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Highly Reduced Organometallics. 32. Cyclopentadienyl- and Pentamethylcyclopentadienyl-Substituted Heptacarbonyls of Zerovalent Titanium, Zirconium, and Hafnium, $[(C_5R_5)M(CO)_4]^-$, and Derivatives Thereof[1]

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Reduction of $(C_5R_5)MCl_3$ (R = H, Me; M = Ti, Zr, Hf) by alkali-metal naphthalenides at low temperature followed by carbonylation at atmospheric pressure provided 40–75% isolated yields of $[(C_5R_5)Ti(CO)_4]^-$ as Et_4N^+ salts and 15–40% isolated yields of the corresponding zirconium and hafnium salts. Also, $[(C_5Me_5)Hf(CO)_4]^-$ was isolated in 40–50% yields as pure $[K(cryptand\ 2.2.2)]^+$ or $[K(15\text{-crown-}5)_2]^+$ salts. Except for unsolvated $Na[(C_5H_5)Ti(CO)_4]$, which proved to be *explosive* at room temperature, the other compounds were quite thermally stable materials and were easily handled in the absence of oxygen and moisture. Interactions of the carbonyltitanates and -zirconates with Ph_3SnCl and Ph_3PAuCl provided what are believed to be the first series of heterobimetallic complexes to contain tin and gold atoms bound to Ti(II) and Zr(II). Although the zirconium complexes $(C_5R_5)Zr(CO)_4E$ (E = $SnPh_3$, $AuPPh_3$) proved to be too thermally unstable for isolation, their spectral properties were very similar to those of the significantly more robust titanium analogs. Reaction of $[(C_5Me_5)Ti(CO)_4]^-$ with I_2 provided the very thermally unstable $(C_5Me_5)Ti(CO)_4I$, which in turn gave a more stable dmpe derivative, $(C_5Me_5)Ti(CO)_2(dmpe)I$ (dmpe = 1,2-bis(dimethylphosphino)ethane). The IR and NMR spectral properties of the latter substance are compared to those of $(C_5Me_5)Zr(CO)_2(dmpe)Cl$ and $(C_5Me_5)Hf(CO)_2(dmpe)Cl$, which are believed to have quite similar half-sandwich molecular structures. The divalent Zr and Hf carbonyl chlorides were obtained by the reductive carbonylation of the corresponding $(C_5Me_5)MCl_3$ in the presence of dmpe. Of the three halo–carbonyl–dmpe complexes described herein, only the hafnium complex was sufficiently robust to be isolated as a pure substance.

Introduction

Our development of a successful atmospheric-pressure reductive carbonylation route to the previously almost inaccessible hexacarbonylmetalates(1–), $[M(CO)_6]^-$, of niobium and tantalum[2] suggested that zero- or lower-valent carbonyls of titanium, zirconium, and hafnium might also be prepared by employing similar procedures. We were particularly excited about the prospects of securing carbonylmetalates of these elements, since none had been reported previously in the scientific literature.[3–5] The relatively high thermal stabilities of group 5 half-sandwich complexes of the general formula $(C_5R_5)M(CO)_4$ (R = H, CH_3; M = V, Nb, Ta)[6] suggested that the isoelectronic group 4 monoanions were suitable targets. In this paper the first full account of the syntheses and properties of these compounds is presented, along with that of a related divalent hafnium complex, $(C_5Me_5)Hf(CO)_2(dmpe)Cl$. X-ray structural characterizations of the latter substance and $[Ph_4As][(C_5H_5)Ti(CO)_4]$ have been previously reported.[7] A portion of the research presented herein has appeared previously in communication form.[7]

Experimental Section

General Procedures and Starting Materials. Operations were performed under an atmosphere of nitrogen, argon, or carbon monoxide further purified by passage through columns of activated BASF catalyst and molecular sieves. All connections involving the gas purification systems were made of glass, metal, or other materials which are impermeable to air.[8] In addition, the carbon monoxide was passed through a column of Ascarite to remove carbon dioxide. Solutions were transferred via stainless steel cannulas whenever possible. Otherwise, syringes or standard Schlenk techniques[9] were used in conjunction with a double-manifold vacuum line.[8] Previously published comments concerning our reductive carbonylation procedures should be

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(4) Claims for the synthesis of alkali-metal salts of $[Cp^{‡}M(CO)_4]^-$ ($Cp^{‡}$ = various substituted cyclopentadienyl groups; M = Ti, Zr, Hf) from "the reaction of the appropriate inorganic metal carbonyl with the cyclopentadienyl alkali metal compound" in *refluxing* THF were the basis of a 1962 patent issued to Ethyl Corp. (U.S. Patent 3069445). No supporting data were provided for any of these formulations. Since "inorganic carbonyls" of all three group 4 elements were not established before a 1988 report on the synthesis and characterization of $[MeC(CH_2PMe_2)_3]M(CO)_4$,[5] these early claims are without merit.

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consulted prior to attempting these syntheses.[10] Solvents were dried, freed of oxygen, and distilled under argon before use. All reactants and solvents were obtained from commercial sources except for the following substances, which were prepared according to previously established procedures: $Me_2PCH_2CH_2PMe_2$,[11] $C_5H_5TiCl_3$,[12] $C_5H_5ZrCl_3$,[13] $C_5H_5HfCl_3{\cdot}2THF$[14] (note that the $(C_5H_5)_2Mg$ used in the preparation of the preceding hafnium complex is best obtained by the method of Lappert et al.[15]), $C_5Me_5TiCl_3$,[16] and $C_5Me_5MCl_3$ (M = Zr, Hf).[17] More recent syntheses for some of these precursors became available after this research was completed.[18] Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer in 0.1-mm sealed NaCl or CaF_2 cells fitted with three-way Nylon stopcocks (Ace Glass 5851) to permit filling outside of the drybox. Nujol (mineral oil) mulls of air-sensitive compounds were prepared in a Vacuum Atmospheres Corp. drybox filled with nitrogen. NMR samples were sealed into 5-mm tubes (Wilmad 505-PS9) and were run on Nicolet NT-300 WB and IBM NR-200 AF and NR-300 AF spectrometers. Carbon spectra were acquired with a 45° pulse and a 4-s delay between pulses to aid in the detection of carbonyl ^{13}C resonances. Melting points are uncorrected and were obtained in sealed capillaries on a Thomas-Hoover Unimelt apparatus. Microanalyses were carried out by H. Malissa and G. Reuter Analtische Laborotorien, Engelskirchen, West Germany. In the experimental section C_5H_5 and C_5Me_5 are often designated by Cp and Cp*, respectively. Also, the following abbreviations are employed: THF = tetrahydrofuran, DMSO = dimethyl sulfoxide, DME = 1,2-dimethoxyethane, 15-C-5 = 15-crown-5 = 1,4,7,10,-13-pentaoxacyclopentadecane, crypt 2.2.2 = cryptand 2.2.2 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane. Celite = filter aid or diatomaceous earth.

$[Et_4N][CpTi(CO)_4]$ (1). Naphthalene (6.13 g, 47.9 mmol) was dissolved in 150 mL of THF, cooled to 0 °C, and added to a stirred suspension of sodium metal (1.65 g, 71.8 mmol) in 150 mL of THF. After it was stirred for 4 h, the green $Na-C_{10}H_8$ solution was transferred to a Morton flask equipped with a mechanical stirrer. $CpTiCl_3$ (2.50 g, 11.4 mmol) was dissolved in 200 mL of THF, and this solution was cooled to −78 °C and added to the rapidly stirred and precooled (−78 °C) $Na-C_{10}H_8$ slurry solution under an Ar atmosphere. The solution turned deep orange-red upon completion of the addition. After 5 min, the reaction vessel was evacuated and CO (~1 atm pressure) was admitted. The reaction mixture immediately turned dark red. After the temperature was raised slowly to room temperature, the IR spectrum of the deep red solution showed ν(CO) bands at 1924 (m), 1821 (w, sh), 1791 (s), and 1723 (m, br) cm^{-1} due to $[Na(THF)_x][CpTi(CO)_4]$. After settling for 1 h, the reaction mixture was filtered through prewashed Celite and the filter cake was rinsed until colorless with THF. The metathesizing salt, $[Et_4N]Br$ (2.40 g, 11.4 mmol), was added to the filtered solution using a bent Schlenk tube. The slurry was stirred for 24 h and filtered through a medium-porosity frit. The solvent was removed from the solution on a rotary evaporator in vacuo at 30–50 °C. The resulting red-violet solid was washed with 3 × 80 mL of pentane and dried in vacuo. By this procedure, 1.90 g (47%) of $[Et_4N][CpTi(CO)_4]$ was obtained. Similar scale reactions typically provide 40–50% yields. Increased yields of up to 70% have been obtained when reductions are done in the presence of excess $C_{10}H_8$. An analytical sample of $[Et_4N][CpTi(CO)_4]$ was obtained by washing the solid with 10 mL of ethanol (which removes trace amounts of $[Et_4N]Br$) followed by 3 × 10 mL of diethyl ether. Anal. Calcd for $C_{17}H_{25}NO_4Ti$: C, 57.47; H, 7.09; N, 3.94. Found: C, 57.29; H, 7.13; N, 4.01.

Crystalline 1 can be handled briefly in air unless it is in the form of a very finely divided solid. However, solutions are extremely air sensitive. When small amounts of air are admitted to solutions of 1, no oxidized titanium carbonyls could be observed by IR spectra at room temperature; i.e., only diminished amounts of $[CpTi(CO)_4]^-$ were seen. IR (Nujol, ν(CO)): 1919 (m), 1753 (s, br) cm^{-1}. NMR (dimethyl-d_6 sulfoxide): ^1H δ 5.05 (s, C_5H_5), 3.20 (q, CH_2 of Et_4N^+), 1.15 (t, CH_3 of Et_4N^+) ppm; $^{13}C\{^1H\}$ δ 289 (s, CO), 93 (s, C_5H_5), 51 (s, CH_2 of Et_4N^+), 7 (s, CH_3 of Et_4N^+) ppm. 1 decomposed at 175–180 °C. Compound 1 is soluble and reasonably stable in a variety of polar solvents, including THF, acetone, and dimethyl sulfoxide but decomposes quickly at room temperature in CH_2Cl_2 and more slowly in CH_3CN. 1 is slightly soluble in anhydrous ethanol and may be recovered intact from this solvent but is unstable in the presence of H_2O.

Unsolvated $Na[CpTi(CO)_4]$ (2). *Caution*! 2 is a potentially explosive product.

Compound 1 (0.50 g, 1.4 mmol) was slurried in 35 mL of cold (0 °C) methanol and added to $Na[BPh_4]$ (0.48 g, 1.4 mmol) in 10 mL of methanol. The reaction mixture immediately turned cloudy. After the mixture was stirred 0.5 h, a white precipitate of $[Et_4N][BPh_4]$ was separated from the red solution by filtration. The methanol was then removed in vacuo to leave a red glass, which was dissolved in 130 mL of diethyl ether, filtered, and then dried. The resulting orange-red powder was transferred to the drybox. When we attempted to remove this solid from the reaction vessel by scraping with a metal spatula, it *violently decomposed*. A Nujol mull spectrum of some remaining pyrophoric red solid showed ν(CO) bands at 1914 (m), 1773 (m), 1727 (sh), 1708 (s), and 1678 (s) cm^{-1}. The solution spectrum of this solid in DME had ν(CO) bands at 1921 (m) and 1783 (s) cm^{-1} corresponding to $[Na(DME)_x][CpTi(CO)_4]$. The latter substance was obtained independently as a powdery red solid from a sodium naphthalenide reductive carbonylation of $CpTiCl_3$ carried out in 1,2-dimethoxyethane. Elemental analyses obtained for this DME solvate showed x varied from 2 to 3 but were not reproducible on independently prepared samples. Due to the explosive nature of unsolvated $Na[[CpTi(CO)_4]$, no attempts were made to obtain elemental analyses on this substance.

$[Ph_4As][CpTi(CO)_4]$ (3). Approximately 50 mL of THF was added to $[Na(DME)_x][CpTi(CO)_4]$ (vide supra; 1.00 g, ca. 2 mmol) and $[Ph_4As]Cl$ (0.81 g, 1.9 mmol), and the red slurry solution was stirred overnight at room temperature. The solution was filtered through a medium frit, which removed some dark solid. Removal of THF left a dark red oil which solidified after trituration with 35 mL of pentane. To ensure complete metathesis, 0.5 g of additional $[Ph_4As]Cl$ was dissolved in 40 mL of oxygen-free ethanol, and the solution was cooled to 0 °C and added to the red solid. Initially, the red solid dissolved, but after 5 min, red crystals precipitated from the solution. The crystals were collected on a medium frit, washed with 3 × 10 mL of ethanol, and dried in vacuo. IR (Nujol) ν(CO)): 1914 (m), 1762 (s) cm^{-1}. ^1H NMR (dimethyl-d_6 sulfoxide): δ 5.03 (s, C_5H_5), 7.59–8.07 (m, $(C_6H_5)_4As^+$) ppm. This sample was used in obtaining the single crystal for the X-ray structure determination of 3 reported previously.[7a] No-elemental analyses were obtained for this spectroscopically pure sample.

$CpTi(CO)_4(SnPh_3)$ (4). $[Et_4N][CpTi(CO)_4]$ (0.50 g, 1.4 mmol) and Ph_3SnCl (0.53 g, 1.3 mmol) were loaded into a reaction vessel, and cold CH_2Cl_2 (35 mL, −60 °C) was transferred via cannula onto the rapidly stirred solids (at −78 °C). When it was warmed to room temperature, the reaction mixture turned cloudy pink and the IR solution spectrum showed a broad ν(CO) band at 1960 cm^{-1}. The compound $CpTi(CO)_4(SnPh_3)$ was thermally unstable in solution, and filtration captured a dark uncharacterized solid. CH_2Cl_2 was removed from the pink solution to

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yield an orange tar, and to it was added about 35 mL of toluene. The toluene solution spectrum showed a ν(CO) band at 1961 cm^{-1}. The toluene solution was filtered, and a dark solid was removed whose IR Nujol mull spectrum showed ν(CO) bands at 1917 (m) and 1767 (s, br) cm^{-1}, corresponding to $[CpTi(CO)_4]^-$. The toluene was removed from the orange-pink solution to yield a glassy pink solid. A Nujol mull spectrum of this solid showed bands at 1982 (w, sh), 1958 (m), and 1933 (m) cm^{-1} due to $CpTi(CO)_4(SnPh_3)$. Attempts to recrystallize this compound from CH_2Cl_2 resulted in further decomposition to $[CpTi(CO)_4]^-$; therefore, a pure sample was not obtained. A solution of $CpTi(CO)_4(SnPh_3)$ was generated in situ by adding CD_2Cl_2 (−78 °C) to precooled $[Et_4N][CpTi(CO)_4]$ and Ph_3SnCl in an NMR tube, to obtain additional spectral data. ^{1}H NMR (−50 °C): δ 7.3–8.2 (m, $(C_6H_5)_3Sn$), 5.20 (s with satellites, J_{Sn-H} = 5.7 Hz, C_5H_5). $^{13}C\{^1H\}$ NMR (−70 °C): δ 246 (s, CO), 148–127 $(C_6H_5)_3Sn$, 92 (s, C_5H_5) ppm. Also observed in the above spectra were signals due to unreacted **1**.

$CpTi(CO)_4(AuPPh_3)$ (5). The reactants $[Et_4N][CpTi(CO)_4]$ (0.85 g, 2.4 mmol) and Ph_3PAuCl (1.2 g, 2.4 mmol) were loaded into a reaction vessel which was cooled to −78 °C, and 70 mL of precooled CH_2Cl_2 (−78 °C) was added via a cannula. The mixture immediately turned deep purple. An IR solution spectrum of this mixture showed ν(CO) bands at 1972 (w, sh) and 1884 (s, br) cm^{-1}. CH_2Cl_2 was removed to leave a purple solid. Approximately 30 mL of cold toluene was added, and the resulting purple solution was filtered at −25 °C using a jacketed low-temperature frit. To the cold solution was added 70 mL of cold pentane (−25 °C). The flask was slowly cooled to −65 °C and stored at this temperature for 24 h. The solid that formed was filtered from the solution onto a jacketed low-temperature frit at −70 °C and was washed with 60 mL of cold pentane. In this reaction, 0.31 g (19%) of pale purple crystalline **5**, of satisfactory purity, was isolated. Anal. Calcd for $C_{27}H_{20}AuO_4PTi$: C, 47.39; H, 2.95; P, 4.53. Found: C, 47.38; H, 3.19; P, 4.66. Compound **5** was air-sensitive and was soluble in toluene, CH_2Cl_2, and THF; however, at room temperature these solutions were unstable. IR (ν(CO)): THF, 1885 (s br) cm^{-1}; Nujol, 1865 (s br) cm^{-1}. NMR (toluene-d_8, −75 °C): ^{1}H, δ 4.83 (s, C_5H_5), 7.01–7.43 (m, $(C_6H_5)_3PAu$) ppm; $^{13}C\{^1H\}$ δ 270 (s, CO), 125–138 (s, C_6H_5), 93 (s, C_5H_5) ppm. The solid decomposed at 126–130 °C to a black solid.

Reaction of 1 with I_2: In Situ Reaction of "$CpTi(CO)_4I$" with NaC_5H_5. Precooled I_2 (0.32 g, 1.3 mmol) in THF (−70 °C, 20 mL) was added to $[Et_4N][CpTi(CO)_4]$ (0.50 g, 1.41 mmol) in THF (−70 °C, 20 mL) to generate a thermally unstable turbid red solution of "$CpTi(CO)_4I$". NaC_5H_5 (0.16 g, 1.7 mmol) was dissolved in 20 mL of THF and added to the reaction mixture. An IR spectrum of the solution showed ν(CO) bands at 1971 and 1883 cm^{-1}, characteristic of $Cp_2Ti(CO)_2$.[3] The solution was warmed to room temperature and filtered and the THF removed in vacuo. After recrystallization from toluene, 0.05 g (15%) of bona fide $Cp_2Ti(CO)_2$ was isolated. No attempts were made to obtain spectral data on the extremely unstable solution of "$CpTi(CO)_4I$".

$[Et_4N][Cp^*Ti(CO)_4]$ (6). By the same procedure used to prepare compound **1**, freshly sublimed Cp^*TiCl_3 (2.30 g, 7.95 mmol) was dissolved in 100 mL of DME and reduced with $NaC_{10}H_8$ (34.2 mmol) in 300 mL of DME. The reduction generated a brown-green solution which turned red after being warmed and stirred under CO overnight. The DME solution spectrum of $Na[Cp^*Ti(CO)_4]$ had ν(CO) bands at 1914 (m), 1772 (s), and 1727 (w) cm^{-1}. After filtration, cation exchange with $[Et_4N]Br$ (1.67 g, 7.94 mmol), and purification as described for **1**, 2.50 g (74%) of homogeneous red crystalline $[Et_4N][Cp^*Ti(CO)_4]$ was obtained. Analytical samples were provided by washing the salt with 10 mL of cold ethanol (to remove excess $[Et_4N]Br$) and then 10 mL of ether. Anal. Calcd for $C_{22}H_{35}NO_4Ti$: C, 62.11; H, 8.29; N, 3.29. Found: C, 61.95; H, 8.11; N, 3.24. IR (Nujol; ν(CO)): 1912 (m), 1801 (sh), 1747 (s, br) cm^{-1}. NMR (dimethyl-d_6 sulfoxide): ^{1}H δ 3.18 (q, CH_2 of Et_4N^+), 1.85 (s, C_5Me_5), 1.14 (t, CH_3 of Et_4N^+) ppm; $^{13}C\{^1H\}$ δ 293 (s, CO), 104 (s, C_5Me_5), 51 (s, CH_2 of Et_4N^+), 12 (s, CH_3 of C_5Me_5), 7 (s, CH_3 of Et_4N^+) ppm. Compound **6** decomposed between 150 and 170 °C.

$Cp^*Ti(CO)_4(SnPh_3)$ (7). Precooled CH_2Cl_2 (30 mL, −78 °C) was added to a flask containing precooled (−78 °C) $[Et_4N][Cp^*Ti(CO)_4]$ (0.50 g, 1.2 mmol) and Ph_3SnCl (0.46 g, 1.2 mmol). The solution was warmed, while being stirred, to −35 °C, and it turned bright red pink. An IR solution spectrum in CH_2Cl_2 exhibited ν(CO) peaks at 2006 (w) and 1948 (br, s) cm^{-1} from the thermally stable $Cp^*Ti(CO)_4SnPh_3$. The CH_2Cl_2 was removed at room temperature, leaving a brown-violet solid. The carbonyl was extracted with 60 mL of toluene, and the solution was filtered. Toluene was removed to give a violet solid which was recrystallized from CH_2Cl_2 to yield 0.50 g (66%) of satisfactorily pure **7**. Anal. Calcd for $C_{32}H_{30}O_4TiSn$: C, 59.57; H, 4.69; Sn, 18.40. Found: C, 59.27; H, 5.02; Sn, 18.50. IR (ν(CO)): toluene 1948 s cm^{-1}. Nujol, 2009 w, 1953 m, 1928 s cm^{-1}. NMR (C_6D_6): ^{1}H δ 7.12–7.97 (m, $(C_6H_5)_3Sn$), 1.44 (s, C_5Me_5) ppm; $^{13}C\{^1H\}$ δ 249 (s, CO), 127–146 (m, $(C_6H_5)_3Sn$), 105 (s, C_5Me_5), 11 (s, CH_3 of C_5Me_5) ppm. Compound **7** was only slightly air sensitive and could be handled in air for brief periods of time. It decomposed in a sealed capillary at 145–155 °C to a black solid.

$Cp^*Ti(CO)_4(AuPPh_3)$ (8). Precooled CH_2Cl_2 (40 mL, −70 °C) was added to a cooled flask (−70 °C) containing $[Et_4N][Cp^*Ti(CO)_4]$ (0.600 g, 1.41 mmol) and PPh_3AuCl (0.698 g, 1.41 mmol). The solution immediately turned deep purple, and it was stirred while being warmed to −40 °C. An IR solution spectrum of the mixture showed ν(CO) bands at 1969 (w) and 1874 (s, br) cm^{-1}. CH_2Cl_2 was removed in vacuo at −30 °C, and the purple solid formed was recrystallized twice from toluene and then washed with 20 mL of pentane. The black crytals of $Cp^*Ti(CO)_4AuPPh_3$ (0.43 g, 40%) were of satisfactory purity. Anal. Calcd for $C_{32}H_{30}AuO_4PTi$: C, 50.95; H, 4.01; P, 4.11. Found: C, 50.91; H, 4.29; P, 4.05. IR (Nujol; ν(CO)): 1982 (w), 1862 (s) cm^{-1}. NMR (C_6D_6): ^{1}H δ 6.92–7.44 (m, $(C_6H_5)_3P$), 1.91 (s, C_5Me_5); $^{13}C\{^1H\}$ δ 271 (s, CO), 128–134 (d, $(C_6H_5)_3P$), 105 (s, C_5Me_5), 11 (s, CH_3 of C_5Me_5) ppm. Compound **8** was more air sensitive and appeared to be slightly less thermally stable than **7**: dec pt 138–144 °C.

Reaction of 6 with I_2. Formation of $Cp^*Ti(CO)_4I$ (9). When equimolar amounts of I_2 and **6** were dissolved in separate portions of cold (−78 °C) CH_2Cl_2 and mixed, a thermally unstable orange-brown substance was obtained. IR spectra of these solutions in the ν(CO) region showed peaks of about the same shape and relative intensity as those for compounds **7** and **8**, only at much higher energies (2046 (w), 1990 (s) cm^{-1}. On the basis of these data and derivative formation (vide infra), the product is formulated as $Cp^*Ti(CO)_4I$ (**9**). This solution decomposed rapidly at room temperature with gas evolution to an uncharacterized non-carbonyl product. All attempts to isolate **9** were unsuccessful.

$Cp^*Ti(CO)_2(dmpe)I$, $Cp^*Ti(^{13}CO)_2(dmpe)I$ (10 and 10-^{13}C). Addition of 1 equiv of dmpe to a cold (−78 °C) solution of $Cp^*Ti(CO)_4I$ as prepared above in THF and warming of this mixture to room temperature resulted in gas evolution and a color change from orange to dark green. An infrared spectrum taken at this time showed bands at 1941 (m) and 1840 (s) cm^{-1} in the ν(CO) region. These slowly decayed at room temperature. Removal of the THF, followed by extraction with toluene, provided a dichroic "red–green" solution (ν(CO): 1934 (m), 1832 (s) cm^{-1}), which on removal of solvent provided a dark solid (IR (Nujol mull; ν(CO)): 1943, 1833 cm^{-1}). Efforts to recrystallize this product from toluene resulted in decomposition to non-carbonyl-containing products.

A solution of $Cp^*Ti(CO)_2(dmpe)I$ was generated as previously described and then stirred at room temperature under an atmosphere of 99% ^{13}CO. IR spectral monitoring indicated complete exchange of CO had occurred after 1 h and showed two new bands in the ν(CO) region: 1891 (m), 1792 (s) cm^{-1}, which are assigned to $Cp^*Ti(^{13}CO)_2(dmpe)I$. NMR (tetrahydrofuran-d_8): $^{31}P\{^1H\}$, (−10 °C) δ 2.7 (br s, 1P), 0.6 br s, 1P), −48 (free dmpe) ppm; $^{13}C\{^1H\}$ (−10 °C) δ 267 (d, J_{C-P} = 7, 0 Hz, 1C), 254 (dd, J_{C-P} = 13, 4 Hz, 1C).

$[Et_4N][CpZr(CO)_4]$ (11). Using the same techniques as described above for the preparation of compound 1, $CpZrCl_3$ (3.00 g, 11.4 mmol) in 200 mL of DME was reacted with 300 mL of $Na–C_{10}H_8$ (48 mmol) in DME at –70 °C, at which time the reaction mixture immediately turned deep purple. The Ar atmosphere was replaced with CO after the reduction was complete, and the solution instantly turned red-brown. After the temperature was raised to –45 °C, a spectrum of the settled solution of $Na[CpZr(CO)_4]$ showed IR ν(CO) bands at 1923 (m) and 1786 (s) cm^{-1}. The solution was warmed to room temperature and filtered through Celite to provide a deep red solution. The filtrate was stirred for 24 h at room temperature with $[Et_4N]Br$ (2.39 g, 11.4 mmol). After the solvent was removed and the residue washed with pentane, ethanol, and ether, 0.67 g (15%) of $[Et_4N][CpZr(CO)_4]$ was isolated as a brown crystalline solid of satisfactory purity. Anal. Calcd for $C_{17}H_{25}NZrO_4$: C, 51.22; H, 6.32; N, 3.51. Found: C, 51.16; H, 6.29; N, 3.49. Compound **11** was air sensitive and violently decomposed in a sealed capillary tube at 184 °C. IR (Nujol; ν(CO)): 1914 (m), 1770 (s, br) cm^{-1}. NMR (DMSO-d_6): ^1H, δ 5.55 (s, C_5H_5), 3.18 (q, CH_2 of Et_4N^+), 1.15 (t, CH_3 of Et_4N^+) ppm; ^{13}C δ 292 (s, CO), 98 (s, C_5H_5), 51 (CH_2 of Et_4N^+), 7 (CH_3 of Et_4N^+) ppm.

$CpZr(CO)_4(SnPh_3)$ (12). The reaction of **11** and Ph_3SnCl in DME yielded only non-carbonyl containing decomposition products. Reaction of the compounds in cold CH_2Cl_2 yielded a thermally unstable carbonyl with a ν(CO) band at 1972 cm^{-1} assigned to $CpZr(CO)_4(SnPh_3)$. Reaction of $[Et_4N][CpZr(CO)_4]$ (0.30 g, 0.075 mmol) and Ph_3SnCl (0.029 g, 0.075 mmol) in a precooled NMR tube (–78 °C) in approximately 1 mL of CD_2Cl_2 (–78 °C) yielded a red-violet thermally unstable solution. Its ^1H NMR spectrum at –50 °C showed resonances at δ 7.2–8.2 ($CpZr(CO)_4Sn\mathit{Ph}_3$), 5.36 (t, J_{Sn-H} = 3.9 Hz, $\mathit{Cp}Zr(CO)_4SnPh_3$), 2.46, and 0.74 ($Et_4N^+$) ppm. In addition, small resonances at δ 5.66, 3.46, and 3.30 ppm were present and not assigned. A partially proton decoupled ^{13}C NMR spectrum showed resonances at δ 241 ($CpZr(\mathit{CO})_4SnPh_3$), 127–145 ($CpZr(CO)_4Sn\mathit{Ph}_3$), 92 (d, $\mathit{Cp}Zr(CO)_4SnPh_3$, J_{C-H} = 18 Hz), 51 (m, Et_4N^+), and 7 (s, Et_4N^+) ppm. Attempts to isolate **12** were unsuccessful.

$CpZr(CO)_4(AuPPh_3)$ (13). Precooled CH_2Cl_2 (50 mL, –78 °C) was added to a precooled flask (–78 °C) containing $[Et_4N][CpZr(CO)_4]$ (0.355 g, 0.891 mmol) and PPh_3AuCl (0.441 g, 0.891 mmol) to generate a dark green thermally unstable solution. CH_2Cl_2 was removed from the product, leaving a green solid. The Nujol mull spectrum of the solid showed a ν(CO) band at 1865 (s, br) cm^{-1}. At room temperature the solid was stable for brief periods, but toluene solutions decomposed to a dark brown solid of unknown composition. Solutions of $CpZr(CO)_4(AuPPh_3)$ generated in situ in CD_2Cl_2 from $[Et_4N][CpZr(CO)_4]$ and PPh_3AuCl showed resonances in ^1H NMR spectra (–75 °C) at δ 6.5–7.5 ($CpZr(CO)_4AuP\mathit{Ph}_3$), 5.49 ($\mathit{Cp}Zr(CO)_4AuPPh_3$), 3.31 (q, Et_4N^+), and 1.26 (t, Et_4N^+) ppm. A partially proton decoupled ^{13}C NMR spectrum of the same solution (–75 °C) showed resonances at δ 273 ($CpZr(\mathit{CO})_4AuPPh_3$), 129–134 ($CpZr(CO)_4AuP\mathit{Ph}_3$), 95 ($\mathit{Cp}Zr(CO)_4AuPPh_3$, J_{C-H} = 13 Hz), 52 (s, Et_4N^+), and 7.4 (d, Et_4N^+) ppm. Due to the thermally unstable nature of **13**, no attempts were made to obtain elemental analyses.

$[Et_4N][Cp^*Zr(CO)_4]$ (14): (a) $NaC_{10}H_8$ Reduction. By the same procedure described for the preparation of $[Et_4N][CpZr(CO)_4]$, Cp^*ZrCl_3 (2.17 g, 6.52 mmol) was reduced with $NaC_{10}H_8$ (27.4 mmol) in a total volume of 350 mL of DME at –60 °C to provide a red-brown mixture. The CO was added at 1 atm pressure, and the red-brown solution was stirred overnight while being warmed to room temperature. The IR solution spectrum of the product $Na[Cp^*Zr(CO)_4]$ had ν(CO) bands at 1914 (m), 1781 (s), and 1754 (w, sh) cm^{-1}. After cation exchange with $[Et_4N]Cl$ (1.08 g, 6.52 mmol) and purification as previously described for **11**, 0.37 g (12%) of maroon crystalline $[Et_4N][Cp^*Zr(CO)_4]$ of satisfactory purity was isolated. Anal. Calcd for $C_{22}H_{35}NO_4Zr$: C, 56.37; H, 7.53; N, 2.99. Found: C, 56.16; H, 7.38; N, 2.98. Compound **14** dissolved in DME and THF to provide deep red and extremely air sensitive solutions. IR (Nujol; ν(CO)): 1913 (s), 1801 (m), 1753 (s) cm^{-1}. NMR (dimethyl-d_6 sulfoxide): ^1H δ 3.21 (q, CH_2 of Et_4N^+), 1.97 (s, C_5Me_5), 1.16 (t, CH_3 of Et_4N^+) ppm; ^{13}C δ 296 (s, CO), 109 (s, C_5Me_5), 51 (CH_2 of Et_4N^+), 12 (s, $C_5\mathit{Me}_5$), 7 (CH_3 of Et_4N^+) ppm.

(b) $KC_{10}H_8$ Reduction. A solution of $KC_{10}H_8$ was prepared by the addition of 80 mL of DME to a flask containing 0.48 g (12.3 mmol) of K and 3.08 g (24.0 mmol) of $C_{10}H_8$. The solution was stirred 4 h at room temperature and then transferred into a cold (–60 °C). Morton flask equipped with a mechanical stirring assembly made entirely of glass. A flask containing 1.00 g (3.00 mmol) of freshly sublimed Cp^*ZrCl_3 was cooled to –78 °C, and 120 mL of DME was added to give a clear, pale yellow solution. After this mixture was stirred 10 min to cool thoroughly, it was transferred into the cold (–60 °C) solution of $KC_{10}H_8$. The dark green-brown reaction mixture was stirred for 22 h at –60 °C. The argon was then removed in vacuo and replaced with CO, whereupon the mixture was observed to change to a dark red-orange. It was stirred for 14 h under CO at –60 °C and then warmed over a 4-h period to room temperature. The solution was stirred an additional 2 h and then allowed to settle for 0.5 h. The solution was then filtered through Celite, and 0.50 g (3.03 mmol) of $[Et_4N]Cl$ was added to the deep red-violet filtrate. The resulting mixture was stirred overnight. It was then filtered through Celite with thorough rinsing, and the DME was then removed in vacuo. Pentane (150 mL) was added, and after mixing the dark red-violet solid was transferred to a frit and rinsed with 20 mL of fresh pentane. After drying in vacuo, 0.56 g (40% yield) of dark violet, microcrystalline $[Et_4N][Cp^*Zr(CO)_4]$ was isolated. The product was spectroscopically identical with bona fide compound **14**.

Reaction of 14 and Ph_3SnCl. Formation of $Cp^*Zr(CO)_4(SnPh_3)$ (15). When cold CH_2Cl_2 (–78 °C) was added to a 1:1 mixture of $[Et_4N][Cp^*Zr(CO)_4]$ and Ph_3SnCl, the solution immediately turned green-brown. IR solution spectra of the thermally unstable solutions could not be obtained, and removal of the CH_2Cl_2 at low temperature afforded an orange-red solid with no IR ν(CO) absorptions. When the compound, postulated to be **15**, was generated in a NMR tube in CD_2Cl_2 at –70 °C, ^1H NMR spectra of the dichroic green-red solution showed resonances at δ 7.2–7.4 ($Cp^*Zr(CO)_4Sn\mathit{Ph}_3$), 2.9 (br s, Et_4N^+), 1.94 and 1.93 (s, $\mathit{Cp}^*Zr(CO)_4^-$ and $\mathit{Cp}^*Zr(\mathit{CO})_4SnPh_3$), and 1.0 ($\mathit{Et}_4N^+$) ppm. The ^{13}C NMR spectrum showed resonances at δ 296 ($Cp^*Zr(CO)_4^-$), 244 ($Cp^*Zr(\mathit{CO})_4SnPh_3$), 127–147 ($Cp^*Zr(CO)_4Sn\mathit{Ph}_3$), 110 ($\mathit{C}_5(CH_3)_5Zr(CO)_4^-$), 106 ($\mathit{C}_5(CH_3)_5Zr(CO)_4SnPh_3$), 51 ($\mathit{Et}_4N^+$), 12 ($C_5(\mathit{CH}_3)_5Zr(CO)_4^-$), 11 ($C_5(\mathit{CH}_3)_5Zr(CO)_4SnPh_3$), and 7 ($\mathit{Et}_4N^+$) ppm. Attempts to isolate **15** were unsuccessful.

Reaction of 14 and Ph_3PAuCl. Formation of $Cp^*Zr(CO)_4(AuPPh_3)$ (16). The reaction of equimolar amounts of precooled $[Et_4N][Cp^*Zr(CO)_4]$ and PPh_3AuCl in cold (–78 °C) CH_2Cl_2 produced an extremely thermally unstable solution of what is believed to be **16**. Solutions generated at –78 °C in CD_2Cl_2 were monitored by ^{13}C NMR spectroscopy. At –78 °C a ^{13}C NMR spectrum showed resonances at 296 ($Cp^*Zr(CO)_4^-$), 275 ($Cp^*Zr(\mathit{CO})_4(AuPPh_3)$), 128–133 ($Cp^*Zr(CO)_4AuPPh_3$), 110 ($\mathit{Cp}^*Zr(CO)_4^-$), 107 ($\mathit{Cp}^*Zr(CO)_4AuPPh_3$), 52 ($\mathit{Et}_4N^+$), 12 ($\mathit{Cp}^*Zr(CO)_4^-$), 11.1 ($\mathit{Cp}^*Zr(CO)_4AuPPh_3$), and 7 ($\mathit{Et}_4N^+$) ppm. Unidentified resonances at 285 and 108 ppm were also observed. After the solution was warmed to –40 °C, the ^{13}C NMR spectrum showed resonances only for a non-carbonyl compound of unknown composition. No ^1H NMR spectra were obtained. Attempts to isolate **16** were unsuccessful.

$[Et_4N][CpHf(CO)_4]$ (17). A solution of $KC_{10}H_8$ was prepared by the addition of 80 mL of DME to a flask containing 0.51 g of K (13.0 mmol) and 3.26 g of $C_{10}H_8$ (25.4 mmol). It was stirred for 4 h at room temperature and then cooled to –60 °C in a Morton flask equipped with a glass mechanical stirring assembly. A flask containing 1.57 g (3.18 mmol) of $CpHfCl_3·2THF$ was cooled to –60 °C, and 120 mL of cold DME was added to give a clear colorless solution. This solution was transferred into the cold (–60 °C) solution of $KC_{10}H_8$ to give a dark red-orange reaction mixture. It was mixed vigorously for 24 h at –60 °C, and then the argon was removed in vacuo and CO was added. After 14 h of stirring under CO, the solution infrared spectrum showed ν-

(CO) bands at 1925 (m), 1782 (s), and 1742 (sh) cm^{-1} for K[CpHf(CO)$_4$]. The solution was then warmed slowly to room temperature under a CO atmosphere with stirring over a 5-h period and then was stirred an additional 1 h. The mixture was allowed to settle for 1 h and then filtered through Celite. After thorough rinsing of the Celite, 0.52 g of [Et_4N]Cl (3.15 mmol) was added via a bent Schlenk tube for cation exchange. The solution was stirred overnight and then filtered through Celite to give a dark red solution. The DME was removed in vacuo, and 100 mL of pentane was added to the solid. After trituration, a red-violet solid was present, and this was transferred onto a frit and rinsed with 20 mL of pentane. The solid was dried in vacuo to give 0.68 g (44% yield) of [Et_4N][CpHf(CO)$_4$]. The sample was recrystallized from THF/Et_2O to give 0.64 g (42% overall yield) of a red microcrystalline solid. The analytical sample was recrystallized a second time from THF/Et_2O. Anal. Calcd for $C_{17}H_{25}HfNO_4$: C, 42.02; H, 5.19; N, 2.88. Found: C, 41.85; H, 5.24; N, 2.98. IR (Nujol; ν(CO)): 1917 (s), 1783 (sh), 1760 (s) cm^{-1}. NMR (dimethyl-d_6 sulfoxide): ^1H, δ 5.51 (s, C_5H_5), 3.18 (q, J = 7.1 Hz, CH_2 of Et_4N^+), 1.14 (t, J = 7.2 Hz, CH_3 of Et_4N^+), $^{13}C\{^1H\}$ 290.6 (s, CO), 96.6 (s, C_5H_5), 51.4 (s, CH_2 of Et_4N^+), 7.1 (s, CH_3 of Et_4N^+). The solid decomposed at 135–136 °C.

[K(cryptand 2.2.2)][Cp*Hf(CO)$_4$] (18). A solution of $KC_{10}H_8$ was prepared by addition of 80 mL of DME to a flask containing 0.43 g (11.0 mmol) of K and 2.73 g (21.3 mmol) of $C_{10}H_8$. After 3.5 h of stirring at room temperature, the solution was cooled to −60 °C. A flask containing 1.12 g (2.67 mmol) of Cp*HfCl$_3$ (freshly sublimed) was cooled to −70 °C, and 120 mL of DME was added to give a clear, pale yellow solution. After it was stirred 10 min to ensure complete cooling, the solution of Cp*HfCl$_3$ was transferred into the cold (−60 °C) $KC_{10}H_8$ solution. The orange-brown mixture was then stirred 24 h at −60 °C. The solution was filtered through a Celite pad on a large-diameter, medium-porosity frit at room temperature. The filtration removed a light brown solid. After thorough rinsing a dark orange-brown filtrate was obtained that appeared to be quite stable at room temperature. The mixture was then cooled to −20 °C, and a solution of 1.00 g (2.66 mmol) of cryptand 222 in 10 mL of DME was added. There was no visual evidence of a reaction upon addition of the cryptand, and the reaction mixture was quickly warmed to room temperature and stirred for 0.5 h. The dark orange-brown mixture was then transferred into a Morton flask equipped with a glass mechanical stirring assembly and cooled to −60 °C. The argon atmosphere was then removed in vacuo, and CO was admitted. The reaction mixture appeared to change to a slightly more yellow-brown color after 5 min under CO. It was vigorously mixed overnight under CO at −60 °C. An infrared solution spectrum showed ν(CO) bands at 1916 (m) and 1775 (s) cm^{-1}. The reaction mixture was warmed over a 4-h period to room temperature and then stirred an additional 0.5 h. After a 0.5-h settling period, the solution was filtered through Celite to remove a dark brown solid. The solid was rinsed with DME to give a dark red-brown solution. The DME was removed in vacuo to leave a dark red-brown oil, which was dried in vacuo for an additional 0.5 h. Pentane (150 mL) was added, and the oil was triturated to give a red-brown insoluble solid. The solid was transferred onto a frit and rinsed with 20 mL of pentane. Drying in vacuo gave 1.10 g (49% yield) of a light brown powdery solid. A 0.5-g sample of the solid was recrystallized from DME/pentane to give 0.32 g (64% recrystallized yield) of a brown powder. Anal. Calcd for $C_{32}H_{51}HfKN_2O_{10}$: C, 45.68; H, 6.11; N, 3.33. Found: C, 46.59; H, 5.99; N, 3.12. IR (Nujol; ν(CO)): 1913 (s), 1763 (s, br) cm^{-1}. NMR (dimethyl-d_6 sulfoxide): ^1H δ 3.48, 3.43, 2.44 (cryptand 222), 1.97 (s, $C_5\mathit{Me}_5$); $^{13}C\{^1H\}$ δ 297.5 (s, CO), 108.8 (s, C_5Me_5), 71.4, 68.6, 55.0 (s, crypt 2.2.2), 12.5 (s, $C_5\mathit{Me}_5$) ppm. Compound **18** decomposed without melting at 146 °C.

[K(15-crown-5)$_2$][Cp*Hf(CO)$_4$] (19). In a procedure very similar to that described above for compound **18**, a cold (−70 °C) solution of 1.00 g (2.38 mmol) of Cp*HfCl$_3$ in 120 mL of DME was added via cannula to a cold (−70 °C) solution/slurry of $KC_{10}H_8$ (prepared from 0.38 g (9.7 mmol) of K and 2.44 g (19.0 mmol of $C_{10}H_8$ in 80 mL of DME). The resulting dark orange-brown reaction mixture was stirred for 1 h at −70 °C and then slowly warmed to room temperature over a period of 12 h while stirring. After filtration, 3.9 mL (19.6 mmol) of 15-crown-5 was added and the mixture was stirred for 2 h. After transfer to a Morton flask, equipped with a mechanical stirring assembly, the mixture was cooled to −60 °C prior to exchange of the argon for carbon monoxide at atmospheric pressure. The mixture was stirred for 12 h under CO at −60 °C, warmed to room temperature over a 4-h period, and filtered. After removal of most DME in vacuo, the resulting red-brown oil slowly solidified after vigorous and prolonged trituration under pentane. After drying in vacuo, 1.18 g (55% yield) of a brown powdery solid was isolated. The sample was recrystallized from THF/pentane to give 0.98 g (45% overall yield) of a brown powder which gave satisfactory analyses. Anal. Calcd for $C_{34}H_{55}HfKO_{14}$: C, 45.10; H, 6.12. Found: C, 45.36; H, 6.06. IR (ν(CO)): DME, 1916 (m), 1776 (s) cm^{-1}; Nujol, 1908 (s), 1756 (s) cm^{-1}. NMR (dimethyl-d_6 sulfoxide): ^1H δ 3.54 (s, 15-C-5), 1.97 (s, C_5Me_5) (small peaks due to HC_5Me_5 were also present at δ 1.75, 1.69, and 0.93 ppm); $^{13}C\{^1H\}$, δ 296.6 (s, CO), 108.3 (s, C_5Me_5), 68.8 (s, 15-C-5), 12.0 (s, $C_5\mathit{Me}_5$) (small peaks due to decomposition products were also present at δ 48.5, 26.0, 21.7, 13.9, 11.5, and 10.9 ppm). Compound **19** decomposed at 128 °C.

[Et_4N][Cp*Hf(CO)$_4$] (20). In a procedure very similar to that employed in the synthesis of compound **19**, 1.00 g (2.38 mmol) of Cp*HfCl$_3$ was reduced by $KC_{10}H_8$ (from 0.38 g of K and 2.44 g of $C_{10}H_8$) in 200 mL of DME and subsequently carbonylated at −60 °C. After 24 h of stirring at −60 °C under CO (atmospheric pressure), the solution showed peaks in the ν(CO) region at 1918 (m), 1777 (m), and 1740 (sh) cm^{-1} due to [K(DME)$_x$][Cp*Hf(CO)$_4$]. The deep red-brown mixture was filtered through Celite and stirred with dry [Et_4N]Cl (0.40 g, 2.42 mmol) for 12 h to complete the cation exchange. The mixture was then filtered through Celite again, and the solvent was removed in vacuo. After thorough drying, 150 mL of pentane was added and the solid was triturated. The solid was then transferred to a medium-porosity frit and rinsed with 2 × 10 mL of pentane. After drying in vacuo, 0.33 g (25% yield) of a bright red-brown microcrystalline solid was isolated. A 0.30-g sample of the solid was recrystallized from DME/Et_2O to give 0.11 g (8% overall yield) of an orange-brown crystalline solid. Anal. Calcd for $C_{22}H_{35}HfNO_4$: C, 47.52; H, 6.35; N, 2.52. Found: C, 47.52; H, 5.82; N, 2.46. IR (Nujol mull; ν(CO)): 1908 (s), 1750 (s, v br) cm^{-1}. NMR (dimethyl-d_6 sulfoxide): ^1H δ 3.19 (q, CH_2 of Et_4N^+), 1.99 (s, C_5Me_5), 1.16 (t, CH_3 of Et_4N^+); $^{13}C\{^1H\}$, δ 296.4 (s, CO), 108.2 (s, C_5Me_5), 51.3 (s, CH_2 of Et_4N^+), 12.0 (s, $C_5\mathit{Me}_5$), 7.1 (s, CH_3 of Et_4N^+). Compound **20** decomposed at 158–160 °C.

Cp*Hf(CO)$_2$(dmpe)Cl (21). Approximately 100 mL of DME was added to a vessel containing Na (0.343 g, 14.9 mmol) and $C_{10}H_8$ (3.18 g, 24.9 mmol), and the mixture was stirred for 3 h to give a deep green solution of Na–$C_{10}H_8$. The Na–$C_{10}H_8$ solution was transferred to and cooled to −60 °C in a Morton flask equipped with a mechanical stirrer. Neat dmpe (0.91 mL, 5.4 mmol) was added to a yellow DME solution (100 mL) of Cp*HfCl$_3$ (2.09 g, 4.98 mmol). The cold Cp*HfCl$_3$/dmpe mixture (−60 °C) was added to the rapidly stirred Na–$C_{10}H_8$ slurry solution, and the resulting reaction mixture slowly turned orange-brown. The Ar atmosphere was evacuated from the reaction vessel immediately upon complete addition, and approximately 1 atm of CO was added. While it was stirred under CO for 2 h, the reaction mixture slowly turned yellow-green. The CO atmosphere was replaced by Ar, and the stirring was stopped. An IR spectrum of the clear dichroic red–green solution had ν(CO) bands at 1913 (m) and 1800 (s) cm^{-1}. After it was warmed to −25 °C, the solution was filtered through Celite and the DME was removed at 0 °C in vacuo. The resulting brown-green solids were washed with 100 mL of hexane. The product was extracted with 100 mL of toluene, and the toluene was removed in vacuo at room temperature to yield 0.51 g (18%) of green crystalline **21**. In a similar reduction of Cp*HfCl$_3$/dmpe with 4 equiv of Na–$C_{10}H_8$, an analytically pure sample was obtained in lower yields (7%) using the same purification methods. Anal. Calcd for $C_{18}H_{31}ClHfO_2P_2$: C, 38.93; H, 5.66; Cl, 6.38. Found: C, 38.79; H, 5.63; Cl, 6.38. Compound

21 was slightly soluble in pentane, hexane, and diethyl ether and very soluble in toluene, DME, and THF. These solutions were unstable at room temperature except under a CO atmosphere. The compound dissolved but rapidly decomposed with gas evolution in DMSO and ethanol. IR (Nujol; ν(CO)): 1904 (s), 1788 (s) cm^{-1}. NMR (toluene-d_8): ^{1}H, δ 1.95 (s, C_5Me_5) 1.21–1.32 (m, C_2H_4 of dmpe), 1.05 (d, J_{H-P} = 6.4 Hz, CH_3 of dmpe), 0.90 (d, J_{H-P} = 5.1 Hz, CH_3 of dmpe) ppm; $^{31}P\{^1H\}$ (25 °C), δ −7.8 s; $^{31}P\{^1H\}$ (−90 °C) δ −6.2 ("s", 1P), −8.8 ("s", 1P).

Cp*Hf(^{13}CO)$_2$(dmpe)$_2$Cl. A toluene solution of compound 21 was stirred under 99% ^{13}CO for 45 min at room temperature. After this period the IR spectrum in the ν(CO) region showed absorptions due only to Cp*Hf(^{13}CO)$_2$(dmpe)Cl at 1871 (m) and 1755 (s) cm^{-1}. Removal of toluene provided a green solid, identical in appearance with compound 21. IR (Nujol; ν(CO)): 1862 (s), 1749 (s) cm^{-1}. NMR (C_6D_6, 25 °C): $^{31}P\{^1H\}$, δ −7.8 (br s, coord dmpe); $^{13}C\{^1H\}$, δ 283 (br s, CO), 184 (free ^{13}CO), 100 (s, C_5Me$_5$), 12 (s, C_5*Me*$_5$) ppm.

Cp*Zr(CO)$_2$(dmpe)Cl (22). By the same procedure employed for the synthesis of 21, an equimolar mixture of Cp*ZrCl$_3$ and dmpe was reduced by 2 equiv of $NaC_{10}H_8$ in DME at −60 °C under argon, followed by treatment with CO. The resulting solution on warming was green-brown in appearance and had the following spectroscopic properties. IR (DME; ν(CO)): 1923 (m), 1810 (s) cm^{-1}. NMR (DME-d_{10}): $^{31}P\{^1H\}$ (−10 °C), δ −8.1 (br s, assigned to product). Impurities were present at δ −2.8 (br s) and −12.6 (br s) (unknown) and at δ −48.3 (free dmpe).

Following filtration, removal of solvent, and extraction of the residue with toluene, a low yield (<10%) of impure deep green solid was obtained that had an IR spectrum (Nujol mull) in the ν(CO) region which was very similar to that of compound 21: 1913 (s), 1800 (s) cm^{-1}. Attempts to obtain satisfactory elemental analyses for the product were unsuccessful. Treatment of a toluene solution of this substance with 99% ^{13}CO at 1 atm pressure provided an obviously impure product that was presumed to contain Cp*Zr(^{13}CO)$_2$(dmpe)Cl, on the basis of the similarity of its spectral properties in the carbonyl region with those of the 99% ^{13}C-labeled hafnium analog. IR (Nujol; ν(CO)): 1871, 1760 cm^{-1}. $^{13}C\{^1H\}$ NMR (toluene-d_8, 25 °C): δ 279 (br s, CO), 185 (free ^{13}CO), 100.1 (C_5Me$_5$), 13.3–11.4 (C_5*Me*$_5$, dmpe) ppm. No further attempts were made to characterize this unstable species.

Results and Discussion

Alkali-Metal Naphthalenide Reductions of (C_5R_5)MCl$_3$ (R = H, Me; M = Ti, Zr, Hf). While the reduction chemistry of the bis(cyclopentadienyl)dihalides of the group 4 elements had been studied extensively,[3,19,20] that for the mono(cyclopentadienyl) trihalides remained virtually unexplored when we began this study in 1983. The cyclopentadienyl group has proven to be very useful for stabilizing group 4 metal carbonyl complexes. Thus armed with the cyclopentadienyl trihalides, available by facile synthetic methods,[12–18] we decided to attack the problem of group 4 carbonylmetalate synthesis. Addition of cold (−65 to −70 °C) solutions of (C_5H_5)MCl$_3$ in THF for Ti or DME for Zr to cold (78 °C) slurry solutions of sodium naphthalenide in the same solvent under an argon atmosphere provided thermally unstable solutions of deep red-brown (Ti) or bright purple (Zr) intermediates. Likewise, reductions of the permethylcyclopentadienyl chlorides (C_5Me_5)MCl$_3$ in DME gave brown-green (Ti) or red-brown (Zr) solutions.

Many attempts to extend this procedure to hafnium were initially unsuccessful. Almost invariably the reduction of (C_5R_5)HfCl$_3$ by $NaC_{10}H_8$ did not proceed to completion. Although reasons for this circumstance are not yet clear, there have been several reports in the literature in which reductions of zirconium complexes appear to proceed faster or more cleanly than those of corresponding hafnium species.[21] Surprisingly, we discovered that $KC_{10}H_8$ reduced (C_5R_5)HfCl$_3$ significantly faster and more completely at low temperature than did $NaC_{10}H_8$, under otherwise identical conditions. After the hafnium reductions were complete, either red-orange (R = H) or orange-brown (R = CH_3) solutions were obtained.

All of these reductions are believed to initially provide labile naphthalene-bound mono(cyclopentadienyl)metalates(1−), but attempts to unambiguously characterize these highly reactive intermediates have been unsuccessful thus far. However, in this regard it is noteworthy that our group has recently shown that reductions of TiCl$_4$ by arene radical anions provide bis(arene)titanates which undergo carbonylation to yield [Ti(CO)$_6$]$^{2-}$.[22a] In related work, Gardner and Girolami have isolated a neutral zerovalent titanium complex containing a labile naphthalene group, i.e., (η^6-$C_{10}H_8$)Ti(tBuSi(CH$_2$PMe$_2$)$_3$), which readily carbonylates to provide the corresponding (triphos)Ti(CO)$_4$.[22b] Also, Jonas et al. have prepared a 17-electron vanadium species, K[$C_{10}H_8$)V(C_5H_5)], which undergoes disproportionation in the presence of CO as shown in eq 1.[23] On this basis, it seems reasonable to propose that

$$2[(C_5H_5)V(C_{10}H_8)]^- + 7CO \xrightarrow{20\,°C} (C_5H_5)V(CO)_4 + [(C_5H_5)V(CO)_3]^{2-} \quad (1)$$

species of similar compositions are initially generated in the alkali-metal naphthalenide reductions described herein. Characterization of these reactive intermediates and exploration of their general reactivity patterns with a variety of small molecules remain significant objectives of our research program.

Carbonylation of Intermediates: Synthesis and Isolation of [(C_5R_5)M(CO)$_4$]$^-$. Carbon monoxide was generally added within 5–10 min after all alkali-metal naphthalenide reacted in the case of the titanium or zirconium reactions. The carbonylations appeared to proceed rapidly at low temperature. However, for the corresponding hafnium reactions not only was a longer reaction time necessary prior to carbonylation (up to 12 h) but the carbon monoxide uptake period was significantly longer. In order to isolate the alkali-metal salts of the hafnium anions, it was necessary to add effective alkali-metal-ion complexants such as 15-crown-5 or cryptand 2.2.2 for potassium ion. It is unclear whether the alkali-metal complexant was necessary to provide a better cation–anion size match, which would presumably lead to a more stable crystalline lattice, or to prevent alkali-metal-cation-promoted decomposition of the carbonylmetalate ion. Attempts to isolate unsolvated alkali-metal salts of [(C_5R_5)M(CO)$_4$]$^-$ were only made for Na[(C_5H_5)Ti(CO)$_4$], which proved to be an *explosive* material. Comments concerning the potentially explosive nature of unsolvated alkali-metal salts of highly reduced carbonylmetalates of

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(19) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood: West Sussex, England, 1986; p 18.

(20) Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 1.

(21) (a) Katabua, M.; Rolland, P.; Mamantor, G.; Huleh, L. *Inorg. Chem.* **1982**, *21*, 3569. (b) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

(22) (a) Blackburn, D. W.; Britton, D.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1495. (b) Gardner, T. G.; Girolami, G. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1693.

(23) Jonas, K.; Rüsseler, W.; Krüger, C.; Raabe, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 925.

the early transition metals have been summarized previously.[24] Metathesis of the alkali-metal salts (in the absence of 15-crown-5 or crypt 2.2.2) of $[(C_5R_5)M(CO)_4]^-$ with tetraethylammonium chloride or bromide in THF or DME provided a facile route to the alkali-metal and solvent-free forms of these carbonylmetalates. All of the tetraethylammonium salts proved to be thermally robust and survived indefinitely at room temperature under an inert atmosphere and in the dark as dry crystalline substances, although the carbonylhafnates were less thermally stable, especially in solution, than the corresponding titanium and zirconium complexes. While $[Et_4N]^+$ salts of $[(C_5H_5)Ti(CO)_4]^-$ and $[(C_5Me_5)Ti(CO)_4]^-$ were routinely isolated in yield higher than 50% based on the corresponding $(C_5R_5)TiCl_3$, the zirconium and hafnium analogs were more difficult to prepare and were often obtained in yields of only 15–25% as pure substances.

Possible improvements in the syntheses of the latter species include conducting the reductive carbonylations at pressures higher than atmospheric,[25] doing the entire reaction under an atmosphere of carbon monoxide,[26] employing $(C_5R_5)MBr_3$ or $(C_5R_5)MI_3$ instead of the corresponding chlorides with the hope that more facile reductions might occur,[27] adding donor ligands such as PMe_3 to help stabilize otherwise unsaturated intermediates,[28–31] adding the reducing agent slowly to the metal halide complex rather than the "inverse" addition procedure used in these syntheses,[32] and employing arene radical anions other than naphthalenide.[33] One major difference between zirconium and hafnium halide chemistry and that of titanium is the ease with which potentially unreactive zirconium and hafnium halide clusters form on reduction; e.g., while $TiCl_3$ and $TiCl_2$ are easily obtained as appropriately ligated monomers, corresponding paramagnetic zirconium and hafnium analogs are unknown.[34] It is believed that the naphthalene binds to the $(C_5R_5)M$ unit at some stage during the reduction process to ultimately provide a zerovalent metal intermediate. The relatively low yields of the carbonylzirconates and -hafnates obtained in these reactions may indicate that the presumed zerovalent metal intermediates are unstable or are formed in relatively low yields. The latter situation would obtain if naphthalene is not very effective at stabilizing paramagnetic intermediates containing the heavier metals in positive oxidation states. However, these low yields could also arise if the carbonylation step is less efficient for zirconium and hafnium than for titanium. Assessing and understanding the relative importance of these various factors, including the role of the solvent in these reactions, may prove to be difficult endeavors.

Table I. IR and NMR Spectral Data for $[(C_5R_5)M(CO)_4]^-$ in the Carbonyl Region

compd[a]	IR ν(CO), cm^{-1} [b]	$^{13}C\{^1H\}$ NMR δ(CO), ppm[c]
$[(C_5H_5)Ti(CO)_4]^-$ (**1**)	1921 m, 1777 s	289
$[(C_5Me_5)Ti(CO)_4]^-$ (**6**)	1914 m, 1769 s	293
$[(C_5H_5)Zr(CO)_4]^-$ (**11**)	1923 m, 1781 s	292
$[(C_5Me_5)Zr(CO)_4]^-$ (**14**)	1916 m, 1781 s	296
$[(C_5H_5)Hf(CO)_4^-$ (**17**)	1920 m, 1780 s	291
$[(C_5Me_5)Hf(CO)_4]^-$ (**20**)	1915 m, 1774 s	296

[a] Numbers after the compounds correspond to those shown in the Experimental Section; all compounds are tetraethylammonium salts. [b] Solvent = tetrahydrofuran. [c] Solvent = $(CD_3)_2SO$ at 20 °C.

IR and NMR Spectral Properties of $[(C_5R_5)M(CO)_4]^-$. Infrared and ^{13}C NMR spectral data for the monoanions in the carbonyl region are collected in Table I. ^1H NMR spectra are in complete accord with the assigned formulations and are shown in the Experimental Section. Infrared spectra of the anions in the ν(CO) region closely resemble those of the neutral group 5 analogs $(C_5R_5)M(CO)_4$ (M = V, Nb, Ta),[6] except corresponding bands are shifted to lower energies (ca. 100–130 cm^{-1}), as expected for the more electron rich anionic group 4 species.[35a] Also, since the positions, shapes, and relative intensities of the ν(CO) bands for all of these species are very similar to those of $[Ph_4As][(C_5H_5)Ti(CO)_4]$ in solution and in the solid state (except for unsolvated $Na[(C_5H_5)Ti(CO)_4]$, vide infra), there is no doubt that they all have the same basic half-sandwich structure as that previously established for $[(C_5H_5)Ti(CO)_4]^-$ in the $[Ph_4As]^+$ salt.[7a] Figure 1 shows the IR solution spectrum of $Na[(C_5H_5)Zr(CO)_4]$ in 1,2-dimethoxyethane in the ν(CO) region. This band pattern is characteristic for an anionic $(C_5R_5)M(CO)_4$ unit which is not substantially perturbed by ion pairing. For comparison, Figure 2 depicts the mineral oil mull IR spectrum of unsolvated (and *explosive*) $Na[(C_5H_5)Ti(CO)_4]$, which shows ν(CO) bands at quite low energies due to strong interactions of Na^+ with oxygen atoms of the carbonylmetalate.[35b] It seems possible that the latter interaction may help to destabilize the carbonyltitanate in much the same fashion, as electrophilic triorganosilyl units have been shown by Lippard and coworkers[35c] to promote reductive coupling of electron-rich substituted carbonylmetalates of the group 5 elements. However, presently, we know very little concerning the decomposition products of unsolvated $Na[(C_5H_5)Ti(CO)_4]$. Carbonyl ^{13}C NMR positions for $[(C_5R_5)M(CO)_4]^-$ are of interest in that they are among the most positive δ values known for any terminal carbonyl complexes and are about 10 ppm downfield of these previously established for the structurally similar 4:3 piano-stool complexes $(TRMPE)M(CO)_4$ (TRMPE = $CH_3C(CH_2PMe_2)_3$; M = Ti, Zr, Hf).[5] While carbonyl ^{13}C chemical shifts generally shift upfield as the atomic number of the metal increases in a

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[24] Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1.

[25] Synthesis of $Hf(CO)_4(trmpe)$ at CO pressures of 1 and 5 atm pressure provided about 2 and 20% yields, respectively.[5]

[26] While CO reacts with alkali-metal naphthalenides at room temperature (Büchner, W. *Chem. Ber.* **1966**, *99*, 1485) corresponding reactions at −40 °C or lower appear to be quite slow.

[27] In the synthesis of other classes of *zerovalent* group 4 carbonyls we have not found any advantage to date in using bromide or iodide precursors instead of the more readily available corresponding chlorides.

[28] Addition of PMe_3 has been found to be extremely important in other syntheses of low-valent group 4 metal complexes,[29–31] but this strategy has not yet been examined in these preparations.

[29] Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1979**, 127. Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1938.

[30] Chi, K. M.; Frerichs, S. R.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.* **1988**, 1013.

[31] Ellis, J. E.; Chi, K. M.; DiMaio, A. J.; Frerichs, S. R.; Stenzel, S. R.; Rheingold, A. L.; Haggerty, B. S. *Angew. Chem., Int. Ed. Engl.* **1990**, *30*, 194.

[32] In the synthesis of $Ti(CO)_3(dmpe)_2$,[10] no advantage was established in adding the alkali-metal naphthalenide slowly to the metal halide complex. Since the former salts are often poorly soluble at low temperatures, our procedure is usually easier to carry out.

[33] Recently, we have initiated a general study on the interaction of arene radical anions with substituted early-transition-metal halides.[22a]

[34] (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988. (b) Cotton, F. A.; Feng, X.; Shang, M.; Wojtczak, W. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1050 and references cited therein.

[35] (a) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975. (b) An excellent discussion of the effects of ion pairing on the infrared spectra of carbonylmetalates appears in: Darensbourg, M. Y. *Prog. Inorg. Chem.* **1986**, *33*, 221. (c) Carnahan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1992**, *114*, 4166 and references cited therein.

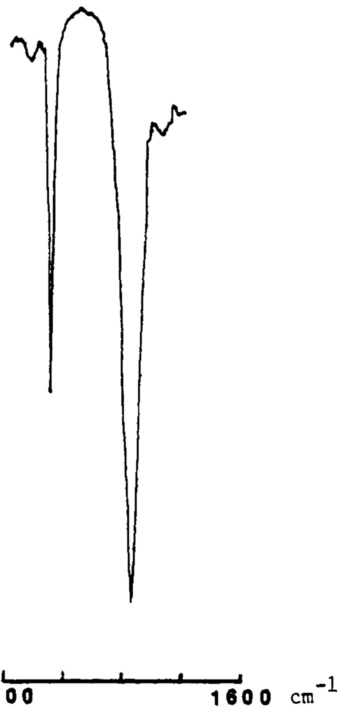

Figure 1. Infrared spectrum of Na[$(C_5H_5)Zr(CO)_4$] in 1,2-dimethoxyethane: ν(CO) 1923 (m), 1786 (s) cm^{-1}.

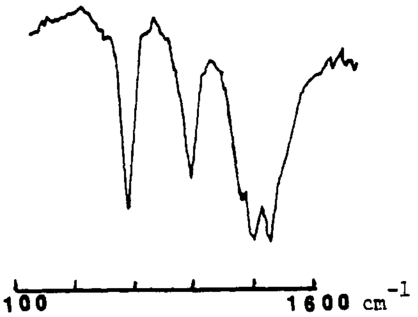

Figure 2. Infrared spectrum of unsolvated and explosive Na[$(C_5H_5)Ti(CO)_4$] as a mineral oil mull: ν(CO) 1914 (m), 1773 (m), 1727 (sh), 1708 (s), 1678 (s) cm^{-1}.

triad for a given type of binary or substituted metal carbonyl,[36] the carbonyl ^{13}C chemical shifts for these zerovalent group 4 carbonyls (including the neutral TRMPE complexes) are unusual in that they are most positive (i.e., shifted farthest downfield) for zirconium and hafnium and are both shifted downfield by about 2–3 ppm relative to those for the analogous titanium species. It has been previously suggested that the surprisingly downfield carbonyl ^{13}C δ values of zerovalent group 4 carbonyls indicate that these metal centers function as unusually strong π donors to the carbonyl group.[22b,37] However, the anomalous carbonyl ^{13}C chemical shift trends mentioned above are not understood. The only other presently reported Hf(0) carbonyl, $(1,3,5\text{-}tBu_3C_6H_3)_2HfCO$, has a rather unremarkable carbonyl ^{13}C δ value of 239.9 ppm,[38] which is not much different from that of $[Hf(CO)_6]^{2-}$, 244.4 ppm.[39a]

Table II. IR and NMR Spectral Data for $(C_5R_5)M(CO)_4E$ and $(C_5R_5)M(CO)_2(dmpe)X$ in the Carbonyl Region

compd[a]	IR ν(CO), cm^{-1} [b]	$^{13}C\{^1H\}$ NMR δ(CO), ppm (solvent; temp °C)
$(C_5H_5)Ti(CO)_4(SnPh_3)$ (**4**)	2020 w, 1960 s	246 (CD_2Cl_2; −70)
$(C_5Me_5)Ti(CO)_4(SnPh_3)$ (**7**)	2006 w, 1948 s	249 ($C_6D_5CD_3$; 20)
$(C_5H_5)Zr(CO)_4(SnPh_3)$ (**12**)	1972 s	241 (CD_2Cl_2; −50)
$(C_5Me_5)Zr(CO)_4(SnPh_3)$ (**15**)	*c*	244 (CD_2Cl_2; −70)
$(C_5H_5)Ti(CO)_4(AuPPh_3)$ (**5**)	1972 w, 1884 s	270 ($C_6D_5CD_3$; −75)
$(C_5Me_5)Ti(CO)_4(AuPPh_3)$ (**8**)	1969 w, 1874 s	271 (C_6D_6; 20)
$(C_5H_5)Zr(CO)_4(AuPPh_3)$ (**13**)	1887 s	272 (CD_2Cl_2; −75)
$(C_5Me_5)Ti(CO)_4I$ (**9**)	2046 w, 1990 s	*d*
$(C_5Me_5)Ti(CO)_2(dmpe)I$ (**10**)	1934 m, 1832 s	267, 254 (C_4D_8O; −10)
$(C_5Me_5)Zr(CO)_2(dmpe)Cl$ (**22**)	1955 m, 1885 s	279 ($C_6D_5CD_3$; 25)
$(C_5Me_5)Hf(CO)_2(dmpe)Cl$ (**21**)	1950 m, 1870 s	283 (C_6D_6; 25)

[a] Numbers after the compounds correspond to those shown in the Experimental Section; only $(C_5H_5)Ti(CO)_4(AuPPh_3)$, $(C_5Me_5)Ti(CO)_4E$ (E = $SnPh_3$, $AuPPh_3$), and $(C_5Me_5)Hf(CO)_2(dmpe)Cl$ could be isolated as pure substances at 20 °C. [b] Solvent = CH_2Cl_2 at 20 °C. [c] Compound was too thermally unstable to obtain the IR spectrum at 20 °C. [d] This spectrum was not obtained.

Synthesis and Properties of Divalent Metal Derivatives of $[(C_5R_5)M(CO)_4]^-$. Divalent metal derivatives of $[(C_5R_5)M(CO)_4]^-$ have been obtained by two routes, as summarized by eqs 2 and 3. Protonation or alkylation

$$[(C_5R_5)M(CO)_4]^- + EX \rightarrow (C_5R_5)M(CO)_4(E) + X^- \quad (2)$$

$$R = H, Me; M = Ti, Zr, EX = Ph_3SnCl, Ph_3PAuCl, I_2$$

$$(C_5R_5)MCl_3 + dmpe \xrightarrow[2.\ CO]{1.\ 2NaC_{10}H_8} (C_5R_5)M(CO)_2(dmpe)Cl + 2NaCl \quad (3)$$

$$R = Me; M = Zr, Hf$$

of these anions provided quite thermally unstable products which have not been characterized. Attempts to obtain stable derivatives of these products were not carried out, although carbonyl halides of the types $(C_5R_5)Ti(CO)_2(dmpe)H$ (R = H, Me) have been accessed by alternative routes.[39b]

Reactions of $[(C_5R_5)M(CO)_4]^-$ with Ph_3SnCl and Ph_3PAuCl have only been examined for titanium and zirconium to date and provide red to purple carbonyl products of varying thermal stabilities (except for the reaction of $[(C_5H_5)Zr(CO)_4]^-$ with Ph_3SnCl, which gave only decomposition products even at low temperatures (−70 °C)). Analytically pure products formulated as $(C_5H_5)Ti(CO)_4(AuPPh_3)$, $(C_5Me_5)Ti(CO)_4(AuPPh_3)$, and $(C_5Me_5)Tf(CO)_4(SnPh_3)$ were isolated as thermally stable (20 °C) and red-violet to purple microcrystalline solids. Although $(C_5H_5)Zr(CO)_4(AuPPh_3)$ could be isolated as a green solid for brief periods at room temperature, it was too thermally unstable to obtain satisfactory elemental analyses. Attempts to isolate the other zirconium compounds resulted in the formation of non-carbonyl-containing decomposition products of unknown nature.

On the basis of infrared and ^{13}C NMR spectral data (Table II), these heterobimetallic compounds are formulated to contain metal–metal bonds. The relatively simple IR spectra in the ν(CO) region (cf. Figure 3 and 4) are consistent with octahedral (or in these cases pseudooc-

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(36) For example, carbonyl ^{13}C δ values for $(C_6Me_6)M(CO)_3$ are 236.3, 225.9, and 215.7 ppm for M = Cr, Mo, and W, respectively: Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1973**, 2012.

(37) Morris, R. J.; Girolami, G. J. *Inorg. Chem.* **1990**, *29*, 4169 and references cited therein.

(38) Cloke, F. G. N.; Lappert, M. F.; Lawless, G. A.; Swain, A. C. *J. Chem. Soc., Chem. Commun.* **1987**, 1667. Cloke, F. G. N.; Courtney, K. A. E.; Sarneh, A. A.; Swain, A. C. *Polyhedrin* **1989**, *8*, 1641.

(39) (a) Ellis, J. E.; Chi, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 6022. (b) Ellis, J. E.; Stein, B. K.; Frerichs, S. R. *J. Am. Chem. Soc.*, in press.

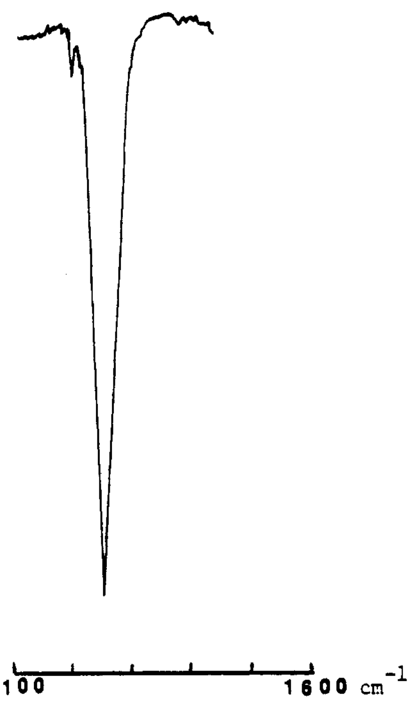

Figure 3. Infrared spectrum of $(C_5Me_5)Ti(CO)_4(SnPh_3)$ in CH_2Cl_2 in the $\nu(CO)$ region: 2006 (w), 1948 (s) cm^{-1}.

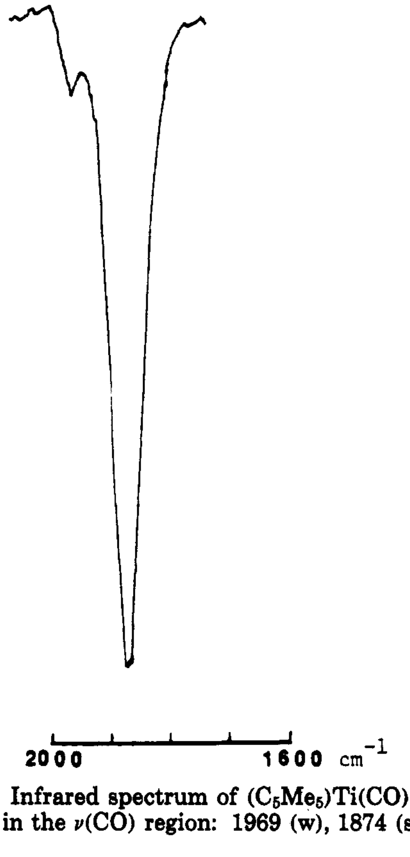

Figure 4. Infrared spectrum of $(C_5Me_5)Ti(CO)_4(AuPPh_3)$ in CH_2Cl_2 in the $\nu(CO)$ region: 1969 (w), 1874 (s) cm^{-1}.

tahedral) structures of the general formula *trans*-LL′M-$(CO)_4$, where the symmetrically bound η^5-C_5R_5 groups are approximately opposite the Ph_3Sn or Ph_3PAu units. We envision the molecular structure of these species to be very similar to that of the structurally characterized $(C_5H_5)Zr(dmpe)_2Cl$, in which the coordination geometry about the metal has been described as a slightly distorted octahedron with the Cp ring centroid occupying the vertex trans to the chlorine atom.[40] Perhaps the most interesting features of the spectral data are the dramatic differences in the $\nu(CO)$ and carbonyl ^{13}C positions for corresponding Ph_3Sn and Ph_3PAu complexes. For example, the most intense $\nu(CO)$ band and the carbonyl ^{13}C resonance positions for $(C_5Me_5)Ti(CO)_4(SnPh_3)$ and (C_5Me_5)-$Ti(CO)_4(AuPPh_3)$ differ by 64 cm^{-1} and 22 ppm, respectively. Both shifts indicate that the Ph_3PAu unit is a much better donor than the Ph_3Sn group in these complexes. While similar infrared spectral comparisons have been previously noted for related monotin and monogold transition-metal complexes,[41] to our knowledge corresponding carbonyl ^{13}C resonances data have not been reported before on analogous tin and gold derivatives of metal carbonyls. Despite the fact that we could not obtain elemental analyses for the corresponding zirconium derivatives, the very similar $\nu(CO)$ and ^{13}C carbonyl NMR values observed for these species and those of the well-characterized titanium analogs provide good support for our formulations of these relatively unstable products.

Attempts were also made to obtain iodo carbonyls of the general formulation $(C_5R_5)M(CO)_4I$ (M = Ti, Zr) by the interaction of the corresponding anions with I_2. In the case of the interaction of $[(C_5R_5)Zr(CO)_4]^-$, no evidence for the existence of the doubtlessly very unstable iodo derivative was obtained. If $(C_5R_5)Zr(CO)_4I$ formed, it decomposed rapidly and completely at −70 °C. Although we could not obtain IR spectral evidence for the existence of $(C_5H_5)Ti(CO)_4I$ at room temperature, when equimolar amounts of $[(C_5H_5)Ti(CO)_4]^-$ and I_2 were mixed at −70 °C in THF and then reacted with $Na[C_5H_5]$, a 15% yield of bona fide $(C_5H_5)_2Ti(CO)_2$ was isolated. It is presumed that the latter formed by the interaction of $(C_5H_5)Ti(CO)_4I$ with $C_5H_5^-$, i.e.

$$[(C_5H_5)Ti(CO)_4]^- + I_2 \rightarrow (C_5H_5)Ti(CO)_4I + I^- \quad (4)$$

$$(C_5H_5)Ti(CO)_4I + C_5H_5^- \rightarrow (C_5H_5)_2Ti(CO)_2 + 2CO + I^- \quad (5)$$

Interaction of $[(C_5Me_5)Ti(CO)_4]^-$ with I_2 at low temperature in CH_2Cl_2 provided a somewhat more stable product whose infrared spectrum in the $\nu(CO)$ region (2046 (w), 1990 (s) cm^{-1}) is consistent with the presence of $(C_5Me_5)Ti(CO)_4I$. The carbonyl absorption in the infrared region were of about the same shape and relative intensities as those of the well-characterized complexes (C_5Me_5)-$Ti(CO)_4(SnPh_3)$ and $(C_5Me_5)Ti(CO)_4(AuPPh_3)$ but were shifted to considerably higher energies. Treatment of the resulting orange solution with 1 equiv of dmpe provided a deep green product, which could be isolated, albeit in impure form. This substance underwent facile and quantitative exchange with excess ^{13}CO at room temperature within 1 h in solution. Its IR and ^{13}C and ^{31}P NMR spectra were consistent with the formulation (C_5Me_5)-$Ti(^{13}CO)_2(dmpe)I$. Inequivalent CO and Me_2P groups were present and indicate that the product is likely to have the same structure as that previously determined for $(C_5Me_5)Hf(CO)_2(dmpe)Cl$[7d] (vide infra). These series of interconversions are depicted in eqs 6 and 7.

Early attempts to prepare $[(C_5R_5)Hf(CO)_4]^-$ were unsuccessful, but when the reductive carbonylation of $(C_5Me_5)HfCl_3$ was carried out in the presence of dmpe (eq

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[40] Gambarotta, S.; Chiang, M. Y. *J. Chem. Soc., Chem. Commun.* 1987, 698.

[41] See for example: (a) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315. (b) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 114.

$$[(C_5Me_5)Ti(CO)_4]^- + I_2 \rightarrow (C_5Me_5)Ti(CO)_4I + I^- \quad (6)$$

$$(C_5Me_5)Ti(CO)_4I + \text{dmpe} \rightarrow (C_5Me_5)Ti(CO)_2(\text{dmpe})I + 2CO \quad (7)$$

3), a neutral green product was obtained which proved to be the divalent hafnium complex $(C_5Me_5)Hf(CO)_2(dmpe)Cl$. Although this substance was isolated only in 18% yield, it provided the first example of a well-characterized group 4 halocarbonyl.[7d] Shortly thereafter, Gambarotta and co-workers reported on the preparation of the related $(C_5H_5)M(CO)_2(dmpe)Cl$ (M = Zr, Hf) by similar methods and the X-ray structure of $(C_5H_5)Zr(CO)_2(dmpe)Cl$.[42] This zirconium complex is closely related structurally to the aforementioned $(C_5H_5)Zr(dmpe)_2Cl$, in that the C_5H_5 ring centroid is opposite or trans to the chlorine atom with the result that both carbonyls and Me_2P groups on the dmpe are equivalent. However, perhaps due to the greater steric bulk of the C_5Me_5 ring compared to the cyclopentadienyl group, the structure of $(C_5Me_5)Hf(CO)_2(dmpe)Cl$ is markedly different in that the Cp* ring centroid is trans to a Me_2P group of the dmpe.[7d] Thus, both CO and Me_2P groups are inequivalent.[43] While this inequivalence is also observed in solution by ^{13}C and ^{31}P NMR spectra at −90 °C, at room temperature the carbonyl and dmpe units become equivalent by an exchange process. In contrast, $(C_5Me_5)Ti(CO)_2(dmpe)I$ in solution (at −10 °C) appears to have the static structure adopted by the hafnium chloride analog in the solid state or at −90 °C in solution. Unfortunately, the titanium iodide complex was sufficiently unstable at elevated temperatures that no variable-temperature NMR studies could be carried out.

In contrast to Gambarotta's $(C_5H_5)Zr(CO)_2(dmpe)Cl$,[42] for which good analytical data were obtained, the C_5Me_5–zirconium analog proved to be quite unstable in the solid state at room temperature. However, on the basis of the great similarity of its IR and ^{13}C NMR spectra with those of the hafnium analog (Table II), it seems very likely that our formulation of the carbonylation product as $(C_5Me_5)Zr(CO)_2(dmpe)Cl$ is correct. Although the titanium chloride analog was originally reported to have been obtained from a corresponding reductive carbonylation of an equimolar mixture of $(C_5Me_5)TiCl_3$ and dmpe, attempts to isolate this complex led to total decomposition and the spectral data reported previously are not sufficient to justify our earlier claim for the existence of this substance.[44]

Concluding Remarks

Reduction of $(C_5R_5)MCl_3$ by alkali-metal naphthalenides followed by treatment with CO at atmospheric temperature has been shown to provide zerovalent group 4 half-sandwich carbonyls of the general formulation $[(C_5R_5)M(CO)_4]^-$ in yields ranging from about 20% for $[(C_5H_5)Zr(CO)_4]^-$ to 75% for $[(C_5Me_5)Ti(CO)_4]^-$. Since the principal objective of our research program has been to explore the stabilization of low-valent early transition metals with different ligand sets,[45] the reaction chemistry of $[(C_5R_5)M(CO)_4]^-$ with electrophiles has not been examined in detail. However, we believe that these materials will prove to have a rich chemistry and represent valuable new precursors for the exploration of the organometallic chemistry of the group 4 elements. The ready availability of the zerovalent hafnium complexes $[(C_5R_5)Hf(CO)_4]^-$, for which the chemistry remains totally unexplored, promises to be of particular significance.

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(42) Wielstra, Y.; Gambarotta, S.; Roedelof, J. B.; Chiang, M. Y. *Organometallics* 1988, 7, 2177.

(43) In this connection, it is noteworthy that Gambarotta et al.[42] was unable to prepare $(C_5Me_5)Z(dmpe)_2Cl$ by the same route used for the C_5H_5 analog.[40] In the former (unknown) complex, three Me_2P units would be forced to be relatively close to the bulky C_5Me_5 ring.

(44) See footnote 16 of ref 7d.

(45) Ellis, J. E. *Polyhedron* 1989, *8*, 1611.