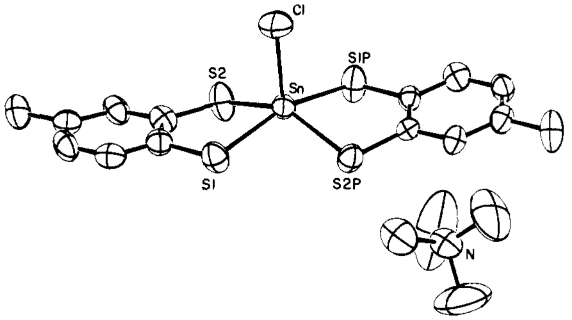

Figure 1. ORTEP plot of the complex $[(CH_3)_4N]^+[(C_7H_6S_2)_2SnCl]^-$ (**1**), with thermal ellipsoids at the 50% probability level. Some Sn-ligand bond parameters: S2-Sn-S2P = 147.6 (1)°, S1P-Sn-S1 = 161.3 (1)°; Sn-Cl = 2.413 (4) Å, Sn-S2 = 2.437 (4) Å, Sn-S2P = 2.447 (3) Å, Sn-S1P = 2.458 (4) Å, Sn-S1 = 2.463 (3) Å; Cl-Sn-S1 = 98.9 (1)°; Cl-Sn-S2 = 106.0 (1)°; Cl-Sn-S1P = 99.8 (2)°; Cl-Sn-S2P = 106.4 (1)°.

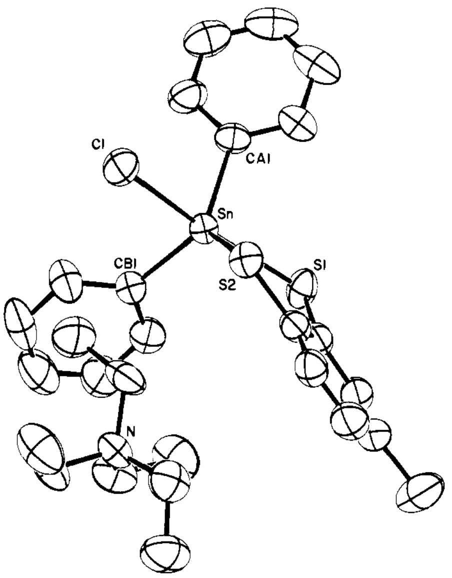

Figure 2. ORTEP plot of $[(C_2H_5)_4N]^+[(C_7H_6S_2)Ph_2SnCl]^-$ (**5**), with thermal ellipsoids at the 50% probability level. Some Sn-ligand bond parameters: Cl-Sn-S1 = 165.9 (1)°, CA1-Sn-CB1 = 121.2 (3)°, CA1-Sn-S2 = 120.6(2)°, CB1-Sn-S2 = 118.0(2)°; Sn-Cl = 2.588 (2) Å, Sn-CA1 = 2.152 (6) Å, Sn-CB1 = 2.146 (7) Å, Sn-S2 = 2.436 (2) Å, Sn-S1 = 2.544 (2) Å.

hydrogen atoms, fixed isotropic for nonmethyl hydrogen atoms). For **1**, a final conventional unweighted residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.039 was obtained on the basis of 1775 independent reflections having $I \geq 2\sigma(I)$. For **5** the final R value was 0.048 for the 3438 reflections having $I \geq 2\sigma(I)$.

Figures 1 and 2 show ORTEP plots of the molecular geometries of **1** and **5**, respectively. It is evident from the bond parameter data given in the legends that the spirocyclic derivative **1** is near rectangular pyramidal and the monocyclic derivative **5** is trigonal bipyramidal. On the basis of the dihedral angle method, as applied to cyclic phosphoranes,[7,8] **1** is displaced 77.0% (unit bond lengths) from a trigonal bipyramid toward a rectangular pyramid, and **5** is 14.3% displaced. These structural distortions are similar to those found in monocyclic and spirocyclic benzodioxaphosphoranes.[7,8] This may mean that the extent of stereochemical nonrigidity of pentacoordinated phosphorus and tin are closely related. However, further examples of substituent effects for tin(IV) are needed to make the comparison more meaningful.

The precursor in the preparation of **1**, $Sn(TDT)_2$, has been used for a long time in the calorimetric estimation of tin.[9] Its solid-state structure, although not known, has been inferred from Mössbauer[10,11] and infrared[12] data to be polymeric. The data support intermolecular Sn-S bonding and the presence of hexacoordinated tin. Hence, the pentacoordinated structure of tin(IV) in **1** is all the more unique. The discovery of this new structural form for **1**, similar to the structure we recently established for the germanium derivative, $[Et_4N]^+[(C_6H_4O_2)_2GeCl]^-$,[13] suggests the existence of a rectangular-pyramidal geometry for silicon(IV).

Acknowledgment. The support of this research by the National Science Foundation is greatly appreciated, as is the generous allocation of computing time by the University of Massachusetts Computing Center.

Supplementary Material Available: Atomic coordinates (Tables I and II) and anisotropic thermal parameters (Tables III and IV) for **1** and **5**, respectively (6 pages). Ordering information is given in any current masthead page.

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(6) The function minimized was $\sum w(|F_o| - |F_c|)^2$. Mean atomic scattering factors were taken from ref 5, Vol. IV, 1974, pp 72-98. Real and imaginary dispersion corrections for Sn, Cl, and S were taken from the same source, pp 149-150.

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New Syntheses and Molecular Structures of the Decamethylmetallocene Dicarbonyls $(\eta^5\text{-}C_5Me_5)_2M(CO)_2$ (M = Ti, Zr, Hf)

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In view of the high current interest in η^5-pentamethylcyclopentadienyl derivatives of the transition and actinide metals,[1-14]

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Table I. Synthesis and Spectra of Group 4B Metallocene Dicarbonyls

compound	yield, %	IR (hexane), cm^{-1}	^{1}H NMR (C_6D_6), ppm	MS: M$^+$, *m/e*^{b}
$Cp_2Ti(CO)_2$ (4)	87^a	1977, 1899	4.65	234
$(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$ (1)	65	1940, 1858	1.67	374
$Cp_2Zr(CO)_2$ (5)	50	1975, 1885	4.95	276^c
$(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ (2)	80	1945, 1852	1.73	416
$Cp_2Hf(CO)_2$ (6)	30	1969, 1878	4.81	366^c
$(\eta^5\text{-}C_5Me_5)_2Hf(CO)_2$^{d} (3)	25	1940, 1844	1.74	506

^{a} Prepared by the method of Demerseman et al.[17] ^{b} Based on the most abundant isotope. ^{c} Reference 20. ^{d} Anal. Calcd for $C_{22}H_{30}O_2Hf$: C, 52.32; H, 5.99. Found: C, 52.18; H, 5.95.

it was of interest to determine the effect of the electron-rich pentamethylcyclopentadienyl ligand on the chemical reactivity and structural features of the group 4B metallocene dicarbonyls. Although $(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$ (**1**) and $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ (**2**) have been described in the literature,[1,2,5] their molecular structures have not yet been examined, and facile synthetic routes to these substances are lacking. In a continuation of our joint program on the formation, reactions, and structures of group 4B metallocene dicarbonyls,[15-17] we now report on a convenient new synthesis of **1**, **2**, and the currently unknown hafnium analogue $(\eta^5\text{-}C_5Me_5)_2Hf(CO)_2$ (**3**) as well as on the results of single-crystal X-ray diffraction studies of all three substances.

During the course of our recent studies concerning the thermal and photochemical reactions of $Cp_2Ti(CO)_2$ (**4**),[18,19] it was desirable to investigate the corresponding zirconium and hafnium analogues, $Cp_2Zr(CO)_2$ (**5**) and $Cp_2Hf(CO)_2$ (**6**), for comparative purposes.[16] However, existing syntheses of these compounds were of low yield and/or required severe reaction conditions.[20-22] We subsequently developed a facile synthetic route to **5** and **6**, utilizing magnesium metal activated by mercuric chloride as the reducing agent. The reaction proceeds smoothly at room temperature and 1-atm CO pressure; yield and pertinent spectral data are given in Table I.

Extensions of this procedure have been found to work equally well for the formation of the decamethylmetallocene dicarbonyls **1** and **2**, starting with the respective decamethyltitanocene[1] and zirconocene dichlorides.[23,24] Decamethylhafnocene dichloride[25] proved to be resistant to reduction under these conditions; however, use of "super"-activated Rieke magnesium[26] was sufficient for reduction and afforded **3** in moderate yield.[27] Pertinent spectral data for **1**–**3** are also given in Table I.

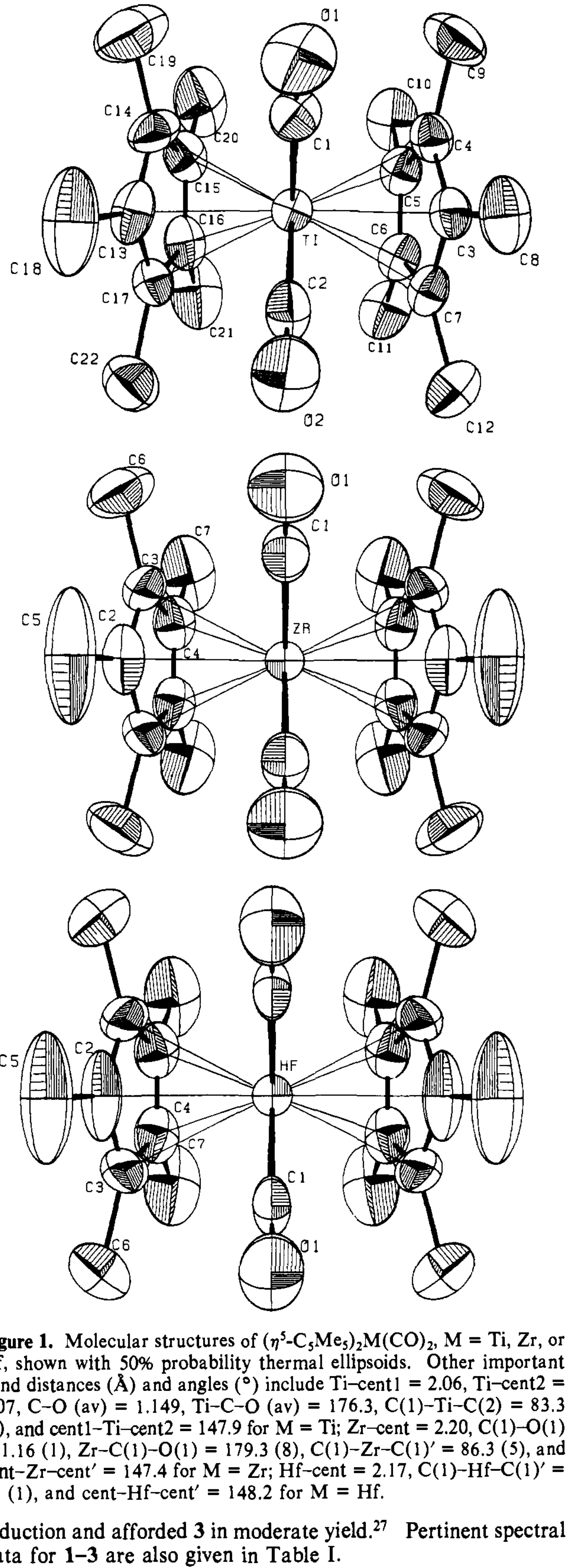

Figure 1. Molecular structures of $(\eta^5\text{-}C_5Me_5)_2M(CO)_2$, M = Ti, Zr, or Hf, shown with 50% probability thermal ellipsoids. Other important bond distances (Å) and angles (°) include Ti–cent1 = 2.06, Ti–cent2 = 2.07, C–O (av) = 1.149, Ti–C–O (av) = 176.3, C(1)–Ti–C(2) = 83.3 (3), and cent1–Ti–cent2 = 147.9 for M = Ti; Zr–cent = 2.20, C(1)–O(1) = 1.16 (1), Zr–C(1)–O(1) = 179.3 (8), C(1)–Zr–C(1)′ = 86.3 (5), and cent–Zr–cent′ = 147.4 for M = Zr; Hf–cent = 2.17, C(1)–Hf–C(1)′ = 87 (1), and cent–Hf–cent′ = 148.2 for M = Hf.

The IR spectra of **1**, **2**, and **3** are of special interest when compared to the spectra of the cyclopentadienyl analogues **4**, **5**,

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(24) In a typical run, 800 mg (1.85 mmol) of $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ in 20 mL of THF was treated with 225 mg (9.26 mmol) of magnesium powder followed by 500 mg (1.84 mmol) of $HgCl_2$. The reaction mixture was stirred vigorously (sharp vortex) under an atmosphere of CO for 24 h. The resulting dark red solution was concentrated to dryness, the residue was extracted with ca. 30 mL of heptane, the extracts were filtered under argon, and the filtrate was concentrated and cooled to −20 °C, producing 620 mg (80%) of black needles of **2**. The titanium analogue **1** was prepared in an analogous manner.

(25) Prepared by a method analogous to that for $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$. ^{1}H NMR δ 2.05 $(\eta^5\text{-}C_5Me_5)$.

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(27) Activated magnesium was prepared from anhydrous $MgCl_2$ (1.90 g) and potassium (1.11 g) in THF according to literature.[26] The mixture was allowed to cool to room temperature and purged with CO. $(\eta^5\text{-}C_5Me_5)_2HfCl_2$ (1.50 g, 2.89 mmol) and $HgCl_2$ (0.50 g, 1.84 mmol) were added and the reaction mixture stirred under CO for 24 h. Workup as described above for **2** produced 360 mg (25%) of **3** as purple needles.

Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compound	$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti(CO)}_2$	$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr(CO)}_2$	$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Hf(CO)}_2$
mol wt	374.4	417.7	505.0
space group	$P2_12_12_1$	*Fmm*2	*Fmm*2
cell constant, *a*, Å	8.517 (3)	15.137 (4)	15.135 (4)
b, Å	10.774 (4)	16.860 (4)	16.807 (4)
c, Å	22.195 (6)	8.280 (3)	8.268 (3)
cell vol, Å^3	2036.7	2113.1	2103.2
molecules/unit cell	4	4	4
ρ(calcd), g cm^{-3}	1.22	1.31	1.59
μ(calcd), cm^{-1}	4.49	5.23	52.23
radiation	Mo Kα	Mo Kα	Mo Kα
max crystal dimensions, mm	0.75 × 0.40 × 1.50	0.10 × 0.10 × 1.80	0.10 × 0.20 × 1.50
scan width	$0.80 + 0.20 \tan \theta$	$0.80 + 0.20 \tan \theta$	$0.80 + 0.20 \tan \theta$
standard reflections	400 008	400 060	400 060
decay of standards	±2%	±2%	±2%
reflections measured	2176	548	546
2θ range	50°	50°	50°
obsd reflections	1366	507	544
no. of parameters varied	226	64	64
GOF	1.15	1.09	1.31
R	0.040	0.030	0.032
R_w	0.045	0.034	0.037

and **6**, respectively. In particular, it is noteworthy that the carbonyl stretching frequencies for both the A_1 and B_1 modes of **1**, **2**, and **3** are shifted to ca. 29–41-cm^{-1} lower energy relative to corresponding values for **4**, **5**, and **6**. These shifts are approximately those predicted[28] for the introduction of 10 methyl substituents onto the cyclopentadienyl rings of **4–6**, and can be attributed to enhanced π backbonding to the CO ligands as a result of increased electron density on the metal atom caused by the methyl groups. Analogous trends in the case of titanium complexes **1** and **4** have also been observed by Brintzinger and co-workers.[1]

Attempts to promote substitution of the carbonyl ligands in **1–3** by phosphines and phosphites under both thermal and photochemical conditions have thus far proved to be largely unsuccessful, in contrast to the cyclopentadienyl analogues **4–6**.[16] The results are consistent with enhanced thermal and photochemical stabilities of the permethylated complexes **1–3** relative to their cyclopentadienyl counterparts.[29] Further studies concerning the reactivities of **1–3** are in progress.

The crystal data for all three compounds and a summary of the refinement parameters are presented in Table II. In each case the hydrogen atoms were included, and all nonhydrogen atoms were refined with anisotropic temperature factors. For the hafnium structure the intensities were corrected for absorption effects.[30]

The molecular structures and atom-numbering schemes for the three compounds are shown in Figure 1. For titanium the molecule contains no crystallographically imposed symmetry, whereas the zirconium and hafnium molecules are isostructural and each metal atom resides on the intersection of two mirror planes. The average Ti–C(π) bond length, 2.384 (12) Å, is larger than the 2.35 (1) Å found in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(CO)}_2$[15] despite the fact that the pentamethylcyclopentadienyl ligand is more electron rich. The lengthening is doubtless due to nonbonded methyl–methyl repulsion. This is also evidenced by the fact that the methyl carbon atoms reside 0.2 Å out of the plane of the ring atoms. The average Ti–C(σ) bond distance, 2.01 (1) Å, is shorter than the 2.03 (1) Å value found in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(CO)}_2$,[15] as might be expected from the longer ring approach with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti(CO)}_2$.

The three unique Zr–C(π) lengths average 2.498 (9) Å compared to 2.48 (1) Å in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr(CO)}_2$.[31] However, the Zr–C($\sigma$) bond is much shorter in the title compound: 2.145 (9) Å vs. 2.187 (4) Å in the $\eta^5\text{-C}_5\text{H}_5$ complex. Following this trend the Hf–C(σ) distance, 2.14 (2) Å, is marginally shorter than the 2.16(2) Å found in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf(CO)}_2$.

Acknowledgment. We are grateful to the National Science Foundation for support of this research program.

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(29) For example, when **3** was photolyzed in C_6D_6 solution for 55 h, starting material was still observed to be present. In contrast, **6** when photolyzed under analogous conditions is completely consumed in 3–4 h.[16]

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Transformation of Coordinatively Unsaturated η^1-Vinylmolybdenum Complexes into Three-Electron η^2-Bonded Cyclic Alkylidene Species

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In an elegant series of investigations Bercaw and co-workers were led to postulate[1] a facile rearrangement of coordinatively unsaturated zirconium η^1-acyl complexes into three-electron η^2-bonded zirconium oxycarbene species, which were unstable and underwent further reactions. A driving force for this interesting rearrangement was considered to be the stability of the zirconium–oxygen bond. Recently a similar "switch" in bonding mode has been reported[2] with acylbis(pentamethylcyclopentadienyl)-thorium complexes. In this paper we report that coordinatively unsaturated vinylmolybdenum complexes can undergo a related transformation into stable three-electron η^2-bonded cyclic alkylidene complexes.

Reaction (−78 °C) of a purple tetrahydrofuran solution of bis(trimethyl phosphite)diphenylacetylene(η^5-cyclopentadienyl)-molybdenum tetrafluoroborate[3] with 1 molar equiv of potassium selectride [KBH(*sec*-Bu)$_3$] led to a rapid reaction and the formation of the green crystalline (from tetrahydrofuran at −30 °C) complex **1** [^{1}H NMR (CD_2Cl_2) τ 2.4–3.4 (m, 10 H, Ph), 4.76 (s, 5 H, C_5H_5), 6.17 (dd, 1 H, MoC*H*Ph, $^3J_{\text{trans-PH}} = 13$ Hz, $^3J_{\text{cis-PH}} = 6$ Hz), 6.66 (d, 9 H, PO*Me*, $^3J_{\text{PH}} = 11.5$ Hz), 6.76 (d, 9 H, PO*Me*, $^3J_{\text{PH}} = 11.5$ Hz); ^{31}P (CD_2Cl_2, ^{1}H decoupled) AB system δ_A 164.7, δ_B 158.1 $J_{\text{PP}} = 155$ Hz; ^{13}C (CD_2Cl_2, ^{1}H decoupled) δ 255.5 (d, alkylidene carbon, $^2J_{\text{PC}} = 40$ Hz), 157.1, 143.9, 130.9, 128.2, 126.8, 126.3, 121.1 (Ph), 91.4 (C_5H$_5$), 51.9, 51.7, 51.4, 51.1, 26.8 (d, Mo*C*HPh, $^2J_{\text{PC}} = 30$ Hz)]. Elemental analysis and mass

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