

ratio of 80:20 was determined by  $^1\text{H}$  NMR integrated ratios of the cyclopentadienyl resonances. Only approximately 10% of the initial 11 was collected.

**Reaction of Carbonyl( $\eta^5$ -cyclopentadienyl)( $\eta^1$ -7-methoxy-1-cycloheptenyl)(triphenylphosphine)iron (11) with 0.5 Equiv of Trimethylsilyl Triflate.** To a solution of a 60:40 mixture of 11-A and 11-B (0.63 g, 1.17 mmol) in 15 mL of a 1:1 pentane/benzene solvent mixture at room temperature was added, dropwise, trimethylsilyl triflate (0.11 mL, 0.6 mmol). The mixture was allowed to stir for  $1/2$  h, after which the solvent was removed. 13 was precipitated from the residue with ethyl acetate to give 0.33 g (85% based on trimethylsilyl triflate) of an orange solid with a 60:40 diastereomeric composition. The solvent was removed from the filtrate, and the residue was chromatographed through a  $1 \times 1/2$  in. column with benzene. A red band was collected. Removal of solvent afforded 0.30 g of 11 with a 10:90 diastereomeric composition.

**Reaction of Carbonyl( $\eta^5$ -cyclopentadienyl)( $\eta^1$ -7-methoxy-1-cycloheptenyl)(triphenylphosphine)iron (11) with**

**Trimethylsilyl Triflate in Pentane.** To a cold (0 °C) solution of a 60:40 mixture of 11-A and 11-B (0.20 g, 0.35 mmol) in 20 mL of pentane was added, dropwise, trimethylsilyl triflate (0.10 mL, 0.4 mmol). An orange precipitate was formed immediately and was collected via filtration. 13 was purified by dissolving the orange solid in a small amount of cold methylene chloride, followed by precipitation from ethyl acetate. The diastereomeric composition of 80:20 was determined by  $^1\text{H}$  NMR integrated areas of the cyclopentadienyl resonances.

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**Registry No.** 5, 87792-69-6; ( $\pm$ )-8, 115513-75-2; 8, 95865-49-9; 9, 95865-47-7; 10, 95865-41-1; 11-A, 115649-09-7; 11-B, 115649-10-0; 13-A, 115649-12-2; 13-B, 115649-14-4; FpCl, 12107-04-9;  $\text{Me}_3\text{SiOTf}$ , 27607-77-8; ( $\pm$ )-1-bromo-7-methoxycycloheptene, 115513-74-1; methanol, 67-56-1; ferrocenium tetrafluoroborate, 1282-37-7.

## Mono(cyclopentadienyl)zirconium(II) and -hafnium(II) Chemistry: Synthesis and Reactivity of $\text{CpM}(\text{CO})_2(\text{dmpe})\text{Cl}$ [M = Zr, Hf; Cp = Cyclopentadienyl; dmpe = 1,2-Bis(dimethylphosphino)ethane] via Mild-Condition Carbonylation Reaction of $\text{CpM}(\text{dmpe})_2\text{Cl}$ . The Crystal Structure of $\text{CpZr}(\text{CO})_2(\text{dmpe})\text{Cl}$

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The Na reduction of  $\text{CpMCl}_3(\text{THF})_2$  (M = Zr, Hf; Cp = cyclopentadienyl; THF = tetrahydrofuran) in the presence of a slight excess of dmpe [dmpe = 1,2-bis(dimethylphosphino)ethane] led to the formation of the two isostructural species  $\text{CpM}(\text{dmpe})_2\text{Cl}$  [M = Zr (1), 68%; M = Hf (2), 58%]. Easy replacement of one of the two coordinated dmpe by two molecules of CO was achieved by either a carbonylation reaction under mild conditions or CO abstraction from  $[\text{CpFe}(\text{CO})_2]_2$ . The resulting carbonyl derivatives  $\text{CpM}(\text{CO})_2(\text{dmpe})\text{Cl}$  [M = Zr (3), 73%; M = Hf (4), 63%] have been isolated and fully characterized. The close similarity in their spectroscopic properties suggested that the two complexes are isostructural. Compound 3 crystallizes in a monoclinic space group of  $P2_1/a$  symmetry with  $a = 15.664$  (10) Å,  $b = 7.208$  (3) Å,  $c = 16.869$  (9) Å,  $\beta = 112.89$  (4)°,  $V = 1754$  (2) Å<sup>3</sup>, and  $Z = 4$ . The presence of a fast CO exchange in solution has been demonstrated for both 3 and 4 by using  $^{13}\text{C}$ O. In agreement with its dynamic behavior in solution, an easy ligand-exchange reaction occurs between 3 and 1 forming the pyrophoric light green carbonyl derivative  $[\text{CpZr}(\text{CO})(\text{dmpe})\text{Cl}]_2(\text{dmpe})$  (5). Complex 5 can be more conveniently synthesized by carrying the carbonylation reaction on saturated solutions of 1 in ether. Easy ligand-exchange reactions of both 1 and 3 with butadiene afforded the new butadiene derivative  $\text{CpZr}(\eta^4\text{-butadiene})(\text{dmpe})\text{Cl}$  (6). Vigorous reaction of 3 with 2 equiv of ethylene (1 atm, room temperature) led instead to the evolution of 1 equiv of CO with formation of a yellow solid product, probably  $\text{CpZr}[\eta^2\text{-C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2]\text{Cl}^{1/2}(\text{dmpe})$  (7). Chemical degradation of 7 with 2 equiv of anhydrous HCl gave cyclopentanol in 75% yield.

### Introduction

The coordination of CO in its intact form, which is the prerequisite for its activation,<sup>1</sup> has been reported in the chemistry of zirconium and hafnium in only few cases:  $\text{Cp}'_2\text{M}(\text{CO})\text{L}$  (Cp' =  $\text{C}_5\text{H}_5$ ,  $\text{RC}_5\text{H}_4$ ,  $\text{C}_5\text{Me}_5$ ; L = CO,  $\text{PR}_3$ ;

M = Zr, Hf)<sup>2</sup> and  $\text{Cp}'\text{M}(\text{CO})_4^-$  (Cp' =  $\text{C}_5\text{H}_5$ ,  $\text{C}_5\text{Me}_5$ ; M = Zr, Hf)<sup>3</sup> in which the metal is in the oxidation state II and

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0, respectively. A labile coordination has been observed with the zerovalent zirconium derivative  $[\text{Zr}(\eta^4\text{-C}_4\text{H}_6)_2(\text{dmpe})_2](\text{dmpe})$ ,<sup>4</sup> and while this work was in progress, a bis(arene) hafnium carbonyl derivative<sup>5</sup> and a mono(cyclopentadienyl)hafnium halocarbonyl<sup>6</sup> have been reported and fully characterized.

The synthetic potential of the low-valent group IV organometallic complexes in this field<sup>7</sup> contrasts with the quite poor development of this chemistry in terms of new classes of low-valent derivatives which, apart from the bis(cyclopentadienyl) systems, are limited to only few clearly characterized compounds.<sup>8</sup> This paucity in the literature prompted us to attempt the synthesis of new divalent zirconium and hafnium derivatives which could possibly work as starting materials for further reactivity studies. In a previous paper<sup>9</sup> we have communicated the facile synthesis and characterization of the Zr(II) species  $\text{CpZr}(\text{dmpe})_2\text{Cl}$  [ $\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{-ethane}$ ] via a reduction reaction of  $\text{CpZrCl}_3(\text{THF})_2$ .

Herein we report the extension to the Hf analogue and a study on the reactivity of these complexes with CO.

### Experimental Section

All the operations were performed under dry nitrogen with use of standard Schlenk techniques or in a nitrogen-filled drybox (Braun MB 200).  $\text{CpZrCl}_3(\text{THF})_2$  and  $\text{CpHfCl}_3(\text{THF})_2$  have been prepared according to published methods.<sup>10</sup> Solvents were dried and distilled following standard procedures. Dmpe has been synthesized as published (*caution*: danger of serious explosions).<sup>11</sup> Ethylene, butadiene, CO (Matheson), and 2,2-dimethyl-2-butene (Aldrich) have been used without further purification. Solvents used for nuclear magnetic resonance (benzene- $d_6$ , THF- $d_8$ ) were vacuum-transferred from a Na-K alloy. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian VXR 300 and Bruker WH 90 spectrometers. Chemical shifts are reported in units of  $\delta$ , referenced to the tetramethylsilane and calculated from the position of the solvent absorption. Infrared (IR) spectra were obtained on a Unicam SP3-300 instrument. Nujol mulls were prepared in the drybox. Elemental analysis were carried out at the Chemistry Department of the University of Groningen. [<sup>13</sup>C]Carbon monoxide (90%; Merck Sharp & Domne) has been used without further purification.

**Preparation of  $\text{CpZr}(\text{dmpe})_2\text{Cl}$  (1).** A THF solution (1.2 L) of  $\text{CpZrCl}_3(\text{THF})_2$  (65.1 g, 0.16 mol) was stirred with an excess of Na sand (8.45 g, 0.37 mol) in presence of dmpe (58.0 g, 0.38 mol). The reaction progress was monitored by NMR. After 10 days the resulting deep orange-brown solution was filtered and evaporated to dryness. The remaining crystalline matter was extracted with ether (1.3 L) and concentrated to a small volume (300 mL). After the solution was left standing overnight at  $-30^\circ\text{C}$ , 56 g of orange-brown crystals of 1 were obtained (0.11 mol,

68.7% yield). Anal. Calcd for  $\text{C}_{17}\text{H}_{37}\text{P}_4\text{ClZr}$  (Found): C, 41.50 (41.28); H, 7.53 (7.35); P, 25.23 (25.22), Cl, 7.22 (7.41); Zr, 18.51 (18.47). <sup>1</sup>H NMR (90 MHz,  $\text{C}_6\text{D}_6$ ,  $27^\circ\text{C}$ ):  $\delta$  4.36 (qt,  $J_{\text{P-H}} = 1.8$  Hz, 5 H, Cp), 1.65 (m, 4 H,  $\text{CH}_2$  dmpe), 1.44 (br s, 12 H,  $\text{CH}_3$  dmpe), 0.95 (br s, 12 H,  $\text{CH}_3$  dmpe), 0.81 (m, 4 H,  $\text{CH}_2$  dmpe). <sup>13</sup>C NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  83.9 (dt,  $J_{\text{C-H}} = 170.2$  Hz,  $J_{\text{P-H}} = 6.5$  Hz, Cp), 30.9 (t,  $J_{\text{C-H}} = 130.1$  Hz,  $\text{CH}_2$  dmpe), 19.6 (q,  $J_{\text{C-H}} = 127.6$  Hz,  $\text{CH}_3$  (dmpe)), 16.7 (q,  $J_{\text{C-H}} = 128.4$  Hz,  $\text{CH}_3$  dmpe).

**Preparation of  $\text{CpHf}(\text{dmpe})_2\text{Cl}$  (2).** A THF solution (70 mL) of  $\text{CpHfCl}_3(\text{THF})_2$  (3.0 g, 6.1 mmol) was stirred for 10 days with 0.35 g of Na sand (14.6 mmol) in the presence of 2 g of dmpe (13.3 mol). The resulting deep orange-brown solution was worked up as above, and brown-orange crystals were obtained (2.1 g, 3.62 mmol, 58% yield). Anal. Calcd for  $\text{C}_{17}\text{H}_{37}\text{P}_4\text{ClHf}$  (Found): C, 35.23 (35.21); H, 6.34 (6.58); Cl, 6.13 (6.21); Hf, 30.82 (31.01). <sup>1</sup>H NMR (90 MHz,  $\text{C}_6\text{D}_6$ ,  $28^\circ\text{C}$ ):  $\delta$  4.21 (qt,  $J_{\text{P-H}} = 1.9$  Hz, 5 H, Cp), 1.68 (m, 4 H,  $\text{CH}_2$  dmpe), 1.48 (br s, 12 H,  $\text{CH}_3$  dmpe), 1.04 (br s, 12 H,  $\text{CH}_3$  dmpe), 0.81 (br s, 4 H,  $\text{CH}_2$  dmpe). <sup>13</sup>C NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  81.1 (d,  $J_{\text{C-H}} = 170.9$  Hz, Cp), 32.7 (t,  $J_{\text{C-H}} = 129.7$  Hz,  $\text{CH}_2$  dmpe), 20.6 (q,  $J_{\text{C-H}} = 127.8$  Hz,  $\text{CH}_3$  (dmpe)), 17.2 (q,  $J_{\text{C-H}} = 128.1$  Hz,  $\text{CH}_3$  dmpe).

**Preparation of  $\text{CpZr}(\text{CO})_2(\text{dmpe})\text{Cl}$  (3).** A deep orange solution of 1 (1.08 g, 2.2 mmol) in ether (300 mL) was exposed to CO (room temperature, 1 atm). When the solution was left standing 24 h, deep purple crystals (0.65 g, 1.6 mmol) were obtained (73% yield). Anal. Calcd for  $\text{C}_{13}\text{H}_{21}\text{P}_2\text{O}_2\text{ClZr}$  (Found): C, 39.24 (39.23); H, 5.03 (5.38); Cl, 8.93 (8.83); Zr, 22.89 (23.12). IR ( $\nu(\text{CO})$ ,  $\text{cm}^{-1}$ ) 1955, 1885. <sup>1</sup>H NMR (90 MHz, THF- $d_8$ ,  $25^\circ\text{C}$ ):  $\delta$  4.87 (t,  $J_{\text{P-H}} = 1.5$  Hz, Cp), 1.73 (m, 4 H,  $\text{CH}_2$  dmpe), 1.36 (d,  $J_{\text{P-H}} = 6.3$  Hz, 6 H,  $\text{CH}_3$  dmpe), 1.26 (d,  $J_{\text{P-H}} = 5.0$  Hz, 6 H,  $\text{CH}_3$  dmpe). <sup>13</sup>C [<sup>1</sup>H] NMR (75 MHz, THF- $d_8$ ,  $25^\circ\text{C}$ ):  $\delta$  249.8 (d,  $J_{\text{P-C}} = 16$  Hz after <sup>13</sup>CO enrichment), 91.6 (d,  $J_{\text{C-H}} = 172.8$  Hz, Cp), 29.0 (t,  $J_{\text{C-H}} = 128.3$  Hz,  $\text{CH}_2$  dmpe), 14.4 (q,  $J_{\text{C-H}} = 129.1$  Hz,  $\text{CH}_3$  dmpe), 14.0 (q,  $J_{\text{C-H}} = 129.1$  Hz,  $\text{CH}_3$  dmpe).

**Preparation of  $\text{CpHf}(\text{CO})_2(\text{dmpe})\text{Cl}$  (4):** quantities and procedure as above; yield, 63%. Anal. Calcd for  $\text{C}_{13}\text{H}_{21}\text{P}_2\text{O}_2\text{ClHf}$  (Found): C, 32.16 (32.65); H, 4.32 (4.26); Cl, 7.32 (7.20); Hf, 36.80 (36.37). IR ( $\nu(\text{CO})$ ,  $\text{cm}^{-1}$ ): 1950, 1870. <sup>1</sup>H NMR (90 MHz, THF- $d_8$ ,  $28^\circ\text{C}$ ):  $\delta$  4.80 (t,  $J_{\text{P-H}} = 1.7$  Hz, 5 H, Cp), 1.76 (m, 4 H,  $\text{CH}_2$  dmpe), 1.43 (d,  $J_{\text{P-H}} = 6.4$  Hz, 6 H,  $\text{CH}_3$  dmpe), 1.33 (d,  $J_{\text{P-H}} = 5.2$  Hz, 6 H,  $\text{CH}_3$  dmpe). <sup>13</sup>C [<sup>1</sup>H] NMR (75 MHz, THF- $d_8$ ,  $25^\circ\text{C}$ ):  $\delta$  251.9 (d,  $J_{\text{P-C}} = 17$  Hz, CO after <sup>13</sup>CO enrichment), 89.6 (d,  $J_{\text{C-H}} = 174$  Hz, Cp), 29.8 (t,  $J_{\text{C-H}} = 127$  Hz,  $\text{CH}_2$  dmpe), 14.4 (q,  $J_{\text{C-H}} = 130.3$  Hz,  $\text{CH}_3$  dmpe), 13.9 (q,  $J_{\text{C-H}} = 131.2$  Hz,  $\text{CH}_3$  dmpe).

**<sup>13</sup>CO Exchange.** THF solutions (10 mL) of 3 and 4 (0.2 g) were transferred in an IR cell and the spectra recorded. After exposure to <sup>13</sup>CO (1 atm, room temperature), IR spectra were recorded showing the disappearance of the two carbonylic resonances and the almost quantitative formation of two new absorptions [1925, 1845  $\text{cm}^{-1}$  (3); 1940, 1840  $\text{cm}^{-1}$  (4)]. <sup>13</sup>CO-Enriched samples of 3 and 4 suitable for NMR spectroscopy were obtained when the above solutions were cooled at  $-80^\circ\text{C}$ .

**Preparation of  $[\text{CpZr}(\text{CO})(\text{dmpe})\text{Cl}]_2(\text{dmpe})$  (5). Method a.** An ether solution (30 mL) of 1.3 g of 1 (2.64 mmol) was exposed to CO (1 atm, room temperature). After the solution was left standing overnight, large-size purple crystals of 3 mixed together with a light green microcrystalline product were present in the reaction flask. The CO was replaced with nitrogen and the mixture gently stirred for 2 days. When the purple crystals of 3 disappeared, the green microcrystalline solid was collected on a filter and thoroughly washed with THF until the filtrate was colorless (1.0 g, 1.12 mmol, 85% yield). Anal. Calcd for  $\text{C}_{30}\text{H}_{58}\text{P}_8\text{O}_2\text{Cl}_2\text{Zr}_2$  (Found): C, 40.49 (40.53); H, 6.52 (6.50); P, 20.92 (21.05); Cl, 7.98 (7.93); Zr, 20.47 (19.98). IR (KBr, Nujol mull,  $\nu$ ,  $\text{cm}^{-1}$ ) 3065 (w), 1840–1830 (vs), 1420 (m), 1400 (w), 1295 (w), 1120 (mb), 1000 (s), 938 (s), 925 (s), 900 (s), 888 (m), 831 (w), 808 (m), 772 (m), 720 (s), 690 (m), 662 (w), 630 (m).

**Method b.** A deep red solution prepared by dissolving equimolar amounts (1.0 mmol) of 1 and 3 in 25 mL of THF afforded light green pyrophoric crystals of 5 in 60% yield within 2 h.

**Method c.** A deep red solution of 3 prepared by dissolving 0.5 mmol in 15 mL of THF was exposed to vacuum for 30 min. The initially purple color turned orange, and light green crystals of 5 separated in 25% yield.

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**Reaction of 1 with  $[CpFe(CO)_2]_2$ .** To a THF solution (100 mL) of 1 (0.95 g, 1.93 mmol) was added 0.682 g (1.92 mmol) of  $[CpFe(CO)_2]_2$ . The resulting deep red solution separated almost immediately bright red crystals of  $[CpFe(dmpe)(CO)][CpFe(CO)_2]$  (0.75 g, 1.56 mmol, 82% yield). Anal. Calcd for  $C_{19}H_{26}O_3P_2Fe_2$  (Found): C, 47.89 (48.02); H, 5.46 (5.55); P, 13.02 (12.93); Fe, 23.52 (23.50). IR ( $\nu(CO)$ ,  $cm^{-1}$ ): 1940, 1850, 1770.  $^1H$  NMR (90 MHz,  $py-d_5$ , 25 °C):  $\delta$  5.02 (s, 5 H, Cp), 4.87 (s, 5 H, Cp), 2.07 (m, 2 H,  $CH_2$  dmpe), 1.85 (m, 2 H,  $CH_2$  dmpe), 1.76 (m, 6 H,  $CH_3$  dmpe), 1.63 (m, 6 H,  $CH_3$  dmpe).  $^{13}C$  NMR (75 MHz,  $py-d_5$ , 25 °C):  $\delta$  229.8 (CO), 214.9 (CO), 83.5 (d,  $J_{C-H}$  = 104.4 Hz, Cp), 77.0 (d,  $J_{C-H}$  = 101.0 Hz, Cp), 29.5 (m,  $CH_2$  dmpe), 18.9 (m,  $CH_3$  dmpe), 18.3 (m,  $CH_3$  dmpe).

The IR spectrum of the solution showed the characteristic absorptions of 3 as the main carbonylic product present in solution.

**Preparation of  $CpZr(\eta^4\text{-butadiene})(dmpe)Cl$  (6). Method a (Reaction of 1 with Butadiene).** An ether solution (70 mL) of 1 (2.05 g, 4.16 mmol) was saturated with butadiene (room temperature, 1 atm). The color changed rapidly to light orange, and the crystalline 6 separated (1.36 g, 3.43 mmol, 82% yield). Anal. Calcd for  $C_{15}H_{27}P_2ClZr$  (Found): C, 45.51 (45.53); H, 6.83 (6.95); Cl, 8.97 (8.93); Zr, 23.04 (23.16). IR (Nujol,  $\nu$ ,  $cm^{-1}$ ): 1475 (m), 1413 (s), 1300 (m), 1280 (s), 1205 (m), 1155 (m), 1120 (m), 1030 (s), 1012 (s), 1005 (s), 930 (vs), 890 (m), 860 (w), 842 (w), 800 (vs), 730 (s), 700 (s), 675 (w), 640 (m), 605 (w), 495 (w), 445 (w).  $^1H$  NMR (90 MHz,  $C_6D_6$ , 80 °C):  $\delta$  6.04 (m, 2 H, butadiene), 5.53 (s, 5 H, Cp), 1.68 (m, 2 H, butadiene), 1.10 (pseudo t, 4 H,  $CH_2$  dmpe), 0.89 (t, 12 H,  $CH_3$  dmpe), 0.66 (m, 2 H, butadiene).  $^{13}C$  NMR (75 MHz, THF- $d_6$ , -80 °C):  $\delta$  131.2 (d,  $J_{P-C}$  = 2.6 Hz, butadiene), 104.8 (s, Cp), 96.9 (s, butadiene), 55.3 (d,  $J_{P-C}$  = 6.4 Hz, butadiene), 40.0 (d,  $J_{P-C}$  = 13 Hz, butadiene), 28.3 (dd, butadiene), 24.6, 14.5, 13.3 (m, dmpe), 10.4 (d,  $J_{P-C}$  = 16 Hz, butadiene).

**Method b (Reaction of 3 with Butadiene).** In a flask connected with a Toepler pump system, a THF solution (10 mL) of 3 (0.095 g, 0.24 mmol) was reacted with 1 equiv of butadiene at room temperature. The color suddenly changed to orange, and a vigorous evolution of 2 equiv of CO was observed (Toepler pump, GC). The resulting solution was evaporated to dryness, and the residual yellow solid was identified by IR and NMR spectroscopy (see above).

**Reaction of 3 with Ethylene.** In a flask connected with a Toepler pump system, a THF solution (10 mL) of 3 (0.2 g, 0.5 mmol) was reacted with 2 equiv of ethylene. The color changed from deep red to pale yellow, and evolution of 1 equiv of CO (GC) was observed. The remaining solution was frozen at -196 °C, added with 2 equiv of anhydrous HCl, and warmed at room temperature. The solution separated solid material, and no gas evolution was observed at the Toepler pump. All the volatiles were vacuum-transferred and analyzed by GC-MS, showing cyclopentanol as the major organic product (75%). The residual solid was isolated and analyzed to be pure  $[CpZrCl_3(dmpe)]$ . Anal. Calcd for  $C_{11}H_{21}P_2Cl_3Zr$  (Found): C, 31.99 (31.86); H, 5.09 (5.00); Cl, 25.82 (25.37); P, 15.03 (14.98); Zr, 22.06 (22.16).  $^1H$  NMR (350 MHz,  $py-d_5$ , 25 °C):  $\delta$  6.65 (d,  $J_{P-H}$  = 1.7 Hz, 5 H, Cp), 1.79 (pseudo d, 4 H,  $CH_2$  dmpe), 1.50 (d,  $J_{P-H}$  = 7.8 Hz, 6 H,  $CH_3$  dmpe), 1.39 (d,  $J_{P-H}$  = 7.8 Hz, 6 H,  $CH_3$  dmpe).

Attempts to isolate the intermediate species led to a yellow amorphous solid that gave analytical results consistent with the formulation  $CpZr[\eta^2-C(O)CH_2CH_2CH_2]Cl^{1/2}(dmpe)$ . The NMR spectra showed very broad peaks probably due to fluxional behavior in the range -50 to +50 °C.

**X-ray Crystallography.** Selected crystals of 3 were mounted in capillaries and transferred onto a Nicolet R3m diffractometer. The crystal quality was tested by  $\omega$  scans on some data points. Many crystals were rejected due to bad features shown on the peak scans. Finally a "best" crystal was chosen although shoulder peaks can still be seen on some scans. Twenty-five centered reflections gave a monoclinic cell. Crystal data and details of the parameters associated with data collection and structure refinement are given in Table I. The structure amplitudes were obtained after the empirical absorption correction and the usual Lorentz and polarization correction. Data reduction, structure solution, and refinement were carried out on a Data General NOVA 4 computer using a SHELXTL program system. The Zr

Table I. Crystal Data and Structural Analysis results for 3

(A) Crystal Data	
formula	$C_{13}H_{21}O_2P_2ClZr$
fw	397.93
cryst system	monoclinic
space group	$P2_1/a$
Z, no. of formulas per unit cell	4
cell parameters	
a (Å)	15.664 (10)
b (Å)	7.208 (3)
c (Å)	16.869 (9)
$\beta$ (deg)	112.89 (4)
V (Å <sup>3</sup> )	1754 (2)
$d_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.51
cryst size (mm)	0.11 × 0.31 × 0.45
$\mu_{\text{calcd}}$ (cm <sup>-1</sup> ), absorp. coeff	9.4
F (000)	808
(B) Data Measurement Parameters and Analysis Results (298 K)	
diffractometer type	Nicolet R3m
radiatn	$Mo$ ( $\lambda$ = 0.71073 Å)
scan type	$\omega$ scan
scan speed (deg min <sup>-1</sup> )	3.91–29.3
scan width (deg)	1.0
(sin $\theta$ )/ $\lambda$ limit (Å <sup>-1</sup> )	0.54 ( $2\theta_{\text{max}}$ = 45°)
range of hkl	(+h, +k, ±l)
no. of reflectns mesd	2616
no. of unique reflectns	2286
$N_o$ , no. of reflectns used in analysis	1691
[I > 3 $\sigma$ (I)]	
$N_v$ , no. of variable parameters	172
final agreement factor	
$R$ ( $= \sum   F_o  -  F_c   / \sum  F_o $ )	0.062
$R_w$ ( $= [\sum ( F_o  -  F_c )^2 / \sum w F_o ^2]^{1/2}$ )	0.074
goodness-of-fit indicators (GOF = $[\sum w( F_o  -  F_c )^2 / (N_o - N_v)^2]^{1/2}$ )	1.497
largest shift/esd, final cycle	0.004

<sup>a</sup> For  $R_w$  and GOF,  $w = 1/[\sigma^2(F_o) + 0.0016(F_o)^2]$ .

position was determined by the Patterson method. The P and Cl atoms were located from the difference Fourier map after refining the Zr position. Subsequent map based on these atomic positions revealed all the non-hydrogen atoms. Anisotropic refinements were applied to all the non-hydrogen atoms. Most hydrogen positions can be found from difference Fourier map. Their positions were calculated on the basis of idealized geometry at the carbon atoms and  $d_{C-H} = 0.96$  Å. Each hydrogen atom was assigned with a temperature factor ( $U$ ) 1.2 times of that of the carbon attached. The final residuals for 172 variables refined against the 1691 data for which  $I > 3\sigma(I)$  were  $R = 0.062$ ,  $R_w = 0.074$ , and  $GOF = 1.497$ . The quantity minimized by the least-squares program was  $w = \sum (|F_o| - |F_c|)^2$ , where  $w$  is the weight of a given observation. The  $g$  factor, used to reduce the weight of the intense reflections, was set to 0.0016 throughout the refinement. In the final least-squares refinement all shifts are less than 0.004 esd. However, four large false peaks (0.84–1.60 e/Å<sup>3</sup>) can still be found near the Zr atom within 1.14 Å. Their occurrence is presumably due to insufficient amount of high-angle data in the data set. Scattering factors for neutral atoms were used. Anomalous scattering corrections were included in all structure factor calculations.<sup>12</sup> The positional and equivalent thermal parameters of non-hydrogen atoms are given in Table II. Some selected bond distances and angles are given in Table III. Anisotropic thermal parameters, the positions of the hydrogen atoms, and a listing of the values of  $F_o$  and  $F_c$  are available as supplementary material.

**Electrochemical Measurements.** Cyclic voltammetry and pulse (normal and differential) voltammetry experiments were carried out with a PAR 174A polarographic analyzer, driven by a PAR 175 universal programmer. Internal resistance was compensated by positive feedback. All the measurements were performed in a one-compartment cell placed in a drybox, equipped with a Pt wire working electrode and a Pt coil auxiliary electrode.

(12) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) p 99, (b) p 149.

**Table II. Atom Coordinates ( $\times 10^4$ ) and Temperature Factors ( $\text{\AA}^2 \times 10^3$ )**

atom	x	y	z	$U_{eq}^a$
Zr	3587 (1)	6097 (1)	7391 (1)	34 (1)
Cl	2628 (2)	8780 (3)	7672 (2)	48 (1)
P(1)	1785 (2)	4918 (3)	6629 (1)	38 (1)
P(2)	3144 (2)	4675 (4)	8696 (1)	42 (1)
O(1)	5181 (5)	9017 (11)	8707 (4)	71 (3)
O(2)	3262 (7)	9143 (11)	5791 (5)	93 (5)
C(1)	4651 (6)	8012 (14)	8259 (6)	46 (4)
C(2)	3382 (7)	8068 (14)	6323 (6)	55 (4)
C(3)	3832 (8)	3609 (15)	6483 (7)	69 (5)
C(4)	4014 (7)	2860 (13)	7278 (6)	54 (4)
C(5)	4812 (7)	3719 (15)	7853 (7)	67 (5)
C(6)	5102 (7)	5005 (15)	7365 (9)	82 (6)
C(7)	4489 (8)	4887 (17)	6546 (8)	85 (7)
C(8)	956 (6)	6459 (13)	5846 (6)	55 (4)
C(9)	1481 (6)	2678 (12)	6100 (6)	54 (4)
C(10)	1321 (5)	4753 (14)	7471 (5)	46 (4)
C(11)	1969 (5)	3659 (13)	8243 (5)	48 (4)
C(12)	3077 (8)	6302 (16)	9502 (6)	74 (5)
C(13)	3803 (7)	2758 (15)	9378 (6)	69 (5)

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

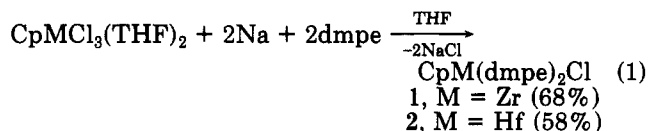
**Table III. Selected Bond Distances and Angles**

Distances, \AA			
Zr-Cl	2.602 (3)	Zr-P(1)	2.742 (3)
Zr-P(2)	2.750 (3)	Zr-C(1)	2.221 (9)
Zr-C(2)	2.218 (10)	C(1)-O(1)	1.139 (11)
C(2)-O(2)	1.145 (13)	Zr-Cp(centroid)	2.200 (2)
Angles, deg			
Cl-Zr-P(1)	75.8 (1)	Cl-Zr-P(2)	77.8 (1)
P(1)-Zr-P(2)	74.1 (1)	Cl-Zr-C(1)	75.9 (3)
P(1)-Zr-C(1)	150.9 (3)	P(2)-Zr-C(1)	93.6 (3)
Cl-Zr-C(2)	76.1 (3)	P(1)-Zr-C(2)	91.2 (3)
P(2)-Zr-C(2)	152.5 (3)	C(1)-Zr-C(2)	88.4 (3)
Zr-C(2)-O(2)	176.9 (10)	Zr-C(1)-O(1)	178.4 (9)

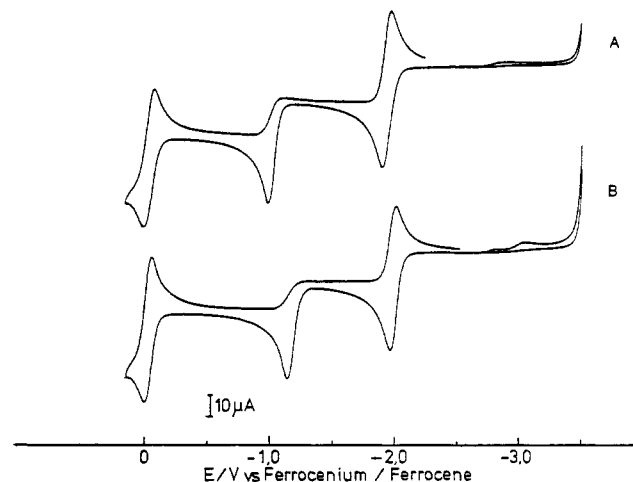
A silver wire (placed directly in the solution and positioned as close as possible to the working electrode by using a Luggin capillary) served as pseudoreference electrode. Calibration was achieved by adding after the measurements some ferrocene or cobaltocene to the solution and repeating the measurements.<sup>13</sup> No significant difference in the measurements was observed by using ferrocene as an internal standard. All potentials were referenced against the ferrocene/ferrocenium couple ( $E^\circ = 0.400$  V vs NHE).<sup>13b</sup> Voltammograms were obtained in THF with scan rates between 50 and 800 mV/s for cyclic voltammetry and 5 mV/s for pulse voltammetry. Solutions were 1–2 mM in electroactive material and 0.1 M in supporting electrolyte ( $\text{Bu}_4\text{NPF}_6$ ).

### Discussion and Results

According to eq 1, room-temperature reduction of  $\text{CpMCl}_3(\text{THF})_2$  ( $M = \text{Zr}, \text{Hf}$ ) with 2 equiv of Na in the presence of a slight excess of dmpe led to the formation of deep orange-brown solutions from which after workup,  $\text{CpM}(\text{dmpe})_2\text{Cl}$  could be isolated in good yield. Sur-



prisingly, a large excess of reducing agent eventually present in the reaction mixture did not affect the yield even after long reaction periods (30 days), and any attempt to further reduce the metal to lower oxidation states was unsuccessful. To clarify this point, we have run cyclic



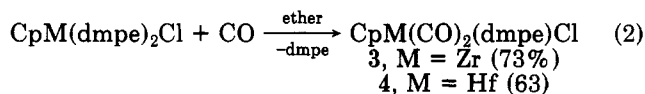
**Figure 1.** Cyclic voltammogram of 1 (curve A) and 2 (curve B) in THF ( $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6$ ) vs (ferrocene/ferrocenium). Scan rate: 50 mV/s.

voltammetry experiments on complexes 1 and 2 with respect to both the oxidation and reduction cycles.

The cyclic voltammograms (Figure 1) did not show any significant reduction, even after the potential was lowered to values where the electrolyte decomposes ( $E = -3.50$  V). This surprising inertness of 1 and 2 toward the reduction reaction is probably responsible for the absence of unwanted byproducts. This makes Na a "selective" reducing agent ( $E_{1/2} = -2.71$  V versus NHE) to allow the metal (Zr, Hf) to achieve the oxidation state (II). However, one-electron oxidations (as indicated by differential pulse voltammetry experiments) to Zr(III) and Hf(III) species were reversible (until scan rates as low as 50 mV/s,  $E_{1/2} = -1.89$  for 1 and  $-1.95$  for 2), while further oxidations to Zr(IV) and Hf(IV) species were irreversible ( $E_p = -0.96$  and  $-1.12$ , respectively).

It is interesting at this point to remember that the reduction to the Zr(0) species can be easily achieved in presence of other stabilizing ligands (carbon monoxide<sup>3</sup> or butadiene/dmpe<sup>4</sup>). Furthermore any attempt to use either small or sterically demanding phosphines ( $\text{PMe}_3$ ,  $\text{PEt}_3$ ,  $\text{PCy}_3$ ) as well as the permethylation of the Cp ring ( $\text{C}_5\text{Me}_5$ ) led only to intractable materials. This indicates that the simultaneous utilization of dmpe and Cp fulfills the steric and electronic requirements for Zr and Hf (no identifiable products have been obtained in the case of Ti) to form stable compounds.

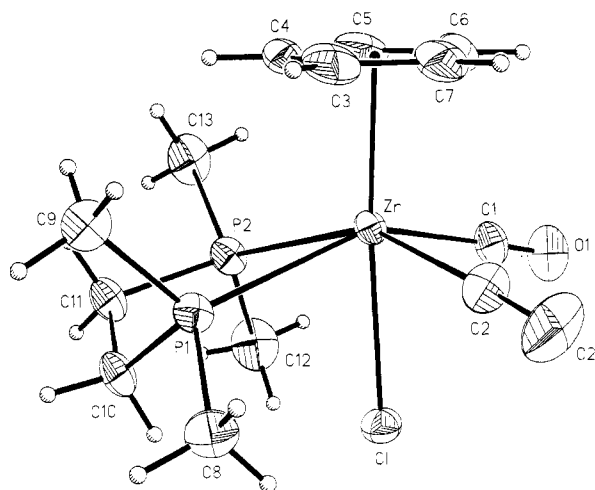
In spite of their high steric shielding and the 18-electron configuration, 1 and 2 show a great tendency to dissociate one of the two coordinated dmpe ligands, providing a mild condition pathway to several ligand-substitution reactions. Smooth reactions of 1 and 2 with CO at room temperature and 1 atm form the corresponding halocarbonyl derivatives  $\text{CpM}(\text{CO})_2(\text{dmpe})\text{Cl}$  [ $M = \text{Zr}$  (3),  $\text{Hf}$  (4)] in good yield.



Complexes 3 and 4 are indefinitely stable at room temperature in both the solid state and solution (under CO atmosphere) but decompose completely within 1 h at higher temperatures ( $80^\circ\text{C}$ ).

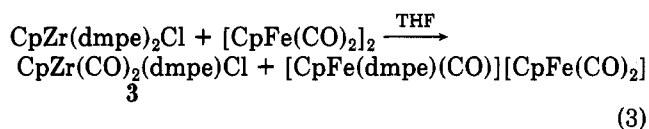
A possible alternative carbonylation reaction of 1 is the CO abstraction from a transition-metal carbonyl complex. For example, a fast reaction takes place between 1 and  $[\text{CpFe}(\text{CO})_2]_2$  with formation of a mixture of products. The formation of 3 is revealed by the presence of the

(13) (a) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* 1984, 56, 461. (b) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* 1980, 19, 2854.



**Figure 2.** ORTEP drawing of  $\text{CpZr}(\text{CO})_2(\text{dmpe})\text{Cl}$  showing the labeling scheme.

characteristic absorptions in the IR spectrum, while the insoluble  $[\text{CpFe}(\text{dmpe})(\text{CO})][\text{CpFe}(\text{CO})_2]^{14}$  can be isolated in good yield as bright red crystals. The structure of **3**



determined by X-ray diffraction analysis reveals that the crystal is composed of discrete molecules of  $\text{CpZr}(\text{CO})_2(\text{dmpe})\text{Cl}$  (Figure 2). The coordination around the metal can be described as slightly distorted octahedral with the Cp ring centroid occupying the vertex trans to the chlorine atom. The four equatorial positions of the octahedron are occupied by the phosphorus atoms of dmpe and two molecules of CO. The coordination geometry is significantly different from the closely related hafnium carbonyl derivative reported by Ellis.<sup>6</sup> In  $\text{Me}_5\text{C}_5\text{Hf}(\text{CO})_2(\text{dmpe})\text{Cl}$  the chelating phosphine is equatorially-axially arranged, probably the result of increased steric hindrance introduced by the permethylation of the Cp ring. The Zr-Cp centroid distance [2.200 (2) Å] falls in the range expected for this moiety.<sup>9</sup> The halide-metal distance [2.602 (3) Å] is rather long<sup>15</sup> and comparable to that of  $\text{CpZr}(\text{dmpe})_2\text{Cl}$ ,<sup>9</sup> suggesting that electronic effects instead of steric hindrance are responsible for such elongation. No significant deviation from the linearity is observed for the vector Cl-Zr-Cp(centroid). The angle subtended at Zr by the two carbon monoxide molecules [88.4 (3)°] compares well with the angles observed for  $\text{Cp}_2\text{Zr}(\text{CO})_2$  and  $\text{Cp}^*\text{Zr}(\text{CO})_2$ , while the Zr-C(CO) distances [2.221 (9) and 2.218 (10) Å] are slightly longer [ $\text{Cp}_2\text{Zr}(\text{CO})_2$ , 2.187 Å;  $\text{Cp}^*\text{Zr}(\text{CO})_2$ , 2.145 Å]. All the other bond distances and angles are normal.

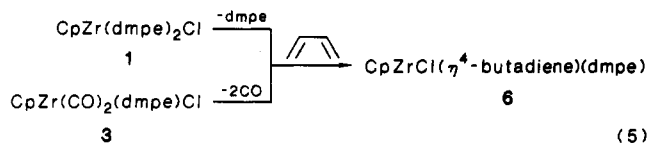
The spectroscopic and analytical data for **3** and **4** are consistent with the solid-state structure. The  $^1\text{H}$  NMR spectrum shows splitting of the Cp ring signal due to coupling with the phosphorus ( $t$ ,  $J_{\text{P-H}} = 1.5$  Hz). No resonance has been observed in the  $^{13}\text{C}$  NMR spectrum in the range 400–100 ppm attributable to the coordinated CO. However, the carbonyl stretching frequencies for both the  $A_1$  and  $B_1$  modes fall within the usual range in the IR spectrum [1955, 1885  $\text{cm}^{-1}$  for **3** and 1950, 1870  $\text{cm}^{-1}$  for

**4**.<sup>2a</sup> The failure to observe the CO resonance in the  $^{13}\text{C}$  NMR spectrum suggests the presence of a fast CO exchange in solution. In agreement with this hypothesis, the treatment of a concentrated solution of **3** and **4** with an excess of 90%  $^{13}\text{C}$  at 1 atm resulted in a quantitative disappearance of the two carbonylic resonances in the IR spectrum and the simultaneous formation of two new absorptions [1925, 1845  $\text{cm}^{-1}$  for **3** and 1940, 1840  $\text{cm}^{-1}$  for **4**) within minutes. After  $^{13}\text{C}$  enrichment an intense resonance can be finally observed in the  $^{13}\text{C}$  NMR spectrum at 249.8 and 251.9 ppm for **3** and **4**, respectively. Further evidence for the dynamic behavior of the coordinated CO in solution is provided by the reactivity of **3**. A slow and irreversible ligand exchange reaction occurs between **1** and **3** forming the highly insoluble  $[\text{CpZr}(\text{CO})(\text{dmpe})\text{Cl}]_2(\text{dmpe})$  (**5**) as light green pyrophoric crystals. The formation of **5**, which can be competitive

$$\text{CpZr}(\text{dmpe})_2\text{Cl} + \text{CpZr}(\text{CO})_2(\text{dmpe})\text{Cl} \rightarrow \text{CpZr}(\text{CO})(\text{dmpe})\text{Cl} + [\text{CpZr}(\text{CO})(\text{dmpe})\text{Cl}]_2(\text{dmpe}) \quad (4)$$

with the synthesis of  $\text{CpZr}(\text{CO})_2(\text{dmpe})\text{Cl}$ , is highly dependent on the concentration of  $\text{CpZr}(\text{dmpe})_2\text{Cl}$  in solution. In fact when a saturated solution of **1** is allowed to react with CO, **5** is formed almost quantitatively and the occasionally present red crystals of **3** are easily removed by washing with THF. Conversely, reaction **4** can be completely avoided when a rather diluted solution of  $\text{CpZr}(\text{dmpe})_2\text{Cl}$  (e.g. 1 g/300 mL) is used in the carbonylation reaction. Finally, when a THF solution of **3** is exposed to vacuum, complex **5** is formed in significant amounts within 30 min. Satisfactory analytical and IR data have been obtained for **5**. Its insolubility in the most common organic solvents (it dissolves only in pyridine with decomposition) prevents any NMR investigation on its structure as well as the growth of a single crystal suitable for X-ray diffraction analysis.

As can be expected from its highly dynamic behavior in solution,  $\text{CpM}(\text{CO})_2(\text{dmpe})\text{Cl}$  ( $M = \text{Zr}, \text{Hf}$ ) undergoes a number of easy ligand exchange reactions. In a first approach we have focused attention on the reactivity with olefins. Reaction of **3** with butadiene under mild conditions led to a vigorous and quantitative evolution of CO with formation of  $\text{CpZr}(\eta^4\text{-butadiene})(\text{dmpe})\text{Cl}$  (**6**) in good yield (eq 5). As expected, complex **6** can also be obtained



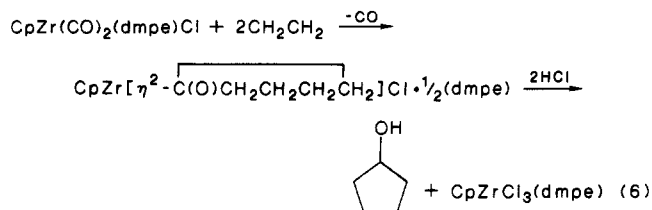
by easy phosphine displacement with butadiene on complex **1**. It is noteworthy that in the bis(cyclopentadienyl) systems it is the butadiene ligand which is irreversibly displaced by CO and not vice versa.<sup>16</sup> The 18-electron configuration of complex **6** inhibits the deoxygenation of CO otherwise observed in the case of the electronically unsaturated species  $\text{Cp}^*\text{M}(\eta^4\text{-butadiene})\text{Cl}$  ( $M = \text{Zr}, \text{Hf}$ ).<sup>8a</sup>

A vigorous reaction occurs between **3** and ethylene (room temperature, 1 atm) with evolution of only 1 equiv of CO and formation of a pale yellow solid, probably  $\text{CpZr}[\eta^2\text{-}\overline{\text{C}}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2]\text{Cl}^{1/2}(\text{dmpe})$  (eq 6). After chemical degradation with 2 equiv of anhydrous HCl, cyclopentanol has been recovered in 75% yield. The absence of hydrogen (even in traces) excludes the formation of the

(14) The IR resonances are quite similar but not identical with the literature data: King, R. B.; Pannell, K. H.; Eggers, C. A.; Houk, L. W. *Inorg. Chem.* 1968, 7, 2353.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175.

(16) Thomas, J. L.; Brown, K. T. *J. Organomet. Chem.* 1976, 111, 297.



enolate-hydride complex  $[\text{CpZrClH}(\text{OC}=\text{CHCH}_2\text{CH}_2\text{CH}_2)] \cdot \frac{1}{2}(\text{dmpe})$  which could be expected on the basis of a similar cocyclization, obtained by prolonged photolysis of  $\text{Cp}^*\text{Zr}(\text{CO})_2$  solutions under an ethylene atmosphere.<sup>17</sup> Reaction 6 seems specific for ethylene, and attempts to react **3** with differently substituted olefins (propylene, isobutene, *cis*-2-butene, 2,3-dimethyl-2-butene) were unsuccessful.

(17) Manriquez, J. M.; McAlister, A. M.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* 1978, 100, 2716.

A further investigation on the reactivity of complexes **3** and **4** is included in our continuing studies on these systems.

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**Registry No.** 1, 114238-07-2; 2, 116148-79-9; 3, 116129-35-2; 3-<sup>13</sup>C<sub>2</sub>, 116129-39-6; 4, 116129-36-3; 4-<sup>3</sup>C<sub>2</sub>, 116129-40-9; 5, 116129-37-4; 6, 115227-38-8; CpZrCl<sub>3</sub>(THF)<sub>2</sub>, 114238-08-3; dmpe, 23936-60-9; CpHfCl<sub>3</sub>(THF)<sub>2</sub>, 66349-82-4; [CpFe(CO)<sub>2</sub>]<sub>2</sub>, 12154-95-9; [CpFe(dmpe)(CO)][CpFe(CO)<sub>2</sub>], 116129-38-5; CpZrCl<sub>3</sub>(dmpe), 115227-37-7; butadiene, 106-99-0; ethylene, 74-85-1; cyclopentanol, 96-41-3.

**Supplementary Material Available:** Tables of anisotropic thermal parameters, atomic coordinates for the hydrogen atoms, and bond lengths and angles (4 pages); a listing of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

## Preparation and Properties of New Methyl(alkoxo)- and Methyl(thiolato)nickel and Methyl(alkoxo)- and Methyl(thiolato)palladium Complexes. CO and CS<sub>2</sub> Insertion into the Alkoxo-Palladium Bond

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Reactions of fluorinated alcohols ( $\text{HOCH}(\text{CF}_3)_2$ ,  $\text{HOCH}_2\text{CF}_3$ , and  $\text{HOCH}(\text{CF}_3)\text{C}_6\text{H}_5$ ) or aromatic thiols ( $\text{HSC}_6\text{H}_5$  and  $\text{HSC}_6\text{H}_4\text{-}p\text{-CH}_3$ ) with dialkylnickel and -palladium complexes ( $\text{NiMe}_2(\text{bpy})$ ,  $\text{NiEt}_2(\text{bpy})$  ( $\text{bpy} = 2,2'$ -bipyridine),  $\text{NiMe}_2(\text{dpe})$ , and  $\text{PdMe}_2(\text{dpe})$  ( $\text{dpe} = 1,2$ -bis(diphenylphosphino)ethane)) give the corresponding monoalkyl complexes with an alkoxo or a thiolato ligand ( $\text{NiMe}(\text{OR})(\text{bpy})$ ,  $\text{NiEt}(\text{OR})(\text{bpy})$ ,  $\text{MMe}(\text{OR})(\text{dpe})$ , and  $\text{MMe}(\text{SAr})(\text{dpe})$  ( $\text{M} = \text{Ni}, \text{Pd}$ ;  $\text{R} = \text{CH}(\text{CF}_3)_2$ ,  $\text{CH}_2\text{CF}_3$ ,  $\text{CH}(\text{CF}_3)\text{C}_6\text{H}_5$ ). These complexes have been characterized by elemental analysis and NMR ( $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}\{^1\text{H}\}$ ) spectroscopy. The methyl(alkoxo)nickel(II) and -palladium(II) complexes thus obtained react with carbon monoxide at normal pressure to give carboxylic esters in high yields. Reaction of carbon monoxide with  $\text{NiMe}(\text{SAr})(\text{dpe})$  ( $\text{Ar} = \text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$ ) also gives the corresponding carbothioic esters in good yields, while  $\text{PdMe}(\text{SPh})(\text{dpe})$  is unreactive with carbon monoxide under similar conditions. The  $^{31}\text{P}\{^1\text{H}\}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the reaction mixture of  $\text{PdMe}(\text{OCH}(\text{CF}_3)_2)(\text{dpe})$  with an equimolar amount of  $^{13}\text{CO}$  at  $-60^\circ\text{C}$  show the formation of  $\text{PdMe}(\text{COOCH}(\text{CF}_3)_2)(\text{dpe})$  produced through insertion of the carbon monoxide into the Pd-O bond. When the reaction temperature is raised to  $-20^\circ\text{C}$ , this alkoxycarbonyl complex undergoes reductive elimination to give 1,1,1,3,3,3-hexafluoro-2-propyl acetate. The reaction is accompanied by simultaneous decarbonylation of the alkoxycarbonyl ligand to regenerate  $\text{PdMe}(\text{OCH}(\text{CF}_3)_2)(\text{dpe})$ . The reaction of  $\text{PdMe}(\text{OCH}(\text{CF}_3)\text{Ph})(\text{dpe})$  with carbon disulfide gives an isolable palladium complex,  $\text{PdMe}(\text{SCSOCH}(\text{CF}_3)\text{Ph})(\text{dpe})$ , formed by insertion of  $\text{CS}_2$  into the Pd-O bond, while  $\text{PdMe}(\text{SPh})(\text{dpe})$  is unreactive with  $\text{CS}_2$ .

### Introduction

In comparison with alkoxides of non-transition-metal elements and early transition metals,<sup>1</sup> examples of isolated late transition metals are still limited.<sup>2-10</sup> The chemistry

of these late-transition-metal alkoxides merits study in its own right and also in view of the important roles these

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