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Thermally generated  $(\eta^2-1,2-didehydrobenzene)$  titanocene and -zirconocene react with hexacarbonylmolybdenum or -tungsten at 90 °C to give five-membered metallacyclic titan- and zirconoxycarbene

complexes 4. The carbon complex  $Cp_2ZrOC[=W(CO)_5]C_6H_4$  (4a) is an organometallic Lewis acid. At room temperature 4a adds 1 equiv of acetophenone giving the adduct 9 [IR  $\Delta \nu_{C=0} = -37$  cm<sup>-1</sup>; <sup>13</sup>C NMR (acetophenone carbonyl C)  $\Delta \delta = +10$  ppm]. Complex 4a is oligometric 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,  $(Me_3CCp)_2ZrOC = W(CO)_5]C_6H_4$  (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<sub>2</sub>Zr(OPh)OC[=W(CO)<sub>5</sub>]C<sub>6</sub>H<sub>5</sub> (10). Complex 10 crystallizes in space group  $P2_{12}2_{12}$  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.<sup>1</sup> They are usually prepared from metal carbonyls by variations of the two-step reaction sequence developed by E. O. Fischer et al.<sup>2</sup> 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.<sup>3</sup>

We have recently developed a new method of preparing metallacyclic metaloxycarbene complexes from metal carbonyls using very reactive  $(\eta^2$ -olefin)metallocenes as reagents.<sup>4</sup> This reaction type has nonnucleophilic reaction characteristics. It has been suggested that a bimetallic  $M(\eta^2-alkene)(\mu-\eta^1:\eta^2-carbonyl)M'$  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),<sup>4</sup>  $Cp*_{2}Th(butadiene)$ ,<sup>5</sup> and  $Cp*_{2}Ti(CH_{2}=CH_{2})$ .<sup>6</sup> We have recently observed that thermally generated  $(\eta^2$ -aryne)MCp<sub>2</sub> complexes (M = Ti, Zr; bearing normal  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> ligands or substituted Cp's) are effective reagents for the metal  $carbonyl \rightarrow metal carbene complex conversion according$ to eq 1.7 In addition, some of the resulting benzannelated



five-membered metallacyclic metaloxycarbene complexes

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derived from the group 6 metal carbonyls exhibit quite unusual structural features and remarkable chemical reactivity. Typical examples are described in this paper.

## **Results and Discussion**

The "Nonnucleophilic" Carbene Complex Synthesis Using  $(\eta^2$ -Aryne)MCp<sub>2</sub> Reagents.  $(\eta^2$ -1,2-Didehydrobenzene)MCp<sub>2</sub> complexes (M = Ti, Zr) can readily be generated thermally from the corresponding diphenylmetallocenes. Trapping with PMe<sub>3</sub> has recently resulted in the isolation and X-ray characterization of stable  $(\eta^2$ - $C_6H_4)ZrCp_2(PMe_3).^8$  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

(6) Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. J. Chem. Soc., Chem. Commun. 1986, 1145. (7) Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C. Angew.

Chem. 1985, 97, 572

(8) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. J. Am. Chem. Soc. 1986. 108. 7411

<sup>&</sup>lt;sup>†</sup> Max-Planck-Institut Mülheim.

<sup>(1) (</sup>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.

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

 <sup>(3)</sup> 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

<sup>(4)</sup> Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R.-D.; Petersen, J. L. J.
Am. Chem. Soc. 1984, 106, 7649. Erker, G.; Lecht, R. J. Organomet.
Chem. 1986, 311, 45. Erker, G.; Lecht, R.; Schlund, R.; Angermund, K.;
Krüger, C. Angew. Chem. 1987, 99, 708. Erker, G.; Lecht, R.; Petersen, J. L.; Bönnemann, H. Organometallics 1987, 6, 1962. Erker, G.; Lecht, R.; Krüger, C.; Tsay, Y.-H.; Bönnemann, H. J. Organomet. Chem. 1987, 326, C75. Erker, G.; Lecht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G.; Lecht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G.; Decht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G.; Decht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G.; Decht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G.; Decht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G.; Decht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G.; Decht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G.; Decht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G.; Decht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G.; Decht, R.; Tsay, Y.-H.; Krüger, C. Chem. Ber. 1987, 326, C75. Erker, G. In Organometer Bise in Generative Science Chem. 1987, 326, C75. Erker, G. In Organometer Bise in Generative Science Chem. 1987, 326, C75. Erker, G. In Organometer Bise in Generative Science Chem. 1987, 326, C75. Erker, G. In Organometer Bise in Generative Science Chem. 1987, 326, C75. Erker, G. In Organometer Bise in Generative Science Chem. 1987, 326, C75. Erker, G. In Organometer Bise in Generative Science Chem. 1987, 326, C75. Erker, G. In Organometer Bise in Generative Science Chem. 1987, 326, C75. Erker, G. In Organometer Bise in Generative Science Chem. 1987, 326, C75. Erker, G. In Organometer Bise in Generative Science Chem. 1987, 326, C75. Erker, G. In Organometer Bise in Generative Science Chem. 1987, 326, C75. Erker, G. In Organometer Bise in Gene 120, 1763. Erker, G. In Organometallics in Organic Synthesis; de Mei-Jee, A., tom Dieck, H., Eds.; Springer-Verlag: Berlin, Heidelberg, 1987;
p 143. Erker, G.; Lecht, R.; Sosna, F.; Uhl, S.; Tsay, Y.-H.; Krüger, C.; Grondey, H.; Benn, R. Chem. Ber. 1988, 121, 1069.
(5) Erker, G.; Mühlenbernd, T.; Benn, R.; Rufinska, A. Organometallics 1986, 5, 402.

methylene transfer to form metallacyclobutabenzenes.<sup>9</sup> Various  $\pi$ -systems (olefins, acetylenes, ketones, carbon dioxide, even dinitrogen) have been added to the reactive  $(\eta^2 - C_6 H_4) MCp_2$  intermediates to yield benzannelated five-membered metallacycles or compounds derived from them.<sup>10</sup>



In a related reaction, thermally generated  $(\eta^2-1,2-di$ dehydrobenzene)zirconocene reacts readily with W(CO)<sub>6</sub> 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  $\sigma$ 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  $\mu$ -oxo-bridged ZrCp<sub>2</sub>-O-ZrCp<sub>2</sub> 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  $(\eta^2 - C_6 H_4) ZrCp_2$  with Mo(CO)<sub>6</sub> 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.<sup>11</sup>

It was shown by a labeling experiment that aryne complexes were involved in the formation of the Cp<sub>2</sub>ZrOC- $[=M(CO)_5]C_6H_4$  carbene complexes. Di-(p-tolylzirconocene is expected to produce the unsymmetrically labeled  $(\eta^2-1, 2-didehydro-4-methylbenzene)$ zirconocene intermediate.<sup>9</sup> 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.



 $(\eta^2-1,2-Didehydrobenzene)$ 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<sub>2</sub>TiOC- $[=W(CO)_5]C_6H_4$  (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<sub>2</sub>TiOC[=Mo(CO)<sub>5</sub>]C<sub>6</sub>H<sub>4</sub> (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  $(Me_3C-Cp)_2Zr(\eta^2-C_6H_4)$  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 carboncarbon coupling with common organic electrophiles is remarkable. The zirconoxycarbene complex 4a turned out to be unreactive toward a variety of alkvl 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

<sup>(9)</sup> Erker, G. J. Organomet. Chem. 1977, 134, 189. Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. Organometallics 1985, 4, 1310. de Boer, H. J. R.; Akkerman, O. S.; Bickelhaupt, F.; Erker, G.; Czisch, P.; Mynott, R.; Wallis, J. M.; Krüger, C. Angew. Chem. 1986, 98, 641. Erker, G.; Mühlenbernd, T. J. Organomet. Chem. 1987, 319, 201. (10) (a) Erker, G.; Kropp, K. J. Am. Chem. Soc. 1979, 101, 3659. Kropp, K.; Erker, G. Organometallics, 1982, 1, 1246. (b) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. J. Am. Chem. Soc. 1987, 109, 7137 (loc. cit.)

<sup>109, 7137 (</sup>loc. cit.).

<sup>(11)</sup> Erker, G.; Dorf, U.; Krüger, C.; Tsay, Y.-H. Organometallics 1987, 6, 680.

bond at C(6) in the condensed aromatic ring system very effectively protects the adjacent Zr–C(1)  $\sigma$ -bond from attack by reagents approaching in the plane of the metallcyclic system bisecting the CpZrCp unit.<sup>10a</sup>



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<sup>12</sup> adjacent to the carbene oxygen, thereby avoiding the unfavorable interaction with the aromatic C(6)-H(6) bond.

The Cp<sub>2</sub>ZrOC[=W(CO)<sub>5</sub>]C<sub>6</sub>H<sub>4</sub>-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  $\nu_{C=0} = 1684 \text{ cm}^{-1}$ for free acetophenone to  $\nu_{C=0} = 1647 \text{ cm}^{-1}$  for the coordinated ketone ligand. The small shift of the C=O frequency ( $\Delta \nu = -37 \text{ cm}^{-1}$ ) on coordination of acetophenone indicates that the zirconium center of complex 4a has only a moderate Lewis acidity. Lewis acids HgCl<sub>2</sub> ( $\Delta \nu = -18$ cm<sup>-1</sup>) and ZnCl<sub>2</sub> ( $\Delta \nu = -47 \text{ cm}^{-1}$ ) exert similar effects on coordinated acetophenone, while adduct formation with many other typical Lewis acids leads to larger reductions of the  $\nu_{C=0}$  stretching frequency [ $\Delta \nu = -116 \text{ cm}^{-1}$  (BF<sub>3</sub>), -118 (TiCl<sub>4</sub>), -120 (AlCl<sub>3</sub>), and -130 cm<sup>-1</sup> (FeCl<sub>3</sub>)].<sup>13</sup>



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): <sup>1</sup>H NMR (ortho, meta, para methyl hydrogens)  $\delta$  8.11, 7.66, 7.80, 3.10 ppm vs  $\delta$  7.94, 7.47, 7.59, 2.58 ppm]. The <sup>13</sup>C NMR (C=O) resonance of acetophenone is shifted from  $\delta$  198.2 to  $\delta$  208.4 upon complexation with 4a.

In contrast, the zirconium-carbon  $\sigma$ -bond of the metallacyclic carbene complex is rapidly cleaved at ambient temperature by protic reagents. Thus, addition of phenol to 4a affords Cp<sub>2</sub>Zr(OPh)[OC(=-W(CO)<sub>5</sub>)C<sub>6</sub>H<sub>5</sub>] (10). The composition of this product was confirmed by an independent synthesis, starting from the hydrozirconation reagent [Cp<sub>2</sub>Zr(H)Cl]<sub>x</sub> via Cp<sub>2</sub>Zr(OPh)Cl (12), which in turn was treated with (CO)<sub>5</sub>W=CPhO<sup>-</sup>Li<sup>+</sup>. The structure of the acyclic zirconoxycarbene complex 10 was determined by X-ray diffraction (see below).

Casey et al. have shown that the carbone complex  $(CO)_5W=C(Ph)OCH_3$  reacts with  $Ph_3P=CH_2$  to give  $(CO)_5W(PPh_3)$  and the enol ether  $H_2C=C(Ph)OCH_3$ .<sup>14a</sup>



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.<sup>15</sup>

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.<sup>14b</sup>



NMR Spectra. In the <sup>13</sup>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 <sup>13</sup>C,<sup>1</sup>H heteronuclear correlation experiment (RELAY).<sup>16</sup> 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 <sup>13</sup>C NMR spectrum with selective proton decoupling was required to identify H-3. In the "gated" decoupled spectrum the signal from the carbon is a doublet ( $J_{CH} = 4$  Hz) which must be due to coupling with H-3 rather than H-6

<sup>(12)</sup> 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.

<sup>(14) (</sup>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.

 <sup>(15)</sup> Evans, D. A.; McGee, L. R. Tetrahedron Lett. 1980, 21, 3975.
 Yamamoto, Y.; Maruyama, K. Ibid. 1980, 21, 4607.
 (16) Bolton, T. H. J. Magn. Reson. 1982, 48, 336. For general refer-

<sup>(16)</sup> Bolton, T. H. J. Magn. Reson. 1982, 48, 336. For general references, see: Bax, A. Top. Carbon-13 NMR Spectrosc. 1984, 4, 197. Ernst, R. R.; Bodenhausen, G.; Wokaun, A. Principles of NMR in One and Two Dimensions; Oxford University Press: Oxford, 1987.



Figure 1. Part of the contour plot of the <sup>1</sup>H-<sup>1</sup>H-<sup>13</sup>C relayed <sup>13</sup>C,<sup>1</sup>H heteronuclear correlated NMR spectrum (RELAY)<sup>16</sup> 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 carbone carbonC-7 has a long-range coupling with D, which must therefore be H-3.

Table I. Selected <sup>13</sup>C NMR Data (in ppm) for the Metallacyclic Carbene Complexes 4a-g (CD<sub>2</sub>Cl<sub>2</sub>)

	<b>4a</b>	4c	4d	4e	4f	4g <sup>a</sup>
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	ь
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 <sub>carbene</sub> )	329.7	329.3	326.8	320.1	337.2	332.1
$-CH_3$		21.3	21.8			
Ср	115.7	115.5	115.5	118.9	118.8	с
CO <sub>trans</sub>	206.7	206.7	206.7	206.4	216.4	205.0
CO <sub>cis</sub>	200.4	200.5	200.5	200.5	208.8	200.5

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>b</sup> Not observed. <sup>c</sup>Me<sub>3</sub>C-Cp: 116.9, 115.4, 109.2, 107.0, 33.0 (q), 30.8 (s) ppm.

(i.e.,  ${}^{3}J_{CH}$ , not  ${}^{4}J_{CH}$ ). 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  $\delta_{\rm H} = 7.00$  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 <sup>13</sup>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<sub>2</sub>Zr(OPh)OC[=W- $(CO)_5$ ]C<sub>6</sub>H<sub>5</sub>] (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)<sub>5</sub>W=C(OC<sub>2</sub>H<sub>5</sub>)C<sub>5</sub>H<sub>4</sub>RuCp;<sup>17</sup> 2.18





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)	01-C1	1.263 (9)					
Zr-01	2.056 (5)	O7-C13	1.37 (1)					
Zr-07	1.971 (6)	C1–C7	1.53(1)					
Bond Angles								
07-Zr-01	100.0 (2)	C7-C1-O1	109.8 (6)					
C1-O1-Zr	166.1 (5)	C7-C1-W	125.9 (5)					
C1307Zr	154.7 (5)	01-C1-W	124.1 (5)					

(1) and 1.29 (2).  $(CO)_5W=C(OC_2H_5)C_5H_8CH=CPh_2$ ,<sup>18</sup> 2.13 (1) and 1.33 (2),  $(CO)_4W=C(OC_2H_5)C_4H_7$ ,<sup>19</sup> 2.198 (10) and 1.262 (11), (CO)<sub>5</sub>W=C(OZrCp<sub>2</sub>)C<sub>4</sub>H<sub>6</sub><sup>4a</sup>]. The O-C-(carbene) bond (1.263 (9) Å) in 10 is somewhat shorter than typically found for ordinary (CO)<sub>5</sub>W=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- $(W-C) = 2.005 (13) Å^{20}$ .

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  $100.0 (2)^{\circ}$ . 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 carbone moiety is oriented toward the central sector. The Zr,O(7),C(13)angle  $(154.7 (5)^{\circ})$  is noticeably smaller than the Zr,O(1),C(1) angle (166.1 (5)°). Both the large Zr,O,Cangles indicate increased oxygen to metal  $\pi$ -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<sub>2</sub>Zr- and -W(CO)<sub>5</sub> 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<sub>5</sub>M-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.

<sup>(18)</sup> Daran, J.-C.; Jeannin, Y. Acta Crystallogr., Sect. B 1980, B36, 1392

<sup>(19)</sup> Toledano, C. A.; Levisalles, J.; Rudler, M.; Rudler, H.; Daran,
J.-C.; Jeannin, Y. J. Organomet. Chem. 1982, 228, C7.
(20) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. J. Am. Chem.

Soc. 1979, 101, 218.



Figure 3. Two views of the helical chain solid-state structure of oligomeric  $[Cp_2ZrOC[=W(CO)_5]C_6H_4]_n$  ((4a)<sub>n</sub>) (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 fivemembered 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



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

deficiency of the zirconium centers in complexes  $(RCp)_2ZrOC[=W(CO)_5]C_6H_4$  (4a, R = H; 4g, R = CMe<sub>3</sub>) 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.

It is the aromatic C-H bond [here C(9)-H] in ortho position to the Zr-C  $\sigma$  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)<sub>2</sub>Zr 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 <sub>30</sub> H <sub>30</sub> O <sub>6</sub> WZr	C <sub>28</sub> H <sub>20</sub> O <sub>7</sub> WZr
М.	761.6	743.5
space group	P4 <sub>3</sub> (No. 78)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (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 <sup>3</sup>	2931.8	2762.3
Z	4	4
$d_{\rm cald}$ , g cm <sup>-3</sup>	1.72	1.79
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	43.92	46.62
F(000), e	1488	1432
T, °C	20	20
cryst dimens (max), mm	$0.30 \times 0.34 \times 0.56$	$0.24 \times 0.04 \times 0.06$
radiatn (Mo Kα), Å	0.71069	0.71069
scan mode	$\theta - 2\theta$	$\theta - 2\theta$
scan range	1.77 - 27.34	1.25 - 29.90
hkl range	$\pm 14, \pm 28, \pm 14$	+15,+21,+22
analyt abs cor	2.879-4.179	1.164 - 1.482
refletns 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 <sub>w</sub>	0.037	0.031
$\rho(\max), e/Å^3$	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<sup>14b</sup> have shown that the zirconoxycarbene complex 10 has to be placed near the unreactive end of the carbonyl reactivity sequence X-C- $(R)=0 > RO - C(R) = W(CO)_5 > [Zr]O - C(R) = W(CO)_5$ > -O - C(R) = 0. 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  $(RCp)_2$  $ZrOC[=M(CO)_5]C_6H_4$  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<sup>21</sup> 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 (<sup>1</sup>H, 80 MHz), WM 300-FT (<sup>13</sup>C, 75.5 MHz), WH 400-FT (<sup>1</sup>H, 400 MHz, <sup>13</sup>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.<sup>22</sup>

Synthesis of  $Cp_2ZrOC[=W(CO)_5]C_6H_4$  (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 (<sup>1</sup>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 (<sup>1</sup>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<sup>+</sup>), 620 (M<sup>+</sup> – CO); IR (C<sub>6</sub>D<sub>6</sub>)  $\nu$ (CO) 2061 (s), 1973 (m), 1933 (vs), 1917 cm<sup>-1</sup> (sh); <sup>1</sup>H NMR  $(CD_2Cl_2, atom numbering scheme as used in the text) \delta 8.31 (m,$ 1 H, H3), 7.12, 7.20 (m, 2 H, H4/5), 7.00 (m, 1 H, H6), 6.46 (s, 10 H, Cp),  ${}^{3}J_{HH} = 7.5$  Hz (H3/4), 7.2 Hz (H4/5), 6.8 Hz (H5/6),  ${}^{4}J_{\rm HH} = 1.4$  Hz (H3/5), 1.5 Hz (H4/6),  ${}^{5}J_{\rm HH} = 0.6$  Hz (H3/6);  ${}^{13}C$ NMR (CD<sub>2</sub>Cl<sub>2</sub>, 40 °C)  $\delta$  329.7 (s, <sup>1</sup>J<sub>WC</sub> = 93 Hz, carbene-C), 206.7 (s, 4 C,  ${}^{1}J_{WC} = 125$  Hz, W-carbonyl), 200.4 (s, 1 C,  ${}^{1}J_{WC} = 128$ Hz, W–carbonyl), 194.0 (s, C-1), 169.8 (s,  ${}^{1}J_{WC} = 14$  Hz, C-2), 140.3 (d,  ${}^{1}J_{CH} = 159$  Hz, C-3), 138.1 (d,  ${}^{1}J_{CH} = 158$  Hz, C-6), 130.4 (d,  ${}^{1}J_{CH} = 159$  Hz, C-5), 126.3 (d,  ${}^{1}J_{CH} = 161$  Hz, C-4), 115.7 (d,  ${}^{1}J_{CH} = 175$  Hz, Cp).  ${}^{13}C$  and  ${}^{1}H$  assignments confirmed by 2D heteronuclear RELAY experiment and decoupling experiments. Anal. Calcd for C22H14O6ZrW (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): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) & 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),  ${}^{3}J_{HH} = 7.3$  Hz (H5/6),  ${}^{4}J_{HH} = 1.7$  Hz (H3/5), 0.6 Hz (H3/Me), 0.7 Hz (H5/Me);  ${}^{13}C$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 40 °C) δ 329.3 (s, carbene-C), 206.7 (s, 1 C, W-carbonyl), 200.5 (s, 4 C,  ${}^{1}J_{WC}$  = 128 Hz, W–carbonyl), 189.9 (s, C-1), 169.8 (s, C-2), 141.0 (d,  ${}^{1}J_{CH} = 155$  Hz, C-3), 138.1 (d,  ${}^{1}J_{CH} = 157$  Hz, C-6), 135.9 (s, C-4), 131.7 (d,  ${}^{1}J_{CH} = 156$  Hz, C-5), 115.5 (d,  ${}^{1}J_{CH} = 174$  Hz, Cp), 21.3 (q,  ${}^{1}J_{CH} = 126$  Hz, CH<sub>3</sub> on C-4). 4d (major component, methyl group at C5): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) 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),  ${}^{3}J_{HH} = 8.1$  Hz (H3/4),  ${}^{4}J_{HH} = 1.8$  Hz (H4/6), 0.7 Hz (H4/Me), 0.6 Hz (H6/Me);  ${}^{13}C$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 40 °C)  $\delta$ 326.8 (s, carbene-C), 206.7 (s, 1 C, W-carbonyl), 200.5 (s,  ${}^{1}J_{WC}$ = 128 Hz, W-carbonyl), 194.4 (s, C-1), 167.7 (s, C-2), 141.1 (s, C-5), 140.3 (d,  ${}^{1}J_{CH}$  = 157 Hz, C-3), 138.8 (d,  ${}^{1}J_{CH}$  = 155 Hz, C-6), 127.2

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

<sup>(22)</sup> 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.).

## Metallacyclic Metaloxycarbene Complexes

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)<sub>6</sub>. Recrystallization from 30 mL of refluxing benzene gave crystalline 5b (380 mg, 29%): IR ( $C_6D_6$ )  $\nu$ (CO) 2061 (s), 1980 (s), 1938 (vs), 1920 cm<sup>-1</sup> (sh); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.50 (m, 6 H, Ph), 7.20 (m, 4 H, Ph), 6.19 (s, 20 H, Cp); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 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,  ${}^{1}J_{CH}$  = 161 Hz, Ph para), 128.7 (d,  ${}^{1}J_{CH}$  = 160 Hz, Ph meta), 122.2 (d,  ${}^{1}J_{CH} = 157$  Hz, Ph ortho), 114.3 (d,  ${}^{1}J_{CH} = 173$  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<sub>6</sub>D<sub>6</sub>)  $\nu$ (CO) 2061 (s), 1974 (m), 1933 (vs), 1912 cm<sup>-1</sup> (sh); <sup>1</sup>H NMR  $(CD_2Cl_2) \delta$  7.55 (m, 6 H, Ph), 7.25 (m, 4 H, Ph), 6.20 (s, 20 H, Cp); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 40 °C)  $\delta$  335.7 (s, <sup>1</sup>J<sub>WC</sub> = 99 Hz, carbene-C), 205.5 (s, 1 C,  ${}^{1}J_{WC}$  = 120 Hz, W–carbonyl), 199.6 (s, 4 C,  ${}^{1}J_{WC}$  = 128 Hz, W-carbonyl), 161.2 (s,  ${}^{1}J_{WC} = 11$  Hz, Ph ipso), 130.1 (d,  ${}^{1}J_{CH} = 162$  Hz, Ph para), 128.7 (d,  ${}^{1}J_{CH} = 160$  Hz, Ph meta), 122.4  $(d, {}^{1}J_{CH} = 159 \text{ Hz}, \text{Ph ortho}), 114.4 (d, {}^{1}J_{CH} = 173 \text{ Hz}, \text{Cp}).$  Anal. Calcd for C44H30O13Zr2W2 (1316.85): C, 40.13; H, 2.30. Found: C, 40.49; H, 2.28.

Synthesis of Cp<sub>2</sub>TiOC[=W(CO)<sub>5</sub>]C<sub>6</sub>H<sub>4</sub> (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)<sub>6</sub>, which was not removed upon recrystallization from benzene): IR (C<sub>6</sub>D<sub>6</sub>)  $\nu$ (CO) 2056 (s), ca. 2000 (obscured by W(CO)<sub>6</sub>), 1940 (sh), 1923 cm<sup>-1</sup> (vs); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  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), <sup>3</sup>J<sub>HH</sub> = 7.1 Hz (H3/4), 7.1 Hz (H4/5), 7.7 Hz (H5/6); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 40 °C)  $\delta$  320.1 (s, <sup>1</sup>J<sub>WC</sub> = 91 Hz, carbene-C), 208.2 (s, C-1), 206.4 (s, 1 C, <sup>1</sup>J<sub>WC</sub> = 127 Hz, W-carbonyl), 200.5 (s, 4 C, <sup>1</sup>J<sub>WC</sub> = 127 Hz, W-carbonyl), 167.1 (s, C-2), 139.6 (d, <sup>1</sup>J<sub>CH</sub> = 158 Hz, C-3), 136.4 (d, <sup>1</sup>J<sub>CH</sub> = 157 Hz, C-6), 130.6 (d, <sup>1</sup>J<sub>CH</sub> = 177 Hz, Cp).

Synthesis of Cp<sub>2</sub>TiOC[=Mo(CO)<sub>5</sub>] $C_6H_4$  (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)<sub>6</sub>, part of which was separated from the remaining 4f by vacuum sublimation at 60 °C: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  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), <sup>3</sup>J<sub>HH</sub> = 7.7 Hz (H3/4), 7.1 Hz (H4/5), 7.3 Hz (H5/6); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 40 °C)  $\delta$  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, <sup>1</sup>J<sub>CH</sub> = 156 Hz, C-3), 136.3 (d, <sup>1</sup>J<sub>CH</sub> = 158 Hz, C-6), 130.5 (d, 158 Hz, C-5), 125.5 (d, <sup>1</sup>J<sub>CH</sub> = 162 Hz, C-4), 118.8 (d, <sup>1</sup>J<sub>CH</sub> = 177 Hz, Cp).

Synthesis of  $(t-BuCp)_2 ZrOC[=W(CO)_5]C_6H_4$  (4g). A sample of 0.53 g (1.09 mmol) of  $(Me_3CCp)_2 ZrPh_2$  (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<sub>6</sub>D<sub>6</sub>) 2060 (s), 1970 (s), 1920 (vs), 1910 cm<sup>-1</sup> (sh); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz)  $\delta$  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), <sup>3</sup>J<sub>HH</sub> = 7.5 Hz (H3/4, H4/5, H5/6), <sup>4</sup>J<sub>HH</sub> = 1.0 Hz (H3/5, H4/6); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz)  $\delta$  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<sub>3</sub>)<sub>3</sub>), 30.8 (s, C(CH<sub>3</sub>)<sub>3</sub>).

Formation of the  $Cp_2ZrOC[=W(CO)_5]C_6H_4$ -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 vellow-orange precipitate. Acetophenone (1 mL) was added. The reaction mixture was filtered while still hot. A vellow 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 ( $C_6 D_6$ ) v-(C=0) 2061, 1934, 1918 cm<sup>-1</sup>,  $\nu$ (C=0) 1647 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, -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); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, -80 °C)  $\delta$  323.1 (carbene-C), 206.4 (W-CO<sub>trans</sub>), 200.4 (W-CO<sub>cis</sub>), 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<sub>30</sub>H<sub>22</sub>O<sub>7</sub>ZrW (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 phenvllithium (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<sub>2</sub>Zr(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 ( $C_6D_6$ )  $\nu$ (CO) 2060 (s), 1931 cm<sup>-1</sup> (vs); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.62, 7.51, 7.46, 7.19, 6.85, 6.65 (aromatic H), 6.46 (Cp); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 331.5 (s, carbene-C), 205.5 (s, W-CO<sub>trans</sub>), 199.7 (s, W-CO<sub>cis</sub>), 165.3 (s), 157.0 (s), 132.1 (d,  ${}^{1}J_{CH} = 159$  Hz), 129.7 (d,  ${}^{1}J_{CH} = 161$  Hz), 128.5 (d,  ${}^{1}J_{CH} = 163$  Hz), 126.6 (d,  ${}^{1}J_{CH} = 159$  Hz), 120.3 (d,  ${}^{1}J_{CH} = 163$ Hz), 118.1 (d,  ${}^{1}J_{CH} = 161$  Hz, aromatic C), 114.6 (d,  ${}^{1}J_{CH} = 181$  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<sub>2</sub>Zr(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: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.17, 6.86, 6.68 (aromatic H), 5.94 (Cp); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  165.8, 129.7, 120.3, 119.0 (aromatic C), 114.3 (Cp). Anal. Calcd for C<sub>16</sub>H<sub>15</sub>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<sub>2</sub>Zr(OPh)<sub>2</sub> and Cp<sub>2</sub>Zr[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): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) & 7.81, 7.25, 6.96, 6.75 (aromatic H), 5.98 (Cp), 4.84, 4.22 (=CH<sub>2</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ 166.0, 165.5 (C=CH<sub>2</sub>, OPh<sub>ipso</sub>), 139.2 (=CPh<sub>ipso</sub>), 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 <sup>1</sup>H NMR spectroscopy. 15: <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta$  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  $(1 \text{ H}, \text{ dd}, {}^{2}J_{\text{HH}} = 15.8 \text{ Hz}, -CH_{2}), 2.75 (1 \text{ H}, \text{ dd}, -CH_{2}).$ 

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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)<sub>6</sub>, 14040-11-0; Mo(CO)<sub>6</sub>, 13939-06-5; H<sub>3</sub>CCOPh, 98-86-2; Ph<sub>3</sub>P=CH<sub>2</sub>, 3487-44-3; Cp<sub>2</sub>Zr-[OC(Ph)=CH<sub>2</sub>]<sub>2</sub>, 121253-44-9; Cp<sub>2</sub>Zr(OPh)<sub>2</sub>, 12303-50-3; PhCHO, 100-52-7;  $(\eta^2-1, 2-didehydrobenzene)$ 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 $[(Me_5C_5)Ca(\mu-I)(THF)_2]_2$

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Potassium pentamethylcyclopentadienide and CaI<sub>2</sub> 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)<sub>2</sub> 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,  $\beta = 98.66$  (1)°, and  $D_{calcd} = 1.47$  g cm<sup>-3</sup> 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  $[Ca(\mu-I)]_2$  core is flanked by an  $\eta^5$ -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 alkalineearth  $(Ae)^1$  element calcium was reported over 80 years ago,<sup>2</sup> the chemistry of organocalcium, -strontium, and barium compounds remains among the least developed of any similar group of metals.<sup>3</sup> 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.<sup>3,4</sup>

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.<sup>5</sup> Consequently, the use of sterically demanding ligands to suppress oligomerization and block decomposition pathways could be expected to im-

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<sup>(1)</sup> 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).

 <sup>(3)</sup> 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.

<sup>(4)</sup> Mochida, K.; Yamanishi, T. J. Organomet. Chem. 1987, 332, 247-252 and references therein. (5) (a) Marks, T. J. Science (Washington, DC) 1982, 217, 989-997. (b)

Evans, W. J. Adv. Organomet. Chem. 1985, 24, 131-177.