J. Am. Chem. Soc. 1986, 108, 2251-2257

The Metallaoxirane-Type Structure of $Cp_2ZrCl(CPh_2OCH_3)$ and the Question of Modeling the Chemistry of Alkylidene Units on a Metal Oxide Surface

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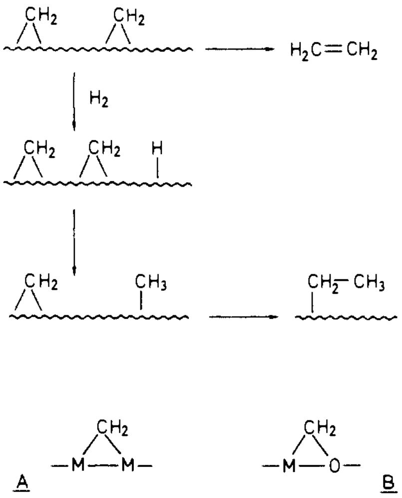
Abstract: The reaction of lithiated benzhydryl methyl ether with zirconocene dichloride yields $Cp_2ZrCl(CPh_2OCH_3)$ (**8**). The molecular structure of **8** in the crystal was determined by X-ray diffraction. **8** crystallizes in the space group $P2_12_12_1$ with cell constants $a = 7.593$ (2) Å, $b = 11.599$ (3) Å, $c = 22.933$ (6) Å, and $g_{calcd} = 1.49$ g cm^{-1} for $Z = 4$. The most remarkable structural feature of **8** is the strong intramolecular coordination of the ether oxygen to the zirconium center. The oxygen binds to the available central position in the bent metallocene σ-ligand plane. The resulting metallaoxirane structural subunit is characterized by bond distances 2.395 (6) Å (Zr–C), 2.215 (4) Å (Zr–O), and 1.450 (7) Å (O–C). Upon heating to 40 °C, **8** decomposes to give tetraphenylethylene and $Cp_2Zr(OCH_3)Cl$ as the major components. With zirconium hydrides $Cp_2Zr(H)Cl$ or Cp_2ZrH_2 **8** reacts by intra- and intermolecular insertion reactions of the CPh_2 group into the zirconium–hydrogen bond to give two pairs of compounds: $Cp_2Zr(OCH_3)Cl$ (**9**)/$Cp_2Zr(CHPh_2)Cl$ (**24**) and Cp_2ZrCl_2 (**6**)/$Cp_2Zr(CHPh_2)OCH_3$ (**25**). These reactions are strongly reminiscent of the chemistry of the CH_2 species on a Fischer–Tropsch catalyst surface. Metallaoxiranes as **8** might, therefore, be considered to serve as molecular models for Fischer–Tropsch type chemistry on metal oxide surfaces. This view is supported by the observation that the bridging metallaoxirane unit in (μ-formaldehyde)$(Cp_2ZrCl)_2$ (**1**) undergoes the same type of insertion reaction. Its CO-derived methylene unit is transferred to form $(Cp_2ZrCl)_2O$ (**29**) and $Cp_2Zr(CH_3)Cl$ (**22**) when treated with the oligomeric zirconocene (hydrido) chloride **3** at 55 °C.

Detailed experimental studies have substantially contributed to the understanding of the mechanistic path of the Fischer–Tropsch (FT) reaction in recent years.[2] From the outcome of model reactions[3] as well as ingenious investigations at active catalytic systems[4] the carbon–carbon bond forming step in the FT reaction sequence at present seems to be best described as a chemistry of methylene units on the catalyst surface.[5]

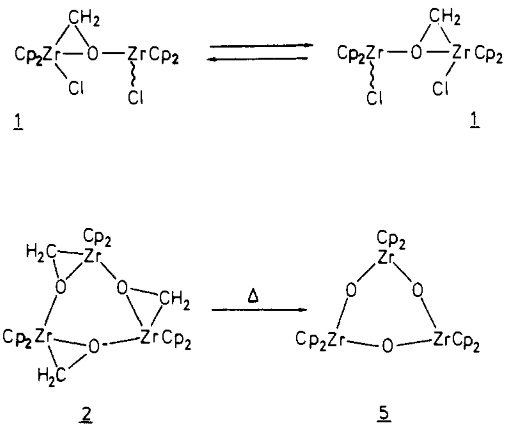
It has been suggested that surface CH_2 moieties, as formed from CO by reduction or introduced from methylene-releasing sources such as diazomethane, rapidly dimerize to give ethylene or (in the presence of hydrogen) insert into surface-H bonds to form a surface-bound methyl group. Further insertion of methylene into the surface–C(alkyl) linkage results in the growth of hydrocarbon chains as is typical for the Fischer–Tropsch synthesis (Scheme I).

Obviously, binuclear transition-metal μ-methylene complexes (A, Scheme I) should be good molecular models for many aspects of the chemistry of methylene groups on a *metal surface*. Accordingly, such complexes have been investigated in great detail in the past.[6] However, it is common knowledge that many oxygen-containing organic compounds rapidly release oxygen upon contact with the surface atoms of a large group of bulk transition metals under FT conditions to form metal oxides.[7] Therefore, it is at least questionable if the μ-methylene species A are indeed reminiscent of the chemistry of the active species in Fischer–Tropsch processes on metal catalysts derived from the elements belonging to this group of metals. To us it appeared more likely

Scheme I



Scheme II



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[2] For reviews see: (a) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79–172. Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103. Rofer-De Poorter, C. K. *Chem. Rev.* **1981**, *81*, 447–474. Herrmann, W. A. *Angew. Chem.* **1982**, *94*, 118–131. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103–109.

[3] See, e.g.: Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503–505. Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7–C10.

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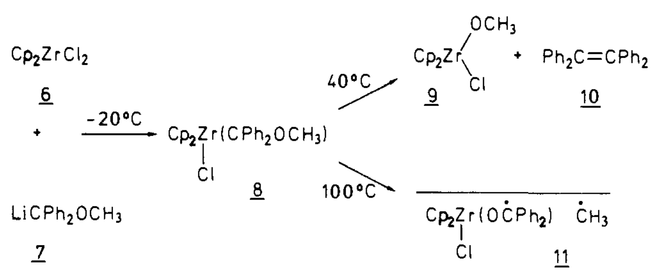
[7] Kugler, E. L.; Steffgen, F. W. *Adv. Chem. Ser.* **1979**, 178. Sung, S.-S.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 578–584 and references cited therein.

Scheme III



that in these cases complexes containing the three-membered metallaoxirane ring structural subunit B might be more suitable molecular models for FT catalysts derived from the oxygenophilic transition metals of the left side of the periodic table, describing the chemistry of methylene units on a *metal oxide surface*.[8]

There is a large number of d- and f-block organometallic compounds known containing M–C–O three-membered ring units.[9] Some of these complexes, among them many derived from the early transition metals, bear the potential of being suitable substrates for modeling single steps of CO-converting reaction sequences.[2b]

Among the many examples studied by us and others, the zirconaoxirane containing complexes **1** and **2** may serve as typical examples. The bridging formaldehyde units in both compounds are directly derived from carbon monoxide. **1** has been obtained by the reduction of the CO molecule by using the zirconium hydride $[Cp_2Zr(H)Cl]_x$ (**3**),[10] while **2** is prepared by the reaction of the oligomeric zirconocene dihydride $[Cp_2ZrH_2]_x$ (**4**) with CO.[11]

Both (formaldehyde)$ZrCp_2$ complexes exhibit rather unusual chemical features that might bear some similarity to the chemistry of the CH_2 unit on a real metal oxide surface. In solution, **1** undergoes an extremely rapid automerization process ($\Delta G^{\ddagger}_{-129°C}$ = 7 kcal/mol), a "dyotropic rearrangement",[12] in the course of which the CH_2 group migrates back and forth between the two metal centers on the Zr–O–Zr skeleton.[13] This process is in a way reminiscent of the rapid migration of methylene groups on a surface, a necessary prerequisite for CH_2 reactions to take place on a heterogeneous catalyst. On the other hand, the cyclotrimeric (formaldehyde)zirconocene complex **2** loses all three methylene units at elevated temperature to leave behind the intact $(-Cp_2Zr-O-)_3$ metal oxide framework.[11,14]

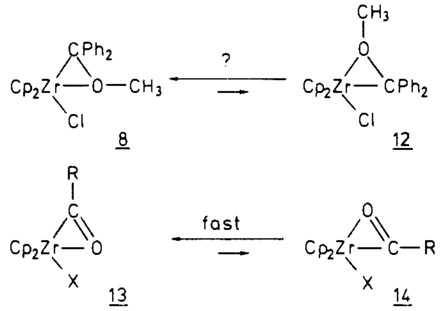
Table I. Molecular Structure of **8** in the Crystal

atoms	bond distance, Å	atoms	bond distance, Å
Zr–Cl	2.531 (2)	Zr–O	2.215 (4)
Zr–C(1)	2.395 (6)	Zr–Cp(1)	2.525 (7)
Zr–Cp(2)	2.543 (7)	Zr–Cp(3)	2.518 (7)
Zr–Cp(4)	2.557 (7)	Zr–Cp(5)	2.543 (7)
Zr–Cp(6)	2.595 (7)	Zr–Cp(7)	2.542 (6)
Zr–Cp(8)	2.520 (7)	Zr–Cp(9)	2.522 (7)
Zr–Cp(10)	2.551 (7)	Zr–Cnt(1)	2.244
Zr–Cnt(2)	2.256	Zr–Ave(1)	2.54 (1)
Zr–Ave(2)	2.55 (3)	O–C(1)	1.450 (7)
O–C(14)	1.450 (7)	C(1)–C(2)	1.510 (9)
C(1)–C(8)	1.483 (9)		

Table II. Molecular Structure of **8** in the Crystal

atoms	bond angle, deg	atoms	bond angle, deg
Cl–Zr–O	78.8(1)	Cl–Zr–C (1)	108.6 (2)
O–Zr–C(1)	36.4 (2)		
Cl–Zr–Cnt(1)	102.955	O–Zr–Cnt(1)	133.318
C(1)–Zr–Cnt(1)	105.125	Cl–Zr–Cnt(2)	106.432
O–Zr–Cnt(2)	99.013	C(1)–Zr–Cnt(2)	109.075
Cnt(1)–Zr–Cnt(2)	123.838	Zr–O–C(1)	78.6 (3)
Zr–O–C(14)	151.6 (4)	C(1)–O–C(14)	125.4 (5)
Zr–C(1)–O	65.0 (3)	Zr–C(1)–C(2)	121.8 (4)
O–C(1)–C(2)	109.3 (5)	Zr–C(1)–C(8)	118.9 (4)
O–C(1)–C(8)	113.1 (5)	C(2)–C(1)–C(8)	115.9 (5)

Scheme IV



In this respect, the observed decomposition pathways of α-metallated ethers like the 1:1 reaction product **8** of Cp_2ZrCl_2 (**6**) with $LiCPh_2OCH_3$ (**7**) should be of substantial interest. We had noticed previously that **8** underwent a thermally induced O–C bond homolysis at surprisingly low temperature. Even more remarkable was the observed competing reaction sequence yielding the "decomposition products" methoxyzirconocene chloride (**9**) and tetraphenylethylene (**10**).[15] The latter reaction represented by far the major reaction pathway at low temperature.[16]

We have now been able to determine the structure of the zirconium-substituted benzhydryl methyl ether **8** in the crystal by X-ray diffraction. The surprising outcome of this analysis stimulated several additional chemical studies. These are reported below and discussed in view of their relevance regarding the above-mentioned search for molecular models reflecting the chemistry of alkylidene units on a metal oxide surface.[17]

X-ray Crystal Structure Analysis of 8

$Cp_2ZrCl(CPh_2OCH_3)$ **8** was prepared by reacting zirconocene dichloride with 1 equiv of lithiated benzhydryl methyl ether (**7**) as described previously.[15] Recrystallization of the crude reaction product from refluxing benzene upon slowly cooling to ambient temperature yielded bright yellow colored crystals suitable for a

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[17] For different types and purposes of models for metal oxide surfaces see: Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1234–1241 and references cited therein.

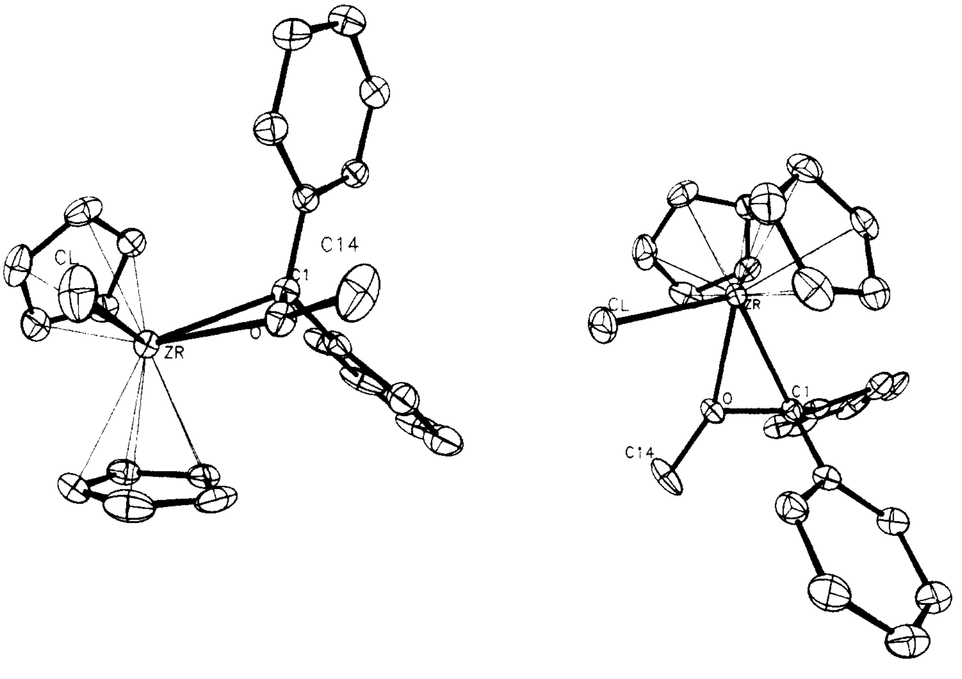
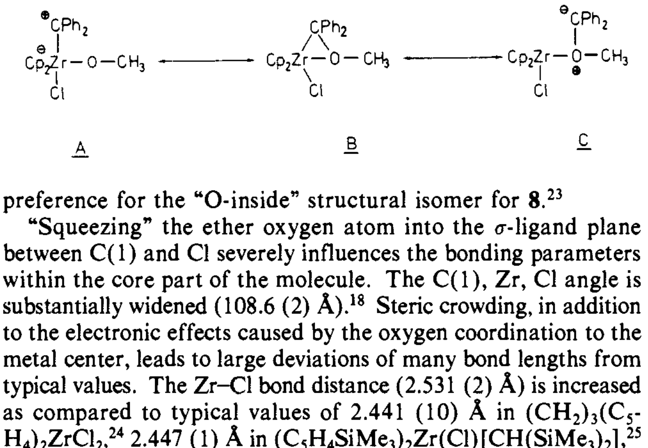


Figure 1. Two different views of the molecular structure of **8** and the numbering scheme for the core atoms.

structure determination by X-ray diffraction. **8** crystallizes in the space group $P2_12_12_1$. Two different views of the molecular structure of **8** in the crystal are given in Figure 1. Also given is the numbering scheme of the core atoms of this organometallic compound. The bent metallocene unit in **8** does not deviate much from typical values, as is exemplified by average Zr–C(Cp) bond distances of 2.55 (3) and 2.54 (1) Å, respectively.[18] The bonding features of the phenyl substituents connected to C(1) are as usually found (see Table I for details).

However, the arrangement of the C(1), O, and Cl atoms (and consequently C(14)) around the zirconium center makes **8** an unusual organometallic compound. The striking feature of the molecular structure of this zirconium-substituted benzhydryl ether is that the ether-oxygen is strongly coordinated to the early transition metal.[19] This leads to an arrangement of ligands where both the ether oxygen (O connected to C(14)) and the α-carbon atom C(1) together with the Cl ligand occupy the sector in the Cp, Zr, Cp bisecting plane that is available for bonding in a bent metallocene complex.[18a] In this ligand plane two orientations of the Zr, O, C(1) three-membered ring structural subunit relative to the Cl atom should represent local minima on the energy surface. The ether oxygen can either occupy a central place between C(1) and Cl ("O-inside") or alternatively be found in the lateral ("O-outside") position. This situation is reminiscent of the geometrical isomerism found for (η^2-acyl)metallocene complexes (see Scheme IV).[20] For the respective (η^2-acetyl)- or (η^2-benzoyl)zirconocene complexes a pronounced thermodynamic preference on the "O-inside"-type structure has clearly been observed experimentally[21] and rationalized on a theoretical basis.[22] In view of these results it is not too surprising to find an analogous preference for the "O-inside" structural isomer for **8**.[23]

Scheme V



"Squeezing" the ether oxygen atom into the σ-ligand plane between C(1) and Cl severely influences the bonding parameters within the core part of the molecule. The C(1), Zr, Cl angle is substantially widened (108.6 (2) Å).[18] Steric crowding, in addition to the electronic effects caused by the oxygen coordination to the metal center, leads to large deviations of many bond lengths from typical values. The Zr–Cl bond distance (2.531 (2) Å) is increased as compared to typical values of 2.441 (10) Å in $(CH_2)_3(C_5H_4)_2ZrCl_2$,[24] 2.447 (1) Å in $(C_5H_4SiMe_3)_2Zr(Cl)[CH(SiMe_3)_2]$,[25] or 2.452 (2) Å in $(C_5H_4CMe_3)_2Zr(Cl)[CH(SiMe_3)_2]$.[26] The value observed for **8** almost approaches the range typically found for bridging μ-Zr-Cl situations as exemplified by the Zr–Cl bond distances of 2.538 (2) and 2.629 (2) Å in $Cp_2Zr(\mu\text{-}CH{=}CHPh)(\mu\text{-}Cl)ZrCp_2$.[26]

The Zr, O, C(1) three-membered ring is the most important structural subunit in **8**. Partitioning bonding electrons between three different groups causes an increase in bond distances around the ether oxygen. This is true for the O–C(14) linkage (1.450 (7) Å as compared to typical values around 1.41 Å observed for simple alphatic ethers)[27] but also for the C–O (1.450 (7) Å) and Zr–O bond (2.215 (4) Å) within the three-membered metallacycle. The latter two values should be compared with the carbon–oxygen and zirconium–oxygen bond lengths found in typical zirconaoxirane structural subunits (e.g., 1.338 (2), 2.126 (1) Å in $(CH_2{=}C{=}O)ZrCp_2(pyridine)$[28] (**15**); 1.339 (9), 2.181 (5) Å in

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(19) This seems also to be true for the related α-zirconated dimethyl thioethers: Gregory, A. R.; Lindeman, J. A.; Mintz, E. A.; Tangvald, T.; Ward, A. S. XI International Conference on Organometallic Chemistry, Calloway Gardens, Oct. 1983, Abstract 60.

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(22) Hofmann, P.; Stauffert, P.; Tatsumi, K.; Nakamura, A.; Hoffmann, R. *Organometallics* **1985**, *4*, 404–406. Hofmann, P.; Tatsumi, K.; Hoffmann, R., personal communication to G.E.

(23) In contrast, there is evidence that "O-outside" and "O-inside" η^2-acyl isomers may be of a similar energy content for bent-metallocene complexes of an actinide element: Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206–2220.

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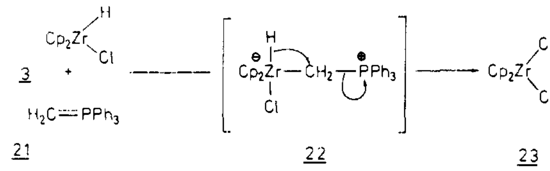
Scheme VI



the ($CH_2{=}C{=}O$)Zr(CH_3)Cp_2 anion[29] (**16**); 1.406 (7), 2.181 (4) Å in an $AlMe_3{\cdot}2(C_5H_{11})CH{=}C{=}OZrCp_2$ adduct[30] (**17**); 1.371 (4), 2.164 (2) Å in dimeric ($Ph_2C{=}C{=}O$)$ZrCp_2$[31] (**18**); 1.412 (4), 2.124 (1) Å in the ($CH_3CH{=}O$)$ZrCp_2/Cp_2ZrH_2$ 1:1 adduct[13b] (**19**); 1.422 (4), 2.111 (2) Å in dimeric ($Ph_2C{=}O$)$ZrCp_2$[32] (**20**); 1.43 (2),2.13 (1) Å in ($CH_2{=}O$)(Cp_2ZrCl)$_2$[10] (**1**); and 1.427 (13), 2.135 (5) Å in [($CH_2{=}O$)$ZrCp_2$]$_3$[11] (**2**)).

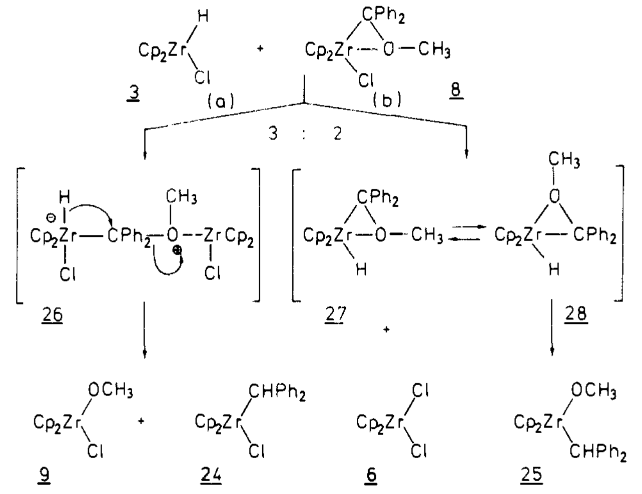
In view of the structural features of the above-mentioned compounds the Zr–C(1) bond length (2.395 (6) Å) in **8** is most remarkable as it appears to mark the longest Zr–C σ-bond so far observed for a zirconaoxirane-type ring system (to be compared with **15**, 2.181 (2) Å; **17**, 2.185 (6) Å; **1**, 2.19 (1) Å; **16**, 2.196 (8) Å; **18**, 2.204 (3) Å; **2**, 2.275 (10) Å; **19**, 2.277 (3) Å; and **20**, 2.348 (3) Å).

The long Zr–C(1) bond and the somewhat lengthened C(1)–O linkage make it tempting to describe the zirconium complex **8** as an adduct of diphenylcarbene to methoxyzirconocene chloride, the latter acting as an alkylidene-accepting organometallic π-system.[34] In terms of the resonance structures which can be written for such an adduct a situation between the extremes B (metallaoxirane-type[9]) and C (oxoniumylide-type,[35] see Scheme V) seems to represent the bonding features best, as they appear from the X-ray analysis. The special bonding situation should manifest itself in the chemical reactivity of **8**. This has been investigated. Several typical experiments and their results are described below.

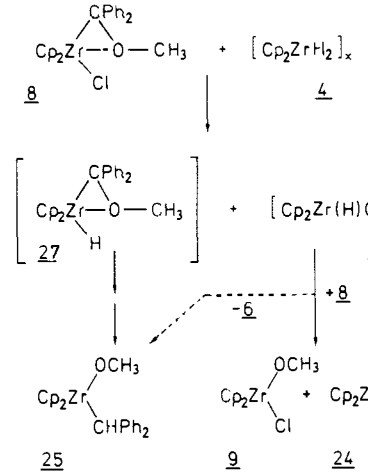
Chemical Studies

There has been evidence that ylides react with electron-deficient 16-electron zirconocene hydrides by a formal alkylidene insertion into the zirconium–hydrogen bond.[36] We have shown that, e.g., methylene triphenylphosphorane (**21**) reacts with the oligomeric (hydride)zirconocene chloride (**3**) to yield methylzirconocene chloride (**23**) plus triphenylphosphine.[37] The methylene insertion is probably occuring stepwise via an intermediate **22** (see Scheme VI). The oxonium ylide character of $\overline{Cp_2Zr(Cl)\text{-}CPh_2O}\text{-}CH_3$ (**8**) could principally manifest itself in a similar reactivity, i.e., the reaction of **8** with electron-deficient zirconocene hydrides could proceed by an "insertion" of the diphenylcarbene moiety into the metal–hydrogen bond of the added substrate. Such reaction type was indeed observed.

Scheme VII



Scheme VIII



The reaction of **8** with [$Cp_2Zr(H)Cl$]$_n$ (**3**) at 50 °C produces four different products: methoxyzirconocene chloride (**9**), benzhydrylzirconocene chloride (**24**), zirconocene dichloride (**6**), and benzhydrylzirconocene methoxyde (**25**) (Scheme VII). The identity of these compounds was established unequivocally by a comparison with authentic material. For this purpose we carried out independent syntheses of the complexes **9**, **24**, and **25**. Methoxyzirconocene chloride was obtained from the reaction of [$Cp_2Zr(H)Cl$]$_x$ with methanol at low temperature. Treatment of benzhydryllithium (generated in situ from diphenylmethane and *n*-butyllithium) with 1 equiv of zirconocene dichloride yielded **24**. Finally, **25** was obtained by reacting **9** with Ph_2CHLi.

The four organometallic reaction products are not formed in equimolar amounts but in an approximate ratio of **9**:**24**:**6**:**25** = 3:3:2:2. This specific product ratio points to a mechanistic scheme for the reaction of **8** and **3** characterized by two competing reaction paths giving a pair of products each (**9**/**24** and **6**/**25**, respectively, see Scheme VII). The two competing reaction sequences a/b take place at a 3:2 ratio.

The observed major reaction path a constitutes the expected oxonium ylide type reactivity[35] of **8** toward the zirconium hydride

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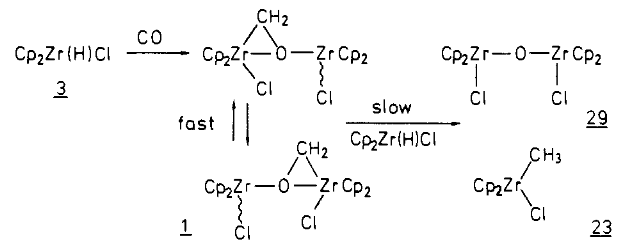
Scheme IX



reagent. Analogous to the reaction of the phosphorous ylide **21** (as outlined in Scheme VI) the CPh_2 carbon center of **8** appears to attack the electron deficient metal center of **3** to form the 1:1 adduct **26**. This, in turn, can readily be stabilized by a 1,2-hydride shift and displacement of the leaving group $Cp_2Zr(OCH_3)Cl$ (**9**). Along this pathway, the CPh_2-insertion product $Cp_2Zr(CHPh_2)Cl$ (**24**) and the diphenylcarbene matrix **9** are formed in an equimolar ratio.

The competing reaction b seems to be initiated by another typical early transition metal hydride reaction sequence, i.e., halide vs. hydride exchange, here leading to Cp_2ZrCl_2 (**6**) and a metallaoxirane-containing zirconocene hydride **27**.[26] In contrast to **27**, its geometrical isomer **28**[21,22] has the possibility undergoing an *intramolecular* version of the $CPh_2/Zr-H$ insertion reaction observed along path a. The final product of reaction b in this sequence is $Cp_2Zr(CHPh_2)OCH_3$ (**25**) which is formed together with Cp_2ZrCl_2 in a 1:1 ratio.

A similar reaction was observed upon treatment of **8** with the oligomeric zirconocene dihydride **4**. The complexes **9**, **24**, and **25** were clearly identified as the major products obtained. Although the reaction of **8** with $(Cp_2ZrH_2)_x$ (**4**) was less clean, a product ratio being considerably different from the one obtained from $[Cp_2Zr(H)Cl]_x$ (**3**, see above) could clearly be established. The reaction of $Cp_2ZrCl(CPh_2OCH_3)$ with zirconocene dihydride produced considerably larger amounts of $Cp_2Zr(CHPh_2)OCH_3$. **9**, **24**, and **25** were obtained in relative ratios which differed not very much from unity.

This observation can readily be explained by a reaction scheme starting with Zr–H/Zr–Cl metathetical exchange (Scheme VIII) to produce (hydrido)zirconocene chloride and the reactive intermediate **27**. The latter rearranges to give the major reaction product $Cp_2Zr(CHPh_2)OCH_3$ (**25**) (as described above); the former could react further with the starting material $Cp_2ZrCl(CPh_2OCH_3)$ (**8**) according to Scheme VII to produce as main reaction products of this secondary reaction sequence the complexes $Cp_2Zr(OCH_3)Cl$ (**9**) and $Cp_2Zr(CHPh_2)Cl$ (**24**).

It remained to be tested whether the observed alkylidene-insertion reactions into the zirconium–hydrogen linkage were specific to the substrate used, i.e., the $Cp_2ZrCl(CPh_2OCH_3)$ complex **8**, or if this insertion might represent a more general reaction type, typical for zirconium complexes possessing a metallaoxirane structural subunit. We therefore exposed the binuclear (μ-formaldehyde)$(ZrCp_2Cl)_2$ complex **1** to a zirconium hydride. **1** can directly be prepared from carbon monoxide.[10] Carbonylation of $Cp_2Zr(H)Cl$ yields the dynamic $Cp_2ZrCl(CH_2O)ZrCp_2Cl$, rapidly undergoing a thermally induced degenerate intramolecular methylene group migration at ambient temperature.[13] Upon treatment with a suspension of the oligomeric (hydrido)zirconocene chloride (**3**) at elevated temperature, **1** was slowly consumed (14 h 55 °C). The newly appearing products $(Cp_2ZrCl)_2O$ (**29**) and methylzirconocene chloride (**23**) were positively identified by comparison with authentic material.[38] **29** and **23** were formed in an equimolar ratio. $Cp_2Zr(CH_3)Cl$ (**23**) is the product of insertion of a CH_2 group into the Zr–H bond of the zirconium hydride reagent. This methylene unit, whose carbon atom originates from the carbon monoxide used to prepare **1**, apparently was slowly transferred from the binuclear (μ-formaldehyde)zirconium complex to leave behind the metal oxide framework in **29**.

Table III. Crystal Data for **8**

compd	$C_{24}H_{23}ClOZr$
mol wt	454.09
space group	$P2_12_12_1$
cell constants	
a, Å	7.593 (2)
b, Å	11.599 (3)
c, Å	22.933 (6)
cell vol, Å^3	2019.6
molecules/unit cell	4
ρ(calcd), g cm^{-3}	1.49
μ(calcd), cm^{-1}	6.79
radiation	Mo Kα
max cryst dimens, mm	0.31 × 0.20 × 0.15
scan width, deg	$0.8 + 0.2 \tan \theta$
std reflectns	200, 020, 002
decay of stds	2%
reflctns measd	2158
2θ range	1–25
obsd reflctns	1635
no. of parameters varied	244
GOF	1.29
R	0.026
R_w	0.033

Table IV. X-ray Crystal Structure Analysis of **8**: Positional Parameters of the Non-Hydrogen Atoms

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eqv)
Zr	−0.17270 (8)	−0.03893 (5)	−0.08304 (2)	0.031
Cl	−0.4574 (3)	−0.1324 (2)	−0.0505 (1)	0.062
O	−0.3653 (5)	0.0992 (3)	−0.1026 (2)	0.039
C(1)	−0.2410 (8)	0.1130 (5)	−0.1501 (3)	0.035
C(2)	−0.333 (1)	0.0899 (5)	−0.2072 (3)	0.037
C(3)	−0.2951 (9)	0.1533 (6)	−0.2581 (3)	0.044
C(4)	−0.385 (1)	0.1332 (7)	−0.3093 (3)	0.052
C(5)	−0.513 (1)	0.0493 (8)	−0.3122 (3)	0.058
C(6)	−0.5513 (9)	−0.0153 (6)	−0.2632 (3)	0.054
C(7)	−0.4642 (9)	0.0041 (6)	−0.2117 (3)	0.045
C(8)	−0.140 (1)	0.222 (6)	−0.1467 (3)	0.044
C(9)	0.020 (1)	0.2300 (8)	−0.1761 (3)	0.061
C(10)	0.118 (1)	0.333 (1)	−0.1747 (4)	0.085
C(11)	0.055 (2)	0.427 (1)	−0.1431 (4)	0.093
C(12)	−0.097 (1)	0.4184 (7)	−0.1133 (4)	0.080
C(13)	−0.196 (1)	0.3184 (6)	−0.1150 (3)	0.056
C(14)	−0.5420 (9)	0.1466 (7)	−0.1010 (4)	0.069
Cp(1)	−0.182 (1)	−0.1925 (7)	−0.1610 (4)	0.061
Cp(2)	−0.054 (1)	−0.1160 (7)	−0.1791 (3)	0.052
Cp(3)	0.083 (1)	−0.1212 (7)	−0.1392 (3)	0.051
Cp(4)	0.043 (1)	−0.2059 (6)	−0.0971 (3)	0.059
Cp(5)	−0.121 (1)	−0.2487 (6)	−0.1105 (4)	0.065
Cp(6)	−0.145 (1)	0.1177 (7)	−0.0028 (3)	0.065
Cp(7)	−0.175 (1)	0.0134 (8)	0.0246 (3)	0.069
Cp(8)	−0.030 (1)	−0.0573 (7)	0.0158 (3)	0.059
Cp(9)	0.0888 (9)	0.0029 (6)	−0.0186 (3)	0.050
Cp(10)	0.017 (1)	0.1110 (7)	−0.0312 (3)	0.051

Conclusions

Structure and chemistry of $Cp_2ZrCl(CPh_2OCH_3)$ (**8**) are characterized by the intramolecular coordination of the ether oxygen to the zirconium center. This results in the formation of a remarkable metallaoxirane structural unit, the metal center formally adopts an 18-electron configuration.

We think there are some remarkable similarities between the chemistry of the CPh_2 group of **8**, bound to the $Cp_2Zr-OCH_3$ matrix, with reactions of alkylidenes on a catalyst surface in Fischer–Tropsch type processes. Like surface-bound CH_2 in Pettit's experiment[4] forming $H_2C{=}CH_2$ in the absence of hydrogen, CPh_2 is expelled from **8** upon heating to yield $Ph_2C{=}CPh_2$ (and $Cp_2Zr(OCH_3)Cl$). Surface-bound CH_2 reacts with H_2 (probably via a surface hydride) to form CH_3 groups, which then initiate the hydrocarbon chain growth at the heterogeneous catalyst, whereas the diphenylcarbene moiety undergoes the same type of metal–hydrogen insertion on a molecular level (intra- as

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Table V. X-ray Crystal Structure Analysis of **8**: Thermal Parameters of the Non-Hydrogen Atoms

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	0.0284 (2)	0.0313 (2)	0.0343 (2)	0.0003 (3)	0.0049 (3)	−0.0005 (3)
Cl	0.042 (1)	0.056 (1)	0.090 (1)	−0.008 (1)	0.016 (1)	0.023 (1)
O	0.026 (2)	0.038 (2)	0.053 (3)	0.001 (2)	0.004 (2)	−0.000 (2)
C(1)	0.029 (3)	0.035 (3)	0.041 (4)	−0.006 (3)	0.004 (3)	0.001 (3)
C(2)	0.032 (3)	0.036 (3)	0.044 (3)	0.004 (4)	−0.004 (3)	0.001 (3)
C(3)	0.041 (4)	0.040 (4)	0.053 (4)	−0.002 (3)	−0.007 (3)	0.005 (3)
C(4)	0.055 (5)	0.053 (4)	0.051 (4)	0.005 (4)	−0.008 (4)	0.006 (4)
C(5)	0.055 (5)	0.068 (5)	0.053 (4)	0.001 (5)	−0.020 (4)	−0.002 (4)
C(6)	0.042 (4)	0.057 (5)	0.063 (5)	−0.009 (4)	−0.012 (4)	−0.004 (4)
C(7)	0.037 (4)	0.048 (4)	0.053 (4)	−0.004 (3)	−0.012 (3)	0.002 (3)
C(8)	0.045 (5)	0.041 (4)	0.048 (4)	−0.013 (4)	−0.018 (4)	0.017 (3)
C(9)	0.048 (5)	0.090 (6)	0.045 (4)	−0.034 (5)	−0.013 (4)	0.021 (4)
C(10)	0.063 (6)	0.15 (1)	0.045 (5)	−0.057 (7)	−0.019 (4)	0.041 (6)
C(11)	0.12 (1)	0.100 (9)	0.059 (6)	−0.072 (8)	−0.048 (6)	0.037 (6)
C(12)	0.125 (9)	0.045 (5)	0.071 (6)	−0.026 (5)	−0.043 (6)	0.012 (4)
C(13)	0.066 (6)	0.037 (4)	0.065 (5)	−0.010 (4)	−0.018 (5)	0.007 (3)
C(14)	0.028 (3)	0.056 (5)	0.124 (8)	0.010 (4)	0.018 (4)	−0.017 (5)
Cp(1)	0.054 (5)	0.056 (5)	0.075 (5)	0.002 (5)	−0.002 (5)	−0.033 (4)
Cp(2)	0.063 (5)	0.051 (4)	0.043 (4)	0.015 (4)	0.003 (4)	−0.012 (4)
Cp(3)	0.041 (4)	0.059 (5)	0.055 (5)	0.011 (4)	0.009 (4)	−0.018 (4)
Cp(4)	0.064 (5)	0.052 (5)	0.064 (6)	0.028 (4)	0.003 (4)	−0.005 (4)
Cp(5)	0.082 (7)	0.034 (4)	0.080 (6)	0.004 (4)	0.026 (5)	−0.001 (4)
Cp(6)	0.063 (6)	0.075 (6)	0.058 (5)	0.023 (5)	−0.023 (5)	−0.040 (4)
Cp(7)	0.067 (5)	0.106 (7)	0.037 (4)	−0.010 (7)	0.011 (4)	−0.013 (4)
Cp(8)	0.086 (6)	0.059 (5)	0.034 (4)	0.004 (5)	−0.012 (4)	0.006 (4)
Cp(9)	0.041 (4)	0.069 (5)	0.041 (4)	0.003 (4)	−0.008 (3)	−0.007 (3)
Cp(10)	0.059 (5)	0.056 (5)	0.039 (4)	−0.008 (4)	−0.015 (4)	−0.007 (3)

well as intermolecularly) when **8** is exposed to a zirconium hydride.

Unfortunately, one of the many limitations of **8** serving as a molecular model in Fischer–Tropsch type chemistry is that subsequent CC-forming steps could not be observed so far under the conditions applied. However, the fact that the same type of insertion reaction as found for **8** was observed starting from the (μ-formaldehyde)zirconocene complex **1** (which is a direct reduction product of the carbon monoxide molecule) indicates that studying the rapidly increasing number of d- and f-block element metallaoxiranes might help to answer some of the many open questions in Fischer–Tropsch type chemistry.

Experimental Section

All reactions were conducted under argon with use of standard Schlenk techniques. Solvents were dried and freshly distilled from $LiAlH_4$ under argon before use. Deuterated benzene was treated overnight with Na/K alloy, distilled in vacuo, and stored under argon. Deuterated methylene chloride was stirred for an hour with P_4O_{10} (Siccapent, Fa, Merck), distilled in vacuo, and stored under argon. NMR spectra were recorded on Bruker WP 80 (^1H), Bruker WM 300 (^{13}C: 75.5 MHz), and Bruker WH 400 (^1H) spectrometers. Chemical shifts are given in ppm relative to Me_4Si. Mass spectra were obtained on a Finnegan 311 A mass spectrometer (70 eV). IR spectra were recorded on a Nicolet 7199 FT-IR spectrometer. Microanalyses were performed by Dornis & Kolbe Mikroanalytisches Laboratorium, Mülheim/Ruhr. Lithium aluminum hydride, *n*-butyllithium (solution in hexane, 1.6 M), diphenylmethane, and methanol (anhydrous) were obtained from commercial sources. Cp_2ZrCl_2, μ-O-$(Cp_2ZrCl)_2$, $[Cp_2Zr(Cl)H]_x$, $(Cp_2ZrH_2)_x$, and $Cp_2Zr(Cl)CH_3$ were prepared by standard procedures.[38] μ-$(CH_2{=}O)$-$(Cp_2ZrCl)_2$ was synthesized according to the literature.[10] $Cp_2Zr(Cl)CPh_2OCH_3$ had previously been prepared and characterized by Dr. F. Rosenfeldt.[15]

Crystallization of $Cp_2Zr(Cl)CPh_2OCH_3$ (8). Raw material of **8** (5.1 g, contaminated with, e.g., Cp_2ZrCl_2) was dissolved in 50 mL of refluxing benzene. The hot solution was allowed slowly to cool to room temperature. Overnight, crystallization of several yellow needles took place. After the mother liquor was removed and short drying in vacuo 2.4 g (5.3 mmol) of pure product could be isolated as robust yellow needles. ^1H NMR (C_6D_6) δ 7.12, 6.96 (m, 10 H, Ph), 5.57 (s, 10 H, Cp), 3.65 (s, 3 H, CH_3).

X-ray Data Collection and Structure Determination for 8. Crystals of **8** obtained from benzene as described above proved suitable for an X-ray crystal structure determination. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $(\sin\theta/\lambda)^2$ values for 15 reflections ($2\theta > 40°$) accurately centered on the diffractometer are given in Table III. The space group was uniquely determined as $P2_12_12_1$ from systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. The method has been previously described.[39] A summary of the data collection parameters is given in Table III. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[40] Neutral atom scattering factors for non-hydrogen atoms were taken from Cromer and Waber,[41] and the scattering for zirconium was corrected for real and imaginary components of anomalous dispersion with use of the table of Cromer and Liberman.[42] Scattering factors for H were from ref 43.

The position of the zirconium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the zirconium atom readily revealed the positions of the non-hydrogen atoms. Hydrogen atoms on the cyclopentadienyl and phenyl groups were placed in calculated positions, while those on the methyl carbon atom were located on a difference map. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.026$ and $R_w = 0.033$. A final difference Fourier showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table IV.

Preparation of Methoxyzirconocene Chloride (9). $[Cp_2Zr(H)Cl]_x$ (**3**) (7.4 g, 28.7 mmol) suspended in 200 mL of toluene was cooled down to −90 °C and treated with 1.15 mL (28.4 mmol) of anhydrous methanol in one portion. The stirred mixture was allowed to warm to room temperature overnight. The resulting colorless solution was filtered from a small amount of unreacted educt and stripped. Product (7.5 g, 91%) was obtained as a white powder which is pure enough for most purposes. Anal. Calcd for $C_{11}H_{13}OClZr$: C, 45.89; H, 4.51. Found: C, 46.25; H, 4.30. ^1H NMR (C_6D_6) δ 5.92 (s, 10 H, Cp), 3.65 (s, 3 H, CH_3). A crystalline sample of **9** was obtained by recrystallization of this material from toluene/pentane (1:1) at −30 °C.

Preparation of Benzhydrylzirconocene Chloride (24).[44] A solution of 2.7 g (16 mmol) diphenylmethane in 100 mL of tetrahydrofuran was slowly treated at room temperature with 10 mL of a 1.6 M solution of *n*-butyllithium in hexane. After the mixture was stirred 2 h, the resulting red solution was transferred slowly into a stirred solution of 5.0 g (17

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[41] Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104–109.

[42] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

[43] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

[44] The synthetic pathway follows the known preparation of $Cp_2Zr(CHPh_2)_2$, see ref 33c.

mmol) of zirconocene dichloride in 100 mL of tetrahydrofurane. After being stirred overnight the red solution was stripped. The resulting orange residue was extracted twice with 150 mL of pentane. The combined extracts were cooled to −15 °C. The obtained first crystal fraction was very impure. Subsequent crystallization of the same solution at −15 °C resulted in small orange crystals of **24**. Concentration of the mother liquor to about 200 mL followed by crystallization at −30 °C yielded another orange crystal portion of **24**. After the combined fractions of **24** were dried in vacuo, 2.9 g (43%) of product remained. Anal. Calcd for $C_{23}H_{21}ClZr$: C, 65.15; H, 4.96. Found: C, 65.79; H, 5.28. ^1H NMR (C_6D_6) δ 6.7–7.2 (m, 10 H, Ph), 5.62 (s, 10 H, Cp), 3.35 (s, 1 H, C*H*Ph$_2$). ^{13}C NMR (CD_2Cl_2) δ 150.5 (s, q-Ph), 128.6, 128.7 (d each, 158, *o*- and *m*-Ph), 123.5 (d, 162, *p*-Ph), 114.6 (d, 175, Cp), 80.1 (d, 116, *C*HPh$_2$). IR (KBr) ν (cm^{-1}) 2810 (CPh_2–H). MS *m/e* 422 (M^+).

Preparation of Benzhydrylzirconocene Methoxide (25). A solution of 0.65 g (3.9 mmol) of diphenylmethane in 50 mL of tetrahydrofurane was slowly treated at room temperature with 2.4 mL (3.9 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. After the mixture was stirred for 1 h the resulting red solution was transferred slowly into a stirred solution of 1.05 g (3.65 mmol) of methoxyzirconocene chloride in 30 mL of tetrahydrofurane. After the mixture was stirred for an additional 2 h the orange solution was stripped. The resulting yellow residue was extracted with 100 mL of pentane. The pentane solution was filtered over a G4-frit and stripped. The resulting yellow oil consisted of a mixture of **25** and diphenylmethane. Because of similar solubilities no further purification took place upon attempted recrystallization. ^1H NMR (C_6D_6) δ 6.9–7.2 (m, 10 H, Ph), 5.56 (s, 10 H, Cp), 3.80 (s, 1 H, C*H*Ph$_2$), 3.65 (s, 3 H, CH_3). ^{13}C NMR (C_6D_6) δ 152.0 (s, q-Ph), 128.3 (d, 155, *m*-Ph), 128.2 (d, 156, *o*-Ph), 122.6 (d, 158, *p*-Ph), 112.1 (d, 172, Cp), 67.6 (d, 118, *C*HPh$_2$), 61.8 (q, 140, OCH_3).

Reaction of $Cp_2Zr(Cl)CPh_2OCH_3$ (8) with $[Cp_2Zr(H)Cl]_x$ (3). $[Cp_2Zr(H)Cl]_x$ (**3**) (15 mg, 0.06 mmol) was placed in a 5-mm NMR tube and suspended with a solution of 25 mg (0.06 mmol) of $Cp_2Zr(Cl)CPh_2OCH_3$ (**8**) in 0.5 mL of deuterated benzene. The NMR tube was sealed and heated at 55 °C with constant agitation for 7 h. The progress of the reaction was controlled by ^1H NMR. The products were identified by comparison of their ^1H NMR signals with those of authentic samples. A mixture of the products zirconocene dichloride (**6**) (20%), methoxyzirconocene chloride (**9**) (30%), benzhydrylzirconocene chloride (**24**) (30%), and benzhydrylzirconocene methoxide (**25**) (20%) was obtained after 7 h. ^1H NMR (C_6D_6) δ 5.89 (**6**), 5.92/3.65 (**9**), 6.9–7.2/5.62/3.35 (**24**), 6.9–7.2/5.56/3.80/3.65 (**25**).

Reaction of $Cp_2Zr(Cl)CPh_2OCH_3$ (8) with $(Cp_2ZrH_2)_x$ (4). $(Cp_2ZrH_2)_x$ (**4**) (15 mg, 0.07 mmol) was placed in a 5-mm NMR tube and suspended with a solution of 25 mg (0.06 mmol) of $Cp_2Zr(Cl)CPh_2OCH_3$ (**8**) in 0.5 mL of deuterated benzene. The NMR tube was sealed and thermolyzed at 55 °C with constant agitation for 2 h. The analysis was carried out as described above for the analogous reaction between **8** and **3**. Eventually, a mixture of zirconocene dichloride (**6**) (5%), methoxyzirconocene chloride (**9**) (30%), benzhydrylzirconocene chloride (**24**) (30%), and benzhydrylzirconocene methoxide (**25**) (30%) was obtained besides several unidentified products (5%).

Reaction of μ-(CH_2=O)(Cp_2ZrCl)$_2$ (1) with $[Cp_2Zr(H)Cl]_x$ (3). $[Cp_2Zr(H)Cl]_x$ (**3**) (15 mg, 0.06 mmol) was placed in a 5-mm NMR tube and suspended with a solution of 30 mg (0.06 mmol) of **1** in 0.5 mL of deuterated benzene. The NMR tube was sealed and thermolyzed at 55 °C for 14 h as described above. A clean mixture of μ-O-(Cp_2ZrCl)$_2$ (**29**) (50%) and $Cp_2Zr(Cl)CH_3$ (**23**) (50%) was obtained. ^1H NMR (C_6D_6) δ 6.02 (s, 20 H, Cp, **29**), 5.76 (s, 10 H, Cp, **23**), 0.42 (s, 3 H, CH_3, **23**).

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie (grant to G.E.) and by a NATO Research Grant (No. 0425/83; J.L.A. and G.E.). J.L.A. is indepted to the National Science Foundation for support of this work.

Registry No. **1**, 83385-36-8; **3**, 86953-31-3; **4**, 85442-81-5; **8**, 100909-17-9; **9**, 11087-26-6; **23**, 1291-45-8; **24**, 85959-82-6; **25**, 100909-18-0; **29**, 12097-04-0; diphenylmethane, 101-81-5; zirconocene dichloride, 1291-32-3.

Supplementary Material Available: Tables of bond distances, angles, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Kinetic and Thermodynamic Acidity of Hydrido Transition-Metal Complexes. 3. Thermodynamic Acidity of Common Mononuclear Carbonyl Hydrides

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Abstract: The pK_a values of the common mononuclear carbonyl hydrides have been determined in acetonitrile by IR measurement of the position of deprotonation equilibria with various nitrogen bases and potassium phenolate. The resulting values cover a range of about 20 pK_a units, from 8.3 for $HCo(CO)_4$ to 26.6 for $CpW(CO)_2(PMe_3)H$. Hydrides with η^5-C_5Me_5 ligands are appreciably weaker acids than the corresponding hydrides with η^5-C_5H_5 ligands (e.g., the pK_a of (η^5-C_5Me_5)$Fe(CO)_2H$ is 26.3, while that of (η^5-C_5H_5)$Fe(CO)_2H$ is 19.4). The acidities of the group 8 carbonyl hydrides $H_2M(CO)_4$ decrease in the order Fe > Ru > Os.

Despite the 1971 comment[1] that "there is a definite need for the measurement of the acidity functions of a systematic series of metal hydrides under controlled, identical conditions", few such measurements have been made until recently. Early German workers carefully determined the pK_a of a few carbonyl hydrides in H_2O,[2] but the scope of this approach is limited by the low solubility of transition-metal hydrides in that solvent (and sometimes by their reactivity with it). Using polarographic and IR techniques, Vlcek and co-workers[3] attempted the *qualitative* determination of the relative thermodynamic acidities in THF of several common carbonyl hydrides and published a preliminary report; however, all measurements in THF are complicated by the tendency of carbonylmetallate anions to form ion pairs in that solvent.[4] More recently, Walker, Ford, and Pearson[5] determined

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