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Preliminary communication

Synthesis of the first anionic derivatives of $Hf(CO)_7$: $[(C_5H_5)Hf(CO)_4]^-$ and $[(C_5Me_5)Hf(CO)_4]^-$

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Abstract

Potassium naphthalenide reductions of $[(C_5R_5)HfCl_3]$ (R = H, Me) in 1,2-dimethoxyethane at − 60 °C followed by carbonylation at atmospheric pressure provide 25–50% isolated yields of the first examples of carbonyl anions of hafnium(0), $[(C_5H_5)Hf(CO)_4]^-$ and $[(C_5Me_5)Hf(CO)_4]^-$. These were isolated as tetraethylammonium salts as well as K(cryptand-2.2.2) and $K(15\text{-Crown-}5)_2{}^+$ salts for the latter anion and now represent two of only four presently known Hf^0 carbonyls. They were characterized by elemental analyses, IR and ^1H and ^{13}C NMR spectra.

Recent communications on the syntheses of the first examples of zerovalent hafnium carbonyls, $[Hf(1,3,5\text{-}tBu_3C_6H_3)_2CO]$ [1] and $[Hf(CO)_4\{CH_3C(CH_2PMe_2)_3\}]$ [2], prompt us to report on the preparation of the initial anionic zerovalent hafnium compounds, $[(C_5R_5)Hf(CO)_4]^-$ (R = H, Me). While corresponding anions of titanium and zirconium have been obtained by low temperature reductive carbonylations using sodium naphthalenide [3], many attempts to extend this procedure to hafnium have been uniformly unsuccessful [4]. However, by substituting potassium naphthalenide for the sodium compound, employing significantly longer reduction and carbonylation periods and by adding the effective potassium ion complexants, 15-Crown-5 or cryptand-2.2.2, before carbonylation (for R = Me), moderate yields (40–50%) of the half sandwich carbonyls, $[(C_5R_5)Hf(CO)_4]^-$ have been obtained for the first time from the corresponding $(C_5R_5)HfCl_3$. A typical synthesis, represented by Scheme 1, is as follows:

$$(C_5Me_5)HfCl_3 \xrightarrow[\text{DME}]{\text{i–iii}} [K(15\text{-}C\text{-}5)_2][(C_5Me_5)Hf(CO)_4] \qquad (1)$$

Reagents, conditions: (i) 4 $KC_{10}H_8$, $4C_{10}H_8$, Ar, − 70 to + 20 °C (12 h); (ii) remove KCl, add 15-Crown-5 (2 equiv.); (iii) cool to − 60 °C, remove Ar, add CO (1 atm) − 60 °C (12 h); warm to + 20 °C (4 h); DME = 1,2-dimethoxyethane.

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* Reference number with asterisk indicates a note in the list of references.

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Freshly sublimed $(C_5Me_5)HfCl_3$ [5] (2.4 mmol) in DME (120 ml) was cooled to − 70 °C and added to a vigorously stirred mixture of $KC_{10}H_8$ and $C_{10}H_8$ (both 4 equiv.) in cold DME (80 ml at − 70 °C) [6*]. Over a period of about 12 h the resulting orange brown mixture was warmed to room temperature. After filtration, neat 15-Crown-5 (4 equiv.) was added, stirring was resumed for 2 h and then the solution was cooled to − 60 °C. Argon was removed in vacuo, carbon monoxide (99.9% pure, anaerobic and free of CO_2) was introduced and for 12 h the solution was mechanically stirred at − 60 °C and then warmed to room temperature over a 4 h period. Following filtration, solvent was removed and the resulting deep red oil was induced to solidify by vigorous trituration with pentane. Recrystallization of this very air sensitive product from tetrahydrofuran/pentane provided a 45% yield of microcrystalline brown powder which provided satisfactory analyses for the composition $[K(15\text{-Crown-}5)_2][(C_5Me_5)Hf(CO)_4]$ (**1**), dec. 128 °C. More thermally stable brown crystalline $[K(2.2.2)][(C_5Me_5)Hf(CO)_4]$ (**2**), dec. 146 °C, was obtained in 49% yield by an analogous procedure. In the absence of 15-Crown-5 or Crypt-2.2.2, deep red brown needles of $[Et_4N][(C_5Me_5)Hf(CO)_4]$ (**3**), dec. 158–160 °C, and deep red crystalline $[Et_4N][(C_5H_5)Hf(CO)_4]$ (**4**), darkens above 136 °C, were obtained in 25 and 40% yields, respectively, from the potassium salts, following metathesis and recrystallization from tetrahydrofuran/ether. Solutions of these hafnium compounds deteriorate slowly at room temperature unlike the apparently more thermally stable zirconium analogs [3]. There was no spectroscopic evidence for the presence of the latter species in these products and elemental analyses also indicated that contamination by zirconium was minimal (≤ 5 mole %) [7*,8*].

Selected infrared and ^{13}C NMR spectral data for $(C_5R_5)Hf(CO)_4^-$, the corresponding titanium and zirconium compounds and the recently reported neutral $M(CO)_4\{CH_3C(CH_2PMe_2)_3\}$ [2] are collected in Table 1. These data show fairly consistent trends in descending the triad and indicate that the relative donor abilities of the substituent ligands decrease in the order $C_5Me_5^- > C_5H_5^- > CH_3C(CH_2PMe_2)_3$. Although ^{13}C NMR spectral data for the previously known neutral group 5 analogs, $(C_5R_5)M(CO)_4$, R = H, Me; M = V, Nb, Ta, have apparently not been reported, IR spectra of these materials in the $\nu(CO)$ region [9] have a similar appearance to those of the group 4 monoanions. Corresponding carbonyl absorptions of $(C_5R_5)M(CO)_4$ are shifted about 100–130 cm^{-1} to higher energies due to the less electron rich nature of the uncharged group 5 molecules. On this basis the molecular structures of $[(C_5R_5)M(CO)_4]^z$ for the analogous group 4 and 5 elements are likely to be quite similar in all cases. Previously it was established that the X-ray structure of $(C_5H_5)Ti(CO)_4^-$ was very much like that of $C_5H_5V(CO)_4$ [3]. It has been observed that carbonyl ^{13}C NMR resonance positions steadily become less positive (i.e., shift upfield) as the atomic number of the metal increases in a triad for a given type of binary or substituted metal carbonyl [10]. 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 [11]. In contrast, the carbonyl ^{13}C resonance positions for our group 4 carbonyls are farthest downfield for zirconium in all three classes of compounds and corresponding values for the hafnium carbonyls are more downfield by about 2–3 ppm than those for the analogous titanium species. The

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* Reference numbers with asterisks indicate notes in the list of references.

Table 1

Selected spectroscopic data for zerovalent metal carbonyls of Ti, Zr and Hf

Entry	Compound [a]	IR ν(CO) (cm^{-1}) [b]	$^{13}C\{^1H\}$ NMR [c] δ(CO) (ppm)	Ref.
1	$C_5H_5Ti(CO)_4^-$	1921 m, 1777s	288.9	3
2	$C_5H_5Zr(CO)_4^-$	1923 m, 1781 s	291.7	3
3	$C_5H_5Hf(CO)_4^-$ [d]	1920 m, 1780 s	290.6	This work
4	$C_5Me_5Ti(CO)_4^-$	1914 m, 1769 s	293.4	3
5	$C_5Me_5Zr(CO)_4^-$	1916 m, 1781 s	296.5	3
6	$C_5Me_5Hf(CO)_4^-$ [e]	1915 m, 1774 s	296.4	This work
7	(TRMPE)Ti$(CO)_4$	1931 m, 1810 s	278.9	2
8	(TRMPE)Zr$(CO)_4$	1938 m, 1820 s	284.4	2
9	(TRMPE)Hf$(CO)_4$	1934 m, 1814 s	282.1	2

[a] All anions are tetraethylammonium salts. TRMPE = $CH_3C(CH_2PMe_2)_3$. [b] Solvent: tetrahydrofuran (THF) for entries 1,7; 1,2-dimethoxyethane (DME) for others. [c] NMR spectra (20 °C) were obtained for entries 1–6 in $(CD_3)_2SO$ and for entries 7–9 in THF-d_8. [d] ^1H NMR (300 MHz), δ 5.51 (s, 5H); $^{13}C\{^1H\}$ NMR (75 MHz) δ 290.6, 96.6 (C_5H_5), cation not shown. [e] ^1H NMR (300 MHz), δ 1.99 (s, 15 H); $^{13}C\{^1H\}$ NMR (75 MHz) δ 296.4, 108.2 (C_5Me_5), 12.0 (C_5Me_5), cation not shown. The anions in the K(15-Crown-5)$_2^+$ and K(Cryptand-2.2.2)$^+$ salts (compounds **1** and **2** in the text) have the same IR, ^1H and ^{13}C NMR spectra as the tetraethylammonium salt.

large positive carbonyl ^{13}C shifts observed for all of these zerovalent group 4 carbonyls are rather impressive and also are 40 to 50 ppm downfield of the carbonyl ^{13}C resonance (δ 239.9) of the only previously known Hf^0 carbonyl, [Hf(1,3,5-$tBu_3C_6H_3)_2CO$] [1].

Potassium naphthalenide reduced $(C_5R_5)HfCl_3$ significantly faster at low temperature than did $NaC_{10}H_8$, under otherwise identical conditions, but the reasons

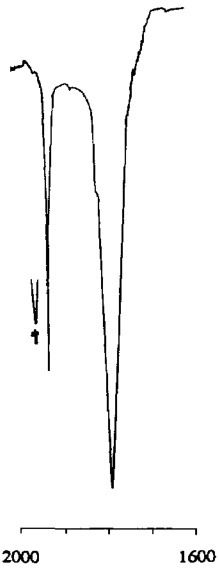

Fig. 1. Infrared solution spectrum of $[Et_4N][(C_5Me_5)Hf(CO)_4]$ in 1,2-dimethoxyethane in the carbonyl stretching frequency region. Position of bands: 1915(m), 1774(s) cm^{-1}. A polystyrene reference band at 1944 cm^{-1} is indicated with a dagger.

for this difference are unclear at present. While infrared solution spectra of the initially formed K[(C_5R_5)Hf(CO)$_4$] could be obtained without difficulty in DME and closely resemble those of the Et_4N^+ salts (Fig. 1), the corresponding sodium salts were much less thermally stable in solution. This cation effect may account for our inability to prepare the hafnium anions previously using Na[$C_{10}H_8$] as the reductant. Surprisingly, we recently reported just the opposite trend for [(C_5H_5)Ti(CO)$_2$($Me_2PCH_2CH_2PMe_2$)]$^-$, where the Na^+ salt is far more thermally stable (in THF) than the K^+ salt [12]. Clearly, the nature of the counterion is often of crucial importance in the synthesis and isolation of highly reduced carbonyl anions of the early transition metals, including the recently reported Ti(CO)$_6^{2-}$ [13]. Alkali metal cations appear to promote the decomposition of these carbonyl anions but how this occurs and the nature of the resulting decomposition product(s) remain interesting and presently unsolved problems.

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6 The need for additional naphthalene over that required to form $KC_{10}H_8$ in this synthesis has not been established, however, 2–4 equivalents of free naphthalene has been shown to substantially improve the yields of other low valent group 4 carbonyls prepared by the alkali metal naphthalenide method (see: K.M. Chi, S.R. Frerichs, B.K. Stein, D.W. Blackburn and J.E. Ellis, J. Am. Chem. Soc., 110 (1988) 163). Excess naphthalene should aid in the formation and stabilization of possible labile naphthalene complexes which we believe are intermediates in many of these syntheses.

7 Compound 1 Anal. Found: C, 45.36; H, 6.06. $C_{34}H_{55}O_{14}$HfK calcd.: C, 45.10; H, 6.12%. (2) Anal. Found: C, 45.59; H, 5.99; N, 3.12. $C_{32}H_{51}O_{10}$HfKN$_2$ calcd.: C, 45.68; H, 6.11; N, 3.33%. (3) Anal. Found: C, 47.52; H, 5.82; N, 2.46. $C_{22}H_{35}O_4$HfN calcd.: C, 47.52; H, 6.35; N, 2.52%. (4) Anal. Found: C, 41.85; H, 5.24; N, 2.98. $C_{17}H_{25}O_4$HfN calcd.: C, 42.02; H, 5.19; N, 2.88%.

8 Since commercial sources of hafnium compounds generally contain 2–4% zirconium which cannot always be easily removed by physical processes such as sublimation or recrystallization and there is precedent for organozirconium compounds undergoing reduction more readily and/or cleanly than their hafnium analogs (see for example Ref. 2 or D.M. Roddick, M.D. Fryzuk, P.F. Seidler, G.L. Hillhouse and J.E. Bercaw, Organometallics, 4 (1985) 97), we were concerned that the reductive carbonylations described herein, which provide 25–50% yields of products, could result in significant enrichment in zirconium. Although there is no evidence for any such problem in this study, zirconium enrichment must always be considered a possibility when less than quantitative yields of products are obtained from a hafnium precursor which is contaminated by zirconium.

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