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On the Mechanisms of Carbon Monoxide Reduction with Zirconium Hydrides

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The conversion of carbon monoxide and dihydrogen to larger molecules, especially those with carbon number greater than one, has become a conspicuously challenging problem. In light of recent energy issues, "syngas" chemistry has assumed increased importance. Consequently there has been a renewed interest in Fischer–Tropsch, methane, and methanol synthesis using heterogeneous catalysts and a genesis of activity in the development of homogeneous catalysts for these and possibly other processes.[1] Whereas the desirability of a homogeneous analogue of the 55-year-old Fischer–Tropsch synthesis has been questioned, there is a general consensus concerning the need for the catalysis of CO and H_2 to oxygenates such as alcohols, esters, and carboxylic acids. The conversion of CO and H_2 to water and saturated hydrocarbons is thermodynamically favored over oxygenates. Hence a key factor needed in new catalysts is selectivity, and it is here that homogeneous systems could play an important role.

The catalytic conversion of CO and H_2 to methane and ethane has been reported for an iridium carbonyl cluster in $NaAlCl_4/AlCl_3$ melt at 180 °C.[2] $HCo(CO)_4$ has been reported to catalyze the conversion of syngas to alcohols and formates at 200 °C,[3] although rates were rather low. More recently the hydrogenation of carbon monoxide to methanol and methyl formate at 1300 atm and 250 °C has been catalyzed with ruthenium carbonyls.[4] The remarkable selectivity of certain rhodium carbonyls in the conversion of CO and H_2 to ethylene glycol[1b] clearly demonstrates the potential utility of homogeneous catalysts. Whereas the mechanisms of the catalytic processes mentioned above remain for the most part undefined, a number of research groups have undertaken the deliberate synthesis of transition-metal compounds containing partially reduced CO fragments such as formyl (CHO) and hydroxymethyl (CH_2OH) which have been proposed as intermediates in the reduction of CO by H_2.[5,6] This recent activity is directed toward an understanding of the mechanisms of carbon monoxide reduction by H_2 at metal sites.

Our entry into this area of research was an outgrowth of some studies of organic derivatives of one of the early transition metals, zirconium. A search for stable dinitrogen complexes of zirconium had led to the synthesis of a crystalline N_2 adduct of bis(pentamethylcyclopentadienyl)zirconium(II), $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (**1**).[7] While our initial interest in **1** was centered on its structure (Figure 1) and the unusual reactivity of its N_2 ligands, we soon discovered that it could be used as an extremely convenient and versatile starting material; olefins, acetylenes, nitriles, isocyanides, carbon monoxide, and H_2 rapidly displace N_2 to yield a variety of stable, crystalline adducts with "permethylzirconocene". Thus, for example, treatment of **1** with CO leads sequentially to $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ (**2**) and $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ (**3**).[8] Similarly, $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (**4**) may be obtained in quantitative yield by simply stirring a toluene solution of **1** with 1 atm of H_2 (eq 1).[9]

$$\underset{\mathbf{1}}{\{Cp^*{}_2ZrN_2\}_2N_2} + 2H_2 \rightarrow \underset{\mathbf{4}}{2Cp^*{}_2ZrH_2} + 3N_2 \qquad (1)$$

$$Cp^* \equiv \eta^5\text{-}C_5Me_5$$

Soon after the synthesis and isolation of these carbonyl and hydride derivatives of permethylzirconocene, we found our first indication that some remarkable chemistry of CO and H_2 was possible for this system. Treatment of **3** with H_2 affords $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$ (**5**) in nearly quantitative yield (eq 2).[8] While

$$\underset{\mathbf{3}}{Cp^*{}_2Zr(CO)_2} + 2H_2 \xrightarrow[110\ °C]{2\text{ atm}} \underset{\mathbf{5}}{Cp^*{}_2Zr(H)(OCH_3)} + CO \qquad (2)$$

the high stability of **5** appears to preclude a catalytic synthesis of methanol from H_2 and CO for this system, reaction 2 represents a clean reduction of carbon mon-

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Peter T. Wolczanski was born in upstate New York and received his S.B. from the Massachusetts Institute of Technology. There he helped harness the photon under the direction of Professor Mark S. Wrighton. Deciding to tackle the energy problem in the thermal sense, he joined Professor John E. Bercaw's research group in 1976. He is currently a J. S. Fluor Fellow at Caltech.

[†] Contribution No. 6106.

[1] (a) C. Masters, *Adv. Organomet. Chem.*, **17**, 61 (1979); (b) R. L. Pruett and W. E. Walker (Union Carbide Corp.), German Offen. 2 262 318 (1973); *U.S. Appl.*, **210**, 538 (1971). (c) M. A. Vannice, *Catal. Rev. Sci. Eng.*, **14** (2), 153 (1976).

[2] G. C. Demitras and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 2796 (1977).

[3] J. W. Rathke and H. M. Feder, *J. Am. Chem. Soc.*, **100**, 3623 (1978).

[4] J. S. Bradley, *J. Am. Chem. Soc.*, **101**, 7419 (1979).

[5] (a) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973); (b) C. P. Casey and S. M. Neumann, *ibid.*, **98**, 5395 (1976); (c) C. P. Casey and S. M. Neumann, *ibid.*, **100**, 2544 (1978); (d) J. A. Gladysz and W. Tam, *ibid.*, **100**, 2545 (1978); (e) C. P. Casey, M. A. Andrews, and J. E. Rinz, *ibid.*, **101**, 741 (1979); (f) W. Tam, W. Wong, and J. A. Gladysz, *ibid.*, **101**, 1589 (1979); (g) G. R. Clark, C. E. L. Headford, K. Marsden, and W. R. Roper, *ibid.*, **101**, 503 (1979).

[6] (a) C. P. Casey, M. A. Andrews, and D. R. McAlister, *J. Am. Chem. Soc.*, **101**, 3371 (1979); (b) J. A. Gladysz, J. C. Selover, and C. E. Strouse, *ibid.*, **100**, 6766 (1978).

[7] (a) J. M. Manriquez and J. E. Bercaw, *J. Am. Chem. Soc.*, **96**, 6229 (1974); (b) J. M. Manriquez, R. D. Sanner, R. E. Marsh, and J. E. Bercaw, *ibid.*, **98**, 3042 (1976); (c) R. D. Sanner, J. M. Manriquez, R. E. Marsh, and J. E. Bercaw, *ibid.*, **98**, 8351 (1976); (d) J. M. Manriquez, D. R. McAlister, E. Rosenberg, A. M. Shiller, K. L. Williamson, S. I. Chan, and J. E. Bercaw, *ibid.*, **100**, 3078 (1978).

[8] J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, **98**, 6733 (1976).

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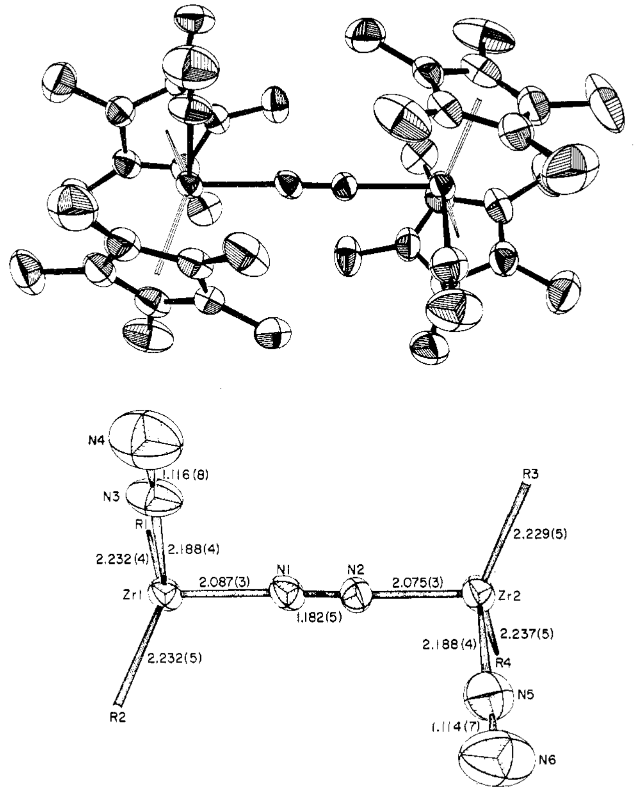


Figure 1. The molecular configuration and skeletal view of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (1).

oxide by H_2 under relatively mild conditions and thus offered a rare opportunity to examine certain features of its mechanism. Our studies of this reaction led us to examine the reactivity of alkyl and hydride derivatives of permethylzirconocene with CO, isocyanides, and other transition-metal carbonyls. This review summarizes our present understanding of the mechanism for reaction 2 and discusses possible mechanisms for several related reactions.

Reactivity of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ with Carbon Monoxide

The evolution of 1 equiv of free CO in reaction 2 suggests the intermediacy of the coordinatively unsaturated species, $[(\eta^5\text{-}C_5Me_5)_2Zr(CO)]$. Such a suggestion is supported by the fact that 2 also reacts with H_2 at room temperature to yield predominantly 5 (eq 3).

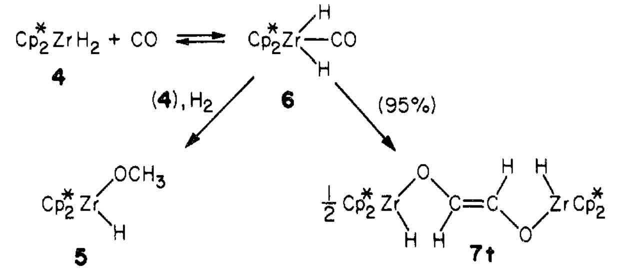
$$\underset{2}{\{Cp^*{}_2Zr(CO)\}_2N_2} + 4\ H_2 \xrightarrow[25\ ^\circ C]{1\text{atm}} \underset{5}{2Cp^*{}_2Zr(H)(OCH_3)} + N_2 \quad (3)$$

Oxidative addition of H_2 to $[(\eta^5\text{-}C_5Me_5)_2Zr(CO)]$ to generate $(\eta^5\text{-}C_5Me_5)_2ZrH_2(CO)$ (6) also appears plausible. An independent route to 6 was therefore investigated, and indeed $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (4) was found to reversibly absorb 1 equiv of carbon monoxide at −80 °C (eq 4). The two hydride ligands of 6 give rise to a

$$\underset{4}{Cp^*{}_2ZrH_2} + CO \rightleftarrows \underset{6}{Cp^*{}_2ZrH_2(CO)} \quad (4)$$

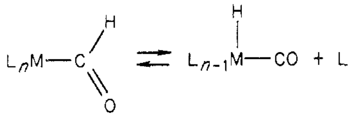
singlet in its ^1H NMR spectrum (220 MHz, −64 °C), which splits into a doublet for $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (^{13}CO) with $J_{^{13}C\text{-}H} = 25$ Hz. These data indicate a symmetric structure for 6, with CO occupying the central equatorial position mutually cis to both hydride ligands.

Scheme I



As the solution of 6 is slowly warmed to −50 °C, the ^1H NMR spectrum attributed to 6 decays concomitant with the growth of the spectrum of a new species, subsequently identified as *trans*-$\{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2(\mu\text{-}OCH{=}CHO)$ (**7t**). No intermediates are observed by ^1H NMR spectrometry. When solutions of 6 are warmed under 1 atm of H_2, 5–10% of the methoxy hydride derivative 5 is formed; **7t** is the still major product. When 6 is warmed in the presence of both 4 and H_2, however, increasing amounts of 5 are observed with the ratio of 5:**7t** responding to the amount of 4 added. These observations are outlined in Scheme I.

A mechanism in accord with Scheme I would involve rearrangement of 6 to an intermediate which is intercepted by 4 and reduced with H_2 to 5 in competition with its dimerization to **7t**. An immediate candidate for such an intermediate is the formyl species $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CHO)$ (8), generated by migratory insertion of CO into one of the Zr–H bonds of 6. There is, however, an apparent difficulty with this proposal: rearrangement of a carbonyl hydride to a formyl complex is thus far unprecedented. Furthermore, a favored pathway for decomposition of transition-metal formyl complexes that are prepared by indirect methods involves dissociation of a ligand and rearrangement to the corresponding carbonyl hydrides (eq 5).[5] The con-



$$L_nM{-}C(H){=}O \rightleftarrows L_{n-1}M(H){-}CO + L \quad (5)$$

version of $(CO)_5MnH$ to $(CO)_5Mn(CHO)$ has been estimated to be endothermic by roughly 20 kcal mol^{-1},[10] so that the equilibrium position for eq 5 appears to lie far to the right, at least for the "late" transition metals.

On the other hand, an unconventional η^2 bonding of the formyl ligand may be expected for 8 by analogy to the structures recently established by Floriani and coworkers[11] for the closely related acyl derivatives $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)(CH_3CO)$ and $(\eta^5\text{-}C_5H_5)_2TiCl(CH_3CO)$. This η^2 coordination may be rationalized on the following basis: dative interaction of an oxygen lone pair of electrons with the empty, low-lying orbital located in the equatorial plane of the "bent-sandwich" moiety[12]

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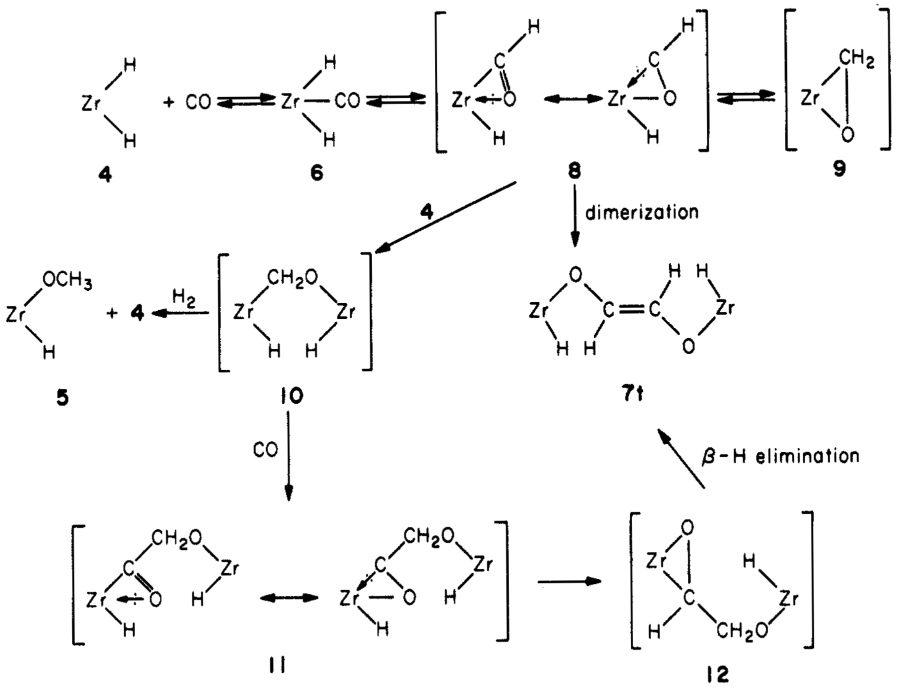
[10] Assuming $D[(CO)_5Mn\text{–}H] = 65$ kcal mol^{-1}, $D[(CO)_5Mn\text{–}CHO] = 25$ kcal mol^{-1}, and $D[H\text{–}CO] = 20$ kcal mol^{-1}; J. Halpern, private communication.

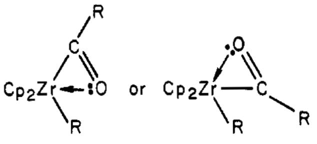
[11] (a) G. Fachinetti, C. Floriani, F. Marchetti, and S. Merlino, *J. Chem. Soc., Chem. Commun.*, 522 (1976); (b) F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, **16**, 299 (1977); (c) G. Fachinetti, G. Fochi, and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 1946 (1977); (d) G. Fachinetti, C. Floriani, and H. Stoeckli-Evans, *ibid.*, 2297 (1977).

[12] (a) J. C. Green, M. L. H. Green, and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, **30**, 373 (1972); (b) H. H. Brintzinger and L. S. Bartell, *J. Am. Chem. Soc.*, **92**, 1105 (1970); (c) A. J. Petersen and L. F. Dahl, *ibid.*, **96**, 2248 (1974); (d) J. W. Lauher and R. Hoffmann, *ibid.*, **98**, 1729 (1976).

Scheme II



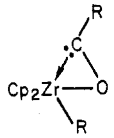
enables the zirconium atom to achieve a full 18-electron valence shell (**8a** and **8b**). There is evidence which



8a **8b**

R = H, alkyl, aryl

implicates **8b** as the kinetic product of migratory insertion, which subsequently rearranges to **8a**.[13] This high oxygen affinity of the early transition metals may thus be invoked to override the otherwise adverse thermodynamics of the migratory insertion of CO into a Zr–H bond of **6**. Furthermore, an additional resonance structure (**8c**) is suggested. In this representation

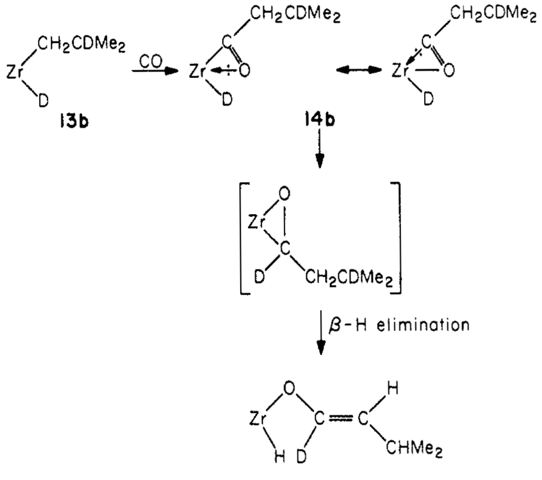


8c, R = H, alkyl, aryl

the acyl group is bonded by a full covalent Zr–O bond and a dative interaction of the oxycarbene lone pair completing the valence shell at zirconium.

The resultant carbenoid character of the formyl ligand provides a basis for understanding the results of Scheme I. As shown in Scheme II simple dimerization of the oxycarbene moieties of **8** could be invoked as a reasonable pathway to **7t**. In the presence of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$, insertion of the oxymethylene center into one of the zirconium hydride bonds to afford **10** could compete with dimerization. Subsequent reductive elimination induced by H_2 would thus yield **5**, regenerating **4**. This final step ($\mathbf{10} + H_2 \rightarrow \mathbf{5} + \mathbf{4}$) is in close analogy to the facile reductive elimination of isobutane

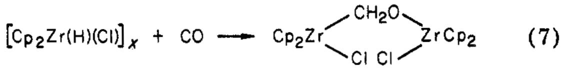
Scheme III



from $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (**13**) induced by H_2 (eq 6).[14] Further support for the intermediacy of **10**

$$\underset{\mathbf{13}}{Cp^*{}_2Zr(H)(CH_2CHMe_2)} + H_2 \xrightarrow{-15\,°C} \underset{\mathbf{4}}{Cp^*{}_2ZrH_2} + CH_3CHMe_2 \quad (6)$$

has been reported by Floriani and co-workers;[15] treatment of $[(\eta^5\text{-}C_5H_5)_2Zr(H)(Cl)]_x$ with carbon monoxide was shown to afford initially $\{(\eta^5\text{-}C_5H_5)_2ZrCl\}_2(\mu\text{-}CH_2O)$ (eq 7). The further absorption of a second equivalent



$$[Cp_2Zr(H)(Cl)]_x + CO \longrightarrow Cp_2Zr\overset{CH_2O}{\underset{Cl\ \ Cl}{\quad}}ZrCp_2 \quad (7)$$

$(Cp \equiv \eta^5\text{-}C_5H_5)$

of CO was observed; however, the resulting complex has not been characterized.

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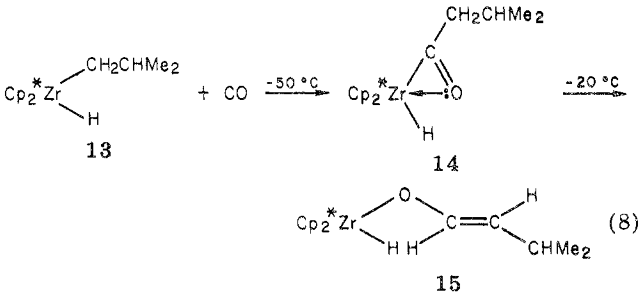
[13] G. Erker and F. Rosenfeldt, *Angew. Chem., Int. Ed. Engl.*, 17, 605 (1978).

[14] (a) D. R. McAlister, D. K. Erwin, and J. E. Bercaw, *J. Am. Chem. Soc.*, **100**, 5966 (1978); (b) M. D. Seidler and J. E. Bercaw, unpublished results.

[15] G. Fachinetti, C. Floriani, A. Roselli, and S. Pucci, *J. Chem. Soc., Chem. Commun.*, 269 (1978).

The reactivity of **13** with carbon monoxide[16,17] suggests a structure for this secondary product as well as an alternative mechanism for the formation of **7t**. Treatment of **13** with carbon monoxide is observed to proceed via the acyl hydride derivative **14** to the final product, *trans*-(η^5-$C_5Me_5)_2Zr(H)(OCH{=}CHCHMe_2)$ (**15**) (eq 8). The results of a deuterium labeling experiment implicate the intermediacy of the isovaleraldehyde adduct formed by insertion of the oxycarbene into the Zr–D bond in the rearrangement **14** → **15** (Scheme III). Simple extension of this process to **10** provides an attractive alternative pathway to **7t** (Scheme II), thus neatly accounting for the exclusive trans geometry observed for the enediolate dimer **7t**.



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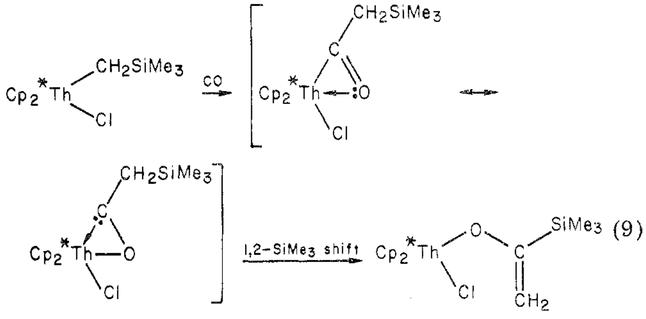
14

15

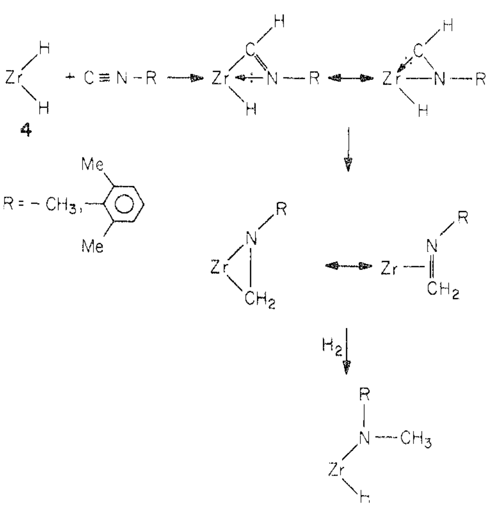
Explicit in the discussions of all possible mechanisms thus far is the proposed oxycarbenoid reactivity imparted to the carbon center by the unusual η^2 coordination of the acyl (or formyl) group to the permethylzirconocene moiety. More recently Manriquez et al.[18] have capitalized on the facility of trimethylsilyl migration to demonstrate the oxycarbenoid character of acyl derivatives of the closely related thorium system. Thus treatment of (η^5-$C_5Me_5)_2Th(Cl)(CH_2SiMe_3)$ with CO affords (η^5-$C_5Me_5)_2Th(Cl)(OC(SiMe_3){=}CH_2)$ (eq 9).

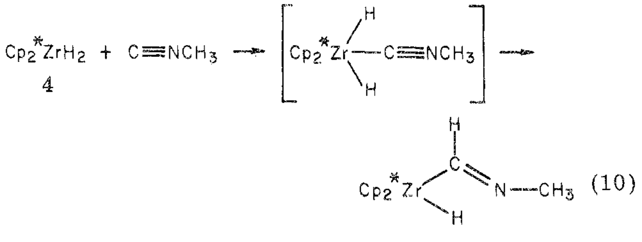


These (η^5-$C_5Me_5)_2M$ (M = Th, U) derivatives which are often very similar in reactivity to the corresponding (η^5-$C_5Me_5)_2Zr$ derivatives.[18,19]

As will become apparent in the next section, an issue crucial to the viability of Scheme II concerns the question of *intra*molecular migratory insertion of CO into a Zr–H bond (i.e., **6** → **8**, Scheme II). In light of previous findings that isoelectronic isocyanides (but not CO) undergo migratory insertion into Ru–H, Os–H, and Pt–H bonds,[20] it appeared necessary to establish whether or not this process could be observed for (η^5-$C_5Me_5)_2ZrH_2$ (**4**).[21] Methyl isocyanide does indeed react rapidly with **4** at −65 °C to afford directly the formimidoyl hydride (η^5-$C_5Me_5)_2Zr(H)(CH{=}NCH_3)$ (**16**) (eq 10).

Scheme IV





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A pathway for migratory insertion of isocyanides, and hence CO, into the Zr–H bonds of **4** is thus established. It should be reemphasized, however, that similar reactivity has been observed with isocyanides but not with carbon monoxide for some of the later transition-metal hydrides, so our findings are more appropriately viewed as necessary but insufficient evidence for Scheme II. It was nonetheless gratifying to find a close similarity between the proposed intermediates and products for **4** with CO (Scheme II) and the products obtained from reactions of **4** with methyl isocyanide and 2,6-dimethylphenyl isocyanide (Scheme IV).[21]

Reactivity of (η^5-$C_5Me_5)_2ZrH_2$ with Coordinated Carbon Monoxide

Our studies of the reactivity of (η^5-$C_5Me_5)_2ZrH_2$ (**4**) with CO do appear to have some bearing on the mechanism for the H_2 reduction of (η^5-$C_5Me_5)_2Zr(CO)_2$ (**3**) to (η^5-$C_5Me_5)_2Zr(H)(OCH_3)$ (**5**) (eq 2): slow addition of CO to **4** does afford **5**, albeit at much lower temperatures than those required for the reduction of **3** to **5**. It could therefore be argued that, according to eq 11, **3** is simply a source of **4** under the reaction condi-

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[16] J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, **100**, 2716 (1978).

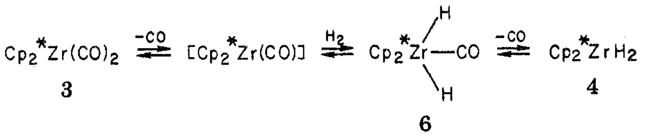
[17] For similar chemistry with the parent $Cp_2ZrH(R)$ see K. I. Gell and J. Schwartz, *J. Organomet. Chem.*, **162**, C11 (1978).

[18] J. M. Manriquez, P. J. Fagan, T. J. Marks, C. S. Day, and V. W. Day, *J. Am. Chem. Soc.*, **100**, 7112 (1978).

[19] (a) J. M. Manriquez, P. J. Fagan, and T. J. Marks, *J. Am. Chem. Soc.*, **100**, 3939 (1978); (b) J. M. Manriquez, P. J. Fagan, T. J. Marks, S. H. Vollmer, C. S. Day, and V. W. Day, *ibid.*, **100**, 5075 (1979); (c) R. W. Broach, A. J. Schultz, J. M. Williams, G. M. Brown, J. M. Manriquez, P. J. Fagan, and T. J. Marks, *Science*, **203**, 172 (1979).

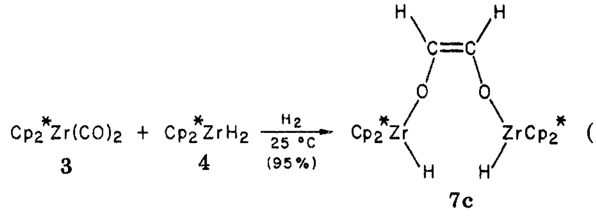
[20] (a) D. F. Christian, G. R. Clark, W. R. Roper, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 458 (1972); (b) R. D. Adams and N. M. Golembeski, *J. Am. Chem. Soc.*, **101**, 2579 (1979); (c) D. F. Christian and W. R. Roper, *J. Organomet. Chem.*, **80**, C35 (1974); (d) G. R. Clark, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Dalton Trans.*, 2556 (1975); (e) D. F. Christian, H. C. Clark, and R. F. Stepaniak, *J. Organomet. Chem.*, **112**, 209 (1976).

[21] P. T. Wolczanski and J. E. Bercaw, *J. Am. Chem. Soc.*, **101**, 6450 (1979).



$$Cp_2^*Zr(CO)_2 \underset{3}{} \xrightleftharpoons{-CO} [Cp_2^*Zr(CO)] \xrightleftharpoons{H_2} \underset{6}{Cp_2^*Zr(H)_2{-}CO} \xrightleftharpoons{-CO} \underset{4}{Cp_2^*ZrH_2} \qquad (11)$$

tions (110 °C, 2 atm of H_2), so that Scheme II still obtains in the hydrogenation of the dicarbonyl (**3**) to yield the methoxy hydride (**5**) (reaction 2). An acceleration of reaction 2 on addition of **4** would be in accord with the above proposal. Indeed solutions containing an equimolar mixture of **3** and **4** (1 atm of H_2) do undergo a reaction at room temperature; however, **5** is obtained in only 5% yield; the major product is now the *cis*-enediolate bridged dimer **7c** (eq 12).[22] This startling result prompted us to reexamine the product mixture from the reaction of **4** with free carbon monoxide, and **7c** was found to be completely absent. Similarly **7t** was not obtained in reaction 12. Since **7c** is *not* among the products obtained from **4** and free CO, one is forced to conclude that **7c** arises via a direct reaction of **4** with **3**, possibly by hydride transfer to a coordinated CO of **3** to generate a binuclear carbene complex.[23] Consideration of this general reaction type (eq 13) appears warranted in any case, since unlike group 6–8 transition-metal hydrides which behave chemically more like protonated metal complex anions, the hydride ligands of **4** are distinctly hydridic, comparable with trialkylborohydrides in reactivity.[9] The latter have been shown to convert a number of transition-metal carbonyls to the corresponding formyl anions.[5b–f]



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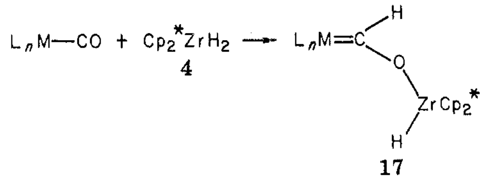
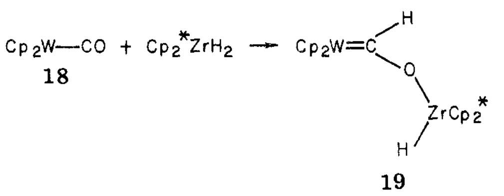


(13)

In view of the large number of stable carbene complexes of molybdenum and tungsten reported, we carried out our initial study of the reactions of **4** with $(\eta^5\text{-}C_5H_5)_2M(CO)$ (M = Cr, Mo, W) in hopes of observing directly the product of the proposed reaction type (eq 13).[22] $(\eta^5\text{-}C_5H_5)_2W(CO)$ (**18**) does indeed react smoothly with **4** at −80 °C to afford $(\eta^5\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$ (**19**) in 95% yield (eq 14).



(14)

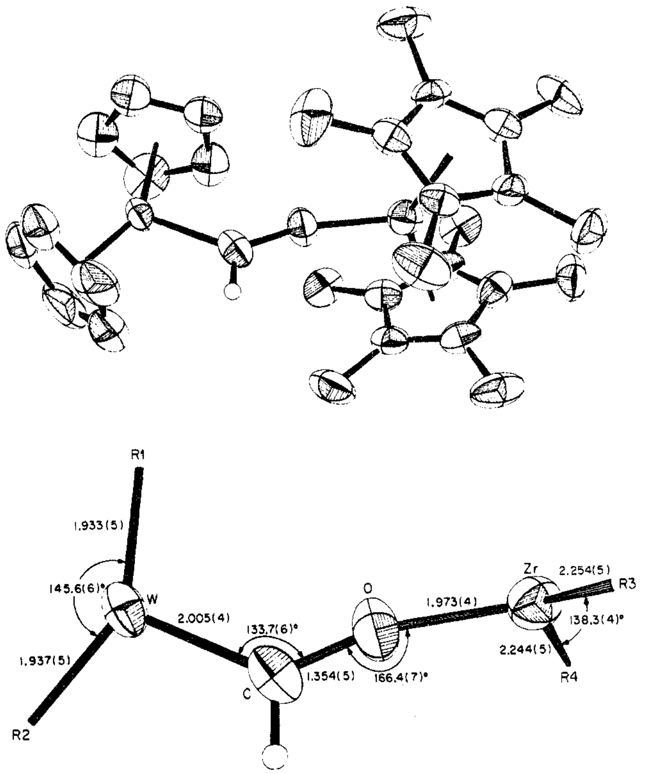
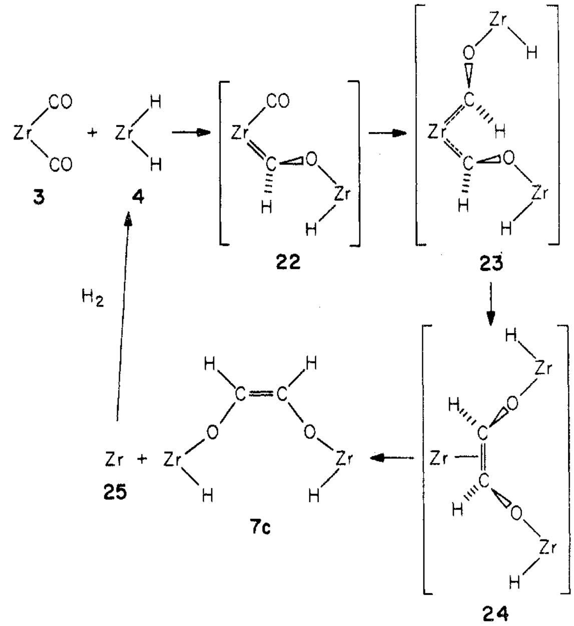


Figure 2. The molecular configuration and skeletal view of $(\eta^5\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$.

Scheme V



Similarly $(\eta^5\text{-}C_5H_5)_2Mo{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$ (**20**) and $(\eta^5\text{-}C_5H_5)_2Cr{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$ (**21**) may be also prepared. The "zirconoxy" carbene complexes **19** and **20** are remarkably robust; toluene solutions remain unchanged for hours at 150 °C. The structure **19** which was deduced by NMR spectrometry was confirmed by X-ray diffraction methods (Figure 2). Thus the NMR inequivalence of the two $(\eta^5\text{-}C_5H_5)$ rings is attributable to the π interaction of the carbon p orbital with the filled b_2 orbital in the equatorial plane of the Cp_2W moiety, firmly locking the carbene with its hydrogen directed toward one cyclopentadienyl ligand and oxygen toward the other.

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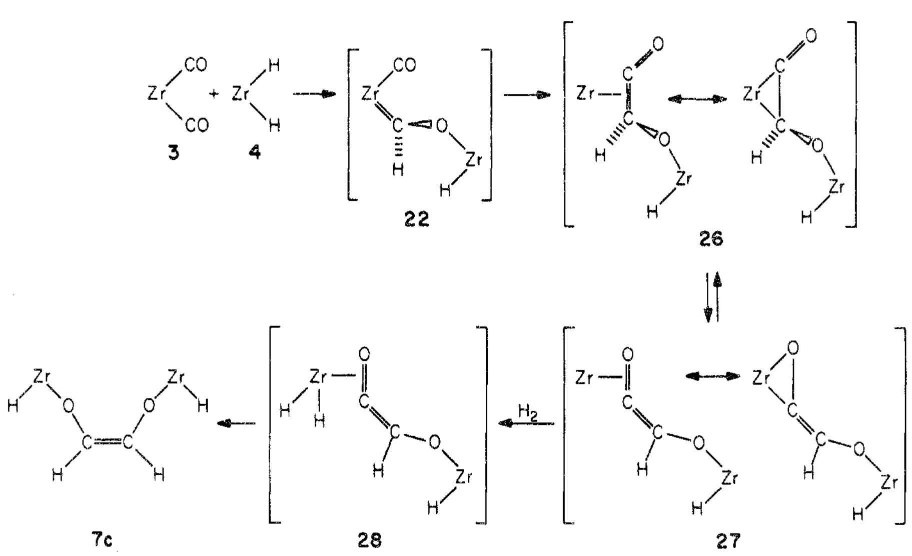
[22] P. T. Wolczanski, R. S. Threlkel, and J. E. Bercaw, *J. Am. Chem. Soc.*, **101**, 218 (1979).

[23] This reaction may be expected to proceed via a transient adduct of the type $[L_nM{-}C{\equiv}O{:}{\rightarrow}ZrH_2Cp^*_2]$.

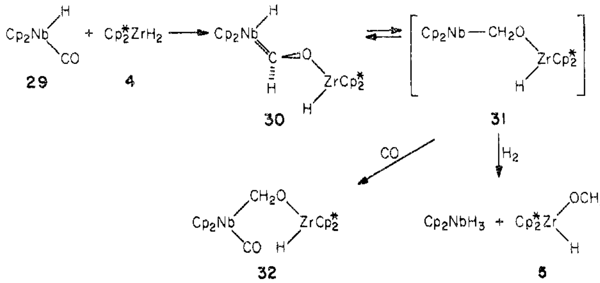
Scheme VI



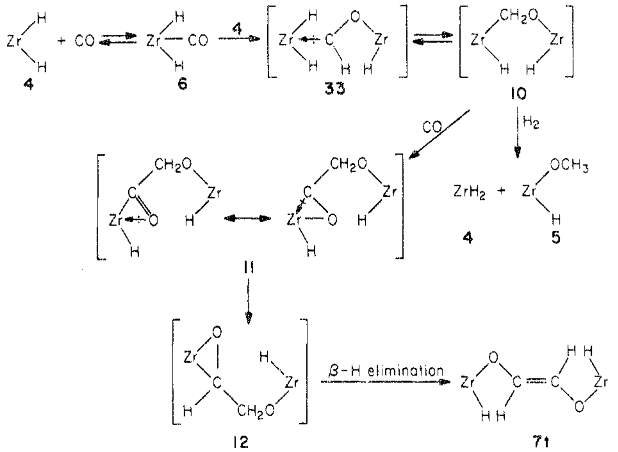
In view of the validity of the proposed reaction type (eq 13), at least for $(\eta^5\text{-}C_5H_5)_2M(CO)$ (M = Cr, Mo, W), a tentative mechanism for the formation of **7c** in reaction 12 may be proposed (Scheme V). Sequential addition of **4** to both carbonyl ligands would lead to the bis(carbene) complex **23** for which C=C bond formation leading to **24** might be anticipated to be rapid.[24] Dissociation of **7c** leaves $(\eta^5\text{-}C_5Me_5)_2Zr$ (**25**), which is known to react rapidly with H_2, affording **4**. The major difficulties with Scheme V are that the steric constraints imposed by the bulky $(\eta^5\text{-}C_5Me_5)$ ligands should disfavor formation of **7c**. Interaction of the carbon pπ orbitals with the filled equatorial orbitals for the unique $(\eta^5\text{-}C_5Me_5)_2Zr$ moiety for both **23** and **24** directs the carbene and olefin substituents, respectively, toward the pentamethylcyclopentadienyl rings. By analogy to the great steric preference for trans olefins exhibited by $(\eta^5\text{-}C_5Me_5)_2Ti$,[25] the bulky $(\eta^5\text{-}C_5Me_5)_2Zr(H)(O-)$ substituents should be trans (not cis as shown in Scheme V) in the sterically favored geometries for **23** and **24**, so that **7t** rather than **7c** should be the formed via the mechanism outlined in Scheme V.

An alternative mechanism which predicts the observed cis geometry involves rearrangement of the carbonyl–carbene intermediate **22** to the ketene adduct **26** (Scheme VI). Recent evidence appears to indicate that intramolecular coupling of CO and carbene ligands to yield coordinated ketenes may be a facile process.[26] The subsequent rearrangement **26** → **27** is analogous to similar fluxional processes for complexed allenes,[27] and should be driven by the high oxygen affinity of zirconium. The preferred geometry for **27** is expected to be that shown in Scheme VI, since for this isomer the distance between the large $[(\eta^5\text{-}C_5Me_5)_2Zr]$ moieties is maximized. It is this rearrangement that determines the geometry about the C=C double bond. Oxidative addition of H_2 followed by reductive elimination of the final C–H bond from **28** would indeed lead to **7c**.

Scheme VII



Scheme VIII



We have further investigated the scope of reaction 13, and have found that carbonyl complexes for a number of transition metals (Ti, Zr, Hf, Nb, Cr, Mo, W, Mn, Fe, Co) do react with $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (**4**); however, thus far only those complexes with a single carbonyl ligand (apart from the group 4 dicarbonyls) undergo clean conversions to the corresponding zirconoxycarbenes according to eq 13.[28] Particularly notable is the reaction of $(\eta^5\text{-}C_5H_5)_2Nb(H)(CO)$ with **4** (Scheme VII).[22,29] Here the expected zirconoxycarbene **30** is generated in nearly quantitative yield. The NMR and

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(24) M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 2172 (1977). Such coupling of carbenes does not, however, appear to be general; see R. R. Schrock, *Acc. Chem. Res.*, 12, 98 (1979).

(25) P. R. Auburn, S. A. Cohen, and J. E. Bercaw, manuscript in preparation.

(26) (a) W. A. Herrmann and J. Plank, *Angew. Chem., Int. Ed. Eng.*, 17, 525 (1978); (b) A. D. Redhouse and W. A. Herrmann, *ibid.*, 15, 615 (1976).

(27) (a) R. Ben-Shosan and R. Pettit, *J. Am. Chem. Soc.*, 89, 2231 (1967); (b) B. Foxman, D. Marten, A. Rosan, S. Raghu, and M. Rosenblum, *ibid.*, 99, 2160 (1977).

(28) P. T. Barger and J. E. Bercaw, unpublished results.

(29) R. S. Threlkel and J. E. Bercaw, unpublished results.

kinetic data indicate that **30** is in rapid equilibrium with its coordinatively unsaturated tautomer **31**, which may be trapped with CO, affording **32**, or with 2 equiv of H_2, affording $(\eta^5\text{-}C_5H_5)_2NbH_3$ and **5**.

In light of these new data (Schemes VI and VII) it is entirely justifiable to question, once again, the occurrence of an intramolecular migratory insertion of CO into a Zr–H bond of $(\eta^5\text{-}C_5Me_5)_2ZrH_2(CO)$ (**6**) (Scheme II), since an equally likely mechanism which avoids such a step may be formulated (Scheme VIII) from the aforementioned precedents. The primary difference between the two alternatives concerns the pathway to the proposed common intermediate **10**. Scheme II invokes reduction of the formyl hydride **8** by **4**; Scheme VIII direct reduction of **6**, the precursor to **8**. Migratory insertion into a Zr–H bond of the resultant zirconoxycarbene (**33**) would be closely analogous to **30** → **31** (Scheme VII). These are subtle but important differences which have thus far proven frustratingly difficult to test experimentally.

Conclusions and Prospects

At the outset of our investigation of the mechanism of reaction 2 we could scarcely imagine the wealth and commensurate complexity of the chemistry of carbon monoxide with $(\eta^5\text{-}C_5Me_5)_2ZrH_2$. Indeed, one of the great remaining enigmas is the clean, stoichiometric character of reaction 2, which yields only $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$ without detectable amounts of either of the enediolate-bridged dimers **7t** or **7c**. Perhaps the most important unsettled issue, however, centers around the proposal of intramolecular migratory insertion of CO into a Zr–H bond of $(\eta^5\text{-}C_5Me_5)_2ZrH_2(CO)$. Any mechanism for the H_2 reduction of carbon monoxide would appear to require a hydride transfer to carbon monoxide.[30] The unusual η^2 coordination anticipated for the formyl hydride $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CHO)$ could be argued to compensate for the otherwise adverse thermodynamics of the carbonyl hydride-to-formyl transformation.[31] Furthermore, the extremely facile migratory insertion of isocyanides into Zr–H bonds and rapid migratory insertion of CO into Zr–alkyl bonds establish a pathway for the intramolecular rearrangement of $(\eta^5\text{-}C_5Me_5)_2ZrH_2(CO)$ to $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CHO)$ (Scheme II). On the other hand, the apparent generality of the reduction of *coordinated* carbon monoxide by $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and the facility of the migratory insertion of the resultant zirconoxy carbene into a Nb–H bond are clearly supportive of a binuclear hydride transfer to CO (Scheme VIII). The consequences of our future findings relevant to these questions could have important implications concerning the number[2,32] and types of transition-metal centers required to "activate" H_2 reduction of CO.

The formation of the C=C coupled products, *cis*- and *trans*-$\{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2(\mu\text{-}OCH{=}CHO)$ (**7c** and **7t**, respectively), is an intriguing and unexpected result, as is the remarkable selectivity of the reactions which generate them. In retrospect our initial proposal that **7t** arises from coupling of the oxycarbene centers of the putative intermediate $(\eta^5\text{-}C_5Me_5)_2Zr(H)(\eta^2\text{-}CHO)$ is undoubtedly simplistic. The insertion of CO into the Zr–C bond of the common intermediate **10** leading to **7t** (Schemes II and VIII) is, on the other hand, closely modeled by the reactivity of CO with $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (Scheme III). Whereas the mechanism for the formation of **7c** remains rather speculative, the carbonyl–carbene coupling to afford a coordinated ketene (Scheme VI) would be expected to afford the observed cis geometry. Indeed, the possibility that such a carbene carbonyl → ketene transformation could be an elementary C–C coupling step in catalytic CO reducing systems does not yet appear to have been given serious consideration.

We are presently pursuing these questions with group 4 transition-metal hydrides analogous to $(\eta^5\text{-}C_5Me_5)_2ZrH_2$[33] and extending our synthetic efforts to group 5[34] and beyond in search of catalytic systems for the homogeneous H_2 reduction of CO.

Our studies have been generously supported by the National Science Foundation, Alfred P. Sloan Foundation, and Camille and Henry Dreyfus Teacher-Scholar Program. We wish to acknowledge the enthusiastic hard work of the students and postdoctoral fellows whose names appear in the references. Special thanks go to Richard S. Threlkel for permission to cite some of his results prior to publication.

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(30) Heterogeneous catalysts for which CO is dissociatively adsorbed are possible exceptions.

(31) The strong Al–O interaction is the apparent driving force for CO reduction by aluminum hydrides. See (a) L. I. Schoer and J. Schwartz, *J. Am. Chem. Soc.*, **99**, 5831 (1977); (b) C. Masters, C. van der Woude, and J. A. van Doorn, *ibid.*, **101**, 1633 (1979).

(32) (a) E. L. Muetterties, *Science*, **196**, 839 (1977); (b) M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976); (c) E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, **79**, 91 (1979).

(33) M. D. Fryzuk, D. M. Roddick, P. Seidler, and J. E. Bercaw, unpublished results.

(34) J. M. Mayer, C. J. Curtis, and J. E. Bercaw, unpublished results.