

$\Delta S = 1$, $\Delta V = 1$. This difference is observed in the two cases. The spectral analysis can be extended to begin a theory of photoreactivity. It was shown above that reactions can occur promptly from quartets of Cr(III) complexes. Thus, we may look to the vibrations excited in the absorption process to suggest the coordinates for relaxation, i.e., the unspecified direction in the abscissa of Figure 4. If we do so, attention is drawn to the t_{1u} buckle, which is fruitful because it suggests stereochemical rearrangement that is, independently, a well-recognized feature of photosubstitution at Cr(III)

centers. This stereochemistry has been discussed effectively by Kirk.³⁵

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Carbonylation of Zirconocene Complexes

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Organometallic carbonylation reactions sometimes follow complicated pathways. As a typical and important example for this often undesirable feature, transition-metal-mediated synthesis gas conversions of the Fischer-Tropsch type usually proceed unspecifically, yielding a broad spectrum of compounds ranging from complex hydrocarbon mixtures to oxygen-containing products alcohols, aldehydes, or ketones.¹ For future rational design of specific catalysts for carbon monoxide utilization,² a fundamental understanding of the complex possibilities of competing pathways is required. This understanding is now beginning to emerge from recent detailed mechanistic studies on well-defined molecular model systems.³

Bis(η -cyclopentadienyl) group 4 transition-metal systems have turned out to be interesting model substrate for CO conversion. Some of these systems have been shown to activate dihydrogen quite easily even in a high oxidation state of the metal.⁴ Specific stoichiometric reduction and/or reductive coupling of carbon monoxide has been achieved starting from group 4 metallocene complexes. For example, methane is formed from $Cp_2Ti(CO)_2$ and H_2 .⁵ Similarly, methanol precursors are formed from various zirconocene hydrides,^{6,7} some of which also induce coupling of CO units to form endiolates⁷ or, promoted by aluminum alkyls, a mixture of precursors of linear alcohols.⁸

In some carbon-carbon bond-forming reactions of bis(η -cyclopentadienyl)zirconium complexes with carbon monoxide, the interplay of kinetic^{7,10,11} and thermodynamic effects^{12,13} has made it possible to trace major pathways leading to thermodynamically favored final products through a variety of isolated intermediates. As typical examples, carbonylation reactions of bis(η -cyclopentadienyl)zirconium alkyl, aryl, and hy-

dride complexes are discussed in this Account.

The Problem of the Initial CO Coordination

In pseudotetrahedral bent metallocene complexes, Cp_2MR_2 , eight out of the available nine metal valence orbitals are used for making metal-to-ligand bonds. For the remaining ninth orbital, which determines the chemical reactivity of such complexes to a considerable

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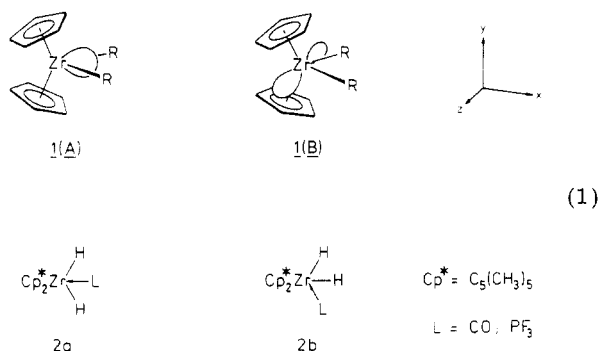
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Table I
Thermal Isomerization of (η^2 -Acyl)zirconocene Complexes $\text{Cp}_2\text{Zr}(\text{COR}^1)\text{R}^2$ **3** \rightarrow **4**

3/4	a	b	c	d	e ^b	f	g	h
R ¹	CH ₃	Ph	<i>p</i> -tolyl	<i>p</i> -anisyl	Ph	Ph	Ph	Ph
R ²	CH ₃	Ph	<i>p</i> -tolyl	<i>p</i> -anisyl	CH ₃	Cl	Br	SPH
T _{isom} , °C	-123	-59	-59	-63	-53	-70	-65	-57
ΔG^\ddagger_T ^a	11.4	15.2	15.6	15.6	15.1	c	c	c

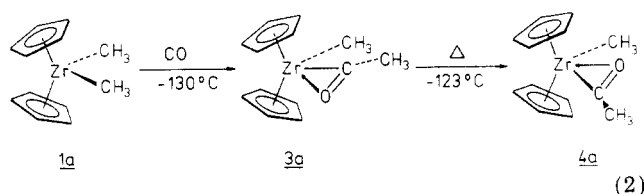
^a kcal mol⁻¹. ^b Only carbonylation product obtained from $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Ph}$ **1e**. ^c $\tau_{1/2} \approx 10$ min.

extent, two spatial arrangements have been discussed.^{14,15} In coordinatively unsaturated 16-electron Cp_2ZrR_2 complexes, this empty orbital in principle could either occupy a *central* position (**1A**)⁷ between the σ -ligands R or be aligned along the *z* axis (**1B**), making the complex more amenable to nucleophilic attack from *lateral* positions (**2b**).¹⁶ Unfortunately,

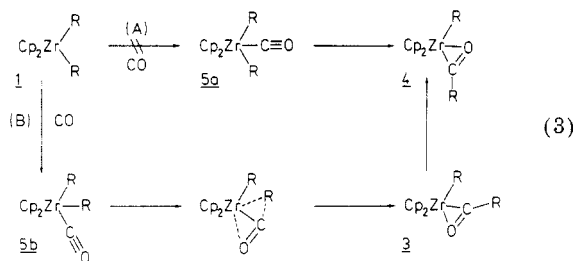


simple adducts of bis(η -cyclopentadienyl)zirconium(IV), which could help to distinguish between these alternatives, have rarely been observed. Though $\text{Cp}_2\text{ZrR}_2(\text{CO})$ complexes are too reactive to allow a clear and direct identification of the *kinetically* preferred adduct, a distinction between central and lateral carbon monoxide addition can be achieved indirectly by transfer of the initial stereochemical information to a stable isolable carbonylation product. A detailed investigation of the carbonylation of **1a** has revealed that the known carbonylation product **4a**¹⁷ is not the primarily formed (η^2 -acyl)zirconocene complex.^{18a} Treatment of dimethylzirconocene with carbon monoxide at temperatures as low as -130 °C cleanly proceeds to a different product, the (η^2 -acetyl)methylzirconocene isomer **3a**. This example of the hitherto unknown η^2 -acyl group **4** metallocene isomer with an acyl oxygen in a lateral position is a thermally very unstable compound. At -123 °C it rearranges to **4a** with a first-order rate constant of $k_{-123} = (9.03 \pm 0.4)10^{-5} \text{ s}^{-1}$. Exactly the same

reaction course is taken in the carbonylation of many other zirconocene complexes¹⁸ (see Table I.)



The fact that (η^2 -acyl)zirconocenes **3** are formed exclusively in the carbonylation of **1** under kinetic control, in combination with the fortunate incident that complexes **3** are of substantially lower thermodynamic stability compared to their (η^2 -acyl)zirconocene isomers **4**,¹⁹ allows a clear differentiation between the possible modes of initial CO attack on **1**. The former observation clearly rules out a two-step formation (A) of a (η^2 -acyl)zirconocene complex after central CO coordination to give intermediate **5a**; the latter contradicts the involvement of an equilibrating (η^1 -acyl)zirconocene intermediate being formed directly following the formation of either of the two possible $\text{Cp}_2\text{ZrR}_2(\text{CO})$ intermediates.²⁰ Therefore, it is a reasonable conclusion that **3** is a true image of the not-directly-observable bis(η -cyclopentadienyl)zirconium(IV) carbonyl complex **5b**, the intermediate formed by addition of carbon monoxide to a lateral coordination site of **1**.



Carbonylation of a Metallacyclic Substrate: 1-Zirconocenaindan

Acyl complexes **3** possess two reactive carbon centers adjacent to each other. If the rapid rearrangement to **4** could be prevented, such substrates should be suitable starting materials to follow the favored further C-C bond formation pathways taken in carbonylation reactions of zirconocene complexes **1**. This approach has been applied successfully with 1,1-bis(η -cyclopentadienyl)-1-zirconaindan (**6**) as a substrate for the

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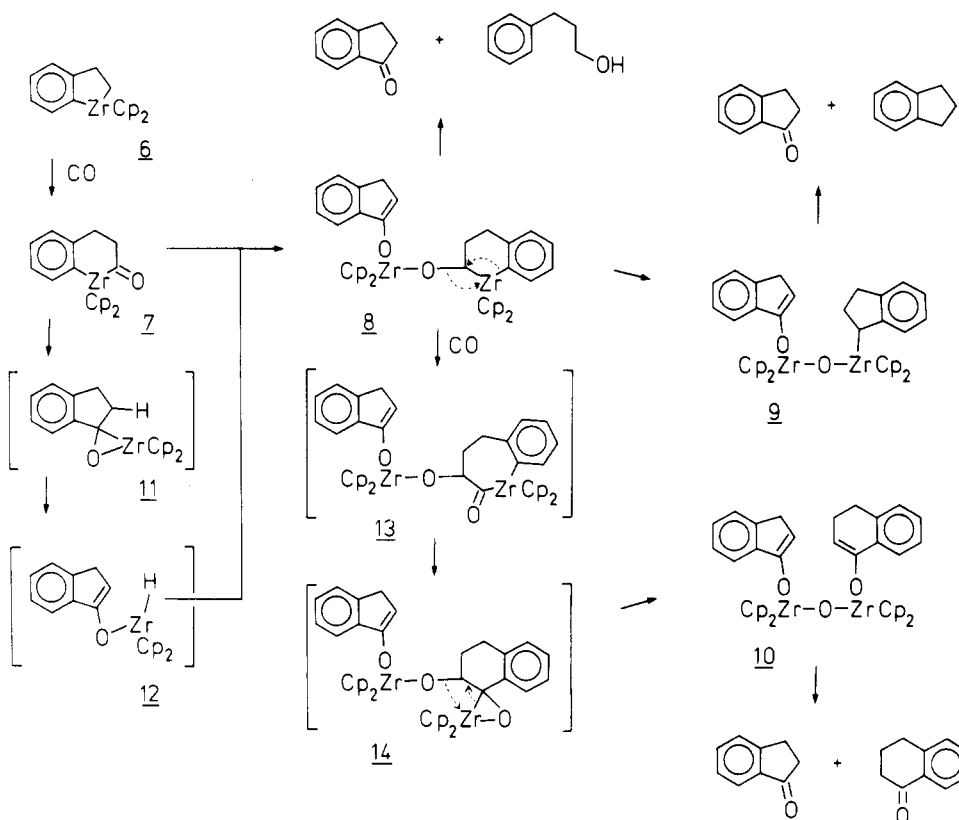
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Scheme I
Reaction Pathways followed in the Carbonylation of Zirconaindan 6



reaction with CO. Compound 6, which is readily available from the thermolysis (70 °C) of diphenylzirconocene in the presence of ethylene,²¹ rapidly takes up carbon monoxide.²² Above room temperature a complex mixture of organometallic products is formed, which yields four organic products upon hydrolysis: 1-indanone, 3-phenylpropanol, indan, and 1-tetralone. Indanone makes up ca. 50% of this mixture; the ratio of the remaining three organic products varies considerably with the conditions of the carbonylation reaction. By carefully adjusting the reaction conditions it was possible to trace the reaction course taken to these final products through various isolated intermediates representing different stages in the conversion of the incorporated carbon monoxide (Scheme I).

Below -40 °C the carbonylation of zirconaindan 6 is specific, yielding a single reaction product: the cyclic acylzirconocene 7 formed by CO insertion into the Zr-C(sp³) σ -bond. Compound 7 is only stable at sufficiently low temperatures. Warming a solution of this acyl complex above -30 °C results in the formation of 8, a binuclear zirconocene complex combining a zirconium center bound to the enolate of the indanone moiety with a metallacycle still showing the basic structural skeleton of its precursor 7. A reaction sequence through intermediates 11 and 12—the latter could be trapped by an added ketone^{22,23}—offers a straightforward explanation for the formation of 8. An equimolar mixture of 1-indanone and 3-phenylpropanol is formed upon hydrolysis. In subsequent transformations of 8, the zirconocene (indanone-enolate) unit re-

mains unchanged. Further reactions are restricted to the second reactive part of the molecule. In the absence of additional carbon monoxide, rearrangement to a zirconium-substituted indan 9 occurs at 70 °C; the free hydrocarbon is produced upon hydrolysis. The thermal rearrangement of 8 to produce 9 under carbocyclic ring closure is formally a double exchange of σ -bonds as indicated in Scheme I. Such reactions, which without a mechanistic implication have been termed (1,2)²-shift²⁴ or coupled σ, σ -exchange,²⁵ have often been observed in cases where energetically favored bonds between electropositive metal centers and electronegative elements can be formed in the course of a rearrangement. Above 0 °C 8 readily takes up another equivalent of CO to form the mixed enolate complex 10. The corresponding ketones 1-indanone and 1-tetralone are liberated upon hydrolysis (Scheme I). It has been demonstrated that (η^2 -ketone and -aldehyde)-zirconocene complexes can, in fact, be isolated if favorable decomposition pathways, which are available for species such as 11 or 14,²⁶ are suppressed by a suitable choice of substituents.²⁷ As a typical example, (η^2 -benzophenone)zirconocene (15) (in equilibrium with its dimer) is formed by thermolysis of (η^2 -benzoyl)-phenylzirconocene 4b. In addition to its spectroscopic features, the chemistry of 15 strongly supports a description of (η^2 -ketone)zirconocenes as being σ -complexes (i.e., metallaoxiranes) rather than (η^2 -ketone)-zirconium(II) π -complexes.²⁸

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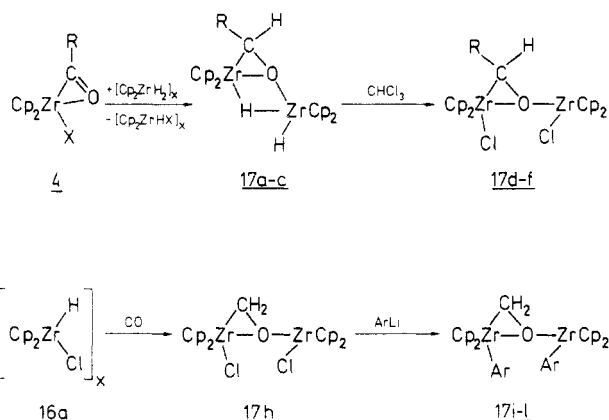
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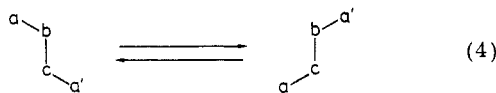
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Scheme II
Syntheses of $(Cp_2ZrX)_2(\mu\text{-aldehyde})$ Complexes 17



Dinuclear (μ -Aldehyde)zirconocene Complexes $(Cp_2ZrX)_2(-OCHR-)$

The problem of understanding the mechanistic course taken in coupled σ,σ -exchange reactions in binuclear zirconocene complexes, of which the rearrangement **8** \rightarrow **9** represents only a special example, has turned out to be closely related to questions concerning structure and reactivity of (η^2 -ketone and -aldehyde) zirconocenes. Most previously described rearrangements of this type are very exothermic reactions.²⁴ Many of these proceed through radical²⁹ or ionic intermediates³⁰ and simply take their driving force from the formation of a very favorable reaction product. However, there are a few examples of such rearrangements known where two groups a and a' exchange places relative to a pivotal group of atoms b-c in a thermoneutral system. As Reetz has demonstrated on the silicon substrates **18** (see below), a concerted automerization process, subsequently named a "dyotropic rearrangement",^{25,31} of a reasonably low activation barrier (**18**: $t_r \geq 170$ °C) explains the observed features of some of these systems. Analogous degenerate rearrangements have been found for binuclear (μ -aldehyde)zirconocene complexes (**17a-g**).^{32,33} From studies on these zirconocene complexes it has to be assumed that dyotropic rearrangements can be extremely rapid for some transition-metal complexes.



Binuclear (μ -aldehyde)zirconocene complexes **17** have been prepared by several related methods. They should in principle be formed in the reaction of suitably sub-

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Table II
Activation Barrier for "Dyotropic" Rearrangements of Selected $(Cp_2ZrX)_2(-OCHR-)$ Complexes 17^a

17	X	R	$T_c, ^\circ C$ ^b	$\Delta G^\ddagger_{T_c}$ ^c
a	H	Ph	120	19.8
b	H	CH ₃	105	19.6
d	Cl	Ph	-15	13.8
e	Cl	CH ₃	-8	13.4
f	Cl	C ₂ H ₅	11	14.4
g	Cl	CH ₂ C ₆ H ₁₁	15	14.7
h	Cl	H	-129	7.0
i	C ₆ F ₅	H	-93	9.5
j	C ₆ H ₅	H	-81	9.9
k	<i>p</i> -CH ₃ C ₆ H ₄	H	-77	10.1
l	<i>p</i> -CH ₃ OC ₆ H ₄	H	-82	10.0

^a From ref 32 and 34 except for 17h (ref 33). ^b Cp coalescence. ^c kcal mol⁻¹.

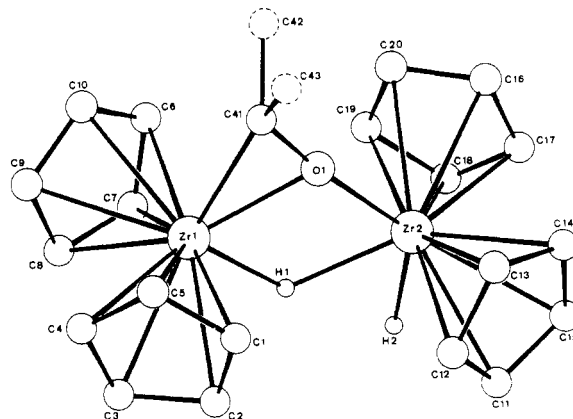


Figure 1. Molecular structure of $(Cp_2ZrH)_2(-OCHMe-)$ **17b**.

stituted (η^2 -acyl)zirconocene complexes **4** with the oligomeric hydrozirconation reagent $[Cp_2Zr(H)Cl]_x$ **16a**. An example prepared by this route, the (μ -cyclohexylacetaldehyde)zirconocene complex **17g**, has in fact been described in the literature.³³ Others have been obtained by treatment of binuclear (μ -aldehyde)zirconocene hydride complexes with alkyl halides (Scheme II).³⁴ The (μ -formaldehyde)zirconocene complex **17h**, which in turn is a convenient starting material for the synthesis of **17i-l** (Scheme II, Table II), is formed in the carbonylation of **16a**.⁶

From a detailed spectroscopic analysis of **17a-l** and a crystallographic structure determination of **17b**, it has to be assumed that $\mu\text{-}\eta^1(O):\eta^2$ -aldehyde ligands are connecting the two zirconium centers in all these complexes;^{32,34} in other words they all contain a (η^2 -aldehyde)zirconocene structural subunit.

The X-ray structure of **17b** shows a terminal (H2) and a bridging (H1) hydride ligand (Figure 1). The carbonyl function of the acetaldehyde ligand is "side-on" coordinated to one metal center. Relatively short Zr1-C (2.275 Å) and Zr1-O (2.123 Å) bond distances³⁵ and a C-O bond length of 1.404 Å point to a substantial

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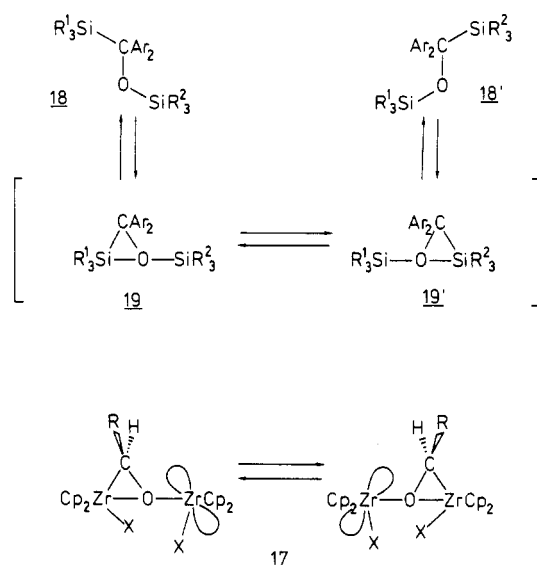
metalloxirane character. The coplanar orientation of the bridging carbonyl group with both metal centers and the crystallography located hydride ligands is in accord with a description of the structure of **17b** as being formally an adduct of two hypothetical monomeric units zirconocene dihydride and (η^2 -acetaldehyde)zirconocene, using the available lateral coordination sites of both these 16-electron species. This type of bridging results in coordinative saturation of both zirconium centers, making effectively use of the typical bonding capability of the bent metallocene units.¹⁵

In solution, zirconocene complexes **17a**–**1** exhibit dynamic behavior. By dynamic NMR spectroscopy³⁶ a degenerate rearrangement effecting the equilibration of Cp_2ZrX units, which have been chemically differentiated by the unsymmetrical bridging μ -aldehyde ligand, can be detected and studied. "Classical" mechanistic investigations³⁷ have revealed many features^{32–34} expected for a degenerate *dyotropic* rearrangement.³¹ Therefore, the observed thermally induced automerization of **17** has to be described as proceeding by a concerted intramolecular exchange of Cp_2ZrX units relative to a pivotal μ -aldehyde ligand bridging both transition-metal centers.

Most remarkable is how easily the dyotropic rearrangement proceeds in the transition-metal system **17** (see Table II). While the observation of an analogous process in the silicon system **18** requires temperatures to be ≥ 170 °C, the activation barrier for the automerization of (μ -aldehyde)(Cp_2ZrX)₂ complexes range from less than 20 kcal mol⁻¹ (**17a,b**) to a value as low as 7 kcal mol⁻¹ for **17h**.³⁸ According to Reetz the exchange of groups in the course of a dyotropic rearrangement does not necessarily have to proceed strictly simultaneously. For **18** it has been assumed that the formation of only one new metal–oxygen linkage, possibly yielding a true intermediate **19**, is preceding the migration of the second metal unit and that this substantially contributes to the overall activation barrier of the dyotropic rearrangement. Following this interpretation the surprisingly low activation barriers observed for the automerization of **17a**–**1** presumably result from a special structural feature of the (μ - η^1 (O): η^2 -aldehyde)(Cp_2ZrX)₂ complexes, i.e., having already formed this additional metal–oxygen bond in the ground state.^{32,34} Therefore, the ground state is structurally much more akin to the transition state of the dyotropic rearrangement for the zirconium complexes **17** than for the silicon compounds **18**. In addition, for the migration of the second metal atom in **17**, a favorable acceptor orbital is ideally located^{15,18} to interact with the carbon center of the pivot (Scheme III).

It is possible that many other transition-metal complexes may have similar structural as well as electronic features. Therefore, the possibility of rapid dyotropic rearrangements in the course of formation and reactions

Scheme III
Dyotropic Rearrangements in Analogous Silicon and Zirconium Systems



of bridged bi- and polynuclear transition-metal complexes should not be underestimated for a variety of bridging ligands,³⁹ not only those typically formed in carbonylation reactions.⁴⁰

Bis(η -cyclopentadienyl)zirconium Hydrides

The reaction course of the enediolate formation⁷ from CO and a zirconium hydride can be traced through different isolable intermediates starting from a well-defined bis(η -cyclopentadienyl)zirconium hydride, the dinuclear aldehyde-bridged zirconocene complex **17a**.³⁴ In the carbonylation of the formal 1:1 adduct **17a** between monomeric zirconocene dihydride Cp_2ZrH_2 and the (η^2 -benzaldehyde)zirconocene unit, the μ -aldehyde ligand has fortunately turned out to be resistant toward CO. The $\text{Cp}_2\text{Zr}(\text{OCHPh})$ unit is not actively taking part in the observed reactions but ultimately acts as an inert matrix for the stabilization of otherwise unobservable monomeric zirconocene complexes, thereby allowing observation and isolation of intermediates formed in the course of the reductive coupling of two CO molecules to the enediolate ligand.

At room temperature and elevated CO pressure (100 bar), **17a** reacts with 2 equiv of carbon monoxide to form the (η^1 -acyl)zirconocene species **26**. This product at ambient pressure readily liberates 1 equiv of CO upon thermolysis (15 min, 70 °C) to yield **24**, a 1:1 adduct of the (η^2 -benzaldehyde)zirconocene unit with $\text{Cp}_2\text{Zr}(\eta^2\text{-formaldehyde})$. Compound **26** is rapidly formed back from **24** with excess carbon monoxide (100 bar). Heating **26** at 100 °C under CO ($p_{\text{CO}} = 100$ bar) to prevent the otherwise rapid decarbonylation eventually results in the thermally induced rearrangement of the $-\text{OCH}_2\text{CO}-$ fragment to the enediolate unit (*cis*- $\text{OCH}=\text{CHO}-$) with clean formation of **27** (Scheme IV).

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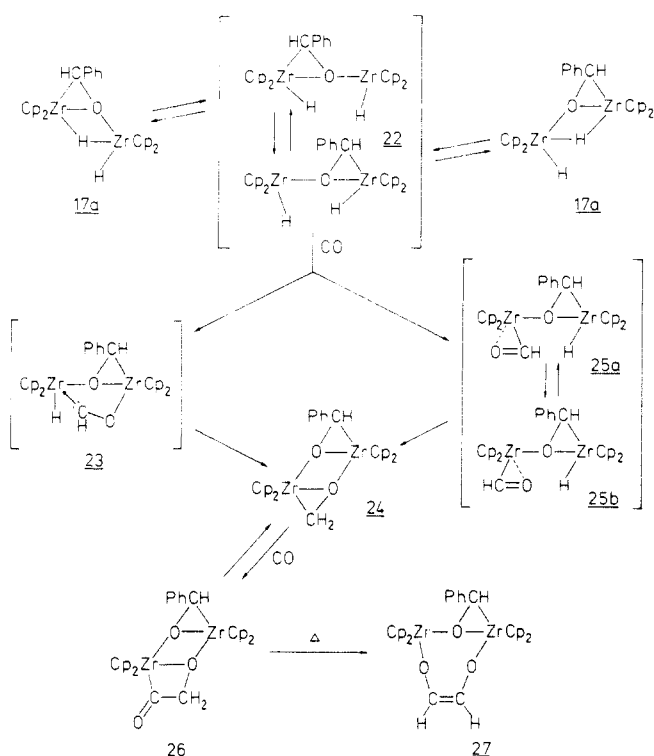
(37) Hoffman, R. W. "Aufklärung von Reaktionsmechanismen"; Georg Thieme Verlag: Stuttgart, 1976. Huisgen, R. *Acc. Chem. Res.* 1977, 10, 117.

(38) It should be noted that bond dissociation energies are not very different for silicon and zirconium systems.¹³ Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978. Hess, G. G.; Lampe, F. W.; Sommer, L. H. *J. Am. Chem. Soc.* 1965, 87, 5327.

(39) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* 1980, 102, 1747. Marsella, J. A.; Foltling, K.; Huffman, J. C.; Caulton, K. G. *Ibid.* 1981, 103, 5596. Maatta, E. A.; Marks, T. J. *Ibid.* 1981, 103, 3576. Longato, B.; Norton, J. R.; Huffman, J. C. *Marsella, J. A.; Caulton, K. G. Ibid.* 1981, 103, 209. Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Ibid.* 1980, 102, 2858. La Croce, S. J.; Cutler, A. R. *Ibid.* 1982, 104, 2312.

(40) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem.* 1976, 88, 688.

Scheme IV
Reaction Sequence in the Carbonylation of
(Cp₂ZrH)₂(μ-benzaldehyde) 17a



The facile carbonylation reaction of the coordinatively saturated zirconium hydride can be understood in view of the observed rapid, thermally induced automerization of 17a (vide supra).³⁴ Cleavage of the hydride bridge yields intermediate 22 whose structure allows a degenerate dyotropic rearrangement with a low activation barrier to occur. From the existing experimental data it cannot be decided at present which of the alternatively possible pathways is followed to form (η^2 -formaldehyde)zirconocene 24 after coordination of CO to the 16-electron zirconocene center of 22. The observation that 3 is obtained in the reaction of zirconocene alkyls and aryls with carbon monoxide under kinetic control (vide supra) indicates that formation of the thermodynamically favorable Zr–O interaction and migration of the σ -ligand occur simultaneously to form (η^2 -acyl)zirconocene species.¹⁸ Therefore, it is not obvious that a reaction mechanism analogous to the “intermolecular” route established for many transition-metal hydride reactions of carbon monoxide,⁴¹ here proceeding through zirconoxycarbene 23,⁴² should be favored over a pathway through intermediate (η^2 -formyl)zirconocene complexes 25.⁴³

(η^2 -Formaldehyde)zirconocene 24 plays a key role in the formation of carbonylation products derived from 17a.⁴⁴ A reactivity of 24 as being expected for a metal alkyl, here a metallaoxirane,⁴⁵ explains that CO is

(41) See for example: Casey, C. P.; Andrews, A.; McAlister, D. R. *J. Am. Chem. Soc.* 1979, 101, 3371. Wong, W. K.; Tam, W.; Gladysz, J. A. *Ibid.* 1979, 101, 5440.

(42) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* 1979, 101, 218. Threlkel, R. S.; Bercaw, J. E. *Ibid.* 1981, 103, 2650.

(43) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* 1981, 103, 6959. Berke, H.; Hoffmann, R. *Ibid.* 1978, 100, 7224 and references cited.

(44) For a discussion of the role of formaldehyde in CO/H₂ conversions, see: Fahey, D. R. *J. Am. Chem. Soc.* 1981, 103, 136 and references therein.

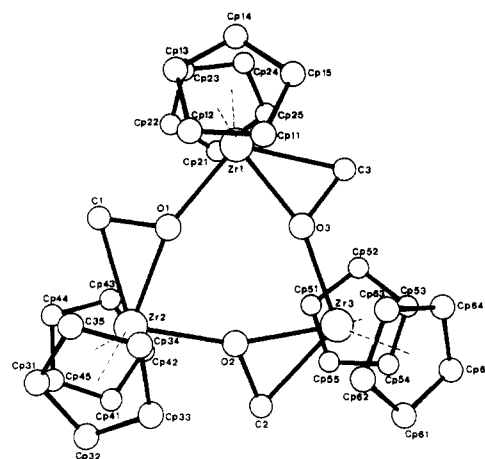
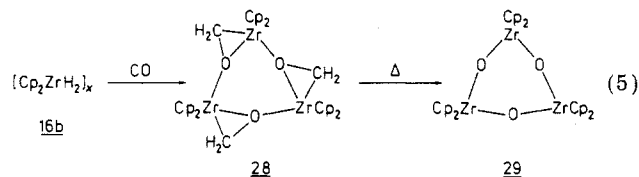


Figure 2. Molecular geometry of [Cp₂Zr(η^2 -CH₂O)]₃ 28.

readily being “inserted” to form 26. Cleavage of only one of the Zr–O–Zr linkages connecting the Cp₂Zr(η^2 -CH₂O) unit with the (benzaldehyde)zirconocene matrix suffices to create the necessary coordination site for this carbonylation reaction.

As in its formation, binuclear structures seem to be retained during the consecutive thermally induced rearrangement process of 26. The formation of the enediolate complex 27 can be described by a sequence of well-established single-reaction steps³⁸ passing through an intermediate dinuclear ketylzirconocene complex. The incorporation of the olefinic double bond into the metallacyclic ring system could simply be responsible for the exclusive formation of the cis isomer of the zirconocene enediolate 27.

The isolation of 24 from the reaction of 17a with CO represents one of the rare examples where the formation of the formaldehyde ligand has been demonstrated to occur in the carbonylation of a transition-metal hydride. Under suitable reaction conditions, (η^2 -formaldehyde)zirconocene complexes have also been isolated from carbonylation mixtures obtained from the oligomeric zirconocene hydrides [Cp₂Zr(H)Cl]_x 16a⁶ and [Cp₂ZrH₂]_x 16b.⁴⁶ Thus, the trimeric (η^2 -formaldehyde)zirconocene 28 was isolated in 14% yield after prolonged treatment of a toluene suspension of 16b with carbon monoxide (150 bar) at room temperature.



The crystal structure of 28 shows an almost regular hexagonal arrangement of metal and oxygen atoms (averaged bond angles: Zr–O–Zr = 160.7°; O–Zr–O = 79.2°) and a nearly coplanar orientation of the zirconium, carbon, and oxygen atoms making up the framework of the [Cp₂Zr(η^2 -CH₂O)]₃ molecule (Figure 2). “Monomeric” (η^2 -formaldehyde)zirconocene substructures are characterized by typical bond distances 2.279 Å (Zr2–C1), 1.411 Å (C1–O1), and 2.129 Å (Zr2–

(45) Dewar, M. J. S.; Dougherty, R. C. “The PMO Theory of Organic Chemistry”; Plenum Press: New York, 1975; p 300. Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* 1979, 101, 783.

(46) Kropp, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* 1983, 105, 3353.

O1).⁴⁷ The connection of the three subunits is accomplished by interaction of the "formaldehyde oxygen" with the available lateral coordination site of the adjacent bent metallocene moiety.¹⁵ In comparison to the Zr–O linkage in the metallacyclic three-membered rings, only slightly longer bond distances have been found for this connection (e.g., Zr1–O1: 2.178 Å).

Compound 28 is a quite remarkable substrate, not only because it appears to represent the first (η^2 -formaldehyde) complex characterized by X-ray diffraction that has been obtained by the carbonylation of a transition-metal hydride⁴⁷ but also because it cleaves all three CO-derived $-\text{CH}_2-$ groups upon thermolysis (200 °C) to form the known ($\text{Cp}_2\text{Zr}=\text{O}$) trimer 29.⁴⁸

Conclusions

It seems that bis(η -cyclopentadienyl)zirconium(IV) alkyl and hydride complexes are informative model substrates for studies directed toward an understanding of metal-induced reduction and coupling processes of the carbon monoxide molecule. In the +4 oxidation state the involved group 4 transition-metal carbonyl complexes lack a considerable backbonding contribution of the M–CO linkage, making d^0 zirconocene carbonyl complexes very unstable and reactive. After initial CO coordination, subsequent stabilizing reactions therefore take place at very low temperature. On the other hand, the pronounced binding affinity for oxygen

(47) To my knowledge, X-ray structures of only three other η^2 -formaldehyde transition-metal complexes had been reported at the time this Account was written. They have all been prepared by reactions of suitable metal complex precursors with formaldehyde solutions (C–O bond lengths of the CH_2O ligand are given in parentheses): (a) $\text{Os}(\eta^2\text{-CH}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2$, (1.59 Å): Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* 1979, 101, 503. (b) $\text{Fe}(\eta^2\text{-CH}_2\text{O})(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2$, (1.32 Å): Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* 1981, 219, 353 (c) $\text{Cp}_2\text{V}(\eta^2\text{-CH}_2\text{O})$, (1.353 Å): Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1982, 104, 2019.

(48) Average Zr–O bond length: 1.959 Å; Zr–O–Zr angle (mean value): 142.5° for 29. Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1979, 101, 1767.

centers from reagents as well as ligands already coordinated to the metallocene moiety provides a considerable additional stabilization for a number of possible reactive intermediates. These factors together have allowed the observation of otherwise undisclosed kinetically controlled pathways in carbonylation reaction sequences under very mild reaction conditions.

(η^2 -Aldehyde)zirconocene complexes are of a special importance as intermediates for the reductive coupling of carbon monoxide at the bent metallocene unit. The occurrence of free formaldehyde in metal-catalyzed transformations of CO/ H_2 mixtures is highly questionable in view of its unfavorable thermodynamics.^{2,44} However, pathways for reductive coupling of the CO molecule through a CH_2O intermediate side-on coordinated to a metal surface is quite possible from the studies on our zirconocene model system.

There is strong evidence that hydrocarbon products in heterogeneously catalyzed Fischer–Tropsch processes are obtained from reactions of methylene groups on a metal surface.⁴⁹ The fact that all three carbon monoxide derived methylene groups are cleaved upon thermolysis of the (η^2 -formaldehyde)zirconocene complex 28 to form the "metal oxide" 29 emphasizes the similarity of our model system with a real Fischer–Tropsch process. Though the fate of the methylene groups "lost" in the model system has not been established at present, this observation may constitute an important basis for future studies directed toward an understanding of the factors controlling Fischer–Tropsch type processes on a well-defined molecular level.

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Conjugate Addition of Alkyl-Grignard Reagents to Mononitroarenes

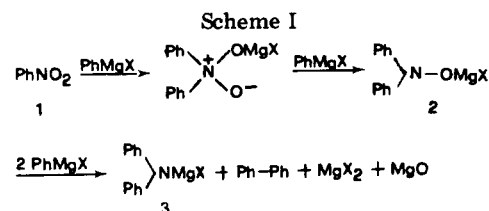
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Until a few years ago some fundamental aspects of the reaction between mononitroarenes and Grignard reagents were unknown or misinterpreted; only the reactions with arylmagnesium halides had been exam-

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ined in detail. Gilman and McCracken,¹ and later on Kursanov and Solodkov,² had explained the formation