Metallacyclic Metaloxycarbene Complexes from 1,2-Didehydrobenzene Group 4 Metallocenes and Metal Carbonyls

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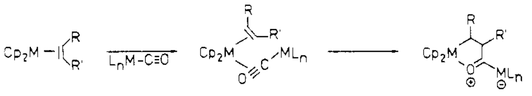
Thermally generated (η^2-1,2-didehydrobenzene)titanocene and -zirconocene react with hexacarbonylmolybdenum or -tungsten at 90 °C to give five-membered metallacyclic titan- and zirconoxycarbene complexes 4. The carbene complex $Cp_2\overline{ZrOC[{=}W(CO)_5]C}_6H_4$ (**4a**) is an organometallic Lewis acid. At room temperature **4a** adds 1 equiv of acetophenone giving the adduct **9** [IR $\Delta\nu_{C=O} = -37$ cm^{-1}; ^{13}C NMR (acetophenone carbonyl C) $\Delta\delta = +10$ ppm]. Complex **4a** is oligomeric in the solid state. Bridging between the monomeric units occurs by formation of [W]—C≡O—[Zr] connections using the CO group at tungsten trans to the carbene ligand. In contrast, $(Me_3CCp)_2\overline{ZrOC({=}W(CO)_5)C}_6H_4$ (**4g**) is monomeric in the crystal; the bulky *tert*-butyl Cp substituents shield the electrophilic zirconium center effectively from nucleophilic attack. Complex **4g** crystallizes in space group $P4_3$ with cell constants a = 11.513 (3) Å, b = 11.513 (3) Å, c = 22.118 (3) Å, Z = 4, R = 0.033, and R_w = 0.037. The metallacycle **4a** reacts with phenol to give the zirconoxycarbene complex $Cp_2Zr(OPh)OC[{=}W(CO)_5]C_6H_5$ (**10**). Complex **10** crystallizes in space group $P2_12_12_1$ with cell constants a = 11.289 (1) Å, b = 15.020 (1) Å, c = 16.291 (1) Å, Z = 4, R = 0.036, and R_w = 0.031. At ambient temperature **10** reacts with the ylide $Ph_3P{=}CH_2$ to yield the zirconium enolate $Cp_2Zr(OPh)OCPh{=}CH_2$ (**14**) which serves as a carbon nucleophile in the aldol condensation reaction with benzaldehyde. The **10** to **14** transformation can be regarded as an organometallic equivalent of the elusive Wittig olefination reaction of a carboxylate salt.

Introduction

Heteroatom-stabilized ("Fischer-type") carbene complexes are of increasing importance as reagents or catalysts in organic synthesis.[1] They are usually prepared from metal carbonyls by variations of the two-step reaction sequence developed by E. O. Fischer et al.[2] However, to successfully carry out this "nucleophilic" M—C≡O to M—carbene conversion, a delicate balance between the stability and the reactivity of the acyl metalate intermediate is required. Therefore, alternative methods for the formation of transition-metal carbene complexes from metal carbonyls are of great value.[3]

We have recently developed a new method of preparing metallacyclic metaloxycarbene complexes from metal carbonyls using very reactive (η^2-olefin)metallocenes as reagents.[4] This reaction type has nonnucleophilic reaction characteristics. It has been suggested that a bimetallic $M(\eta^2\text{-alkene})(\mu\text{-}\eta^1{:}\eta^2\text{-carbonyl})M'$ type intermediate is formed, followed by (probably concerted electrocyclic) ring closure with carbon–carbon bond formation to give the metallacyclic metaloxycarbene complexes. Olefin metallocene type reagents that have been successfully applied include (butadiene)MCp$_2$ complexes (M = Zr, Hf),[4] Cp^*_2Th(butadiene),[5] and $Cp^*_2Ti(CH_2{=}CH_2)$.[6] We have recently observed that thermally generated (η^2-aryne)MCp$_2$ complexes (M = Ti, Zr; bearing normal η^5-C_5H_5 ligands or substituted Cp's) are effective reagents for the metal carbonyl → metal carbene complex conversion according to eq 1.[7] In addition, some of the resulting benzannelated five-membered metallacyclic metaloxycarbene complexes derived from the group 6 metal carbonyls exhibit quite unusual structural features and remarkable chemical reactivity. Typical examples are described in this paper.



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Results and Discussion

The "Nonnucleophilic" Carbene Complex Synthesis Using (η^2-Aryne)MCp$_2$ Reagents. (η^2-1,2-Didehydrobenzene)MCp$_2$ complexes (M = Ti, Zr) can readily be generated thermally from the corresponding diphenylmetallocenes. Trapping with PMe$_3$ has recently resulted in the isolation and X-ray characterization of stable (η^2-C_6H_4)ZrCp$_2$(PMe$_3$).[8] In the absence of a suitable donor ligand, the $Cp_2M(\eta^2\text{-}C_6H_4)$ species have only a fleeting existence. They may react with arenes under C–H bond activation. Activation of ylidic carbon to hydrogen bonds yields metallocene ylides; this reaction competes with

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(1) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983. (b) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573. (c) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

(2) Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645; *Chem. Ber.* **1967**, *100*, 2445.

(3) See, e.g.: Lappert, M. F.; Oliver, A. J. *J. Chem. Soc., Dalton Trans.* **1974**, 65. Doyle, M. J.; Lappert, M. F.; Pyl, P. L.; Terreros, P. *Ibid.* **1984**, 2355.

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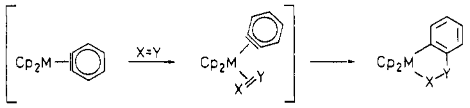
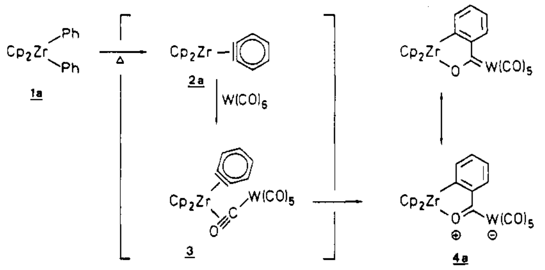
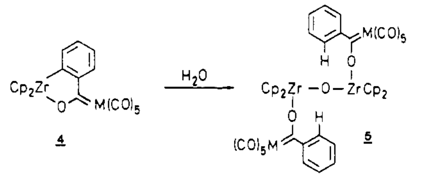
methylene transfer to form metallacyclobutabenzenes.[9] Various π-systems (olefins, acetylenes, ketones, carbon dioxide, even dinitrogen) have been added to the reactive $(\eta^2\text{-}C_6H_4)MCp_2$ intermediates to yield benzannelated five-membered metallacycles or compounds derived from them.[10]



In a related reaction, thermally generated (η^2-1,2-didehydrobenzene)zirconocene reacts readily with $W(CO)_6$ at 90 °C to form the benzannelated five-membered metallacyclic zirconoxycarbene complex **4a**. The carbene complex was obtained as an extremely moisture-sensitive solid in 50% yield. It can be recrystallized from various solvents. Using benzene, toluene, methylene chloride, or heptane produced solids of different elemental compositions. Detailed analyses of the dissolved material by NMR revealed that some of the solvent used for recrystallization was always incorporated in the solid. In the case of toluene, the built-in solvent molecules were located by X-ray diffraction. The incorporated solvent molecules could be removed under vacuum: powdered samples of **4a** thus obtained gave correct analyses for the composition $Cp_2ZrOC[=W(CO)_5]C_6H_4$.

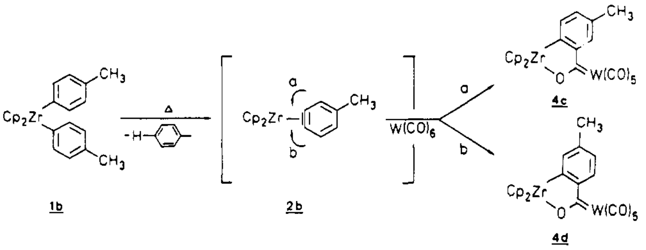


In solution, trace amounts of moisture were taken up by **4a** at once, reacting with the zirconium to carbon σ-bond. One equivalent of water converted two carbene complex moieties, opening up the five-membered metallacyclic structures with formation of the bis(zirconoxycarbene) complex **5a** containing four metal centers and a μ-oxo-bridged $ZrCp_2\text{–}O\text{–}ZrCp_2$ unit. The monocarbene complex **4a** was converted to **5a** on a preparative scale by controlled hydrolysis using the four available water equivalents from $CuSO_4{\cdot}5H_2O$.



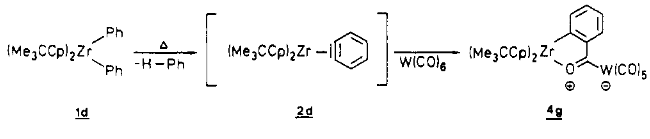
The reaction of $(\eta^2\text{-}C_6H_4)ZrCp_2$ with $Mo(CO)_6$ proceeded similarly. However, complex **4b** was not isolated under the reaction conditions applied. The hydrolysis product **5b** was directly obtained from the reaction mixture (30% yield) instead. Carbene complex **5b** was characterized by an X-ray crystal structure analysis.[11]

It was shown by a labeling experiment that aryne complexes were involved in the formation of the $Cp_2ZrOC[=M(CO)_5]C_6H_4$ carbene complexes. Di-(*p*-tolyl-zirconocene is expected to produce the unsymmetrically labeled (η^2-1,2-didehydro-4-methylbenzene)zirconocene intermediate.[9] Alternative addition of $M(CO)_6$ via pathway a or b followed by carbon–carbon coupling and ring closure should give two differently substituted zirconoxycarbene complexes. The reaction of $W(CO)_6$ with di-*p*-tolylzirconocene at 90 °C yielded the expected carbene complexes **4c** and **4d** in a 40:60 ratio in good yield, indicating that the reaction has indeed proceeded via the proposed aryne metallocene intermediate.



(η^2-1,2-Didehydrobenzene)titanocene (**3c**) can be employed as a reagent for the carbene complex synthesis as well. Complex **3c**, generated in situ from Cp_2TiPh_2 (**1c**) by thermally induced elimination of benzene at 90 °C, was trapped by $W(CO)_6$ present in the reaction mixture to give the metallacyclic titanoxycarbene complex $Cp_2TiOC[=W(CO)_5]C_6H_4$ (**4e**). In contrast to the zirconocene system, the product was obtained free from the bis(carbene complex) hydrolysis product. However, it was difficult to separate **4e** from any small remaining amounts of tungsten hexacarbonyl. Similarly, $Cp_2TiOC[=Mo(CO)_5]C_6H_4$ (**4f**) was obtained by thermolyzing diphenyltitanocene at 90 °C in heptane in the presence of $Mo(CO)_6$.

Very bulky Cp substituents do not hinder this carbene complex synthesis. Bis(*tert*-butylcyclopentadienyl)zirconium diphenyl (**1d**) was employed as a precursor for the $(Me_3C\text{–}Cp)_2Zr(\eta^2\text{-}C_6H_4)$ reagent. Trapping of the in situ generated aryne complex with $W(CO)_6$ at 90 °C resulted in the formation of $(Me_3CCp)_2ZrOC[W(CO)_5]C_6H_4$ (**4g**). This carbene complex was characterized by an X-ray crystal structure analysis (see below).



Reactions of the Metaloxycarbene Complexes. In view of the extreme sensitivity of the carbene complexes **4** toward hydrolysis, their reluctance to undergo carbon–carbon coupling with common organic electrophiles is remarkable. The zirconoxycarbene complex **4a** turned out to be unreactive toward a variety of alkyl halides. It failed to react as a carbon nucleophile with common aldehydes, esters, or ketones. Probably, the remaining zirconium to carbon bond in the five-membered metallacyclic ring system is very effectively shielded. From the chemistry of the structurally related bis(cyclopentadienyl)zirconaindan system **7**, it is well-known that the carbon–hydrogen

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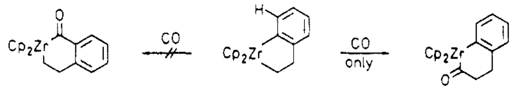
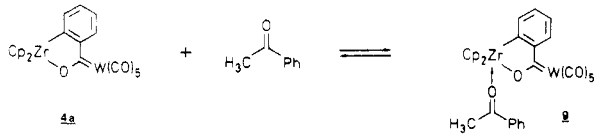
bond at C(6) in the condensed aromatic ring system very effectively protects the adjacent Zr–C(1) σ-bond from attack by reagents approaching in the plane of the metallcyclic system bisecting the CpZrCp unit.[10a]



6 7 8

However, the carbene complex **4a** is not totally unreactive toward organic carbonyl substrates. The zirconium center is sufficiently Lewis acidic to form 1:1 adducts with aldehydes or ketones. Bond formation to the carbonyl oxygen of the organic substrate probably occurs in the metallacyclic ring plane using the available lateral coordination site of the 16-electron early transition metal[12] adjacent to the carbene oxygen, thereby avoiding the unfavorable interaction with the aromatic C(6)–H(6) bond.

The $Cp_2\overline{ZrOC[=W(CO)_5]C_6H_4}$-acetophenone adduct has been characterized in some detail. In the IR spectrum, coordination to zirconium results in a decrease of the organic C=O stretching frequency from $\nu_{C=O}$ = 1684 cm^{-1} for free acetophenone to $\nu_{C=O}$ = 1647 cm^{-1} for the coordinated ketone ligand. The small shift of the C=O frequency ($\Delta\nu$ = −37 cm^{-1}) on coordination of acetophenone indicates that the zirconium center of complex **4a** has only a moderate Lewis acidity. Lewis acids $HgCl_2$ ($\Delta\nu$ = −18 cm^{-1}) and $ZnCl_2$ ($\Delta\nu$ = −47 cm^{-1}) exert similar effects on coordinated acetophenone, while adduct formation with many other typical Lewis acids leads to larger reductions of the $\nu_{C=O}$ stretching frequency [$\Delta\nu$ = −116 cm^{-1} (BF_3), −118 ($TiCl_4$), −120 ($AlCl_3$), and −130 cm^{-1} ($FeCl_3$)].[13]

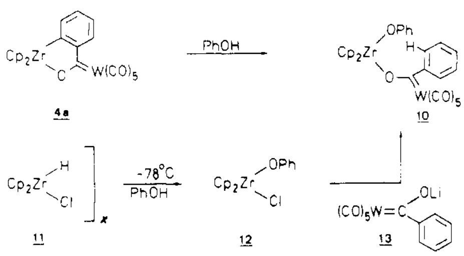


4a 9

The rather weak coordination of the ketone to zirconium allows rapid exchange with excess acetophenone in solution. Accordingly, dynamic NMR spectra have been observed. The NMR features of the coordinated acetophenone ligand were obtained from the low-temperature limiting spectra (−80 °C in CD_2Cl_2 at 9.4 T). They deviate characteristically from the NMR spectra of uncoordinated acetophenone measured under similar conditions [(coordinated vs free O=CMePh): ^{1}H NMR (ortho, meta, para methyl hydrogens) δ 8.11, 7.66, 7.80, 3.10 ppm vs δ 7.94, 7.47, 7.59, 2.58 ppm]. The ^{13}C NMR (C=O) resonance of acetophenone is shifted from δ 198.2 to δ 208.4 upon complexation with **4a**.

In contrast, the zirconium–carbon σ-bond of the metallacyclic carbene complex is rapidly cleaved at ambient temperature by protic reagents. Thus, addition of phenol to **4a** affords $Cp_2Zr(OPh)[OC(=W(CO)_5)C_6H_5]$ (**10**). The composition of this product was confirmed by an independent synthesis, starting from the hydrozirconation reagent $[Cp_2Zr(H)Cl]_x$ via $Cp_2Zr(OPh)Cl$ (**12**), which in turn was treated with $(CO)_5W{=}CPhO^-Li^+$. The structure of the acyclic zirconoxycarbene complex **10** was determined by X-ray diffraction (see below).

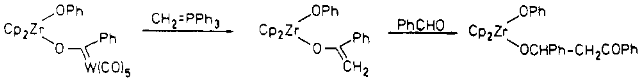
Casey et al. have shown that the carbene complex $(CO)_5W{=}C(Ph)OCH_3$ reacts with $Ph_3P{=}CH_2$ to give $(CO)_5W(PPh_3)$ and the enol ether $H_2C{=}C(Ph)OCH_3$.[14a]



4a 10 11 12 13

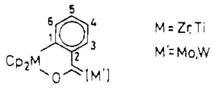
This transformation is related to the Wittig olefination reaction of organic carbonyl compounds. Using zirconoxycarbene complexes as substrates gives this reaction a new dimension, producing zirconium enolates. Enolate anion systems modified by early transition metals have served as valuable carbon nucleophiles in aldol-type carbon–carbon coupling reactions. Suitably substituted zirconium enolates undergo highly syn-selective aldol condensation reactions.[15]

The zirconoxycarbene complex **10** rapidly reacted with 1 equiv of $Ph_3P{=}CH_2$ at ambient temperature in benzene solution to give the zirconium enolate $Cp_2Zr(OPh)(O{-}C(Ph){=}CH_2)$ (**14**). Subsequent reaction with benzaldehyde afforded the zirconium aldolate **15**.[14b]



10 14 15

NMR Spectra. In the ^{13}C NMR spectrum of **4a** seven signals are observed in addition to the metal carbonyl and the Cp resonances. Three signals arise from quaternary carbons: that from the carbene carbon is found at 329.7 ppm, while the signal from C-1 (194.0 ppm) is shifted to lower field than that of C-2 (169.8 ppm) because of the directly bonded Zr atom. The remaining signals arise from the four CH carbons of the *o*-phenylene group, and their unambiguous assignment was essential for the interpretation of the marking experiment with methyl groups where di-*p*-tolylzirconocene has been used as the starting material.



Atom numbering scheme used for assigning NMR resonances of the carbene complexes **4a–4g**.

First the sequence of signals from the carbon atoms C-3 to C-6 in **4a** was determined by using a 2D relayed ^{13}C,^{1}H heteronuclear correlation experiment (RELAY).[16] In the 2D NMR spectrum, cross peaks are observed not only between a given carbon and its directly attached proton but also to other protons to which the first couples, allowing adjacent carbon atoms to be identified (see Figure 1). To establish which of the resonances from the carbon atoms at the end of the sequence is due to C-3, a ^{13}C NMR spectrum with selective proton decoupling was required to identify H-3. In the "gated" decoupled spectrum the signal from the carbene carbon is a doublet (J_{CH} = 4 Hz) which must be due to coupling with H-3 rather than H-6

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[12] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[13] Susz, B. P.; Chalandon, P. *Helv. Chim. Acta* **1958**, *41*, 1332. See also: Crist, D. R.; Hsieh, Z.-H.; Jordan, G. J.; Schinco, F. P. Maciorowski, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 4932.

[14] (a) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 6543. (b) A competition experiment has revealed that the ylide $Ph_3P{=}CH_2$ reacts about twice as fast with $(CO)_5W{=}CPh(OC_2H_5)$ than with the zirconoxycarbene complex **10**.

[15] Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, *21*, 3975. Yamamoto, Y.; Maruyama, K. *Ibid.* **1980**, *21*, 4607.

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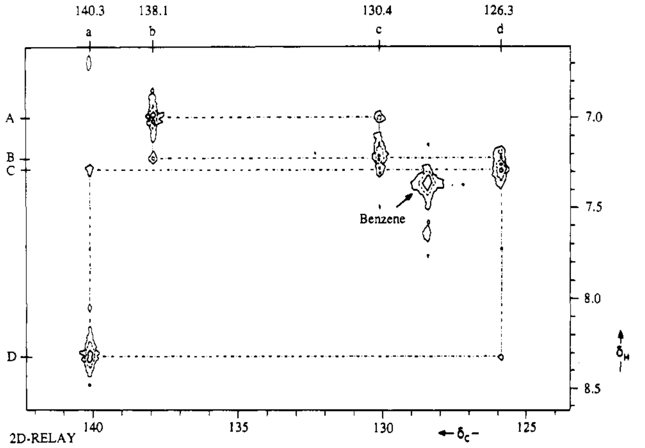

Figure 1. Part of the contour plot of the ^1H-^1H-^{13}C relayed ^{13}C,^1H heteronuclear correlated NMR spectrum (RELAY)[16] of **4a**. The main peaks arise from carbon a directly bonded to proton D, d to C, c to B, and b to A, while weaker cross peaks reveal that the carbon atoms are connected a–d–c–b. Decoupling experiments showed that the carbene carbonC-7 has a long-range coupling with D, which must therefore be H-3.

Table I. Selected ^{13}C NMR Data (in ppm) for the Metallacyclic Carbene Complexes 4a–g (CD_2Cl_2)

	4a	**4c**	**4d**	**4e**	**4f**	**4g**[a]
C-1	194.0	189.9	194.4	208.2	208.1	194.3
C-2	169.8	169.8	167.7	167.1	165.3	*b*
C-3	140.3	141.0	140.3	139.6	139.1	140.6
C-4	126.3	135.9 (s)	127.2	125.6	125.5	126.2
C-5	130.4	131.7	141.1 (s)	130.6	130.5	129.8
C-6	138.1	138.1	138.8	136.4	136.3	138.1
C-7 ($C_{carbene}$)	329.7	329.3	326.8	320.1	337.2	332.1
$-CH_3$		21.3	21.8			
Cp	115.7	115.5	115.5	118.9	118.8	*c*
CO_{trans}	206.7	206.7	206.7	206.4	216.4	205.0
CO_{cis}	200.4	200.5	200.5	200.5	208.8	200.5

[a] In C_6D_6. [b] Not observed. [c] Me_3C–Cp: 116.9, 115.4, 109.2, 107.0, 33.0 (q), 30.8 (s) ppm.

(i.e., $^3J_{CH}$, not $^4J_{CH}$). Irradiation at $\delta_H = 8.31$ ppm (the corresponding proton is directly bonded to the carbon resonating at 140.3 ppm) caused the carbene doublet to collapse, while irradiation at $\delta_H = 7.00$ had no effect upon it.

The structures of the methyl-substituted compounds **4c** and **4d** were assigned by using estimates of their chemical shifts based upon the assigned shifts of **4a** and chemical shift increments for the introduction of a methyl group in a benzene ring. The fine structures of all the multiplets in the proton-coupled ^{13}C NMR spectra of **4c** and **4d** are also entirely consistent with the replacement of H-4 and H-5, respectively, by a methyl group. Some selected NMR parameters are collected in Table I. A characteristic feature of the proton spectra of these cyclic carbene complexes is that the signal for H-3 always lies to the low-field side of 8 ppm. The RELAY and decoupling experiments on **4a** also confirm the assignments made to H-3 to H-6.

X-ray Crystal Structures. The X-ray crystal structure analysis reveals a pronounced acyl metalate character of the zirconoxycarbene complex $Cp_2Zr(OPh)OC[{=}W(CO)_5]C_6H_5]$ (**10**). The W–C(carbene) bond length is 2.188 (7) Å, which is in the range typically found for many oxygen-stabilized $(CO)_5W$–carbene complexes [W–C(carbene) and O–C(carbene) bond distances (in Å) for comparison: 2.23 (2) and 1.35 (2), $(CO)_5W{=}C(OC_2H_5)C_5H_4RuCp$;[17] 2.18 (1) and 1.29 (2). $(CO)_5W{=}C(OC_2H_5)C_5H_8CH{=}CPh_2$,[18] 2.13 (1) and 1.33 (2), $(CO)_4W{=}C(OC_2H_5)C_4H_7$,[19] 2.198 (10) and 1.262 (11), $(CO)_5W{=}C(OZrCp_2)C_4H_6$[4a]]. The O–C(carbene) bond (1.263 (9) Å) in **10** is somewhat shorter than typically found for ordinary $(CO)_5W{=}C(OR)Ar$ complexes (range 1.35 (2)–1.29 (2) Å[1a]). It is even shorter than that in the complex $Cp_2W{=}C(H)OZr(H)Cp^*_2$ (1.35 (2) Å; *d*(W–C) = 2.005 (13) Å[20]).

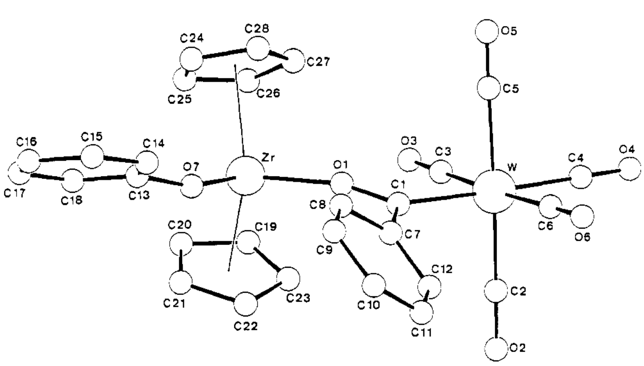

Figure 2. Molecular geometry of the carbene complex **10** in the crystal.

Table II. Selected Bond Lengths (Å) and Angles (deg) of $Cp_2Zr(OPh)OC[{=}W(CO)_5]Ph$ (10)

Bond Distances			
W–C1	2.188 (7)	O1–C1	1.263 (9)
Zr–O1	2.056 (5)	O7–C13	1.37 (1)
Zr–O7	1.971 (6)	C1–C7	1.53 (1)
Bond Angles			
O7–Zr–O1	100.0 (2)	C7–C1–O1	109.8 (6)
C1–O1–Zr	166.1 (5)	C7–C1–W	125.9 (5)
C13–O7–Zr	154.7 (5)	O1–C1–W	124.1 (5)

It is interesting to compare the bonding parameters around the two oxygen centers in **10** that are connected to zirconium. Their bond angles and bond distances are quite different from one another. The O–Zr–O angle at the metal center is 100.0 (2)°. This allows for a rather large separation between O(7) and O(1). The PhO oxygen is closer to zirconium [*d*(Zr–O(7)) = 1.971 (6) Å] than the carbene oxygen atom [*d*(Zr–O(1)) = 2.056 (5) Å]. The adjacent groups [phenyl at O(7), the $-C(Ph){=}W(CO)_5$ unit at O(1)] are both oriented near the CpZrCp bisecting major plane of the bent metallocene unit. The bond angles at both oxygen atoms are quite large. Nevertheless, the phenyl group at O(7) is oriented outward toward a lateral position of the Cp_2Zr core, while the large carbene moiety is oriented toward the central sector. The Zr,O(7),C(13) angle (154.7 (5)°) is noticeably smaller than the Zr,O(1),C(1) angle (166.1 (5)°). Both the large Zr,O,C angles indicate increased oxygen to metal π-interaction. The obtained numerical value of the Zr,O(1),C(1) angle deviates sufficiently from a linear M–O–C(carbene) arrangement to allow a defined stereochemical assignment of groups at the $-O{=}C$(carbene) moiety. The bulky $(PhO)Cp_2Zr-$ and $-W(CO)_5$ units occupy E-oriented positions; the carbene-C bound phenyl group points to the central sector of the bent metallocene fragment. Rather uncommon for octahedral L_5M–carbene complexes is the eclipsed orientation of the O(1),C(1),C(7) carbene ligand plane with the W-bound C(3),O(3) and C(6),O(6) ligands observed for **10** in the solid state.

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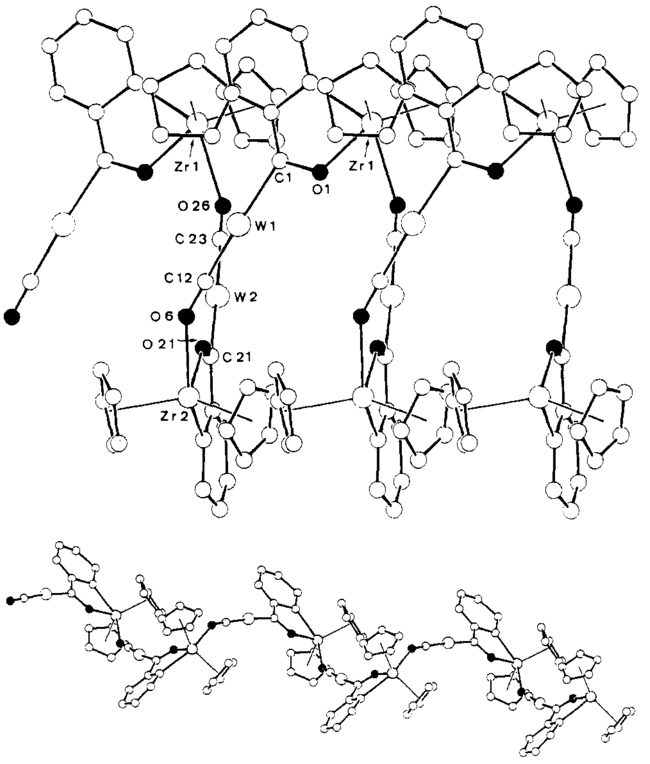

Figure 3. Two views of the helical chain solid-state structure of oligomeric $[Cp_2ZrOC[=W(CO)_5]C_6H_4]_n$ ($(\mathbf{4a})_n$) (the cis CO ligands at tungsten have been omitted for clarity).

Incorporation of the carbene oxygen atom into the five-membered metallacyclic framework of the zirconoxycarbene complex **4a** results in a dramatic reduction of the bond angles of the Zr(Ar)OC(carbene) unit. This almost completely eliminates the Zr—O=C[W] conjugative interaction and makes the early transition metal very Lewis acidic. In the solid state this leads to intermolecular adduct formation between individual $Cp_2ZrOC[=W(CO)_5]C_6H_4$ units through bonds between the carbonyl oxygen at tungsten trans to the carbene ligand and zirconium. In the crystal, lining up of the $Cp_2ZrOC[=W(CO)_5]C_6H_4$ monomers results in the formation of oligomeric helically shaped chains. Single chains of the organometallic polymers are separated by built-in solvent molecules.

Two slightly different individual zirconoxycarbene molecules were found in the asymmetric unit. Consequently, two different connecting zirconium to carbonyl oxygen bond distances are found [2.40 (2) Å, Zr(1)-O(26); 2.49 (2) Å, Zr(2)-O(6)]. Typically, the carbene complex unit containing the less electrophilic early-transition-metal center Zr(2) exhibits markedly less acyl metalate character [O(21)-C(21) = 1.36 (2) Å, W(2)-C(21) = 2.25 (1) Å, Zr(2)-O(21) = 2.15 (1) Å] than the carbene unit coordinated to Zr(1) [O(1)-C(1) = 1.21 (2) Å, W(1)-C(1) = 2.250 (8) Å, Zr(1)-O(1) = 2.16 (2) Å].

The (*t*-Bu)Cp-substituted zirconoxycarbene complex $(Me_3CCp)_2ZrOC[=W(CO)_5]C_6H_4$ (**4g**) has a similar five-membered metallacyclic framework. Typical bonding parameters are as follows: *d*(Zr-O(1)) = 2.082 (7) Å, *d*(O(1)-C(1)) = 1.31 (2) Å, *d*(C(1)-W) = 2.229 (8) Å, and *d*(Zr-C(8)) = 2.284 (9) Å; angles C(8),Zr,O(1) = 72.7 (3)° and Zr,O(1),C(1) = 126.8(4)°. According to the X-ray crystal structure analysis, the acyl metalate character of **4g** is very similar to that of **4a**. Although the electron deficiency of the zirconium centers in complexes $(RCp)_2ZrOC[=W(CO)_5]C_6H_4$ (**4a**, R = H; **4g**, R = CMe_3) have to be regarded as comparable, the aggregation state of the two complexes in the solid state is very different. Attachment of the bulky *tert*-butyl groups at the Cp rings completely shuts down oligomer formation that makes use of the lateral coordination site at the zirconium adjacent to the carbene oxygen O(1). Complex **4g** exhibits discrete monomeric units in the crystal.

Table III. Selected Bond Lengths (Å) and Angles (deg) of 4g

	Bond Distances		
W-C1	2.229 (8)	C7-C12	1.41 (2)
Zr-O1	2.082 (7)	C8-C9	1.40 (1)
Zr-C8	2.284 (9)	C9-C10	1.39 (2)
O1-C1	1.31 (2)	C10-C11	1.38 (2)
C1-C7	1.47 (1)	C11-C12	1.38 (1)
C7-C8	1.41 (1)		
	Bond Angles		
C8-Zr-O1	72.7 (3)	C9-C8-C7	117 (1)
C1-O1-Zr	126.8 (4)	C9-C8-Zr	131.1 (9)
C7-C1-O1	110.6 (8)	C7-C8-Zr	111.9 (5)
C7-C1-W	132.0 (9)	C10-C9-C8	121 (1)
O1-C1-W	117.4 (4)	C11-C10-C9	120.9 (7)
C12-C7-C8	120.6 (7)	C12-C11-C10	119 (1)
C12-C7-C1	122 (1)	C11-C12-C7	121 (1)
C8-C7-C1	117 (1)		

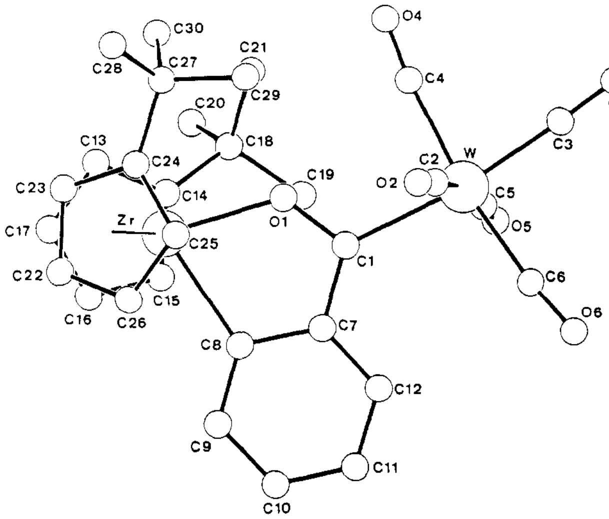

Figure 4. Molecular geometry of the carbene complex $(Me_3CCp)_2ZrOC[=W(CO)_5]C_6H_4$ (**4g**) as revealed by X-ray diffraction.

It is the aromatic C-H bond [here C(9)-H] in ortho position to the Zr-C σ bond that again appears to determine the chemical behavior of the benzannelated metallacyclic zirconoxycarbene system. We assume that repulsive steric interaction with the (*t*-Bu)Cp substituents causes the bent metallocene system to adopt the unusual conformation observed for **4g**. Both bulky *tert*-butyl groups are found quite close to each other in the lateral sector of the $(RCp)_2Zr$ unit adjacent to the Zr-O(1) bond. Concentrating both bulky alkyl substituents above and below the only position available for incoming donor ligands very effectively blocks coordination at the Lewis acidic zirconium center.

Conclusions

Two major conclusions can be drawn from our observations. In many respect Fischer-type carbene complexes are organometallic analogues of organic carbonyl compounds, the C=W(CO)$_5$ unit serving as a substitute of the

Table IV. Data for the X-ray Crystal Structure Analyses of the Zirconoxycarbene Complexes 10 and 4g

	4g	10
formula	$C_{30}H_{30}O_6WZr$	$C_{28}H_{20}O_7WZr$
M_r	761.6	743.5
space group	$P4_3$ (No. 78)	$P2_12_12_1$ (No. 19)
a, Å	11.513 (3)	11.289 (1)
b, Å	11.513 (3)	15.020 (1)
c, Å	22.118 (3)	16.291 (1)
V, Å^3	2931.8	2762.3
Z	4	4
d_{cald}, g cm^{-3}	1.72	1.79
μ(Mo Kα), cm^{-1}	43.92	46.62
F(000), e	1488	1432
T, °C	20	20
cryst dimens (max), mm	0.30 × 0.34 × 0.56	0.24 × 0.04 × 0.06
radiatn (Mo Kα), Å	0.71069	0.71069
scan mode	θ–2θ	θ–2θ
scan range	1.77–27.34	1.25–29.90
hkl range	±14,±28,+14	+15,+21,+22
analyt abs cor	2.879–4.179	1.164–1.482
reflctns measd	13234	4461
reflctns unique	6611	4431
reflctns obsd	5444 ($I > 2\sigma(I)$)	2855 ($I > 2\sigma(I)$)
refined parameters	344	335
max shift/esd	0.14	0.03
R	0.033	0.036
R_w	0.037	0.031
ρ(max), e/Å^3	2.93 (around W)	

C=O functional group. Zirconoxycarbene complexes may therefore be regarded as organometallic equivalents of metal carboxylate systems. There is more than just a formal analogy between the [Zr]OC(R)=W(CO)$_5$ moiety and the salt of a carboxylic acid. Our structural work on **10** shows that there is in fact a rather pronounced electron delocalization present, although not leading to a complete disappearance of carbonyl activity as is characteristic for a true carboxylate anion. Preliminary qualitative competition experiments[14b] have shown that the zirconoxycarbene complex **10** has to be placed near the unreactive end of the carbonyl reactivity sequence X—C(R)=O > RO—C(R)=W(CO)$_5$ > [Zr]O—C(R)=W(CO)$_5$ > -O—C(R)=O. Nevertheless, the residual carbonyl-like character is just sufficient to use **10** as a substrate in an organometallic analogue of the Wittig olefination reaction. This remarkable reaction produces a metal enolate which is a strong carbon nucleophile for aldol-type carbon–carbon coupling reactions.

It is also noteworthy that the carbene oxygen–Zr conjugative interaction appears to be almost completely eliminated by incorporating the [Zr]OC(R)=W(CO)$_5$ unit into a five-membered metallacyclic system. The electron-withdrawing features of the -O=C(R)W(CO)$_5$ unit make the early-transition-metal center in the (RCp)$_2$$\overline{\text{ZrOC[=M(CO)}_5\text{]C}_6}H_4$ species **4** very electrophilic. It is tempting to use these Lewis acids as catalysts in organic synthesis. A simple variation of Cp substituents would make chiral organometallic Lewis acids[21] available from the systems described above. We are actively investigating this possibility at present.

Experimental Section

All reactions were carried out in an inert atmosphere (argon) by using Schlenk type glassware. Solvents were dried and freshly distilled from potassium/benzophenone, lithium aluminum hydride, or P_4O_{10} (Sikapent, Merck; methylene chloride, chloroform) prior to use. Deuterated solvents benzene-d_6 and toluene-d_8 were treated with sodium/potassium alloy, distilled, and stored under argon. The following spectrometers were used: NMR, Bruker WP 80-FT (^{1}H, 80 MHz), WM 300-FT (^{13}C, 75.5 MHz), WH 400-FT (^{1}H, 400 MHz, ^{13}C 100.6 MHz); IR, Nicolet 7199 and 5DXC FT-IR spectrometer; MS, Finnigan 311 A (70 eV). The m/z values given correspond to isotopes of highest natural abundance. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, FRG. Melting points are uncorrected. Starting materials Cp_2ZrPh_2, Cp_2TiPh_2, $[Cp_2Zr(H)Cl]_x$, and $(Me_3CCp)_2ZrPh_2$ were prepared according to published procedures.[22]

Synthesis of Cp$_2$$\overline{\text{ZrOC[=W(CO)}_5\text{]C}_6}H_4$ (4a). A mixture of 7.9 g (21 mmol) of diphenylzirconocene **1a** and 7.0 g (20 mmol) of hexacarbonyltungsten in 1000 mL of heptane was thermolyzed for 5 h at 90 °C. The hot solution was filtered from a dark brown precipitate. The resulting orange-red solution was kept at dry ice temperature for 12 h. A precipitate formed that was recovered by filtration at low temperature and dried in vacuo to give 6.7 g (52%) of pure **4a** (^{1}H NMR control). Cryoscopic molecular weight determination was unsuccessfully tried; product **4a** precipitated from the benzene solution upon cooling. Recrystallization of a 3.1-g (4.8-mmol) sample of **4a** from 40 mL of refluxing benzene gave 2.4 g (62.5%) of brown crystals that contained 2 molar equiv of benzene (^{1}H NMR integration). The incorporated benzene was evaporated in vacuo or under a stream of dry argon with decomposition of the crystals. Analogously prepared toluene containing crystals of **4a** were more stable (mp 132 °C dec). Solvent-free sample: MS m/z 648 (M$^+$), 620 (M$^+$ – CO); IR (C_6D_6) ν(CO) 2061 (s), 1973 (m), 1933 (vs), 1917 cm^{-1} (sh); ^{1}H NMR (CD_2Cl_2, atom numbering scheme as used in the text) δ 8.31 (m, 1 H, H3), 7.12, 7.20 (m, 2 H, H4/5), 7.00 (m, 1 H, H6), 6.46 (s, 10 H, Cp), $^3J_{HH}$ = 7.5 Hz (H3/4), 7.2 Hz (H4/5), 6.8 Hz (H5/6), $^4J_{HH}$ = 1.4 Hz (H3/5), 1.5 Hz (H4/6), $^5J_{HH}$ = 0.6 Hz (H3/6); ^{13}C NMR (CD_2Cl_2, 40 °C) δ 329.7 (s, $^1J_{WC}$ = 93 Hz, carbene-C), 206.7 (s, 4 C, $^1J_{WC}$ = 125 Hz, W–carbonyl), 200.4 (s, 1 C, $^1J_{WC}$ = 128 Hz, W–carbonyl), 194.0 (s, C-1), 169.8 (s, $^1J_{WC}$ = 14 Hz, C-2), 140.3 (d, $^1J_{CH}$ = 159 Hz, C-3), 138.1 (d, $^1J_{CH}$ = 158 Hz, C-6), 130.4 (d, $^1J_{CH}$ = 159 Hz, C-5), 126.3 (d, $^1J_{CH}$ = 161 Hz, C-4), 115.7 (d, $^1J_{CH}$ = 175 Hz, Cp). ^{13}C and ^{1}H assignments confirmed by 2D heteronuclear RELAY experiment and decoupling experiments. Anal. Calcd for $C_{22}H_{14}O_6ZrW$ (649.42): C, 40.69; H, 2.17. Found: C, 39.79; H, 2.56.

Thermolysis of Cp$_2$Zr(*p*-tolyl)$_2$ in the Presence of W(CO)$_6$. Di-*p*-tolylzirconocene (**1b**) (800 mg, 2 mmol) and 650 mg (1.8 mmol) of hexacarbonyltungsten were thermolyzed for 2 h at 90 °C in 100 mL of heptane. Hot filtration yielded 500 mg of crude reaction product. From the mother liquor an additional 300 mg of crystalline product was obtained after 12 h at −35 °C (total yield 67%). NMR analysis revealed that both fractions contained products **4c** and **4d** in slightly different ratios (precipitated raw material, 40/60; crystals from heptane, 30/70). Subsequent recrystallization of the crude reaction product mixture (ca. 300 mg) from refluxing benzene (20 mL) yielded an analytically pure sample of the **4c**/**4d** mixture. Anal. Calcd for $C_{23}H_{16}O_6ZrW$ (663.44): C, 41.64; H, 2.43. Found: C, 42.33; H, 2.39. **4c** (minor component, methyl group at C4): ^{1}H NMR (CD_2Cl_2) δ 8.13 ("s", 1 H, H3), 7.06 (m, 1 H, H5), 6.88 (m, 1 H, H6), 6.44 (s, 10 H, Cp), 2.41 ("s", 3 H, $-CH_3$ on C4), $^3J_{HH}$ = 7.3 Hz (H5/6), $^4J_{HH}$ = 1.7 Hz (H3/5), 0.6 Hz (H3/Me), 0.7 Hz (H5/Me); ^{13}C NMR (CD_2Cl_2, 40 °C) δ 329.3 (s, carbene–C), 206.7 (s, 1 C, W–carbonyl), 200.5 (s, 4 C, $^1J_{WC}$ = 128 Hz, W–carbonyl), 189.9 (s, C-1), 169.8 (s, C-2), 141.0 (d, $^1J_{CH}$ = 155 Hz, C-3), 138.1 (d, $^1J_{CH}$ = 157 Hz, C-6), 135.9 (s, C-4), 131.7 (d, $^1J_{CH}$ = 156 Hz, C-5), 115.5 (d, $^1J_{CH}$ = 174 Hz, Cp), 21.3 (q, $^1J_{CH}$ = 126 Hz, CH_3 on C-4). **4d** (major component, methyl group at C5): ^{1}H NMR (CD_2Cl_2) δ 8.19 (m, 1 H, H3), 7.08 (m, 1 H, H4), 6.80 ("s", 1 H, H6), 6.45 (s, 10 H, Cp), 2.30 ("s", 3 H, $-CH_3$ on C5), $^3J_{HH}$ = 8.1 Hz (H3/4), $^4J_{HH}$ = 1.8 Hz (H4/6), 0.7 Hz (H4/Me), 0.6 Hz (H6/Me); ^{13}C NMR (CD_2Cl_2, 40 °C) δ 326.8 (s, carbene-C), 206.7 (s, 1 C, W–carbonyl), 200.5 (s, $^1J_{WC}$ = 128 Hz, W–carbonyl), 194.4 (s, C-1), 167.7 (s, C-2), 141.1 (s, C-5), 140.3 (d, $^1J_{CH}$ = 157 Hz, C-3), 138.8 (d, $^1J_{CH}$ = 155 Hz, C-6), 127.2

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(21) See, e.g.: Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310 and references cited therein.

(22) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986. Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*; Academic Press: New York, 1974 (loc. cit.).

(d, $^1J_{CH}$ = 159 Hz, C-4), 115.5 (d, $^1J_{CH}$ = 174 Hz, Cp), 21.8 (q, $^1J_{CH}$ = 126 Hz, CH_3 on C-5).

Thermolysis of Diphenylzirconocene (1a) in the Presence of Hexacarbonylmolybdenum. Diphenylzirconocene (**1a**) (1.1 g, 2.9 mmol) and hexacarbonylmolybdenum (600 mg, 2.3 mmol) in 100 mL of heptane were thermolyzed for 2 h at 90 °C. The mixture was filtered while still hot and then kept at −35 °C for 12 h. The resulting voluminous precipitate was recovered by filtration at low temperature giving ca. 1 g of a product mixture still containing $Mo(CO)_6$. Recrystallization from 30 mL of refluxing benzene gave crystalline **5b** (380 mg, 29%): IR (C_6D_6) ν(CO) 2061 (s), 1980 (s), 1938 (vs), 1920 cm^{-1} (sh); ^{1}H NMR (CD_2Cl_2) δ 7.50 (m, 6 H, Ph), 7.20 (m, 4 H, Ph), 6.19 (s, 20 H, Cp); ^{13}C NMR (CD_2Cl_2, 40 °C) δ 354.2 (s, carbene-C), 215.5 (s, 1 C, Mo–carbonyl), 207.6 (s, 4 C, Mo–carbonyl), 159.5 (s, Ph ipso), 130.0 (d, $^1J_{CH}$ = 161 Hz, Ph para), 128.7 (d, $^1J_{CH}$ = 160 Hz, Ph meta), 122.2 (d, $^1J_{CH}$ = 157 Hz, Ph ortho), 114.3 (d, $^1J_{CH}$ = 173 Hz, Cp). Complex **5b** was characterized by an X-ray crystal structure analysis.

Controlled Hydrolysis of the Metallacyclic Zirconoxycarbene Complex 4a. A sample of 4.3 g (6.6 mmol) of **4a** in 200 mL of methylene chloride was stirred overnight with 200 mg (0.8 mmol = 4.0 mmol of water) of $CuSO_4{\cdot}5H_2O$. The brown reaction mixture was filtered. Solvent was removed in vacuo. The brown residue was dissolved in 50 mL of refluxing benzene and left for 12 h at ambient temperature for crystallization. Filtration gave 1.55 g (36%) of orange crystals of **5a**: mp 192 °C; IR (C_6D_6) ν(CO) 2061 (s), 1974 (m), 1933 (vs), 1912 cm^{-1} (sh); ^{1}H NMR (CD_2Cl_2) δ 7.55 (m, 6 H, Ph), 7.25 (m, 4 H, Ph), 6.20 (s, 20 H, Cp); ^{13}C NMR (CD_2Cl_2, 40 °C) δ 335.7 (s, $^1J_{WC}$ = 99 Hz, carbene-C), 205.5 (s, 1 C, $^1J_{WC}$ = 120 Hz, W–carbonyl), 199.6 (s, 4 C, $^1J_{WC}$ = 128 Hz, W–carbonyl), 161.2 (s, $^1J_{WC}$ = 11 Hz, Ph ipso), 130.1 (d, $^1J_{CH}$ = 162 Hz, Ph para), 128.7 (d, $^1J_{CH}$ = 160 Hz, Ph meta), 122.4 (d, $^1J_{CH}$ = 159 Hz, Ph ortho), 114.4 (d, $^1J_{CH}$ = 173 Hz, Cp). Anal. Calcd for $C_{44}H_{30}O_{13}Zr_2W_2$ (1316.85): C, 40.13; H, 2.30. Found: C, 40.49; H, 2.28.

Synthesis of $Cp_2\overline{TiOC[{=}W(CO)_5]C_6H_4}$ (4e). Diphenyltitanocene (**1c**) (1.8 g, 5.4 mmol) and hexacarbonyltungsten (1.0 g, 2.8 mmol) in 100 mL of heptane were thermolyzed at 90 °C for 12 h. The resulting dark red solution was separated from some precipitate by filtration while still hot and then left at −35 °C for 12 h. The resulting crystals were collected by filtration to give 650 mg (39%) of **4e** (contaminated by some $W(CO)_6$, which was not removed upon recrystallization from benzene): IR (C_6D_6) ν(CO) 2056 (s), ca. 2000 (obscured by $W(CO)_6$), 1940 (sh), 1923 cm^{-1} (vs); ^{1}H NMR (CD_2Cl_2) δ 8.11 (m, 1 H, H3), 7.08, 7.18 (m, 2 H, H4/5), 6.47 (s, 10 H, Cp), 6.45 (m, 1 H, H6), $^3J_{HH}$ = 7.1 Hz (H3/4), 7.1 Hz (H4/5), 7.7 Hz (H5/6); ^{13}C NMR (CD_2Cl_2, 40 °C) δ 320.1 (s, $^1J_{WC}$ = 91 Hz, carbene-C), 208.2 (s, C-1), 206.4 (s, 1 C, $^1J_{WC}$ = 127 Hz, W–carbonyl), 200.5 (s, 4 C, $^1J_{WC}$ = 127 Hz, W–carbonyl), 167.1 (s, C-2), 139.6 (d, $^1J_{CH}$ = 158 Hz, C-3), 136.4 (d, $^1J_{CH}$ = 157 Hz, C-6), 130.6 (d, $^1J_{CH}$ = 158 Hz, C-5), 125.6 (d, $^1J_{CH}$ = 161 Hz, C-4), 118.9 (d, $^1J_{CH}$ = 177 Hz, Cp).

Synthesis of $Cp_2\overline{TiOC[{=}Mo(CO)_5]C_6H_4}$ (4f). A mixture of 10.2 g (30.9 mmol) of diphenyltitanocene (**1c**) and 6.9 g (26.1 mmol) of hexacarbonylmolybdenum was thermolyzed in 1000 mL of heptane for 12 h at 90 °C. The hot reaction mixture was filtered. The resulting solution was kept at dry ice temperature for 12 h. The precipitate was recovered by filtration. The product (6.2 g, 46%), contained some $Mo(CO)_6$, part of which was separated from the remaining **4f** by vacuum sublimation at 60 °C: ^{1}H NMR (CD_2Cl_2) δ 8.17 (m, 1 H, H3), 7.05, 7.19 (m, 2 H, H4/5), 6.46 (s, 10 H, Cp), ca. 6.5 (1 H, hidden by solvent), $^3J_{HH}$ = 7.7 Hz (H3/4), 7.1 Hz (H4/5), 7.3 Hz (H5/6); ^{13}C NMR (CD_2Cl_2, 40 °C) δ 337.2 (s, carbene-C), 216.4 (s, 1 C, Mo–carbonyl), 208.8 (s, 4 C, Mo–carbonyl), 208.1 (s, C-1), 165.3 (s, C-2), 139.1 (d, $^1J_{CH}$ = 156 Hz, C-3), 136.3 (d, $^1J_{CH}$ = 158 Hz, C-6), 130.5 (d, 158 Hz, C-5), 125.5 (d, $^1J_{CH}$ = 162 Hz, C-4), 118.8 (d, $^1J_{CH}$ = 177 Hz, Cp).

Synthesis of $(t\text{-BuCp})_2\overline{ZrOC[{=}W(CO)_5]C_6H_4}$ (4g). A sample of 0.53 g (1.09 mmol) of $(Me_3CCp)_2ZrPh_2$ (**1d**) was reacted with 0.35 g (1.00 mmol) of $W(CO)_6$ in 100 mL of heptane at 90 °C (3 h). The reaction mixture was filtered, and the product precipitated during 14 h at dry ice temperature. Filtration yielded 0.45 g (54%) of a fine crystalline brown product, **4g**, containing ca. 15% of hydrolysis product. Recrystallization from toluene gave deep red crystals of **4g**, suitable for X-ray crystal structure analysis: mp (DTA): 131 °C, endothermic; IR (C_6D_6) 2060 (s), 1970 (s), 1920 (vs), 1910 cm^{-1} (sh); ^{1}H NMR (C_6D_6, 400 MHz) δ 8.79 (m, 1 H, H3), 7.09, 6.97 (m, 1 H each, H4/5), 6.60 (m, 1 H, H6), 6.03, 5.78, 5.64, 5.25 (m, 2 H each, Cp), 1.01 (s, 18 H, *t*-Bu), $^3J_{HH}$ = 7.5 Hz (H3/4, H4/5, H5/6), $^4J_{HH}$ = 1.0 Hz (H3/5, H4/6); ^{13}C NMR (C_6D_6, 100.6 MHz) δ 332.1 (s, carbene-C), 205.0 (s, 1 H, W–carbonyl), 200.5 (s, 4 C, W–carbonyl), 194.1 (s, C-1), 145.6 (s, Cp), 140.6 (d, C-3), 138.1 (d, C-6), 129.8 (d, C-5), 126.2 (C-4), 116.9, 115.4, 109.2, 107.0 (all d, CH of Cp), 33.0 (q, $C(CH_3)_3$), 30.8 (s, $C(CH_3)_3$).

Formation of the $Cp_2\overline{ZrOC[{=}W(CO)_5]C_6H_4}$–Acetophenone Adduct 9. A suspension of diphenylzirconocene (2.20 g, 5.86 mmol) and hexacarbonyltungsten (2.00 g, 5.68 mmol) in 100 mL of heptane was heated for 5 h at 90 °C to give a deep red solution containing a fine yellow-orange precipitate. Acetophenone (1 mL) was added. The reaction mixture was filtered while still hot. A yellow precipitate formed as the filtrate cooled to room temperature. Product **9** was collected by filtration yielding 0.75 g (19%) of fine microcrystalline yellow material: IR (C_6D_6) ν(C≡O) 2061, 1934, 1918 cm^{-1}, ν(C=O) 1647 cm^{-1}; ^{1}H NMR (CD_2Cl_2, −80 °C) δ 8.28 (H3), 7.19–7.36 (H4–6), 6.06 (Cp), 8.11, 7.66, 7.80, 3.10 (coordinated acetophenone); ^{13}C NMR (CD_2Cl_2, −80 °C) δ 323.1 (carbene-C), 206.4 (W–CO_{trans}), 200.4 (W–CO_{cis}), 195.0, 162.1, 139.3, 123.4, 129.0, 136.8 (C1–C6), 111.5 (Cp), 208.4, 135.7, 133.0, 128.2, 127.8, 26.3 (coordinated acetophenone). Anal. Calcd for $C_{30}H_{22}O_7ZrW$ (769.57): C, 46.82; H, 2.88. Found: C, 47.13; H, 3.11.

Preparation of $Cp_2Zr(OPh)(OC(Ph)[{=}W(CO)_5]$ (10). Procedure A. A mixture of 3.6 g (9.5 mmol) of diphenylzirconocene (**1a**) and 3.3 g (9.5 mmol) of hexacarbonyltungsten in 150 mL of heptane was stirred for 6 h at 90 °C. The resulting product mixture was cooled to 50 °C, and 0.9 g (9.5 mmol) of phenol was added. The mixture was stirred for 5 min and then filtered and the filtrate solution kept at −29 °C for 12 h. The crude reaction product precipitated as a fine red solid. The solution was decanted and the product dissolved in benzene (50 mL). After filtration, 50 mL of heptane was added and then the total volume of the solution reduced in vacuo to 30 mL. Complex **10** (2.0 g, 29%) was isolated as a red microcrystalline solid. **Procedure B.** An ethereal solution of phenyllithium (0.99 M, 22 mL) was added to a suspension of 7.0 g (20 mmol) of hexacarbonyltungsten in 150 mL of diethyl ether. The solution was stirred for 30 min at ambient temperature; then 5 mL of methylene chloride was added to quench unreacted phenyllithium reagent. At −78 °C a solution of 6.7 g (20 mmol) of $Cp_2Zr(OPh)Cl$ (**12**) in 50 mL of toluene was added. The mixture was stirred for 2.5 h at −78 °C and then allowed to warm to room temperature during 4 h. Volatiles were removed in vacuo. Complex **10** was purified as described above and recovered in 70% yield (8.20 g): IR (C_6D_6) ν(CO) 2060 (s), 1931 cm^{-1} (vs); ^{1}H NMR (CD_2Cl_2) δ 7.62, 7.51, 7.46, 7.19, 6.85, 6.65 (aromatic H), 6.46 (Cp); ^{13}C NMR (CD_2Cl_2) δ 331.5 (s, carbene-C), 205.5 (s, W–CO_{trans}), 199.7 (s, W–CO_{cis}), 165.3 (s), 157.0 (s), 132.1 (d, $^1J_{CH}$ = 159 Hz), 129.7 (d, $^1J_{CH}$ = 161 Hz), 128.5 (d, $^1J_{CH}$ = 163 Hz), 126.6 (d, $^1J_{CH}$ = 159 Hz), 120.3 (d, $^1J_{CH}$ = 163 Hz), 118.1 (d, $^1J_{CH}$ = 161 Hz, aromatic C), 114.6 (d, $^1J_{CH}$ = 181 Hz, Cp). Anal. Calcd for $C_{28}H_{20}O_7WZr$ (743.5): C, 45.23; H, 2.71. Found: C, 44.97; H, 2.47.

Preparation of $Cp_2Zr(OPh)Cl$ (12). A solution of 2.5 g (26 mmol) of phenol in 100 mL of toluene was added dropwise at −78 °C to a suspension of $[Cp_2Zr(H)Cl]_x$ (**11**) in 150 mL of toluene. The resulting solution was filtered at ambient temperature. The solvent was removed in vacuo to give 8.7 g (96%) of **12** as a colorless oil. Complex **12** may be precipitated from pentane at −78 °C to give a fine white powder that melts upon warming to 20 °C to give a colorless oil: ^{1}H NMR (C_6D_6) δ 7.17, 6.86, 6.68 (aromatic H), 5.94 (Cp); ^{13}C NMR (C_6D_6) δ 165.8, 129.7, 120.3, 119.0 (aromatic C), 114.3 (Cp). Anal. Calcd for $C_{16}H_{15}OClZr$ (349.97): C, 54.91; H, 4.32. Found: C, 55.18; H, 4.17.

"Carbene Complex Wittig Olefination Reaction" of the Zirconoxycarbene Complex 10. A solution of 0.21 g (0.77 mmol) of $Ph_3P{=}CH_2$ in 10 mL of benzene was added to 0.57 g (0.77 mmol) of the carbene complex **10** in 15 mL of benzene at ambient temperature. The solution was stirred for 5 min. The volatiles were then removed in vacuo. The oily residue was extracted with pentane (25 mL) and filtered. The zirconium enolate product **14** (0.29 g) precipitated from the pentane solution at -78 °C together with small amounts of $Cp_2Zr(OPh)_2$ and $Cp_2Zr[OC(Ph){=}CH_2]_2$ which could not be separated. Complex **14** was identified by NMR spectra and its aldol reaction with benzaldehyde (see below): ^{1}H NMR (C_6D_6) δ 7.81, 7.25, 6.96, 6.75 (aromatic H), 5.98 (Cp), 4.84, 4.22 ($=CH_2$); ^{13}C NMR (C_6D_6) δ 166.0, 165.5 ($C{=}CH_2$, OPh_{ipso}), 139.2 ($=CPh_{ipso}$), 129.8, 125.7, 119.6, 118.6 (aromatic C, some hidden by solvent peaks), 113.1 (Cp), 86.6 ($C{=}CH_2$).

Aldol Condensation Reaction of 14 with Benzaldehyde. Slightly less than 1 molar equiv of benzaldehyde was added to a solution of **14** in benzene-d_6 at ambient temperature. The reaction was complete within 15 min as determined by ^{1}H NMR spectroscopy. **15**: ^{1}H NMR (C_6D_6) δ 6.7-7.5 (m, Ph), 5.94, 5.95 (5 H each, Cp), 5.87 (1 H, dd, $^3J_{HH}$ = 2.8, 8.3 Hz, $-OCHPh-$), 3.37 (1 H, dd, $^2J_{HH}$ = 15.8 Hz, $-CH_2-$), 2.75 (1 H, dd, $-CH_2-$).

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Registry No. **1a**, 51177-89-0; **1b**, 63672-39-9; **1c**, 1273-09-2; **1d**, 83076-03-3; **2a**, 71191-32-7; **4a**, 96896-91-2; **4c**, 96896-94-5; **4d**, 96896-93-4; **4e**, 121253-38-1; **4f**, 121253-39-2; **4g**, 121253-40-5; **5a**, 106625-46-1; **5b**, 106625-47-2; **5g**, 121253-46-1; **9**, 121253-41-6; **10**, 121253-42-7; **11**, 37342-97-5; **12**, 109550-91-6; **13**, 52573-30-5; **14**, 121253-43-8; **15**, 121253-45-0; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; H_3CCOPh, 98-86-2; $Ph_3P{=}CH_2$, 3487-44-3; $Cp_2Zr[OC(Ph){=}CH_2]_2$, 121253-44-9; $Cp_2Zr(OPh)_2$, 12303-50-3; PhCHO, 100-52-7; (η^2-1,2-didehydrobenzene)titanocene, 12679-36-6.

Supplementary Material Available: Tables of bond lengths and angles, positional parameters, and temperature factors for the zirconoxycarbene complexes **4g** and **10** (21 pages); listings of calculated and observed structure factors for **4g** and **10** (35 pages). Ordering information is given on any current masthead page.

Synthesis of a Monopentamethylcyclopentadienyl Halide Complex of Calcium. The X-ray Crystal Structure of $[(Me_5C_5)Ca(\mu\text{-}I)(THF)_2]_2$

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Potassium pentamethylcyclopentadienide and CaI_2 react in a 3:2 molar ratio in THF to yield a nearly equimolar mixture of the complexes $Cp^*CaI(THF)_2$ and $Cp^*_2Ca(THF)_2$ ($Cp^* = Me_5C_5$). The metallocene can be removed with hexane, leaving the colorless, toluene-soluble organometallic halide in 57% yield. At 20 °C, the equilibrium constant in THF for the system $Cp^*_2Ca(THF)_2 + CaI_2(THF)_2 \rightleftharpoons 2Cp^*CaI(THF)_2$ is 4. $Cp^*CaI(THF)_2$ crystallizes from toluene in the monoclinic space group $P2_1/a$, with a = 14.837 (4) Å, b = 13.022 (4) Å, c = 21.125 (7) Å, β = 98.66 (1)°, and D_{calcd} = 1.47 g cm^{-3} for Z = 4 (dimers). Least-squares refinement on the basis of 4437 observed reflections measured at 118 K led to a final R value of 0.036. Two independent iodide-bridged dimers appear in the asymmetric cell, each with a crystallographically imposed center of inversion. Each calcium in the $[Ca(\mu\text{-}I)]_2$ core is flanked by an η^5-Cp* ring with average Ca-C distances in both dimers of 2.67 (1) Å and by two THF molecules with average Ca-O distances of 2.422 (6) Å in one dimer and 2.387 (7) Å in the other. The Ca-I and Ca-I′ distances differ by 0.06 and 0.146 Å in the two dimers; a quantitative comparison of these values with those in related organolanthanide species provides a method for ranking structural distortions in bridged homometallic dimers.

Introduction

Although an organometallic complex of the alkaline-earth (Ae)[1] element calcium was reported over 80 years ago,[2] the chemistry of organocalcium, -strontium, and -barium compounds remains among the least developed of any similar group of metals.[3] The low solubility in common organic solvents and marginal thermal stability of many Ca, Sr, and Ba complexes have hindered their investigation, so that even the optimum methods of preparation of the long-known "pseudo-Grignard" reagents (RAeX) are still under study.[3,4]

Such experimental problems stem partly from the use of small, compact organic groups as ligands (e.g., Me, Et), which are unable to supply the steric saturation required to stabilize the complexes against irreversible polymerization or decomposition.[5] Consequently, the use of sterically demanding ligands to suppress oligomerization and block decomposition pathways could be expected to im-

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(1) We would like to suggest the use of the symbol "Ae" to represent the alkaline-earth metals, analogous to the use of "Ln" for the lanthanides and "An" for the actinides. The symbol "Ae" emphasizes the common divalent, electropositive nature of these elements and does not conflict with the symbols for the metals Al and Ac.

(2) The synthesis of PhCaI was reported in 1905 (Beckman, E. *Chem. Ber.* **1905**, *38*, 904-906).

(3) For the most recent general review of organometallic Ae chemistry, see: Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, 1982; Vol. I, Chapter 4.

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