seems to be a more reliable technique.

Conclusions

The yttrium–carbon bond in 14-electron permethylyttrocenes Cp^*_2YR reacts readily with CX multiple bonds (X = =O, =S, N) provided that the substrate can coordinate to yttrium. In this respect the steric bulk of the carbyl R is very important. Too large a ligand may prevent an insertion reaction, either by inhibiting the formation of adducts $Cp^*_2YR{\cdot}S$ or by blocking the transition state for insertion. The insertion reactions presented above clearly demonstrate that a rich organometallic chemistry is accessible on the basis of carbyls Cp^*_2YR. The insertion products are in general 16-electron systems if the inserted substrate is a bidentate functionality. Even in these seemingly congested molecules space for additional ligands is available. This is convincingly demonstrated in the molecular structure of **11**, an η^2-iminoacyl THF adduct, it shows that in the organoyttrium systems under discussions the size of the coordination sphere is very large. It means that not only 18-electron systems are possible but also further, interesting reactions of the newly formed yttrium complexes may be anticipated.

Registry No. **1**, 95197-83-4; **2**, 108366-50-3; **3**, 108366-51-4; **4**, 108366-52-5; **5**, 108366-53-6; **6**, 108366-54-7; **7**, 108366-55-8; **8**, 108366-56-9; **9**, 108366-57-0; **10**, 108366-58-1; **11**, 108366-59-2; CO_2, 124-38-9; *t*-BuCN, 630-18-2; *t*-BuNC, 7188-38-7; CS_2, 75-15-0; (2,6-xylyl)NC, 2769-71-3.

Supplementary Material Available: Tables of atom coordinates, anisotropic thermal parameters, bond distances and (torsion) angles, and least-squares planes and atomic deviations therefrom, analysis of ring puckering, and analysis of the coordination or metal–metal geometry and ORTEP structure of $C_{42}H_{50}D_8NOY$ (**11**) showing the thermal ellipsoids (20 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Chemistry of Titanium(IV), Titanium(III), Zirconium(IV), and Hafnium(IV) Complexes of Phosphine Sulfides and Selenides. The Crystal and Molecular Structures of $Cp_2Ti(SPCy_2)_2$, $Cp_2Ti(S_2PCy_2)$, and $Cp_2Ti(Se_2PPh_2)$

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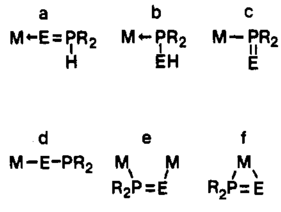
The complexes $Cp_2M(SPR_2)_2$ (M = Ti, R = Cy (**1**); M = Zr, R = Ph (**2**), R = Cy (**3**); M = Hf, R = Ph (**4**), R = Cy (**5**)) were prepared by reaction of $LiSPR_2$ with the appropriate metallocene dihalide. **1** crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.999$ (2) Å, $b = 13.102$ (5) Å, $c = 16.626$ (6) Å, $\alpha = 96.71$ (3)°, $\beta = 101.43$ (3)°, $\gamma = 91.14$ (3)°, $V = 1694$ (1) Å^3, and $Z = 2$. Species **2**–**5** could also be prepared from the reaction of $Cp_2M(PR_2)_2$ (M = Zr, Hf) with elemental sulfur. Reactions of Cp_2TiCl_2 with $LiXPR_2$ (X = S, R = Ph; X = Se, R = Ph, Cy) or solutions of **1** on standing yield Ti(III) species by reductive elimination of $(XPR_2)_2$. These Ti(III) complexes are formulated as "Cp_2TiXPR_2" (X = S, R = Ph (**6**), Cy (**7**); X = Se, R = Ph (**8**), R = Cy (**9**)) on the basis of EPR data. These Ti(III) compounds are unstable and slowly convert by chalcogen atom abstraction to the complexes $Cp_2TiX_2PR_2$ (X = S, R = Ph (**12**), R = Cy (**13**); X = Se, R = Ph (**14**), R = Cy (**15**)). **13** crystallizes in the orthorhombic space group *Pbna*, with $a = 9.075$ (3) Å, $b = 34.052$ (5) Å, $c = 14.318$ (5) Å, $V = 4424$ (3) Å^3, and $Z = 8$. **14** crystallizes in the monoclinic space group $P2_1/c$, with $a = 8.471$ (3) Å, $b = 29.868$ (9) Å, $c = 8.336$ (3) Å, $\beta = 104.47$ (3)°, $V = 2030$ (1) Å^3, and $Z = 4$. **12**–**15** as well as the analogues (X = S, R = Me (**10**), R = Et (**11**)) can also be prepared by photolysis of $Cp_2Ti(CO)_2$ in the presence of $(SPR_2)_2$ or XPR_2H. Alternatively, **12**–**15** can be prepared by reaction of either $LiXPR_2$ or LiX_2PR_2 with $[Cp_2TiCl]_2$. Complexes **2**–**5** slowly convert to the complexes $[Cp_2MX]_2$ (M = Zr, X = S (**16**), X = Se (**17**); M = Hf, X = S (**18**), X = Se (**19**), respectively). The preparation of **16**–**19** can also be achieved by direct reaction of **2**–**5** with $Cp_2M(PR_2)_2$. The differences between the Ti chemistry and that of Zr and Hf are attributed to the ease of reduction of Ti(IV) to Ti(III).

Introduction

Over the past several years, interest in early–late heterobimetallics has led us to develop several synthetic routes to such complexes. The methods we have devised are based on the use of early-transition-metal metalloligands as synthons.[1-7] In efforts to expand the arsenal of metalloligands available for heterobimetallic complex synthesis, we have investigated reactions of early transition metals with secondary phosphine chalcogenides. The high affinity of early metals for chalcogenide atom donors and

Chart I. Coordination Modes of Secondary Phosphine Chalcogenides and Their Conjugate Bases



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low affinity for phosphorus suggests that it may be possible to link early and late metals together with these ligands.

At least six different types of bonding of transition metals to secondary phosphine chalcogenides or their conjugate bases have been reported[8-23] and reviewed[24] (Chart I). The various modes of bonding include those involving bonding only through chalcogenide (X), those bound only through P, and those in which both X and P bond to a metal. Although numerous reports of such complexes are present in the literature, the chemistry of the early metals Ti, Zr, and Hf with such ligands has not been explored. In related work, others have previously investigated dithio- and diselenophosphate and dithio- and diselenophosphinate complexes of both V[25-35] and Ti.[36-38] Recent reports have described related thiophosphoryl complexes[39,40] and polychalcogen complexes[41-43] of these metals. In this paper, we describe the chemistry of secondary phosphine sulfide or selenide complexes of Ti, Zr, and Hf. The chemistry of the Ti complexes is contrasted with that of the Zr and Hf analogues and discussed in light of the results of X-ray structural studies.

Experimental Section

All preparations were done under an atmosphere of dry O_2-free N_2. Solvents were reagent grade, distilled from the appropriate drying agents under N_2, and degassed by the freeze–thaw method at least three times prior to use. ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer located at Wayne State University, using the trace of protonated solvent (benzene) as the reference. The chemical shifts are reported in parts per million relative to $SiMe_4$ for the ^1H NMR data. ^{31}P NMR spectra were recorded on a Bruker CXP-90 spectrometer or on a General Electric GN-300 spectrometer located at Wayne State University. ^{31}P NMR chemical shifts are reported in parts per million relative to external 85% H_3PO_4. UV–vis data were recorded on a Shimadzu 240 spectrometer or a Hewlett-Packard 8451A diode array spectrophotometer. EPR spectra were obtained by using a Varian E-12 spectrometer. EPR spectra were computer-simulated by Dr. P. E. Doan (Boudoin College) and J. Cornelius (University of Illinois). Combustion analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, or by Spang Laboratories, Eagle Harbor, MI. Cp_2TiCl_2, Cp_2ZrCl_2, and Cp_2HfCl_2 were purchased from the Aldrich Chemical Co. $(SPMe_2)_2$, $(SPEt_2)_2$, PPh_2H, and PCy_2H were purchased from the Strem Chemical Co. $Cp_2Ti(CO)_2$, $[Cp_2TiCl]_2$, $Cp_2Zr(PPh_2)_2$, $Cp_2Hf(PPh_2)_2$, $Cp_2Zr(PCy_2)_2$, $Cp_2Hf(PCy_2)_2$, $SPPh_2H$, $SPCy_2H$, $(SPPh_2)_2$, and $SePCy_2H$ were prepared by literature methods.[44-48]

Preparation of $Cp_2M(SPR_2)_2$ (M = Ti, R = Cy (1); M = Zr, R = Ph (2), R = Cy (3); M = Hf, R = Ph (4), R = Cy (5)). (i) From Cp_2MCl_2. Cp_2MCl_2 (300 mg) was dissolved in 25 mL of THF. Two equivalents of the appropriate $LiSPR_2$ reagent[24] were added. After 5 min of vigorous stirring, the solution was filtered and concentrated to 5 mL. Addition of 20 mL of diethyl ether resulted in formation of a precipitate, which was isolated by filtration. The compound was washed with three 5-mL portions of diethyl ether. Yields: **1**, 380 mg (60%); **2**, 425 mg (65%); **3**, 475 mg (70%); **4**, 500 mg (65%); **5**, 575 mg (75%).

(ii) From $Cp_2M(PR_2)_2$ (M = Zr or Hf; R = Ph or Cy) and SPR_2H. $Cp_2M(PR_2)_2$ 300 mg was dissolved in 25 mL of THF. Two equivalents of the appropriate SPR_2H were added. After 5 min of vigorous stirring, the resulting solution was concentrated to 2 mL under vacuum and chromatographed on neutral alumina. The product was eluted with THF, the yellow band collected and concentrated to 2 mL, and the product precipitated upon addition of hexane. Yields obtained by using $Cp_2M(PPh_2)_2$: **2**, 230 mg (70%); **3**, 275 mg (80%); **4**, 265 mg (80%); **5**, 240 mg (70%). Yields obtained by using $Cp_2M(PCy_2)_2$: **2**, 210 mg (65%); **3**, 240 mg (70%); **4**, 255 mg (80%); **5**, 245 mg (75%).

(iii) From $Cp_2M(PR_2)_2$ (M = Zr or Hf; R = Ph or Cy) and S. Two equivalents of S_8 were added to 300 mg of $Cp_2M(PR_2)_2$ dissolved in 20 mL of benzene. The solution was vigorously stirred for 5 h. Yields (based on $^{31}P\{^1H\}$ NMR integration): **2**, 185 mg (55%); **3**, 245 mg (70%); **4**, 200 mg (60%), **5**, 260 mg (80%). Anal. Calcd for $C_{34}H_{54}P_2S_2Ti$ (1): C, 64.13; H, 8.54; S, 9.73. Found: C, 63.63; H, 8.51; S, 9.70. 1: ^1H NMR (C_6D_6) δ 6.16 (s, 10 H), 1–2 (m, 44 H); $^{31}P\{^1H\}$ NMR (THF) δ 64.3 (s); UV–vis (THF; λ, nm (ϵ, $M^{-1}\ cm^{-1}$)) 342 (3900), 526 (1700). 2: ^1H NMR (C_6D_6) δ

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7–8 (m, 20 H), 5.73 (s, 10 H); $^{31}P\{^1H\}$ NMR (THF) δ 25.7 (s); UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 535 (380). Anal. Calcd for $C_{34}H_{54}P_2S_2Zr$ (**3**): C, 60.04; H, 8.00. Found: C, 59.72; H, 8.17. **1**: ^1H NMR (C_6D_6) δ 6.16 (s, 10 H), 1–2 (m, 44 H); $^{31}P\{^1H\}$ NMR (THF) δ 64.3 (s); UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 350 (650). **4**: ^1H NMR (C_6D_6) δ 7–8 (m, 10 H), 5.89 (s, 10 H); $^{31}P\{^1H\}$ NMR (THF) δ 25.8 (s); UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 235 (3500), 335 (600). **5**: ^1H NMR (C_6D_6) δ 6.12 (s, 10 H), 1–2 (m, 44 H); $^{31}P\{^1H\}$ NMR (THF) δ 63.8 (s); UV–vis (THF; λ, nm (ϵ, M^{-1})) 232 (3100), 325 (400).

Formation of "Cp_2TiXPR_2" (X = S, R = Ph (6), Cy (7); X = Se, R = Ph (8), R = Cy (9)). Cp_2TiCl_2 (300 mg) was added to a stirring THF solution (15 mL) of 2 equiv of the appropriate $LiXPR_2$.[24] The solution was stirred for 5 min, 10 mL of *n*-hexane was added, and the solution was filtered. The filtrate exhibited an EPR signal attributable to the species "Cp_2TiXPR_2". **6**: $g = 1.995$, $a\langle ^{47}Ti/^{49}Ti\rangle = 6.7$ G, $a\langle ^{31}P\rangle = 20.7$ G, $a\langle ^1H\rangle = 0.4$ G. **7**: $g = 1.988$, $a\langle ^{47}Ti/^{49}Ti\rangle = 6.5$ G, $a\langle ^{31}P\rangle = 17.8$ G, $a\langle ^1H\rangle = 0.5$ G. **8**: $g = 1.990$, $a\langle ^{47}Ti/^{49}Ti\rangle = 6.6$ G, $a\langle ^{31}P\rangle = 21.0$ G, $a\langle ^1H\rangle = 0.4$ G. **9**: $g = 1.994$, $a\langle ^{47}Ti/^{49}Ti\rangle = 6.5$ G, $a\langle ^{31}P\rangle = 20.0$ G, $a\langle ^1H\rangle = 0.5$ G.

Preparation of $Cp_2TiX_2PR_2$ (X = S, R = Me (10), R = Et (11), R = Ph (12), R = Cy (13); X = Se, R = Ph (14), R = Cy (15)). (i) From Cp_2TiCl_2. Upon standing in THF/hexane solution, the Ti(III) species **6–9** undergo complete conversion to **12–15**, respectively, within 24 h. The solvent was removed under reduced pressure, the residue extracted with hexane (5 × 10 mL portions), and the volume reduced to 5 mL. Upon cooling (−20 °C overnight), a very air-sensitive green solid precipitated and was isolated by filtration. Yields: **12**, 44 mg (25%); **13**, 55 mg (30%); **14**, 60 mg (30%); **15**, 70 mg (35%).

(ii) From $[Cp_2TiCl]_2$ and $LiXPR_2$. $[Cp_2TiCl]_2$ (300 mg) was added to 25 mL of THF containing 2 equiv of the appropriate $LiXPR_2$.[24] The solution was allowed to stir for 3 h and filtered and the solvent removed under reduced pressure. The residue was extracted with hexane (5 × 10 mL portions) and the volume reduced to 5 mL. When the solution was cooled to −20 °C, a green precipitate formed. The solid was isolated by filtration. Yields: **12**, 65 mg (15%); **13**, 110 mg (25%); **14**, 80 mg (15%); **15**, 110 mg (20%).

(iii) From $[Cp_2TiCl]_2$ and LiX_2PR_2. $[Cp_2TiCl]_2$ 300 mg in THF (10 mL) was added to a THF solution (15 mL) containing 2 equiv of the appropriate LiX_2PR_2 (X = S or Se; R = Ph or Cy). The solution was allowed to stir overnight and filtered and the solvent removed under reduced pressure. The residue was extracted with hexane (5 × 10 mL portions) and the volume reduced to 5 mL. When the solution was cooled to −20 °C, a green solid precipitated, which was isolated by filtration. Yields: **12**, 160 mg (45%); **13**, 220 mg (60%); **14**, 260 mg (70%); **15**, 270 mg (70%).

(iv) From $Cp_2Ti(CO)_2$. Photolysis of a THF solution (25 mL) containing 200 mg of $Cp_2Ti(CO)_2$ and 1 equiv of $(SPR_2)_2$ (R = Me, Et, Ph, Cy) or $HXPR_2$ (X = S, Se; R = Ph, Cy) gave rise to a green brown solution. Removal of the solvent under reduced pressure followed by several extractions of the residue with hexane (5 × 10 mL portions) gave an emerald green solution. The volume of this hexane extract was reduced to 5 mL and cooled to −10 °C overnight, yielding a green solid, which was isolated by filtration. Yields: **10**, 12 mg (8%); **11**, 17 mg (10%); **12**, 43 mg (20%); **13**, 55 mg (30%); **14**, 50 mg (20%); **15**, 65 mg (25%). **10**: $g = 1.980$, $a\langle ^{47}Ti/^{49}Ti\rangle = 11.3$ G, $a\langle ^{31}P\rangle = 43.2$ G. **11**: $g = 1.979$, $a\langle ^{47}Ti/^{49}Ti\rangle = 11.9$ G, $a\langle ^{31}P\rangle = 38.9$ G. **12**: UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 312 (3800), 358 (1900); $g = 1.978$, $a\langle ^{47}Ti/^{49}Ti\rangle = 10.8$ G, $a\langle ^{31}P\rangle = 41.3$ G. Anal. Calcd for $C_{22}H_{32}P_1S_2Ti$ (**13**): C, 60.12; H, 7.34. Found: C, 59.92; H, 7.42. **13**: UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 318 (3000), 370 (3100); $g = 1.981$, $a\langle ^{47}Ti/^{49}Ti\rangle = 10.8$ G, $a\langle ^{31}P\rangle = 37.6$ G. **14**: UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 310 (4200), 365 (1300); $g = 1.981$, $a\langle ^{47}Ti/^{49}Ti\rangle = 10.9$ G, $a\langle ^{31}P\rangle = 50.8$ G. **15**: UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 323 (2400), 375 (2300); $g = 1.980$, $a\langle ^{47}Ti/^{49}Ti\rangle = 10.8$ G, $a\langle ^{31}P\rangle = 44.8$ G.

Preparation of $[Cp_2MX]_2$ (M = Zr, X = S (16), X = Se (17); M = Hf, X = S (18), X = Se (19)). (i) From Cp_2MCl_2. To a THF solution (20 mL) of 300 mg of Cp_2MCl_2 were added 2 equiv of the appropriate $LiXPR_2$.[24] In the case where X = Se, products precipitate immediately. For X = S, stirring for 24–48 h results in the formation of the products. In all cases, the product was isolated by reduction of the volume to 5 mL, followed by filtration. Yields: **16**, 140 mg (50%); **17**, 280 mg (90%); **18**, 160 mg (60%); **19**, 290 mg (95%).

(ii) From $Cp_2M(SPR_2)_2$. $Cp_2M(PR_2)_2$ (600 mg) was added to THF solution containing either 1 equiv of **2–5** or 1 equiv of $LiXPR_2$. The solutions were allowed to stir overnight resulting in the slow formation of the crystalline products **16–19**. The products were isolated by filtration. Yields: **16**, 230 mg (90%); **17**, 280 mg (95%); 18, 270 mg (90%); **19**, 315 mg (95%). Anal. Calcd for $C_{20}H_{20}S_2Zr_2$ (**16**): C, 47.36; H, 3.79; S, 12.65. Found: C, 47.41; H, 4.12; S, 12.66. **16**: ^1H NMR (C_6D_6) δ 6.23 (s); UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 410 (3400), 602 (120). Anal. Calcd for $C_{20}H_{20}Se_2Zr_2$ (**17**): C, 39.99; H, 3.36. Found: C, 39.64; H, 3.39. **17**: ^1H NMR (C_6D_6) 6.19 (s). UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 452 (2400), 686 (150). Anal. Calcd for $C_{20}H_{20}S_2Hf$ (**18**): C, 35.25; H, 2.96. Found: C, 35.88; H, 2.72. **18**: ^1H NMR (C_6D_6) δ 6.31 (s); UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 374 (2400), 546 (60). Anal. Calcd for $C_{20}H_{20}Se_2Hf_2$ (**19**): C, 30.99; H, 2.60. Found: C, 30.97; H, 2.75. **19**: ^1H NMR (C_6D_6) δ 6.25 (s). UV–vis (THF; λ, nm (ϵ, M^{-1} cm^{-1})) 412 (1800), 636 (80).

X-ray Data Collection and Reduction. Purple and green crystals of **1** and **13**, respectively, were obtained by slow evaporation of a THF/hexane (50:50) solution of **1** after 14 days. Green crystals of **14** were obtained by vapor diffusion of *n*-hexane into a THF solution of **14**.

Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrix for each compound was obtained from 15 machine-centered reflections selected from rotation photographs. These data were used to determine the crystal systems. Partial rotation photographs around each axis were consistent with triclinic, orthorhombic, and monoclinic crystal systems for **1**, **13**, and **14**, respectively. Ultimately, 30 high-angle reflections (15° < 2θ < 30°) were used to obtain the final lattice parameters and the orientation matrices. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space groups $P\bar{1}$ for **1**, *Pbna* for **13**, and $P2_1/c$ for **14**. The $\pm h,\pm k,+l$ data were collected for **1** over the range 4.5° < 2θ < 35.0°; $+h,+k,+l$ data were collected for **13** and $\pm h,+k,+l$ data were collected for **14** both over the range 4.5° < 2θ < 40.0°. Three standard reflections, for each species, were recorded regularly throughout data collection. In each case, some decay was observed, **1** (5%), **13** (18%), and **14** (10%), and an appropriate decay correction was applied. The data were processed by using the SHELX-76 program package on the computing facilities at the University of Windsor. The total number of reflections with $F_o^2 > 3\sigma(F_o^2)$, for each compound, are listed in Table I. The absorption coefficients were small, and the crystals used were not anisotropic; therefore, no absorption corrections were applied to the data.

Structure Solutions and Refinements. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[49-51] Initial positions for the Ti, P, S, or Se atoms were obtained by direct methods (SHELX-76). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where the weight, *w*, is defined as $4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of refinement, the Ti, P, S, or Se atoms were assigned anisotropic temperature factors, while carbon atoms were described by isotropic thermal parameters. The phenyl ring geometries of **14** were constrained to that of regular hexagons with C–C bond distances of 1.39 Å. Hydrogen atom positions were allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the thermal parameter of the carbon atom to which they are bonded. In all cases, the hydrogen atom contributions were calculated,

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(49) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

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

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Table I. Crystallographic Parameters

	1	13	14
formula	$C_{34}H_{54}S_2P_2Ti$	$C_{22}H_{32}S_2PTi$	$C_{22}H_{32}Se_2PTi$
cryst color, form	purple blocks	green blocks	green blocks
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	*Pbna*	$P2_1/c$
a, Å	7.999 (2)	9.075 (3)	8.471 (3)
b, Å	13.102 (5)	34.052 (5)	29.868 (9)
c, Å	16.626 (6)	14.318 (5)	8.336 (3)
α, deg	96.71 (3)		
β, deg	101.43 (3)		104.47 (3)
γ, deg	91.14 (3)		
V, Å^3	1694 (1)	4424 (3)	2030 (1)
d, g cm^{-3}	1.25	1.32	1.74
Z	2	8	4
cryst dimens, mm	0.4 × 0.2 × 0.5	0.4 × 0.4 × 0.6	0.4 × 0.3 × 0.4
abs coeff, μ, cm^{-1}	4.40	5.93	20.32
radiatn λ, Å	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
temp, °C	24	24	24
scan speed, deg/min	2.0–5.0	2.0–5.0	2.0–5.0
scan range, deg	1.0 below Kα_1 1.1 above Kα_2	1.0 below Kα_1 1.0 above Kα_2	1.0 below Kα_1 1.1 above Kα_2
bkgd/scan time ratio	0.5	0.5	0.5
unique data	2259	2418	2515
data $F_o^2 > 3\sigma(F_o^2)$	1649	1204	1287
no. of variables	182	125	102
R	6.41	8.15	8.09
R_w	7.42	8.81	8.54
max Δ/σ in final cycle	0.001	0.001	0.001
largest residual electron density, e/Å^3	0.54	0.82	0.99
atom assoc with residual density	C44–C45	C8–C9–C10	Se2

but not refined. The final values of $R = \sum||F_o| - |F_c|/\sum|F_o||$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ for each species and the maximum Δ/σ on any of the parameters in the final cycles of refinement are given in Table I. Final difference Fourier map calculations showed no peaks of chemical significance. The magnitudes and locations of the largest residual peaks are described in Table I. The following data are tabulated: positional parameters (Table II), selected bond distances and angles (Table III). Thermal parameters (Table S1), hydrogen atom parameters (Table S2), bond distances and angles (Table S3), and values of $10|F_o|$ and $10|F_c|$ (Table S4) have been deposited as supplementary material.

Results and Discussion

Secondary phosphine sulfides react with alkyllithium reagents to generate the species, $Li(SPR_2)$.[24] These salts react rapidly with Ti, Zr, or Hf metallocene dichlorides in THF to give complexes of the form $Cp_2M(SPR_2)_2$ in reasonable yields. For M = Ti, this type of complex could only be isolated when R = Cy. This complex (1) is an intense purple color similar to that observed for complexes of the form $Cp_2Ti(SR)_2$,[1,6,7] suggesting that the phosphine sulfide moieties are bound to the Ti through sulfur (Chart I, d). This was confirmed by a crystallographic study of 1 (vide infra). The isolation of 1 from reaction mixtures must be performed quickly as decomposition via reduction occurs rapidly. Similar reductions occur so rapidly when R = Ph or when phosphine selenides are employed that isolation of analogues of the Ti(IV) species is not possible.

The nature of the Ti(III) products formed on reaction of Cp_2TiCl_2 with $SPPh_2H$ or phosphine selenides was investigated by EPR spectroscopy. In all cases, the reaction mixtures showed EPR signals with *g* values of ca. 1.99 and hyperfine coupling to ^{47}Ti and ^{49}Ti, typical of Ti(III) species. Values of the spectral parameters were obtained from computer simulations of the observed spectra. Couplings to a single phosphorus nucleus of approximately 20 G and to 10 equivalent protons of about 0.5 G were observed in these spectra (Figure 1). Similar hyperfine coupling to cyclopentadienyl ring protons has been observed for the Ti(III) hydrides $[Cp_2TiH_2]^-M^+$ where M = Na, MgBr, $AlCl_2$, or AlH_2.[52] The similarity of the $a\langle^{31}P\rangle$ values of these Ti(III) species to that observed for the Zr(III) species, $Cp_2Zr(CH_2PPh_2)$,[53] suggests formulation of the reduction products as "Cp_2TiXPR_2" (X = S, R = Ph (**6**), R = Cy (**7**); X = Se, R = Ph (**8**), R = Cy (**9**)). By analogy to the Zr(III) species, the structures of **6–9** are proposed to involve both S and P bonding to Ti(III) (Chart I, f) although this has not been confirmed, as these complexes are unstable. The formation of the complexes **6–9** presumably occurs via reductive elimination of $(XPR_2)_2$

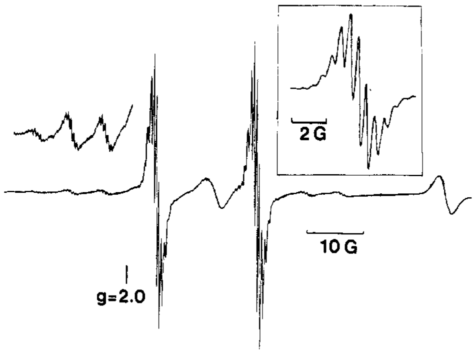

Figure 1. EPR spectrum of **9** in THF solution at 25 °C.

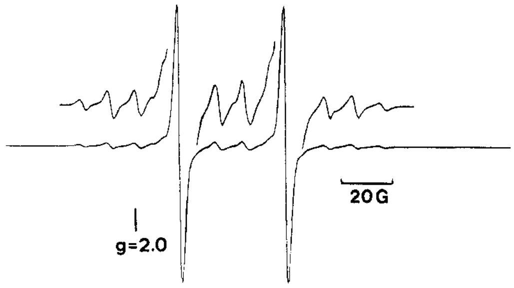

Figure 2. EPR spectrum of **12** in THF solution at 25 °C.

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[52] Kenworthy, J. G.; Myatt, J. *J. Chem. Soc. A* **1971**, 1020.

[53] Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1985**, *224*.

Table II. Positional Parameters[a]

atom	x	y	z	atom	x	y	z
Molecule 1							
Ti	−1027 (2)	4219 (1)	3060 (1)	S1	−1799 (3)	3240 (2)	1698 (2)
S2	1104 (3)	3112 (2)	3690 (2)	P1	−117 (4)	3396 (2)	888 (2)
P2	482 (4)	1800 (2)	4215 (2)	C1	−3568 (13)	4908 (9)	3362 (7)
C2	−2618 (13)	4626 (8)	4085 (7)	C3	−2518 (14)	3576 (9)	3996 (7)
C4	−3378 (14)	3206 (9)	3211 (7)	C5	−4045 (14)	4030 (8)	2824 (7)
C6	224 (13)	5859 (8)	3647 (7)	C7	1577 (13)	5263 (8)	3529 (7)
C8	1383 (13)	4967 (8)	2671 (6)	C9	−56 (13)	5433 (8)	2282 (7)
C10	−760 (13)	5974 (8)	2869 (6)	C11	−1625 (14)	3322 (8)	−117 (7)
C12	−2780 (15)	2368 (9)	−357 (8)	C13	−3947 (18)	2390 (9)	−1129 (9)
C14	−4908 (18)	3349 (9)	−1237 (10)	C15	−3814 (17)	4291 (11)	−999 (8)
C16	−2632 (15)	4291 (9)	−0147 (8)	C21	873 (14)	2135 (8)	841 (6)
C22	1829 (16)	2022 (10)	130 (8)	C23	2763 (18)	1011 (11)	127 (9)
C24	3957 (16)	940 (11)	945 (8)	C25	3050 (16)	1050 (10)	1641 (8)
C26	2064 (14)	2057 (9)	1654 (7)	C31	262 (13)	747 (7)	3359 (6)
C32	361 (15)	−300 (8)	3684 (7)	C33	121 (15)	−1174 (9)	2967 (7)
C34	−1554 (16)	−1117 (10)	2369 (8)	C35	−1696 (17)	−76 (9)	2061 (8)
C36	−1412 (14)	803 (9)	2752 (7)	C41	2617 (11)	1600 (7)	4822 (6)
C42	4066 (12)	1551 (8)	4360 (6)	C43	5766 (13)	1413 (8)	4916 (7)
C44	6166 (15)	2233 (9)	5664 (7)	C45	4755 (14)	2218 (9)	6143 (7)
C46	3005 (13)	2366 (8)	5595 (66)				
Molecule 13							
Ti	5792 (2)	5200 (3)	3645 (1)	S1	4015 (2)	4688 (4)	3625 (1)
P	4295 (3)	2574 (4)	3738 (1)	S2	5687 (3)	2343 (4)	3724 (1)
C1	5768 (12)	4700 (19)	2957 (5)	C2	5513 (12)	6117 (19)	2994 (5)
C3	6220 (11)	6870 (20)	3152 (5)	C4	6978 (13)	5963 (18)	3208 (5)
C5	6676 (10)	4585 (18)	3082 (4)	C6	5404 (13)	5858 (18)	4297 (5)
C7	6111 (11)	4990 (21)	4336 (5)	C8	6865 (13)	5574 (20)	4162 (5)
C9	6619 (13)	6901 (20)	4017 (5)	C10	5654 (13)	7145 (20)	4095 (5)
C11	3728 (9)	1387 (13)	3383 (4)	C12	3922 (9)	1803 (16)	2969 (4)
C13	3380 (11)	866 (16)	2669 (4)	C14	3592 (12)	−793 (18)	2741 (5)
C15	3438 (10)	−1223 (16)	3155 (4)	C16	3975 (9)	−284 (15)	3440 (5)
C21	3784 (11)	2025 (20)	4204 (5)	C22	2788 (10)	2418 (20)	4237 (5)
C23	2338 (16)	2022 (28)	4623 (7)	C24	2925 (18)	1814 (28)	4930 (7)
C25	3867 (14)	1264 (25)	4916 (7)	C26	4312 (18)	1908 (30)	4533 (8)
Molecule 14							
Ti	4892 (3)	8633 (1)	108 (3)	Se1	1600 (2)	8652 (1)	−26 (2)
Se2	4902 (2)	8631 (1)	3414 (2)	P	2360 (5)	8801 (1)	2580 (5)
C1	4190 (23)	7970 (6)	−1494 (24)	C2	5597 (27)	8106 (8)	−1751 (31)
C3	6810 (25)	8085 (7)	−329 (27)	C4	6117 (26)	7916 (7)	880 (29)
C5	4517 (22)	7853 (6)	177 (24)	C6	6920 (20)	9115 (6)	−502 (21)
C7	5557 (21)	9132 (6)	−1860 (25)	C8	4251 (20)	9323 (6)	−1378 (21)
C9	4770 (22)	9428 (6)	314 (25)	C10	6388 (23)	9313 (6)	788 (24)
C12	212 (14)	8692 (3)	4618 (15)	C13	−737 (14)	8437 (3)	5433 (15)
C14	−715 (14)	7968 (3)	5342 (15)	C15	247 (14)	7753 (3)	4437 (15)
C16	1192 (14)	8008 (3)	3622 (15)	C11	1175 (14)	8477 (3)	3713 (15)
C22	664 (12)	9609 (4)	1963 (12)	C23	359 (12)	10057 (4)	2280 (12)
C24	1378 (12)	10281 (4)	3615 (12)	C25	2701 (12)	10057 (4)	4633 (12)
C26	3005 (12)	9608 (4)	4316 (12)	C21	1987 (12)	9384 (4)	2981 (12)

[a] Multiplied by 10^4.

from the initially formed Ti(IV) species.

The unstable Ti(III) complexes **6**–**9** undergo conversions to other Ti(III) species over the 24 h period following initial observation of the EPR signals. The initial signals diminish and are replaced with a second set of resonances. The new species show EPR spectra with g values of ca. 1.98 and couplings to phosphorus of about 37–50 G (Figure 2). These compounds can be isolated from the reaction mixtures as dark green crystals; however, the yields are only 15–25%. On the basis of the EPR data, as well as elemental analyses, the complexes were formulated as $Cp_2Ti(X_2PR_2)$ (X = S, R = Ph (**12**), R = Cy (**13**); X = Se, R = Ph (**14**), R = Cy (**15**)). Crystallographic data for **13** and **14** confirm these formulations (vide infra). Hyperfine couplings to phosphorus of similar magnitude have been previously observed for Ti(III)[54] and V(IV)[26–33] complexes of dithiophosphates and -phosphinates. Extended Hückel molecular orbital calculations performed by Lorenz and Wasson[36] suggest that in spite of the Ti–P distance being 3.221 (5) Å, the large superhyperfine coupling occurs primarily via a through-space interaction of the metal d and the trans annular phosphorus s orbitals. The formation of these dithio- and diselenophosphinate complexes from **6**–**9** presumably occurs via abstraction of a chalcogen atom from any available source. The strain of the three-membered rings in **6**–**9** and the poor affinity of Ti for phosphorus donors may be factors that enhance the Lewis acidity of the Ti(III) atoms and thus account for the observed chalcogen atom abstraction reactions.

The complexes **12**–**15** can also be generated in several other ways. Photochemical reactions of $Cp_2Ti(CO)_2$ with $(SPR_2)_2$ or XPR_2H (X = S or Se) led to $Cp_2Ti(S_2PR_2)$ (R = Me (**10**); R = Et (**11**)) and **12**–**15**, although the yields from this route are also low (8–30%). The mechanisms of these photochemical processes are not known; however, the initial step is thought to involve replacement of the photolabilized CO by the phosphine chalcogenide yielding a Ti(II) intermediate. Intramolecular one-electron oxi-

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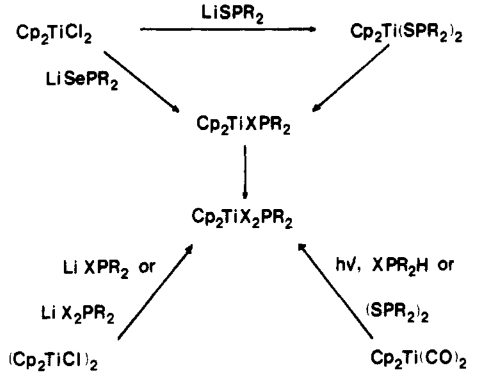
Table III. Selected Bond Distances and Angles

Molecule 1			
Distances, Å			
Ti–S1	2.420 (3)	Ti–S2	2.427 (3)
P1–S1	2.107 (4)	P2–S2	2.110 (3)
P1–C11	1.85 (1)	P1–C21	1.85 (1)
P2–C31	1.84 (1)	P2–C41	1.844 (9)
Ti–C1	2.36 (1)	Ti–C2	2.34 (1)
Ti–C3	2.36 (1)	Ti–C4	2.35 (1)
Ti–C5	2.37 (1)	Ti–C6	2.37 (1)
Ti–C7	2.41 (1)	Ti–C8	2.38 (1)
Ti–C9	2.37 (1)	Ti–C10	2.37 (1)
Angles, deg			
Ti–S1–P1	122.9 (1)	Ti–S2–P2	116.5 (2)
S1–P1–C11	101.3 (4)	S2–P2–C31	104.0 (3)
S1–P1–C21	102.6 (4)	S2–P2–C41	98.4 (3)
C11–P1–C21	103.2 (5)	C31–P2–C41	101.8 (4)
S1–Ti–S2	98.5 (1)		
Molecule 13			
Distance, Å			
Ti–S1	2.586 (4)	Ti–S2	2.611 (5)
P–S1	1.997 (5)	P–S2	2.005 (5)
P–C11	1.81 (1)	P–C21	1.82 (2)
Ti–C1	2.39 (2)	Ti–C2	2.40 (2)
Ti–C3	2.34 (2)	Ti–C4	2.36 (2)
Ti–C5	2.36 (2)	Ti–C6	2.37 (2)
Ti–C7	2.41 (2)	Ti–C8	2.36 (2)
Ti–C9	2.32 (2)	Ti–C10	2.35 (2)
Ti···P	3.221 (5)		
Angles, deg			
S1–Ti–S2	78.0 (1)	S1–P–S2	107.2 (2)
Ti–S1–P	88.3 (2)	Ti–S2–P	87.5 (2)
S1–P–C11	110.8 (4)	S2–P–C11	111.6 (5)
S1–P–C21	110.5 (6)	S2–P–C21	113.1 (6)
C11–P–C21	103.8 (7)		
Molecule 14			
Distances, Å			
Ti–Se1	2.764 (3)	Ti–Se2	2.754 (3)
Se1–P	2.151 (4)	Se2–P	2.151 (4)
Ti–C1	2.37 (2)	Ti–C2	2.38 (2)
Ti–C3	2.39 (2)	Ti–C4	2.39 (2)
Ti–C5	2.34 (2)	Ti–C6	2.39 (2)
Ti–C7	2.38 (2)	Ti–C8	2.38 (2)
Ti–C9	2.37 (2)	Ti–C10	2.38 (2)
P–C11	1.82 (1)	P–C21	1.81 (1)
Ti···P	3.361 (4)		
Angles, deg			
Se1–Ti–Se2	78.0 (1)	Se1–P–Se2	107.5 (2)
Ti–Se1–P	85.3 (2)	Ti–Se2–P	85.6 (1)
Se1–P–C11	110.6 (4)	Se2–P–C11	110.3 (4)
Se1–P–C21	111.2 (4)	Se2–P–C21	111.9 (4)
C11–P–C21	105.4 (4)		

dation of these Ti(II) species with concomitant loss of ·PR_2 would then give the observed products. Compounds **12–15** can also be prepared by reaction of $[Cp_2TiCl]_2$ with $LiXPR_2$. Although **6–9** are expected to be formed in the initial step, these species are not observed during these reactions. The rapid formation of **12–15** suggests that abstraction of a chalcogen atom from $LiXPR_2$ is facile. A direct route to **12–15** involves reaction of $[Cp_2TiCl]_2$ with LiX_2PR_2. This route, which presumably proceeds by a simple nucleophilic substitution mechanism, offers the highest yields. The reactions involving Ti complexes are summarized in Scheme I.

Scheme I. General Reaction Scheme for the Ti Complexes of Phosphine Sulfides or Selenides



Reactions of $LiSPR_2$ with Cp_2MCl_2, where M = Zr or Hf, yield complexes of the form $Cp_2M(SPR_2)_2$ (M = Zr, R = Ph (**2**), R = Cy (**3**); M = Hf, R = Ph (**4**), R = Cy (**5**)). The ^1H NMR and $^{31}P\{^1H\}$ NMR data suggest that these Zr and Hf complexes are structurally similar to **1**. Complexes **2–5** can also be generated by reaction of $Cp_2M(PR_2)_2$ with elemental sulfur. Alternatively, **2–5** can be prepared by reaction of $Cp_2M(PR_2)_2$ with SPR_2H. The susceptibility of the diphosphide complexes to substitution by other protic reagents has been previously reported.[46] In this case, the reaction was monitored by $^{31}P\{^1H\}$ NMR. Replacement of both phosphides by the SPR_2 moieties occurs rapidly with liberation of PR_2H. No evidence was found for an intermediate monosubstitution product (i.e., $Cp_2M(PR_2)(SPR_2)$). The reactions of $Cp_2Zr(PR_2)_2$ with SPR'_2H gave exclusively $Cp_2Zr(SPR'_2)_2$, thus confirming that the reaction does not proceed by sulfur atom transfer but rather through a substitution mechanism. On standing for 24–48 h in solution, complexes **2–5** convert to $[Cp_2MS]_2$ (M = Zr (**16**); M = Hf (**18**)) and SPR_2PR_2 is eliminated. The observation of $SPCy_2PPh_2$, as a major byproduct from the conversion of a solution containing **2** and **3** to **16**, suggests a bimolecular process. The complexes **16** and **18** were formulated on the basis of ^1H NMR and elemental analyses. In addition, the formulation of **16** was confirmed by crystallographic data.[55] During the course of this work, Bottomley et al. structurally characterized **16**, which was prepared by photolysis of $Cp_2Zr(CO)_2$ in the presence of S_8[56]. **16** or **18** are rapidly formed by reaction of **2–5** with $Cp_2M(PR'_2)_2$. In these reactions, $PR_2PR'_2$ is the only byproduct. This suggests that formation of **16** or **18**, via this route, also proceeds through a bimolecular process.

Attempts to prepare the Se analogues of **2–5**, via reaction of Cp_2MCl_2 with $LiSePR_2$, yielded only the complexes $[Cp_2MSe]_2$ (M = Zr (**17**); M = Hf (**19**)). Similarly, the reactions of $Cp_2M(PR_2)_2$ with either $SePR_2H$ or elemental Se yielded **17** or **19**. These Se-bridged dimers[57] and the Zr–Te[58] analogues have been previously prepared and reported. The reactions involving Zr or Hf complexes are summarized in Scheme II.

Structure Descriptions. An X-ray crystallographic study of **1** revealed that the crystals are made up of triclinic unit cells each containing two discrete molecules. The closest approach between molecules is 2.255 Å (H43B···H43B). Selected bond distances and angles are given in Table III. An ORTEP drawing of **1** is shown in Figure 3. The Ti coordination sphere is comprised of two cyclo-

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(55) Blue crystals of **16** were obtained by recrystallization from THF. The crystal system is monoclinic of the space group $P2_1/n$ with $a = 13.681$ (2) Å, $b = 8.267$ (1) Å, $c = 8.417$ (4) Å, $\beta = 94.68$ (1)°, $V = 948.6$ (2) Å^3, and $Z = 2$. A total of 1420 data with $F_o^2 > 3\sigma(F_o^2)$ were used to refine the 109 variables to $R = 0.0260$ and $R_w = 0.0375$. The results of this study are not statistically different from those reported by Bottomley et al.,[56] and thus no further details are reported here.

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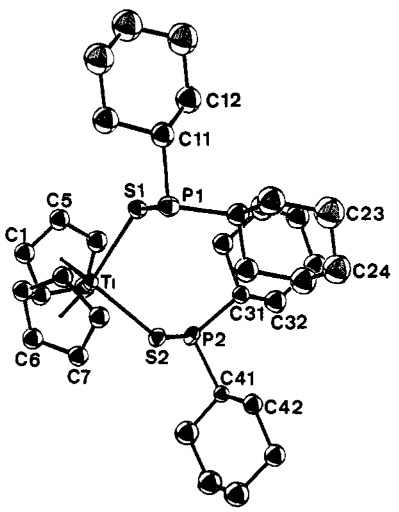


Figure 3. ORTEP drawing of 1. 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.

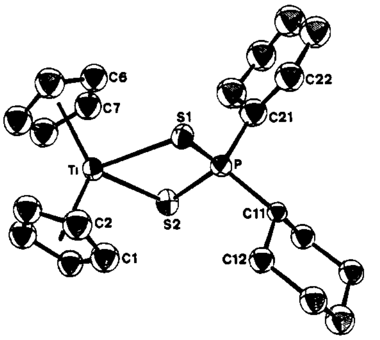


Figure 4. ORTEP drawing of 13. 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.

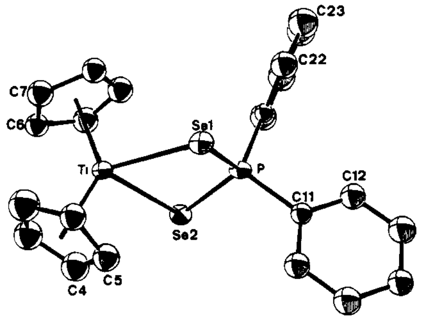
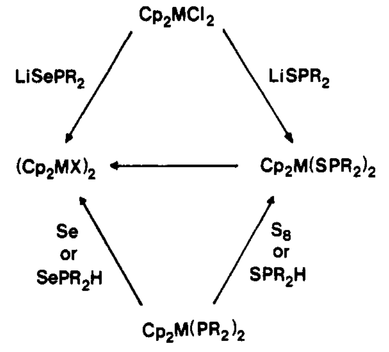


Figure 5. ORTEP drawing of 14. 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.

Scheme II. General Reaction Scheme for the Zr and Hf Complexes of Phosphine Sulfides or Selenides



pentadienyl groups and two sulfur-bound SPR_2 moieties. The geometry about the Ti atom is pseudotetrahedral with typical Ti–C distances.[1,6,7,34,41] The average Ti–S bond length is 2.423 (3) Å, which is similar to that found in $Cp^*{}_2Ti(SH)_2$.[41] The Ti–S distance is slightly longer than the average Ti–S bond distances of 2.381 (6) Å found in the thiolato complex[7] $Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2$ (**20**). This can be attributed to the greater electron-withdrawing ability of the phosphido group in **1** vs. that of the alkyl substituent in **20**. The S–P bond lengths average 2.108 (4) Å and are typical of those found in phosphine sulfide complexes.[13,17]

X-ray data for **13** shows that the crystals are comprised of orthorhombic unit cells that contain eight distinct, symmetry-related molecules. The closest approach between molecules is 2.449 Å (H4···H5). The coordination sphere of the Ti atom consists of two Cp rings as well as the two sulfur atoms of the bound dicyclohexyldithiophosphinate group (Table III, Figure 4). The Ti–C bond lengths average 2.36 (3) Å, similar to that seen in the Ti(IV) complex **1**. The Ti–S bond lengths are 2.611 (5) and 2.586 (4) Å, which are substantially longer than those found in **1** or in the Ti(IV) dithiophosphinate complex $TiCl_2(S_2PEt_2)_2$ (**21**).[37] This is consistent with both the change in oxidation state of Ti and the delocalized donor nature of the dithiophosphinate ligand. The S–Ti–S angle of 76.6 (1)°, which is considerably smaller than the S–Ti–S angle of 98.5 (1)° found in **1**, is a result of the symmetrical four-membered ring formed by coordination of the dithiophosphinate ligand to Ti. The larger bite angle of 79.9 (1)° found in **21**[37] is attributed to the trans influence present in that pseudooctahedral species. The Ti–S–P angles 87.5 (2)° and 88.3 (2)° and the pseudotetrahedral geometry about P are typical of dithiophosphinate chelation.[37] The shorter S–P bond lengths found in **13** (av 2.001 (5) Å) compared to those found in **1** (av 2.109 (4) Å) are consistent with the delocalized P–S multiple-bond character expected in the dithiophosphate ligand.

A crystallographic study of **14** shows that crystals are made up of monoclinic units cells that contain four discrete molecules. The closest approach between molecules is 2.243 Å (H12···H24). The structure of **13** is similar to that of **14** (Table III, Figure 5). The Ti atom is bound to two Cp rings and the two Se atoms of the diselenophosphinate.

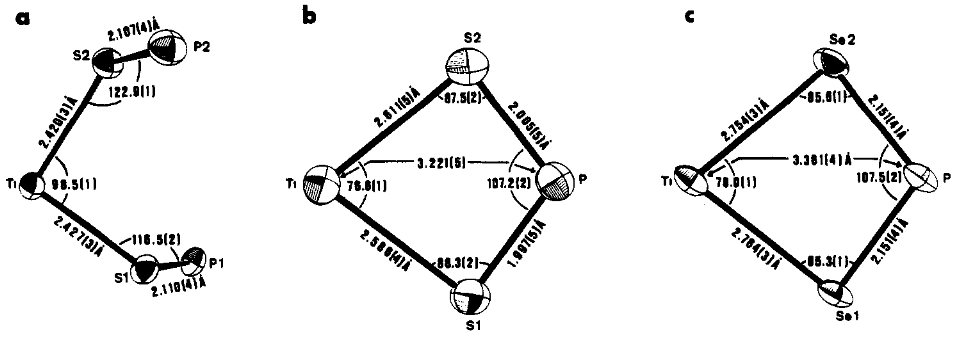


Figure 6. The core geometries of molecules (a) **1**, (b) **13**, and (c) **14**.

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Ti-Se distances average 2.759 (3) Å, while the P-Se are identical at 2.151 (4) Å. The bite angle (i.e., Se1-Ti-Se2) is slightly greater than the analogous S1-Ti-S2 angle found in **13**, while the Ti-Se-P angles (average 85.4 (1)°) is approximately three degrees smaller than the corresponding Ti-S-P angles. A comparison of the core structures of **1**, **13**, and **14** is illustrated in Figure 6.

Summary. Herein, we have described reactions of phosphine sulfides and selenides with Ti, Zr, and Hf metallocene dihalides. The chemistry of the titanium complexes is directed by the ease of reduction of Ti(IV) to Ti(III). In contrast, no corresponding redox chemistry was observed for Zr or Hf complexes. These observations are typical of the chemistry of group 4.

The utility of the chemistry described herein for the synthesis of heterobimetallic complexes is the subject of current studies. In particular, we have found that complexes **1-5** are capable of acting as metalloligands, chelating to late transition metals forming early-late heterobimetallic species. This chemistry will be the subject of a future publication.

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Supplementary Material Available: Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and bond distances and angles associated with cyclopentadienyl, cyclohexyl, and phenyl rings (Table S3) (10 pages); values of $10|F_o|$ and $10|F_c|$ (Table S4) (17 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of a Neutral Tungsten(0) Alkyl Complex. Insertion of CO_2 into the W-CH_3 Bond of *trans,trans*-$W(CH_3)(CO)_2(NO)(PPh_3)_2$ and the Structural Characterization of *trans*-$W(\eta^2\text{-}O_2CCH_3)(CO)(NO)(PPh_3)_2$

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Reaction of *trans,trans*-$WCl(CO)_2(NO)(PPh_3)_2$ (**1**) with CH_3Li or $(CH_3)_2Zn$ affords *trans,trans*-$W(CH_3)(CO)_2(NO)(PPh_3)_2$ (**2**) in good yields. Treatment of **2** with DCl gives **1** and CH_3D quantitatively. Reaction of **2** with carbon monoxide (2 atm, 80 °C) results in a reversible substitution of CO for PPh_3 to give *mer*-$W(CH_3)(CO)_3(NO)(PPh_3)$ (**3**). Carbon dioxide undergoes a 1,2-insertion reaction with **2** to give the monodentate acetate complex *trans,trans*-$W[\eta^1\text{-}OC(O)CH_3](CO)_2(NO)(PPh_3)_2$ (**4**), which reversibly loses CO on heating to yield the bidentate acetate derivative *trans*-$W(\eta^2\text{-}O_2CCH_3)(CO)(NO)(PPh_3)_2$ (**5**). Monoclinic prisms of **5** were grown from a dichloromethane/benzene solution and crystallized in space group $P2_1/a$ with $Z = 4$, $a = 20.864$ (5) Å, $b = 9.729$ (2) Å, $c = 17.504$ (4) Å, and $\beta = 103.21$ (1)°. An X-ray diffraction study at -91 ± 3 °C showed that the acetate ligand is bound in an asymmetric fashion to the tungsten center and that the nitrosyl and carbonyl ligands are *not* substantially disordered. Salient metrical parameters of the structure include the following: W(1)-O(4) = 2.249 (5) Å, W(1)-O(5) = 2.217 (5) Å, O(4)-C(6) = 1.270 (10) Å, O(5)-C(6) = 1.302 (10) Å, W(1)-C(8) = 1.914 (8) Å, C(8)-O(9) = 1.171 (9) Å, W(1)-N(10) = 1.836 (7) Å, N(10)-O(11) = 1.203 (9) Å, and W(1)-N(10)-O(11) = 178.3 (6)°. The least-squares refinement converged to $R(F) = 0.036$ and $R_w(F) = 0.036$ for 3518 unique data with $F > 3\sigma(F)$.

Introduction

Insertion reactions of small molecules into transition-metal-carbon σ-bonds are key features in a variety of important stoichiometric and catalytic chemical processes. As a result, considerable research attention has been focused on the elucidation of the scope and the mechanistic details of the insertions of CO, CO_2, CS_2, C_2H_4, SO_2, etc. into M-R bonds.[1] Several simple metal systems have yielded valuable information in this regard, such as the classic studies of CO migratory insertion into the alkyl bond of $Mn(CO)_5R$,[2] as well as the more recent investigations of the insertions of CO and CO_2 into the tungsten-alkyl bond of $[W(CO)_5R^-]$ and $[W(CO)_4(PR_3)R^-]$.[3] Indeed, it has been sugggested by Darensbourg et al. that the group 6 metal anionic carbonyl aryl and alkyl complexes of the type $[M(CO)_5R^-]$ (M = Cr, W) might prove

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