Organometallics 1991, *10*, 3559–3568

moving crystal–moving counter technique, at the beginning and end of each scan. As a check on instrument and crystal stability, two representative reflections were measured every 2 h for **5**, **8a**, and **9**. Three such reflections were used in the collection of data for **6a**. Lorentz, polarization, and decay corrections were applied, as was an empirical absorption correction based on a series of ψ scans. The number of data observed and used for least-squares refinement with $F_o > 3\sigma(F_o)$ for each crystal are listed in Table I. All other reflections were considered to be unobserved.

Each of the structures was solved by the Patterson method using SHELXS-86,[22] which revealed the positions of the metal atoms. All other non-hydrogen atoms were found by successive difference Fourier syntheses. The hydride positions were calculated by using the program Hydex.[12] No other hydrogens were located. The hydride positions were included in the structure factor calculations but not refined in the final least-squares cycles. All non-hydrogen atoms were refined anisotropically. Selected bond distances and angles are given in Tables II–V and the residual electron densities in the final structures are listed in Table I.

Scattering factors were taken from Cromer and Waber.[23] Anomalous dispersion corrections were those of Cromer.[24] All calculations were carried out on a DEC MicroVax II computer, using the SDP/VAX system of programs.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation (CHE-9016495) for support of this research. We thank the NATO Science Program for a travel grant (E.R. and L.M.) and the Consiglio Nazionale delle Ricerche and the Ministero dell Universita (L.M). We also acknowledge Prof. A. Fratiello and R. Perrigan at California State University, Los Angeles, for help in obtaining 400-MHz ^{1}H NMR spectra and Johnson-Matthey for a loan of osmium tetroxide (D.O.).

Supplementary Material Available: Tables 6–9, listing atomic positions, Tables 10–13, listing anisotropic displacement factors, and Tables 14–17, listing bond distances and angles for **5**, **6a**, **8a**, and **9** (29 pages); Tables 18–21, listing calculated and observed structure factors for **5**, **6a**, **8a**, and **9** (167 pages). Ordering information is given on any current masthead page.

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(23) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(24) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Formation of Metallacyclic (Zirconoxycarbene)vanadium Complexes from CpV(CO)$_4$ and Their Conversion into Ordinary Fischer-Type Carbene Complexes of Vanadium

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(*s-trans*-Butadiene)zirconocene (**8**) adds to a carbonyl ligand of CpV(CO)$_4$ to give the [(π-allyl)zirconoxycarbene]vanadium complex $\mathrm{Cp_2\overline{ZrOC[{=}VCp(CO)_3]C}_4H_6}$ (**11b**). (butadiene)HfCp$_2$ reacts similarly to give a mixture of the [(π-allyl)hafnoxycarbene]- and seven-membered metallacyclic [(σ-allyl)hafnoxycarbene]vanadium species (**11a**/**12a**). These complexes subsequently add a ketone (acetone, acetophenone, methyl vinyl ketone), aldehyde (acrolein), or nitrile (pivalonitrile) to yield nine-membered metaloxycarbene vanadium complexes, such as $\mathrm{Cp_2\overline{HfOC[{=}VCp(CO)_3]CH_2CH{=}CHCH_2C(CH_3)_2O}}$ (**13a**), exhibiting analogous chiral *trans*-cycloalkene dioxametalla-*trans*-cyclononene frameworks. The (carbene)vanadium complex **13a** was characterized by X-ray diffraction. Complex **13a** crystallizes in space group $P2_1/c$ with cell constants $a = 11.741$ (1) Å, $b = 14.244$ (2) Å, $c = 15.824$ (1) Å, $\beta = 109.57$ (1)°, $Z = 4$, $R = 0.028$, $R_w = 0.023$. Treatment of the nine-membered metaloxycarbene complexes with tetrabutylammonium fluoride trihydrate in tetrahydrofuran solution gave the Zr,Hf-free vanadium acylmetalate complexes $\mathrm{[Cp(CO)_3VC({=}O)CH_2CH{=}CHCH_2CR^1R^2OH](NBu_4)}$, which were subsequently O-alkylated with triethyloxonium tetrafluoroborate to yield the ordinary Fischer-type (carbene)vanadium complexes $\mathrm{Cp(CO)_3V{=}C(OC_2H_5)CH_2CH{=}CHCH_2CR^1R^2OH}$. Treatment of $\mathrm{Cp_2\overline{ZrOC[{=}VCp(CO)_3]C}_4H_6}$ (**11b**) with TBAF·3H$_2$O followed by the reaction with Meerwein's reagent gave $\mathrm{Cp(CO)_3V{=}C(OC_2H_5)CH_2CH{=}CHCH_3}$ (**24**).

Heteroatom-stabilized carbene complexes play an important role as stoichiometric reagents in organic synthesis. They are becoming increasingly important as catalysts for the selective conversion of unsaturated organic substrates.[1] Carbene complexes are readily available for most transition metals. However, there are a few situations where carbene complexes of neither the Fischer nor the Schrock type seem to be obtained easily. Among others, this applies for the d-block element vanadium. To our knowledge only a very limited number of heteroatom-stabilized (carbene)vanadium complexes have been mentioned in the literature. So far, notable examples are complexes **3** and **5**,[2] both of which were prepared by synthetic routes avoiding the

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(1) See, e.g.: Casey, C. P. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, p 190. Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. Schubert, U.; Fischer, H.; Hofmann, P.; Weiss, K.; Dötz, K. H.; Kreissl, F. R. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983.

(2) Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, 348. Martin, J.; Moise, C.; Tirouflet, J. *C. R. Hebd. Seances Acad. Sci., Ser. 2* **1981**, *292*, 1143.

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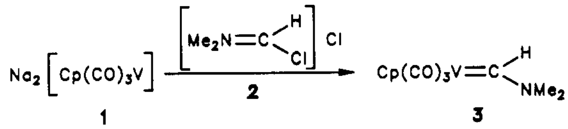
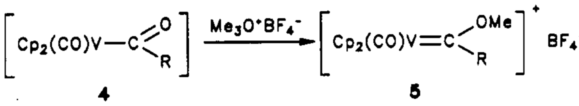
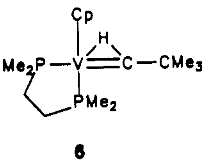
acylmetalate anion intermediates typically encountered in the variants of Fischer's classical M—C≡O to M=C(R)(OR′) conversion.[3]

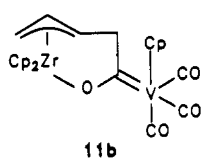




It seems that the molecular structures of only two (carbene)vanadium complexes have been determined by X-ray diffraction previously. Teuben et al. have prepared and described the (alkylidene)V(dmpe) complex **6**.[4] We have communicated the structure of the (zirconoxycarbene)vanadium complex **11b**.[5] The latter was synthesized by means of a novel way of converting metal carbonyls into metal carbene complexes.[6,7] To achieve this, the L_nM—C≡O starting material is treated with a very reactive (olefin)metallocene such as (butadiene)zirconocene or -hafnocene. This probably leads to an unstable $L_nM(\mu\text{-C}{\equiv}O)M(\text{diene})Cp_2$ intermediate which rapidly undergoes ring closure to form a metallacyclic zirconoxycarbene complex of the respective ML_n system (see below).



6



11b

In this paper it is shown that metallacyclic (metaloxycarbene)vanadium complexes with varying substitution pattern and ring size can readily be obtained by means of this rather general synthetic entry. The resulting zirconoxy- or hafnoxycarbene complexes possess a very high metal acyl complex character and hence lack typical electrophilic carbene complex reactivities almost completely.[8] However, we have developed ways to transform such "protected" Fischer-type carbene complexes into the ordinary acyclic $L_nM{=}C(R)(OR')$ species.[9] Applying these pathways of zirconocene (or hafnocene) removal allowed for the conversion of the readily available protected metaloxycarbene complexes into functionalized real Fischer carbene complexes of the element vanadium that were previously not available by the conventional synthetic procedures starting from a vanadium carbonyl. Some typical examples are described in the following text.

Results and Discussion

Synthesis of (Metaloxycarbene)vanadium Complexes. The starting materials for our complex synthesis were (*s-trans*-η^4-butadiene)zirconocene and -hafnocene (**8**). The former is a stable and isolable compound at ambient temperature (albeit at equilibrium with its (*s-cis*-diene)metallocene isomer);[10] the latter is readily available from the thermodynamically favored (*s-cis*-η^4-C_4H_6)$HfCp_2$ isomer by means of thermal or photochemical activation.[11]

The (butadiene)metallocenes react readily with a large variety of metal carbonyl complexes by coupling of the butadiene with a CO ligand to yield metallacyclic metaloxycarbene complexes.[6a,7] This reaction very nicely complements the Fischer procedure which has nucleophilic reaction characteristics and thus has made carbene complexes from quite a number of L_nM fragments available that could not readily be obtained otherwise.[12] The mechanism of the new method is rather different from the conventional L_nM—C≡O to L_nM(carbene) transformation. Probably, the metal carbonyl is added to the (η^2-diene)metallocene moiety to generate a reactive μ-C≡O intermediate (**9**) which is kinetically favoring subsequent (electrocyclic) ring closure. The primary product **10** is usually not stable under the reaction conditions but undergoes rapid subsequent σ-allyl ⇌ π-allyl rearrangements[13] to give **11** or **12** (see below).

(Butadiene)zirconocene adds readily to a carbonyl ligand of cyclopentadienyltetracarbonylvanadium to give a (π-allyl)zirconoxycarbene complex (**11b**).[5] Carrying out this reaction on a preparative scale is complicated by its rapid reversibility and unfavorable equilibrium ratio. Starting from an equimolar mixture of the starting materials, one reaches an equilibrium state at ambient temperature in homogeneous solution which contains about a 1:1 mixture of $\overline{Cp_2ZrOC[{=}VCp(CO)_3]C_4H_6}$ (**11b**) and $Cp_2Zr(C_4H_6)$

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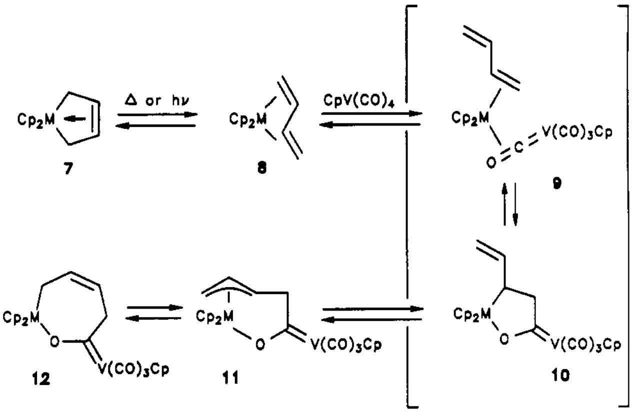
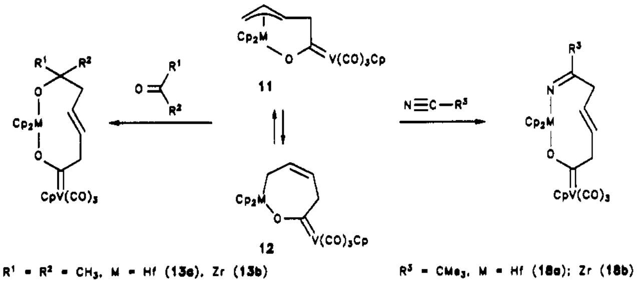


M = Hf(a), Zr(b)

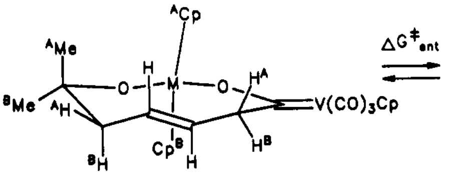
plus $CpV(CO)_4$. However, the low solubility of the product **11b** easily allows finding the experimental conditions to generate an open system where the precipitating product drives the addition reaction almost to completion (82% yield of **11b** isolated).

Thermochemistry helped us to solve the synthetic problem caused by the rapid and (in the case of the zirconium reagent unfavorable) equilibrium more elegantly. There is convincing evidence that hafnium to carbon σ-bonds are shorter[14] and about 3–5 kcal/mol stronger than corresponding Zr–C linkages.[15] As expected, this turned out to be completely sufficient to shift the $Cp_2M(C_4H_6) + CpV(CO)_4 \rightleftharpoons Cp_2\overline{MOC[{=}VCp(CO)_3]C}_4H_6$ equilibrium to the carbene product side. Reacting photochemically generated (*s-trans*-η^4-butadiene)hafnocene with the vanadium carbonyl at low temperature gave the corresponding hafnoxycarbene complex in >60% isolated yield. Different from the zirconium system, two isomeric hafnoxycarbene products were observed and identified by their NMR spectra in solution. In addition to the usual (π-allyl)metaloxycarbene complex the seven-membered-ring ((σ-allyl)hafnoxycarbene)vanadium complex **12a** is of a comparable thermodynamic stability because of the somewhat higher hafnium to carbon σ-bond dissociation energy.

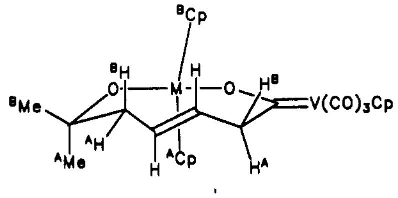
The equilibrating system of isomeric ((σ-/π-allyl)hafnoxycarbene)vanadium complexes **11a**/**12a** behaves as a carbon nucleophile. It cleanly adds 1 molar equiv of acetone at room temperature over 3 h in toluene solution to give **13a**. Carbon–carbon coupling has occurred exclusively at the allyl CH_2 terminus to form a nine-membered metallacyclic framework, part of which is the (hafnoxycarbene)vanadium moiety.[8,9,16] The $CpV(CO)_3$ subunit gave rise to strong IR absorptions at ν(CO) = 1941, 1847, and 1832 cm^{-1} (KBr). The NMR spectra of **13a** have revealed the presence of a chiral conformation of the nine-membered metallacycle. This became evident from the appearance of signals of pairwise diastereotopic cyclopentadienyl ligands at hafnium ($^1H/^{13}C$ NMR at ambient temperature in benzene-d_6: δ 6.21, 6.18/111.9, 111.6) and methyl substituents (introduced with the acetone reagent) at the ring carbon atom C(2) (δ 1.21, 1.14/32.2, 28.2). The methylene carbon atoms C(3) and C(6) gave ^{13}C NMR resonances at δ 66.4 and 47.8; the signals of the olefinic carbon centers C(4)/C(5) appeared at δ 131.3 and 128.7. The ^1H NMR lines of the corresponding pairs of diastereotopic methylene hydrogens were observed at δ 1.90, 1.60 (^2J = 11.9 Hz, 3-H, 3-H′) and 3.49, 4.31 (^2J = 19.0 Hz, 6-H, 6-H′). The olefinic hydrogen resonances were found at δ 4.9 (^3J = 15.1 Hz, 4-H, 5-H). The numerical value of the vicinal 4-H, 5-H coupling constant is consistent with a trans-configurated carbon–carbon double bond in the ring. The overall appearance of the ^1H and ^{13}C NMR spectra at ambient temperature suggests that complex **13a** is a metallaheterocyclic analogue of a chiral medium-sized *trans*-cycloalkene.[17]



R¹ = R² = CH₃, M = Hf (**13a**), Zr (**13b**)
R¹ = CH₃, R² = CMe₃, M = Hf (**14a**), Zr (**14b**)
R¹ = CH₃, R² = Ph, M = Hf (**15a**), Zr (**15b**)
R¹ = CH₃, R² = -CH=CH₂, M = Hf (**16a**)
R¹ = H, R² = -CH=CH₂, M = Hf (*trans*-**17a**, *cis*-**17a**)
R³ = CMe₃, M = Hf (**18a**); Zr (**18b**)



13 [4,5,6-pR]



ent-**13** [4,5,6-pS]

The observed dynamic behavior of **13a** in solution is in accord with the suggested chiral ring structure. Increasing the monitoring temperature rapidly results in broadening and pairwise coalescence of the ^1H NMR methyl singlets and the Cp lines as well as the 3-H/H′ and 6-H/H′ multiplets. At the temperature of the ^1H NMR Cp coalescence a Gibbs activation energy of $\Delta G^*(321\ K) = 16.5 \pm 0.3$ kcal/mol was estimated for the thermally induced enantiomerization process of the chiral metallacycle. This is a value very similar to that previously observed for the analogous topomerization process of a variety of similarly structured metaloxycarbene complexes 4,5-*trans*-$Cp_2\overline{ZrOC[{=}ML_n]CH_2CH{=}CHCH_2CMe_2O}$ ($ML_n = W(CO)_5$, $Mo(CO)_5$, $Cr(CO)_5$; $\Delta G^*(323\ K) = 16.6 \pm 0.4$ kcal/mol).[8,18] The racemization activation barrier of the chiral hydrocarbon *trans*-cyclononene, having a similar

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Table I. Selected Spectroscopic Data for the (Metaloxycarbene)vanadium Complexes 13–23

complex	IR ν(C=O), cm$^{-1\,a}$			^{1}H NMR^c		^{13}C NMR^c			
				δ(CpV)	^3J(CH=CH)	δ((OC)CH$_2$–)	δ(–CH=CH–)		δ(–CH$_2$–)
13a	1941	1847	1832	4.92^b	15.1	66.4	131.3	128.7	47.8
13b	1939	1846	1830	5.18	15.1	66.0	131.2	129.5	48.0
14a	1946	1853	1839	5.24	15.2	66.0	132.0	128.9	40.1
14b	1945	1861	1837^e	5.23	*d*	65.4	131.9	128.9	40.0
15a (A)^f	1943	1856	1838^g	5.22	*d*	66.0	131.2	128.1	48.0
15′a (B)				5.39	*d*	66.0	130.8	127.9	46.0
15b (A)	*d*			5.22	*d*	*d*	130.7	127.8	48.0
16a (A)	1942	1856	1833^g	4.97	*d*	66.5	130.8	130.0	47.2
16′a				4.97	*d*	66.5	130.1	129.5	46.0
17a (trans)	1945	1856	1826^g	5.20	*d*	67.0^b	131.1	129.7	42.4
17′a (cis)				5.15	*d*	61.1^b			36.8
18a	1937	1860	1821	5.15	*d*	66.3	130.7	129.2	37.3
18b	1935	1857	1819	5.13	*d*	66.6	130.4	129.4	38.6
19	1908	1800	1794^h	5.23^b	15.2	67.2^b	134.8	126.5	39.7
20	1964	1868	1848^h	4.90^b	15.2	66.9^b	134.8	126.5	39.7
21	1911	1801^e		5.26^b	15.1	69.6^e	133.5	125.6	48.2
22	*d*			4.89^h	15.2	66.0^b	126.0	124.8	35.1
23^g	1911	1801	1781^e	5.29^b	*d*	64.9^e	131.0	123.1	18.4^i
						60.0^e	129.9	121.2	14.5^j
24^g	1964	1867^h		4.87^b	*d*	62.4	128.3	126.4	18.0^i
						d	125.0	124.0	13.3^j

[a] In KBr, unless otherwise stated. [b] In C_6D_6. [c] In $CDCl_3$. [d] Not determined. [e] In tetrahydrofuran. [f] Legend: A, major isomer; B, minor isomer. [g] Mixture of isomers. [h] In methylene chloride. [i] Methyl group, trans isomer. [j] Methyl group, cis isomer.

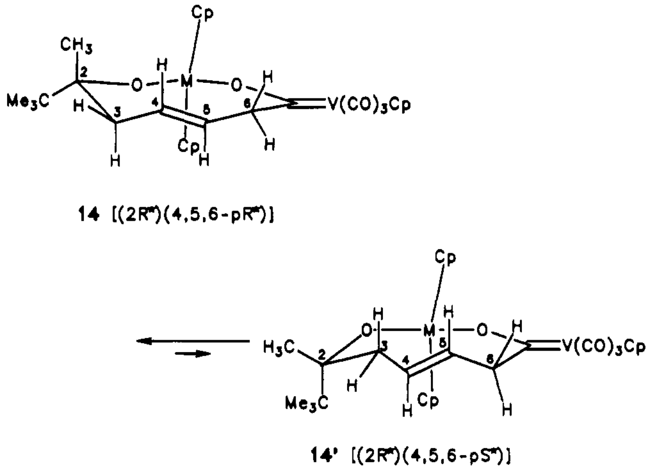
parameter, is only slightly higher at $\Delta G^‡$(263 K) = 19 kcal/mol.

The reaction of the ((π-allyl)zirconoxycarbene)vanadium complex **11b** with acetone is less straightforward. Attempts to react **11b** in a way similar to that for the hafnium complex **11a**/**12a** with equimolar amounts of acetone resulted in the formation of rather complex product mixtures. This is probably due to the reversibility of the (π-allyl)zirconoxycarbene complex formation from (butadiene)$ZrCp_2$ and $CpV(CO)_4$.[5] This reverse reaction, which is considerably more favorable for zirconium than for hafnium (see above), makes the starting materials available for other reactions with the added organic carbonyl compound.

This problem is easily overcome by allowing a suspension of solid $Cp_2ZrOC[{=}VCp(CO)_3]C_4H_6$ (**11b**) to react with a large excess of acetone. Under these conditions the unfavorable CC cleavage reaction is much less important and can sufficiently be suppressed to allow for the preparation of $Cp_2ZrOC[{=}VCp(CO)_3]CH_2CH{=}CHCH_2C(CH_3)_2O$ (**13b**) in good yield (>70% isolated). The spectroscopic features of **13b** (see Table I) again indicated the presence of a persistent chiral ring conformation caused by the incorporation of a trans-configurated C=C double bond (C(4)–C(5)) in the rather rigid dioxametallacyclononene. From the dynamic ^{1}H NMR spectra, a Gibbs activation energy of $\Delta G^‡$(316 K) = 16.4 ± 0.3 kcal/mol was derived for the ring-topomerization process.

The situation gets slightly more complicated when the $Cp_2MOC[{=}VCp(CO)_3]C_4H_6$ complexes are coupled with a prochiral ketone, such as pinacolone. The resulting nine-membered metallacyclic metaloxycarbene complexes may now contain two chirality elements, the chiral dioxametalla-*trans*-cyclononene conformer plus the chirality center C2. Therefore, two diastereoisomers could be formed. This is usually observed experimentally (see below); however, the reaction between $Cp_2MOC[{=}VCp(CO)_3]C_4H_6$ (M = Zr, Hf) with a very bulky ketone such as pinacolone represents an exception from the rule.

Scheme I. Schematic Drawing of the Diastereoisomeric Nine-Membered-Ring (Metaloxycarbene)vanadium Complexes with Systematic Numbering Scheme Used for the NMR Description and Correct IUPAC Naming of the Compounds



As usual, the reaction between $Cp_2ZrOC[{=}VCp(CO)_3]C_4H_6$ and methyl *tert*-butyl ketone requires a large excess of the organic compound to go to completion, whereas the ketone addition to the corresponding hafnium complex **11a**/**12a** can be carried out at a 1:1 stoichiometry. In each case only a single $Cp_2MOC[{=}VCp(CO)_3]CH_2CH{=}CHCH_2C(CH_3)(CMe_3)O$ diastereoisomer (**14b**, M = Zr; **14a**, M = Hf) was obtained. This situation is quite similar to that encountered in the formation of the analogously structured tungsten carbene complex $Cp_2ZrOC[{=}W(CO)_5]CH_2CH{=}CHCH_2C(CH_3)(CMe_3)O$ from the sequential coupling of butadiene with $W(CO)_6$ and pinacolone at the zirconocene template.[8,9] In that case, an X-ray crystal structure analysis had revealed that the C2-bonded bulky *tert*-butyl substituent is placed in a pseudoequatorial position on the crown-shaped metallacyclic framework and the product, favored under thermodynamic control, has to be assigned the relative stereochemical descriptor of (2*R**)(4,5,6-p*S**). A comparison of characteristic ^{1}H and ^{13}C NMR data (see Table I) indicates the close structural relation between $Cp_2ZrOC[{=}W(CO)_5]CH_2CH{=}CHCH_2C(CH_3)(CMe_3)O$ and the newly formed carbene vanadium complexes **14b** (Zr)/**14a** (Hf). Therefore, it has to be assumed that the diastereoselective addition of pinacolone to **11b** or **11a**/**12a** leads to the formation of (2*R**)(4,5,6-p*S**) configurated metaloxycarbene vanadium complexes **14b** (M = Zr) and **14a** (M = Hf), respectively.

The reaction of $Cp_2HfOC[{=}VCp(CO)_3]C_4H_6$ (**11a**/**12a**) with acetophenone (equimolar) gives a 70:30 mixture of two stereoisomeric nine-membered-ring $Cp_2HfOC[{=}VCp(CO)_3]CH_2CH{=}CHCH_2C(CH_3)PhO$ complexes. According to their spectroscopic data both contain the chiral *trans*-cyclononene-like framework. It has to be assumed that in the phenyl-substituted system the energy separation of the two possible diastereoisomers is smaller than observed for the tert-butyl analogue. Hence, the complexes formed have to be assigned the structures **15a** ((2*R**)(4,5,6-p*S**)) and **15′a** ((2*R**)(4,5,6-p*R**)), respectively. The reaction of the (π-allyl)zirconoxycarbene complex **11b** with acetophenone proceeds similarly to give a mixture of **15b** and **15′b**.

Methyl vinyl ketone reacts with $Cp_2HfOC[{=}VCp(CO)_3]C_4H_6$ (**11a**/**12a**) regioselectively. Only CC coupling at the carbonyl carbon atom of the added reagent is observed. However, similar to the example described above (**15a**, **15′a**), a 60:40 mixture of the respective hafnadioxa-*trans*-4,5-nonene diastereoisomers **16a** and **16′a** was obtained.

The reaction of **11a**/**12a** with acrolein also produces a mixture of two isomeric nine-membered metallacyclic (hafnoxycarbene)vanadium complexes (80:20). However, the outcome of this reaction differs somewhat from the other examples mentioned so far. The major isomer exhibits NMR spectra which closely compare to those of the other examples of the nine-membered *trans*-cyclononene-like metallacyclic metaloxycarbene complexes. However, the minor isomer has some distinctly different spectral features (see Table I), indicating that in this special case the metallacyclic cis isomer **17′a** was formed along with the "ordinary" *trans*-C=C metallacycle **17a**. This is not an unusual observation. A completely analogous behavior was found in many reactions of $Cp_2ZrOC[{=}W(CO)_5]C_4H_6$ complexes with organic carbonyl compounds: the reaction with aldehydes invariably gave mixtures of the corresponding *cis*- and *trans*-$Cp_2ZrOC[{=}W(CO)_5]CH_2CH{=}CHCH_2CHRO$ isomers, whereas the addition of ketones or nitriles produced only the chiral nine-membered metallacycles exhibiting trans-configurated carbon–carbon double bonds in the medium-sized ring system.[18]

The (carbene)vanadium complexes $Cp_2MOC[{=}VCp(CO)_3]C_4H_6$ also insert nitriles to form the corresponding nine-membered metallacycles.[19] The reaction of the (zirconoxycarbene)vanadium complex **11b** required a ca. 3-fold excess of pivalonitrile to go to completion. The stable (carbene)vanadium product **18b** was isolated in ca. 70% yield. Complex **18b** also exhibits a chiral ring conformation, as is evident from the ambient-temperature ^1H and ^{13}C NMR spectra at 4.7 T. In $CDCl_3$ solution the ^1H NMR singlets of the diastereotopic cyclopentadienyl ligands at zirconium are well separated (δ 6.07, 6.04), as are the pairwise diastereotopic allylic methylene hydrogen resonances at carbon centers C(3) and C(6) (details are given in the Experimental Section).

The $Cp_2HfOC[{=}VCp(CO)_3]CH_2CH{=}CHCH_2C(CMe_3){=}N$ complex **18a** was prepared analogously. In this case it was sufficient to react the $Cp_2HfOC[{=}VCp(CO)_3]C_4H_6$ starting material (**11a**/**12a**) with an equimolar quantity of Me_3CCN to achieve a clean and regioselective nitrile addition reaction to the hafnium-bonded allyl group. The (hafnoxycarbene)vanadium complex **18a** was isolated in >70% yield.

Molecular Structure of the Nine-Membered Metallacyclic (Hafnoxycarbene)vanadium Complex 13a. As mentioned above, only two X-ray crystal structure analyses of (carbene)vanadium complexes seem to have been described in the literature so far.[4,5] Teuben's alkylidenevanadium complex **6** is characterized by a rather strong α-agostic M—H—C interaction between the $=CH(CMe_3)$ moiety and the group 5 metal.[20] The corresponding V=C(carbene) bond is very short at 1.809 (3) Å. This is in contrast to the molecular structure of the (zirconoxycarbene)vanadium complex $Cp_2ZrOC[{=}VCp(CO)_3]C_4H_6$ (**11b**), which is characterized by a much longer vanadium—C(carbene) linkage at 2.102 (3) Å. Here the adjacent metal—CO bonds at the $VCp(CO)_3$ unit are shorter by about 0.2 Å (1.899 (4), 1.889 (4), and 1.921 (4) Å).

The molecular structure of the (hafnoxycarbene)vanadium complex $Cp_2HfOC[{=}VCp(CO)_3]CH_2CH{=}CHCH_2C(CH_3)_2O$ (**13a**) features a pseudotetrahedrally coordinated group 4 transition-metal center which is incorporated in a rigid nine-membered metallacyclic ring system. To the hafnium center are coordinated two cyclopentadienyl ligands and the ring oxygen atoms O(1) and O(2). The O(1)HfO(2) angle is rather large at 109.6 (1)°.[21] The oxygen centers are close to sp-hybridized, as is evident from their corresponding bond angles HfO(1)C(1) (163.6 (3)°) and HfO(2)C(6) (174.0 (2)°), which both do not deviate much from a linear three-atom arrangement. These bonding parameters are indicative of a pronounced oxygen–metal π-interaction. This interpretation is further supported by the short hafnium to oxygen distances observed (Hf–O(1) = 2.063 (3) Å; Hf–O(2) = 1.906 (2) Å).

Such a pronounced group 4 metallocene to oxygen π-interaction is typically found in many Cp_2M–O-containing metallacycles having a ring size greater than five,[22] whereas in various five-, four-, and three-membered $Cp_2M{-}O{-}(CR_x)_n{-}Y$ ring systems a bonding angle at oxygen too small for extensive π-bonding is enforced.[23]

The crown-shaped metallacyclic framework of complex **13a** is chiral.[17,24] It exhibits a trans-configurated car-

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[19] See for a comparison: Erker, G.; Sosna, F.; Zwettler, R.; Krüger, C. *Z. Anorg. Allg. Chem.* **1990**, *581*, 16.

[20] Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710. Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.

[21] See for a comparison: Erker, G.; Frömberg, W.; Krüger, C.; Raabe, E. *J. Am. Chem. Soc.* **1988**, *110*, 2400.

[22] Stephan, D. W. *Organometallics* **1990**, *9*, 2718.

[23] For typical examples, see: Takaya, H.; Yamakawa, M.; Mashima, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1283. Kropp, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Erker, G.; Czisch, P.; Schlund, P.; Angermund, K.; Krüger, C. *Angew. Chem.* **1986**, *98*, 356; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 364. Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**,1 *5*, 668. Erker, G.; Hoffmann, U.; Betz, P.; Krüger, C. *Angew. Chem.* **1989**, *101*, 644; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 630.

Table II. Selected Bond Distances (Å) and Angles (deg) for 13a

Hf-O(1)	2.063 (3)	Hf-O(2)	1.906 (2)
Hf-C(9)	2.507 (6)	Hf-C(10)	2.487 (5)
Hf-C(11)	2.503 (5)	Hf-C(12)	2.542 (5)
Hf-C(13)	2.553 (5)	Hf-C(14)	2.502 (6)
Hf-C(15)	2.490 (5)	Hf-C(16)	2.495 (6)
Hf-C(17)	2.518 (5)	Hf-C(18)	2.524 (8)
V-C(1)	2.080 (4)	O(1)-C(1)	1.276 (5)
O(2)-C(6)	1.413 (5)	C(1)-C(2)	1.527 (6)
C(2)-C(3)	1.446 (7)	C(3)-C(4)	1.272 (7)
C(4)-C(5)	1.429 (7)	C(5)-C(6)	1.531 (7)
C(6)-C(7)	1.513 (7)	C(6)-C(8)	1.493 (7)
O(2)-Hf-O(1)	109.6 (1)	C(25)-V-C(1)	118.3 (2)
C(24)-V-C(1)	72.4 (2)	C(26)-V-C(1)	75.9 (2)
C(1)-O(1)-Hf	163.6 (3)	C(6)-O(2)-Hf	174.0 (2)
C(2)-C(1)-O(1)	112.1 (3)	C(2)-C(1)-V	123.7 (3)
O(1)-C(1)-V	124.3 (3)	C(3)-C(2)-C(1)	114.8 (4)
C(4)-C(3)-C(2)	133.8 (5)	C(5)-C(4)-C(3)	133.1 (5)
C(6)-C(5)-C(4)	113.2 (4)	C(8)-C(6)-C(7)	109.7 (4)
C(8)-C(6)-C(5)	111.5 (4)	C(8)-C(6)-O(2)	109.8 (4)
C(7)-C(6)-C(5)	109.4 (4)	C(7)-C(6)-O(2)	108.6 (4)
C(5)-C(6)-O(2)	107.8 (3)		

Table III. Atomic Coordinates (with Esd's) for 13a

atom	*x*	*y*	*z*
Hf	0.1750 (1)	0.2078 (1)	0.2121 (1)
V	−0.2646 (1)	0.2220 (1)	0.0350 (1)
O(1)	0.0016 (2)	0.2388 (2)	0.1301 (2)
O(2)	0.2813 (2)	0.3067 (2)	0.2064 (2)
O(3)	−0.2618 (5)	0.4152 (3)	0.1171 (4)
O(4)	−0.4621 (3)	0.3378 (3)	−0.0996 (4)
O(5)	−0.2123 (4)	0.2201 (3)	−0.1422 (3)
C(1)	−0.0896 (3)	0.2742 (3)	0.0697 (3)
C(2)	−0.0552 (4)	0.3597 (3)	0.0253 (3)
C(3)	0.0470 (4)	0.4123 (3)	0.0822 (4)
C(4)	0.1537 (4)	0.4265 (3)	0.0817 (3)
C(5)	0.2611 (4)	0.4617 (3)	0.1472 (4)
C(6)	0.3497 (4)	0.3844 (3)	0.1951 (3)
C(7)	0.4275 (5)	0.4189 (4)	0.2867 (4)
C(8)	0.4281 (5)	0.3556 (4)	0.1424 (4)
C(9)	0.1013 (6)	0.1485 (4)	0.3338 (3)
C(10)	0.2261 (6)	0.1540 (5)	0.3700 (3)
C(11)	0.2582 (5)	0.2448 (4)	0.3760 (3)
C(12)	0.1552 (5)	0.3004 (4)	0.3438 (3)
C(13)	0.0568 (4)	0.2408 (5)	0.3181 (3)
C(14)	0.2275 (7)	0.1348 (4)	0.0862 (4)
C(15)	0.3189 (5)	0.1107 (4)	0.1644 (4)
C(16)	0.2708 (7)	0.0517 (4)	0.2108 (4)
C(17)	0.1519 (7)	0.0384 (4)	0.1640 (6)
C(18)	0.1260 (6)	0.0889 (5)	0.0868 (5)
C(19)	−0.3359 (9)	0.0738 (4)	0.0207 (4)
C(20)	−0.2189 (7)	0.0708 (4)	0.0731 (6)
C(21)	−0.2087 (6)	0.1168 (5)	0.1487 (4)
C(22)	−0.3204 (9)	0.1505 (4)	0.1427 (5)
C(23)	−0.3985 (5)	0.1209 (5)	0.0625 (6)
C(24)	−0.2630 (5)	0.2416 (4)	0.0872 (4)
C(25)	−0.3912 (4)	0.2905 (4)	−0.0488 (4)
C(26)	−0.2316 (4)	0.2213 (4)	−0.0745 (3)

bon–carbon double bond (C(3)–C(4) = 1.272 (7) Å) which is oriented as a bisector to the metallacyclic mean plane. However, there is no significant transannular interaction between the endocyclic carbon–carbon double bond and the hafnium metal center, as is illustrated by a projection of the molecular structure of **13a** showing the extension of the hafnadioxacyclononene ring system (see Figure 1).

The carbene carbon atom (C(1)) is tricoordinate planar. It is connected to the C(2) methylene group originating from the former butadiene ligand by a carbon–carbon single bond (C(1)–C(2) = 1.527 (6) Å). The C(1)–O(1) bond distance is short (1.276 (5) Å). It is within the range of a carbon to oxygen double bond.[25] The adjacent C(1) to vanadium linkage is rather long at 2.080 (4) Å: i.e much longer than the vanadium to carbonyl C bonds (1.891 (6), 1.897 (6), 1.898 (5) Å). Therefore, it must be concluded that the (hafnoxycarbene)vanadium complex **13a** exhibits a quite substantial metal acyl character. The bonding features of the heteroatom-stabilized carbene complex **13a** as observed in the crystal by X-ray diffraction may be described by a pronounced contribution of the acylmetalate resonance structure **13a′**. There is quite some precedence for this structural behavior: group 4 metaloxycarbene complexes derived from a variety of metal carbonyls have been characterized by X-ray diffraction and shown to exhibit similar acylmetalate type structures.[6-9,19]

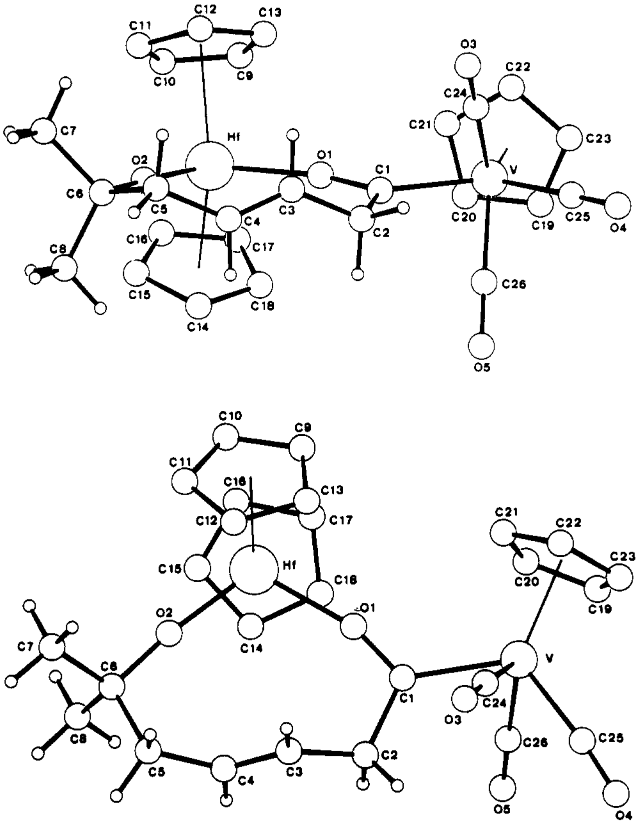
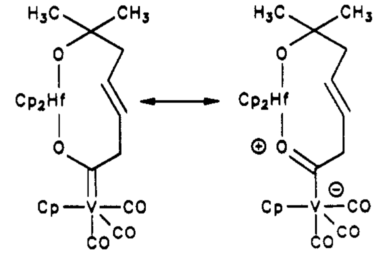


Figure 1. Two projections of the molecular structure of the chiral nine-membered metallacyclic (hafnoxycarbene)vanadium complex **13a** (a nonsystematic numbering scheme was used for the X-ray structure description).



13a **13a′**

Generation of Ordinary Fischer-Type (Carbene)-vanadium Complexes from the Metaloxycarbene Metallacycles. The metallacyclic zirconoxy- and hafnoxycarbene complexes are generally very unreactive carbene complexes. Under the usual conditions they do not

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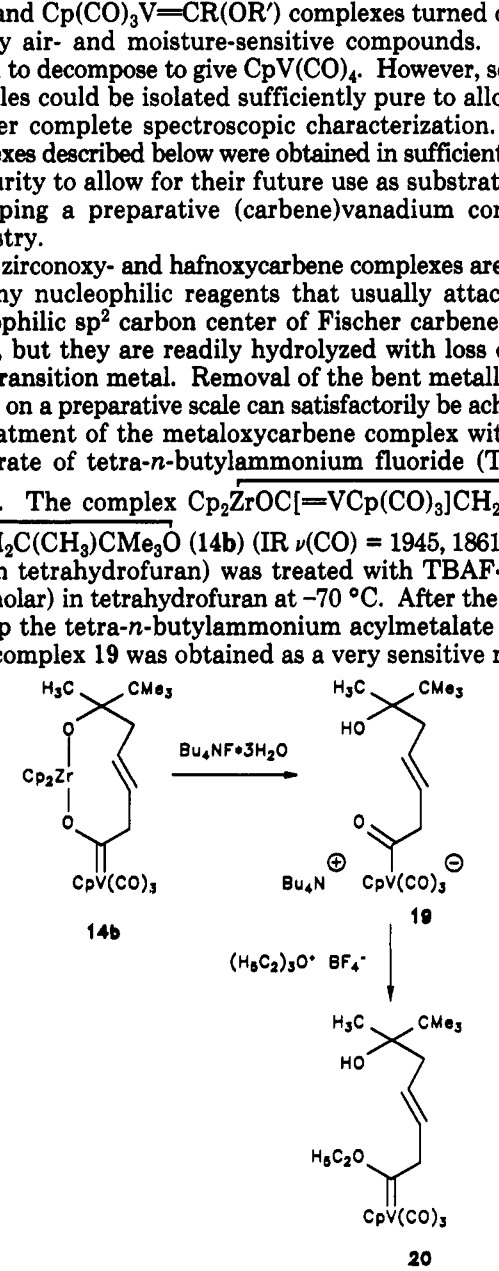
(24) For analogous carbocyclic ring systems see: Binsch, G.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 5157. Noe, E. A.; Wheland, R. C.; Glazer, E. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 3488. Cope, A. C.; Pawson, B. A. *J. Am. Chem. Soc* **1965**, *87*, 3649. See also: Marshall, J. A. *Acc. Chem. Res.* **1980**, *13*, 213.

(25) Allen, F. A.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

easily undergo many of the characteristic reactions that the ordinary $L_nM{=}CR(OR')$ complexes allow for. It seems that the $L_nM{=}CR[O(M'Cp_2X)]$ (M' = Ti, Zr, Hf) species[7,26] may be regarded as "protected carbene complexes".[9] We have used this for carrying out selective reactions at the related $Cp_2MOC[{=}W(CO)_5]CH_2{=}CHCH_2CR^1R^2O$ complexes[8] and developed methods for the subsequent elimination of the auxiliary group 4 metal to give ordinary heteroatom-stabilized carbene complexes or metal-free organic products.[9]

This methodology was used here to convert some of the metallacyclic (metaloxycarbene)vanadium complexes described above into ordinary Fischer-type carbene complexes of vanadium. The obtained $Cp(CO)_3V{=}CR(O^-)NR_4^+$ and $Cp(CO)_3V{=}CR(OR')$ complexes turned out to be very air- and moisture-sensitive compounds. They tended to decompose to give $CpV(CO)_4$. However, several examples could be isolated sufficiently pure to allow for a rather complete spectroscopic characterization. The complexes described below were obtained in sufficient yield and purity to allow for their future use as substrates for developing a preparative (carbene)vanadium complex chemistry.

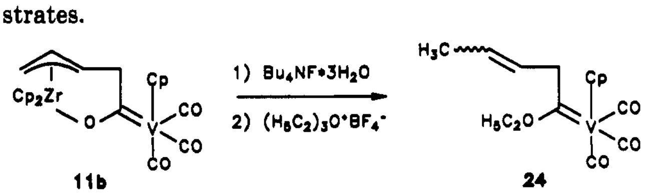
The zirconoxy- and hafnoxycarbene complexes are inert to many nucleophilic reagents that usually attack the electrophilic sp^2 carbon center of Fischer carbene complexes, but they are readily hydrolyzed with loss of the early transition metal. Removal of the bent metallocene moiety on a preparative scale can satisfactorily be achieved by treatment of the metaloxycarbene complex with the trihydrate of tetra-*n*-butylammonium fluoride (TBAF·$3H_2O$). The complex $Cp_2ZrOC[{=}VCp(CO)_3]CH_2CH{=}CHCH_2C(CH_3)CMe_3O$ (**14b**) (IR ν(CO) = 1945, 1861, 1837 cm^{-1} in tetrahydrofuran) was treated with TBAF·$3H_2O$ (equimolar) in tetrahydrofuran at −70 °C. After the usual workup the tetra-*n*-butylammonium acylmetalate vanadium complex **19** was obtained as a very sensitive red oil (IR ν(CO) = 1911, 1802 cm^{-1} in tetrahydrofuran solution; ν(CO) = 1908, 1800, 1794 cm^{-1} in dichloromethane). The ^{1}H NMR VCp resonance of **19** is at δ 5.23 in C_6D_6 (**14b**: δ 5.00), the methylene hydrogens at C(2), adjacent to the "carbene" carbon center, are still diastereotopic (δ 4.15 (2-H), 3.86 (2-H')). The C(3)–C(4) carbon–carbon double bond is trans-configurated (δ 5.45, 5.70, ^3J = 15.2 Hz; ^{13}C NMR chemical shifts of the $(OC)CH_2CH{=}CHCH_2-$ moiety δ 67.2, 134.8, 126.5, 39.7).



The anionic acylmetalate complex **19** was O-alkylated to give an ordinary Fischer-type (carbene)vanadium complex. For this purpose a sample of **19** was reacted at low temperature (−80 to −20 °C) with an equimolar quantity of triethyloxonium tetrafluoroborate in methylene chloride. Removal of the solvent followed by repeated extraction of decomposition products with pentane gave the neutral heteroatom-stabilized (carbene)vanadium complex $Cp(CO)_3V{=}C(OC_2H_5)CH_2CH{=}CHCH_2C(CH_3)(CMe_3)OH$ (**20**) in ca. 70% yield (IR ν(CO) = 1964, 1868 cm^{-1} in CH_2Cl_2; see for a comparison $Cp(CO)_3V{=}C(H)NMe_2$ (**6**) ν(CO) = 1956, 1881, 1863 (sh) in hexane[4]). The $({=}C)CH_2CH{=}CHCH_2-$ unit of **20** has retained the *trans*-C=C bond of the starting material **14b**. This is evident from the ^{1}H NMR (C_6D_6 (–*CH*=*CH*–) δ 5.57, 5.34, ^3J = 15.2 Hz) and ^{13}C NMR spectra (δ 66.9, 134.8, 126.5, 39.7).

The acetone-derived (hafnoxycarbene)vanadium complex $Cp_2HfOC[{=}VCp(CO)_3]CH_2CH{=}CHCH_2C(CH_3)_2O$ (**13a**) can be similarly degraded to give the acylmetalate anion **21**, albeit in rather low yield. The removal of the Cp_2Zr unit from the nitrile addition product **18b** can be analogously achieved by exposure of the metallacycle to TBAF·$3H_2O$ to yield the corresponding iminoacylmetalate complex of vanadium (**22**) $(Cp(CO)_3V{=}C(O^-NBu_4^+)CH_2CH{=}CHCH_2C(CMe_3){=}NH$; ^{13}C NMR δ 149.0 (*C*=N)).

It turned out that zirconium removal with TBAF·$3H_2O$ is taking place rapidly enough to successfully compete with the otherwise rather favorable CC bond-cleaving equilibration of the carbene complex $Cp_2ZrOC[{=}VCp(CO)_3]C_4H_6$ (**11b**) with its synthetic components (butadiene)$ZrCp_2$ and $CpV(CO)_4$. Treatment of the (zirconoxycarbene)vanadium complex **7** with TBAF·$3H_2O$ (equimolar quantity) at low temperature (−78 to −30 °C) in tetrahydrofuran solution resulted in a clean formation of $Cp(CO)_3V{=}C(O^-NBu_4^+)CH_2CH{=}CHCH_3$ (**23**, mixture of cis and trans isomers, 70% isolated). Subsequent O-alkylation of **23** with Meerwein's reagent led to the formation of a cis/trans mixture of the neutral Fischer carbene complex of vanadium (**24**). We have begun to investigate whether (carbene)vanadium complexes isolated or in situ generated by the procedures outlined above exhibit novel reaction patterns that can be used for the stoichiometric or catalytic transformation of organic substrates.



Experimental Section

General Procedures and Materials. All reactions with organometallic compounds were carried out under an inert atmosphere (argon) with use of Schlenk-type glassware. Solvents were dried and distilled under argon prior to use. The following spectrometers were used: Bruker WP 200 SY NMR spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz; ^1J(C,H) coupling constants (Hz) are given in parentheses); Nicolet 5 DXC FT IR spectrometer.

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Melting points were determined in sealed glass capillaries and are uncorrected. Cp_2Zr(butadiene) (**8b**), Cp_2Hf(butadiene) (**8a**), and $CpV(CO)_4$ were prepared according to literature procedures.[10,11,27] Experimental details of the preparation of the (metaloxycarbene)vanadium complex precursors used for the syntheses of complexes **13–24** were described previously.[5] Most of the very sensitive anionic and neutral open-chain (carbene)vanadium complexes gave C, H (N) analyses deviating slightly from the expected values. They were characterized spectroscopically.

Bis(cyclopentadienyl)[μ-(1-η:7-η)-2,2-dimethyl-7-oxo-1-oxahept-4-ene-1,7-diyl-*O*](tricarbonylcyclopentadienylvanadium)hafnium (13a). To a suspension of 308 mg (0.52 mmol) of the hafnoxyvanadium complex **11a**/**12a** in 20 mL of toluene was added dropwise 39 μL (0.52 mmol) of acetone. The mixture was stirred for 3 h at ambient temperature until the solid had dissolved. The resulting black solution was filtered from a small amount of an unidentified solid. The clear filtrate was stripped in vacuo to give 290 mg (85%) of **13a**, mp 173 °C dec (DSC). Anal. Calcd for $C_{26}H_{27}O_5VHf$ (648.9): C, 48.12; H, 4.19. Found: C, 48.11; H, 4.22. ^1H NMR ($CDCl_3$): δ 6.21, 6.18 (s, 5 H each, Cp_2Hf), 5.20 (s, 5 H, CpV), 5.07 (ddd, 1 H, 4-H), 4.97 (ddd, 1 H, 5-H), 4.39 (dd, 1 H, 6-H′), 3.52 (dd, 1 H, 6-H), 2.11 (dd, 1 H, 3-H′), 1.79 (t, 1 H, 3-H), 1.21, 1.14 (s, 3 H each, CH_3); coupling constants (Hz) ^2J = 11.9 (3-H′), 19.0 (6-H, 6-H′), ^3J = 11.1 (3-H, 4-H), 2.8 (3-H′, 4-H), 15.1 (4-H, 5-H), 8.1 (5-H, 6-H), 3.5 (5-H, 6-H′). ^{13}C NMR ($CDCl_3$): δ 131.3, 128.7 (153, 154, C(4)/C(5)), 111.6, 111.9 (173, Cp_2Hf), 93.3 (175, CpV), 81.6 (C(2)), 66.4 (C(6)), 47.8 (127, C(3)), 32.3, 28.2 (126, CH_3), carbene and carbonyl carbon atoms at vanadium not observed. IR (KBr): ν(CO) 1941, 1847, 1832 cm^{-1}.

X-ray Crystal Structure Analysis of 13a. $C_{26}H_{27}O_5HfV$, mw 648.9, space group $P2_1/c$, a = 11.741 (1) Å, b = 14.244 (2) Å, c = 15.824 (1) Å, β = 109.57 (1)°, V = 2493 (2) $Å^3$, d_{calc} = 1.73 g cm^{-3}, μ = 45.18 cm^{-1}, Z = 4, λ = 0.710 69 Å, 6093 measured reflections ($\pm h,+k,+l$), $(\sin\theta)/\lambda_{max}$ = 0.65, empirical absorption correction (minimum 0.84, maximum 1.0), 5660 independent and 4910 observed reflections ($I > 2\sigma I$), 298 refined parameters, R = 0.028, R_w = 0.023, ρ_{max} = 0.54 e $Å^{-3}$. The structure was solved by the heavy-atom method, and hydrogen atom positions were calculated and kept fixed in the final refinement.

Bis(cyclopentadienyl)[μ-(1-η:7-η)-2,2-dimethyl-7-oxo-1-oxahept-4-ene-1,7-diyl-*O*](tricarbonylcyclopentadienylvanadium)zirconium (13b). A sample of 160 mg (0.318 mmol) of **11b** was suspended in a solution containing 0.5 mL (12.7 mmol) of acetone in 5 mL of toluene, and the mixture was stirred for 3 h at ambient temperature. This mixture was then filtered and the clear black filtrate evaporated in vacuo. The residue was washed with pentane and dried to give 130 mg (73%) of **13b**, mp 155 °C dec. Anal. Calcd for $C_{26}H_{27}O_5VZr$ (561.7): C, 55.60; H, 4.85. Found: C, 55.74; H, 5.03. ^1H NMR ($CDCl_3$): δ 6.25, 6.24 (s, 5 H each, Cp_2Zr), 5.18 (s, 5 H, CpV), 5.08 (ddd, 1 H, 4-H), 4.90 (ddd, 1 H, 5-H), 4.41 (d, 1 H, 6-H′), 3.45 (dd, 1 H, 6-H), 2.13 (d, 1 H, 3-H′), 1.80 (t, 1 H, 3-H), 1.21, 1.15 (s, 3 H each, CH_3); coupling constants (Hz) ^2J = 11.6 (3-H, 3-H′), 16.2 (6-H, 6-H′) ^3J = 15.1 (4-H, 5-H), 9.1 (6-H, 5-H), 11.0 (3-H, 4-H). ^{13}C NMR ($CDCl_3$): δ 131.2, 129.5 (C(4)/C(5)), 113.3, 113.1 (Cp_2Zr), 93.6 (CpV), 82.6 (C(2)), 66.0 (C(6)), 48.0 (C(3)), 31.8, 27.9 (CH_3), C(7) and CO carbon atoms at vanadium not observed. IR (KBr): ν(CO) 1939, 1846, 1830 cm^{-1}.

Bis(cyclopentadienyl)[μ-(1-η:7-η)-2-*tert*-butyl-2-methyl-7-oxo-1-oxahept-4-ene-1,7-diyl-*O*](tricarbonylcyclopentadienylvanadium)hafnium (14a). The (hafnoxycarbene)vanadium complex **11a**/**12a** (690 mg, 1.17 mmol) was suspended in 20 mL of toluene. Pinacolone (160 μL, 1.29 mmol) was added and the mixture stirred for 3 h at room temperature. The reaction mixture was then filtered and solvent removed from the filtrate in vacuo to give 700 mg (87%) of **14a**, mp 152 °C dec. Anal. Calcd for $C_{29}H_{33}O_5VHf$ (691.0): C, 50.41; H, 4.81. Found: C, 50.58; H, 4.76. ^1H NMR ($CDCl_3$): δ 6.23, 6.18 (s, 5 H each, Cp_2Hf), 5.24 (s, 5 H, CpV), 5.16 (ddd, 1 H, 4-H), 5.00 (ddd, 1 H, 5-H), 4.20 (dd, 1 H, 6-H′), 3.97 (dd, 1 H, 6-H), 2.05 (dd, 1 H, 3-H′), 1.92 (t, 1 H, 3-H), 1.10 (s, 3 H, CH_3), 0.95 (s, 9 H, *tert*-butyl); coupling constants (Hz) ^2J = 11.3 (3-H, 3-H′), 17.7 (6-H, 6-H′), ^3J = 10.8 (3-H, 4-H), 3.9 (3-H′, 4-H), 8.6 (5-H, 6-H), 3.7 (5-H, 6-H′), 15.2 (4-H, 5-H). ^{13}C NMR ($CDCl_3$): δ 132.0, 128.9 (151, 157, C(4)/C(5)), 112.4, 111.8 (both 173, Cp_2Hf), 93.7 (172, CpV), 88.6 (C(2)), 66.0 (C(6)), 40.1 (128, C(3)), 38.8 (CMe_3), 26.0 (120, $C(CH_3)_3$), 22.0 (125, CH_3); C(7) and V—C≡O not observed. IR (KBr): ν(CO) 1946, 1853 (sh), 1839 cm^{-1}.

Bis(cyclopentadienyl)[μ-(1-η:7-η)-2-*tert*-butyl-2-methyl-7-oxo-1-oxahept-4-ene-1,7-diyl-*O*](tricarbonylcyclopentadienylvanadium)zirconium (14b). To a solution consisting of 30 mL of toluene and 5 mL (40 mmol) of pinacolone was added 1.81 g (3.59 mmol) of **11b**. The mixture was stirred for 3 h and filtered. The filtrate was stripped and the solid residue washed with pentane to yield 1.80 g (83%) of **14b**, mp 156 °C dec. Anal. Calcd for $C_{29}H_{33}O_5VZr$ (603.7): C, 57.69; H, 5.51. Found: C, 57.34; H, 5.61. ^1H NMR ($CDCl_3$): δ 6.29, 6.25 (s, each 5 H, Cp_2Zr), 5.23 (s, 5 H, CpV), 5.20–4.94 (m, 2 H, 4-H, 5-H), 4.25 (br d, 1 H, 6-H′), 3.87 (dd, 1, 6-H), 2.06 (dd, 1 H, 3-H′), 1.95 (t, 1 H, 3-H), 1.14 (s, 3 H, CH_3), 0.96 (s, 9 H, *tert*-butyl); coupling constants (Hz) ^2J = 12.3 (3-H, 3-H′), 17.7 (6-H, 6-H′), ^3J = 10.9 (3-H, 4-H), 3.6 (3-H′, 4-H), 8.8 (5-H, 6-H), 3.7 (5-H, 6-H′). ^{13}C NMR ($CDCl_3$): δ 131.9, 128.9 (156, 154, C(4)/C(5)), 113.6, 113.0 (both 179, Cp_2Zr), 93.3 (174, CpV), 90.4 (C(2)), 65.4 (C(6)), 40.0 (126, C(3)), 38.5 (CMe_3), 25.8 (125, $C(CH_3)_3$), 21.7 (126, CH_3). IR (KBr): ν(CO) 1940, 1852 (sh), 1839 cm^{-1}.

Bis(cyclopentadienyl)[μ-(1-η:7-η)-2-methyl-2-phenyl-7-oxo-1-oxahept-4-ene-1,7-diyl-*O*](tricarbonylcyclopentadienylvanadium)hafnium (15a). Complex **11a**/**12a** (265 mg, 0.45 mmol) was suspended in 5 mL of toluene, and then 54 μL (0.45 mmol) of acetophenone was added. The mixture was stirred for 5 h at 25 °C and then filtered from a small amount of an unidentified precipitate. The resulting clear solution was stripped in vacuo. The solid residue was washed with some pentane and dried to give 280 mg of **15a** (89%), mp 148 °C dec (DSC). Anal. Calcd for $C_{31}H_{29}O_5VHf$ (711.0): C, 52.39; H, 4.11. Found: C, 51.89; H, 4.24. Mixture of two isomers (A:B = 70:30; see Table I). ^1H NMR ($CDCl_3$): δ 7.35–7.10 (m, Ph), 6.24, 6.20 (each s, Cp_2Hf (A)), 6.38, 6.16 (each s, Cp_2Hf (B)), 5.39 (s, CpV (B)), 5.22 (s, CpV (A)), 5.40 (m, 4-H and 5-H (A,B)), 4.40 (m, 6-H′ (A,B)), 3.70 (m, 6-H (A,B)), 2.17 (m, 3-H′ (A,B)), 1.85 (m, 3-H (A,B)), 1.53 (s, CH_3 (A)), 1.42 (s, CH_3 (B)). ^{13}C NMR ($CDCl_3$): A, δ 150.1 (ipso C (Ph)), 131.2, 129.4, 128.1, 126.6, 124.2 (C(Ph) C(4), C(5)), 112.4, 112.0 (Cp_2Hf), 90.7 (CpV), 84.5 (C(2)), 66.0 (C(6)), 48.0 (C(3)), 30.0 (CH_3); B, δ 147.4 (ipso C (Ph)), 130.8, 129.0, 127.9, 125.4, 125.3 (C(Ph), C(4), C(5)), 112.7, 112.4 (Cp_2Hf), 89.9 (CpV), 84.8 (C(2)), 66.0 (C(6)), 46.0 (C(3)), 24.4 (CH_3). IR (KBr, mixture of isomers): ν(CO) 1943, 1856, 1838 cm^{-1}.

Bis(cyclopentadienyl)[μ-(1-η:7-η)-2-methyl-2-phenyl-7-oxo-1-oxahept-4-ene-1,7-diyl-*O*](tricarbonylcyclopentadienylvanadium)zirconium (15b). The ((π-allyl)zirconoxycarbene)vanadium complex **11b** (230 mg, 0.46 mmol) was suspended in 10 mL of toluene. Acetophenone (160 μL, 0.46 mmol) was added. The mixture was then stirred for 3 h at room temperature and filtered. Solvent was removed in vacuo. The residue was washed with pentane and dried to give **15b** (225 mg, ca. 75%) as a brown powder that contained some 10–15% of unidentified additional organometallic compounds. Complex **15b** was formed as a mixture of two isomers. Only the NMR signals of the major component were assigned. ^1H NMR ($CDCl_3$): δ 7.60–7.30 (m, 5 H, Ph), 6.38, 6.16 (s, 5 H each, Cp_2Zr), 5.22 (s, 5 H, CpV), 4.43 (d, 1 H, 6-H′), 3.70 (dd, 1 H, 6-H), 2.16 (m, 1 H, 3-H′), 1.82 (m, 1 H, 3-H), 1.43 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 146.9 (ipso C (Ph)), 130.7, 127.8, 126.5, 125.2, 124.8 (C (Ph), C(4), C(5)), 113.9, 113.4 (Cp_2Zr), 90.0 (CpV), 84.5 (C(2)), C(6) not localized, 48.0 (C(3)), 28.5 (CH_3).

Bis(cyclopentadienyl)[μ-(1-η:7-η)-2-methyl-2-ethenyl-7-oxo-1-oxahept-4-ene-1,7-diyl-*O*](tricarbonylcyclopentadienylvanadium)hafnium (16a). The **11a**/**12a** mixture (150 mg, 0.25 mmol) was suspended in 5 mL of toluene. Methyl vinyl ketone (23 μL, 0.24 mmol) was added. After 1.5 h at room temperature the black reaction mixture was filtered. The resulting solution was stripped in vacuo and the residue washed with pentane and dried to give 113 mg (67%) of **16a**, mp 140 °C dec. Anal. Calcd for $C_{27}H_{27}O_5VHf$ (660.9): C, 49.07; H, 4.12. Found: C, 48.80; H, 4.22. Mixture of two isomers (A:B = 60:40). ^1H NMR

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(C_6D_6): δ 6.04 (s, CpHf (B)), 6.01 (s, CpHf (A)), 5.91 (s, CpHf (A,B)), 5.90–5.65 (m, ethenyl –CH= (A,B)), 4.97 (s, CpV (A,B)), 4.99–4.85 (m, 4-H, 5-H, ethenyl =CH_2 (A,B)), 4.38–4.10 (m, 6-H′ (A,B)), 3.74–3.40 (m, 6-H (A,B)), 2.16, 1.99 (m, 3-H′ (A)(B)), 1.80–1.60 (m, 3-H (A,B)), 1.05 (s, CH_3 (A)), 0.97 (s, CH_3 (B)). ^{13}C NMR (C_6D_6): δ 147.6 (ethenyl –*C*H= (A)), 144.9 (ethenyl –*C*H= (B)), 130.8, 130.0 (C(4), C(5) (A)), 130.1, 129.5 (C(4), C(5) (B)), 112.4, 112.2, 112.1 (double intensity) (Cp_2Hf (A,B)), 111.3 (ethenyl =CH_2 (A)), 110.1 (ethenyl =CH_2 (B)), 93.3 (CpV (A,B)), 66.5 (C(6) (A,B)), 47.2 (C(3) (A)), 46.0 (C(3) (B)), 28.9 (CH_3 (A)), 26.3 (CH_3 (B)). IR (KBr, mixture of isomers): ν(CO) 1942, 1856, 1833 cm^{-1}.

Bis(cyclopentadienyl)[μ-(1-η:7-η)-2-ethenyl-7-oxo-1-oxahept-4-ene-1,7-diyl-*O*](tricarbonylcyclopentadienylvanadium)hafnium (17a). To a suspension of 339 mg (0.58 mmol) of **11a/12a** in 10 mL of toluene were added 42 μL (0.63 mmol) of acrolein. The mixture was stirred for 1 h at ambient temperature. A clear black solution was obtained after filtration which was stripped in vacuo. The remaining dark brown solid was washed with pentane and dried in vacuo to yield 220 mg (79%) of **17a**, mp 140 °C dec. Anal. Calcd for $C_{26}H_{25}O_5VHf$ (646.9): C, 48.27; H, 3.90. Found: C, 48.56; H, 3.97. Mixture of two isomers (A:B = 80:20). ^1H NMR ($CDCl_3$): δ 6.26, 6.21 (s, Cp_2Hf (A)), 6.25, 6.16 (s, Cp_2Hf (B)), 5.73, 5.65 (each dd, ethenyl –CH=, (A)(B)), 5.20 (s, CpV (A)), 5.15 (s, CpV (B)), 5.06–4.78 (m, 4-H, 5-H, ethenyl =CH_2 (A,B)), 4.42 (br d, 6-H′ (A,B)), 4.19 (m, 2-H (A,B)), 3.45 (dd, 6-H (A)), 2.87 (dd, 6-H (B)), 2.22 (m, 3-H′ (A)), 2.10–1.70 (m, 3-H, 3-H′ (B)), 1.48 (m, 3-H (A)). ^{13}C NMR (C_6D_6): δ 143.1 (ethenyl –*C*H= (A)), 142.7 (ethenyl –*C*H= (B)), 131.1, 129.7 (C(4), C(5) (A,B)), 126.0 (C(8) (A,B)), 112.0, 111.5 (Cp_2Hf (B)), 112.6, 111.4 (Cp_2Hf (A)), 93.6 (CpV (A,B)), 84.0 (C(2) (B)), 82.9 (C(2) (A)), 67.0 (C(6) (A)), 61.1 (C(6) (B)), 42.4 (C(3) (A)), 36.8 (C(3) (B)). IR (KBr, mixture of isomers): ν(CO) 1945, 1856, 1826 cm^{-1}.

Bis(cyclopentadienyl)[μ-(1-η:7-η)-2-*tert*-butyl-7-oxo-1-azahepta-1,4-diene-1,7-diyl-*O*](tricarbonylcyclopentadienylvanadium)hafnium (18a). Pivalonitrile (155 μL, 1.05 mmol) was added to a suspension of 620 mg (1.05 mmol) of the **11a/12a** mixture in 30 mL of toluene and the reaction mixture then stirred for 5 h at room temperature. A small amount of a precipitate was filtered off and the filtrate stripped in vacuo. The residue was washed with pentane and dried to yield 500 mg (71%) of **18a**, mp 156 °C dec. Anal. Calcd for $C_{28}H_{30}NO_4VHf$ (674.0): C, 49.46; H, 4.49; N, 2.08. Found: C, 50.05; H, 4.74; N, 1.99. ^1H NMR (C_6D_6): δ 5.77, 5.71 (s, 5 H each, Cp_2Hf), 4.98 (s, 5 H, CpV), 4.64–4.45 (m, 3 H, 4-H, 5-H, 6-H′), 3.19 (dd, 1 H, 6-H), 2.83 (dd, 1 H, 3-H′), 2.12 (dd, 1 H, 3-H), 0.90 (s, 9 H, *tert*-butyl), coupling constants (Hz) ^2J = 15.1 (3-H, 3-H′), 15.4 (6-H, 6-H′), ^3J = 8.4 (3-H, 4-H), 3.9 (3-H′, 4-H), 7.0 (5-H, 6-H). ^{13}C NMR ($CDCl_3$): δ 182.4 (C(2)), 130.7 (C(5)), 129.2 (C4), 109.6 (174, Cp_2Hf), 93.2 (173, CpV), 66.3 (120, C6), 41.7 (*C*Me_3), 37.3 (127, C3), 27.7 (126, C(*C*H_3)$_3$). IR (KBr): ν(CO) 1937, 1860, 1821 cm^{-1}; ν(CN) 1666, 1654 cm^{-1}.

Bis(cyclopentadienyl)[μ-(1-η:7-η)-2-*tert*-butyl-7-oxo-1-azahepta-1,4-diene-1,7-diyl-*O*](tricarbonylcyclopentadienylvanadium)zirconium (18b). To a solution of 200 μL (1.58 mmol) of pivalonitrile in 5 mL of toluene was added 290 mg (0.53 mmol) of the ((π-allyl)zirconoxycarbene)vanadium complex **11b** at room temperature. After it was stirred for 5.5 h, the mixture was filtered and the solvent removed from the filtrate in vacuo to give an oily residue which was solidified by treatment with pentane. Complex **18b** was recovered as a red amorphous solid (220 mg, 70%), mp 159 °C dec. Anal. Calcd for $C_{28}H_{30}NO_4VZr$ (586.7): C, 57.32; H, 5.15; N, 2.39. Found: C, 57.28; H, 5.62; N, 2.22. ^1H NMR ($CDCl_3$): δ 6.07, 6.04 (s, 5 H each, Cp_2Zr), 5.13 (s, 5 H, CpV), 4.66–4.60 (m, 2 H, 4-H, 5-H), 4.45 (dd, 1 H, 6-H′), 3.22–3.05 (m, 2 H, 6-H, 3-H′), 2.38 (dd, 1 H, 3-H), 1.13 (s, 9 H, *tert*-butyl); coupling constants (Hz) ^2J = 17.4 (3-H, 3-H′), 16.2 (6-H, 6-H′), ^3J = 10.1 (3-H, 4-H), 4.3 (3-H′, 4-H), 8.9 (5-H, 6-H), 4.4 (5-H, 6-H′). ^{13}C NMR ($CDCl_3$): δ 182.6 (C(2)), 130.4 (C(5)), 129.4 (C(4)), 110.8 (Cp_2Zr), 93.1 (CpV), 66.6 (C(6)), 41.0 (*C*Me_3), 38.6 (C(3)), 27.7 (C(*C*H_3)$_3$). IR (KBr): ν(CO) 1935, 1857, 1819 cm^{-1}; ν(CN) 1683, 1663 cm^{-1}.

Tetrabutylammonium (η^1-6-Hydroxy-1-oxo-6,7,7-trimethyloct-3-en-1-yl)tricarbonylcyclopentadienylvanadate (19). The (zirconoxycarbene)vanadium complex **14b** (470 mg, 0.78 mmol) was dissolved in 30 mL of tetrahydrofuran and the solution then cooled to –70 °C. A 700-μL amount of a 1.1 M TBAF·3H_2O solution in THF was added dropwise. The mixture was stirred for 15 min at low temperature to allow the reaction to go to completion. The solution was warmed to –25 °C and kept at that temperature for 14 h. Then the red solution was decanted from a brown precipitate and the solvent removed to give **19** as a red oil (360 mg, 75%). ^1H NMR (C_6D_6): δ 5.70 (ddd, 1 H, 4-H), 5.45 (ddd, 1 H, 3-H), 5.23 (s, 5 H, CpV), 4.15 (dd, 1 H, 2-H′), 3.86 (dd, 1 H, 2-H), 3.13 (s, 1 H, OH), 2.19 (dd, 1 H, 5-H′), 2.11 (dd, 1 H, 5-H), 1.13 (s, 3 H, CH_3), 1.04 (s, 9 H, *tert*-butyl); coupling constants (Hz) ^2J = 14.9 (2-H, 2-H′), 14.4 (5-H, 5-H′), ^3J = 15.2 (3-H, 4-H), 5.2 (4-H, 5-H), 6.4 (4-H, 5-H′), 8.9 (2-H, 3-H), 5.0 (2-H′, 3-H); tetrabutylammonium δ 2.87 (br s, 8 H, CH_2N), 1.30 (br m, 16 H, CH_2), 0.90 (br m, 12 H, CH_3). ^{13}C NMR (C_6D_6): δ 134.8, 126.5 (both 151, C(3), (C4)), 92.8 (172, CpV), 74.6 (C(6)), 67.5 (C92), signal broadened), 39.7 (126, C(5)), 37.7 (*C*Me_3), 24.4 (C(*C*H_3)$_3$), 22.6 (CH_3), C(1) and CO carbon atoms at vanadium not observed; tetrabutylammonium δ 58.4 (CH_2N), 25.9 (CH_2), 19.9 (CH_2), 13.8 (CH_3). IR (CH_2Cl_2): ν(CO) 1908, 1800, 1794 cm^{-1}.

Tricarbonyl[ethoxy(5-hydroxy-5,6,6-trimethylhept-2-en-1-yl)carbene]cyclopentadienylvanadium (20). Complex **19** (185 mg, 0.30 mmol) was dissolved in dichloromethane and cooled to –80 °C. A 300-μL amount of a 1.0 M solution of triethyloxonium tetrafluoroborate (0.30 mmol) in dichloromethane was added dropwise. The mixture was stirred for 10 min at low temperature and then warmed up to –20 °C over 2 h. Solvent was then removed in vacuo. The resulting red-brown residue was extracted with pentane. Removal of the pentane solvent gave **20** (86 mg, 70%) as a dark red oil. ^1H NMR (C_6D_6): δ 5.57 (ddd, 1 H, 3-H), 5.34 (ddd, 1 H, 2-H), 4.90 (s, 5 H, CpV), 4.41 (q, 2 H, C*H*$_2$CH$_3$), 3.64 (m, 2 H, 1-H, 1-H′), 2.25 (dd, 1 H, 4-H′), 1.98 (dd, 1 H, 4-H), 1.14 (t, 3 H, CH$_2$C*H*$_3$), 1.00 (s, 3 H, CH_3), 0.89 (s, 9 H, *tert*-butyl), O*H* not localized; coupling constants (Hz) ^2J = 13.1 (4-H, 4-H′), ^3J = 15.2 (2-H, 3-H), 7.4 (1-H, 2-H), 7.3 (3-H, 4-H), 5.4 (3-H, 4-H′), 7.0 (–CH_2CH_3). ^{13}C NMR (C_6D_6): δ 134.8, 126.5 (C(2), C(3)), 92.9 (CpV), 74.6 (C(5)), 67.8 (O*C*H$_2$), 66.9 (C(1)), 39.7 (C(4)), 37.7 (*C*Me_3), 24.0 (C(*C*H_3)$_3$), 22.6 (CH_3), 14.3 (CH$_2$*C*H$_3$); C(1) and CO at vanadium not localized. IR (CH_2Cl_2): ν(CO) 1964, 1868, 1848 (sh) cm^{-1}.

Tetrabutylammonium (η^1-6-Hydroxy-1-oxo-6,6-dimethylhept-3-en-1-yl)tricarbonylcyclopentadienylvanadate (21). The (hafnoxycarbene)vanadium complex **13a** (740 mg, 1.25 mmol) was dissolved in 40 mL of tetrahydrofuran at 0 °C. A 1.25-mL volume of a 1.0 M TBAF·3H_2O solution (1.25 mmol) in THF was added. A brown precipitate was formed. The mixture was stirred for 1 h at room temperature and then stripped in vacuo. The black oily residue was extracted with four 20-mL portions of ether. The solvent was removed from the ethereal solution in vacuo to give 70 mg (10%) of **21** as an orange-red oil. ^1H NMR (THF-*d*$_8$): δ 5.43, 5.13 (2 dt, 1 H each, 3-H, 4-H), 4.78 (s, 5 H, CpV), 3.45 (d, 2 H, 2-H, 2-H′), 1.99 (d, 2 H, 5-H, 5-H′), 1.07 (s, 6 H, CH_3); coupling constants (Hz) ^3J = 7.4 (4-H, 5-H), 7.0 (2-H, 3-H), 15.1 (3-H, 4-H); tetrabutylammonium δ 3.37 (8 H, CH_2N), 1.73, 1.44 (8 H each, CH_2), 1.02 (12 H, CH_3). ^{13}C NMR (THF-*d*$_8$): δ 133.5, 125.6 (C(3), C(4)), 93.6 (CpV), 69.6 (C(2)), 65.5 (C(6)), 48.2 (C(5)), 29.6 (CH_3); tetrabutylammonium δ 59.3 (*C*H$_2$N), 24.7, 20.6 (CH_2), 14.0 (CH_3). IR (THF): ν(CO) 1911, 1801 cm^{-1}.

Tetrabutylammonium [η^1-6-Imino-1-oxo-7,7-dimethyloct-3-en-1-yl]tricarbonylcyclopentadienylvanadate (22). To a solution of 380 mg (0.65 mmol) of the (zirconoxycarbene)vanadium complex **18b** in 20 mL of tetrahydrofuran was added 610 μL (0.65 mmol) of a 1 M solution of TBAF·3H_2O in THF at –40 °C. During 1 h the mixture was warmed to –20 °C. Solvent was then removed in vacuo at –5 °C to give 490 mg of a red oil containing **22** and some unidentified Cp_2Zr-containing compounds. ^1H NMR of the **22** anion (THF-*d*$_8$): δ 5.82 (dd, 1 H, 3-H), 5.37 (dt, 1 H, 4-H), 4.76 (s, 5 H, CpV), 3.70 (m, 2 H, 2-H, 2-H′), 3.50 (m, 2 H, 5-H, 5-H′), 1.70 (s, 9 H, *tert*-butyl). ^{13}C NMR (C_6D_6): δ 149.0 (C=N), 126.0, 124.8 (C(3), C(4)), 93.9 (CpV), 66.0 (C(2)), 41.9 (*C*Me_3), 35.1 (C(5)), 29.1 (C(*C*H_3)$_3$); tetrabutylammonium 59.4 (CH_2N), 24.6, 20.5 (CH_2), 14.2 (CH_3).

Tetrabutylammonium (η^1-1-Oxopent-3-en-1-yl)tricarbonylcyclopentadienylvanadate (23). The (zirconoxycarbene)vanadium complex **11b** (1.01 g, 2.0 mmol) was dissolved in 30 mL of tetrahydrofuran at –78 °C. During 1 h 1.82 mL of a 1.1 M TBAF·$3H_2O$ solution (2.0 mmol) in THF was added. The clear red solution was warmed to −30 °C over 3 h and then kept at this temperature for 14 h. A brown precipitate was filtered off and the resulting red solution stripped in vacuo to yield 810 mg (70%) of **23** as a red oil. Anal. Calcd for $C_{29}H_{48}NO_4V$ (525.7): C, 66.26; H, 9.20; N, 2.66. Found: C, 67.87; H, 9.41; N, 2.72. Mixture of trans and cis isomers (70:30). *trans*-**23**: ^1H NMR (C_6D_6) δ 6.00, 5.50 (m, 1 H each, 3-H, 4-H), 5.29 (s, 5 H, CpV), 4.07, 3.97 (d, 1 H each, 2-H), 1.72 (br d, 3 H, CH_3), coupling constants (Hz) ^3J = 6.3 (2-H, 3-H), 6.5 (4-H, 5-H), tetrabutylammonium δ 2.90 (8 H, CH_2N), 1.26 (16 H, CH_2), 0.89 (12 H, CH_3); ^{13}C NMR (THF-d_8) δ 305 (br, C(1)), 265 (br, V–CO), 131.0 (158, C(4)), 123.1 (157, C(3)), 93.3 (171, CpV), 64.9 (C(2)), 18.4 (125, C(5)), tetrabutylammonium δ 59.3 (137, NCH_2), 24.7 (CH_2), 20.6 (121, CH_2), 14.1 (CH_3). *cis*-**23** (=minor isomer) δ 129.9 (158, C(4)), 121.2 (157, C(3)), 14.5 (C95)), remainder hidden under trans-**23** and tetrabutylammonium signals.

Tricarbonyl[ethoxy(but-2-en-1-yl)carbene]cyclopentadienylvanadium (24). The tetrabutylammonium vanadium salt **23** (550 mg, 1.05 mmol) was dissolved in 40 mL of dichloromethane and then cooled to −78 °C. During 2 h 1.05 mL of a 1.0 M triethyloxonium tetrafluoroborate solution in dichloromethane was added with stirring. The mixture was warmed up to −30 °C over 3 h. The resulting dark red solution was concentrated in vacuo to a volume of 10 mL. A 30-mL amount of cold pentane was added and the mixture kept at −30 °C for 14 h. The solution was then decanted from a brown precipitate at −30 °C. Removal of the solvent from the clear red solution at −30 °C gave 170 mg (52%) of **24**, which contained some $CpV(CO)_4$ and ammonium salts. The product was very sensitive toward further decomposition and was, therefore, stored at −78 °C. Mixture of two isomers (A:B $\approx$ 70:30). Major isomer: ^1H NMR (C_6D_6) δ 5.32, 5.29 (m, 2 H, 2-H, 3-H), 4.87 (s, 5 H, CpV), 4.41 (q, 2 H, OCH_2), 3.58 (m, 2 H, 1-H, 1-H′), 1.50 (d, 3 H, CH_3; the methyl resonance of the minor isomer was observed at δ 1.43), 1.11 (t, 3 H, OCH_2CH_3); ^{13}C NMR (CD_2Cl_2): δ 128.3, 126.4 (C(2), C(3); Minor isomer δ 125.0, 124.0), 94.2 (CpV), 73.6 (OCH_2), 62.4 (broad, C(1)), 18.0 (C(4), trans isomer; minor (cis) isomer δ 13.3), 14.8 (OCH_2CH,, carbonyl and carbene carbon atoms at vanadium not localized. IR (CH_2Cl_2): ν(CO) 1964, 1867 cm^{-1}.

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Supplementary Material Available: Description of the X-ray crystal structure analysis of **13a** and listings of final positional and thermal parameters, distances, and angles (6 pages); a listing of final observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Indium Compounds That Contain Two Different Organic Substituents. Crystal Structure of $[In(CH_2CMe_3)(CH_2SiMe_3)Cl]_2$. An Interesting Case of Partial Ligand Disorder in the Solid State

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Three new indium compounds containing two different organic substituents, $In(CH_2CMe_3)(CH_2SiMe_3)Cl$, $In(CH_2CMe_3)(C_6H_5)Cl$, and $(Me_3CCH_2)(Me_3SiCH_2)InPEt_2$, have been prepared, purified, and characterized. All compounds were characterized by partial elemental analysis (C, H, and P as appropriate), cryoscopic molecular weight studies in benzene solution, and NMR and IR spectroscopic studies. All compounds exist as dimeric molecules in solution. NMR spectral data were consistent with the presence of mixtures of cis and trans isomers in solution. $[In(CH_2CMe_3)(CH_2SiMe_3)Cl]_2$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (C_i^1, No. 2) with a = 6.1000 (10) Å, b = 10.337 (3) Å, c = 12.190 (3) Å, α = 77.28 (2)°, β = 84.41 (2)°, γ = 84.50 (2)°, V = 744.0 (3) Å^3, and Z = 1. Diffraction data (Mo Kα, 2θ = 5–50°) were collected on a Siemens R3m/V automated four-circle diffractometer, and the structure was solved and refined to R = 5.39% and R_w = 7.65% for those 1752 unique data with $|F_o| > 4\sigma(|F_o|)$ (R = 8.30% for all 2629 data). Distances within the centrosymmetric dimeric molecule in the trans conformation include $In–CH_2CMe_3$ = 2.140 (13) Å, $In–CH_2SiMe_3$ = 2.125 (12) Å, and In–Cl (bridging) = 2.572 (3) and 2.659 (3) Å. There is some slight disorder of CH_2CMe_3 and CH_2SiMe_3 ligands (~73%:27%), and there are weak intermolecular In···Cl interactions at 3.528 (3) Å along the a-direction. Attempts to prepare the related organogallium compounds, $Ga(Me)(CH_2CMe_3)Cl$ and $Ga(CH_2CMe_3)(CH_2CMe_2Ph)Cl$, were unsuccessful. Ligand redistribution reactions led to the formation and subsequent isolation of mixtures of the appropriate symmetrized products.

Introduction

The chemistry of organoindium compounds is important for gaining a more complete understanding of the reactions involved in the organometallic chemical vapor deposition process for making InP, an important electronic material. The most common organoindium compounds[1] employed in producing InP are $InMe_3$[2] and $InEt_3$[3,4], although a variety of other simple homoleptic trialkylindium compounds including $In(n\text{-}Pr)_3$,[4] $In(i\text{-}Pr)_3$,[4] $In(n\text{-}Bu)_3$,[4] $In(sec\text{-}Bu)_3$,[4] $In(t\text{-}Bu)_3$,[5] $In(CH_2CMe_3)_3$,[6] and $In(CH_2SiMe_3)_3$[7] are known.

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