Dimeric (η^2-Benzophenone)zirconocene: Its Remarkable Structure and Chemistry

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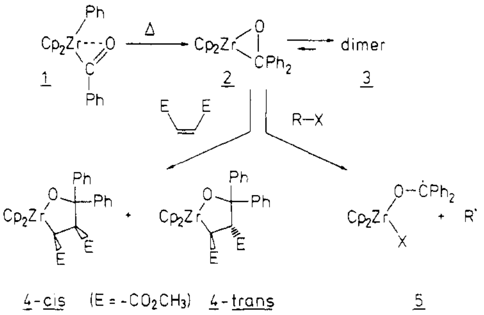
(η^2-Benzophenone)zirconocene has been obtained by the thermolysis of (η^2-benzoyl)phenylzirconocene. In the solid state this (η^2-ketone)metallocene complex adopts a dimeric structure and crystallizes in the monoclinic space group $P2_1/n$ with lattice parameters a = 13.765 (4) Å, b = 18.220 (3) Å, c = 14.182 (5) Å, β = 93.20 (2)°, V = 3551.3 (1.6) Å^3, and Z = 4. In $[(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}OC(C_6H_5)_2)]_2$ (**3**), the two independent three-membered Zr–O–C rings, which contain short zirconium–oxygen bonds (Zr1–O1 = 2.109 (2), Zr2–O2 = 2.112 (2) Å) and long zirconium–carbon distances (Zr1–C1 = 2.346 (3), Zr2–C2 = 2.350 (3) Å), are linked together by relatively weak Zr1–O2 (2.304 (2) Å) and Zr2–O1 (2.287 (2) Å) bonds. In contrast to many other oligomeric (η^2-ketone)- and (η^2-aldehyde)MCp$_2$ complexes, the central four-membered Zr$_2$O$_2$- unit in **3** is nonplanar with a folding angle of 17.2°. In solution **3** reacts with electron-deficient transition metal or main-group metal hydrides to form 1:1 adducts containing the monomeric (η^2-benzophenone)zirconocene unit. The reaction of **3** with $(Cp_2ZrH_2)_x$ yields the binuclear complex $Cp_2Zr(\mu\text{-}\eta^1(O)\text{:}\eta^2\text{-}OC(C_6H_5)_2)(\mu\text{-}H)ZrCp_2H$ (**17**). The corresponding 1:1 adduct between $Cp_2Zr(\eta^2\text{-}OC(C_6H_5)_2)$ and hafnocene dihydride undergoes a thermally induced "dyotropic" rearrangement to give an equilibrium mixture of $Cp_2Zr(\mu\text{-}\eta^1(O)\text{:}\eta^2\text{-}OC(C_6H_5)_2)(\mu\text{-}H)HfCp_2H$ (**18**) and $Cp_2Hf(\mu\text{-}\eta^1(O)\text{:}\eta^2\text{-}OC(C_6H_5)_2)(\mu\text{-}H)ZrCp_2H$ (**19**). The reaction of **3** with methylenetriphenylphosphorane proceeds with ring opening of the metallaoxirane structural subunit. Transfer of one ylide hydrogen to the carbonyl carbon atom of the former η^2-ketone ligand leads to the formation of the metallocene-substituted phosphorus ylide $Cp_2Zr(OCHPh_2)(CHPPh_3)$ (**25**).

Introduction

(η^2-Olefin)transition-metal complexes are among the most important substrates in organometallic chemistry. Their "heteroanalogues", the (η^2-ketone)- and (η^2-aldehyde)metal complexes, are far less in number but are attracting a rapidly increasing interest.[2] The reaction of a suitable metal complex fragment with an organic carbonyl compound is a common preparative route for those complexes containing late-transition elements. η^2-Ketone/aldehyde complexes of the early-transition metals[3-12] (and the oxophilic f elements[13]) are usually obtained in a different way: the side-on bound organic carbonyl

Scheme I



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[1] (a) MPI Mülheim. (b) West Virginia University; X-ray crystal structure analysis.

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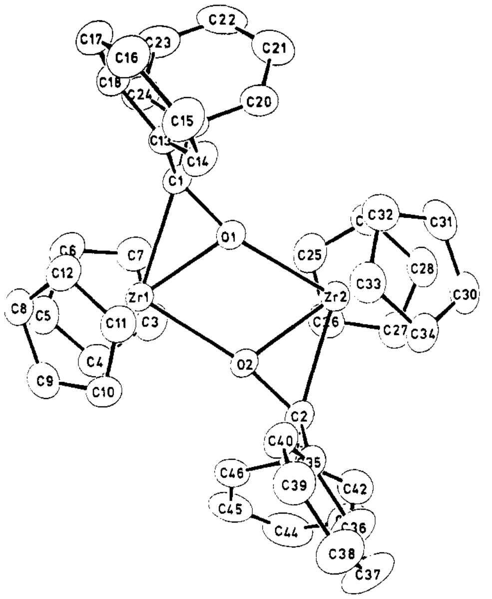


Figure 1. A perspective view of the molecular structure of $[(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}OC(C_6H_5)_2)]_2$ with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 50% probability. The hydrogen atoms have been omitted for clarity. Atoms C19, C29, and C41 are hidden behind C15, C32, and C35, respectively.

ligands[14] are often formed in the coordination sphere of the metal. Typically, these $(\eta^2\text{-}R^1R^2C{=}O)ML_n$ complexes are formed in a multistep reaction via carbonylation of the metal alkyl or hydride complexes $R^1R^2ML_n$ as precursors.

The formation of (η^2-benzophenone)$ZrCp_2$ (**2**) is a typical example. We have shown previously that the carbonylation of diphenylzirconocene occurs rapidly even at −70 °C. The observed kinetic product, an "O-outside" (η^2-acyl)zirconocene complex, rapidly rearranges above −50 °C to the thermodynamically favored "O-inside" (η^2-aroyl)-$ZrCp_2R$ geometric isomer **1**.[15] At +70 °C 1,2 migration of the remaining σ-bonded aryl ligand of **1** from zirconium to the acyl–carbon occurs with the formation of a side-on coordinated diaryl ketone ligand. The (η^2-benzophenone)$ZrCp_2$ complex had been characterized by elemental analysis, cryoscopic molecular weight determination, spectroscopic analysis, and several chemical reactions (Scheme I).[16] The molecular structure of this remarkable dimeric (η^2-ketone)metallocene in the solid state has now been determined by an X-ray structural analysis. This structural result has subsequently stimulated additional studies of the reactivity of this metallaoxirane with several electrophilic substrates, including $(Cp_2MH_2)_x$, M = Zr and Hf, $Al(i\text{-}C_4H_9)_2H$, and $CH_2{=}PPh_3$. The results from these investigations are described herein.

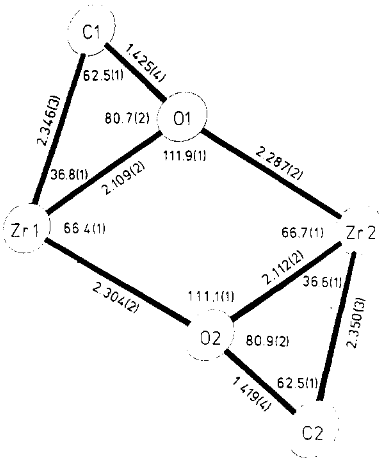
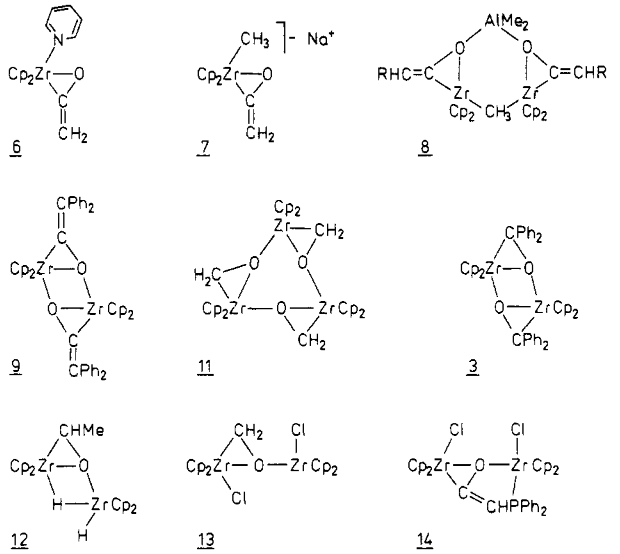


Figure 2. $Zr_2(\eta^2\text{-}OC)_2$ core of **3** with pertinent interatomic distances and bond angles included.

Scheme II



The Molecular Structure of the (η^2-Benzophenone)zirconium Complex $[(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}OC(C_6H_5)_2)]_2$

The molecular structure of the dimeric (η^2-benzophenone)zirconocene complex (**3**) is depicted in Figure 1 with the appropriate atom labeling scheme. The positional parameters for all of the atoms in this dinuclear compound are given in Table I. Pertinent interatomic separations and bond angles are given in Table II. The coordination environment about each independent Zr atom consists of two π-cyclopentadienyl rings, a side-on bonded benzophenone unit, and the oxygen atom of the other benzophenone which provides an asymmetric bridge between the two Zr centers. The average Zr–C(Cp) bond length of 2.557

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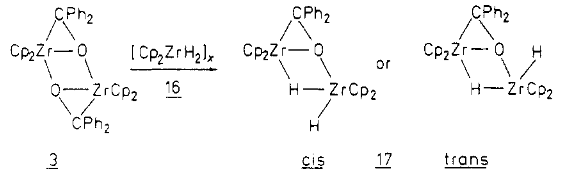
Table I. Positional Parameters for $[(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}OC(C_6H_5)_2)]_2$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Zr1	0.39228 (2)	0.20952 (2)	0.48525 (2)	C42	0.7797 (3)	0.1675 (2)	0.3623 (3)
Zr2	0.50592 (2)	0.21308 (2)	0.25940 (2)	C43	0.8452 (3)	0.1144 (3)	0.3951 (4)
O1	0.3660 (1)	0.2222 (1)	0.3382 (2)	C44	0.8326 (4)	0.0793 (3)	0.4788 (4)
O2	0.5312 (1)	0.2305 (1)	0.4059 (2)	C45	0.7570 (4)	0.0987 (2)	0.5317 (3)
C1	0.2689 (2)	0.2098 (2)	0.3643 (2)	C46	0.6917 (3)	0.1526 (2)	0.5000 (3)
C2	0.6268 (2)	0.2427 (2)	0.3768 (2)	H1	0.512 (3)	0.071 (2)	0.467 (3)
C3	0.4627 (3)	0.0820 (2)	0.5009 (3)	H2	0.525 (3))	0.125 (2)	0.625 (3)
C4	0.4702 (3)	0.1111 (2)	0.5926 (3)	H3	0.362 (3)	0.132 (2)	0.681 (3)
C5	0.3766 (3)	0.1161 (2)	0.6240 (3)	H4	0.254 (3)	0.095 (2)	0.559 (3)
C6	0.3114 (3)	0.0951 (2)	0.5520 (3)	H5	0.339 (3)	0.054 (2)	0.417 (3)
C7	0.3642 (3)	0.0722 (2)	0.4752 (3)	H6	0.277 (3)	0.250 (2)	0.654 (3)
C8	0.3185 (3)	0.2743 (2)	0.6228 (3)	H7	0.457 (3)	0.255 (2)	0.686 (3)
C9	0.4200 (3)	0.2791 (2)	0.6417 (3)	H8	0.520 (3)	0.334 (2)	0.573 (3)
C10	0.4573 (3)	0.3237 (2)	0.5736 (3)	H9	0.388 (3)	0.381 (2)	0.459 (3)
C11	0.3797 (3)	0.3473 (2)	0.5123 (3)	H10	0.237 (3)	0.325 (2)	0.517 (3)
C12	0.2948 (3)	0.3172 (2)	0.5442 (3)	H11	0.297 (3)	0.348 (2)	0.312 (3)
C13	0.2027 (2)	0.2747 (2)	0.3514 (2)	H12	0.194 (3)	0.447 (2)	0.299 (3)
C14	0.2337 (3)	0.3433 (2)	0.3220 (3)	H13	0.034 (3)	0.434 (2)	0.330 (3)
C15	0.1717 (3)	0.4028 (2)	0.3151 (3)	H14	−0.016 (3)	0.325 (2)	0.379 (3)
C16	0.0763 (3)	0.3962 (2)	0.3364 (3)	H15	0.077 (3)	0.226 (2)	0.388 (3)
C17	0.0430 (3)	0.3289 (2)	0.3638 (3)	H16	0.271 (3)	0.171 (2)	0.186 (3)
C18	0.1049 (3)	0.2691 (2)	0.3706 (3)	H17	0.186 (3)	0.084 (2)	0.112 (3)
C19	0.2200 (2)	0.1453 (2)	0.3140 (3)	H18	0.089 (3)	0.003 (2)	0.171 (3)
C20	0.2319 (3)	0.1374 (2)	0.2174 (3)	H19	0.067 (3)	0.018 (2)	0.327 (3)
C21	0.1834 (4)	0.0836 (3)	0 1650 (3)	H20	0.150 (3)	0.098 (2)	0.417 (3)
C22	0.1216 (3)	0.0375 (2)	0.2069 (4)	H21	0.428 (3)	0.060 (2)	0.291 (3)
C23	0.1087 (3)	0.0435 (2)	0.3007 (4)	H22	0.600 (3)	0.068 (2)	0.344 (3)
C24	0.1570 (3)	0.0969 (2)	0.3541 (3)	H23	0.677 (3)	0.117 (2)	0.205 (3)
C25	0.4724 (3)	0.0755 (2)	0.2585 (3)	H24	0.561 (3)	0.132 (2)	0.079 (3)
C26	0.5706 (3)	0.0818 (2)	0.2851 (3)	H25	0.405 (3)	0.099 (2)	0.132 (3)
C27	0.6178 (3)	0.1090 (2)	0.2081 (3)	H26	0.605 (3)	0.268 (2)	0.082 (3)
C28	0.5494 (3)	0.1175 (2)	0.1336 (3)	H27	0.434 (3)	0.233 (2)	0.054 (3)
C29	0.4586 (3)	0.0987 (2)	0.1647 (3)	H28	0.335 (3)	0.299 (2)	0.164 (3)
C30	0.5562 (3)	0.2832 (2)	0.1126 (3)	H29	0.459 (3)	0.376 (2)	0.268 (3)
C31	0.4581 (3)	0.2661 (2)	0.0949 (3)	H30	0.621 (3)	0.353 (2)	0.215 (3)
C32	0.4050 (3)	0.3037 (2)	0.1595 (3)	H31	0.801 (3)	0.305 (2)	0.375 (3)
C33	0.4695 (3)	0.3448 (2)	0.2174 (3)	H32	0.850 (3)	0.425 (2)	0.387 (3)
C34	0.5638 (3)	0.3333 (2)	0.1874 (3)	H33	0.742 (3)	0.515 (2)	0.409 (3)
C35	0.6611 (2)	0.3200 (2)	0.3900 (2)	H34	0.587 (3)	0.482 (2)	0.418 (3)
C36	0.7588 (3)	0.3397 (2)	0.3849 (3)	H35	0.537 (3)	0.368 (2)	0.409 (3)
C37	0.7887 (3)	0.4123 (3)	0.3925 (4)	H36	0.787 (3)	0.188 (2)	0.303 (3)
C38	0.7235 (3)	0.4677 (2)	0.4051 (3)	H37	0.890 (3)	0.105 (2)	0.359 (3)
C39	0.6277 (3)	0.4495 (2)	0.4122 (3)	H38	0.874 (3)	0.046 (2)	0.502 (3)
C40	0.5976 (3)	0.3774 (2)	0.4055 (3)	H39	0.749 ((3)	0.077 (2)	0.593 (3)
C41	0.7004 (2)	0.1868 (2)	0.4131 (3)	H40	0.645 (3)	0.168 (2)	0.541 (3)

[a] The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figures.

(4) Å and Cp(*n*)–Zr–Cp(*n*) angles of 119.9 (2) and 120.6 (2)°, respectively, are comparable to the corresponding values reported for many other zirconocene complexes.[17]

Scheme III



The two three-membered Zr–O–C rings of 3 are structurally similar (Figure 2) but not coplanar. By comparison with typical bond distance data, the three bond distances within each triangular ring are relatively long. The C–O bonds of the coordinated benzophenone ligands are substantially longer than that reported for parent ketone.[18] The values of 1.425 (4) and 1.419 (4) Å for the C1–O1 and C2–O2 bond distances, respectively, reflect the presence of a carbon–oxygen single bond.[19] They also compare favorably with the C(sp^2)–oxygen single bond distances[20] found in the few known examples of mononuclear (η^2-diphenylketene)zirconocene complexes (**6** and **7**) as well as dinuclear zirconocene complexes containing (η^2-ketene)-metallocene structural subunits (**8**, **9**, and **14** in Table III and Scheme II). The C–O bond lengths are close to the expected C(sp^3)–O bond length found for the (η^2-aldehyde)$ZrCp_2$ complexes **11**, **12**, and **13**. Although the Zr–O bonds within each (η^2-benzophenone)$ZrCp_2$ moiety of **3** are slightly shorter than the comparable Zr–O bonds in the examples cited in Table III, they are clearly longer than the Zr–O bonds in simple (μ-oxo)zirconocene complexes such as $(Cp_2ZrCl)_2O$ (1.95 Å)[21] or $(Cp_2ZrO)_3$ (1.94 Å).[22] The Zr–C(carbonyl) bonds in **3** of 2.346 (3) and 2.350 (3) Å are also rather long. The corresponding Zr–C bond

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[17] X-ray data (Cp_2Zr) - unit (examples): Wailes, P. C.; Coutts, R. S. P.; Weigold, H. "Organometallic Chemistry of Titanium, zirconium, and Hafnium"; Academic Press: New York, 1974; p 122 and references cited therein. For many additional examples see: Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

[18] C=O double bond lengths of $Ph_2C{=}O$: 1.23 Å (X-ray value): Fleischer, E. B.; Sung, N.; Hawkinson, S. *J. Phys. Chem.* **1968**, *72*, 4311.

[19] C—O single bond values, e.g., CH_3OCH_3: 1.410 ± 0.003 Å (microwave value): Blukis, U.; Kasai, P. H.; Myers, R. J. *J. Chem. Phys.* **1963**, *38*, 2753.

[20] Add 0.03 Å for comparison with bond distances to sp^3-hybridyzed carbon.

[21] Clarke, J. F.; Drew, M. G. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 2267.

[22] Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767.

Table II. Interatomic Separations (Å) and Bond Angles (deg) for Non-Hydrogen Atoms in $[(\eta^5\text{-}C_5H_5)_2Zr(\eta^3\text{-}OC(C_6H_5)_2)]_2$[a,b]

A. Interatomic Separations

Zr1–O1	2.109 (2)	Zr2–O2	2.112 (2)	C6–C7	1.406 (6)	C28–C29	1.390 (6)
Zr1–O2	2.304 (2)	Zr2–O1	2.287 (2)	C7–C3	1.396 (6)	C29–C25	1.398 (6)
Zr1–C1	2.346 (3)	Zr2–C2	2.350 (3)	C8–C9	1.412 (6)	C30–C31	1.395 (6)
O1–C1	1.425 (4)	O2–C2	1.419 (4)	C9–C10	1.382 (6)	C31–C32	1.385 (6)
Zr1–C3	2.522 (4)	Zr2–C25	2.548 (4)	C10–C11	1.407 (6)	C32–C33	1.395 (6)
Zr1–C4	2.550 (4)	Zr2–C26	2.571 (4)	C11–C12	1.391 (6)	C33–C34	1.404 (6)
Zr1–C5	2.620 (4)	Zr2–C27	2.573 (4)	C12–C8	1.386 (6)	C34–C30	1.399 (6)
Zr1–C6	2.569 (4)	Zr2–C28	2.587 (4)	C13–C14	1.392 (5)	C35–C36	1.398 (5)
Zr1–C7	2.535 (4)	Zr2–C29	2.544 (4)	C14–C15	1.381 (5)	C36–C37	1.387 (6)
Zr1–C8	2.541 (4)	Zr2–C30	2.570 (4)	C15–C16	1.369 (6)	C37–C38	1.369 (6)
Zr1–C9	2.566 (4)	Zr2–C31	2.576 (4)	C16–C17	1.373 (6)	C38–C39	1.369 (6)
Zr1–C10	2.563 (4)	Zr2–C32	2.538 (4)	C17–C18	1.383 (5)	C39–C40	1.380 (6)
Zr1–C11	2.547 (4)	Zr2–C33	2.517 (4)	C18–C13	1.392 (5)	C40–C35	1.389 (5)
Zr1–C12	2.544 (4)	Zr2–C34	2.562 (4)	C19–C20	1.396 (6)	C41–C42	1.386 (5)
Zr1–Cp(1)	2.268 (5)	Zr2–Cp(3)	2.276 (5)	C20–C21	1.380 (6)	C42–C43	1.386 (6)
Zr1–Cp(2)	2.259 (5)	Zr2–Cp(4)	2.260 (5)	C21–C22	1.356 (7)	C43–C44	1.368 (8)
C1–C13	1.498 (5)	C2–C35	1.494 (5)	C22–C23	1.356 (8)	C44–C45	1.362 (7)
C1–C19	1.513 (5)	C2–C41	1.507 (5)	C23–C24	1.382 (6)	C45–C46	1.390 (6)
C3–C4	1.403 (6)	C25–C26	1.389 (6)	C24–C19	1.381 (5)	C46–C41	1.391 (5)
C4–C5	1.391 (6)	C26–C27	1.393 (6)	Zr1···Zr2	3.6428 (4)		
C5–C6	1.376 (5)	C27–C28	1.384 (6)				

B. Bond Angles

Cp(1)–Zr1–Cp(2)	119.9 (2)	Cp(3)–Zr2–Cp(4)	120.6 (2)	C12–C8–C9	107.7 (4)	C34–C30–C31	108.2 (4)
O1–Zr1–O2	66.4 (1)	O2–Zr2–O1	66.7 (1)	C8–C9–C10	107.8 (4)	C30–C31–C32	108.2 (4)
C1–Zr1–O1	36.8 (1)	C2–Zr2–O2	36.6 (1)	C9–C10–C11	108.3 (3)	C31–C32–C33	108.2 (4)
C1–Zr1–O2	103.3 (1)	C2–Zr2–O1	102.7 (1)	C10–C11–C12	107.5 (4)	C32–C33–C34	108.1 (4)
Zr1–O1–Zr2	111.9 (1)	Zr2–O2–Zr1	111.1 (1)	C11–C12–C8	108.7 (4)	C33–C34–C30	107.3 (4)
Zr1–O1–C1	80.7 (2)	Zr2–O2–C2	80.9 (2)	C18–C13–C14	116.2 (3)	C40–C35C36	115.5 (3)
Zr2–O1–C1	160.6 (2)	Zr1–O2–C2	167.6 (2)	C13–C14–C15	121.9 (3)	C35–C36–C37	121.5 (4)
Zr1–C1–O1	62.5 (1)	Zr2–C2–O2	62.5 (1)	C14–C15–C16	120.7 (4)	C36–C37–C38	121.3 (4)
Zr1–C1–C13	120.1 (2)	Zr2–C2–C35	120.7 (2)	C15–C16–C17	118.8 (4)	C37–C38–C39	118.2 (4)
Zr1–C1–C19	128.9 (2)	Zr2–C2–C41	121.5 (2)	C16–C17–C18	120.6 (4)	C38–C39–C40	120.8 (4)
O1–C1–C13	114.6 (3)	O2–C2–C35	113.8 (3)	C17–C18–C13	121.8 (3)	C39–C40–C35	122.6 (4)
O1–C1–C19	113.5 (3)	O2–C2–C41	114.2 (3)	C24–C19–C20	116.7 (3)	C46–C41–C42	117.1 (3)
C13–C1–C19	107.8 (3)	C35–C2–C41	113.2 (3)	C19–C20–C21	121.4 (4)	C41–C42–C43	121.3 (4)
C7–C3–C4	108.1 (4)	C29–C25–C26	108.2 (4)	C20–C21–C22	120.0 (4)	C42–C43–C44	120.4 (4)
C3–C4–C5	107.5 (4)	C25–C26–C27	107.8 (4)	C21–C22–C23	120.1 (4)	C43–C44–C45	119.6 (4)
C4–C5–C6	108.7 (4)	C26–C27–C28	108.1 (4)	C22–C23–C24	120.5 (4)	C44–C45–C46	120.4 (4)
C5–C6–C7	108.3 (4)	C27–C28–C29	108.4 (4)	C23–C24–C19	121.2 (4)	C45–C46–C41	121.1 (4)
C6–C7–C3	107.2 (4)	C28–C29–C25	107.4 (4)				

[a] Cp(n) denotes the centroid of the cyclopentadienyl ring. [b] The esd's for the interatomic distances and bond angles were calculated from the standard errors of the fractional coordinates of the corresponding atomic positions.

Table III. A Comparison of Selected Structural Data of Complexes Containing a Bis(η-cyclopentadienyl)zirconaoxirane Subunit

compd[a]	η^2-ligand	Zr–C	O–C	Zr–O[b]	Zr–O′[c]	type[d]	ref
6	$CH_2{=}C{=}O$	2.181 (2)	1.338 (2)	2.126 (1)		m	5
7	$CH_2{=}C{=}O$	2.196 (8)	1.339 (9)	2.181 (5)		m	6
8[e]	$C_5H_{11}CH{=}C{=}O$	2.185 (6)	1.406 (7)	2.181 (4)		b	7
9	$Ph_2C{=}C{=}O$	2.204 (3)	1.371 (4)	2.164 (2)	2.165 (2)	d	8
11[e]	$CH_2{=}O$	2.275 (10)	1.427 (13)	2.135 (5)	2.179 (5)	t	9
3[e]	$Ph_2C{=}O$	2.348 (3)	1.422 (4)	2.111 (2)	2.296 (2)	d	this work
12[e]	$CH_3CH{=}O$	2.277 (3)	1.412 (4)	2.124 (1)	2.131 (9)	b	10
13	$CH_2{=}O$	2.19 (1)	1.43 (2)	2.13 (1)	2.10 (1)	b	11
14	$Ph_2PCH{=}C{=}O$	2.265 (6)	1.319 (10)	2.311 (4)	2.360 (5)	b	12

[a] Structures are given in Scheme II; bond distances are given in Å. [b] Within the zirconaoxirane structural subunit. [c] Connecting bond between different monomeric units. [d] Structural type: m = monomer; d = cyclodimer; t = cyclotrimer in the crystal; b = bimetallic complex. [e] Averaged bond distances from several independent monomeric units are given.

distances within the η^2-ketone and η^2-aldehyde units for the examples given in Table III are comparable to the typical values observed for Zr–C σ-bonds.[23] The Zr–C-(carbonyl) bond lengths in **3** are near the upper limit but clearly lie within the typical range for a zirconium to sp^3-carbon σ-interaction. Consequently, within the family of structurally related (η^2-$R^1R^2C{=}O$)zirconocene complexes (Table III and Scheme II), the monomeric (η^2-benzophenone)$ZrCp_2$ units of **3** represent one of the possible extremes, which is characterized by a strong metal–oxygen interaction coupled with a normal C–O single bond and a relatively weak metal–carbon bond. Under these circumstances, however, the (η^2-ketone)metallocene subunits still retain a pronounced metallaoxirane character.[24]

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[23] Values around 2.273 (5) and 2.280 (5) Å as observed for $Cp_2Zr(CH_3)_2$/$Cp_2ZrCl(CH_3)$ seem to be typical for unstrained Zr–C σ-bonds. A normal zirconium–carbon σ-bond distance of 2.284 (4) Å is observed for $Cp_2Zr(CH_2SiMe_3)_2$, whereas steric interaction leads to a substantially longer Zr–C σ-bond distance in $Cp_2Zr(CHPh_2)_2$ of 2.388 (12) Å. Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750 and references cited therein. Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1593. Atwood, J. L.; Barker, G. K.; Holton, J.; Hunter, W. E.; Lappert, M. F.; Pearce, R. *J. Am. Chem. Soc.* **1977**, *99*, 6645. For additional examples see: Krüger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *4*, 215.

[24] Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783.

Table IV. Selected ^1H NMR Data of $Cp_2Zr(\mu\text{-}\eta^1(O){:}\eta^2\text{-Aldehyde})(\mu\text{-}H)ZrCp_2H$ Complexes 12a–c[a] and the $(\mu\text{-}\eta^1(O){:}\eta^2\text{-Benzophenone})$zirconocene and Hafnocene Hydrides 17–20[b]

compd	bridging ligands	metals	terminal hydride	bridging ligands	$^2J_{HH}$[c]	Cp
12a[d]	$CH_3CH{=}O$	Zr, Zr	4.2	−1.62	13.8	5.50, 5.20 5.40, 5.20
12b[d]	$C_2H_5CH{=}O$	Zr, Zr	4.3	−1.55	13.6	5.58, 5.33 5.31, 5.30
12c[d]	$PhCH{=}O$	Zr, Zr	4.3	−1.40	13.5	5.67, 5.42 5.26, 5.03
17[e]	$Ph_2C{=}O$	Zr, Zr	5.04	−1.43	7.5	5.94, 5.40
18[e]	$Ph_2C{=}O$	Zr, Hf	8.19	−0.80	7.7	5.89, 5.43
19[e]	$Ph_2C{=}O$	Hf, Zr	4.39	−0.76	5.8	5.96, 5.39
20[e]	$Ph_2C{=}O$	Hf, Hf	7.74	−0.09	5.6	5.91, 5.43

[a] From ref 10. **12a** was characterized by an X-ray crystal structure analysis. [b] This work (for formulas see Scheme IV); chemical shifts given in ppm relative to internal Me_4Si (δ-scale). [c] Geminal coupling constant between hydride ligands given in Hz. [d] NMR in C_6D_6. [e] NMR in THF-d_8.

Although the structure parameters within the Zr–O–C rings are comparable, this similarity does not extend to all structural features of the two independent monomeric units. For example, the dihedral angles between the planes of the two phenyl rings attached to the same carbonyl carbon differ for the two benzophenone ligands. The dihedral angles between the planes containing C13–C18 and C19–C24 and between the planes containing C35–C40 and C41–C46 are 79.7° and 64.3°, respectively. This conformational variation presumably is a consequence of the crystal packing forces in the lattice.

The two Zr–C–O rings are bonded to each other through the carbonyl oxygen atoms, O1 and O2, which coordinate to the available lateral coordination site of the zirconium center of the adjacent bent metallocene unit.[25] Pseudotetrahedral bis(η^5-cyclopentadienyl)zirconium(IV) complexes under certain conditions can coordinate a fifth donor ligand by utilizing this unoccupied "ninth" valence orbital.[15,26] The extremely small in-plane interligand angles of C1–Zr1–O1 = 36.8 (1)° and C2–Zr2–O2 = 36.6 (1)° in **3** clearly favor this mode of interaction. Several cyclodimeric and -trimeric structures resulting from this type of interaction have been reported in the literature. For these adducts the connecting Zr–O bonds are usually strong[27] (Table III) and the resulting $(Zr\text{–}C\text{–}O)_n$ frameworks are generally planar. However, these two characteristic features are not observed in **3**. First, a small but significant deviation of the $Zr_2C_2O_2$ skeleton from planarity is observed. The dihedral angle between the Zr1–C1–O1 and Zr2–C2–O2 rings is 15.0°. The central four-membered Zr_2O_2 ring is also puckered[28] by 17.2°. As a result, atoms Zr2, C1, and C2 are displaced by 0.542 (1) Å above, 0.277 (4) Å below, and 0.280 (4) Å above the Zr1–O1–O2 plane, respectively. The nature of the Zr–O interactions in **3** is also notably different than those reported for related dinuclear and trinuclear zirconaoxirane oligomers. For example, in the dimeric (η^2-diphenylketene)$ZrCp_2$ complex **9**, the four Zr–O bonds of the corresponding $Zr_2C_2O_2$ core are essentially equal. In the cyclic trimer **11**, however, the Zr–O bonds of each monomeric unit are consistently ca. 0.04 Å shorter than the corresponding Zr–O bonds that link together the three (η^2-formaldehyde)zirconocene units. This latter trend becomes even more evident in **3**. Here, the Zr–O bonds in the two Zr–O–C rings are the shortest ones observed to date for a zirconaoxirane. In contrast, the connecting Zr–O linkages are substantially longer than the corresponding Zr–O bonds of 2.234 (7) Å in dimeric $[(\eta^5\text{-}C_5H_5)_2ZrOCH_2CH_2CHMe]_2$ (**15**).[30] Of the examples cited in Table III, only the phosphorane-substituted binuclear zirconocene ketene complex **14** exhibits a longer Zr–O linkage than **3**.[12] From this structural analysis, it is evident that **3** is best described as a loosely bound dimer of two (η^2-benzophenone)$ZrCp_2$ units held together by two unusually long Zr–O linkages. This structural feature presumably plays an important role in governing the chemical behavior of **3** in solution (vide infra).

Reactions of (η^2-Benzophenone)zirconocene in Solution

Previously studied[16] reactions of (η^2-benzophenone)zirconocene have taken advantage of the metal–alkyl character of the zirconaoxirane moiety. This species serves as an electron donor in the reaction with alkyl halides and behaves as a nucleophile toward α,β-unsaturated esters. The formal cycloaddition reaction with dimethyl maleate proceeds with partial loss of the stereochemistry as expected for a stepwise reaction mechanism (Scheme I).[31]

In view of the structural results for *3*, an investigation was undertaken to search for reactions of this dimer that yield products containing the zirconaoxirane moiety intact. Presumably, the already weakened Zr–O linkages of **3** can be readily broken by coordinatively unsaturated substrates which form stronger adducts with (η^2-benzophenone)$ZrCp_2$ than it does with itself. Our investigation indeed revealed that electron-deficient metal hydrides readily bind to the (η^2-benzophenone)zirconocene moiety to form stable 1:1 complexes. Treatment of **3** with a slight excess of the zirconium dihydride $(Cp_2ZrH_2)_x$ under mild reaction con-

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[25] Brintzinger, H. H.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 1105. Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[26] For leading references see: Ballhausen, C. J.; Dahl, J. P. *Acta Chem. Scand.* **1961**, *15*, 1333. Alcock, N. W. *J. Chem. Soc. A* **1967**, 2001. Green, J. C.; Green, M. L. H.; Prout, C. K. *J. Chem. Soc., Chem. Commun.* **1972**, 421. Green, J. C.; Jackson, S. E.; Higginson, B. *J. Chem. Soc., Dalton Trans.* **1975**, 403. Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6416, 6422. Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433. Marsella, J. A.; Curtis, C. J.; Bercaw, J. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 7244.

[27] Dimeric $Cp_2Ti(\eta^2\text{-}Ph_2C{=}C{=}O)$ (**10**) appears to be an exception of the rule with the Ti—O bond in the three-membered ring being substantially shorter (2.037 (2) Å) than the connecting Ti—O′ bond (2.250 (30) Å) in the four-membered Ti_2O_2 unit; see ref. 4.

[28] In contrast, even the carbocyclic analogues, the bis(η-cyclopentadienyl)metallacyclobutanes of the group 4 elements seem to favor a planar ring structure: Lee, J. B.; Gaida, G. J.; Schaefer, U. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358. Tikkanen, W. R.; Egan, J. W., Jr.; Petersen, J. L. *Organometallics* **1984**, *3*, 1646. Tikkanen, W. R.; Liu, J. Z.; Egan, J. W., Jr.; Petersen, J. L. *Organometallics* **1984**, *3*, 825. Ruppé, K.; Goddard III, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 297.

[29] For a related example of a planar metallacyclic ring system containing two zirconium and two selenium atoms, see: Gautheron, B.; Tainturier, G.; Pouly, S. *J. Organomet. Chem.* **1984**, *268*, C56.

[30] Takaya, H.; Yamakawa, M.; Mashima, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1283.

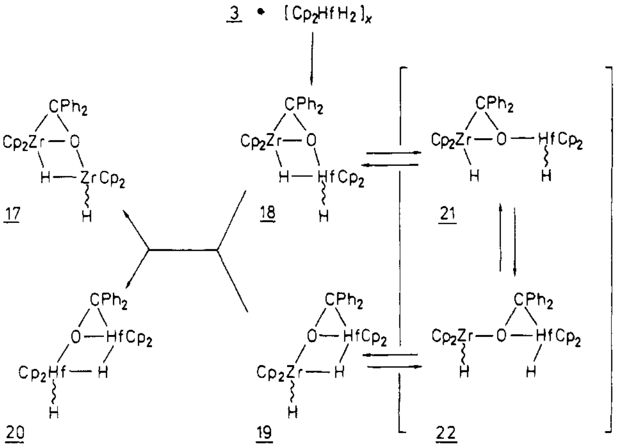
[31] In contrast, the related bis(olefin)metallocene metallacyclopentane type ring closure seems to be characterized by a stereospecific reaction course: Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246 and references cited therein.

ditions (48 h at ambient temperature) results in breaking the oligomeric structures of both reagents. The newly formed bimetallic compound is a 1:1 adduct of the monomeric building blocks (η^2-benzophenone)zirconocene and Cp_2ZrH_2. The product exhibits two different ^{1}H NMR Cp singlets each representing 10 hydrogen atoms. The presence of two different types of hydride ligands is also revealed by the ^{1}H NMR spectrum.[32] A terminal zirconium-bound hydride ligand is present (δ 5.04, see Table IV). A high-field resonance signal at δ −1.43 points to a μ-hydride bridging two zirconium centers. From these NMR data a structure for this (η^2-benzophenone)zirconocene/zirconocene dihydride adduct similar to the well-characterized $Cp_2Zr(\mu\text{-}\eta^1(O){:}\eta^2\text{-aldehyde})(\mu\text{-}H)ZrHCp_2$ complexes **12** is indicated.[10] For such complexes two different inplane arrangements of the hydride ligands within the bent metallocene moiety are possible. The addition of a fifth ligand to the pseudotetrahedral Cp_2ZrH_2 unit can occur in either a central or lateral position[15,25,26] of the ZrH_2 plane. These geometrical isomers are characterized by either a trans or cis orientation of the geminal hydride ligands, respectively. The location of both hydride ligands in the X-ray structure analysis of **12a** established a cis orientation for this binuclear zirconocene complex.[10] In principal, we initially did not see any obvious reason why **17** should adopt a different structure. However, one important difference is observed in the ^{1}H NMR spectra of **12** and **17**. While the *cis*-dihydridozirconocene moiety of **12** gives rise to a geminal $^2J_{HH}$ coupling constant of 13.8 Hz, only about half this value ($^2J_{HH}$ = 7.5 Hz, see Table IV) is found for **17**. ^{1}H NMR NOE experiments have provided an additional indication that the trans structure **17** may be favored over the *cis*-dihydride geometry.[32a] However, at the moment we have no obvious explanation for this apparent structural difference.

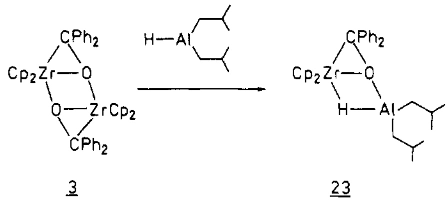
An analogous adduct is formed upon treatment of **3** with oligomeric hafnocene dihydride. Again the ^{1}H NMR spectrum greatly helps in the evaluation of the structure of the reaction product **18** (see Table IV).[33] The ^{1}H resonance of the μ-hydride ligand bridging between zirconium and hafnium is only slightly influenced by the variation of the metal centers. However, the introduction of the hafnocene unit causes a drastic downfield shift of the terminal hydride resonance for **18** relative to the bis(zirconocene) complex **17**. Again the Cp_2MH_2L unit is characterized by a rather small geminal coupling constant of the two different hydride ligands ($^2J_{HH}$ = 7.7 Hz).

Binuclear μ-aldehyde group 4 metallocene complexes often exhibit a remarkable dynamic behavior.[34] For complexes of the type $Cp_2Zr^1X(\mu\text{-}\eta^1(O){:}\eta^2\text{-}CHR{=}O)\text{-}Zr^2Cp_2X$ substantial evidence has been found to support the presence of a concerted exchange process[35] (termed "dyotropic rearrangement" or "simultaneous σ,σ-exchange")[36] which results in the mutual exchange of metal centers (Zr^1 vs. Zr^2) relative to the unsymmetrical bridging ligand. This intramolecular rearrangement process may proceed rapidly with an activation energy as low as 7 kcal/mol. (μ-Aldehyde)zirconocene complexes such as **12** also undergo this type of rearrangement, albeit at much lower rates.[10] For **17** or **18** this process most likely would involve the mutual exchange of Zr centers and the hydride ligands with the rate-determining step being the opening of the hydride bridge. For **17**, however, we did not observe this exchange process by dynamic NMR spectroscopy. In this case the reaction rate is apparently too low.[37] However, the availability of the "labeled" compound $Cp_2Zr(\mu\text{-}\eta^1(O){:}\eta^2\text{-}OC(C_6H_5)_2)(\mu\text{-}H)HfCp_2H$ (**18**) permitted an analysis of the exchange process by classical means. Thermolysis of **18** (THF-d_8, 2 h, 60 °C) rapidly resulted in the formation of the new isomeric binuclear complex **19**, which is produced from **18** by a formal exchange of the metal centers (see Scheme IV). The ^{1}H NMR spectrum clearly shows the presence of a hydride ligand bridging the zirconium and hafnium centers.[32] However, a terminal hydride now is bonded to zirconium in **19** rather than to hafnium as in **18** (see Table IV).

Scheme IV



Scheme V



A closer inspection of the NMR spectra revealed that the organometallic product mixture slowly became more complicated upon prolonged thermolysis. In addition to the **18**/**19** equilibrium mixture (70:30 ratio at 60 °C) two further products appeared, one of which was positively identified as the Zr,Zr complex **17** by comparison with the authentic material. On the basis of available ^{1}H NMR data (Table IV), the other product being formed in the thermolysis is apparently the analogous Hf,Hf compound **20**. These observations are consistent with a reversible formation of the $Cp_2Zr(\eta^2\text{-benzophenone})/Cp_2MH_2$ adducts. Therefore, by this reversible reaction sequence of adduct

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[32] (a) The chemical shift differences for bridging and terminal hydride ligands at zirconocene centers has been well documented. For leading references see: (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246. Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846. (c) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889. (d) Bickley, D. G.; Hao, N.; Bougerard, P.; Sayer, B. G.; Burns, R. C.; McGlinchey, M. J. *J. Organomet. Chem.* **1983**, *246*, 257. (b) Schroth, G.; Benn, R.; Dorf, U.; Erker, G., unpublished observations. A detailed discussion of the structural characteristics of binuclear (μ-ketone)- and (μ-aldehyde)metallocene dihydrides will be given in a forthcoming publication.

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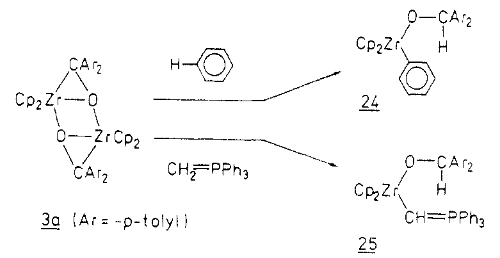
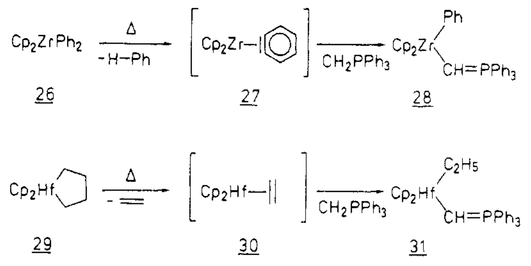
[36] Reetz, M. T.; Kliment, M.; Plachky, M. *Chem. Ber.* **1976**, *109*, 2716. Reetz, M. T.; Kliment, M.; Plachky, M.; Greif, N. *Chem. Ber.* **1976**, *109*, 2728. Reetz, M. T. *Adv. Organomet. Chem.* **1977**, *16*, 33. Reetz, M. T. *Chem. Ber.* **1977**, *110*, 954, 965.

[37] Günther, H. "NMR-Spektroskopie"; Georg Thieme Verlag: Stuttgart, 1973. Kessler, H. *Angew. Chem.* **1970**, *82*, 237.

Scheme VI



Scheme VII



formation and dyotropic exchange, $Cp_2M(\mu\text{-}\eta^1(O)\text{:}\eta^2\text{-ketone})(\mu\text{-}H)MCp_2H$ complexes, which currently cannot be prepared by direct reaction routes, are accessible (Scheme IV).

The adduct formation is not limited to the reaction of **3** with the group 4 metallocene hydrides but can be observed with electron-deficient main-group metal hydrides as well. An example is the straightforward reaction of **3** with diisobutylaluminum hydride to give the binuclear mixed main-group/transition-metal complex **23**.[38]

During a previous investigation of the ring-opening reactions of (η^2-diaryl ketone)metallocenes, we had noticed the remarkable ability of **3** to react with aromatic hydrocarbons via activation of a carbon–hydrogen bond to form **24**.[16,39] In this particular study we have found an example of a related reaction. Dimeric (η^2-4,4′-dimethylbenzophenone)zirconocene complex (**3a**) at 70 °C in hexane reacts with the phosphorus ylide methylenetriphenylphosphorane by activating a C(ylide)–hydrogen bond. The Cp_2Zr(*O*-benzhydryl)-substituted ylide **25** is formed via hydrogen abstraction and transfer to the carbonyl carbon atom of the former η^2-diaryl ketone ligand. Considering the ability of **3** to furnish (η^2-benzophenone)$ZrCp_2$ in solution, the formation of a mononuclear zirconium-substituted ylide upon treatment of the dimeric **3** with CH_2=PPh_3 is not surprising. The hydrogen transfer leading to the formation of **25** may well be a simple intramolecular analogue of the intermolecular route to $Cp_2ZrCl(CHPPh_3)$ from the reaction of a Cp_2ZrCl_2 and excess methylenetriphenylphosphorane, which was reported by Kaska several years ago.[40] However, such an intramolecular H abstraction route is normally not observed upon the exposure of simple electron-deficient zirconocene σ-hydrocarbyls, such as $Cp_2Zr(CH_3)_2$ and $Cp_2Zr(phenyl)_2$, to CH_2=PPh_3, even under drastic reaction conditions.[41] We have, however, obtained convincing evidence for the formation of the metallocene-substituted ylides **28** or **31** from the reaction of methylenetriphenylphosphorane with **26** or **29**, respectively, via (η^2-alkene)metallocene intermediates[42] (**27** and **30** in Scheme VII). Although it remains to be proven, the reaction of the readily available (η^2-benzophenone)zirconocene with CH_2=PPh_3 may represent a new example of this reaction type.[41,43]

Concluding Remarks

On the basis of the structure analysis of **3**, the kinetic lability of $[(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}OC(C_6H_5)_2)]_2$ toward fragmentation and the opening of the zirconium to carbonyl–carbon linkage during the course of subsequent chemical reactions is understandable. On the other hand, the persistence of the three-membered metallacyclic structural unit in the (η^2-benzophenone)MCp_2/Cp_2MH_2 adducts **17**–**20** seems remarkable. Although these adducts are kinetically labile (as indicated by the **18** ⇄ **19** rearrangement), they show a clear thermodynamic preference for reforming the three-membered metallcyclic ring system on the **17**–**22** energy surface. This dynamic behavior indicates that these binuclear $M^1(\mu\text{-}\eta^1(O)\text{:}\eta^2\text{-aldehyde/ketone})M^2$ complexes may provide important substrates for modeling the chemistry of :CHR and :CR_2 units on a metal oxide framework.[9] Rearrangements like the **18** ⇄ **19** transformation are reminiscent of rapid migration processes of alkylidene units on a metal oxide surface. Conceivably, alkylidene reactions on metal oxide surfaces represent important steps in CO transformations like the Fischer–Tropsch reaction.[44,45] In addition, the ability of **3** to furnish monomeric units of (η^2-benzophenone)$ZrCp_2$, which in turn can be used in the preparation of a variety of binuclear (μ-organyl)transition-metal complexes, introduces a useful alternative to synthetic routes currently available in organometallic chemistry.

Experimental Section

All reactions were conducted under argon by using standard Schlenk techniques. Solvents were dried and freshly distilled from $LiAlH_4$ under argon before use. Deuterated solvents were treated with $LiAlH_4$, distilled, and stored under argon. NMR spectra were recorded on a Bruker WP 80 (^1H and ^{31}P, 32.4 MHz), Bruker WM 300 (^{13}C, 75.5 MHz), and Bruker WH 400 (^1H and ^{13}C, 100.6 MHz; ^{27}Al, 104.3 MHz) spectrometers. Chemical shifts are given relative to Me_4Si (^1H and ^{13}C), H_3PO_4 (^{31}P), or $Al(acac)_3$ (^{27}Al), respectively. Mass spectra were obtained on a Finnigan 311 A mass spectrometer at 70 eV. Microanalyses were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Mülheim/Ruhr. Diphenylzirconocene, zirconocene dihydride, hydridozirconocene chloride, and hafnocene dihydride were prepared by standard procedures.[46] Diisobutylaluminum hydride (DIBAH neat) and

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(38) For other examples of adducts between aluminum hydrides and group 4 transition-metal complexes see: Schoer, L. I.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 5831. Shoer, L. I.; Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1977**, *136*, C19. Kopf, J.; Vollmer, H.-J.; Kaminsky, W. *Cryst. Struct. Commun.* **1980**, *9*, 985. Lobkovskii, E. B.; Soloveichik, G. L.; Sizov, A. I.; Bulychev, B. M. *J. Organomet. Chem.* **1985**, *280*, 53.

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(42) For the generation of the reactive (η^2-ethylene)MCp_2 and (η^2-didehydrobenzene)MCp_2 complexes see: (a) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (b) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 7659. (c) Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 572. (d) Skibbe, V.; Erker, G. *J. Organomet. Chem.* **1983**, *241*, 15. (e) Dorf, U.; Engel, K.; Erker, G. *Angew. Chem.* **1982**, *94*, 916.

(43) Erker, G.; Czisch, P.; Mynott, R. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1985**, *40*, 1177. Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059.

(44) The crucial role of surface bound methylene in heterogeneously catalyzed Fischer–Tropsch reactions has been demonstrated: Brady III, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

(45) For leading references see: Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. Rofer-De Poorter, C. K. *Chem. Rev.* **1981**, *81*, 447. Herrmann, W. A. *Angew. Chem.* **1982**, *94*, 118.

Table V. Data for X-ray Diffraction Analysis of $[(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}OC(C_6H_5)_2)]_2$

A. Crystal Data	
cryst system	monoclinic
space group	$P2_1/n$ (nonstandard setting of $P2_1/c$)
a, Å	13.765 (4)
b, Å	18.220 (3)
c, Å	14.182 (5)
β, deg	93.20 (2)
V, Å^3	3551.3 (1.6)
fw, amu	807.26
d(calcd), g/cm^3	1.510
Z	4
μ, cm^{-1}	6.18
B. Data Collection and Analysis Summary	
cryst dimens, mm	0.350 × 0.225 × 0.325
reflctns sampled	$\pm h,k,l$ ($5° \leq 2\theta \leq 50°$)
2θ range for centered reflctns	30–35°
scan rate	2°/min
scan width, deg	$1.1 + 0.8 \tan \theta$
no. of std reflctns	3
% cryst decay	2
total no. of measd reflctns	4980 ($F_o^2 > \sigma(F_o^2)$)
no. of unique data used	4774
agreement between equivalent data	
$R_{av}(F_o)$	0.017
$R_{av}(F_o^2)$	0.014
transmission coeff	1.0
P	0.03
discrepancy indices	
$R(F_o)$	0.045
$R(F_o^2)$	0.042
$R_w(F_o^2)$	0.065
σ_1	1.17
no. of variables	571
data to parameter ratio	8.36:1

$LiAlH_4$ were obtained from commercial sources. Carbon monoxide (commercial quality grade) was used without further purification. The consumption of CO was followed by a calibrated, mercury-sealed gas burette.

Preparation of (η^2-Benzophenone)zirconocene (3). A solution of diphenylzirconocene (4.9 g, 13.1 mmol) in 100 mL of benzene was exposed to gaseous carbon monoxide with rapid stirring for 30 min at room temperature (consumption 300 mL, 13.3 mmol). The solution was stripped in vacuo. The remaining yellow solid was suspended in heptane (200 mL) and stirred for 4 h at 70 °C. The yellow solid was isolated (G4 frit), washed twice with pentane (100 mL), and dried in vacuo. The product (4.7 g, 89% yield) shows a moderate solubility in aromatic solvents immediately after its preparation but precipitates after being stored for several days. The aged insoluble material was only marginally less reactive than the freshly prepared 3. Single crystals of the dimer 3 were grown by cooling a solution of 1.3 g of freshly prepared 3 in 100 mL of refluxing toluene slowly to room temperature. Several small yellow crystals were isolated by removing the mother liquid from the main part of an amorphous precipitate, carefully washing with 30 mL of pentane, and shortly drying in vacuo. ^1H NMR (C_6D_6): δ 7.35 (m, Ph), 5.76 (s, Cp). ^{13}C NMR (C_6D_6): δ 153.1 (s, *t*-Ph), 127.4, 126.6, 124 (d, *o*-, *m*-, *p*-Ph), 112.1 (d, Cp), 92.6 (s, carbonyl C).

X-ray Data Collection and Structural Analysis for $[(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}OC(C_6H_5)_2)]_2$ (3). An orange rectangular crystal was wedged into a glass capillary tube under a prepurified N_2 atmosphere, sealed, and optically aligned on a Picker goniostat that is controlled by a Krisel Control diffractometer automation system. Analogous procedures to those described previously[32c] were used to determine the lattice parameters of the monoclinic unit cell and the orientation matrix and to collect the intensity data. The systematic absences of $\{h0l\}$, $h + l = 2n + 1$, and $\{0k0\}$, $k = 2n + 1$ are consistent with the space group $P2_1/n$, a nonstandard setting of $P2_1/c$ (no. 14, C_{2h}^5). Specific details regarding the refined lattice parameters and the data collection procedures are given in Table V.

Approximate positions for the two Zr atoms were interpolated from the first E map calculated with MULTAN78[47] and the phase assignments for the set with the highest figure of merit. The remaining non-hydrogen atoms were located from subsequent Fourier summations. All of the hydrogen atoms were determined with difference Fourier methods using low-angle data with ($\sin \theta)/\lambda < 0.40$ Å^{-1}. Full-matrix least-squares refined (based on F_0^2)[48–52] for the positional and anisotropic temperature parameters of the 50 non-hydrogen atoms and the positional parameters for the 40 hydrogen atoms (each with a fixed isotropic temperature factor of $U = 0.063$ Å^2) converged to the final discrepancy indices of $R(F_0) = 0.045$, $R(F_0^2) = 0.042$, and $R_w(F_0^2) = 0.065$ with $\sigma_1 = 1.17$ for 4774 data with $F_0^2 > \sigma(F_0^2)$. The maximum parameter shift to error ratio for any of the 571 varied parameters did not exceed 0.1 during the last refinement cycle. A final difference Fourier map was featureless and did not reveal any residuals greater than 0.5 e/Å^3.[53]

Preparation of $Cp_2Zr(\mu\text{-}\eta^1(O){:}\eta^2$-benzophenone)($\mu$-H)-$ZrCp_2H$ (17). Method A. Dimeric (η^2-benzophenone)zirconocene (3) (4.7 g, 11.7 mmol) and zirconocene dihydride (2.6 g, 11.6 mmol) were stirred in 150 mL of benzene for 48 h at room temperature. The resulting suspension was filtered (G4-frit). After the ivory-colored precipitate was dried in vacuo, 6.7 g (92%) of product was isolated. After recrystallization of 0.5 g of the crude reaction product from 40 mL of refluxing benzene, 17 was obtained as ivory-colored needles with a decomposition point of 168 °C. Crystalline 17 invariably contained about 0.5 equiv of benzene as judged from ^1H NMR and elemental analyses. Anal. Calcd for $C_{33}H_{32}OZr_2{\cdot}0.5C_6H_6$: C, 64.92; H, 5.26. Found (two independently prepared samples): C, 65.40; H, 5.34/C, 64.83; H, 5.11. ^1H NMR (THF-d_8): δ 7.59 (d, 4 H, *o*-Ph), 7.14 (t, 4 H, *m*-Ph), 6.82 (t, 2 H, *p*-Ph), 5.94/5.40 (s, each 10 H, Cp), 5.04 (d, 1 H, term H), −1.43 (d, 1 H, bridged H, $^2J_{HH} = 7.5$ Hz). MS: *m/e* 624 (M^+), 457 ($M^+ - 167$), 167 (phenyltropylium$^+$).

Method B. A benzene-d_6 suspension (0.5 mL) of 3 (20 mg, 0.05 mmol) and $[Cp_2Zr(H)Cl]_x$ (25 mg, 0.1 mmol) was reacted at room temperature by shaking in a sealed 5-mm NMR tube (15 min). In the ^1H NMR spectrum the formation of 17 and 1 equiv of zirconocene dichloride, which was identified by comparison with an authentic sample[54] (^1H NMR (C_6D_6) δ 5.89 (s, Cp)) was observed.

Preparation of $Cp_2Zr(\mu\text{-}\eta^1(O){:}\eta^2$-benzophenone)($\mu$-H)-$HfCp_2H$ (18). Dimeric (η^2-benzophenone)zirconocene (3) (1.25 g, 3.1 mmol) and hafnocene dihydride (0.95 g, 3.1 mmol) were stirred in 50 mL of benzene for 12 h at room temperature. The resultant suspension was filtered through a G4-frit. After the precipitate was dried in vacuo, 1.5 g (68%) of product was isolated. After recrystallization from refluxing benzene (0.5 g in 40 mL) 18 appeared as ivory-colored needles with a decomposition point of 170 °C. Anal. Calcd for $C_{33}H_{32}OHfZr{\cdot}0.5C_6H_6$: C, 57.39; H, 4.65. Found: C, 58.72; H, 4.60. ^1H NMR (THF-d_8): δ 8.19 (d, 1 H, term H), 7.63 (d, 4 H, *o*-Ph), 7.15 (t, 4 H, *m*-Ph), 6.83 (t, 2

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(48) The least-squares refinement[49] of the X-ray diffraction data was based upon the minimization of $\sum\omega_i|F_0^2 - S^2F_c^2|$, where ω_i is the individual weighting factor and S is the scale factor. The discrepancy indices were calculated from the expressions: $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(F_o^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2$, and $R_w(F_o^2) = [\sum\omega_i|F_o^2 - F_c^2|^2/\sum\omega_i F_o^4]^{1/2}$. The standard deviation of an observation of unit weight, σ_1, equals $[\sum\omega_i|F_o^2 - F_c^2|/(n - p)]^{1/2}$, where n is the number of observations and p is the number of parameters varied during the last refinement cycle.

(49) The values of the atomic scattering factors in all of the structure factor calculations were those of Cromer and Mann[50] for the non-hydrogen atoms and those of Stewart et al.[51] for the hydrogen atoms with corrections included for anomalous dispersion.[52]

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(54) King, R. B. *Organomet. Synth.* **1965**, *1*, 75.

H, *p*-Ph), 5.89/5.43 (s, each 10 H, Cp), –0.80 (d, 1 H, bridged H, $^2J_{HH}$ = 7.7 Hz). MS: *m/e* 714 (M^+_{ZrHf}), 633 (M^+_{HfHf} – 167), 545 (M^+_{ZrHf} – 167), 167 (phenyltropylium$^+$).

Thermolysis of $Cp_2Zr(\mu$-η^1(O):η^2-benzophenone)(μ-H)-$HfCp_2H$ (18). Method A. A 0.5-mL THF-d_8 solution of 18 (20 mg, 0.03 mmol) was sealed in a 5-mm NMR tube and placed in an oil bath at 60 °C for 2 h. The sample then consisted of a mixture containing 70% of **18**, 30% of $Cp_2Hf(\mu$-η^1(O):η^2-benzophenone)(μ-H)$ZrCp_2H$ (**19**), and a trace of **17**. The **18**/**19** ratio was not changed upon further heating of the sample.

Method B. A 50-mL toluene solution of **18** (1.0 g, 1.4 mmol) was heated in an oil bath for 2 h at 80 °C. When the darkened solution was cooled to –30 °C (48 h), a few colorless crystals precipitated which consisted of a mixture of **18**, **19**, and the "crossover" products **17** and **20**. Because of the workup step, the observed **17**:**18**:**19**:**20** ratio of about 35:50:10:5 certainly does not represent the true equilibrium ratio of these compounds under the reaction conditions applied. MS (from the mixture): *m/e* 633 (M^+_{HfHf} – 167), 545 (M^+_{HfZr} – 167), 455 (M^+_{ZrZr} – 167), 167 (phenyltropylium$^+$). ^{1}H NMR (from the mixture, THF-d_8) **19**, δ 7.56 (d, 4 H, *o*-Ph), 7.17 (t, 4 H, *m*-Ph), 6.82 (t, 2 H, *p*-Ph), 5.96/5.39 (s, each 10 H, Cp), 4.40 (d, 1 H, term H), –0.76 (d, 1 H, bridged H, $^2J_{HH}$ = 5.8 Hz); **20**, δ 7.74 (d, 1 H, term H), ca. 7.60 (*o*-Ph), ca. 7.15 (*m*-Ph), ca. 6.80 (*p*-Ph), 5.91/5.43 (s, each Cp), 10 H, –0.09 (d, 1 H, bridged H, $^2J_{HH}$ = 5.6 Hz).

Preparation of $Cp_2Zr(\mu$-η^1(O):η^2-benzophenone)(μ-H)Al-(i-$C_4H_9)_2$ (23). To a stirred suspension of **3** (2.8 g, 6.9 mmol) in 100 mL of benzene was added a solution of diisobutylaluminum hydride (DIBAH) (0.7 mL, 4.2 mmol) in 30 mL of benzene over a period of 2 h. The solution was filtered from excess **3** and stripped in vacuo. The resultant brown-yellow oil was dissolved in 100 mL of pentane. The yellow solution was filtered from a small amount of precipitate and stripped in vacuo at –20 °C. A foamy residue was obtained to give 0.7 g of **23** (30%) as a yellow powder at room temperature. Anal. Calcd for $C_{31}H_{39}OAlZr$: C, 68.21; H, 7.20. Found: C, 68.08; H, 6.79. ^{1}H NMR (C_6D_6): δ 7.44 (d, 4 H, *o*-Ph), 7.17 (t, 4 H, *m*-Ph), 6.90 (t, 2 H, *p*-Ph), 5.30 (s, 10 H, Cp), 2.32 (m, 2 H, CH), 1.31/1.34 (each d, 6 H, CH_3), 0.41/0.62 (each 2 H, CH_2), –0.70 (s (br), 1 H, hydride). ^{13}C NMR (C_6D_6): δ 151.8 (s, *t*-Ph), 127.9 (d, 158, Ph), 124.5 (br, Ph), 124.2 (d, 160, *p*-Ph), 105.2 (d, 174, Cp), 83.2 (s, carbonyl C), 28.7/28.9 (each q, 125, CH_3), 26.9 (d, 125, CH), 23.4 (t (br), 110, CH_2). ^{27}Al NMR (C_6D_6): δ 149.

Preparation of $Cp_2Zr[OCH(C_6H_4CH_3)_2](CHPPh_3)$ (25). A suspension of 1.05 g (2.43 mmol) (η^2-4,4′-dimethylbenzophenone)zirconocene (**3a**) (prepared analogously to **3**, see above) and 0.78 (2.80 mmol) of methylenetriphenylphosphorane in 50 mL of hexane was heated at 70 °C for 3 h. The reaction mixture was filtered, and the product **25** was obtained as a bright yellow solid by crystallization from the yellow filtrate at –25 °C (0.82 g, 48%; mp 130 °C dec). Anal. Calcd for $C_{44}H_{41}OPZr$: C, 74.64; H, 5.84. Found: C, 74.29; H, 5.76. ^{1}H NMR (C_6D_6): δ 5.87 (s, 10 H, Cp), 3.88 (d, $^2J_{HP}$ = 12 Hz, 1 H, CH=P), 2.15 (s, 3 H, CH_3), 5.95 (s, 1 H, –C*H*Ar_2), 7.09 and 7.45 (d, each 2 H tolyl-H), 7.73 and 7.09 (m, PPh_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 16.1. ^{13}C NMR (C_6D_6): δ 109.7 (d, $^1J_{CH}$ = 171 Hz, Cp), 72.2 (dd, $^1J_{CH}$ = 120 Hz, $^1J_{CP}$ = 36.4 Hz, CH=P), 21.2 (q, $^1J_{CH}$ = 126 Hz, CH_3), 86.3 (d, $^1J_{CH}$ = 139 Hz, *C*HAr_2); tolyl: δ 146.0 (s, OCH*C*), 135.6 (s, H_3C*C*), 128.9, 127.4 (d, $^1J_{CH}$ = 158.0 Hz, *o*-C, *m*-C); PPh_3, δ 136.7 (d, $^1J_{CP}$ = 79.3 Hz, C(quart)), 133.4 (dd, $^1J_{CH}$ = 162 Hz, $^2J_{CP}$ = 9.2 Hz, *o*-C), 128.3 (dd, $^3J_{CP}$ = 10.9 Hz, *m*-C), 130.4 (dd, $^1J_{CH}$ = 162 Hz, $^4J_{CP}$ = 2.1 Hz, *p*-C). MS: *m/e* 706 (M^+), 431 (M^+ – $CH{=}PPh_3$), 275 ($CH{=}PPh_3$), 195 ($CHTol_2$). IR (KBr): ν (cm^{-1}) 3050, 1435, 1020, 800 (Cp), 950 (PC).

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Supplementary Material Available: Tables of temperature factors, bond distances and angles for hydrogen atoms, pertinent least-squares planes, and observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.