

$C_8H_{12}Cl$].²⁹ Since steric factors probably do not influence the reactivity of these half-sandwich compounds to any large degree, we conclude that electronic effects are largely responsible for the lack of substitutive reactivity in both $[(HBpz_3)Ru(\eta^4-C_8H_{12})Cl]$ and $[(\eta^5-C_5Me_5)Ru(\eta^4-C_8H_{12})Cl]$. Both the steric and electronic similarities between the pentamethylcyclopentadienyl and hydrotris(1-pyrazolyl)borate ligands have already been noted.³⁰

In conclusion, the reactive precursors $[(\eta^4-C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ and $[(\eta^4-C_8H_{12})RuCl(Me)(NCMe)_2]$ provide a unique entry to the coordination chemistry of (dihydrobis(1-pyrazolyl)borato)- and (hydrotris(1-pyrazolyl)boratoruthenium complexes and, through the fragmentation of the pyrazolylborate ligands, also to pyrazolyl- and amidine-ruthenium systems.

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Registry No. 1, 61042-65-7; 2, 109744-70-9; 3, 109744-71-0; 4, 109744-72-1; 6, 109744-76-5; 7, 109744-77-6; $K[H_2B(3,5-Me_2pZ)_2]$, 18583-59-0; $[H(\mu-H)B(3,5-Me_2pZ)_2]Ru(\eta^4-C_8H_{12})Me$, 109764-46-7; $[(\mu-H)B(3,5-Me_2pZ)_2]Ru(dppb)H$, 109744-73-2; $[(\mu-H)B(3,5-Me_2pZ)_2]Ru(dppb)Me$, 109744-74-3; $K[Et_2BpZ_2]$, 109744-75-4; $K[Ph_2BpZ_2]$, 95675-62-0; $K[HBpZ_3]$, 18583-60-3; $[(HBpZ_3)Ru(\eta^4-C_8H_{12})H]$, 109744-69-6.

Supplementary Material Available: Details of the structure determinations and tables of fractional coordinates, temperature factors, and bond lengths and angles for 2 and 4 and elemental analyses and spectroscopic characterization for 2 and 4 (20 pages); listing of observed and calculated structure factors for 2 and 4 (33 pages). Ordering information is given on any current masthead page.

(29) For example, 7 and $[(\eta^5-C_5Me_5)Ru(\eta^4-C_8H_{12})Cl]$ may be converted to the stable cations $[(HBpz_3)Ru(\eta^4-C_8H_{12})(solvent)]^+$ and $[(\eta^5-C_5Me_5)Ru(\eta^4-C_8H_{12})(solvent)]^+$ ²⁸ respectively, whereas in the case of $[(\eta^5-C_5H_5)Ru(\eta^4-C_8H_{12})Cl]$, such species have not been detected and are possibly only intermediates in certain substitution processes of this compound.

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Highly Reduced Organometallics. 21.¹ Halocarbons of Group 4 Elements. Synthesis, Characterization, and Molecular Structure of $(C_5Me_5)Hf(CO)_2(Me_2PCH_2CH_2PMe_2)Cl$

Beatrice Kelsey Stein,² Scott R. Frerichs, and
John E. Ellis*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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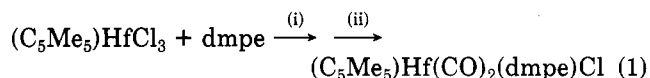
Summary: The first example of a stable halocarbonyl of a group 4 element has been synthesized, isolated, and

(1) Part 20: Chi, K. M.; Frerichs, S. R.; Stein, B. K.; Blackburn, D. W.; Ellis, J. E., submitted for publication.

(2) Present address: Air Products and Chemicals, Allentown, PA 18105.

characterized. Treatment of $(C_5Me_5)HfCl_3$ with sodium naphthalenide in the presence of $Me_2PCH_2CH_2PMe_2$ at $-60^\circ C$ in 1,2-dimethoxyethane followed by atmospheric pressure carbonylation provides $(C_5Me_5)Hf(CO)_2(dmpe)Cl$. The single-crystal X-ray structure of this material has been determined and is discussed in relation to spectroscopic data. Much less thermally stable zirconium and titanium analogues have also been prepared and are characterized on the basis of their spectroscopic properties.

While several classes of titanium and zirconium carbonyls are now known,³ the carbonyl chemistry of hafnium remains poorly explored and has been largely limited to divalent compounds of the type $(\eta^5\text{-ring})_2Hf(CO)L$, where $(\eta^5\text{-ring}) = C_5H_5, C_5Me_5$, or indenyl and $L = CO$, phosphines, or phosphites.⁴ On the basis of the relatively high thermal stability exhibited by $(C_5H_5)Zr(CO)_4$ ^{-3a} and $(C_5Me_5)Zr(CO)_4$ ⁻⁵ we had hoped to extend our low-temperature sodium naphthalenide reductive carbonylation methodology to obtain an analogous hafnium species. Corresponding reductions of $(C_5Me_5)HfCl_3$ provided exceedingly unstable materials. However, we now report that addition of the excellent donor ligand 1,2-bis(dimethylphosphino)ethane, dmpe, before reduction provides the first isolable halocarbonyl of a group 4 element,⁶ $(C_5Me_5)Hf(CO)_2(dmpe)Cl$ (1). Since this material is also the initial "half-sandwich" carbonyl of hafnium and the only known derivative of the unknown $(C_5Me_5)Hf(CO)_4X$ ($X = \text{halogen}$), its constitution has been verified by a single-crystal X-ray diffraction study. Equation 1 summarizes the procedure used for the synthesis of this and related zirconium and titanium complexes. Conditions: (i) 2–4 equiv of $Na-C_{10}H_8$ at -60 to $-70^\circ C$ in 1,2-dimethoxyethane under argon, (ii) evacuation followed by addition of CO (1 atm) and slow warming.)



In a typical synthesis, a solution containing dmpe (0.91 mL, 5.4 mmol) and $(C_5Me_5)HfCl_3$ (2.1 g, 5.0 mmol) in 100 mL of 1,2-dimethoxyethane (dme) was cooled to $-60^\circ C$ and subsequently added via cannula to a mechanically stirred slurry/solution of $Na-C_{10}H_8$ (14.9 mmol) and $C_{10}H_8$ (10.0 mmol) in 100 mL of dme at $-60^\circ C$ in a 500-mL Morton flask. Within 5 min the argon atmosphere was removed under vacuum and replaced by carbon monoxide at about 1-atm pressure. The resulting yellow green reaction mixture was then slowly warmed to $-25^\circ C$ over a 2-h period, filtered through Celite, and evacuated at $0^\circ C$ to remove solvent. After the residue was washed with hexane to remove naphthalene, the product was recrystallized from toluene to provide 0.51 g (18% yield, unoptimized) of a thermally stable bright green crystalline (1) (decomp pt $165\text{--}175^\circ C$) which provided satisfactory analytical data.⁷ Despite the presence of the good electron-donating C_5Me_5 and dmpe groups and the corre-

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(6) Teuben and co-workers have reported infrared spectral evidence for $(C_5Me_5)Hf(2,3\text{-dimethyl-1,3-butadiene})(CO)Cl$, but this material could not be isolated: Blenkins, J.; De Liefde Meijer, H.; Teuben, J. *Organometallics* 1983, 2, 1483.

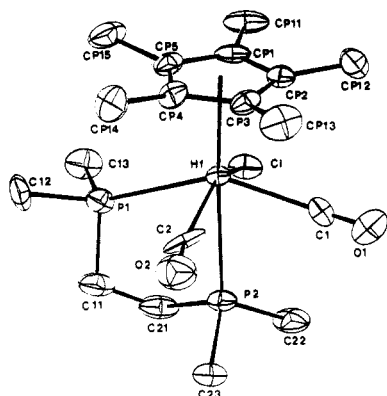


Figure 1. ORTEP diagram of $(C_5Me_5)Hf(CO)_2(dmpe)Cl$ drawn with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Hf–Cent = 2.173 (5), Hf–Cl = 2.568 (1), Hf–C(1) = 2.244 (5), Hf–C(2) = 2.208 (5), Hf–P(1) = 2.755 (1), Hf–P(2) = 2.764 (1), Hf–CP(1) = 2.519 (4), Hf–CP(2) = 2.479 (5), Hf–CP(3) = 2.455 (5), Hf–CP(4) = 2.470 (4), Hf–CP(5) = 2.510 (4); C(1)–Hf–C(2) = 85.6 (2), Cl–Hf–C(1) = 90.8 (1), Cl–Hf–P(1) = 80.07 (4), Cl–Hf–P(2) = 98.9 (1), P(1)–Hf–P(2) = 73.61 (4), C(1)–Hf–P(2) = 74.7 (1), Cl–Hf–C(2) = 149.1 (1), C(1)–Hf–P(1) = 148.3 (1), Cent–Hf–Cl = 111.4 (1), Cent–Hf–C(1) = 100.3 (1), Cent–Hf–C(2) = 99.4 (1), Cent–Hf–P(1) = 111.3 (1), Cent–Hf–P(2) = 172.2 (1) (Cent = centroid of C_5Me_5 ring).

sponding low IR active $\nu(CO)$ values,⁷ the carbonyl groups in **1** are quite labile. For example, treatment of a dilute solution of **1** in toluene at room temperature with excess 99% ^{13}CO at atmospheric pressure resulted in essentially quantitative exchange of coordinated carbon monoxide within 45 min.⁸ While solutions of **1** in toluene under argon decompose within hours at room temperature, they are stable for several weeks under a CO atmosphere at room temperature.

The X-ray structure of **1** is shown in Figure 1⁹ and is structurally related to the recently reported $(C_5H_5)Zr(dmpe)_2Cl$ ¹⁰ and $(C_5H_5)Ti(CO)_2(dmpe)H$.¹¹ However, in **1** a Me_2P unit of the dmpe ligand, rather than a chlorine

or hydrogen atom, is located opposite the centroid of the ring. Unfavorable steric interactions of the methyl groups on the dmpe and C_5Me_5 ligands are likely to favor the observed geometry of **1**. While $^{31}P\{^1H\}$ NMR solution spectra of **1** at room temperature show only one resonance due to equivalent phosphines of coordinated dmpe, corresponding low-temperature spectra at $-90^\circ C$ show two sharp singlets of equal intensities which suggest that the same structure as observed in the solid state is also preferred in solution.⁷ Interatomic distances and angles (see Figure 1) are reasonable for a divalent hafnium species. The Hf– C_5Me_5 centroid distance, 2.17 Å, is the same as that found for $(C_5Me_5)_2Hf(CO)_2$,¹² but all other Hf to element distances appear to be somewhat longer than corresponding values observed previously, perhaps due to the relatively crowded environment about the metal center. For example, the mean Hf–C(carbonyl) distance, of 2.23 (2) Å, is significantly longer than those in $(C_5Me_5)_2Hf(CO)_2$, 2.14 (2) Å,¹² and $(C_5H_5)_2Hf(CO)_2$, 2.16 (2) Å.¹³ Similarly, the mean Hf–P distance of 2.759 (6) Å and Hf–Cl distance of 2.568 (1) Å of **1** are longer than the respective distances found in the formally zerovalent species $Hf(\eta-C_4H_6)_2(dmpe)$, 2.71 (2) Å,¹⁴ and the recently reported $(C_5Me_5)Hf(2,3\text{-dimethyl-1,3-butadiene})Cl$, 2.393 (2) Å, and its pyridine adduct, 2.536 (2) Å.¹⁵

Analogous green zirconium and olive green titanium compounds, $(C_5Me_5)M(CO)_2(dmpe)Cl$, were synthesized by the same procedure and have been characterized by their infrared and NMR spectra.¹⁶ However, these materials are much less stable in solution than the corresponding hafnium compound and have not been isolated as pure substances. Teuben and co-workers have noted similar stability trends for related complexes of the type $(C_5Me_5)M(2,3\text{-dimethyl-1,3-butadiene})Cl$ for $M = Ti, Zr$, and Hf .¹⁵

The reactivity patterns of these new materials have not been investigated in detail; however, they show promise as precursors to new anionic carbonyls of these elements as well as novel classes of heterometallic complexes.

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Supplementary Material Available: Tables of positional parameters, general temperature factor expressions, and bond lengths and angles and X-ray structural analysis (12 pages); a listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

(7) 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. IR (1,2-dimethoxyethane): $\nu(CO)$ 1914 m, 1801 s cm^{-1} . IR (Nujol): 1904 m, 1788 s cm^{-1} . NMR (toluene- d_6 , $23^\circ C$): $^1H\{^{31}P\}$ δ 1.95 (s, C_5Me_5 , 15 H), 1.21–1.33 (m, CH_2 of dmpe, 4 H), 1.05 (s, CH_3 of dmpe, 6 H), 0.90 (s, CH_3 of dmpe, 6 H); $^{31}P\{^1H\}$, δ –8.6 (s, coord dmpe); $-90^\circ C$, δ –6.2 (s, coord dmpe, 1 P), –8.8 (s, coord dmpe, 1 P). Also a small singlet at –48 ppm due to free dmpe was evident. The ^{13}C NMR spectrum of the unenriched material exhibited no CO resonance.

(8) Spectral data for ^{13}C enriched material: IR (dme) $\nu(CO)$ 1871 m, 1755 s cm^{-1} (calculated values: 1871, 1760 cm^{-1} based on $\nu(^{12}CO)$ data). NMR (C_6D_6 , $23^\circ C$): $^{31}P\{^1H\}$, δ –7.8 (s), –47 (weak s, free dmpe); $^{13}C\{^1H\}$, δ 283 (br s, CO), 184 (weak s, free ^{13}CO), 100 (s, $C_5(CH_3)_5$), 12 (s, $C_5(CH_3)_5$), no peaks due to dmpe were observed in this spectrum.

(9) Single crystals of $(C_5Me_5)Hf(CO)_2(dmpe)Cl$ were slowly grown from pentane–toluene at $0^\circ C$ over a 4-day period. Data collection was carried out at $-56^\circ C$ on an Enraf-Nonius CAD 4 automated diffractometer using Mo $K\alpha$ radiation. The compound crystallizes in the monoclinic space group $P2_1/a$ (nonstandard setting of No. 14) and has the cell parameters: $a = 16.428$ (15) Å, $b = 9.425$ (3) Å, $c = 14.190$ (8) Å, $\beta = 99.65$ (6)°, $V = 2166$ (4) Å³, and $Z = 4$. Intensity data were collected for 3655 reflections of which 3468 were unique and measured $F_o^2 \geq 1.0\sigma(F_o)^2$ and were used for structure solution and refinement by using Enraf-Nonius CAD 4-SDP programs. The last cycle of least-squares refinement gave residuals of $R = 0.033$ and $R_w = 0.046$ and a GOF of 1.53 for a fit to 249 variables to 3468 observations. Complete details of the refinement and tables of data are available as supplementary material.

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(16) $(C_5Me_5)Zr(CO)_2(dmpe)Cl$: IR(dme) $\nu(CO)$: 1923 m, 1810 s cm^{-1} , IR (Nujol) 1913 s, 1800 m cm^{-1} ; $^{31}P\{^1H\}$ NMR (dme, $-10^\circ C$) δ –8.1 (br s). $>90\%$ ^{13}C -enriched compound: IR(dme) $\nu(CO)$ 1885 m, 1773 s cm^{-1} ; $^{13}C\{^1H\}$ (toluene- d_8) δ 279 (br s CO), 185 (free ^{13}CO), 100.1 ($C_5(CH_3)_5$); signals due to other carbons were not resolved. $(C_5Me_5)Ti(CO)_2(dmpe)Cl$: IR (dme) $\nu(CO)$ 1923 m, 1826 s cm^{-1} ; $^{31}P\{^1H\}$ NMR (dme, $-10^\circ C$) δ 11.2 (br s). Attempts to isolate the titanium compound led to extensive decomposition.