linearly with time and X-ray exposure to about 64% of the original intensity. Each of the standards behaved in a similar manner, and the stability constant estimates were 0.013, 0.011, and 0.011, indicating that the decline was at least a steady effect. The intensities were corrected with the Lorentz and polarization factors.

Absorption corrections were applied with the use of numerical integration over an (8 × 8 × 8) Gaussian grid. The crystal had 12 well-formed faces, and the shape is given by the following indices and perpendicular distances (in parentheses) in millimeters from an internal origin: 1,1,1 (0.244); –1,–1,–1 (0.152); –1,1,1 (0.195); 1,–1,–1 (0.141); 1,–1,1 (0.211); –1,1,–1 (0.170); 1,1,–1 (0.098); –1,–1,1 (0.177); 0,1,0 (0.175); 0,–1,0 (0.118); 1,0,0 (0.203); –1,0,0 (0.216). The indexing and measurements were done on the diffractometer, and the crystal orientation was given to the program in the form of the diffractometer matrix. The absorption coefficient was 47.5 cm^{-1}, and the corrections were in the range 0.296–0.348.

(C) Crystal Structure Solution and Refinement. The structure was solved by the use of the Patterson function and heavy-atom method. The atomic scattering factors for uncharged atoms were used.[40] The programs used were supplied by Penfold[41] and are based on ORFLS, FORDAP, ORFFE, and ORTEP. The structure was refined by the method of least squares minimizing $\sum w(|F_o| - |F_c|)^2$. A weighting scheme was devised in the final stages of the refinement: $w = (A + Bx + Cx^2 + Dx^3)^{-1}$ where $x = |F_o|$ and $A = 41.388$, $B = -0.53721$, $C = 0.38642 \times 10^{-2}$, and $D = -0.40782 \times 10^{-5}$. This weighting scheme gives a reasonably constant mean value of $w\Delta^2$ when the reflections are analyzed in batches according to the amplitudes of the structure factors. Because of program size limitations, the refinement was done by alternately refining two large blocks of parameters chosen according to chemical grouping and with the six heavy atoms always included. Convergence was reached, and the estimated standard deviations of the anisotropic temperature parameters were obtained. The standard deviations of the bond lengths and angles were then obtained from the inverted matrix of a final cycle including all the fractional coordinate variables. The lithium atom was easily located in difference maps, although the evidence for its identity rests mainly upon the chemical preparation and subsequent analysis of the compound. The final discrepancy indices were $R = 0.100$ and $R_w = 0.109$. There were 2123 observations and 331 variables in the model and $(\sum w\Delta^2/(N_{obsd} - N_{var}))^{1/2} = 2.14$.

We were not able to refine the structure further owing to a difficulty in precisely locating the carbon atoms of the triethylphosphine ligand. This ligand is either in disorder or in high thermal motion, and we finally chose to contour the difference map based on structure factors calculated for all atoms except the six carbons of the triethylphosphine ligand. These were then positioned with the use reasonable torsion angles, molecular models, and our previous experience of the most likely conformation for PEt_3 in square-planar complexes.

Notwithstanding the uncertainty in the PEt_3 ligand, the final difference map has a maximum of 2.11 e Å^{-3} and a minimum of –1.25 e Å^{-3}, and we are confident that the structure is not significantly in error. The fractional atomic coordinates are given in Table V, and tables of structure factors, anisotropic temperature parameters, and intermolecular distances have been deposited.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada and the University of Victoria for research grants and Mrs. K. Beveridge for technical assistance in the crystal structure determination.

Registry No. **5** (R′ = Et, R = Ph, M = Pt), 78610-29-4; **5** (R′ = *n*-Bu, R = Ph, M = Pt), 78610-30-7; **5** (R′ = Et, R = OEt, M = Pt), 78610-31-8; **5** (R = *n*-Bu, R = OEt, M = Pt), 78610-32-9; **5** (R′ = Ph, R = OEt, M = Pt), 78610-33-0; **5** (R′ = Et, R = Ph, M = Pd), 78610-34-1; **6** (R′ = Et, R = Ph, M = Pd), 78610-35-2; **6** (R′ = *n*-Bu, R = OEt, M = Pt), 78610-36-3; $[Pt(PEt_3)_2(acac)][BF_4]$, 78610-38-5; $(EtO)_2P(O)CH_2P(O)(OEt)_2$, 1660-94-2; $Ph_2P(O)CH_2P(O)Ph_2$, 2071-21-8; $Pt_2Cl_4(P(n\text{-}Bu)_3)_2$, 15670-38-9; $Pt_2Cl_4(PEt_3)_2$, 15692-96-3; $Pd_2Cl_4(PEt_3)_2$, 15684-59-0; $Pt_2Cl_4(PPh_3)_2$, 15349-80-1; $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$, 19394-82-2; $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$, 22180-55-8; *cis*-$[PtCl_2(PEt_3)_2]$, 15692-07-6; $PtCl_2(PEt_3)(CH(PPh_2O)_2Na)$, 78610-39-6; $PtCl_2(P\text{-}n\text{-}Bu_3)(CH(PPh_2O)_2Na)$, 78610-40-9; $PtCl_2(PEt_3)(CH(P(OEt)_2O)_2Na)$, 78610-41-0.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (Table S1), intermolecular distances (Table S2), and anisotropic temperature parameters (Table S3) (10 pages). Ordering information is given on any current masthead page.

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Magnesium Butadiene as a Reagent for the Preparation of Transition-Metal Butadiene Complexes: Molecular Structure of Bis(η-butadiene)[1,2-bis(dimethylphosphino)ethane]hafnium

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The conveniently prepared reagent $Mg(C_4H_6)\cdot 2THF$ reacts readily with transition-metal halides, forming butadiene complexes. Thus $Hf(\eta\text{-}C_4H_6)_2(dmpe)$, $Ti(\eta\text{-}C_4H_6)_2(depe)$, $Ti(\eta\text{-}C_4H_6)_2[(MeO)_2PC_2H_4P(OMe)_2]$, $Ti(\eta\text{-}C_4H_6)_2(diphos)$, and $Zr(\eta\text{-}C_4H_6)_2(dmpe)$ are formed when MCl_4 (M = Ti, Zr, Hf) and the appropriate bidentate phosphine (dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, diphos = 1,2-bis(diphenylphosphino)ethane) are treated with $Mg(C_4H_6)\cdot 2THF$. Similarly, $NbCl_4(dmpe)_2$, WCl_6, and $FeCl_2$ or $FeCl_3$ adducts of trimethylphosphine react with the reagent, affording $NbCl(C_4H_6)(dmpe)_2$, $W(\eta\text{-}C_4H_6)_3$, and $Fe(\eta\text{-}C_4H_6)(PMe_3)_3$, respectively. $Ti(C_4H_6)_2(diphos)$ polymerizes ethylene. $Hf(\eta\text{-}C_4H_6)_2(dmpe)$ is triclinic, space group $P\bar{1}$, with $a = 13.274$ (2) Å, $b = 14.952$ (2) Å, $c = 9.319$ (1) Å, $\alpha = 97.14$ (1)°, $\beta = 101.82$ (1)°, $\gamma = 109.76$ (1)°, $Z = 4$, and ρ(calcd) = 1.742 g cm^{-3}. The complex has no crystallographically imposed symmetry but has a structure based on a distorted C_2 octahedral geometry. The $Zr\text{–}C_4H_6$ arrangement is η^4 but distorted toward a 1,4-η^2-C_4H_6 structure, reflecting substantial π interaction.

Transition-metal butadiene complexes are generally prepared by reducing a metal halide or halo complex in the presence of butadiene, by thermal or photolytic ligand displacements, or by metal atom evaporation techniques. All of these methods, although quite useful, have limitations; more general methods would be helpful, especially for the preparation of thermally unstable complexes on a moderate scale. Magnesium is known to react with butadiene in THF under

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controlled conditions to form $[Mg(C_4H_6)\cdot 2THF]_n$ (**1**), a reagent that functions as a source of the butadiene dianion.[1] For example, **1** reacts with $(\eta\text{-}C_8H_8)MCl_2$ (M = Hf, Zr, Ti)[2] and $(C_5H_5)_2ZrCl_2$,[3] forming $(\eta\text{-}C_8H_8)M(C_4H_6)$ and $(C_5H_5)_2Zr(C_4H_6)$, respectively. We find this to be a conveniently prepared, readily available reagent of general utility for butadiene complex preparation. Herein, we report the reaction of **1** with a variety of metal–halo complexes, affording butadiene complexes that are difficult to prepare or inaccessible by more standard procedures.

This technique has, for example, allowed the preparation of a wide range of derivatives of the type $M(\eta\text{-}C_4H_6)_2L_2$ (M = Ti, Zr, Hf). A limited number of compounds of this stoichiometry have been prepared by reductive methods[4] and are of general interest because they are among the few examples of zerovalent group 4 organometallics, they catalyze the oligomerization of olefins,[5] and they function as precursors to novel group 4 phosphine carbonyl complexes.[6] Accordingly, the details of the syntheses of these compounds from **1**, factors affecting their stability, and some aspects of their chemistry and structural features are presented.

Experimental Section

All manipulations were performed under an atmosphere of prepurified nitrogen. Solvents were distilled from sodium benzophenone ketyl. 1,2-Bis(dimethylphosphino)ethane (dmpe),[7] 1,2-bis(dimethoxyphosphino)ethane,[8] 1,2-bis(diethylphosphino)ethane (depe),[9] and $NbCl_4(dmpe)_2$[10] were prepared by literature methods. All other materials were from standard sources. ^1H NMR (90 MHz) and ^{31}P NMR (29.9 MHz) were obtained on EM-390 and FT-80 spectrometers, respectively. Elemental analyses and mass spectra were performed by the Central Research Analytical Division.

$Mg(C_4H_6)\cdot 2THF$ (1). A 1-L flask was charged with 24.4 g of Mg chips (Alfa, resublimed), 400 mL of THF, and 1.2 mL of iodobenzene. The flask was fitted with a stopcock, cooled to −196 °C, and evacuated. Butadiene (0.50 mol), dried by passage through a tube packed with P_2O_5, was condensed into the vessel, which was then sealed. After being warmed to room temperature and shaken for 2 days, the flask contained pale yellow, solid **1** and Mg suspended in THF. The slurry of **1** was decanted from the excess Mg. After filtration, washing with THF, and drying in vacuo, 19.5 g (88 mmol, 18%) of **1** was obtained.

To the recovered Mg chips was added an additional 10 g of Mg, and the mixture was reused in an identical reaction; 87.1 g of **1** (392 mmol, 78%) was obtained.

$Hf(\eta\text{-}C_4H_6)_2(dmpe)$ (2). To a suspension of 3.6 g of $Mg(C_4H_6)\cdot 2THF$ (16.2 mmol) in 75 mL of THF was added a mixture of 2.58 g of $HfCl_4$ (8.05 mmol) and 1.21 g of dmpe (8.05 mmol) in 50 ml of THF in several small portions. The resulting orange solution was heated to boiling, treated with 5 mL of dioxane, and allowed to cool while stirring. After 2 h, the solution was filtered and evaporated to dryness, affording an orange residue, which was extracted with 2 × 100 mL of boiling hexane. After filtration, the pooled extracts were concentrated to 100 mL and allowed to cool. The resulting red crystals of **2** were collected by filtration, washed with hexane, and dried in vacuo (1.15 g, 2.63 mmol, 33%).[8] Concentration of the supernatant gave a smaller second crop (0.65 g, 1.49 mmol, 19%): ^{31}P NMR (benzene-d_6) 9.40 ppm; ^1H NMR (benzene-d_6) τ 4.43 (m, 4 H, $\text{-}CH{=}CH_2$), 8.70 (m, 4 H, $C{=}CHH$), 8.75 (d, 4 H, $CH_2{-}P$), 9.10 (t, 12 H, $P{-}CH_3$), 9.28 (m, 4 H, $C{=}CHH$); mass spectrum, *m/e* 438 $[^{12}C_{14}{}^1H_{28}{}^{180}Hf^{31}P_2]^+$. Anal. Calcd for $C_{14}H_{28}HfP_2$: C, 38.49; H, 6.46. Found: C, 37.96; H, 6.44.

$Ti(\eta\text{-}C_4H_6)_2(depe)$ (3). A solution of 3.0 g of $TiCl_4\cdot 2THF$ (9 mmol) in 50 mL of THF was treated with 1.86 g of depe (9 mmol). To the resulting orange solution was added 4.00 g of $Mg(C_4H_6)\cdot 2THF$ (18 mmol) in small portions. After the exothermic reaction had subsided, the green mixture was stirred for 30 min, treated with 5 mL of dioxane, and filtered. Evaporation of the solvent, extraction of the residue with 2 × 75 mL of boiling hexane, and concentration and cooling afforded 1.70 g (4.69 mmol, 52%) of deep blue crystals of 3: ^{31}P NMR (benzene-d_6) 46.92 ppm; ^1H NMR (benzene-d_6) τ 4.41 (m, 4 H, $\text{-}CH{=}CH_2$), 8.33 (m, 4 H, $C{=}CHH$), 8.8–8.3 (m, 12 H, PCH_2), 9.22 (m, 12 H, CH_2CH_3), 9.79 (m, 4 H, $C{=}CHH$); mass spectrum, *m/e* 362 $[^{12}C_{18}{}^1H_{36}{}^{31}P_2{}^{48}Ti]^+$. Anal. Calcd for $C_{18}H_{36}P_2Ti$: C, 59.67; H, 10.02. Found: C, 57.23; H, 9.76.

$Ti(\eta\text{-}C_4H_6)_2[(MeO)_2PC_2H_4P(OMe)_2]$ (4). In a similar manner, 2.29 g of $TiCl_4\cdot 2THF$ (6.87 mmol) and 1.47 g of $(MeO)_2PC_2H_4P(OMe)_2$ (6.87 mmol) were reacted with 3.05 g of $Mg(C_4H_6)\cdot 2THF$ in 100 mL of THF, affording after recrystallization from hexane 0.240 g of **4** (0.65 mmol, 9%): ^1H NMR (benzene-d_6) τ 4.62 (m, 4 H, $\text{-}CH{=}CH_2$), 7.03 (t, 12 H, $CH_3{-}O$), 8.03 (m, 4 H, $C{=}CHH$), 8.06 (d, 4 H, $P{-}CH_2$), 9.71 (m, 4 H, $C{=}CHH$); mass spectrum, *m/e* 370.0900 $[^{12}C_{14}{}^1H_{28}{}^{16}O_4{}^{31}P_2{}^{48}Ti]^+$ (370.0941 calcd). Anal. Calcd for $C_{14}H_{28}O_4P_2Ti$: C, 45.42; H, 7.62. Found: C, 45.52; H, 7.53.

$Ti(\eta\text{-}C_4H_6)_2(diphos)$ (5). In an identical manner, 3.0 g (9 mmol) of $TiCl_4\cdot 2THF$ and 3.58 g of diphos in 50 mL of THF were treated with 4.0 g of $Mg(C_4H_6)\cdot 2THF$ (18 mmol). After two recrystallizations from hot (70 °C) toluene, 1.53 g of green crystals of a mixture of **5** and diphos were obtained; further recrystallizations did not separate the excess ligand. Integration of the ^{31}P and ^1H NMR spectra indicated the mixture contained 20 mol % of **5**: ^1H NMR (benzene-d_6) τ 3.0 (m, $P{-}C_6H_5$), 4.17 (m, $\text{-}CH{-}CH_2$), 7.05 (m, $CH{=}CHH$), 7.99 (m, $\text{-}CH{=}CHH$), 7.83 (d, $P{-}CH_2$); ^{31}P NMR (benzene-d_6) 65.26 ppm.

$Zr(\eta\text{-}C_4H_6)_2(dmpe)$ (6). Similarly, 6.37 g of $ZrCl_4\cdot 2THF$ (16.9 mmol), 2.53 g of dmpe (16.9 mmol), and 7.5 g of $Mg(C_4H_6)\cdot 2THF$ (33.8 mmol) in 100 mL of THF gave 4.34 g of a mixture of $Zr(\eta\text{-}C_4H_6)_2(dmpe)$ (65%) and $[Zr(\eta\text{-}C_4H_6)dmpe]_2(dmpe)$[4] (35%) (composition determined by ^1H NMR) after recrystallization from hexane.

$NbCl(\eta\text{-}C_4H_6)(dmpe)_2$ (7). To a solution of 5.99 g of $NbCl_4(dmpe)_2$ (11.2 mmol) in 100 mL of THF at 0 °C was added dropwise a slurry of 5.00 g of $Mg(C_4H_6)\cdot 2THF$ (22.5 mmol) in 75 mL of THF. The resulting orange solution was heated briefly to boiling, treated with 5 mL of dioxane, and allowed to cool to room temperature. Activated charcoal was added to the mixture, and it was filtered through a 3-cm layer of alumina on a Celite pad. After evaporation of the solvent, the residue was extracted with 2 × 75 mL of boiling hexane. The pooled extracts were filtered, concentrated at the boiling point to 30 mL, and cooled to −20 °C. The resulting orange crystals of 7 were collected by filtration, washed with cold hexane, and dried in vacuo: yield 1.21 g (2.70 mmol, 24%); ^{31}P NMR (benzene-d_6) broad single line at 30 °C, 27.0 ppm; ^1H NMR (benzene-d_6) τ 6.47 (m, 2 H, $\text{-}HC{=}CH_2$), 8.63 (br, 12 H, $P{-}CH_3$), 9.02 (br, 12 H, $P{-}CH_3$), other butadiene resonances are broad and overlapped with the $\mathbf{P{-}CH_2}$ signals in the region 8–9. Anal. Calcd for $C_{16}H_{38}ClNbP_4$: C, 39.75; H, 7.92; P, 25.62. Found: C, 39.79; H, 7.94; P, 24.48.

$Fe(\eta\text{-}C_4H_6)(PMe_3)_3$ (8). Similarly, 2.85 g of $FeCl_2$ (22.5 mmol) and 5.13 g of PMe_3 (67.5 mmol) in 50 mL of THF were treated with 5.00 g of $Mg(C_4H_6)\cdot 2THF$ (22.5 mmol), and the mixture was stirred overnight. After addition of 5 mL of dioxane and filtration, the solution was evaporated to dryness and the residue recrystallized from hexane, yielding 5.16 g (15.3 mmol, 68%) of yellow, crystalline **8**: mass spectrum, *m/e* 338.1168 $[^{12}C_{13}{}^1H_{33}{}^{31}P_3{}^{56}Fe]^+$ (338.1143 calcd). Anal. Calcd for $C_{13}H_{33}P_3Fe$: C, 46.17; H, 9.84. Found: C, 45.72; H, 9.75.

The same compound was prepared in lower yield (40%) by reaction of 1.83 g (11.3 mmol) of $FeCl_3$, 2.0 g of PMe_3 (33.8 mmol), and 5 g of (22.5 mmol) **1**.

$W(\eta\text{-}C_4H_6)_3$ (9). Similarly, 2 g of WCl_6 (5.04 mmol) in 20 mL of Et_2O was reacted with 3.36 g of $Mg(C_4H_6)\cdot 2THF$ suspended in

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Table I. Data for the X-ray Diffraction Study of $Hf(C_4H_6)_2(dmpe)$

formula	$C_{14}H_{28}P_2Hf$
formula wt	436.82
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	13.274 (2)
b, Å	14.952 (2)
c, Å	9.319 (1)
α, deg	97.14 (1)
β, deg	101.82 (1)
γ, deg	109.76 (1)
V, Å^3	1665.7
Z	4
ρ(calcd), g cm^{-3}	1.742
abs coeff, cm^{-1}	67.73
radiation	Mo Kα (λ = 0.710 69 Å)
monochromator	graphite
cryst dimens, mm	0.30 × 0.15 × 0.52
no. of indep reflctns	5461
no. reflctns, $F_o^2 > 2\sigma(F_o^2)$	4882
no. of variables refined	531
R	0.024
R_w	0.028
error in observn of unit wt, e	1.695

100 mL of THF. After addition of dioxane, filtration, and evaporation of the solvent, the residue was dissolved in toluene and eluted down a short silica column (5 × 1.5 cm). Evaporation of the eluent gave an off-white solid, which afforded 0.65 g of **9** (1.87 mmol, 37%) after recrystallization from hexane. The compound was identified by comparison of its ^{1}H NMR spectrum to that in the literature report.[11]

Polymerization of Ethylene with $Ti(C_4H_6)_2$(diphos). To a 100-mL flask equipped with a magnetic stir bar was charged 170 mg of a mixture of **5** and diphos, shown to contain 18 mol % of **5** (therefore, 0.07 mmol of **5**) by ^{31}P NMR, and 25 mL of toluene. The flask was fitted with a vacuum adaptor, freeze-thaw degassed, and charged with 1 atm of ethylene. After stirring 18 h at 70 °C, polyethylene (310 mg, 11.1 mmol) was collected by filtration and dried in vacuo. This corresponds to 4.0 mg of C_2H_4 polymerized atm^{-1} min^{-1} (mmol of **5**)$^{-1}$.

X-ray Data Collection. A large crystal (0.30 × 0.15 × 0.52 mm) of **2** was selected and sealed into a glass capillary under an atmosphere of prepurified nitrogen. The crystal was mounted on a Syntex P3 diffractometer. The crystal system, space group, and approximate unit cell dimensions were determined from preliminary scans and rotation photographs. A ω scan from a typical reflection gave a peak width at half-maximum of 0.22°, indicating that the crystal was of good quality. The unit cell dimensions were subsequently refined from the Bragg angles of 50 computer-centered reflections. Table I contains a summary of the crystal data.

Intensity data were collected with use of the ω-scan method. 5461 independent reflections were measured in the range $4° < 2\theta < 50°$ with a scan range of 1.0°, a variable scan rate of 4.0–10.0°/min, and total background time equal to scan time. The X-ray tube was operated at maximum output, (60 kV, 40 MA). The crystal temperature was maintained at −100 °C. The intensities of four standard reflections were monitored periodically.

Solution and Refinement of the Structure. Solution and refinement of the structure were done on a PDP-11 computer using local modifications of the structure determination package supplied by the Enraf-Nonius Corp.[12] The atomic scattering factors were taken from the tabulations of Cromer and Waber.[13a] Anomalous dispersion corrections were by Cromer.[13b] In the full-matrix least-squares refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weight, w, was assigned as $[\sigma(F_o)]^{-2}$. The standard deviations of the observed structure factors, $\sigma(F_o)$, were based on counting statistics and an "ignorance factor" p of 0.02.[14]

The positions of the two Hf atoms in the asymmetric unit were determined by interpretation of the Patterson function. The positions of the other 32 nonhydrogen atoms were found from a difference Fourier electron density map. After anisotropic refinement of all the nonhydrogen atoms, the R value was 0.028, and the weighted R was 0.035. A second difference Fourier map yielded positions of all 56 hydrogen atoms. In the final refinement with 531 variables, the hydrogen atoms were refined with isotropic temperature factors, and all of the B_{iso} values were reasonable. The final R value was 0.024, and the weighted R was 0.028.

The positional and thermal parameters of the nonhydrogen atoms are given in Table II; those for the hydrogen atoms are in Table V (supplementary material). Selected bond lengths, angles, and least-squares planes are listed in Table IV. General temperature factors appear in Table III.

Results and Discussion

Preparation and Properties of $[Mg(C_4H_6)\cdot 2THF]_n$. Minor modification of the procedure employed by Yasuda et al.[1g] consistently afforded **1** in good yield. Thus, shaking Mg turnings or chips, activated with a small amount of an alkyl or aryl halide, with butadiene at room temperature gave **1** in ca. 20% yield. Vigorous mechanical shaking was found to be beneficial. In our hands, temperatures above 25 °C, as recommended in reference 1g, resulted in reduced yields. Recycling of the excess Mg chips in subsequent preparations improved the yield to ca. 80%. **1** can be easily prepared on a 0.5-mol scale in a 1-L flask as described in the Experimental Section.

The off-white solid is pyrophoric but may be stored indefinitely under a nitrogen atmosphere. Compound **1** has no appreciable solubility in ethereal solvents but will react with metal halides in THF at 0 °C; little reaction occurs at substantially lower temperatures or in ethyl ether.

Representation Reactions of 1 with Metal Halides. The reaction of a transition-metal halide with **1** to form a butadiene complex appears to be quite general, although in some cases yields are low. Examples from the literature or this work are listed in eq 1–6. Typically, the metal complex and a stoichiometric amount of **1** are combined in THF at room temperature or 0 °C; reaction is rapid and exothermic. Yields vary from nearly quantitative for **6** to poor for **9**.

$$(\eta\text{-}C_8H_8)MCl_2 + Mg(C_4H_6)\cdot 2THF \rightarrow (\eta\text{-}C_8H_8)M(C_4H_6)^2 + MgCl_2 \quad (1)$$

$$M = Ti, Zr, Hf$$

$$(\eta\text{-}C_5H_5)_2ZrCl_2 + Mg(C_4H_6)\cdot 2THF \rightarrow (\eta\text{-}C_5H_5)_2Zr(C_4H_6)^3 + MgCl_2 \quad (2)$$

$$MCl_4 + P\text{–}P + Mg(C_4H_6)\cdot 2THF \rightarrow M(C_4H_6)_2(P\text{–}P) + MgCl_2 \quad (3)$$

$$M = Hf, Ti, Zr$$

P–P = dmpe (**2**), depe (**3**), $(MeO)_2PC_2H_4P(OMe)_2$ (**4**), diphos (**5**), dmpe (**6**)

$$NbCl_4(dmpe)_2 + Mg(C_4H_6)_2\cdot 2THF \rightarrow \underset{\mathbf{7}}{NbCl(\eta\text{-}C_4H_6)(dmpe)_2} + MgCl_2 \quad (4)$$

$$FeCl_2 \text{ or } FeCl_3 + Mg(C_4H_6)\cdot 2THF + PMe_3 \rightarrow \underset{\mathbf{8}}{Fe(C_4H_6)(PMe_3)_3} + MgCl_2 \quad (5)$$

$$WCl_6 + Mg(C_4H_6)\cdot 2THF \rightarrow \underset{\mathbf{9}}{W(C_4H_6)_3} + MgCl_2 \quad (6)$$

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[11] Skell, P. S.; Van Dam, E. M.; Silvon, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 626.

[12] Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthaf-Hazehamp, R., von Konigsveld, H., Gassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

[13] "International Tables for X-ray Crystallography"; Vol. IV, Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B. (b) Table 2.3.1.

[14] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197–204.

[15] Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966.

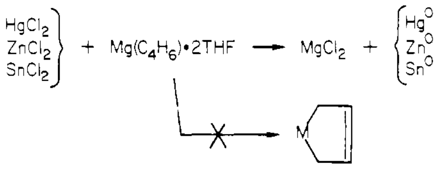
Table II. Fractional Coordinates and Temperature Factors of the Nonhydrogen Atoms of $Hf(\eta\text{-}C_4H_6)_2(dmpe)$[a]

ATOM	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
HF1	0.25041(1)	0.09353(1)	0.25062(2)	0.00226(1)	0.00152(1)	0.00535(2)	0.00098(2)	0.00170(2)	0.00180(2)
HF2	0.75988(1)	0.46307(1)	0.10464(2)	0.00273(1)	0.00140(1)	0.00386(2)	0.00151(2)	0.00176(2)	0.00113(2)
P1	0.1391(1)	-0.06689(9)	0.3390(1)	0.00265(7)	0.00138(5)	0.0067(1)	0.00093(10	0.0028(2)	0.0012(1)
P2	0.3541(1)	0.10799(9)	0.5384(1)	0.00308(7)	0.00158(5)	0.0054(1)	0.00111(10	0.0008(2)	0.0007(1)
P3	0.7211(1)	0.46745(9)	0.3755(1)	0.00266(7)	0.00184(6)	0.0048(1)	0.00106(10	0.0024(1)	0.0006(1)
P4	0.7848(1)	0.30781(9)	0.2022(1)	0.00272(7)	0.00151(5)	0.0053(1)	0.00144(9	0.0014(2)	0.0010(1)
C1	0.1552(4)	-0.0130(4)	0.0166(6)	0.0042(3)	0.0035(3)	0.0060(6)	0.0022(5)	0.0011(7)	0.0005(7)
C2	0.2490(4)	0.0585(4)	-0.0092(6)	0.0048(3)	0.0051(3)	0.0071(6)	0.0044(5)	0.0046(7)	0.0052(7)
C3	0.3557(4)	0.0797(5)	0.0738(6)	0.0040(3)	0.0060(3)	0.0071(6)	0.0032(5)	0.0069(6)	0.0053(8)
C4	0.3837(4)	0.0311(4)	0.1918(6)	0.0044(3)	0.0052(3)	0.0075(6)	0.0057(4)	0.0051(7)	0.0041(7)
C5	0.1290(4)	0.1601(4)	0.3394(6)	0.0044(3)	0.0029(2)	0.0099(7)	0.0034(4)	0.0054(7)	0.0025(7)
C6	0.1485(4)	0.1975(4)	0.2100(6)	0.0039(3)	0.0026(2)	0.0098(7)	0.0034(4)	0.0007(8)	0.0028(7)
C7	0.2551(5)	0.2474(4)	0.1979(7)	0.0056(4)	0.0022(2)	0.0130(8)	0.0028(5)	0.0031(9)	0.0067(7)
C8	0.3506(5)	0.2622(4)	0.3164(8)	0.0052(4)	0.0017(3)	0.0183(10)	-0.0002(5)	0.0034(10)	0.0063(8)
C11	-0.0119(5)	-0.1109(4)	0.2863(7)	0.0040(4)	0.0031(3)	0.0152(9)	0.0018(5)	0.0041(9)	0.0053(8)
C12	0.1623(4)	-0.1777(4)	0.2800(6)	0.0057(4)	0.0018(2)	0.0086(7)	0.0028(4)	0.0019(8)	0.0000(7)
C13	0.1755(4)	-0.0534(4)	0.5437(6)	0.0047(3)	0.0020(2)	0.0099(6)	0.0016(4)	0.0081(7)	0.0051(6)
C14	0.3024(4)	-0.0046(4)	0.6046(5)	0.0040(3)	0.0026(2)	0.0056(6)	0.0019(4)	0.0015(7)	0.0014(6)
C15	0.3401(5)	0.1949(4)	0.6821(6)	0.0059(4)	0.0025(3)	0.0077(7)	0.0019(5)	0.0020(8)	-0.0013(7)
C16	0.5030(5)	0.1391(4)	0.5920(7)	0.0039(4)	0.0038(3)	0.0100(7)	0.0017(5)	0.0011(8)	0.0028(8)
C21	0.7841(4)	0.6277(4)	0.1664(6)	0.0060(3)	0.0024(2)	0.0099(7)	0.0041(4)	0.0063(8)	0.0038(7)
C22	0.8513(4)	0.6223(4)	0.0640(6)	0.0057(3)	0.0021(2)	0.0095(6)	0.0025(5)	0.0068(7)	0.0048(6)
C23	0.9307(4)	0.5819(4)	0.0906(6)	0.0039(3)	0.0019(2)	0.0096(6)	0.0004(4)	0.0070(7)	0.0037(6)
C24	0.9535(4)	0.5433(4)	0.2216(6)	0.0028(3)	0.0031(3)	0.0073(6)	0.0006(5)	0.0019(7)	0.0017(7)
C25	0.5645(4)	0.3712(4)	0.0193(6)	0.0034(3)	0.0035(3)	0.0074(6)	0.0025(4)	0.0006(7)	-0.0006(7)
C26	0.5926(4)	0.4297(4)	-0.0881(6)	0.0046(3)	0.0044(3)	0.0062(6)	0.0054(5)	-0.0005(7)	0.0011(7)
C27	0.6746(5)	0.4291(4)	-0.1584(6)	0.0065(4)	0.0044(3)	0.0048(6)	0.0049(5)	0.0014(8)	0.0030(7)
C28	0.7379(4)	0.3678(4)	-0.1284(6)	0.0053(3)	0.0035(3)	0.0057(6)	0.0036(5)	0.0040(7)	0.0005(7)
C31	0.6057(4)	0.4995(4)	0.4059(6)	0.0041(3)	0.0038(3)	0.0081(6)	0.0035(4)	0.0044(7)	-0.0005(7)
C32	0.8322(4)	0.5506(4)	0.5339(6)	0.0044(3)	0.0046(3)	0.0060(6)	0.0027(5)	0.0021(7)	0.0002(8)
C33	0.6963(4)	0.3506(4)	0.4352(6)	0.0064(3)	0.0029(2)	0.0072(6)	0.0043(4)	0.0078(7)	0.0049(6)
C34	0.7846(4)	0.3117(4)	0.4009(6)	0.0062(3)	0.0030(2)	0.0069(6)	0.0055(4)	0.0038(7)	0.0045(6)
C35	0.6765(4)	0.1881(4)	0.1158(7)	0.0039(3)	0.0022(3)	0.0109(7)	0.0009(5)	0.0025(8)	0.0015(7)
C36	0.9091(4)	0.2839(4)	0.1904(6)	0.0034(3)	0.0029(2)	0.0089(7)	0.0034(4)	0.0015(7)	0.0010(7)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

This procedure employs generally milder conditions than used for thermal or photolytic ligand displacement based preparations of butadiene complexes. Further, it does not require the presence of a strong reductant, as do many procedures for diene complex preparation. For example, **6** can be made by Na/Hg reduction of $ZrCl_4(dmpe)_2$ in the presence of butadiene.[4] However, analogous reactions fail for $HfCl_4$, as it is not reduced by Na/Hg at moderate temperatures[5] and butadiene is incompatible with other powerful reductants (e.g., sodium naphthalene). But as shown in eq 3, $HfCl_4$ reacts directly with **1** and dmpe to form **2**. Indeed, the reagent **1** allows preparation of a broad range of group 4 derivatives. Further, in general its use is more convenient and gives comparable or higher yields than more common synthetic methods. For example, the syntheses of **6** and **8** shown in eq 3 and 5 are superior to the literature methods;[4,13] the preparation of **9** in eq 6 does not require the metal evaporation apparatus used in the original report of the compound.[11] $NbCl(\eta\text{-}C_4H_6)(dmpe)_2$ (**7**) cannot be prepared by Na/Hg reduction of $NbCl_4(dmpe)_2$ in the presence of butadiene.[16]

Main-group, P-block halides do not appear to form stable metallocyclopentenes on treatment with **1**. Thus, $HgCl_2$, $ZnCl_2$, and $SnCl_4$ are quantitatively reduced by **1**, as indicated in eq 7.



(7)

Substituted diene–magnesium adducts, analogous to **1**, have been described[1] and appear to react similarly to **1** with metal

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(16) Datta, S.; Wreford, S. S., unpublished results; see ref 23.

Table III. General Temperature Factors for $Hf(C_4H_6)_2$(dmpe)

	U(1,1)	*U*(2,2)	*U*(3,3)	*U*(1,2)	*U*(1,3)	*U*(2,3)
Hf1	0.01663 (8)	0.01453 (8)	0.02154 (9)	0.00410 (7)	0.00463 (7)	0.00560 (7)
Hf2	0.02006 (8)	0.01338 (8)	0.01557 (8)	0.00633 (6)	0.00478 (6)	0.00350 (7)
P1	0.0195 (5)	0.0132 (5)	0.0269 (6)	0.0039 (4)	0.0075 (4)	0.0036 (5)
P2	0.0226 (6)	0.0152 (5)	0.0216 (6)	0.0047 (4)	0.0022 (4)	0.0021 (5)
P3	0.0195 (5)	0.0177 (5)	0.0192 (5)	0.0044 (4)	0.0065 (4)	0.0018 (5)
P4	0.0200 (5)	0.0144 (5)	0.0215 (6)	0.0061 (4)	0.0037 (4)	0.0030 (5)
C1	0.031 (2)	0.034 (3)	0.024 (2)	0.009 (2)	0.003 (2)	0.001 (2)
C2	0.035 (2)	0.049 (3)	0.029 (2)	0.018 (2)	0.012 (2)	0.016 (2)
C3	0.030 (2)	0.058 (3)	0.029 (2)	0.013 (2)	0.019 (2)	0.016 (2)
C4	0.032 (2)	0.050 (3)	0.030 (2)	0.024 (2)	0.014 (2)	0.013 (2)
C5	0.032 (2)	0.028 (2)	0.040 (3)	0.014 (2)	0.015 (2)	0.008 (2)
C6	0.029 (2)	0.025 (2)	0.039 (3)	0.014 (2)	0.002 (2)	0.009 (2)
C7	0.041 (3)	0.021 (2)	0.052 (3)	0.012 (2)	0.008 (2)	0.021 (2)
C8	0.038 (3)	0.016 (2)	0.074 (4)	−0.001 (2)	0.009 (3)	0.019 (3)
C11	0.030 (3)	0.030 (3)	0.061 (3)	0.008 (2)	0.011 (2)	0.017 (3)
C12	0.042 (3)	0.017 (2)	0.035 (3)	0.012 (2)	0.005 (2)	−0.000 (2)
C13	0.034 (2)	0.019 (2)	0.040 (2)	0.007 (2)	0.022 (2)	0.016 (2)
C14	0.029 (2)	0.024 (2)	0.023 (2)	0.008 (2)	0.004 (2)	0.004 (2)
C15	0.043 (3)	0.024 (3)	0.031 (3)	0.008 (2)	0.005 (2)	−0.004 (2)
C16	0.029 (3)	0.037 (3)	0.040 (3)	0.007 (2)	0.003 (2)	0.009 (3)
C21	0.044 (3)	0.023 (2)	0.040 (3)	0.017 (2)	0.017 (2)	0.012 (2)
C22	0.042 (3)	0.020 (2)	0.038 (3)	0.010 (2)	0.019 (2)	0.015 (2)
C23	0.029 (2)	0.018 (2)	0.039 (2)	0.002 (2)	0.019 (2)	0.011 (2)
C24	0.020 (2)	0.029 (3)	0.030 (2)	0.003 (2)	0.005 (2)	0.005 (2)
C25	0.025 (2)	0.034 (3)	0.030 (3)	0.011 (2)	0.002 (2)	−0.002 (2)
C26	0.034 (2)	0.043 (3)	0.025 (2)	0.023 (2)	−0.001 (2)	0.003 (2)
C27	0.048 (3)	0.042 (3)	0.019 (2)	0.020 (2)	0.004 (2)	0.009 (2)
C28	0.039 (2)	0.034 (3)	0.023 (2)	0.015 (2)	0.011 (2)	0.001 (2)
C31	0.030 (2)	0.037 (3)	0.033 (3)	0.015 (2)	0.012 (2)	−0.002 (2)
C32	0.032 (3)	0.044 (3)	0.024 (2)	0.011 (2)	0.006 (2)	0.001 (2)
C33	0.047 (2)	0.028 (2)	0.029 (2)	0.018 (2)	0.021 (2)	0.015 (2)
C34	0.045 (3)	0.029 (2)	0.028 (2)	0.023 (2)	0.010 (2)	0.014 (2)
C35	0.028 (2)	0.021 (2)	0.044 (3)	0.004 (2)	0.007 (2)	0.005 (2)
C36	0.025 (2)	0.028 (2)	0.036 (3)	0.014 (2)	0.004 (2)	0.003 (2)

halides.[3] However, their preparation and purification is considerably less convenient.[1h]

Properties of $M(C_4H_6)L_2$ (M = Ti, Zr, Hf). The large number of compounds in this class, which may be prepared by use of **1**, has provided some information concerning the criteria for stability and the influence of the donor ligands on the chemistry of these complexes.

The stability of group 4 complexes of the type $M(C_4H_6)_2L_2$ is strongly dependent on the nature of donor ligands. Complexes with monodentate phosphines do not appear to be stable. Treatment of Ti, Zr, and $HfCl_4$ with PMe_3 and **1** in THF gives blue, purple, and orange solutions, indicative of formation of the respective derivatives; however, the solutions each turn brown or black in several minutes, and no butadiene complexes can be isolated. Only Ti forms a stable diphos derivative (**5**); the Zr and Hf analogues can be observed to form on the basis of color changes but are not stable and cannot be isolated.

The complex **5** has been obtained as an inseparable mixture with diphos; the solubility properties of **5** and diphos are too similar to allow separation by crystallization, and the complex does not survive chromatographic conditions. Characterization was based on NMR data. Although **5** is stable in toluene solution to ca. 100 °C, it decomposes slowly in the solid state unless cooled to −20 °C.

Apparently, phosphine donors are a requisite for stability, as the reaction of tetramethylenediamine, **1**, and $HfCl_4$ or $TiCl_4$ does not give a stable complex.

The nature of the bidentate phosphine significantly influences the chemistry of $M(C_4H_6)_2$(P–P).[4] For example, although $Ti(C_4H_6)_2$(dmpe) and $Zr(C_4H_6)_2$(dmpe) oligomerize olefins and butadiene,[5] **4** does not. Presumably, the poorer donor, $(MeO)_2PC_2H_4P(OMe)_2$, destabilizes olefin adducts and inhibits subsequent oligomerization. Similarly, although $Zr(C_4H_6)_2$(dmpe) dimerizes and trimerizes ethylene, **5** polymerizes it. Thus, treatment of **5** in toluene with ethylene at 70 °C at 1 atm or more results in formation of polyethylene. Whether **5** is itself the catalyst or a precursor to the catalyst is unknown, but the catalyst solution does appear to be homogeneous. Filtration of an active solution does not significantly diminish activity. Remarkably, **5** functions in the presence of both coordinated and excess diphos; Lewis bases are generally potent poisons for Ziegler–Natta and modified Ziegler–Natta catalysts.[17]

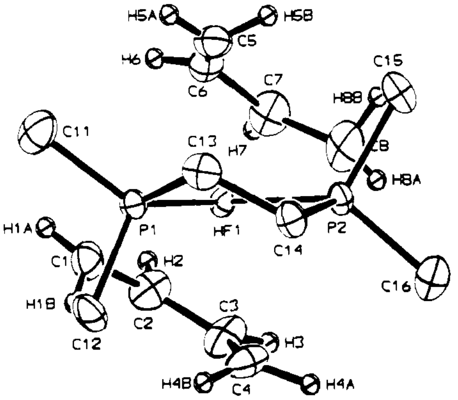

Figure 1. Structure of one of the independent molecules in the unit cell of $Hf(\eta\text{-}C_4H_6)_2$(dmpe). Distances from the C1–C2–C3–C4 least-squares plane are as follows: Hf1, −1.849 (0); H1A, −0.07 (5); H1B, 0.57 (5); H2, −0.25 (6); H3, −0.19 (6); H4A, −0.20 (6); H4B, 0.53 (5) Å. Distances from the C5–C6–C7–C8 least-squares plane are as follows: Hf1, 1.875 (0); H5A, 0.06 (6); H5B, −0.67 (5); H6, 0.24 (6); H7, 0.09 (8); H8A, 0.09 (5); H8B, −0.73 (6) Å.

We note a considerable variation in Lewis acidity of $M(C_4H_6)_2$(P–P) with the metal ion. Although **6** forms weakly

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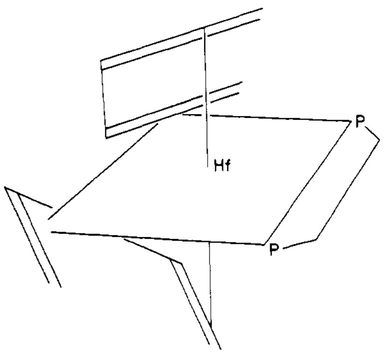
(17) Boor, J. "Ziegler–Natta Catalysts and Polymerizations"; Academic Press: New York, 1979; p 231.

Table IV. Selected Bond Lengths and Angles from the Structure of $Hf(\eta\text{-}C_4H_6)_2(dmpe)$

A. Bond Lengths			
Hf1-P1	2.685 (1)	Hf2-P3	2.675 (1)
Hf1-P2	2.698 (1)	Hf2-P4	2.692 (1)
Hf1-C1	2.353 (5)	Hf2-C21	2.352 (5)
Hf1-C2	2.407 (4)	Hf2-C22	2.397 (4)
Hf1-C3	2.401 (4)	Hf2-C23	2.402 (4)
Hf1-C4	2.385 (5)	Hf2-C24	2.382 (4)
Hf1-C5	2.387 (5)	Hf2-C25	2.392 (5)
Hf1-C6	2.398 (4)	Hf2-C26	2.408 (5)
Hf1-C7	2.394 (4)	Hf2-C27	2.389 (4)
Hf1-C8	2.349 (5)	Hf2-C28	2.349 (4)
C1-C2	1.428 (7)	C5-C6	1.425 (7)
C2-C3	1.376 (7)	C6-C7	1.395 (7)
C3-C4	1.445 (7)	C7-C8	1.432 (8)
C11-P1	1.821 (5)	C31-P3	1.815 (5)
C12-P1	1.825 (5)	C32-P3	1.820 (5)
C13-P1	1.837 (5)	C33-P3	1.844 (4)
C13-C14	1.539 (6)	C33-C34	1.544 (6)
C14-P2	1.826 (4)	C34-P4	1.846 (4)
C15-P2	1.830 (5)	C35-P4	1.830 (5)
C16-P2	1.813 (5)	C36-P4	1.823 (4)
C21-C22	1.446 (6)	C25-C26	1.433 (7)
C22-C23	1.377 (7)	C26-C27	1.385 (7)
C23-C24	1.435 (6)	C27-C28	1.451 (7)
B. Bond Angles			
P1-Hf1-P2	72.00 (3)	P3-Hf2-P4	72.16 (3)
C11-P1-C12	101.3 (3)	C31-P3-C32	100.4 (3)
C11-P1-C13	103.7 (3)	C31-P3-C33	103.9 (2)
C12-P1-C13	101.1 (2)	C32-P3-C33	101.3 (3)
P1-C13-C14	108.7 (3)	P3-C33-C34	108.3 (3)
C13-C14-P2	110.4 (3)	C33-C34-P4	109.7 (3)
C14-P2-C15	101.2 (2)	C34-P4-C35	100.3 (3)
C14-P2-C16	102.4 (2)	C34-P4-C36	103.8 (2)
C15-P2-C16	100.7 (3)	C35-P4-C36	101.0 (2)
C1-C2-C3	122.3 (5)	C21-C22-C23	122.0 (4)
C2-C3-C4	123.7 (5)	C22-C23-C24	122.7 (4)
C5-C6-C7	122.3 (5)	C25-C26-C27	122.9 (5)
C6-C7-C8	120.6 (5)	C26-C27-C28	121.6 (5)

bound adducts with small donors,[4] none of the Ti derivatives or **2** do so with phosphines detectably by NMR.

Molecular Structure of $Hf(C_4H_6)_2(dmpe)$. The structure of **2** is closely related to that proposed earlier for **6** on the basis of NMR data,[4b] i.e., an *approximate* octahedral disposition of ligands, as shown schematically by structure A and in Figure 1. Selected bond lengths, angles, and least-squares planes are presented in Table IV. The structure is triclinic and centrosymmetric. An approximate twofold axis passes through Hf and the center of the C14–C13 bond in the dmpe ligand. The asymmetric unit contains two molecules, one being the approximate mirror image of the other but rotated with respect to the other by about 76° around the pseudotwofold molecular axes. Both molecular axes are essentially parallel to the same nonrational lattice direction. The relationship of the two independent molecules is shown in Figure 2.



A

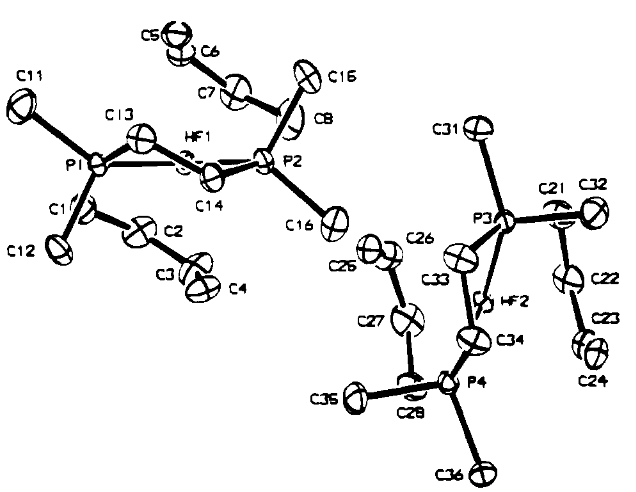


Figure 2. The two independent molecules of $Hf(\eta\text{-}C_4H_6)_2(dmpe)$.

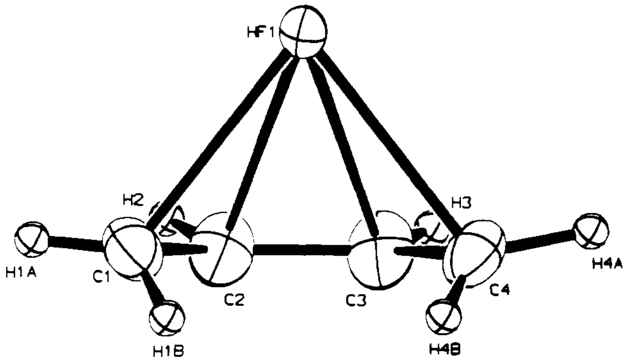


Figure 3. Geometry of one of the four independent η-butadiene ligands.

The butadiene ligands are bound in an η^4 mode with an essentially planar carbon skeleton; one of the four independent ligands is shown in Figure 3. The average distance between the internal butadiene carbon atoms, 1.383 (4) Å, is significantly shorter than those between the terminal and internal carbon atoms, 1.437 (3) Å, by an average of 0.054 (7) Å. This trend is a general feature of diene complexes[18] but is more pronounced in the structure of **2**. For example, high-precision $Fe(CO)_3$(diene) structures show an average difference of 0.02 Å.[19] The larger difference observed for **2** is consistent with the proposal that the M_{IV}(dmpe) unit is a potent electron donor.[4b] The Hf–C bond distances support this hypothesis as well. Typically, transition-metal diene complexes have metal to terminal carbon bond distances that are longer than the metal to internal carbon distances; an average over 13 structures gave a difference of 0.08 Å.[19] In **2** the pattern is reversed. The butadiene ligand in Figure 3, for example, has an average Hf–terminal carbon distance that is 0.035 (6) Å shorter than the average Hf–internal carbon distance, a pattern observable for all the independent butadiene ligands. The recently reported structure of dicyclopentadienyl(2,3-dimethylbutadiene)zirconium[20] shows a similar, but greater, shortening of the metal–carbon terminal bond distances, ca. 0.3 Å.[20] Apparently, **2** and the Zr–dimethylbutadiene complex have ground states intermediate between a 1,4-η^2-butadiene complex, exemplified by (1,5-cyclooctadiene)(η^2-2,3-dimethylbuta-1,4-diene)platinum,[21] and an η^4-butadiene com-

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plex, exemplified by $Fe(CO)_3$(diene) complexes. Indeed, equilibria between 1,4-η^2- and η^4-diene complexes have been observed by NMR for $(C_8H_8)M(C_4H_6)$ (M = Ti, Zr, Hf)[2] and $(C_5H_5)_2Zr$(diene).[3]

The hydrogen atoms of the C_4H_6 ligand have been located. The anti hydrogens attached to C1 and C4 are displaced away from Hf (ca. 0.6 Å out of the C1, C2, C3, C4 plane); the syn hydrogens are nearly in the butadiene plane. The hydrogen atoms attached to C2 and C3 are displaced ca. 0.3 Å toward Hf. Similar parameters have been observed in the structure of $Mn(C_4H_6)_2(CO)$[22] in which the hydrogen atoms have been located.

Each of the butadiene ligands has one Hf-terminal carbon distance that is 0.03 Å shorter than the other, a small but significant difference. This appears to be a trans effect as each short Hf-C distance occurs on the end of the diene trans to the dmpe phosphorus. The internal butadiene carbon-metal distances are unaffected.

The bite angle of the dmpe ligand, 72.0°, is somewhat smaller than the typical range, 75-85°,[23] a consequence of the long Hf-P distances. The conformation of the dmpe chelate ring is similar to other examples.[24]

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Registry No. **1**, 60300-64-3; **2**, 78791-10-3; **3**, 78791-11-4; **4**, 78791-12-5; **5**, 78791-13-6; **6**, 71328-76-2; **7**, 78791-14-7; **8**, 56315-41-4; **9**, 51733-16-5; ethylene, 74-85-1; $TiCl_4·2THF$, 31011-57-1; $ZrCl_4·2THF$, 21959-01-3; $[Zr(n\text{-}C_4H_6)dmpe]_2(dmpe)$, 69878-77-9; $NbCl_4(dmpe)_2$, 61202-65-1.

Supplementary Material Available: Listings of hydrogen atom positions and isotropic temperature factors (Table V) and structure factor amplitudes (Table VI) (37 pages). Ordering information is given on any current masthead page.

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Preparation and Spectral Characterization of Cadmium(II) Thiocyanate Complexes of Tricyclohexyl-, Triphenyl- and Tri-*m*-tolylphosphines and the Crystal and Molecular Structure of the Tri-*m*-tolylphosphine Complex

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The complexes $Cd(SCN)_2PR_3$, where R = cyclohexyl, phenyl, or *m*-tolyl, have been isolated from the reaction of $Cd(SCN)_2$ with the phosphine. Phosphorus-31 NMR, infrared, and Raman spectra of the complexes have been examined, and the structure of the tri-*m*-tolylphosphine complex has been determined by a single-crystal X-ray diffraction study. No satellites due to $^{111}Cd/^{113}Cd-^{31}P$ spin-spin couplings are observed in the ^{31}P NMR spectra even at 183 K. The vibrational spectra of the complexes are consistent with a polymeric structure involving bridging thiocyanates and five-coordinate cadmium. The crystals of the *m*-tolyl compound $Cd(SCN)_2(P(C_7H_7)_3)$ belong to the monoclinic space group $P2_1/c$, with $a = 10.866$ (7) Å, $b = 10.203$ (3) Å, $c = 20.077$ (6) Å, $\beta = 101.14$ (4)°, and $Z = 4$. The structure was solved by the heavy-atom method and refined by least-squares procedures on 1965 nonzero reflections. The final R factor was 0.038. Infinite chains of five-coordinated Cd atoms and bridging SCN groups extend along the b direction in the crystal. The metal shows a distorted trigonal-bipyramid geometry with the equatorial positions being occupied by the phosphine (Cd-P = 2.584 (2) Å), an S-bonded SCN group (Cd-S = 2.595 (2) Å), and the N end of a symmetry-equivalent SCN group (Cd-N = 2.256 (6) Å). The remaining SCN group bridges axial positions along the chain by forming weaker bonds (Cd-S = 2.792 (2) Å, Cd-N = 2.297 (6) Å). The unusual distribution of soft S atoms and hard N atoms in both the axial and equatorial positions undoubtedly results from the intermediate softness of cadmium, since the strongly bonding equatorial sites are filled only by soft P and S atoms in the similar mercury complexes.

Introduction

Tertiary phosphine complexes of cadmium(II) and mercury(II) halides were first reported[1c] 40 years ago. During the last decade, phosphine complexes of a variety of mercury(II) salts such as pseudohalides,[2-11] nitrate,[2,12-14] perchlorate,[2,15] and carboxylates[16-18] have been extensively investigated. However, very little has hitherto been known about phosphine complexes of cadmium(II) derivatives other than the halides. A recent study[16,19] showed that cadmium(II) halides and thiocyanate form 1:1 complexes with tri-*tert*-butylphosphine.

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