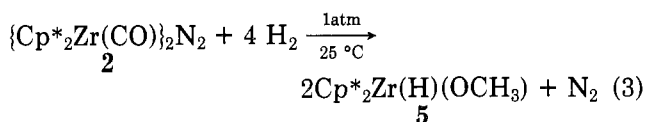


**Figure 1.** The molecular configuration and skeletal view of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrN}_2$  (1).

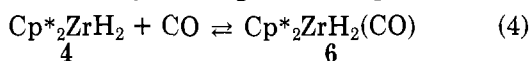
oxide by  $\text{H}_2$  under relatively mild conditions and thus offered a rare opportunity to examine certain features of its mechanism. Our studies of this reaction led us to examine the reactivity of alkyl and hydride derivatives of permethylzirconocene with CO, isocyanides, and other transition-metal carbonyls. This review summarizes our present understanding of the mechanism for reaction 2 and discusses possible mechanisms for several related reactions.

### Reactivity of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ with Carbon Monoxide

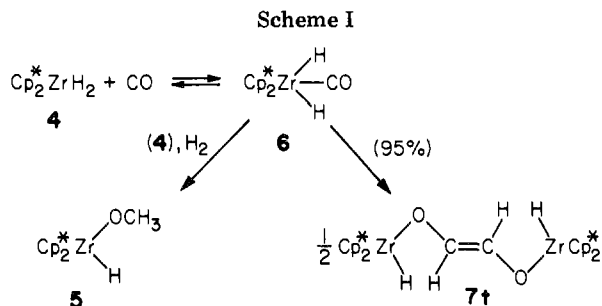
The evolution of 1 equiv of free CO in reaction 2 suggests the intermediacy of the coordinatively unsaturated species,  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})]$ . Such a suggestion is supported by the fact that **2** also reacts with  $\text{H}_2$  at room temperature to yield predominantly **5** (eq 3).



Oxidative addition of  $\text{H}_2$  to  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})]$  to generate  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$  (**6**) also appears plausible. An independent route to **6** was therefore investigated, and indeed  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$  (**4**) was found to reversibly absorb 1 equiv of carbon monoxide at  $-80^\circ\text{C}$  (eq 4). The two hydride ligands of **6** give rise to a

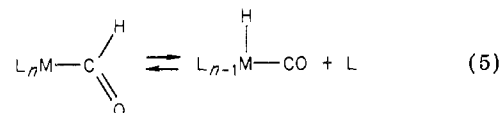


singlet in its  $^1\text{H}$  NMR spectrum (220 MHz,  $-64^\circ\text{C}$ ), which splits into a doublet for  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$  ( $^{13}\text{C}$ ) with  $J_{\text{C-H}} = 25$  Hz. These data indicate a symmetric structure for **6**, with CO occupying the central equatorial position mutually cis to both hydride ligands.



As the solution of **6** is slowly warmed to  $-50^\circ\text{C}$ , the  $^1\text{H}$  NMR spectrum attributed to **6** decays concomitant with the growth of the spectrum of a new species, subsequently identified as *trans*- $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}\}_2(\mu\text{-OCH}=\text{CHO})$  (**7t**). No intermediates are observed by  $^1\text{H}$  NMR spectrometry. When solutions of **6** are warmed under 1 atm of  $\text{H}_2$ , 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  $\text{H}_2$ , 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  $\text{H}_2$  to **5** in competition with its dimerization to **7t**. An immediate candidate for such an intermediate is the formyl species  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{CHO})$  (**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).<sup>5</sup> The con-



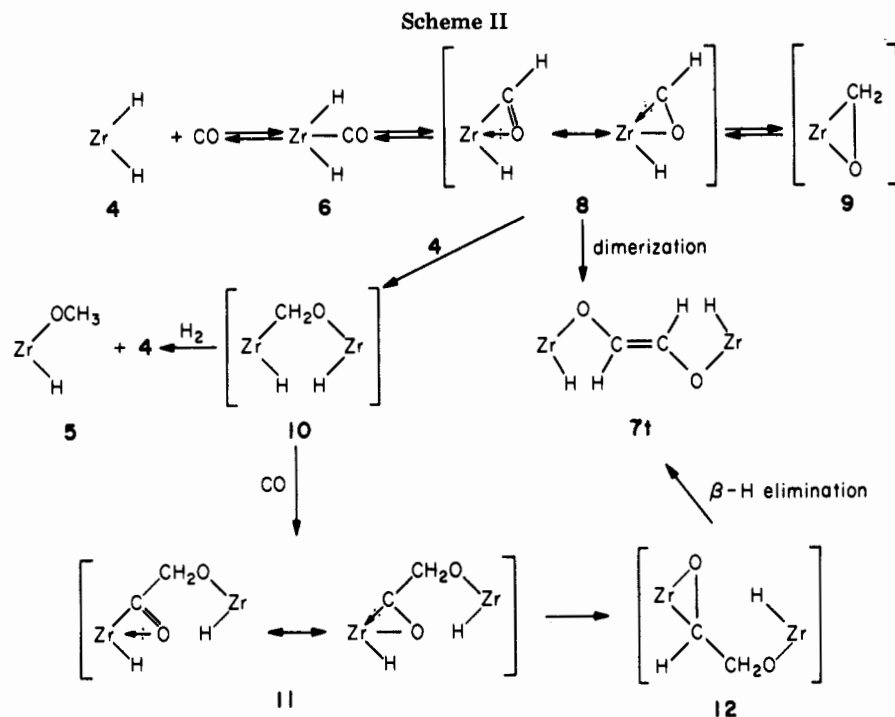
version of  $(\text{CO})_5\text{MnH}$  to  $(\text{CO})_5\text{Mn}(\text{CHO})$  has been estimated to be endothermic by roughly  $20 \text{ kcal mol}^{-1}$ ,<sup>10</sup> so that the equilibrium position for eq 5 appears to lie far to the right, at least for the “late” transition metals.

On the other hand, an unconventional  $\eta^2$  bonding of the formyl ligand may be expected for **8** by analogy to the structures recently established by Floriani and co-workers<sup>11</sup> for the closely related acyl derivatives  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{CH}_3\text{CO})$ . This  $\eta^2$  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<sup>12</sup>

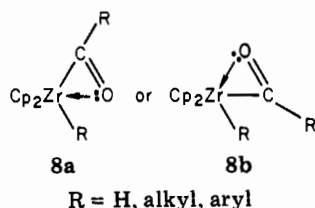
(10) Assuming  $D[(\text{CO})_5\text{Mn-H}] = 65 \text{ kcal mol}^{-1}$ ,  $D[(\text{CO})_5\text{Mn-CHO}] = 25 \text{ kcal mol}^{-1}$ , and  $D[\text{H-CO}] = 20 \text{ kcal mol}^{-1}$ ; J. Halpern, private communication.

(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).

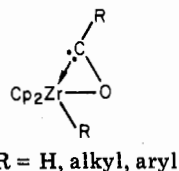
(12) (a) J. C. Green, M. L. H. Green, and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, 30, 373 (1972); (b) H. H. Brintzinger and L. S. Bartell, *J. Am. Chem. Soc.*, 92, 1105 (1970); (c) A. J. Petersen and L. F. Dahl, *ibid.*, 96, 2248 (1974); (d) J. W. Lauher and R. Hoffmann, *ibid.*, 98, 1729 (1976).



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



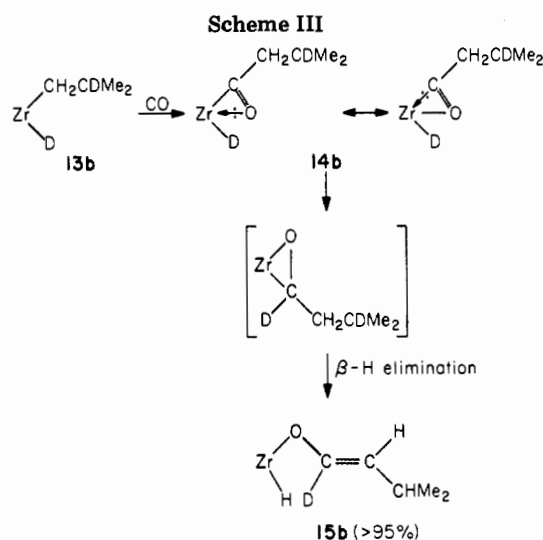
implicates 8b as the kinetic product of migratory insertion, which subsequently rearranges to 8a.<sup>13</sup> This high oxygen affinity of the early transition metals may thus be invoked to override the otherwise adverse thermodynamics of the migratory insertion of CO into a Zr-H bond of 6. Furthermore,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



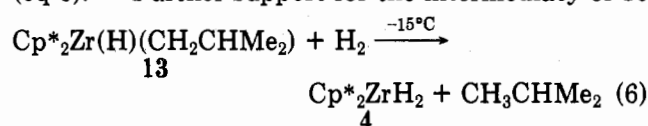
the acyl group is bonded by a full covalent Zr-O bond and a dative interaction of the oxycarbene lone pair completing the valence shell at zirconium.

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 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub>, 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<sub>2</sub> would thus yield 5, regenerating 4. This final step (10 + H<sub>2</sub> → 5 + 4) is in close analogy to the facile reductive elimination of isobutane

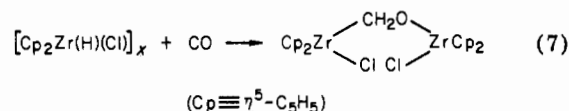
(13) G. Erker and F. Rosenfeldt, *Angew. Chem., Int. Ed. Engl.*, **17**, 605 (1978).



from ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(CH<sub>2</sub>CHMe<sub>2</sub>) (13) induced by H<sub>2</sub> (eq 6).<sup>14</sup> Further support for the intermediacy of 10



has been reported by Floriani and co-workers;<sup>15</sup> treatment of [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(H)(Cl)]<sub>x</sub> with carbon monoxide was shown to afford initially {( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub>( $\mu$ -CH<sub>2</sub>O)} (eq 7). The further absorption of a second equivalent

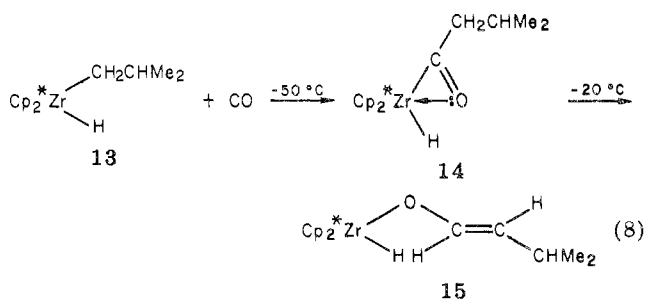


of CO was observed; however, the resulting complex has not been characterized.

(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.

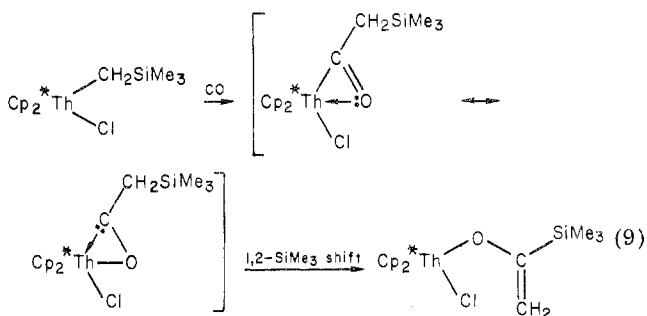
(15) G. Fachinetti, C. Floriani, A. Roselli, and S. Pucci, *J. Chem. Soc., Chem. Commun.*, 269 (1978).

The reactivity of **13** with carbon monoxide<sup>16,17</sup> 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*-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(OCH=CHCHMe<sub>2</sub>) (**15**) (eq 8). The results of a deuterium labeling ex-



periment 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**.

Explicit in the discussions of all possible mechanisms thus far is the proposed oxycarbenoid reactivity imparted to the carbon center by the unusual  $\eta^2$  coordination of the acyl (or formyl) group to the permethylzirconocene moiety. More recently Manriquez et al.<sup>18</sup> 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 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(Cl)(CH<sub>2</sub>SiMe<sub>3</sub>) with CO affords ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(Cl)(OC(SiMe<sub>3</sub>)=CH<sub>2</sub>) (eq 9).



These ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>M (M = Th, U) derivatives which are often very similar in reactivity to the corresponding ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr derivatives.<sup>18,19</sup>

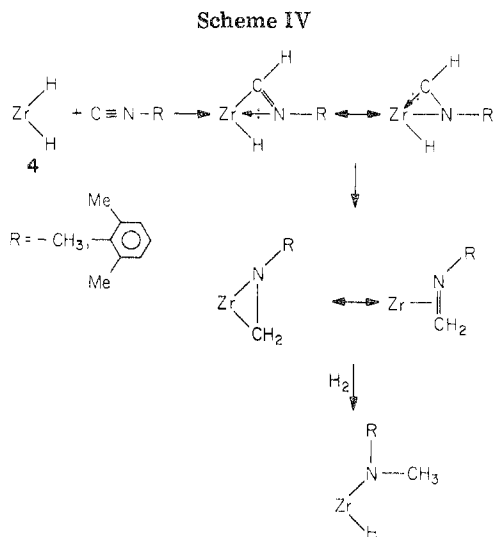
As will become apparent in the next section, an issue crucial to the viability of Scheme II concerns the question of *intramolecular* migratory insertion of CO into a Zr-H bond (i.e., **6** → **8**, Scheme II). In light of previous findings that isoelectronic isocyanides (but not CO) undergo migratory insertion into Ru-H, Os-H, and Pt-H bonds,<sup>20</sup> it appeared necessary to establish

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

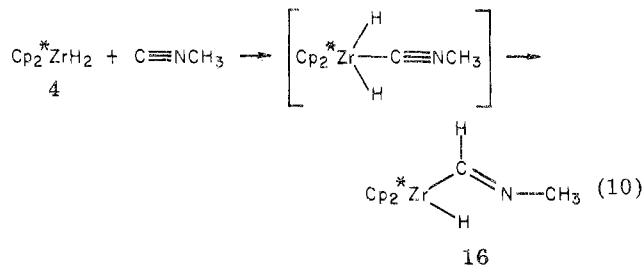
(17) For similar chemistry with the parent Cp<sub>2</sub>ZrH(R) see K. I. Gell and J. Schwartz, *J. Organomet. Chem.*, **162**, C11 (1978).

(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).



whether or not this process could be observed for ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub> (**4**).<sup>21</sup> Methyl isocyanide does indeed react rapidly with **4** at -65 °C to afford directly the formimidoyl hydride ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(CH=NCH<sub>3</sub>) (**16**) (eq 10).



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).<sup>21</sup>

### Reactivity of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub> with Coordinated Carbon Monoxide

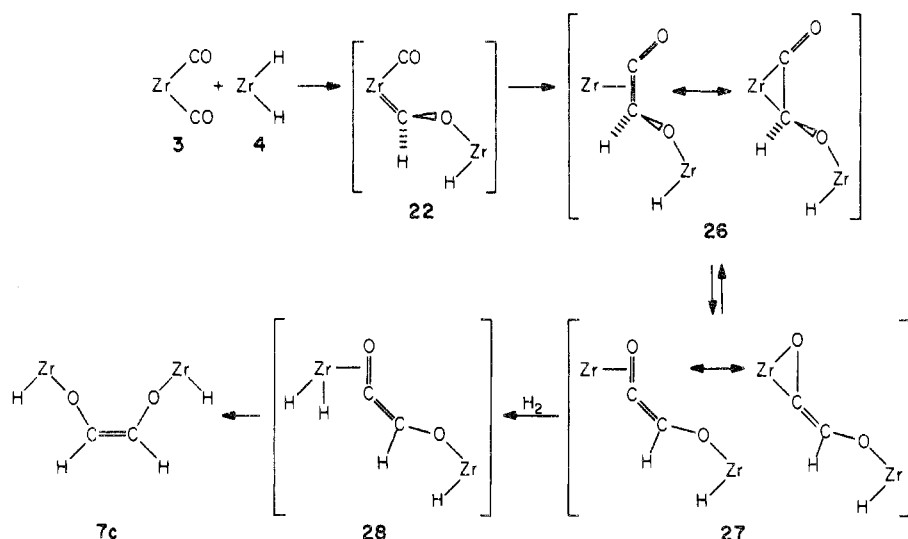
Our studies of the reactivity of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub> (**4**) with CO do appear to have some bearing on the mechanism for the H<sub>2</sub> reduction of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(CO)<sub>2</sub> (**3**) to ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(OCH<sub>3</sub>) (**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-

(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).



Scheme VI



In view of the validity of the proposed reaction type (eq 13), at least for  $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{CO})$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ), 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.<sup>24</sup> Dissociation of **7c** leaves  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}$  (**25**), which is known to react rapidly with  $\text{H}_2$ , affording **4**. The major difficulties with Scheme V are that the steric constraints imposed by the bulky  $(\eta^5\text{-C}_5\text{Me}_5)$  ligands should disfavor formation of **7c**. Interaction of the carbon  $\pi$  orbitals with the filled equatorial orbitals for the unique  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}$  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  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}$ ,<sup>25</sup> the bulky  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{O}^-)$  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.<sup>26</sup> The subsequent rearrangement **26**  $\rightarrow$  **27** is analogous to similar fluxional processes for complexed allenes,<sup>27</sup> 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  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}]$  moieties is maximized. It is this rearrangement that determines the geometry about the C=C double bond. Oxidative

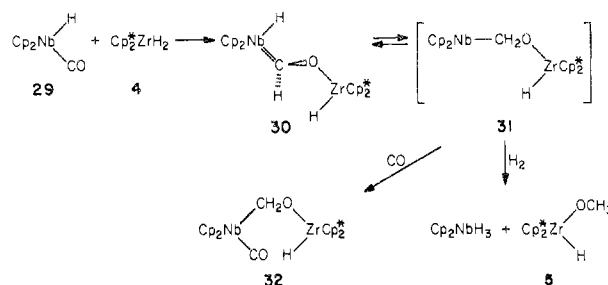
(24) M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 2172 (1977). Such coupling of carbenes does not, however, appear to be general; see R. R. Schrock, *Acc. Chem. Res.*, 12, 98 (1979).

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

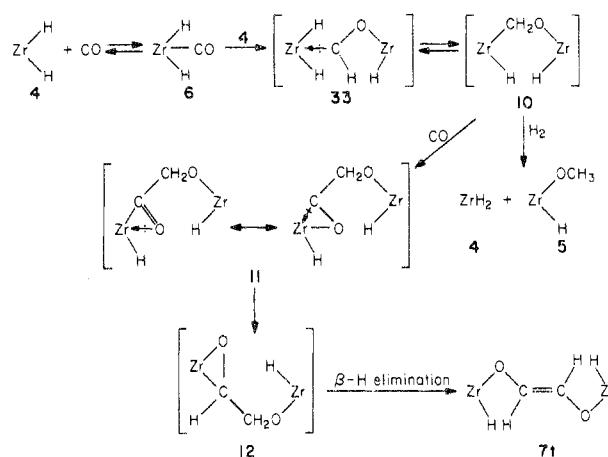
(26) (a) W. A. Herrmann and J. Plank, *Angew. Chem., Int. Ed. Eng.*, 17, 525 (1978); (b) A. D. Redhouse and W. A. Herrmann, *ibid.*, 15, 615 (1976).

(27) (a) R. Ben-Shoshan 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).

Scheme VII



Scheme VIII



addition of  $\text{H}_2$  followed by reductive elimination of the final C-H bond from **28** would indeed lead to **7c**.

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  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$  (**4**); however, thus far only those complexes with a single carbonyl ligand (apart from the group 4 dicarbonyls) undergo clean conversions to the corresponding zircononoxycarbene according to eq 13.<sup>28</sup> Particularly notable is the reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{H})(\text{CO})$  with **4** (Scheme VII).<sup>22,29</sup> Here the expected zircononoxycarbene **30** is generated in nearly quantitative yield. The NMR and

(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<sub>2</sub>, affording (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NbH<sub>3</sub> 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 (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub>(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 (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub>. Indeed, one of the great remaining enigmas is the clean, stoichiometric character of reaction 2, which yields only (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(OCH<sub>3</sub>) 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 (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub>(CO). Any mechanism for the H<sub>2</sub> reduction of carbon monoxide would appear to require a hydride transfer to carbon monoxide.<sup>30</sup> The unusual η<sup>2</sup> coordination anticipated for the formyl hydride (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(CHO) could be argued to compensate for the otherwise adverse thermodynamics of the carbonyl hydride-to-formyl transformation.<sup>31</sup> 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 re-

arrangement of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub>(CO) to (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(CHO) (Scheme II). On the other hand, the apparent generality of the reduction of *coordinated* carbon monoxide by (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub> and the facility of the migratory insertion of the resultant zirconoxycarbene 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<sup>2,32</sup> and types of transition-metal centers required to "activate" H<sub>2</sub> reduction of CO.

The formation of the C=C coupled products, *cis*- and *trans*-{(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH}<sub>2</sub>(μ-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 (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(η<sup>2</sup>-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 (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(CH<sub>2</sub>CHMe<sub>2</sub>) (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 (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub><sup>33</sup> and extending our synthetic efforts to group 5<sup>34</sup> and beyond in search of catalytic systems for the homogeneous H<sub>2</sub> reduction of CO.

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