Zr(N(Cy))$_2$C=PR* **26**, respectively. Crystallographic data are reported for compounds **22**, **25b**, and **26**.

Introduction

Early-metal−ligand multiple bonds have been the subject of great interest since the discovery of metal carbenes.[1] Recent studies of multiply bonded early-metal−heteroatom derivatives have been spurred by their potential for use in the syntheses of organic compounds containing heteroatoms, as well as the possibility of structural and mechanistic insight relating to MOCVD processes. The research groups of Bergman,[2] Bercaw,[3] and Wolczanski[4] among others[5] have prepared or generated early-metal imides (M=NR), oxides (M=O), and sulfides (M=S) and shown that such species demonstrate a rich chemistry. Related studies of metal−phosphorus double bonds (M=PR) have drawn much less attention. Lappert et al.[6] and Cowley et al.[7] have structurally characterized the compounds Cp$_2$M(PR*) (M = Mo, W) and W(CO)Cl$_2$(Ph$_2$PMe)$_2$(PR*) (R* = C$_6$H$_2$-2,4,6-t-Bu$_3$), respectively, while others[8] have studied the chemistry of transient tungsten and molybdenum phosphinidenes. More recently we[9−11] have illustrated the considerable reactivity of the transient early-metal phosphinidenes Cp*$_2$-Zr=PR. In addition, as part of a large study of Zr−P complexes we reported the preparation and structure of the base-stabilized Zr−phosphinidene complex Cp$_2$Zr(PR*)(PMe$_3$) **2**.[11] Furthermore, Schrock et al.[12] have described the terminal Ta−phosphinidene complexes ((Me$_3$SiNCH$_2$CH$_2$)$_3$N)Ta=PR (R = Ph, Cy, t-Bu) while Wolczanski and co-workers[13] have prepared (R$_3$SiO)$_3$Ta=EPh (E = N, P, As). These syntheses and structural studies are recent highlights in the area, but it is the reactivity of stable terminal phosphinidene complexes that is expected to be a fertile and intriguing area of research. High-valent transition metal phosphinidenes all contain nucleophilic phosphorus centers, corresponding to Schrock-type carbenes. They are distinguished from the transient phosphinidene complexes of low-valent transition metals, which are electrophilic and thus

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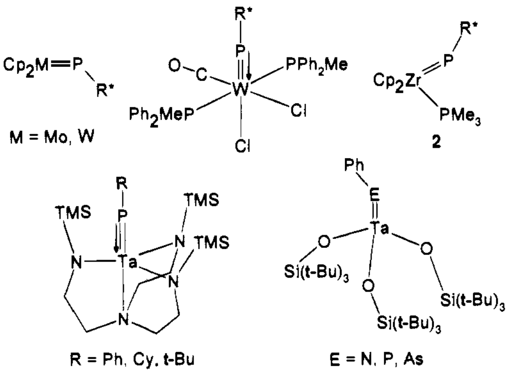

analogous to Fischer carbene complexes.[1] While the reactivity of electrophilic phosphinidenes has been studied,[8] the nucleophilic species have only been examined briefly in the report of Schrock et al.[12] In the present paper we relate the first detailed reactivity study of an isolated terminal phosphinidene complex. Reactions of compound **2** with a variety of organic and other group 14 reagents are described in which phosphinidene group transfer occurs. Mechanistic, structural, and spectroscopic aspects of this chemistry are discussed.

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. 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$_3$PO$_4$, respectively. In some cases, spectral simulations were performed with the software PANIC. Yields calculated by ^{1}H NMR were determined in reference to a CH$_2$Cl$_2$ internal standard which was introduced by means of an Evans NMR tube. 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. PH$_2$(C$_6$H$_2$-*t*-Bu$_3$) was purchased from the Quantum Design Chemical Co. All other reagents were purchased from the Aldrich Chemical Co. Cp$_2$ZrMeCl[14] and LiHPR*·3THF[15] were prepared by literature methods. In all instances, R* and Ar refer to the 2,4,6-*t*-Bu-C$_6$H$_2$ group.

Synthesis of Cp$_2$ZrMe(PHR*) 1. To a benzene solution of Cp$_2$ZrMeCl (272 mg, 1.0 mmol) was added a benzene solution of LiHPR*·3THF (501 mg, 1.0 mmol). After standing for 10 min the LiCl was filtered from the wine-red solution. Yield: 98% (by ^{1}H NMR). ^{1}H NMR (25 °C, C$_6$D$_6$): δ 7.58 (br s, 2H, Ar-*H*), 6.04 (d, $|J_{\mathrm{P-H}}|$ = 263.9 Hz, 1H, P-*H*), 5.53 (s, 10H, Cp), 1.64 (br s, 18H, *o*-^{t}Bu), 1.33 (s, 9H, *p*-^{t}Bu), −0.14 (d, $|^{3}J_{\mathrm{P-H}}|$ = 7.1 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (25 °C, C$_6$D$_6$): δ 148.0 (s, quat), 139.0 (d, $|J|$ = 7.0 Hz, quat), 121.2 (s, arom *C*-H), 108.2 (s, Cp), 38.5 (s, *o*-*C*(CH$_3$)$_3$), 34.7 (s, *p*-*C*(CH$_3$)$_3$), 32.9 (br s, *o*-C(*C*H$_3$)$_3$), 31.3 (s, *p*-C(*C*H$_3$)$_3$), 24.8 (s, *C*H$_3$). ^{31}P NMR (25 °C, C$_6$D$_6$): δ 74.1 (d, $|J_{\mathrm{P-H}}|$ 264.7 Hz).

Synthesis of Cp$_2$Zr(PR*)(PMe$_3$) 2. To a benzene solution of Cp$_2$ZrMeCl (272 mg, 1.0 mmol) and excess PMe$_3$ was added a benzene solution of LiHPR*·3THF (501 mg, 1.0 mmol). The reaction mixture stood for 3 days, after which time the green-black solution was filtered and the solvent removed in vacuo. The oily residue was taken up in diethyl ether, and the solvent was again evaporated under reduced pressure. This produced a flaky green-black solid. Yield: 545 mg (95%). Spectroscopic properties were identical to those previously reported.[11]

Reactions of 2 with Ketones and Aldehydes: Synthesis of PhCH=PR* 3, Ph$_2$C=PR* 4, 1,3-C$_6$H$_2$(CH=PR*)$_2$ 5, and PhN=C=PR* 6. The reactions of **2** with several ketones and aldehydes were performed in a similar manner; thus, only one preparation is described in detail. The reagent employed and the characterization of the products are given. To a benzene solution of **2** (57 mg, 0.1 mmol) was added PhCHO (10.2 μL, 0.1 mmol). The reaction mixture stood overnight, after which time the yellow solution was stirred with activated alumina for 1.5 h. The solvent was evaporated under reduced pressure, and the product was then extracted into pentane. Filtration and removal of the solvent in vacuo gave the pale yellow oil **3**. (**3**) Yield: 80% (by ^{1}H NMR). ^{31}P NMR (25 °C, CDCl$_3$): δ 259.2 (d, $|^{2}J_{\mathrm{P-H}}|$ = 24.9 Hz). ^{1}H NMR and ^{13}C{^{1}H} NMR data were as reported in the literature.[16] (**4**) Reagent: Ph$_2$CO. Yield: 82% (by ^{1}H NMR). ^{31}P NMR (25 °C, C$_6$D$_6$): δ 242.1 (s). ^{1}H NMR and ^{13}C{^{1}H} NMR data were as reported in the literature.[17] (**5**) Reagent: 1,3-C$_6$H$_2$(CHO)$_2$. Yield: 86% (by ^{1}H NMR). ^{31}P NMR (25 °C, C$_6$D$_6$): δ 259.9 (d, $|^{2}J_{\mathrm{P-H}}|$ = 23.8 Hz). ^{1}H NMR and ^{13}C{^{1}H} NMR data were as reported in the literature.[18] (**6**) Reagent: PhNCS. Yield: 81% (by ^{1}H NMR). ^{31}P NMR (25 °C, CDCl$_3$): δ −106.3. ^{1}H NMR and ^{13}C{^{1}H} NMR data were as reported in the literature.[19]

Synthesis of Cp$_2$Zr(PHR*)(OC$_6$H$_9$) 7. To a benzene solution of **2** (114 mg, 0.2 mmol) was added cyclohexanone (20.8 μL, 0.2 mmol). The reaction mixture stood overnight, resulting in the formation of an orange solution. The solvent was then removed in vacuo and the product dissolved in pentane. Orange crystals formed over 12 h at room temperature and were isolated by filtration. Yield: 73 mg (62%). ^{1}H NMR (25 °C, C$_6$D$_6$): δ 7.61 (d, $|^{4}J_{\mathrm{P-H}}|$ = 1.4 Hz, 2H, Ar-*H*), 5.69 (br s, 10H, Cp), 5.11 (d, $|J_{\mathrm{P-H}}|$ = 216.9 Hz, 1H, P-*H*), 4.53 (t, $|J|$ = 3.7 Hz, 1H, =C*H*), 1.76 (s, 18H, *o*-^{t}Bu), 1.55−1.25 (m, 8H, Cy-*H*), 1.34 (s, 9H, *p*-^{t}Bu). ^{13}C{^{1}H} NMR (25 °C, C$_6$D$_6$): δ 160.2 (s, O−*C*=), 150.1 (s, quat), 145.8 (d, $|J|$ = 36.4 Hz, quat), 145.6 (s, quat), 119.4 (s, arom *C*-H), 111.1 (s, Cp), 99.2 (s, =*C*H), 38.3 (s, *o*-*C*(CH$_3$)$_3$), 34.6 (s, *p*-*C*(CH$_3$)$_3$), 33.1 (br s, *o*-C(*C*H$_3$)$_3$), 31.5 (s, *p*-C(*C*H$_3$)$_3$), 30.0 (s, *C*H$_2$), 24.2 (s, *C*H$_2$), 23.5 (s, *C*H$_2$), 23.0 (s, *C*H$_2$). ^{31}P NMR (25 °C, C$_6$D$_6$): δ −31.1 (d, $|J_{\mathrm{P-H}}|$ = 218.1 Hz). HRMS (EI) (*m/e*) for C$_{34}$H$_{49}$OPZr: calcd 594.2564, found 594.2539. Anal. Calcd for C$_{34}$H$_{49}$OPZr: C, 68.52; H, 8.29. Found: C, 68.12; H, 8.14.

Reactions of 2 with Alkylidene Dichlorides: Synthesis of CH$_2$=PR* 8, CHCl=PR* 9, (CH$_2$CH$_2$PR*) 10, 1,2-C$_6$H$_4$(CH$_2$PR*)$_2$ 11, (CH(CH=CH$_2$)CH$_2$PR*) 12, and (C(C=CH$_2$)CH$_2$PR*) 13. The reactions of **2** with several alkylidene dichlorides were performed in a similar manner; thus, only one preparation is described in detail. To a benzene solution of **2** (57 mg, 0.1 mmol) was added CH$_2$Cl$_2$ (6.0 μL, 0.1 mmol). The reaction mixture stood overnight, after which time the yellow solution was stirred with activated alumina for 1.5 h. The solvent was evaporated under reduced pressure and the product then extracted into pentane. Filtration and removal of the solvent in vacuo gave the pale yellow oil **8**. (**8**) Yield: 86% (by ^{1}H NMR). ^{31}P NMR (25 °C, benzene): δ 289.3 (t, $|^{2}J_{\mathrm{P-H}}|$ = 30.4 Hz). ^{1}H NMR and ^{13}C{^{1}H} NMR data were as reported in the literature.[20] (**9**) Reagent: CHCl$_3$. Yield: 76% (by ^{1}H NMR). ^{31}P NMR (25 °C, C$_6$D$_6$): δ 251.0 (d, $|^{2}J_{\mathrm{P-H}}|$ = 18.5 Hz, *E*-isomer), 249.5 (d, $|^{2}J_{\mathrm{P-H}}|$ = 43.2 Hz, *Z*-isomer). ^{1}H NMR and ^{13}C{^{1}H} NMR data were as reported in the literature.[20,21] (**10**) Reagent: ClCH$_2$CH$_2$Cl. Yield: 45% (by ^{1}H NMR). ^{31}P NMR (25 °C, benzene): δ −201.9 (s). ^{1}H NMR and ^{13}C{^{1}H} NMR data were as reported in the literature.[22] (**11**) Reagent: 1,2-C$_6$H$_4$(CH$_2$Cl)$_2$. Yield: 53% (by ^{1}H NMR). ^{1}H NMR (25 °C, C$_6$D$_6$): δ 7.30 (d, $|^{4}J_{\mathrm{P-H}}|$ = 2.3 Hz, 2H, Ar-*H*), 7.52 and 6.85 (m, 4H, Ph), 3.30 (dd, $|^{2}J|$ = 11.8 Hz, $|^{2}J_{\mathrm{P-H}}|$ = 8.9 Hz, 2H, C*H*H), 2.98 (dd, $|^{2}J|$ = 11.8 Hz, $|^{2}J_{\mathrm{P-H}}|$ = 3.9 Hz, 2H, CH*H*), 1.50 (s, 18H, σ-^{t}Bu), 1.26 (s, 9H, *p*-^{t}Bu). ^{13}C{^{1}H}

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NMR (25 °C, C_6D_6): δ 154.7 (s, quat), 146.7 (s, quat), 140.3 (d, $|J| =$ 12.1 Hz, quat), 139.9 (d, $|J|$ 50.0 Hz, quat), 126.1 (d, $|J| = 3.8$ Hz, arom *C*-H), 122.1 (d, $|J|$ 12.1 Hz, arom *C*-H), 122.0 (s, arom *C*-H), 41.9 (d, $|J_{P-C}| = 15.2$ Hz, *C*H_2), 38.9 (s, *o*-*C*(CH_3)$_3$), 34.6 (s, *p*-*C*(CH_3)$_3$), 33.5 (d, $|^4J_{P-C}|$ 7.2 Hz, *o*-C(*C*H_3)$_3$, 31.2 (s, *p*-C(*C*H_3)$_3$). ^{31}P NMR (25 °C, C_6D_6): δ 12.7 (s). HRMS (EI) (*m/e*) for $C_{26}H_{37}P$: calcd 380.2633, found 380.2627. (**12**) Reagent: *cis*-$ClCH_2CH{=}CHCH_2$-Cl. Yield: 38% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 7.52 (d, $|^4J_{P-H}| = 1.9$ Hz, 2H, Ar-*H*), 4.80 (d, $|^3J| = 17.0$ Hz, 1H, =C*H*H), 4.58 (dd, $|^3J| = 10.1$ Hz, $|^4J_{P-H}| = 1.8$ Hz, 1H, CH*H*), 3.99 (dddd, $|^3J| = 17.0$ Hz, $|^3J| = 10.1$ Hz, $|^3J| = 9.9$ Hz, $|^3J_{P-H}| = 2.7$ Hz, 1H, =C*H*). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 154.8 (s, quat), 150.2 (s, quat), 143.1 (d, $|J| = 52.6$ Hz, quat), 139.1 (s, =*C*H), 120.3 (s, arom *C*-H), 113.2 (s, =*C*H_2), 38.3 (s, *o*-*C*(CH_3)$_3$), 34.8 (s, *p*-*C*(CH_3)$_3$), 33.6 (d, $|^4J_{P-C}| =$ 9.1 Hz, *o*-C(*C*H_3)$_3$), 32.5 (d, $|J_{P-C}| = 43.8$ Hz, ring *C*H), 31.1 (s, *p*-C(*C*H_3)$_3$), 21.4 (d, $|J_{P-C}| = 41.4$ Hz, ring *C*H_2). ^{31}P NMR (25 °C, C_6D_6): δ −174.2 (s). HRMS (EI) (*m/e*) for $C_{22}H_{35}P$: calcd 330.2476, found 330.2462. (**13**) Reagent: $ClCH_2C{\equiv}CCH_2Cl$. Yield: 53% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 7.38 (d, $|^4J_{P-H}| = 2.0$ Hz, 2H, Ar-*H*), 3.56 (AB q, $|J| = 2.7$ Hz, 2H, =C*H_2*), 1.60 (s, 18H, *o*-^{t}Bu), 1.28 (s, 9H, *p*-^{t}Bu). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 200.5 (d, $|^2J_{P-C}| = 10.1$ Hz, =*C*=), 155.1 (s, quat), 149.8 (s, quat), 134.6 (d, $|J| =$ 65.5 Hz, quat), 122.4 (s, arom *C*-H), 84.4 (d, $|J_{P-C}| = 46.5$ Hz, ring *C*=), 76.6 (s, =*C*H_2), 38.4 (s, *o*-*C*(CH_3)$_3$), 34.9 (s, *p*-*C*(CH_3)$_3$), 33.6 (d, $|^3J_{P-C}| = 7.4$ Hz, *o*-C(*C*H_3)$_3$), 31.2 (s, *p*-C(*C*H_3)$_3$), 22.2 (d, $|J_{P-C}| = 48.9$ Hz, ring *C*H_2). ^{31}P NMR (25 °C, C_6D_6): δ −149.6 (s). HRMS (EI) (*m/e*) for $C_{22}H_{33}P$: calcd 328.2320, found 328.2309.

Reactions of 2 with Epoxides: Synthesis of (PhCHCH(Ph)PR*) 15, *trans*-($PhCHCH_2PR$*) 16, and Cp_2Zr(PHR*)($OCH_2CH{=}CH_2$) 17. The reactions of **2** with three epoxides were performed in a similar manner; thus, only one preparation is described in detail. To a benzene solution of **2** (57 mg, 0.1 mmol) was added *trans*-stilbene oxide (20 mg, 0.1 mmol). The reaction mixture stood overnight, after which time the solvent was removed under reduced pressure. Extraction into pentane followed by filtration and solvent removal in vacuo gave the yellow product. (**15**) Yield: 53% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 7.49 (d, $|^4J_{P-H}| = 1.9$ Hz, 2H, Ar-*H*), 7.3−6.8 (m, 10H, Ph-*H*), 1.66 (s, 18H, *o*-^{t}Bu), 1.32 (s, 9H, *p*-^{t}Bu), 1.6−1.1 (m, 2H, C*H*). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 156.4 (s, quat), 150.1 (s, quat), 137.6 (s, quat), 137.4 (d, $|J_{P-C}| = 53.3$ Hz, quat), 137.2 (d, $|J_{P-C}| = 12.1$ Hz, quat), 130.1 (s, arom *C*-H), 129.9 (s, arom *C*-H), 128.5 (s, arom *C*-H), 126.7 (s, arom *C*-H), 125.8 (s, arom *C*-H), 121.9 (s, arom *C*-H), 119.4 (s, arom *C*-H), 42.5 (d, $|J_{P-C}| = 37.4$ Hz, ring *C*H), 39.2 (s, *o*-*C*(CH_3)), 34.9 (s, *p*-*C*(CH_3)), 33.9 (d, $|^4J_{P-C}| = 8.6$ Hz, *o*-C(*C*H_3)), 31.5 (s, *p*-C(*C*H_3)). ^{31}P NMR (25 °C, C_6D_6): δ −166.8 (s). HRMS (EI) (*m/e*) for $C_{32}H_{41}P$: calcd 456.2946, found 456.2928. (**16**) Reagent: ($PhCHCH_2O$). Yield: 92% (by ^{1}H NMR). ^{31}P NMR (25 °C, C_6D_6): δ −174.8 (d, $|J| = 20.4$ Hz). ^{1}H NMR and ^{13}C{^{1}H} NMR data were as reported in the literature.[23] (**17**) Reagent: ($MeCHCH_2O$). Yield: 89% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 7.60 (d, $|^4J_{P-H}| = 1.7$ Hz, 2H, Ar-*H*), 5.63 (s, 10H, Cp), 5.00 (m, 3H, C*H*=C*H_2*), 4.95 (d, $|J_{P-H}| = 213.9$ Hz, 1H, P-*H*), 4.17 (m, 2H, O-C*H_2*), 1.76 (s, 18H, *o*-^{t}Bu), 1.37 (s, 9H, *p*-^{t}Bu). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 151.9 (s, quat), 146.3 (d, $|J| = 44.3$ Hz, quat), 145.2 (s, quat), 139.0 (s, =*C*H), 120.8 (s, arom *C*-H), 113.1 (s, =*C*H_2), 111.0 (s, Cp), 74.9 (s, O-*C*H_2), 38.4 (s, *o*-*C*(CH_3)$_3$), 34.5 (s, *p*-*C*(CH_3)$_3$), 33.0 (d, $|^4J_{P-C}| = 6.1$ Hz, *o*-C(*C*H_3)$_3$), 31.4 (s, *p*-C(*C*H_3)$_3$. ^{31}P NMR (25 °C, C_6D_6): δ −43.5 (d, $|J_{P-H}| = 217.2$ Hz). HRMS (EI) (*m/e*) for $C_{31}H_{45}OPZr$: calcd 554.2251, found 554.2274.

Reactions of 2 with Silicon, Germanium, and Tin Dihalides and Tin Sulfides: Synthesis of Cp_2Zr(PR*($SiMe_2Cl$))Cl 18. To a benzene solution of **1** (114 mg, 0.2 mmol) was added dichlorodimethylsilane (24.2 μL, 0.2 mmol). The reaction mixture stood for 3 h, during which time the solution became deep red. The solvent was removed in vacuo and the product dissolved in pentane. A red microcrystalline solid precipitated over 12 h at room temperature and was isolated by filtration. Yield: 95 mg (71%). ^{1}H NMR (25 °C, C_6D_6): δ 7.68 (d, $|^4J_{P-H}| =$ 2.2 Hz, 2H, Ar-*H*), 5.89 (br s, 10H, Cp), 1.69 (s, 18H, *o*-^{t}Bu), 1.28 (d, $|^4J_{P-H}| = 2.9$ Hz, 6H, Me), 1.27 (s, 9H, *p*-^{t}Bu). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 155.2 (s, quat), 147.3 (s, quat), 133.9 (s, quat), 123.9 (s, arom *C*-H), 111.2 (s, Cp), 39.8 (s, *o*-*C*(CH_3)$_3$), 34.8 (s, *p*-*C*(CH_3)$_3$), 34.5 (s, *o*-C(*C*H_3)$_3$), 31.2 (d, $|^2J_{P-C}| = 5.0$ Hz, Me), 31.0 (s, *p*-(C(*C*H_3)$_3$). ^{31}P NMR (25 °C, C_6D_6): δ 117.9 (s). HRMS (EI) (*m/e*) for $C_{30}H_{45}Cl_2PSiZr$: calcd 624.1448, found 624.1471. Anal. Calcd for $C_{30}H_{45}Cl_2PSiZr$: C, 57.48; H, 7.24. Found: C, 57.94; H, 6.91.

Synthesis of PR*($SiMe_2Cl$)$_2$ 19, (Me_2GeCl)$_2$PR* 20, and (Me_2GePR*)$_2$ 21. The reactions of **2** with 2 equiv of Me_2SiCl_2 or 1 and 2 equiv of Me_2GeCl_2 were performed in a similar manner; thus, only one preparation is described in detail. To a benzene solution of **2** (57 mg, 0.1 mmol) was added 2 equiv of Me_2SiCl_2 (24.2 μL, 0.2 mmol). The reaction mixture stood overnight, after which time the solvent was removed under reduced pressure. Extraction into pentane followed by filtration and solvent removal in vacuo gave the yellow product. (**19**) Yield: 92% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 7.48 (d, $|^4J_{P-H}| = 3.3$ Hz, 2H, Ar-*H*), 1.68 (s, 18H, *o*-^{t}Bu), 1.23 (s, 9H, *p*-^{t}Bu), 0.53 (d, $|^3J_{P-H}| = 5.6$ Hz, 12H, Me). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 159.3 (s, quat), 150.8 (s, quat), 122.3 (s, arom *C*-H), 38.6 (s, *o*-*C*(CH_3)$_3$), 34.7 (s, *p*-*C*(CH_3)$_3$), 33.7 (s, *o*-C(*C*H_3)$_3$), 31.0 (s, *p*-(C(*C*H_3)$_3$), 5.6 (d, $|^2J_{P-H}| = 17.1$ Hz, Me). ^{31}P NMR (25 °C, C_6D_6): δ −121.9 (s). HRMS (EI) (*m/e*) for $C_{22}H_{41}Cl_2PSi_2$: calcd 462.1862, found 462.1848. (**20**) Reagent: Me_2GeCl_2 (2 equiv). Yield: 62% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 7.46 (d, $|^4J_{P-H}| = 3.1$ Hz, 2H, Ar-*H*), 1.62 (s, 18H, *o*-^{t}Bu), 1.22 (s, 9H, *p*-^{t}Bu), 0.77 (d, $|^3J_{P-H}| = 4.1$ Hz, 12H, Me). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 159.1 (s, quat), 155.2 (s, quat), 122.4 (s, arom *C*-H), 38.6 (s, *o*-*C*(CH_3)$_3$), 34.7 (s, *p*-*C*(CH_3)$_3$), 33.7 (d, $|^4J_{P-C}| = 6.4$ Hz, *o*-C(*C*H_3)$_3$), 31.2 (s, *p*-(C(*C*H_3)$_3$), 8.6 (d, $|^2J_{P-C}| = 9.8$ Hz, Me). ^{31}P NMR (25 °C, C_6D_6): δ −79.9 (s). HRMS (EI) (*m/e*) for $C_{22}H_{41}Cl_2Ge_2P$: calcd 552.0759, found 552.0864.[24] (**21**) Reagent: Me_2GeCl_2 (1 equiv). Yield: 39% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 7.37 (s, 2H, Ar-*H*), 1.66 (s, 18H, *o*-^{t}Bu), 1.28 (s, 9H, *p*-^{t}Bu), 0.66 (t, $|^3J_{P-H}| = 4.4$ Hz, 6H, Me). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 159.3 (s, quat), 155.1 (s, quat), 122.3 (s, arom *C*-H), 37.9 (s, *o*-*C*(CH_3)$_3$), 34.2 (s, *p*-*C*(CH_3)$_3$), 33.3 (d, $|^4J_{P-C}| = 6.5$ Hz, *o*-C(*C*H_3)$_3$), 31.0 (s, *p*-(C(*C*H_3)$_3$), 8.7 (t, $|^2J_{P-C}| = 11.6$ Hz). ^{31}P NMR (25 °C, C_6D_6): δ −52.7 (s). HRMS (EI) (*m/e*) for $C_{40}H_{70}Ge_2P_2$: calcd 758.3389, found 758.3517.[24]

Synthesis of (*t*-Bu_2SnPR)$_2$ 22. To a benzene solution of **2** (114 mg, 0.2 mmol) was added a benzene solution of di-*tert*-butyltin dichloride (61 mg, 0.2 mmol). The reaction mixture stood overnight, after which time the solvent was removed in vacuo. The product was extracted into pentane, and this solution was filtered. Large orange crystals formed over 3 days at room temperature and were isolated by filtration. Yield: 61 mg (30%). ^{1}H NMR (25 °C, C_6D_6): δ 7.35 (s, 4H, Ar-*H*), 1.83 (s, 36H, ^{t}Bu), 1.46 (s, 36H, ^{t}Bu), 1.30 (s, 18H, *p*-^{t}Bu). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 156.5 (s, quat), 147.8 (s, quat), 121.5 (s, arom *C*-H), 44.3 (s, *C*(CH_3)$_3$), 39.3 (s, *C*(CH_3)$_3$), 34.6 (s, C(*C*H_3)$_3$, 34.3 (s, *C*(CH_3)$_3$), 32.4 (s, C(*C*H_3)$_3$), 31.2 (s, (C(*C*H_3)$_3$). ^{31}P NMR (25 °C, C_6D_6): δ −84.8 (s, $|^1J_{^{117}Sn-P}| = 686.7$ Hz, $|^1J_{^{119}Sn-P}| = 717.4$ Hz). Anal. Calcd for $C_{52}H_{94}Sn_2P_2$: C, 61.31; H, 9.30. Found: C, 60.88; H, 9.01.

Synthesis of (Me_2SnPR*)$_2$ 23. To a benzene solution of **2** (57 mg, 0.1 mmol) was added a benzene solution of dimethyltin sulfide (18 mg, 0.1 mmol). The reaction mixture stood overnight, after which time the solvent was removed under reduced pressure and the product extracted into pentane. Filtration followed by evaporation of the solvent in vacuo gave **23** as a red solid. *Note*: Attempts to recrystallize this compound from pentane only resulted in the decomposition of **23**. Yield: 46% (by ^{1}H NMR). ^{1}H NMR (25 °C, C_6D_6): δ 7.46 (s, 2H, Ar-*H*), 1.76 (s, 18H, *o*-^{t}Bu), 1.28 (s, 9H, *p*-^{t}Bu), 0.65 (br s, 6H, Me). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 157.6 (s, quat), 149.1 (s, quat), 121.5 (s, arom *C*-H), 38.7 (s, *o*-*C*(CH_3)$_3$), 34.6 (s, *p*-*C*(CH_3)$_3$), 33.7 (s, *o*-C(*C*H_3)$_3$), 31.1 (s, *p*-(C(*C*H_3)$_3$), 2.3 (br s, Me). ^{31}P NMR (25 °C, C_6D_6): δ −108.9 (s, $|^1J_{^{117}Sn-P}| = 485.0$ Hz, $|^1J_{^{119}Sn-P}| = 504.7$ Hz). HRMS (EI) (*m/e*) for $C_{40}H_{70}Sn_2P_2$: calcd 852.2997, found 852.3044.

Reactions of 2 with Benzonitrile and Dicyclohexylcarbodiimide: Formation of Cp_2Zr(PMe_3)(NC(Ph)(PR*)) 25a and 25b. To a benzene solution of **2** (57 mg, 0.1 mmol) was added benzonitrile (10.2 μL, 0.1 mmol). The reaction mixture stood for 2 h, after which time the solvent was removed in vacuo and the red product extracted into pentane. This solution was allowed to stand for 2 weeks; after this

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(23) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Chem. Lett.* **1985**, 441.

(24) Despite repeated attempts, high-resolution mass spectral data for the Ge derivatives **21** and **22** agreed only within 15 ppm of the expected values.

Table 1. Crystallographic Data

	22	**25**	**26**
formula	$C_{52}H_{94}P_2Sn_2$	$C_{38}H_{53}NP_2Zr$	$C_{41}H_{61}N_2PZr$
formula weight	1,018.64	768.23	704.14
crystal size	0.30 × 0.25 × 0.25	0.32 × 0.27 × 0.24	0.30 × 0.37 × 0.28
a (Å)	12.062(7)	12.918(3)	14.353(6)
b (Å)	23.090(3)	14.879(4)	13.513(4)
c (Å)	10.543(3)	19.751(4)	21.101(5)
α (deg)	101.67(1)		
β (deg)	99.77(3)	98.57(2)	106.78(3)
γ (deg)	78.99(2)		
space group	$P\bar{1}$	$P2_1/c$	*Cc*
vol (Å^3)	2796(2)	3754(1)	3918(2)
D_{calcd} (g cm^{-3})	1.21	1.36	1.19
Z	2	4	4
abs coeff, μ, cm^{-1}	9.79	6.66	3.50
temp (°C)	24	24	24
no. of data collected	9862	3701	3616
no. of data with $F_o^2 > 3\sigma(F_o^2)$	5988	834	1188
variables	506	97	146
R (%)[a]	4.6	9.0	7.8
R_w (%)[a]	5.9	9.2	6.2

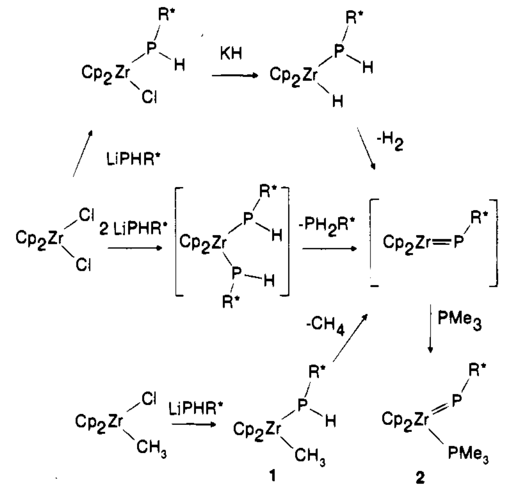
[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum(|F_o| - |F_c|)^2|/\sum|F_o|^2]^{0.5}$.

time two or three thin red crystals of **25b** were obtained. Repeated attempts to isolate larger quantities were unsuccessful. ^{1}H NMR gave an estimated 50% combined yield of **25a** and **25b**. ^{1}H NMR (25 °C, C_6D_6, mixture of **25a** and **25b**): δ 7.71−6.89 (m, 14H, Ph-*H* and Ar-*H*), 5.76 (s, 5H, Cp), 5.75 (s, 5H, Cp), 5.52 (s, 5H, Cp), 5.51 (s, 5H, Cp), 2.05 (s, 18H, *o*-^{t}Bu), 1.92 (s, 18H, *o*-^{t}Bu), 1.48 (s, 9H, *p*-^{t}Bu), 1.39 (s, 9H, *p*-^{t}Bu), 0.36 (d, $|^2J_{P-H}| = 7.10$ Hz, 9H, Me), 0.95 (d, $|^2J_{P-H}| = 7.37$ Hz, 9H, Me). (**25a**) ^{31}P NMR (25 °C, C_6D_6): δ 83.9 (s), −14.7 (s). (**25b**) ^{31}P NMR (25 °C, C_6D_6): δ 92.1 (s), −15.2 (s).

Synthesis of $Cp_2Zr(N(Cy))_2C{=}PR^*$ 26. To a benzene solution of **2** (114 mg, 0.2 mmol) was added dicyclohexylcarbodiimide (42 mg, 0.2 mmol). The reaction mixture stood overnight, after which time the solvent was evaporated in vacuo and the brown solid dissolved in pentane. Dark brown crystals formed over 12 h at room temperature and were isolated by filtration. Yield: 64 mg (46%). ^{1}H NMR (25 °C, C_6D_6): δ 71.57 (d, $|^4J_{P-H}| = 1.5$ Hz, 2H, Ar-*H*), 5.99 (s, 10H, Cp), 4.56 (m, 1H, C-*H*), 2.86 (m, 1H, C-*H*), 2.65−0.60 (m, 20H, C*H*$_2$), 2.00 (s, 18H, *o*-^{t}Bu), 1.44 (s, 9H, *p*-^{t}Bu). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 164.3 (d, $|J| = 121.6$ Hz, *C*=P), 157.1 (d, $|J| = 5.4$ Hz, quat), 147.5 (s, quat), 138.7 (d, $|J| = 72.3$ Hz, quat), 121.2 (s, arom *C*-H), 113.8 (s, Cp), 57.8 (d, $|^3J_{P-C}| = 37.9$ Hz, *C*-H), 57.0 (s, *C*-H), 39.4 (s, *o*-*C*(CH$_3$)$_3$), 37.1 (s, *C*H$_2$), 35.8 (d, $|J| = 3.5$ Hz, *C*H$_2$), 34.9 (s, *p*-*C*(CH$_3$)$_3$), 33.5 (d, $|^4J_{P-C}| = 9.6$ Hz, *o*-C(*C*H$_3$)$_3$), 31.5 (s, *p*-(C(*C*H$_3$)$_3$), 26.7 (s, *C*H$_2$), 25.9 (s, *C*H$_2$), 25.8 (s, *C*H$_2$), 25.5 (s, *C*H$_2$). ^{31}P NMR (25 °C, C_6D_6): δ −9.7 (s). Anal. Calcd for $C_{41}H_{61}N_2PZr$: C, 69.94; H, 8.73. Found: C, 70.38; H, 8.44.

Crystal Structure Determination. X-ray quality crystals of **22**, **25**, and **26** 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 AFC6 diffractometer equipped with graphite-monochromatized Mo Kα radiation. Crystal data and details associated with data collection for **22**, **25b**, and **26** are given in Tables 1 and S1 (Table S1 is in the supporting information). 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. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[25,26] Atom positions were determined using direct methods and 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, all the non-hydrogen atoms in **22** were assigned anisotropic temperature factors. For **25b** and **26** the Zr and P atoms were assigned anisotropic temperature factors while the remaining non-hydrogen atoms were assigned isotropic temperature factors. The cyclopentadienyl and phenyl rings in **25b** and **26** as well as the *tert*-butyl groups in **25b** were refined with a constrained geometry in order to maintain a statistically meaningful data:variable ratio. The correct enantiomorph of **26** was confirmed by inversion and refinement of the model. 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. Crystallographic details, positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as supporting information.

Scheme 1



Results and Discussion

We have previously reported the synthesis of the species $Cp_2Zr(PR^*)(PMe_3)$ **2** from either Cp_2ZrCl_2 or $Cp_2Zr(PHR^*)Cl$ (Scheme 1).[10,11] In either synthesis the yield of the terminal phosphinidene complex **2** was in the range of 40%. Since these reports we have determined that the reaction of $Cp_2ZrMeCl$ with Li(PHR*) and PMe_3 (Scheme 1) is a superior synthetic route to **2**, providing a greater purity and vastly improved yields. The reaction of $Cp_2ZrMeCl$ with phosphide rapidly produced $Cp_2Zr(PHR^*)Me$ **1**, which was unstable with respect to the elimination of methane. When this occurred in the presence of PMe_3, the forest-green terminal phosphinidene species **2** was obtained cleanly, in nearly quantitative isolated yield.

Reactions of 2 with Ketones and Aldehydes. Compound **2** reacted with benzaldehyde to give an insoluble white precipitate (presumably polymeric zirconocene oxides), free PMe_3, and the *E*-isomer of the known phosphaalkene $R^*P{=}CHPh$ **3**.[16] An analogous synthetic procedure using benzophenone provided an 82% yield of the known phosphaalkene $R^*P{=}CPh_2$ **4**;[17] in the same manner the use of 2 equiv of **2** with isophthalaldehyde furnished the benzodiphosphaalkene species $C_6H_2(1,3\text{-}C{=}PR^*)_2$ **5**[18] (Scheme 2). In contrast to the published synthetic route the present procedure resulted in the exclusive formation of the *E,E*-isomer of **5** in 86% yield. The related reaction of **2** with phenyl isothiocyanate gave the heteroallene *trans*-PhN=C=PR* **6** in 81% yield,[19] along with the crystalline blue byproduct $[Cp_2ZrS]_2$.[27]

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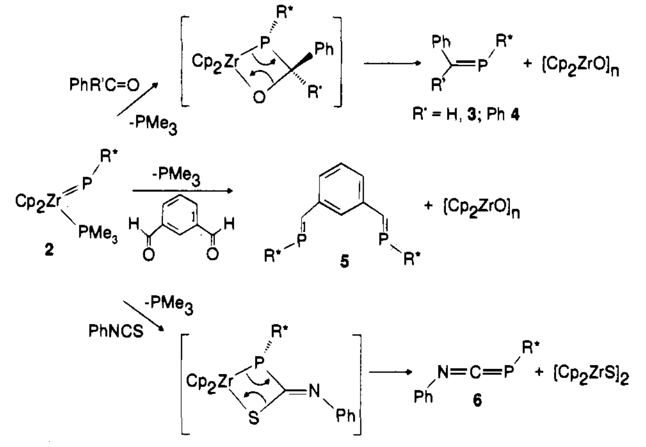
(25) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys. Theor. Gen. Crystallogr.* **1968**, *A24*, 324. (b) *Ibid.* **1968**, *A24*, 390.

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

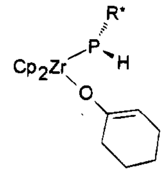
(27) (a) Bottomley, F.; Drummond, D. F.; Egharevba, G. O.; White, P. S. *Organometallics* **1986**, *5*, 1620. (b) Gelmini, L.; Stephan, D. W. *Organometallics* **1987**, *6*, 1515.

Scheme 2



The above reactions are viewed as hetero-olefin metatheses formally resulting in the exchange of Zr=P and C=E double bonds. They are thought to proceed through initial coordination of the carbonyl species followed by intramolecular attack of the carbon atom by phosphorus to give a cyclic intermediate (Scheme 2). Subsequent retrocyclization gives the C=P product and oligomerized Zr=E. The selective regiochemistry resulting in the formation of only the *E*-isomers of the phosphaalkenes corresponds to a minimization of steric crowding in the metallacyclic intermediates. These transformations are analogous to the well-known reaction between tantalum alkylidenes and aldehydes to yield olefins and a Ta=O species,[28] and related reactions yielding phosphaalkenes have also been briefly described for $((Me_3SiNCH_2CH_2)_3N)Ta{=}PR$.[12]

In contrast to the above reactions, **2** reacted with cyclohexanone to give the enolate derivative $Cp_2Zr(PHR^*)(OC_6H_9)$ **7**. The formation of **7** is consistent with the basicity of the phosphinidene group of **2** and the presence of acidic, enolizable protons of cyclohexanone.

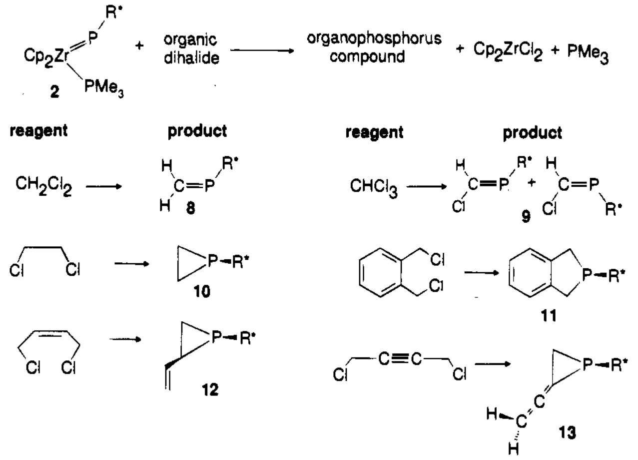


7

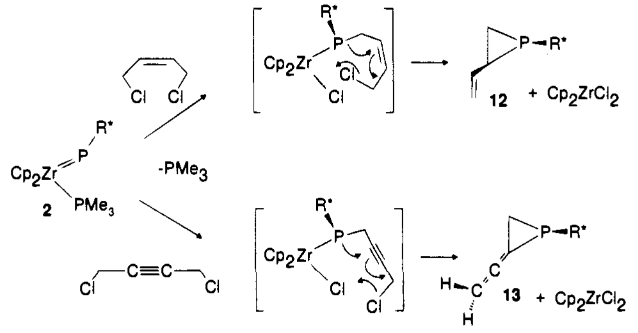
Reactions of 2 with Alkylidene Dichlorides. *gem*-Dichlorides also reacted with **2** to give phosphaalkenes, along with byproducts Cp_2ZrCl_2 and PMe_3. For example, $R^*P{=}CH_2$ **8**[20] was formed in 86% yield via reaction of **2** with CH_2Cl_2, and the analogous reaction with $CHCl_3$ gave a 1:2 ratio of the *cis*- and *trans*-isomers of $R^*P{=}CHCl$ **9**,[20,21] in an overall yield of 76% (Scheme 3). Organophosphacycles were accessible by altering the choice of organic dihalide. For instance, the known phosphirane $CH_2CH_2PR^*$ **10**[22] was prepared in 45% yield by reaction of **2** with 1,2-dichloroethane, and the use of *o*-dichloroxylene produced the new phospholane $C_6H_4(CH_2)_2PR^*$ **11** in 53% yield.

In contrast to these results the reaction of **2** with 1,4-dichloro-2-butene did not produce the anticipated five-membered ring, but rather the *cis*-isomer of the vinyl-substituted phosphirane $(CH_2CH)(CHCH_2PR^*)$ **12** in 38% yield. Likewise, reaction of **2** with 1,4-dichloro-2-butyne produced the species $CH_2C(CCH_2PR^*)$ **13** in 53% yield (Scheme 3). Both **12** and **13** exhibited the high-field ^{31}P chemical shifts typical of three-membered rings.[29] The existence of the vinyl group in **12** was confirmed by ^{13}C and DEPT experiments. Simulations of the ^1H NMR vinyl region showed very small coupling of the vinyl protons to phosphorus, suggesting a *cis* orientation of the supermesityl and vinyl groups. This geometry is consistent with the absence of coupling between phosphorus and the vinyl carbon atoms and is also in accordance with ^{13}C NMR data for related vinylphosphiranes.[30] The presence of the allene fragment in **13** was verified by ^{13}C NMR spectra. The central carbon of this moiety resonates at 220.5 ppm while signals at 76.6 and 84.4 ($|J_{P-C}|$ = 46.5 Hz) ppm were confirmed by DEPT experiments to be the exocyclic methylene and the substituted ring carbons, respectively.

Scheme 3



Scheme 4



The reactions with alkyl halides are thought to involve phosphide–halide intermediates of the form $Cp_2Zr(PR^*R')Cl$, and structurally related compounds $Cp_2Zr(PR^*H)Cl$,[10] $Cp^*{}_2Zr(PR^*H)Cl$,[31] and $Cp_2Zr(PR^*SiMe_3)Cl$[32] have been previously characterized. This view is compatible with observations of transient ^{31}P NMR resonances at 165.6, 180.8, and 173.8 ppm in the formations of **11**, **12**, and **13**, respectively. Although the unusual reactions of **2** with 1,4-dichloro-2-butene and 1,4-dichloro-2-butyne were observed to progress through these intermediates, the completion of the reaction proceeds via an alternate pathway (Scheme 4).

Reactions of 2 with Epoxides. Phosphiranes PhCHCH(Ph)PR* **15** and *trans*-(PhCHCH$_2$PR*) **16** were derived from reactions of **2** with *trans*-stilbene oxide and styrene oxide,

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[28] Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399.

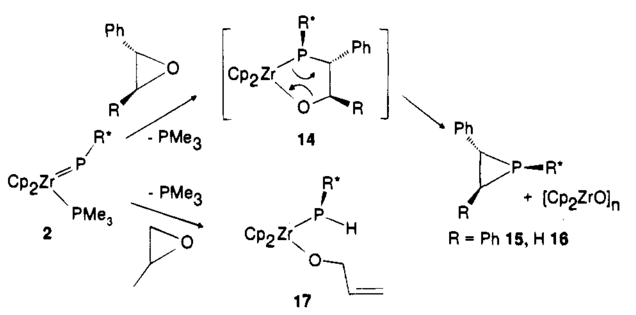
[29] (a) Goldwaite, H.; Rowsell, D.; Vertal, L. E.; Bowers, M. T.; Cooper, M. A.; Manatt, S. L. *Org. Magn. Reson.* **1983**, *21*, 494. (b) *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, FL, 1987.

[30] Richter, W. J. *Chem. Ber.* **1983**, *116*, 3293.

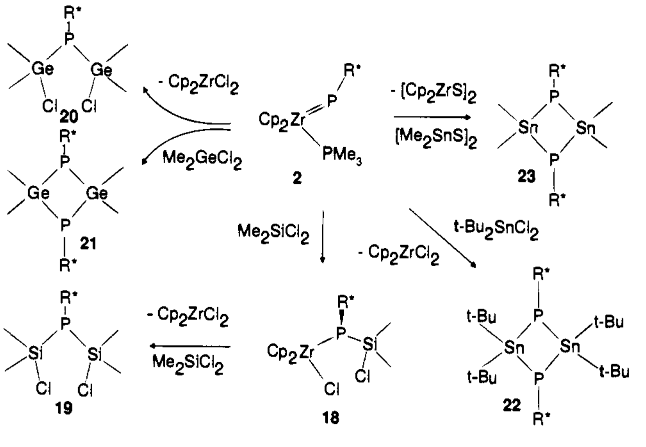
[31] Fermin, M. C.; Ho, J.; Stephan, D. W. *Organometallics*, submitted for publication.

[32] Arif, A. M.; Cowley, A. H.; Nunn, C. M.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1987**, 994.

Scheme 5



Scheme 6



respectively. The ^{31}P NMR spectrum of the reaction of **2** with *trans*-stilbene oxide revealed the initial appearance of a resonance at 136.4 ppm attributable to an intermediate of the form **14** (Scheme 5). This signal gradually receded and was replaced by the resonance due to **15**. The ^{13}C NMR spectrum of **15** revealed the inequivalence of the two phenyl substituents, indicative of a relative *trans* orientation. A similar reaction between **2** and styrene oxide yielded one pair of enantiomers of the known[23] phosphirane **16**, in which the phenyl and R* groups were of a *trans* disposition.

In the related reaction of **2** with propylene oxide the derived product $Cp_2Zr(PR^*H)(OCH_2CHCH_2)$ **17** was formed through enolization. The reaction probably progresses through coordination of the epoxide to the zirconium center followed by abstraction of the enolizable proton and ring opening to give **17**. Similar enolization of isobutylene oxide has been observed by Bergman et al. with the Zr–imido species $Cp_2Zr(NR)$(THF).[2b] The use of epoxides without enolizable protons results in intramolecular nucleophilic attack of the coordinated epoxide by phosphorus to afford ring-opened intermediates akin to **14**.

Reactions of 2 with Silicon, Germanium, and Tin Dichlorides and Tin Sulfides. Interest in phosphinidenes of the heavier main group elements has intensified in recent years.[33] The observed reactivity of **2** suggests the accessibility of main group phosphinidenes through reactions of **2** with various main group dihalides or chalcogenides. Thus, the use of Me_2SiCl_2 furnished a 71% yield of $Cp_2Zr(PR^*(SiMe_2Cl))Cl$ **18** (Scheme 6), which appears to be related to the proposed intermediates in reactions of **2** with organic dihalides. However, upon standing in solution, **18** did not liberate Cp_2ZrCl_2 and the phosphasilene, a fact which may be ascribed to the inherent strength of the Si–Cl bond. Nonetheless, reaction of **18** with 2 equiv of Me_2SiCl_2 furnished Cp_2ZrCl_2 and a 92% yield of the disilylphosphine $PR^*(SiMe_2Cl)_2$ **19**.

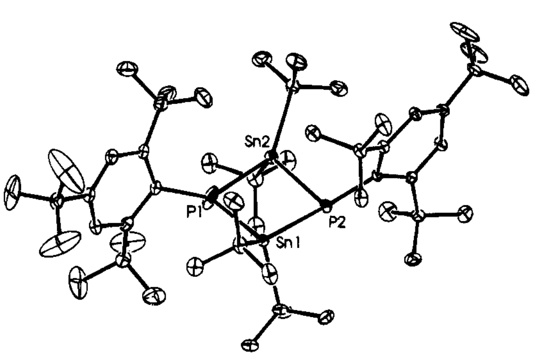


Figure 1. ORTEP drawing of **22**; 30% thermal ellipsoids are shown. Sn(1)–P(1), 2.524(3) Å; Sn(1)–P(2), 2.614(2) Å; Sn(2)–P(1), 2.556(3) Å; Sn(2)–P(2), 2.557(2) Å; P(1)–Sn(1)–P(2), 87.30(9)°; P(1)–Sn(2)–P(2), 87.87(9)°; Sn(1)–P(1)–Sn(2), 93.0(1)°; Sn(1)–P(2)–Sn(2), 90.92(7)°.

The corresponding reaction of **2** with 1 equiv of Me_2GeCl_2 resulted in the total consumption of **2** and the formation of two products, **20** and **21**, in a 55:45 ratio. The methyl protons of **20** appeared as a phosphorus-coupled doublet which supported its formulation as $(Me_2GeCl)_2PR^*$, whereas the triplet observed for the methyl protons of **21** pointed to a cyclic oligomer of the form $(Me_2GePR^*)_n$. High-resolution mass spectrometry confirmed the formulations of **20** and **21** as $(Me_2GeCl)_2PR^*$ and $(Me_2GePR^*)_2$, respectively. The phosphinidene transfer reaction followed by rapid dimerization of the highly unstable germanium phosphinidene intermediate is a likely mechanism for the formation of **21**. Not unexpectedly, the use of 2 equiv of Me_2GeCl_2 greatly improved the yield of **20** to 62% and gave a **20**:**21** ratio of 87:13.

Phosphinidene transfer to a tin center was observed in the reaction of **2** with t-Bu_2SnCl_2. The product **22** was isolated in 30% yield as large orange crystals which exhibited a ^{31}P NMR resonance at −84.8 ppm. ^{1}H and ^{13}C NMR data as well as elemental analyses were consistent with an empirical formulation of t-Bu_2SnPr^*; subsequently the dimeric nature of **22** was verified by X-ray crystallography (Figure 1). Although cyclic Sn–P compounds related to **22** have been synthesized through standard organic preparations, structural data have not been reported.[34] The crystal structure of **22** represents the first crystallographic data to be reported for a tin phosphinidene species. The Sn_2P_2 four-membered ring of **22** is slightly puckered as reflected in the dihedral angle of 170.2(1)° between the two SnP_2 planes. The supermesityl groups adopt a *cisoid* disposition with respect to the Sn_2P_2 core. The P–Sn–P angles average 87.58(9)° while the Sn–P–Sn angles are 93.0(1)° and 90.92(7)°. The Sn(2)–P distances of 2.556(3) and 2.557(2) Å and the Sn(1)–P distances of 2.524(3) and 2.614(2) Å agree well with the Sn–P distances in $Me_2Sn(PR^*H)_2$.[35] The sum of the angles about P(2) is 335.2°, indicating the approximately pyramidal geometry; however, a distortion at P(1) toward trigonal planarity is evidenced in the sum of the angles of only 348.0°. These metric parameters suggest that inversion at P may be facile in this strained four-membered ring system. This

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[33] (a) Ranaivonjatovo, H.; Escudie, J.; Couret, C.; Satge, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1047. (b) Couret, C.; Escudie, J.; Satge, J.; Raharinirina, A.; Andriamizaka, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 8280. (c) Escudie, J.; Couret, C.; Andrianarison, M.; Satge, J. *J. Am. Chem. Soc.* **1987**, *109*, 386. (d) Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156. (e) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Ruiz, J.; Atwood, J. L.; Bott, S. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1150. (f) Hope, H.; Pestana, D. C.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 691. (g) Waggoner, K. M.; Parkin, S.; Pestana, D. C.; Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3597. (h) Atwood, J. L.; Cowley, A. H.; Jones, R. A.; Mardones, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 7050. (i) Weber, L. *Chem. Rev.* **1992**, *92*, 1839.

[34] (a) Baudler, M.; Suchomel, H. *Z. Anorg. Allg. Chem.* **1983**, *505*, 39. (b) Schumann, H.; Benda, H. *Chem. Ber.* **1971**, *104*, 333.

[35] Breen, T. L.; Stephan, D. W. Unpublished results.

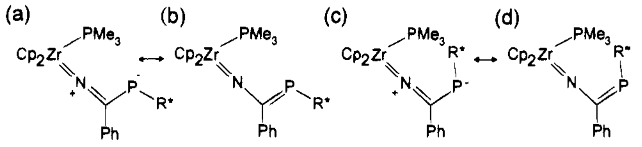
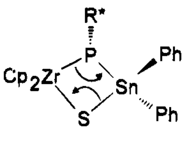


Figure 2. Resonance forms of **25a** and **25b**.

is consistent with the symmetry in solution implied by the ^{1}H and ^{13}C NMR spectra, though attempts to stop such inversion processes by cooling to −80 °C merely resulted in the observation of spectral broadening.

The ready availability of organotin chalcogenides also provided a route to dimerized tin phosphinidenes. **2** reacted with $(Me_2SnS)_3$[36] to give $[Cp_2ZrS]_2$, PMe_3, and a product of empirical formulation Me_2SnPR^*. The dimeric character of **23** was subsequently confirmed by high-resolution mass spectrometric data. The mechanism of this reaction is thought to proceed in a manner similar to that proposed for reactions of **2** with ketones and aldehydes. Since an intermediate to support this claim could not be detected, a comparable reaction was studied. The reaction between **2** and $(Ph_2SnS)_3$[36] progressed slowly; ^{31}P NMR spectroscopy showed the conversion of the starting material to a resonance at 93.4 ppm with $|^1J_{^{119}Sn-P}|$ and $|^1J_{^{117}Sn-P}|$ values of 881 and 925 Hz, respectively. This signal is tentatively assigned to the intermediate $Cp_2Zr(PR^*SnPh_2S)$ **24**. Continued surveillance by ^{31}P NMR spectroscopy showed



24

the slow disappearance of the resonance due to **24** and its replacement by a resonance at −174.3 ppm. By comparison to **22** and **23** this peak is attributed to $(R^*PSnPh_2)_2$, the isolation of which was precluded by its thermal instability.

By analogy to phosphaalkene formation transient terminal germanium and tin phosphinidenes are thought to be intermediates to the dimers **21**, **22**, and **23**, although these intermediates could not be detected even by monitoring the reaction mixtures at −80 °C. Monomeric germanium and tin phosphinidenes are known to be stabilized by bulkier substituents as in $(i\text{-}Pr_3C_6H_2)_2SnPR^*$,[33a] for example. However, the increased steric demands of the substituents in $(Me_3C_6H_2)_2SnCl_2$ inhibited reaction with **2**, and no phosphinidene transfer was observed.

Reactions of 2 with Benzonitrile and Dicyclohexylcarbodiimide. Addition of 1 equiv of benzonitrile to a benzene solution of **2** resulted in a rapid color change to deep red. After 1 h the ^{31}P NMR spectrum showed several byproducts, a major set of resonances at 83.8 and −14.7 ppm (attributable to **25a**), and an absence of free PMe_3. After 24 h the ^{31}P NMR revealed the appearance of a new pair of resonances at +92.1 and −15.2 ppm, which can be attributed to the product of isomerization **25b**. ^{1}H NMR data indicated that two closely related species were present in a 55:45 ratio. Prolonged standing in pentane afforded a few thin red crystals, and a subsequent X-ray crystallographic study established the connectivity of **25b** as $Cp_2Zr(PMe_3)(NC(Ph)(PR^*))$. The Zr−N−C vector is approximately linear, similar to the imido complex $Cp_2Zr{=}NR(THF)$ reported by Bergman et al.[2a,b] There is a *trans* arrangement of the phenyl and supermesityl groups about the C−P bond of the phosphaalkene moiety (Figure 2b, Figure 3).

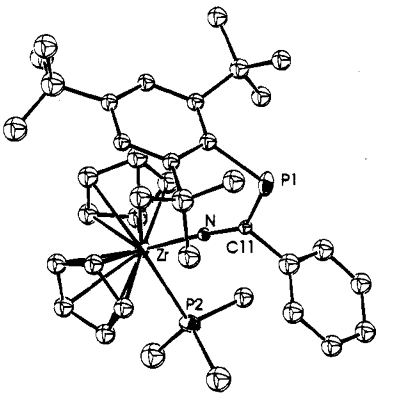


Figure 3. ORTEP drawing of **25b**; 30% thermal ellipsoids are shown. Zr−N, 1.93(2) Å; Zr−P(2), 2.74(1) Å; N−C(11), 1.29(3) Å; P(1)−C(11), 1.81(3) Å; Zr−N−C(11), 176(3)°.

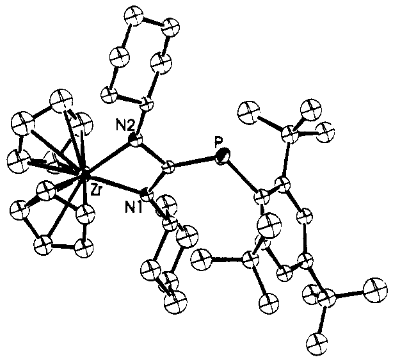
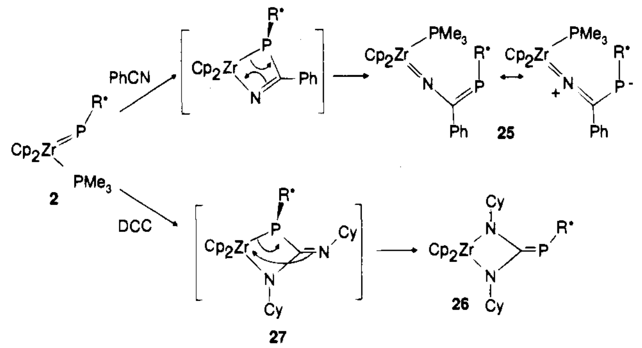


Figure 4. ORTEP drawing of **26**; 30% thermal ellipsoids are shown. Zr−N(1), 2.11(2) Å; Zr−N(2), 2.08(2) Å; N(1)−C(17), 1.44(3) Å; N(2)−C(17), 1.43(3) Å; P−C(17), 1.74(3) Å; N(1)−Zr−N(2), 66.3(8)°.

Scheme 7



The extremely short N−C distance of 1.29(3) Å and the relatively long C−P bond distance of 1.81(3) Å suggests the resonance form depicted in Figure 2c and Scheme 7. The participation of such resonance forms (Figure 2) in solution implies that the conversion of **25a** to **25b** is a result of rotation about the P−C bond. In the proposed reaction mechanism (Scheme 7) the *cis*-isomer **25a** is formed first, and steric congestion provokes isomerization to the less hindered **25b**. While the ^{31}P NMR shifts could be assigned to the two isomers in this way, correlation of the ^{1}H NMR data was precluded by our inability to separate bulk quantities of the unstable species **25a** and **25b**.

The reaction of **2** with dicyclohexylcarbodiimide (DCC) afforded a 46% yield of $Cp_2Zr(N(Cy))_2C{=}PR^*$ **26**, the structure of which was confirmed by X-ray crystallography (Figure 4). The Zr−N bond lengths in **26** of 2.08(2) and 2.11(2) Å are comparable to the terminal amido Zr−N bond distance in $[(Me_2N)_2ZrNCMe_3]_2$ of 2.065(1) Å.[37] The P−C bond length

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(36) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 2.

of 1.74(3) Å, much shorter than the analogous P−C distance in **25b**, substantiates the exocyclic phosphaalkene moiety in **26**.

The reactions of **2** with benzonitrile and DCC are comparable to established reactions of tantalum alkylidenes with nitriles.[38] The present reactions are thought to proceed through cycloaddition intermediates as depicted in Scheme 7, and evidence for this mechanism was acquired by monitoring the reaction mixture of **26** by ^{31}P NMR spectroscopy. A signal at 47.3 ppm, attributable to the intermediate **27**, was observed initially and was subsequently replaced by the product resonance. Rearrangement of the intermediates in both reactions results in the rupture of Zr−P bonds and the formation of P−C double bonds. Coordination of PMe_3 traps the imido compound **25**, which would be expected to be extremely reactive in the absence of PMe_3. This may account for some of the unidentified byproducts and the instability of **25**. In comparison, an intramolecular rearrangement process to give the exocyclic phosphaalkene moiety occurs in the formation of **26**.

Summary

The chemistry described herein demonstrates the significant reactivity of the terminal phosphinidene complex **2**. A variety of organic reagents, as well as some of their lower congeners, participate in reactions with **2**. **2** acts as a source of the phosphinidene moiety, which may be exchanged for an oxo, a sulfido, or two chloride groups. This provides a route to an assortment of organophosphorus derivatives and the corresponding zirconocene oxide, sulfide, or dichloride. Similar reactions of **2** with C−N multiple bonds also effect phosphinidene transfer to carbon. These exchange and transfer reactions reflect the inherent reactivity of the Zr=P double bond.

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Supporting Information Available: Text giving a full description of crystallographic details and tables of crystallographic parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles (26 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(37) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030.

(38) Wood, C. J.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210.