Journal of Organometallic Chemistry, 458 (1993) 97–103

JOM 23625

Structure of a metallacyclic metaloxycarbene vanadium complex prepared from $CpV(CO)_4$

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(Received December 31, 1992)

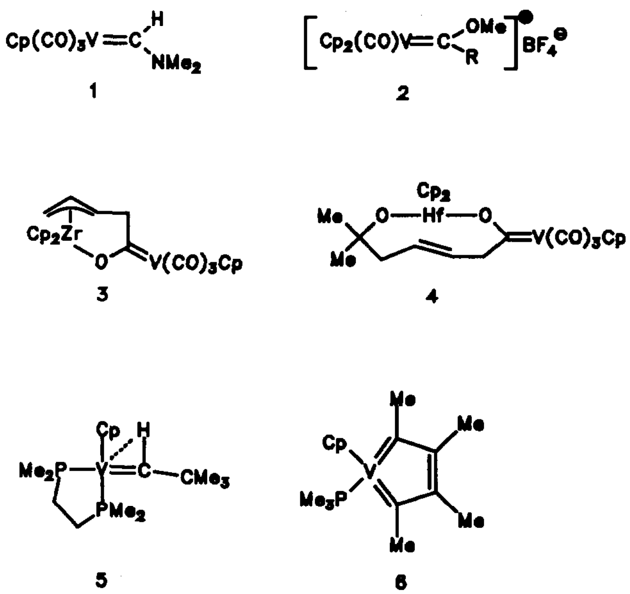
Abstract

Treatment with (butadiene)hafnocene converted $CpV(CO)_4$ into the metaloxycarbene vanadium complex **12**, which was then trapped by coupling with cyclopentanone to give the nine-membered metallacyclic metaloxycarbene vanadium complex $Cp_2\overline{HfOC(C_4H_8)CH_2CHCH{=}CH_2C[{=}VCp(CO)_3]O}$ (**13**), the crystal structure of which was determined. Complex **13** contains a *trans*-configurated C=C double bond inside the medium-size ring system and is chiral. The vanadium–C(carbene) bond length is 2.086(5) Å and the short O(carbene)–C(carbene) distance of 1.282(6) Å indicates considerable acylmetallate character for this metaloxycarbene vanadium complex.

1. Introduction

Carbene complexes of the d-elements play an important role in organometallic chemistry. They find increasing applications in stoichiometric organic synthesis and catalysis [1]. Heteroatom-stabilized ("Fischer-type") carbene complexes are usually synthesized starting from metal carbonyls. Sequential addition of a nucleophilic and electrophilic reagent efficiently converts the coordinated CO ligand into the carbene moiety [2]. This sequence of nucleophilic C-alkylation followed by electrophilic O-alkylation in a few cases cannot be used successfully for making carbene metal complexes. For these cases, other synthetic routes have been developed that either use precursors other than metal carbonyls or circumvent the difficulties encountered in these specific cases by employing reagents that mechanistically and energetically modify the M–C≡O to M–carbene conversion to make it favourable again [3,4].

Carbene complexes of vanadium are notoriously difficult to make from metal carbonyls. A few other routes have been tested up to now (see examples **1** and **2** in Scheme 1) [5]. We have shown that the (butadiene)zirconocene reagent can be used to convert



Scheme 1.

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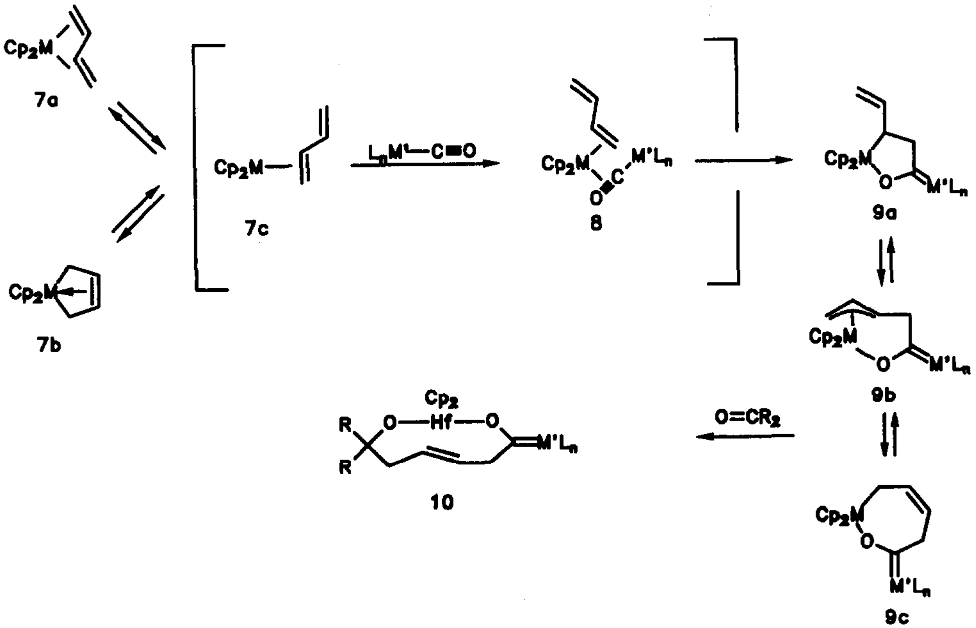
a carbonyl group in cyclopentadienyl(tetracarbonyl)vanadium into a metaloxycarbene vanadium functionality. This special example of a rather general reaction type for converting metal coordinated carbonyl into carbene ligands [3,6,7] produces an O-metallated carbene complex (**3**) which is rather labile owing to reversibility. The replacement of zirconium by hafnium, however, makes the carbene complex thermodynamically more stable [8]. Addition of 1 molar equivalent of acetone converts the initially formed coupling product to the nine-membered metallacyclic carbene complex **4**, which has no tendency to decompose via cycloreversion [9].

Only a few carbene vanadium complexes have so far been characterized by X-ray diffraction. Among the first was Teuben's "Schrock-type" alkylidene vanadium complex **5** [10]. To the best of our knowledge complexes **3** and **4** (and the related product of reaction of **3** with pivalonitrile) represent the only examples of O-metallated derivatives of "Fischer-type" carbene complexes of vanadium for which the crystal structures have been determined [8,9]. Because the characteristic structural features of the metaloxycarbene vanadium moieties are very different from those of the alkylidene vanadium species, we considered it to be important to expand the structural database available for these rather rare examples of the heteroatom-stabilized carbene vanadium complexes. Therefore, we prepared a variety of additional analogues of complexes **3** and **4** [9] by our synthetic methodology. For one of these, we were able to obtain crystals suitable for an X-ray structural analysis, and the results are described.

2. Results and discussion

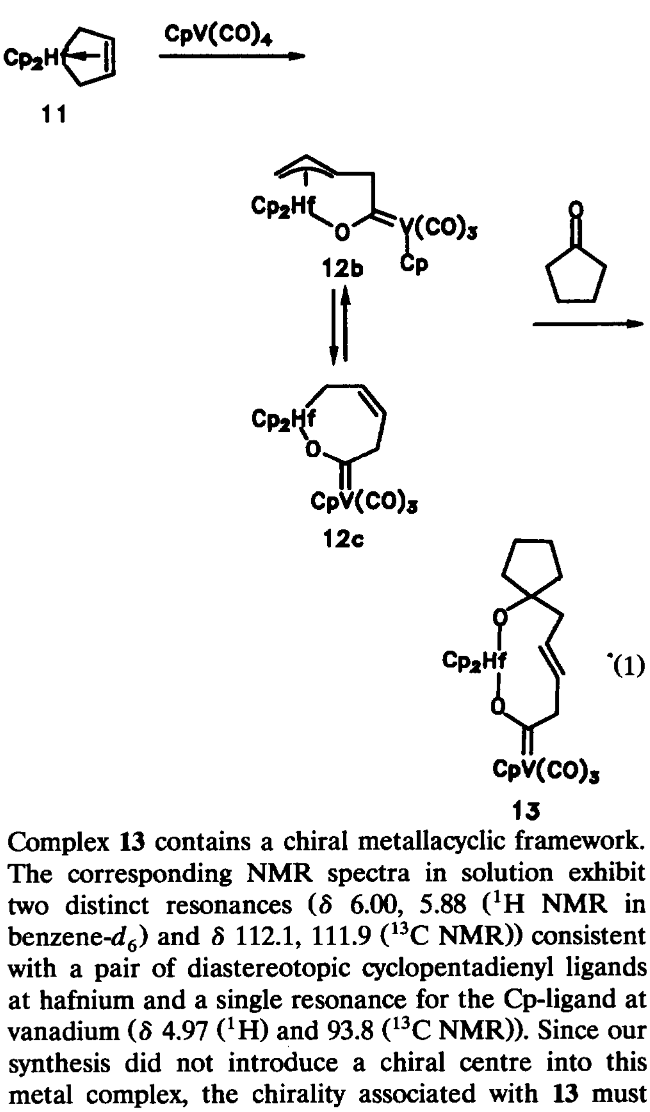
Our new carbene synthesis makes use of the high reactivity of (alkene)metallocene complexes and the high tendency of the Group 4 elements to form thermodynamically very favourable M–O bonds. Thus, (butadiene)MCp$_2$ complexes react with metal carbonyls L$_n$M–C≡O by means of a reaction sequence as depicted in Scheme 2 to yield an equilibrium situation of the 1:1 addition products **9**. We and others have used this route and variations thereof for converting carbonyl complexes of many transition metals into their respective metaloxycarbene complexes [3,6,7].

For this study, we treated (s-*cis*-η^4-butadiene) hafnocene (**11**) with 1 molar equivalent of CpV(CO)$_4$ to give a mixture of the metallacyclic allylic carbene complex isomers (**12b, c**) [8]. Subsequent addition of cyclopentanone proceeded rapidly at room temperature with conversion of both isomers **12(b, c)** into the nine-membered metallacyclic metaloxycarbene vanadium complex **13**. This coupling of the butadiene dianion equivalent in **11** was achieved with very high regioselectivity. Within the limits of detection, only 1,4-addition of the electrophiles employed (first the metal carbonyl and then the organic carbonyl compound) had



Scheme 2.

taken place. Compound **13** is thermodynamically stable and was isolated as crystals in close to 80% yield starting from the **12b, c** mixture of isomers.



Complex **13** contains a chiral metallacyclic framework. The corresponding NMR spectra in solution exhibit two distinct resonances (δ 6.00, 5.88 (^{1}H NMR in benzene-d_6) and δ 112.1, 111.9 (^{13}C NMR)) consistent with a pair of diastereotopic cyclopentadienyl ligands at hafnium and a single resonance for the Cp-ligand at vanadium (δ 4.97 (^{1}H) and 93.8 (^{13}C NMR)). Since our synthesis did not introduce a chiral centre into this metal complex, the chirality associated with **13** must arise from the structural properties of the metallacyclic ring system formed.

This conclusion was confirmed by the X-ray structural analysis of **13**. The central nine-membered metallacyclic framework of **13** contains a *trans*-configurated carbon–carbon double bond between carbon atoms C(3) and C(4) (1.309(6) Å). The pertinent bond angles at C(3) (C(2)–C(3)–C(4) 123.1(5)°) and C(4) (C(3)–C(4)–C(5) 124.6(5)°) are in the typical range for sp^2-hybridized carbon centres. The adjacent C(2)–C(3) (1.500(7) Å) and the C(4)–C(5) bond lengths (1.489(7) Å) are characteristic for C(sp^2)–C(sp^3) single bond distances [11]. It is this arrangement of the *trans*-C=C bond inside the rigid nine-membered metallacycle that makes complex **13** chiral. As is visualized from the projection of the molecular structure of **13** depicted in Fig. 1, the plane of the C(3)–C(4) carbon–carbon double bond is oriented almost perpendicular to the mean plane of the ring. Any intramolecular enantiomerization of this system exhibiting planar chirality proceeding without bond rupture requires rotational movements that force one of the hydrogen atoms attached to C(3) or C(4) to move through the inside of the medium-sized ring. It is known from many related metallacyclic [6] as well as carbocyclic examples [12] that rather high activation barriers (16–19 kcal mol^{-1}) are usual for this conformational equilibration of enantiomeric ring structures, making this inherent chirality information sufficiently persistent for the analytical methods employed (NMR at ambient temperature; X-ray crystal structure analysis).

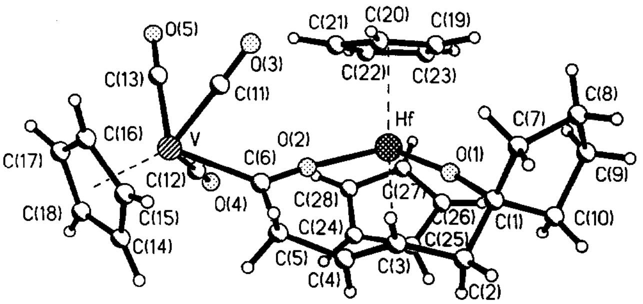


Fig. 1. A view of the molecular structure of complex 13 in the crystal with the atom numbering scheme.

Much of the rigidity of the system originates from the structural features of the incorporated HfO_2 moiety. The hafnium–oxygen bonds are rather short at 2.066(3) Å (O(2)–Hf) and 1.900(3) Å (O(1)–Hf). The angles at both ring oxygen atoms are much larger than expected and nearly approach a linear arrangement with sp-hybridized oxygen atoms (bond angles C(6)–O(2)–Hf 169.0(3); C(1)–O(1)–Hf 172.3(3)°). The C(3)–C(4) carbon–carbon π-bond is oriented directly in front of the Hf atom (angle O(1)–Hf–O(2) 103.9(1)°). However, the Hf $\cdots$ C(3)/C(4) separation is clearly outside the range expected for any bonding interaction (see Fig. 2). Most probably, the very rigid metallacyclic framework keeps the metal atom physically away from the organic C(4)–C(3) π-system. In addition, the electron demand of the electrophilic d^0 hafnium centre which formally possesses a 16-electron count, is likely to be diminished by the strong oxygen–hafnium interactions.

The carbon centre (C(6)) of the carbene ligand in **13** is trigonal planar, exhibiting bond angles of 127.1(3)° (O(2)–C(6)–V), 120.2(3)° (C(5)–C(6)–V), and 112.6(4)° (O(2)–C(6)–C(5)). The C(6)–C(5) bond length is 1.546(7) Å which is at the high limit of a C(sp^2)–C(sp^3) bond [11]. The C(6)–V distance of 2.086(5) Å is similar

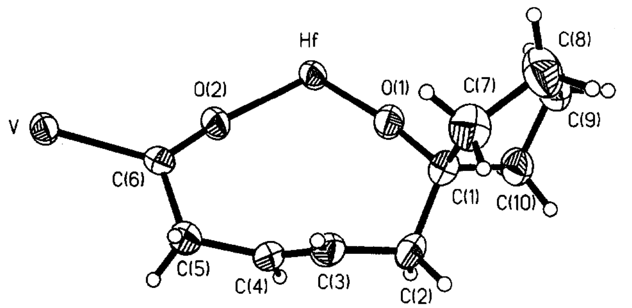
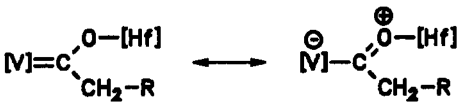


Fig. 2. Projection of the core of the metaloxycarbene vanadium complex 13.

to the corresponding distances found in the metaloxyvanadium complexes **3** (2.102(3) Å) and **4** (2.080(4) Å) [8,9]; in contrast the V–C(carbene) bond in the alkylidene vanadium complex **5** is much shorter at 1.809(3) Å [10].

The carbene oxygen–carbene carbon linkage (C(6)–O(2)) in complex **13** is rather short (1.282(6) Å). The corresponding O–C(carbene) bond length in the related metaloxycarbene vanadium complexes **3** and **4** are at 1.270(4) Å and 1.276(5) Å, respectively. All of these values are in a range typical of carbon–oxygen double bonds [11] and represent a characteristic general feature of such metaloxycarbene complexes. From the X-ray diffraction studies on the complexes **3**, **4**, and **13**, the respective structural features of the carbene vanadium moiety in all these metaloxycarbene vanadium complexes consistently fall within a narrow range, and the rather short C(carbene)–O(carbene) distance points to a pronounced participation of a resonance structure of considerable metal acyl complex character.



$$[\mathrm{V}]{=}\mathrm{C}\begin{smallmatrix}\mathrm{O{-}[Hf]}\\ \mathrm{CH_2{-}R}\end{smallmatrix} \longleftrightarrow \overset{\ominus}{[\mathrm{V}]}{-}\mathrm{C}\begin{smallmatrix}\overset{\oplus}{\mathrm{O}}\mathrm{{-}[Hf]}\\ \mathrm{CH_2{-}R}\end{smallmatrix} \qquad (2)$$

3. Experimental section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or a glovebox. For spectrometers used and general experimental conditions applied, see [9]. The metaloxycarbene complexes **11** were prepared as previously described [9].

3.1. Preparation of 13

To a suspension of 765 mg (1.29 mmol) of the metaloxycarbene complex mixture **12b, c** in 25 ml of toluene was added dropwise 0.13 ml (1.47 mmol) of cyclopentanone. The mixture was stirred for 5 h at room temperature and then filtered. The clear filtrate was kept at −18°C for 14 days. The resulting crystals were collected by filtration. A single crystal of this material was used for the X-ray crystal structure determination of **13**. Solvent was removed *in vacuo* from the mother liquor of the first crystallization to give additional **13** which was washed with pentane and dried *in vacuo*. Combined yield 680 mg (78%); m.p. 113°C (decomp.). Anal. Found (crystalline **13**): C, 52.71; H, 4.69. $C_{28}H_{29}O_5VHf$ (675.0) calcd.: C, 49.83; H, 4.33; $C_{28}H_{29}O_5VHf \times 0.5\ (C_7H_8)$ (721.1) calcd.: C, 52.48; H, 4.61%. IR (KBr): ν 3107, 2962, 1943 vs, 1861 vs, 1828 vs, 1371, 1353, 1048, 814, 802 cm^{-1}. ^{1}H NMR (benzene-d_6, numbering scheme as in Fig. 1): δ 6.00 and 5.88 (s, 5H each, Cp$_2$Hf); 4.97 (s, 5H, CpV); 4.88 (m, 2H, 3H, 4H); 4.35 (m, 1H, 5H); 3.44 (m, 1H, 5H′); 1.96–1.77 (m, 2H, 2H, 2H′); 1.60–1.15 (m, 8H, 7H–10H). ^{13}C NMR (benzene-d_6): δ 133.2, 132.0 (C-3, C-4); 112.1, 111.9 (Cp$_2$Hf); 93.8 (CpV); 92.1 (C-1); 66.6

TABLE 1. Crystallographic data for the X-ray diffraction analysis of $Cp_2Hf(OC(C_4H_8)CH_2CH{=}CHCH_2C[{=}VCp(CO)_3]O)\cdot 1/2C_7H_8$

A. Crystal data	
Empirical formula	$C_{28}H_{29}HfVO_5 \cdot 1/2C_7H_8$
Colour	Green, parallelepiped
Crystal dimensions (mm)	0.10×0.20×0.48
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	8.2967(18)
b (Å)	17.1247(35)
c (Å)	20.4801(46)
β (°)	101.386(15)
Volume (Å^3)	2852.5(14)
Z	4
Formula weight (amu)	721.0
Calculated density (g cm^{-3})	1.679
μ (cm^{-1})	40.03
F(000)	1428
B. Data collection and structural analyses	
Scan type	ω, variable
Scan rate (°/min)	2.00–5.00
2θ range (°)	3.0–50.0
Reflections sampled	$h\ k\ \pm l$
No. of reflections collected	6537
Agreement between equivalent data, $R_{av}(F_o)$	0.010
Total no. of unique data	4990
Observed data criteria	$F_o > 3.0\sigma(F_o)$
No. of observed data	4212
Absorption correction	Empirical
Trans. coefficients	0.348–0.674
p^2	0.0006
Discrepancy indices	
$R(F_o)$	0.0283
$R_w(F_o)$	0.0340
σ_1, GOF	0.98
No. of variables	367
Data to parameter ratio	11.5:1

(C-5); 46.3 (C-2); 42.0, 38.0 (C-7, C-10); 24.1, 23.9 (C-8, C-9); C-6 and C(CO) at vanadium not observed.

3.2. X-Ray structural analysis of 13

A single crystal of 13 · $1/2\ C_7H_8$ was sealed under nitrogen in a capillary tube and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The corresponding lattice parameters and orientation matrix for the sample were determined from a least-squares fit of the orientation angles for 25 reflections at 22°C. The systematic absences are consistent with the centrosymmetric monoclinic space group, $P2_1/n$. The refined lattice parameters and other pertinent crystallographic information are summarized in Table 1.

TABLE 2. Positional parameters ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for all of the non-hydrogen atoms in $Cp_2\overline{Hf(OC(C_4H_8)CH_2CH{=}CHCH_2C[{=}VCp(CO)_3]O})\cdot 1/2C_7H_8$

Atom	x	y	z	U_{eq} [a]
Hf	1862(1)	3355(1)	7631(1)	29(1)
V	25(1)	2088(1)	9556(1)	31(1)
O(1)	581(4)	4221(2)	7250(2)	37(1)
O(2)	984(4)	3116(2)	8486(2)	35(1)
O(3)	−2299(4)	1887(2)	8212(2)	54(1)
O(4)	3709(5)	2200(3)	9537(2)	72(2)
O(5)	891(5)	488(2)	9055(2)	66(2)
C(1)	−356(5)	4905(3)	7055(2)	35(1)
C(2)	−615(7)	5331(3)	7679(3)	43(2)
C(3)	−1203(6)	4781(3)	8152(3)	40(2)
C(4)	−244(6)	4505(3)	8687(2)	37(2)
C(5)	−663(6)	3835(3)	9086(2)	42(2)
C(6)	240(5)	3070(3)	8977(2)	30(1)
C(7)	−1954(6)	4679(3)	6580(3)	50(2)
C(8)	−1599(7)	4714(4)	5871(3)	59(2)
C(9)	177(7)	4996(4)	5942(3)	56(2)
C(10)	528(6)	5411(3)	6612(2)	43(2)
C(11)	−1393(6)	1965(3)	8721(2)	37(2)
C(12)	2338(6)	2167(3)	9549(3)	43(2)
C(13)	575(6)	1077(3)	9254(3)	42(2)
C(14)	−351(7)	2807(3)	10456(2)	47(2)
C(15)	−1876(6)	2603(3)	10091(2)	43(2)
C(16)	−2036(7)	1787(3)	10110(3)	52(2)
C(17)	−577(8)	1490(3)	10493(3)	55(2)
C(18)	476(7)	2116(4)	10710(3)	54(2)
C(19)	360(8)	2738(3)	6568(3)	53(2)
C(20)	−319(7)	2399(3)	7072(3)	52(2)
C(21)	896(7)	1938(3)	7461(3)	50(2)
C(22)	2325(8)	2004(3)	7207(3)	56(2)
C(23)	1998(8)	2513(3)	6653(3)	56(2)
C(24)	4168(6)	3845(4)	8530(3)	59(2)
C(25)	3931(7)	4420(4)	8045(3)	63(2)
C(26)	4341(7)	4107(4)	7465(3)	62(2)
C(27)	4860(7)	3346(4)	7609(3)	63(2)
C(28)	4744(6)	3187(4)	8273(3)	56(2)
C(29) [b]	6265(12)	4651(7)	205(6)	72(8)
C(30) [b]	6835	5190	−208	97(9)
C(31) [b]	5758	5737	−561	109(13)
C(32) [b]	4112	5745	−503	82(7)
C(33) [b]	3542	5206	−91	62(6)
C(34) [b]	4618	4659	263	63(5)
C(35) [b]	3959(19)	4084(12)	701(12)	125(12)

[a] The equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[b] Carbon atoms C(29)–C(34) correspond to the phenyl ring carbons of the disordered toluene and were refined as a rigid group. The methyl carbon atom C(35) was refined with the C(35)–C(34), C(35)–C(29), and C(35)–C(33) distances fixed at 1.51, 2.52 and 2.52 Å, respectively.

TABLE 3. Interatomic distances (Å) for all of the non-hydrogen atoms in $Cp_2\overline{Hf(OC(C_4H_8)CH_2CH{=}CHCH_2C[{=}VCp(CO)_3]O})$

Hf–O(1)	1.900(3)	Hf–O(2)	2.066(3)
Hf–C(19)	2.516(5)	Hf–C(20)	2.539(5)
Hf–C(21)	2.558(5)	Hf–C(22)	2.527(6)
Hf–C(23)	2.488(6)	Hf–C(24)	2.523(5)
Hf–C(25)	2.533(6)	Hf–C(26)	2.506(6)
Hf–C(27)	2.497(6)	Hf–C(28)	2.508(5)
V–C(6)	2.086(5)	V–C(11)	1.887(5)
V–C(12)	1.927(5)	V–C(13)	1.923(5)
V–C(14)	2.288(5)	V–C(15)	2.267(6)
V–C(16)	2.290(6)	V–C(17)	2.314(6)
V–C(18)	2.318(5)	O(1)–C(1)	1.418(5)
O(2)–C(6)	1.282(6)	O(3)–C(11)	1.166(6)
O(4)–C(12)	1.144(7)	O(5)–C(13)	1.139(7)
C(1)–C(2)	1.524(7)	C(1)–C(7)	1.531(6)
C(1)–C(10)	1.541(7)	C(2)–C(3)	1.500(7)
C(3)–C(4)	1.309(6)	C(4)–C(5)	1.489(7)
C(5)–C(6)	1.546(7)	C(7)–C(8)	1.539(8)
C(8)–C(9)	1.531(8)	C(9)–C(10)	1.520(7)
C(14)–C(15)	1.381(7)	C(14)–C(18)	1.414(8)
C(15)–C(16)	1.404(8)	C(16)–C(17)	1.402(8)
C(17)–C(18)	1.399(8)	C(19)–C(20)	1.395(8)
C(19)–C(23)	1.390(9)	C(20)–C(21)	1.399(8)
C(21)–C(22)	1.391(9)	C(22)–C(23)	1.413(8)
C(24)–C(25)	1.384(9)	C(24)–C(28)	1.370(9)
C(25)–C(26)	1.404(10)	C(26)–C(27)	1.386(10)
C(27)–C(28)	1.409(9)		

Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and variable ω scans. Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured periodically during data collection and gave no indication of crystal decay or sample movement. The data were corrected for Lorentz polarization and absorption effects and the symmetry-equivalent reflections were averaged.

Approximate positions for the Hf and V atoms were located using direct methods (SHELXTL PLUS operating on a St. Clair 486 workstation) and all of the remaining non-hydrogen atoms were revealed by successive difference Fourier syntheses. Following anisotropic refinement of the non-hydrogen atoms, idealized positions for the hydrogen atoms were included as fixed contributions using a riding model. Near the end of the refinement, a toluene molecule was located and found

TABLE 4. Bond angles (°) for all of the non-hydrogen atoms in $Cp_2\overline{Hf(OC(C_4H_8)CH_2CH{=}CHCH_2C[{=}VCp(CO)_3]O})$

O(1)–Hf–O(2)	103.9(1)	C(6)–V–C(11)	71.5(2)
C(6)–V–C(12)	75.0(2)	C(11)–V–C(12)	116.4(2)
C(6)–V–C(13)	119.3(2)	C(11)–V–C(13)	75.7(2)
C(12)–V–C(13)	76.1(2)	Hf–O(1)–C(1)	172.3(3)
Hf–O(2)–C(6)	169.0(3)	O(1)–C(1)–C(2)	108.6(4)
O(1)–C(1)–C(7)	109.2(4)	C(2)–C(1)–C(7)	114.0(4)
O(1)–C(1)–C(10)	109.4(4)	C(2)–C(1)–C(10)	112.8(4)
C(7)–C(1)–C(10)	102.8(4)	C(1)–C(2)–C(3)	111.0(4)
C(2)–C(3)–C(4)	123.1(5)	C(3)–C(4)–C(5)	124.6(5)
C(4)–C(5)–C(6)	113.6(4)	V–C(6)–O(2)	127.1(3)
V–C(6)–C(5)	120.2(3)	O(2)–C(6)–C(5)	112.6(4)
C(1)–C(7)–C(8)	106.7(4)	C(7)–C(8)–C(9)	106.4(4)
C(8)–C(9)–C(10)	104.0(5)	C(1)–C(10)–C(9)	103.9(4)
V–C(11)–O(3)	178.5(5)	V–C(12)–O(4)	178.6(5)
V–C(13)–O(5)	177.8(5)	C(15)–C(14)–C(18)	108.3(5)
C(14)–C(15)–C(16)	108.5(5)	C(15)–C(16)–C(17)	107.5(5)
C(16)–C(17)–C(18)	108.4(5)	C(14)–C(18)–C(17)	107.3(5)
C(20)–C(19)–C(23)	108.7(5)	C(19)–C(20)–C(21)	107.7(5)
C(20)–C(21)–C(22)	108.2(5)	C(21)–C(22)–C(23)	107.9(5)
C(19)–C(23)–C(22)	107.4(6)	C(25)–C(24)–C(28)	108.7(6)
C(24)–C(25)–C(26)	108.2(6)	C(25)–C(26)–C(27)	107.2(6)
C(26)–C(27)–C(28)	108.0(6)	C(24)–C(28)–C(27)	107.9(6)

to be disordered about a crystallographic centre of inversion. The positions of the six carbon atoms of the phenyl ring were refined as a rigid body with a C–C distance of 1.395 Å and the methyl carbon was located by a difference Fourier analysis. The methyl carbon position was refined by fixing the C–C bond distance to the phenyl ring at 1.51 Å and the C ··· C distances to the *ortho* carbons at 2.52 Å. Full-matrix least-squares refinement, based upon the minimization of $\Sigma w_i \mid F_o - F_c \mid^2$, with $w_i^{-1} = \sigma^2(F_o) + 0.0006F_o^2$, converged to give final discrepancy indices of $R(F_o) = 0.0283$, $R_w(F_o) = 0.0340$ and $\sigma_1 = 0.98$ for 4212 reflections with $F_o > 3.0\sigma(F_o)$. The discrepancy indices were calculated from the expressions $R(F_o) = \Sigma \mid F_o - F_c \mid / \Sigma F_o$ and $R_w(F_o) = \Sigma (w_i)^{1/2} \mid F_o - F_c \mid / \Sigma (w_i)^{1/2} F_o$ and the standard deviation of an observation of unit weight σ_1 is equal to $[(\Sigma w_i \mid F_o - F_c \mid^2)/(n-p)]^{1/2}$, where n is the number of observations and p is the number of parameters varied during the last refinement cycle. The refined positional parameters are provided in Table 2 and interatomic distances and bond angles for **13** are given in Tables 3 and 4, respectively.

Acknowledgements

Financial support from the Fonds der Chemischen Industrie, the Volkswagen-Stiftung, the Alfried Krupp von Bohlen und Halbach-Stiftung, and NATO is gratefully acknowledged. J.L.P. wishes to acknowledge the financial support provided by the Chemical Instrumentation Program of the National Science Foundation (Grant No. CHE-9120098) for the acquisition of a Siemens P4 X-ray diffractometer by the Department of Chemistry at West Virginia University.

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