Organometallic Reaction Mechanisms: Catalytic Cyclotrimerization of Alkynes, Reduction of Carbon Monoxide and Reductive Elimination from an Alkylhydride Complex.

Thesis by

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to Merrie Jo

(actually it's none of your
business why)

Acknowledgements

It is not without some trepidation that I attempt to appropriately acknowledge those who share responsibility for the work presented in this thesis. On one hand it would be embarrassing to fail to mention anyone actually desirous of inclusion; but on the other hand it would certainly be impolite to risk stigmatizing anyone by unwanted association. Consequently, rather than agonize over subtle nuances of social or scientific values, I have provided a number (3) of blank spaces in which anyone so inclined may place the names of themselves or of their friends and/or enemies as they see fit.

I am sincerely indebted to:

_____

_____

_____

for his/her/their contribution(s).

I am of course very grateful to Marla Turner for her truly elite typing. I also would like to thank my research directors--Dr. R. G. Bergman and Dr. J. E. Bercaw--without whom this thesis would not have been possible. Likewise, I would like to thank my parents--Nina L. and Robert C. McAlister--without whom this thesis would not have been necessary. Finally, I am as always deeply appreciative of anyone who gave me money, including: Caltech, Dr. and Mrs. Zechmeister, my aforementioned research directors and of course ultimately, NSF-that "great mammary in the sky".

Abstract: Chapter I

The cobaltacyclic compound, $(\eta^5\text{-}C_5H_5)\overline{Co(C(CH_3)=C(CH_3)c(CH_3)=C(CH_3)}$ (PPh_3) (3a), formed by reaction of $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (1a) with 2-butyne is shown to be an efficient catalyst for cyclotrimerization of alkynes to provide arenes. An investigation of the substitution reactions of PMe_3 and 2-butyne with 1a and with its PMe_3 containing congeners (1b and 1c) is reported. A mechanism consistent with this data and in accord with the observed dependence of the rate of formation 3a on PPh_3 and 2-butyne concentration is proposed.

The kinetics of the cyclotrimerization of 2-butyne catalyzed by 3a both in the presence and absence of excess PPh_3 and the kinetics of substitution of PEt_3 for PPh_3 in 3a are reported. These results indicate a mechanism involving rate determining coordination of 2-butyne to cobalt. In contrast the reaction of $C_2(CO_2Me)_2$ (dma) with the PMe_3 substituted analog of 3a, (3c), is shown to proceed without prior coordination of the alkyne.

Abstract: Chapter II

Bis (pentamethyl cyclopentadienyl)-dihydrido zirconium (IV) $(\eta^5\text{-}C_5Me_5)_2\ ZrH_2$ (2) forms unstable adducts with PF_3 and CO at -80°. The carbonyl adduct $(\eta^5\text{-}C_5Me_5)_2\ ZrH_2(CO)$ yields $\{(\eta^5\text{-}C_5Me_5)_2\ ZrH\}_2$ (μ-OCH=CHO) and/or $(\eta^5\text{-}C_5Me_5)_2\ ZrH(OCH_3)$ upon warming depending on conditions. Carbonylation of $(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)_2$ provides successively $(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)(C(=O)CH_3)$ and $(\eta^5\text{-}C_5Me_5)_2\ \overline{Zr(OC(Me)=C(Me)O)}$. Reaction of the zirconocyclopentane, $(\eta^5\text{-}C_5Me_5)_2\ \overline{Zr(CH_2(CH_2)_2CH_2)}$, with CO affords $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)\ (\overline{OC=CH(CH_2)_2CH_2})$. Treatment of 2 with isobutylene gives $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)\ (CH_2CHMe_2)$ (13), which reacts with CO to give $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)\ (OCH=CH(CHMe_2))$(15). The results of ^{13}C and deuterium labeling studies indicate that $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)\ (C(=O)CH_2CHMe_2)$ is an intermediate in conversion of 13 to 15. The observed reaction patterns of alkyl and hydride derivatives of zirconium with CO are attributed to carbenoid character of the carbonyl carbon resulting from an unusual "side-on" coordination of acyl or formyl groups.

Abstract: Chapter III

The alkyl hydride complex $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (5a), prepared by reaction of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (4) with isobutylene, is a monomeric, pseudotetrahedral compound. In direct contrast to other transition metal complexes bearing cis hydride and alkyl ligands it is reasonably thermally stable. However, isobutane is evolved from 5a upon thermolysis at 75°. Reaction with H_2 or ethylene also results in generation of isobutane.

The isotopically labeled complexes $(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ (5b) and $(\eta^5\text{-}C_5(CD_3)_5)_2Zr(D)(CH_2CD(CH_3)_2)$ (5c) are prepared by reaction of isobutylene with $(\eta^5\text{-}C_5Me_5)_2ZrD_2$ and $(\eta^5\text{-}C_5(CD_3)_5)_2ZrD_2$, respectively. The deuterium distribution in isobutanes resulting from thermolysis of 5a, b and c and from their reactions with H_2, D_2, C_2H_4 and C_2D_4 were determined. The rates of thermolysis of those complexes are also reported. Mechanisms consistent with these data are proposed. For the cases of thermolysis and reaction with H_2, the suggested mechanisms are similar to those proposed to account for exchange processes between 4 and a deuterium atmosphere.

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Chapter I

Kinetics and Mechanism of Alkyne Cyclotrimerization Catalyzed by Cyclopentadienylcobalt(I) Complexes.

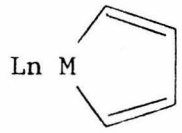
"Mixing memory and desire."

T.S.E.

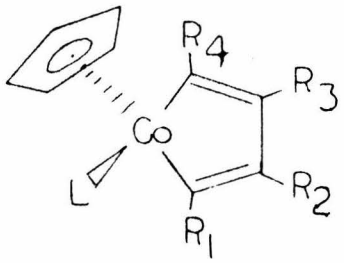
Introduction

Many low valent transition metal compounds promote the cyclotrimerization of alkynes to afford arenes.[2-4] The mechanisms of several catalytic cyclooligomerization systems have been investigated; however, these studies have primarily involved the isolation or identification of intermediates. There has not as yet been an attempt at a detailed analysis of the kinetics of one of these reactions.

The intermediacy of metallocyclopentadienes (metalloles):



is a common feature of many alkyne cyclotrimerization reactions. Metalloles, formed by oxidative cyclization of two alkynes with a low valent metal center, have been detected or inferred in systems employing iridium[5], platinum and palladium[6], iron[7], nickel[8], chromium[9], and cobalt[10] catalysts. Recently, H. Yamazaki[10] has shown $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (1) and resulting metallocycles (3):



with $R_1=R_2=R_3=R_4=$ Me

3a; L = PPh_3

3b; L = PEt_3

3c; L = PMe_3

to be very efficient in promotion of cyclotrimerization of disubstituted acetylenes. Catalytic and stoichiometric procedures for preparation of arenes, pyridines[11,12], cyclohexadienes[13], and benzocyclobutenes[14] from alkynes and nitriles have been developed based on

these and related cyclopentadienylcobalt complexes. In view of the generality and (potential) utility of these reactions a detailed kinetic and mechanistic study appeared to be warranted.

Results

1. Preparation of $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (1a) and its Reactions with 2-Butyne. Cyclopentadienylcobalt (I) bis(triphenylphosphine) (1a) is most conveniently prepared by the method of Rinze et al.[15] (eq 1 and 2).

$$Co(acac)_3 + 3PPh_3 \xrightarrow[N_2,\ \text{toluene}]{Al(\text{iso-}C_4H_9)_3} (PPh_3)_3Co(N_2)H \qquad (1)$$

$$(PPh_3)_3Co(N_2)H + 2\ C_5H_6 \xrightarrow[\text{benzene}]{} (\eta^5\text{-}C_5H_5)Co(PPh_3)_2 + C_5H_8 + PPh_3 \qquad (2)$$

It is isolated as a dark red, crystalline, air-sensitive material. In refluxing benzene $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$(1a) reacts with two equivalents of 2-butyne to afford the metallocycle, triphenylphosphine cyclopentadienylcobalta-2,3,4,5-tetramethylcyclopentadiene (3a) (eq 3) in quantitative yield (nmr).

$$(\eta^5\text{-}C_5H_5)Co(PPh_3)_2 + 2CH_3C{\equiv}CCH_3 \longrightarrow \text{[Me, Me, Co, } Ph_3P\text{, Me, Me]} + PPh_3 \qquad (3)$$

The reaction of 1a with excess 2-butyne can be monitored by ^{1}H-nmr spectrometry. (The ^{1}H-nmr spectral assignments of compounds encountered in this study are collected in Table I.) Initial spectra of a benzene-d_6 solution of 1a with 2.5 molar equivalents of 2-butyne indicate the formation of a mono-acetylene complex, $(\eta^5\text{-}C_5H_5)Co(PPh_3)(CH_3C{\equiv}CCH_3)$ (2a). In contrast to the mono-acetylene complexes prepared

by Yamazaki[13] from reaction of 1a with "activated" acetylenes (i.e., those possessing ester or phenyl substituents) 2a appears to be formed reversibly. This, coupled with its enhanced solubility in hydrocarbon solvents, has prevented its isolation. Heating the sample at 78° for a few hrs causes smooth, quantitative conversion of 1a (and 2a) to the yellow, brown cobaltacycle, 3a, identified by elemental analysis and ^{1}H-nmr spectroscopy (Table I and Experimental Section). Further heating induces (catalytic) cyclotrimerization of the remaining 2-butyne giving hexamethylbenzene (4). No significant decomposition of the cobaltacycle (3a) is observed under these conditions.

2. Substitution Reactions of Cyclopentadienylcobalt (I) Phosphine Complexes. The value of the equilibrium constant for formation of mono-acetylene complex, 2, by reaction of 1a with 2-butyne (eq 4) was determined at various temperatures by ^{1}H-nmr spectrometry (Table II)

$$(\eta^5\text{-}C_5H_5)Co(PPh_3)_2 + CH_3C{\equiv}CCH_3 \rightleftharpoons (\eta^5\text{-}C_5H_5)Co(PPh_3)(CH_3C{\equiv}CCH_3) + PPh_3 \quad (4)$$

A plot of $\ln(K_{eq})$ vs. T^{-1} was linear and gave thermodynamic parameters: $\Delta H° = 3.4(\pm 1.0)$ kcal/mole and $\Delta S° = 10.4(\pm 1.0)$ eu.

It is also possible to substitute other donor ligands for the PPh_3 of 1a. Thus in the presence of excess trimethylphosphine (PMe_3) 1a is very rapidly converted to (^{5}-C_5H_5)$Co(PMe_3)_2$ (1c) as in eq. 5.

$$(\eta^5\text{-}C_5H_5)Co(PPh_3)_2 + 2PMe_3 \longrightarrow (\eta^5\text{-}C_5H_5)Co(PMe_3)_2 + 2PPh_3 \qquad (5)$$

The preference of the electron rich cobalt (I) center for the more basic but smaller trimethylphosphine suggests that steric bulk rather than electronic properties determines the binding of phosphine ligands in these complexes.[16] Treatment of 1a with just one equivalent of PMe_3 provides only the mixed phosphine complex, $(\eta^5\text{-}C_5H_5)Co(PPh_3)(PMe_3)$ (1b) as in eq 6.

$$(\eta^5\text{-}C_5H_5)Co(PPh_3)_2 + PMe_3 \longrightarrow (\eta^5\text{-}C_5H_5)Co(PPh_3)(PMe_3) + PPh_3 \qquad (6)$$

This stepwise replacement of triphenyl by trimethylphosphine suggests a dissociative substitution scheme in which the bulkier ligand is always the more labile. Hence reaction of 1b with 2-butyne was expected to provide $(\eta^5\text{-}C_5H_5)Co(PMe_3)$(2-butyne).

The reaction of 1b, prepared in situ (eq 6) and consequently accompanied by one equivalent PPh_3, with excess 2-butyne was followed by ^{1}H-nmr spectroscopy. At 25° no reaction is observed, apparently because the lability of PPh_3 in 1b is less than in the sterically more crowded complex, 1a. At 75° reaction occurs, however no mono-acetylene complex is detected. Instead, the metallocycle bearing PPh_3 ligand (3a) and the bis trimethylphosphine complex (1c) are initially observed to grow in at equal rates. Eventually both of these products are converted to 3c, the PMe_3 substituted metallocycle, which is the final product. The replacement of the PPh_3 of 3a with PMe_3 to provide 3c is irreversible under these conditions. (Note that

3c does not catalyze cyclotrimerization of 2-butyne at 75°). Formation of 3a requires either preferential substitution of the PMe_3 ligand (rather than the PPh_3) of 1b, which is contraindicated by the substitution patterns with additional PMe_3 reported above, or dissociation of both phosphine ligands of 1b prior to formation of metallocycle. This latter possibility indicates the intermediacy of a bis alkyne complex in metallocycle formation.

3. Kinetics of 2-Butyne Cyclotrimerization. Although formation of metallocycle, 3a, from reaction of 1a with 2-butyne (eq 3) is clearly a complicated, multistep process, the kinetics of the overall transformation were investigated. Reactions at 74° of 1a with greater than ten fold excess 2-butyne in the presence of a pseudo-first-order excess of PPh_3 were monitored by ^{1}H-nmr and by visible absorption spectrometry. Observed pseudo-first-order rates of formation of 3a are reported on Table III as a function of alkyne and phosphine concentration. Unfortunately, the dependence of the rate is complex and it was not possible to satisfactorily fit the data with any simple rate law.[17]

The kinetics of catalyzed cyclotrimerization of 2-butyne to give hexamethylbenzene (4) (eq 7) proved to be more amenable to analysis.

$$3CH_3C{\equiv}CCH_3 \xrightarrow[\text{3a, } PPh_3]{120^\circ,\ \text{benzene-}d_6} C_6(CH_3)_6 \qquad (7)$$

At 120° in benzene-d_6 solution in a sealed nmr tube, the conversion of 2-butyne to hexamethylbenzene (4) catalyzed by 3a could conveniently

be monitored by ^{1}H-nmr spectroscopy. In the presence of excess PPh_3 the pseudo-first-order rates of formation of 4 (see Table IV) fit the expression:

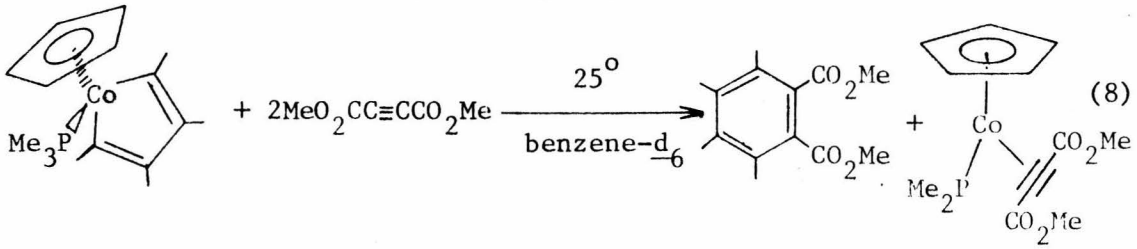
$$\frac{d[4]}{dt} = \frac{k_{obsd}[3a][2\text{-butyne}]}{PPh_3}$$

where $k_{obsd} = (5.1 \pm 0.5) \times 10^{-5} s^{-1}$. The inverse dependence of rate on phosphine concentration and direct dependence on 2-butyne is consistent with a mechanism featuring competition for a coordinatively unsaturated metallocyclic intermediate generated by loss of phosphine from 3a. Moreover, in the absence of excess PPh_3 the rate of appearance of 4 at 74° in a reaction mixture initially 1.9 M in 2-butyne and 0.2 M in 3a was constant $(2.0 \pm 0.2) \times 10^{-5}$ M s^{-1} for over five turnovers of the catalyst. Lack of dependence of rate on alkyne concentration indicates that at this lower temperature and in the absence of excess PPh_3 the rate determining step becomes dissociation of PPh_3 from the catalyst.

The rate of phosphine dissociation from 3a was determined from the kinetics of its substitution reactions. Thus, in benzene-d_6 solution at 74° both PEt_3 and PMe_3 quantitatively replace PPh_3 in 3a providing 3b and 3c, respectively. The first order rate of formation of 3b, $(5.8 \pm 0.5) \times 10^{-5}$ s^{-1}, is independent of PEt_3 concentrations varying from a 3 to a 20 fold molar excess over 3a (Table V). Although the rate was not accurately determined, PMe_3 appears to substitute for PPh_3 in 3a at about the same rate as does PEt_3. Lack of reaction order in entering ligand implies that here, as in the catalytic

reaction of 2-butyne with 3a in the absence of excess phosphine, the rate of the reaction is determined by the rate of dissociation of PPh_3 from 3a. In accord with this hypothesis, it is observed that 3c does not induce cyclotrimerization of 2-butyne at 74° and even after several days at 120° reaction of 3c with 2-butyne in the absence of excess phosphine produces only very little hexamethylbenzene.

4. Reaction of Dimethylacetylenedicarboxylate with 3c. The reactions of these cobaltacycles with dimethylacetylenedicarboxylate (dma) are in striking contrast to their reactions with 2-butyne. Investigation of reaction of dma with 3a is hampered by the very rapid reaction of the diester acetylene with liberated phosphine[18], leading to irreversible decomposition of the metallocycle and a plethora of phosphorous containing organic compounds. However, dissociation of the trialkylphosphines, PEt_3 and PMe_3, from 3b and 3c, respectively, has been shown to be much slower than dissociation of PPh_3 from 3a. In contradistinction to the lack of reaction of 2-butyne with 3c at 74°, dma reacts cleanly and rapidly at 25° in accord with eq 8.



(8)

The products are the expected arene, 3,4,5,6-tetramethylphthalate dimethyl ester (5), and a monoacetylene complex, $(\eta^5\text{-}C_5H_5)Co(PMe_3)(dma)$ (6), identified by their ^{1}H-nmr spectra (see Table I and Experimental Section).

The kinetics of this reaction were monitored by both ^{1}H-nmr and

visible spectrometry. In the presence of excess dma the pseudo-first-order rates (see Table VI) fit the expression:

$$\frac{d[\underline{5}]}{dt} = -\frac{d[\underline{3c}]}{dt} = k_8 [\underline{3c}] [dma]$$

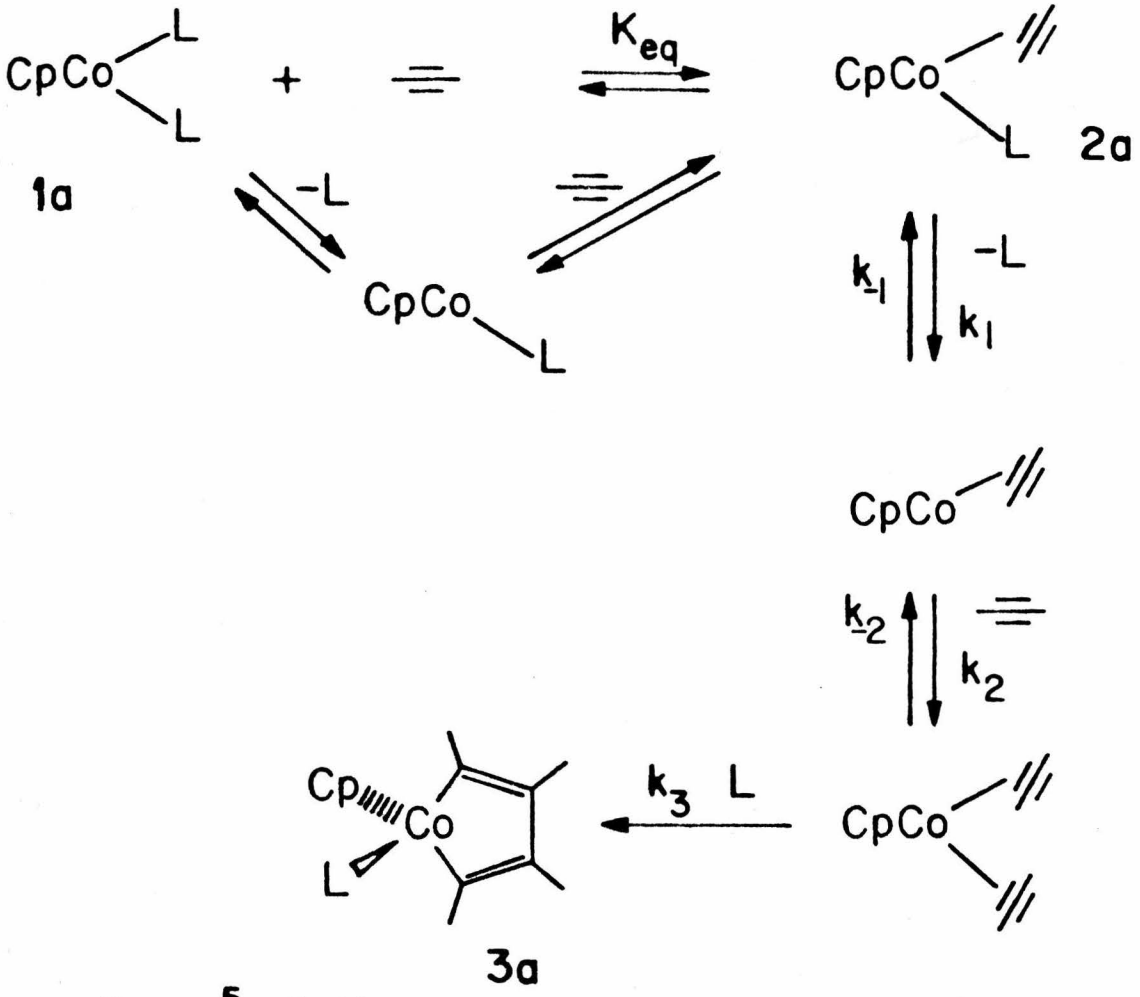
where at 24° the value of the second order rate constant (k_8) is $(2.7 \pm 0.3) \times 10^{-3}$ $\underline{M}^{-1}$ S^{-1}. (Of course, study of the effect of excess phosphine on this process is precluded by the rapid reaction of dma with phosphines[18]). These data clearly indicate that reaction of dma with 3c proceeds readily without prior dissociation of phosphine; and hence, presumably, without entry of dma into the coordination sphere of cobalt.[19]

Discussion

Promotion of the catalytic cyclotrimerization of 2-butyne by $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (1a) proceeds in two steps. First is the formation of the "active catalyst", cobaltacycle (3a), by reaction of 1a with 2-butyne. The subsequent catalysis of hexamethylbenzene(4)formation from reaction of 3a with 2-butyne is a somewhat slower process. The catalytic cycle appears to include regeneration of 3a from cobalt (I) intermediates in a fashion similar to its original formation from 1a and 2-butyne.

The substitution reactions of PMe_3 with 1a provide a framework about which a mechanism of formation of 3a can be constructed. The relative rates of reaction of 1a and 1b with PMe_3 (1a > 1b) and of 1a, 1b and 1c with 2-butyne (1a > 1b > 1c) suggest dissociative substitution processes with the sterically bulkier ligand in the more crowded environment being the most labilized. Thus the equilibrium of eq 4 between 1a and the monoacetylene complex, 2a, almost certainly involves the intermediacy of a coordinatively unsaturated complex bearing a single phosphine ligand, $(\eta^5\text{-}C_5H_5)Co(PPh_3)$. Subsequent loss of the bulkier ligand of 2a, the PPh_3, and addition of 2-butyne affords the bis alkyne complex, $(\eta^5\text{-}C_5H_5)Co(2\text{-butyne})_2$, which was indicated to be an intermediate by the initial formation of 3a in reaction of 1b with 2-butyne discussed above.

Unfortunately, since we were neither able to prepare nor directly detect a bis alkyne complex, little can be concluded regarding the mode of its conversion to metallocycle. The mechanism suggested in Scheme I proposes a bimolecular, i.e. phosphine assisted, oxidative-



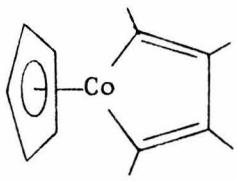
Cp = $\eta^5 - C_5H_5$

L = PPh_3

Scheme I.

cyclization. While such an associative process is not unambiguously required it is consistent with the data for overall rate of formation of 3a from 1a and 2-butyne.[20] However, the kinetics of 2-butyne catalytic cyclotrimerization under conditions of low phosphine concentration do suggest direct regeneration of 3a from reaction of cyclopentadienylcobalt (I) intermediates (presumably including a bis 2-butyne complex) with PPh_3 and 2-butyne as will be discussed below. The direct formation of 3a rather than a coordinatively unsaturated metallocyclic precursor is indicative of phosphine assistance of the oxidative cyclization. The lesser steric requirements of 2-butyne as compared to the PPh_3 ligands might allow such an associative process for the bis alkyne complex.

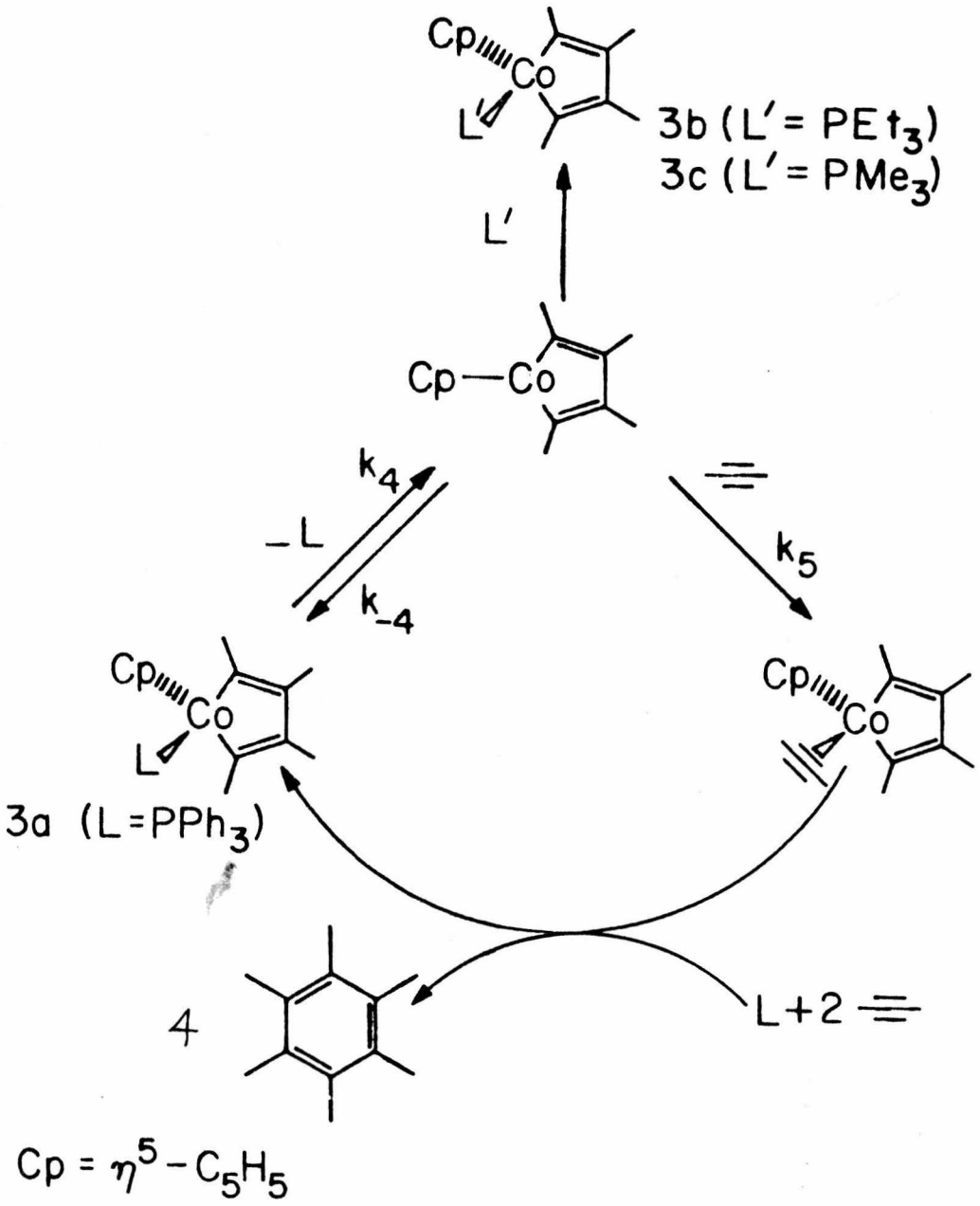
A mechanism for cyclotrimerization of 2-butyne catalyzed by 3a in the presence of PPh_3 is presented in Scheme II. It features rate determining competition between phosphine and 2-butyne for the coordinatively unsaturated metallocyclic intermediate, 7.



(7)

The rate law for formation of hexamethylbenzene (4) derived from this mechanism (assuming steady state concentration of all unobserved species) is

$$\frac{d[4]}{dt} = \frac{k_4 k_5 [3a] [2\text{-butyne}]}{k_{-4} [PPh_3] + k_5 [2\text{-butyne}]} \qquad (9)$$


Cp
Co
L'
3b (L' = PEt3)
3c (L' = PMe3)
L'
Cp—Co
k4
-L
k-4
k5
Cp
Co
L
3a (L=PPh3)
Cp
Co
4
L+2
Cp = η5 - C5H5

Scheme II.

At high phosphine concentration ($k_{-4}[PPh_3] >> k_5[2\text{-butyne}]$) the rate law approaches:

$$\frac{d[4]}{dt} = \frac{k_4 k_5}{k_{-4}} \frac{[3a][2\text{-butyne}]}{[PPh_3]} \tag{10}$$

which agrees with the rate behavior observed under these conditions ($k_{obsd} = \frac{k_4 k_5}{k_{-4}} = (5.1 \pm 0.5) \times 10^{-5}\ s^{-1}$).

At low phosphine concentration ($k_5[2\text{-butyne}] >> k_{-4}[PPh_3]$) the rate law becomes:

$$\frac{d[4]}{dt} = k_4[3a] \tag{11}$$

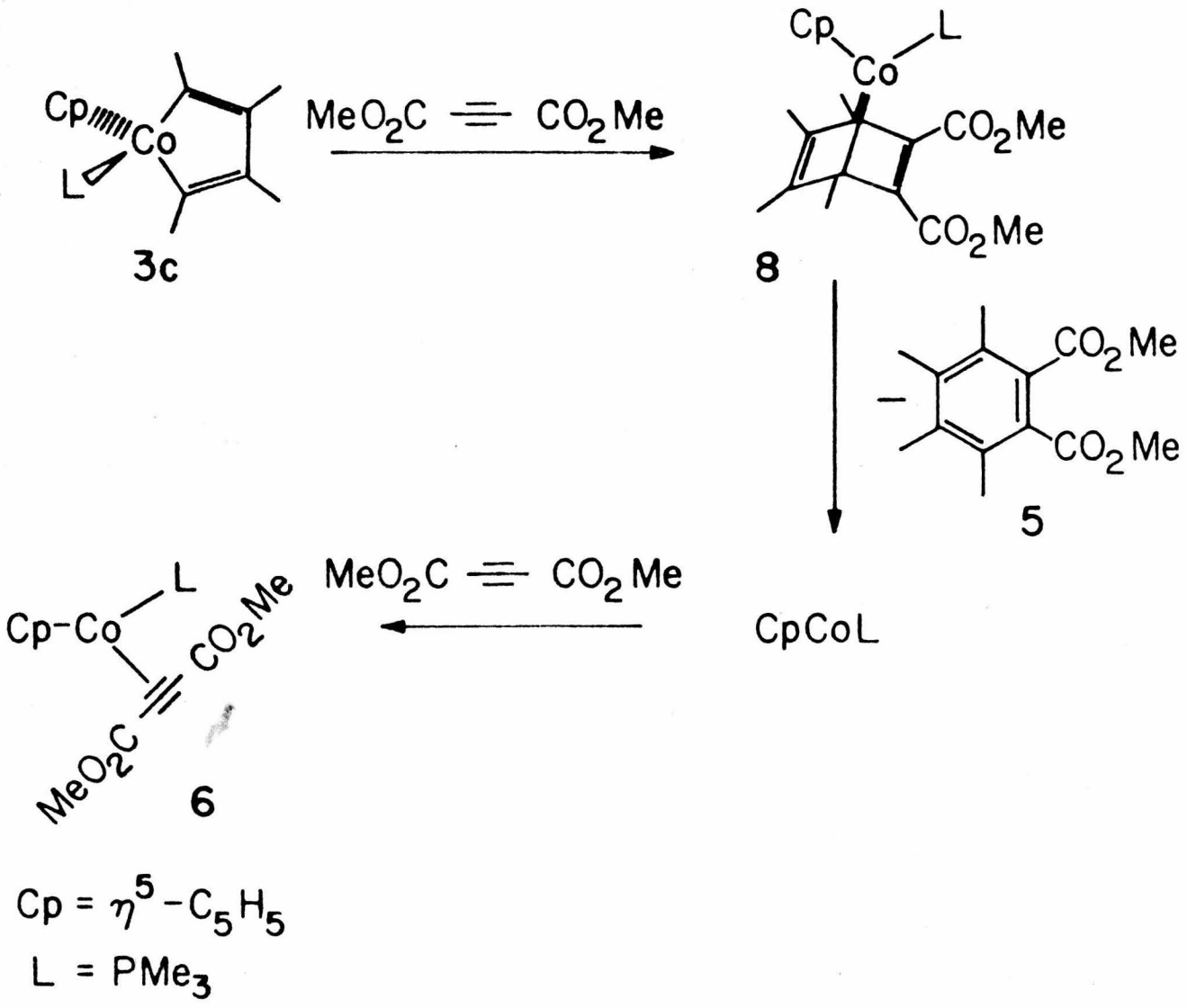
thus giving a rate of formation of 4 that is independent of 2-butyne concentration in accord with experimental observation. The lack of 2-butyne order results because of the requirement in the proposed mechanism (Scheme II) that 3a itself be regenerated in each cycle. Hence, the rate of formation of 4 becomes limited by the rate of dissociation (k_4) of PPh_3 from 3a. Clearly, mechanisms allowing direct regeneration of coordinatively unsaturated metallocycle (7) would display a dependence of rate of hexamethylbenzene (4) production on 2-butyne concentration particularly at very low phosphine concentration.

The observed 0-order rate of hexamethylbenzene (4) production under conditions of low phosphine concentration was $(2.0 \pm 0.2) \times 10^{-5}$ M s^{-1}. Since the concentration of the catalyst (3a) was 0.2 M, from

eq 11 the rate of PPh_3 dissociation from 3a at 74° should be k_4 = $(1.0 \pm .2) \times 10^{-4}$ s^{-1}. This value is in reasonable agreement with the rate of dissociation determined from the kinetics of substitution of PEt_3 for PPh_3 of 3a ($k_4 = (5.8 \pm 0.5) \times 10^{-5}$ s^{-1}) particularly if allowance is made for the considerable difference in reaction media.[22]

The reaction of dimethylacetylenedicarboxylate (dma) with 3c, the metallocycle bearing PMe_3 ligand, in striking contrast with the reactions of 2-butyne with 3a appears to proceed without dissociation of phosphine. Two modes of reaction of alkynes with metalloles can be envisioned: (i) Diels-Alder addition of alkyne to the diene moiety of the metallocycle to give a bicyclic intermediate (cf., 8 in Scheme III) and (ii) insertion of the acetylene into a metal-carbon σ bond to provide an intermediate metallocycloheptatriene. In either case arene could be generated by reductive elimination. The rapidity of the reaction between the powerfully dienophilic alkyne (dma) and the electron rich diene moiety of 3c without preliminary displacement of phosphine is suggestive of the Diels-Alder pathway.

A mechanism for the reaction of dma with 3c incorporating such a Diels-Alder addition as rate determining step is presented in Scheme III. The bicyclic Diels-Alder product (8) provides arene (5) by reductive elimination leaving coordinatively unsaturated (η^5-C_5H_5)Co (PMe_3) which traps excess dma to generate 6. This mechanism accommodates the observed second order kinetics however we cannot, of course, rule out alternate associative processes.[23] In any case the identification of a cobalt (I) complex as product supports the


Cp
Co
L
3c
MeO2C ≡ CO2Me
Cp
L
Co
CO2Me
CO2Me
8
CO2Me
CO2Me
5
L
Cp-Co
CO2Me
MeO2C
6
MeO2C ≡ CO2Me
CpCoL
Cp = η5-C5H5
L = PMe3

Scheme III.

presumption of reductive elimination of arene.

The requirement of dissociative substitution of phosphine by alkyne in reaction of 2-butyne with 3a might perhaps be more in accord with an insertion process than with the Diels-Alder addition suggested for reaction of dma. However, the available data certainly do not necessitate the intermediacy of a metallocycloheptatriene. Despite the existence of at least two modes of reaction of alkynes with metalloles, the general mechanistic features elucidated here--(i) intermediacy of a bis alkyne complex, (ii) oxidative cyclization (perhaps with ligand assistance) to give metallocycle, (iii) incorporation of another alkyne, either by Diels-Alder addition or via ligation and subsequent insertion and (iv) generation of arene by reductive elimination--are very likely typical of alkyne cyclotrimerization reactions induced by low valent transition metal complexes.

Experimental

General Considerations. All manipulations were carried out using either high vacuum line or glove box techniques. Solvents were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene".[24] Nmr solvent, benzene-d_6, (Aldrich Chemical Co.) was dried over activated 4Å molecular sieves and vacuum transferred from "titanocene". Triphenylphosphine was recrystallized from hot Skellysolve "C" and dried under high vacuum. Volatile reagents such as 2-butyne and trimethylphosphine were purifed by vacuum transfer while triethylphosphine and dimethylacetylene dicarboxylate were distilled at reduced pressure. All four were dried over activated 4Å molecular sieves.

^{1}H-nmr spectra were recorded on Varian T-60, A60-A and HR 220 spectrometers. The HR 220 was employed for variable temperature nmr experiments. Visible absorption spectral data were obtained using Cary 14 and 17 spectrophotometers.

Kinetics Measurements. Reaction kinetics were monitored either by ^{1}H-nmr or by visible spectrometry. Typically, nmr samples were prepared as follows: solid, nonvolatile reagents were transferred to an nmr tube sealed to a ground glass joint and fitted with a teflon needle valve adapter under an inert atmosphere (nitrogen or argon) in an evacuable glove box. Solvent (benzene-d_6) and volatile reagents were quantitatively vacuum transferred from calibrated volumes and the tube was sealed with a torch. Because of its very low volatility dimethylacetylenedicarboxylate was transferred via volumetric syringe. The samples were heated by full immersion in a thermostated oil bath

for measured intervals and then cooled rapidly in an ice bath. Relative concentrations of cobalt complexes were determined by integration of the characteristic cyclopentadienyl resonances and of alkyne or arene compounds by integration of relevant methyl resonances. Absolute concentrations were determined by reference to internal standards--TMS or ferrocene.

Samples to be monitored by visible absorption spectroscopy were prepared in an analogous manner in specially designed reaction vessels possessing a teflon needle valve and a 0.1 mm pyrex cell on a side arm, see figure 1. In the case of reactions involving $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (1a) the disappearance of a characteristic absorption at 510 nm was followed. The reaction of dma with PMe_3 substituted metallocycle, 3c, was monitored by the growth of an absorbtion at 530 nm due to the formation of $(\eta^5\text{-}C_5H_5)Co(PMe_3)$(dma) (6).

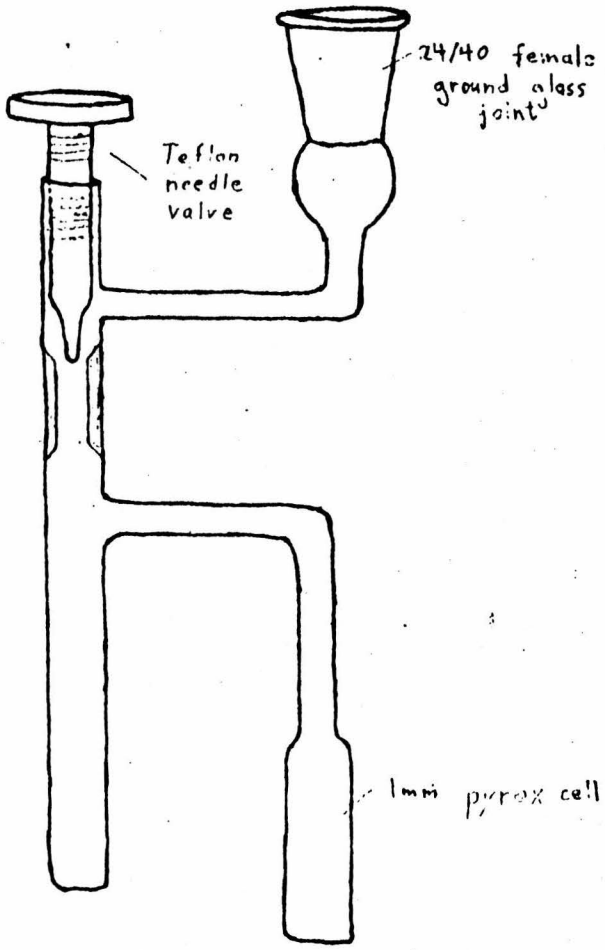


Figure 1

Procedures and Data

1. Preparation of Metallocycle, 3a, (eq 3). A dark red solution of 395 mg (0.6 mmol) $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (1a) (prepared by the method of Rinze et al.[15]) in 20 ml benzene was treated with 1.8 mmol 2-butyne. The solution was heated at 60° for ca. 2 hrs; the color changed to a golden brown. Solvent was removed in vacuo and 3a was isolated from the dark brown residue by either column chromatography on deactivated alumina or by crystallization from benzene-petroleum ether. The dark yellow brown, (almost black in large crystals), material collected in ca. 60% yield is fairly air stable in solid state. Calculated for $C_{31}H_{32}P_2O$: C 75.28, H 6.53, Co 11.93; found: C 75.03, H 6.47, Co 11.87. Melting point (sealed capillary under argon): 166-168°.

2. Equilibrium Constant for Formation of 2a (eq 4). Nmr samples were prepared containing $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (1c), 2-butyne and PPh_3 in benzene-d_6 (Table II); since only relative concentrations were required, no internal standard was included. The relative concentrations at various temperatures of organocobalt complexes 1a, 2a and 3a were determined from integration of the characteristic cyclopentadienyl resonances; relative concentrations of uncomplexed 2-butyne and PPh_3 could be calculated from the stoichiometries of eqs. 3 and 4. Values of the equilibrium constant of reaction 4:

$$K_{eq} = \frac{[2a][PPh_3]}{[1a][2\text{-butyne}]} \quad ,$$

are listed in Table II. A plot of ln (K_{eq}) vs. T^{-1} is linear and indicates thermodynamic parameters: $\Delta H° = 3.4(\pm 1.0)$ kcal/mole and $\Delta S° = 10.4(\pm 1.0)$ eu.

3. Rate of Formation of Metallocycle, 3a (eq 3). The pseudo-first-order rates of formation of 3a from reaction of 1a with excess 2-butyne in the presence of PPh_3 (eq 3) were determined by both ^{1}H-nmr (TMS as internal standard) and visible absorption spectrometry, as described above. The data (Table III) give a fairly good fit to the rate law:

$$\frac{d[3a]}{dt} = \frac{k_1 k_2 k_3 K_{eq} [1a] [2\text{-butyne}]^2}{k_{-1}k_{-2}[PPh_3] + k_{-1}k_3 [PPh_3]^2 + k_2 k_3 [PPh_3] [2\text{-butyne}]},$$

derived from the mechanism of Scheme I.[20] Attempts to fit the data with simpler rate expressions were unsuccessful.[17]

4. Rate of Cyclotrimerization of 2-Butyne Catalyzed by 3a (eq 7). The pseudo-first-order rates of formation of hexamethylbenzene (4) from 3a catalyzed cyclotrimerization of 2-butyne in benzene-d_6 at 120° were determined from ^{1}H-nmr spectral data, employing TMS as an internal standard. The rates (Table IV) under these conditions fit the expression:

$$\frac{d[4]}{dt} = k_{obsd} \frac{[3a] [2\text{-butyne}]}{[PPh_3]}$$

derived from the mechanism of Scheme II at high PPh_3 concentration, where $k_{obsd} = \frac{k_4 k_5}{k_{-4}} = (5.1 \pm 0.5) \times 10^{-5}\ S^{-1}$. The reaction of

2-butyne with 3a at 75° in the absence of excess PPh_3 is described in the Results Section.

The arene, 4, was isolated from the reaction mixture by column chromotography (silica gel) and identified by its ^{1}H-nmr spectrum.

5. Reaction of Metallocycle, 3a, with PEt_3 and PMe_3. The formation of metallocycle, 3a, by reaction of PEt_3 with 3a in benzene-d_6 solution at 74° was monitored by ^{1}H-nmr spectrometry. The rate of formation of 3b was independent of PEt_3 concentration (Table V), fitting the rate expression:

$$\frac{d[3b]}{dt} = k_4 [3a] .$$

consistent with an SN-1 type dissociative substitution where the rate of dissociation of PPh_3 from 3a is $k_4 = (5.8 \pm 0.5) \times 10^{-5} s^{-1}$.

The PMe_3 substituted metallocycle, 3c, is prepared analogously. Reaction of 3a in benzene solution at ca. 70° with excess PMe_3 proceeds at a rate qualitatively similar to the reaction with PEt_3. Orange crystals of 3c (identified by ^{1}H-nmr) can be isolated from the residue remaining after removal of solvent from the reaction mixture in vacuo by recrystallization from benzene-petroleum ether.

6. Reaction of 3c with Dma, eq 8. Trimethylphosphine substituted metallocycle (3c), 55 mg (0.22 mmol), was dissolved in 10 ml toluene. The orange solution was cooled to -78° and 2.2 mmol dma were added via syringe. Gradual warming to 25° caused the reaction mixture to darken to red brown. After 2 hrs stirring at 25°

the mixture was filtered and solvent and unreacted dma were removed *in vacuo*. The resultant dark red oil was chromatographed on deactivated alumina. Elution with benzene provided a white, crystalline material identified as 3,4,5,6-tetramethyldimethylphthalate (5) by its ^{1}H-nmr spectrum and melting point, 127-128° (reported[25], 127°). Further elution with 20% diethylether in benzene provided a dark red brown material identified as the monoacetylene complex (η^5-C_5H_5)Co (PMe_3) (dma)(6) by its ^{1}H-nmr spectrum.

Pseudo-first-order rates of reaction of 3c with dma in benzene solution at 25° were monitored by both ^{1}H-nmr (employing ferrocene as internal standard) and visible absorbtion techniques. (Table VI). The data are in accord with the rate law from Scheme III;

$$\frac{d[5]}{dt} = \frac{d[6]}{dt} = k_8[3c][dma]$$

with second order rate, $k_8 = (2.7 \pm 0.3) \times 10^{-3}\ \underline{M}^{-1}\ s^{-1}$.

Table I. ^{1}H-nmr Spectral Data.

Compound	Moiety		Chemical Shift
$(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (1a)	$C_5\underline{H}_5$	t	4.42δ ($^{3}J_{^{31}P\text{-}^{1}H}$=1 Hz)
	$P(C_6\underline{H}_5)_3$	m	6.5-8.0δ
$(\eta^5\text{-}C_5H_5)Co(PPh_3)(PMe_3)$ (1b)	$C_5\underline{H}_5$	t	4.47δ ($^{3}J_{^{31}P\text{-}^{1}H}$=1 Hz)
	$P(C\underline{H}_3)_3$	d	0.84δ ($^{2}J_{^{31}P\text{-}^{1}H}$=7.5Hz)
$(\eta^5\text{-}C_5H_5)Co(PMe_3)_2$ (1c)	$C_5\underline{H}_5$	t	4.57δ ($^{3}J_{^{31}P\text{-}^{1}H}$=1 Hz)
	$P(C\underline{H}_3)_3$	t	1.10δ ($^{virtual}J_{^{31}P\text{-}^{1}H}$=4 Hz)
$(\eta^5\text{-}C_5H_5)Co(PPh_3)(C_2Me_2)$ (2a)	$C_5\underline{H}_5$	s	4.60δ
	$C\underline{H}_3C_2C\underline{H}_3$	s	2.03δ
$(\eta^5\text{-}C_5H_5)\overline{Co(CMe=CMeCMe=CMe)}(PPh_3)$ (3a)			
	$C_5\underline{H}_5$	s	4.73δ
	methyls	s	1.60 and 2.23 δ
$(\eta^5\text{-}C_5H_5)\overline{Co(CMe=CMeCMe=CMe)}(PEt_3)$ (3b)			
	$C_5\underline{H}_5$	s	4.57δ
	methyls	s	1.95 and 2.33 δ
	$P(C_2\underline{H}_5)_3$	m	0.5-1.3 δ
$(\eta^5\text{-}C_5H_5)\overline{Co(CMe=CMeCMe=CMe)}(PMe_3)$ (3c)			
	$C_5\underline{H}_5$	s	4.52δ
	methyls	s	1.92 and 2.27 δ
	$P(C\underline{H}_3)_3$	d	0.80δ ($^{2}J_{^{31}P\text{-}^{1}H}$ 10 Hz)
C_6Me_6 (4)	$C\underline{H}_3$	s	2.12δ
$1,2\text{-}(CO_2Me)_2(C_6Me_4)$ (5)	$CO_2C\underline{H}_3$	s	3.52δ
	$C_6(C\underline{H}_3)_4$	s	1.75 and 2.13 δ

Table I. ^{1}H-nmr Spectral Data. (Continued)

Compound	moiety			Chemical Shift
$(\eta^5\text{-}C_5H_5)Co(PMe_3)(C_2(CO_2Me)_2)$ (6)				
	$C_5\underline{H}_5$	s	4.58	
	$CO_2C\underline{H}_3$	s	3.51	
	$P(C\underline{H}_3)_3$	d	0.70	$(^2J_{^{31}P-^{1}H}$=10. Hz)

Table II. Temperature Dependence of the Equilibrium Constant,

$$K_{eq} = \frac{[2a][PPh_3]}{[1a][2\text{-butyne}]} \quad \text{(eq 4)}.$$

A. Initial Conditions:

Sample	1a	PPh_3	2-butyne
1	0.06 M	0.2 M	1.0 M
2	0.05	0.5	1.0
3	0.07	0.8	1.0

B. Values of K_{eq}

Sample 1		Sample 2		Sample 3	
Temperature(^{o}C)	K_{eq}	Temperature(^{o}C)	K_{eq}	Temperature(^{o}C)	K_{eq}
8.0^{o}	0.06	19.0^{o}	0.08	19.0	0.08
24.5	.09	21.0	0.07	21.0	0.08
33.0	.11	28.5	0.09	28.5	0.09
40.0	.12	36.5	0.11	36.5	0.11
55.0	.14	45.4	0.13	45.5	0.13
		55.0	0.17	55.0	0.15

Table III. Rate of Formation of Metallocycle, 3a at 74° in benzene-d_6.

PPh_3	2-butyne	$k_{obs}(X10^3)$	Method of Observation	$k_{calc}(X10^3)$[a]
0.45 M	0.11 M	0.02 s^{-1}	vis	0.02
1.12	.38	.06	vis	.05
.82	.41	.07	vis	.09
.45	.34	.13	vis	.16
.64	.43	.16	vis	.14
.44	.44	.26	vis	.24
.73	.74	.27	vis	.30
1.34	1.34	.29	nmr	.29
.14	.21	.30	vis	.29
.36	.45	.31	vis	.33
1.15	1.15	.33	vis	.29
.78	1.02	.38	vis	.39
1.50	1.90	.38	nmr	.41
1.01	1.44	.41	nmr	.43
.99	1.50	.52	nmr	.50
.40	1.00	.82	nmr	.86

(a) The values of k_{calc} derive from a least squares fit of the data to the rate law from Scheme II (see Discussion Section). The expression is:

$$k_{calc} = \frac{\left[\text{2-butyne}\right]^2}{451.0\left[PPh_3\right] + 1080.5\left[PPh_3\right]^2 + 2017.2\left[PPh_3\right]\left[\text{2-butyne}\right]}$$

Table IV. Rate of Cyclotrimerization of 2-butyne Catalyzed by 3a at 120°.

3a	PPh_3	Rate ($X10^4$) of Hexamethylbenzene Formation
0.15 M	1.34 M	0.07 s^{-1}
.14	1.14	.07
.16	.79	.08
.17	.50	.17
.17	.35	.24

Table V. Rates of Reaction of 3a with PEt_3 at 74°.

3a	PEt_3	Rate of Substitution ($X10^5$)
0.16 M	1.29 M	5.7 s^{-1}
.14	1.97	6.0
.13	2.50	5.7
.13	1.33	5.6[b]

(b) This reaction mixture also contained 0.66 M PPh_3.

Table VI. Rate of Reaction of Metallocycle, 3b with Dimethylacetylene dicarboxylate (dma).

dma	Observed Pseudo-first-order Rate ($X10^3$)	Method
0.05 M	0.11 s^{-1}	vis
.10	.23	"
.23	.56	"
.23	.69	"
.25	.72	"
.25	.72	"
.35	1.00	"
.45	.98	"
.49	1.26	"
.50	1.61	"
.67	1.20	nmr
.74	2.20	"
.80	2.10	"
.98	2.60	"
1.14	3.20	"
1.28	4.60	"

Notes and References

(1) This chapter includes previously published results; D. R. Mc Alister, J. E. Bercaw and R. G. Bergman, J. Amer. Chem. Soc., 99, 1666 (1977).

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(17) Single term rate laws such as $C_1[\text{2-butyne}]/[PPh_3]$ and $C_2[\text{2-butyne}]^2/[PPh_3]$, C_1 and C_2 constants, which result from assumption of a "fast preequilibrium" concentration of bis alkyne complex give indistinguishably poor fits to the data. The general trend of rate enhancement at higher alkyne concentration and inhibition by phosphine is, however, clearly apparent.

(18) N. E. Waite, J. C. Tebby, R. S. Ward and D. H. Williams, J. Chem. Soc. C, 110 (1969) and references therein.

(19) An alternative mechanism which can not be rigorously eliminated would involve initial coordination of dma via an 18-electron metallocyclic intermediate possessing an η^3-cyclopentadienyl and retaining PMe_3.

(20) A straightforward treatment of the mechanism of Scheme I assuming a "fast pre-equilibrium" concentration of 2a and steady state concentrations of the 16-electron mono alkyne complex and of the undetected bis alkyne complex provides a rate law of the form:

$$\text{Rate} = \frac{d[3a]}{dt} = -\frac{d[1a]}{dt} = \frac{k_1k_2k_3K_{eq}[1a][\text{2-butyne}]^2}{k_{-1}k_{-2}[PPh_3]+k_{-1}k_3[PPh_3]^2+k_2k_3[PPh_3][\text{2-butyne}]}$$

A least squares fit[21] of the data of Table III to a three parameter function of this form yielded:

$$\text{Rate} = \frac{[1a][2\text{-butyne}]^2}{451.0[PPh_3] + 1080.5[PPh_3]^2 + 2017.2[PPh_3][2\text{-butyne}]}$$

The k_{calc} values of Table III were derived from this expression.

(21) A general non-linear least squares program is presented by: P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, N. Y., 1969. The program was modified to accept functions of more than a single variable.

(22) Typical compositions of the two solutions (by weight) are: (a) 11% 2-butyne, 89% C_6D_6; (b) 34% PEt_3, 66% C_6D_6.

(23) An 18-electron intermediate facilitated by an η^3-cyclopentadienyl ring similar to that proposed in note (19) cannot be ruled out.

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Chapter II

The Reduction of Carbon Monoxide Promoted by Alkyl and Hydride Derivatives of Permethylzirconocene.[1]

"... But like a fool I mixed them,
And they strangled up my mind."

B. D.

Introduction

The catalytic reduction of carbon monoxide with molecular hydrogen to selectively provide alkanes or alcohols is a problem of considerable current interest. Only a few homogeneous systems which can effect this sort of transformation have thus far been developed. These include the Rh based ethylene glycol synthesis[2], methanation promoted by $Os_3(CO)_{12}$ or $Ir_4(CO)_{12}$[3] and the catalytic production of methane, ethane, propane and isobutane by $Ir_4(CO)_{12}$ in molten $NaCl \cdot 2AlCl_3$.[4]

Recently, we reported the stoichiometric reduction of ligated CO by molecular H_2 in certain zirconium complexes[5] (Eq 1 and 2):

$$(\eta^5\text{-}C_5Me_5)_2\ Zr(CO)_2 + 2H_2 \xrightarrow[\text{or } h\nu]{110^\circ} (\eta^5\text{-}C_5Me_5)_2\ Zr(H)(OCH_3) \qquad (1)$$

$$\left\{(\eta^5\text{-}C_5Me_5)_2\ Zr(CO)\right\}_2 (N_2) + 4H_2 \xrightarrow{25^\circ} 2(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(OCH_3) + N_2 \qquad (2)$$

Although this system is not catalytic, it does provide an opportunity to examine certain salient features of the reduction mechanism, in particular the presumed migratory insertion of CO into a metal hydride bond. Hence, we have extended our investigations to include the reactivities of permethylzirconocene derivatives of the types $(\eta^5\text{-}C_5Me_5)_2\ ZrH_2$, $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(R)$ and $(\eta^5\text{-}C_5Me_5)_2\ ZrR_2$ toward CO. Herein we report the results of these studies.

Results

1. Reactions of $(\eta^5\text{-}C_5Me_5)_2\ ZrH_2$ with CO. The preparation of $(\eta^5\text{-}C_5Me_5)_2\ ZrH_2$ (2) by reaction of $\{(\eta^5\text{-}C_5Me_5)_2\ Zr(N_2)\}_2\ (N_2)$[6,7] (1) with H_2 is adequately described elsewhere.[1,8] Its molecular weight, analytical data, ^{1}H-nmr (Table I) and ir spectrum (ν(Zr-H) 1555 cm^{-1}; ν(Zr-D) 1100 cm^{-1}) indicate a monomeric, pseudotetrahedral structure analogous to $(\eta^5\text{-}C_5Me_5)_2\ ZrCl_2$. Although the chemical shift of the hydride hydrogen atoms of 2 (7.46 δ) is unusually low-field compared to the typical high-field resonances of Group V-VIII transition metal hydrides, it is intermediate between the hydride resonances of $(\eta^5\text{-}C_5Me_5)_2\ TiH_2$ (0.28 δ) and $(\eta^5\text{-}C_5Me_5)_2\ HfH_2$ (15.6 δ).[8] The reactions of 2 with CO were investigated in conjunction with other researchers and many of the results were reported in another thesis[9]; they are included here for completeness. The appropriate Experimental data are to be found in references 1 and 9.

$(\eta^5\text{-}C_5Me_5)_2\ ZrH_2$ (2) is formally a 16-electron complex and so might be expected to add small donor molecules. Indeed, in toluene solution at -78° 2 absorbs PF_3 to generate the unstable, 18-electron complex $(\eta^5\text{-}C_5Me_5)_2\ ZrH_2(PF_3)$ (3). On the basis of its ^{1}H-nmr spectrum at -50° (Table I), the structure of 3 appears to be similar to that of $(\eta^5\text{-}C_5H_5)_2\ TaH_3$[10] with PF_3 occupying the central position mutually cis to the two hydride ligands:

$$(\eta^5\text{-}C_5Me_5)_2\ Zr\begin{matrix}H\\ \diagup\\ \diagdown\\ H\end{matrix}\!\!-\!\!-\ PF_3 \qquad (3)$$

Surprisingly, $P(OMe)_3$, $P(C_6H_5)_3$ or PMe_3 do not appear to form analogous adducts; the ^{1}H-nmr spectra of solutions of 2 containing 2-10 molar equivalents of these ligands give no indication of any additional species at 25°. 2 does, however, react readily with CO in toluene solution at -78° providing an unstable carbonyl hydride $(\eta^5\text{-}C_5Me_5)_2 ZrH_2(CO)$ (4). 4 decomposes both in solution and solid state if warmed above -40°, however it has been partially characterized by its reactivity and ^{1}H-nmr spectrum. Reaction of toluene solution of 4 with excess HCl at -78° liberates H_2 (1.78 moles/mole 4) and CO (0.85 moles/mole 4) and gives $(\eta^5\text{-}C_5Me_5)_2 ZrCl_2$ nearly quantitatively in accord with eq 3.

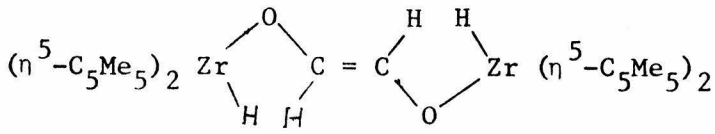
$$(\eta^5\text{-}C_5Me_5)_2ZrH_2(CO) + 2HCl \longrightarrow (\eta^5\text{-}C_5Me_5)_2 ZrCl_2 + 2H_2 + CO \qquad (3)$$

The ^{1}H-nmr spectrum of 4 (Table I) is consistent with a symmetric structure analogous to 3, and the doublet with 25 Hz coupling observed for the hydride resonance of 4-(^{13}CO) is consistent only with a two bond ^{13}C to ^{1}H coupling, indicating a carbon-bonded carbonyl compound, viz.;

$$(\eta^5\text{-}C_5Me_5)_2 \overset{H}{\underset{H}{Zr}} \!\!-\!\!- CO \qquad (4).$$

If solutions of 4 are allowed to warm above -50°, $\{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2 (OCH{=}CHO)_2$ (5) is obtained in nearly quantitative yield. The structure of this rather unexpected compound is supported by analytical data,

infrared spectra (ν(Zr-H) 1580 cm^{-1}, ν(Zr-D) 1130 cm^{-1}; ν(C-O) 1205 cm^{-1}, $\nu(^{13}C\text{-}O)$ 1180 cm^{-1}) and most characteristically by ^{1}H and ^{13}C nmr data for $\{(\eta^5\text{-}C_5Me_5)_2\ ZrH\}_2$ (O $^{13}CH=^{13}CHO$) prepared from 2 and ^{13}CO; an AA'XX' pattern[11] is observed for the ^{1}H and ^{13}C of the (-O $^{13}CH=^{13}CHO$-) bridge (Table I).



(5)

Moreover, 5 reacts readily with CH_3I to generate methane (1.68 mole/mole 5) and $\{(\eta^5\text{-}C_5Me_5)_2\ ZrI\}_2$ (OCH=CHO) (6). The ir spectrum (ν(C-O) 1195 cm^{-1}, $\nu(^{13}C\text{-}O)$ 1175 cm^{-1}) and ^{1}H and ^{13}C nmr data for 6 prepared from normal and from ^{13}CO (Table I) indicate a structure completely analogous to 5. The preliminary results of an x-ray structural determination, presently refined to R=0.08, are fully in accord with this structure[1].

The same reaction leading to 5 is observed if 4 is warmed under H_2; however, in the presence of both H_2 and catalytic amount of $(\eta^5\text{-}C_5Me_5)_2\ ZrH_2$ (2) both 5 and $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)\ (OCH_3)$ (7), fully characterized by analysis, molecular weight and ir and nmr spectroscopy, are formed. 2 is recovered quantitatively. The relative yield of 7 as compared to 5 increases with larger relative amounts of 2.

2. Reactions of $(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)_2$ and $(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_2(CH_2)_2CH_2)$ with CO. It was anticipated that the reactions of CO with zirconium alkyl compounds might provide instructive contrast to the reactions with 2. The parent dimethyl compound, $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$

has been reported to reversibly add CO to afford $(\eta^5\text{-}C_5H_5)_2\ Zr(CH_3)(C(=O)CH_3)$, which has been characterized by x-ray diffraction structural determination.[12] The preparation of the permethyl compound $(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)_2$ (8) parallels that of the parent[13] (eq 4).

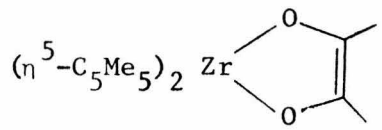
$$(\eta^5\text{-}C_5Me_5)_2\ ZrCl_2 + 2MeLi \longrightarrow (\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)_2 + 2LiCL \qquad (4)$$

It is a white, crystalline, easily sublimable material and has been characterized by analysis, and ^{1}H-nmr (Table I). In benzene solution 8 also reacts reversibly with CO (1 atm) according to eq 5.

$$(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)_2 + CO \longrightarrow (\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)(C(=O)CH_3) \qquad (5).$$

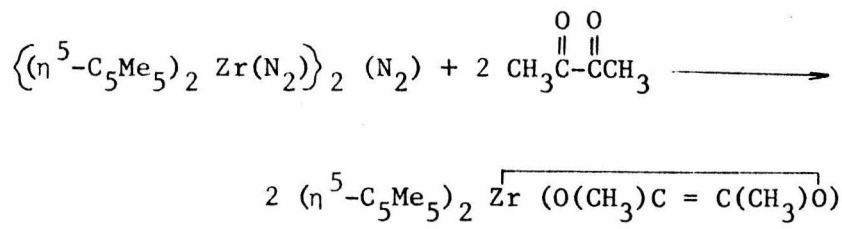
The lability and high solubility of $(\eta^5 - C_5Me_5)_2\ Zr(CH_3)(C(=O)CH_3)$ (9) have prevented its isolation; however, the similarity of its ^{1}H-nmr spectrum (Table I) and ir spectrum (ν(C-O) 1537 cm^{-1} (THF solution)) to those for $(\eta^5\text{-}C_5H_5)_2\ Zr(CH_3)(C(=O)CH_3)$ ($\eta^5\text{-}C_5\underline{H}_5$ singlet, 5.35 δ(10H), $C(=O)C\underline{H}_3$ singlet, 2.41 δ(3H), $ZrC\underline{H}_3$ singlet, 0.45 δ; ν(C-O) 1545 cm^{-1} (Nujol mull)) leaves little doubt that the two acyl methyl compounds are isostructural.

Pyrolysis of benzene solutions of $(\eta^5\text{-}C_5H_5)_2\ Zr(CH_3)(C(=O)CH_3)$ at 70° under CO (1 atm) induces a complicated series of reactions leading to several products. In contrast, the permethyl compound, 9, reacts smoothly with CO in benzene at 70° over a period of several hours to quantitatively provide $(\eta^5\text{-}C_5Me_5)_2\ \overline{Zr(O(CH_3)C = C(CH_3)O)}$ (10).



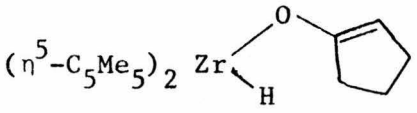
(10)

This structure is supported by ^{1}H nmr (Table I), and by analytical, infrared and mass spectral data (see Experimental section). Moreover, 10 can also be prepared independently by reaction of $\{(\eta^5\text{-}C_5Me_5)_2\ ZrN_2\}_2(N_2)$ with biacetyl (eq 6).



$$\{(\eta^5\text{-}C_5Me_5)_2\ Zr(N_2)\}_2\ (N_2) + 2\ CH_3C(=O)C(=O)CH_3 \longrightarrow 2\ (\eta^5\text{-}C_5Me_5)_2\ Zr\ (O(CH_3)C = C(CH_3)O) + 3N_2 \qquad (6)$$

Another dialkyl permethyl zirconocene complex, the zirconacyclopentane $(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_2(CH_2)_2CH_2)$ (11) has recently been reported[1,14]. It reacts rapidly at 25°C with CO to generate the enolate hydride compound 12 along with a small amount (< 5%) of $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$.



(12)

The ^{1}H nmr spectral data for 11 and 12 are included in Table I.

3. Reaction of $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(CH_2CHMe_2)$ with CO. Solutions (pentane or toluene) of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (2) react with excess isobutylene over a period of several minutes at room temperature to provide $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(CH_2CHMe_2)$ (13a) in nearly quantitative yield (by ^{1}H nmr) in accord with eq 7.

$$(\eta^5\text{-}C_5Me_5)_2\ ZrH_2 + CH_2{=}\ CMe_2 \longrightarrow (\eta^5\text{-}C_5Me_5)_2\ Zr(H)(CH_2CHMe_2) \qquad (7)$$

Despite possession of cis alkyl and hydride ligands, 13 is remarkably stable; benzene solutions are stable at 50° for hours, even in the presence of excess isobutylene. When treated with ethylene or with H_2, however, 13 reacts rapidly with generation of isobutane.[15]

The dideutero analog of 13a, $(\eta^5\text{-}C_5Me_5)_2\ Zr(D)(CH_2CDMe_2)$ (13b) may be prepared according to equations 8 and 9.

$$\left\{(\eta^5\text{-}C_5Me_5)_2\ Zr(N_2)\right\}_2(N_2) + 2D_2 \longrightarrow 2(\eta^5\text{-}C_5Me_5)_2ZrD_2 + 3N_2 \qquad (8)$$

$$(\eta^5\text{-}C_5Me_5)_2\ ZrD_2 + CH_2{=}\ CMe_2 \longrightarrow (\eta^5\text{-}C_5Me_5)_2\ Zr(D)(CH_2CDMe_2) \qquad (9)$$

The sequence must be performed below 5° to avoid deuterium exchange with the hydrogens of the pentamethylcyclopentadienyl groups of $(\eta^5\text{-}C_5Me_5)_2\ ZrD_2$.[8] The ^1H nmr spectrum (Table I) gives no evidence of a similar deuteride with ring methyl hydrogen exchange process for 13b. The nmr spectral data also indicate that the addition of isobutylene is entirely regiospecific, since there appears to be no scrambling (< 5%) of deuterium into the isobutyl methyls, as would be expected if $(\eta^5\text{-}C_5Me_5)_2\ Zr(D)(CMe_2CH_2D)$ were reversibly formed (eq 10).

$$(\eta^5\text{-}C_5Me_5)_2\ ZrD_2 + CH_2{=}\ CMe_2 \not\longrightarrow (\eta^5\text{-}C_5Me_5)_2\ Zr(D)(CMe_2CH_2D) \qquad (10)$$

$(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(CH_2CHMe_2)$ (13a) reacts rapidly with CO in toluene soluation at 25°C producing $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH = CHCHMe_2)$ (15a) (eq 11) together with a small amount of $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$.

$$(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(CH_2CHMe_2) + CO \longrightarrow (\eta^5\text{-}C_5Me_5)_2\ Zr(H)(OCH{=}CHCHMe_2) \quad (11)$$

This reaction was monitored at low temperature by ^1H nmr spectroscopy (toluene-d_8). At -50° under 1 atm CO, 13a reacts slowly to form an adduct which is assigned the structure $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(C(=O)CH_2CHMe_2)$ (14a) on the basis of its ^1H nmr spectrum (Table I) and by analogy with $(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)(C(=O)CH_3)$ (see Scheme II). The identification of this transient intermediate as an acyl rather than a formyl derivative is further supported by ^1H nmr data (Table I) for 14c obtained from 13a and ^{13}CO. The small couplings of 9Hz and 5Hz for the ^{13}C to hydride and to methylene hydrogens, respectively, of $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(^{13}C(=O)CH_2CHMe_2)$ (14c) are incompatible with a one bond $^{13}C\text{-}^1H$ coupling (cf. $^1J_{^{13}C\text{-}^1H}$ = 173 Hz for 15c, Table I). Further warming of these solutions to -20° leads to rearrangement of 14 to the final product $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH{=}CHCHMe_2)$ (15).

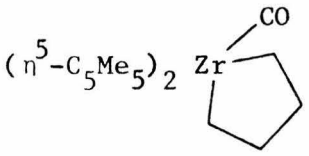
Significantly, treatment of the di-deutero compound $(\eta^5\text{-}C_5Me_5)_2\ Zr(D)(CH_2CDMe_2)$ (13b) with CO affords $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(OCD{=}CHCDMe_2)$ (15b) (eq 12).

$$(\eta^5\text{-}C_5Me_5)_2\ Zr(D)(CH_2CDMe_2) + CO \longrightarrow (\eta^5\text{-}C_5Me_5)_2Zr(H)(OCD{=}CHCDMe_2) \quad (12)$$

The isotopic labeling pattern of 15b indicates that both isobutyl and hydride moieties of 13 are transferred to the carbonyl carbon atom and that the hydrogen atom which appears as the hydride of 15b originated from the methylene carbon of the isobutyl group of 13b. The mechanistic implications of these results are discussed in the following section.

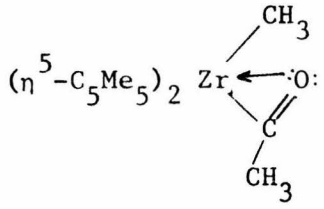
Discussion

The reactions of these alkyl and hydride derivatives of bis (pentamethylcyclopentadienyl) zirconium with carbon monoxide provide in each case a final product in which the carbonyl oxygen has become bonded to zirconium. The initial adduct of carbonylation of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ has been identified and shown to have a structure with CO carbon-bonded to zirconium in the central equitorial position (Scheme I). Similar structures may reasonably be presumed for the initial carbonyl adducts of $(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)_2$ and $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(CH_2CHMe_2)$. For the zirconacyclopentane, $(\eta^5\text{-}C_5Me_5)_2\ \overline{Zr(CH_2(CH_2)_2CH_2)}$, however, initial coordination of CO at the side to give a structure as shown below would be more reasonable, since the alternative places the CO within the five-membered ring and must be highly unfavorable.

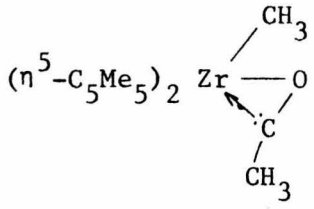


Subsequent migratory insertion of CO into Zr-alkyl or Zr-hydride bonds occurs in each case with remarkable facility. The results of ^1H nmr study of the reaction of $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(CH_2CHMe_2)$ with ^{13}CO establish that alkyl migration is favored over hydride migration for this system. Indeed, initial quantitative conversion of $(\eta^5\text{-}C_5Me_5)_2\ ZrH_2$ to $(\eta^5\text{-}C_5Me_5)_2\ ZrH_2\ (CO)$ upon carbonylation in contrast to direct formation of acyls from CO and $(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)_2$ or $(\eta^5\text{-}C_5Me_5)\ Zr(H)(CH_2CHMe_2)$ without buildup of detectable concentrations of their carbonyl adducts bespeaks the relative ease of alkyl as compared to hydride migration.

The facility of these migratory insertions and the subsequent reactivity of the complexes may in part be ascribed to the unusual bonding mode of the acyl or formyl groups to zirconium. A "side-on" or "π" coordination of the acyl groups have recently been established by Floriani and coworkers for $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)(C(=O)CH_3)$[12] and $(\eta^5\text{-}C_5H_5)_2Ti\ Cl(C(=O)CH_3)$.[16] Analogous "side-on" bonding of acyl or formyl is strongly inferred in these <u>bis</u> (pentamethylcyclopentadienyl) zirconium systems in light of the structural features shared by all these compounds. Indeed, the close correspondence between ir and ^1H nmr spectral data for $(\eta^5\text{-}C_5Me_5)_2\ Zr(CH_3)(C(=O)CH_3)$ and $(\eta^5\text{-}C_5H_5)_2\ Zr(CH_3)(C(=O)CH_3)$ dictates nearly identical structures. Interaction of an acyl oxygen lone pair of electrons with the empty, low energy orbital located in the equitorial plane of the $(\eta^5\text{-}C_5Me_5)_2Zr$ moiety enables the zirconium atom to achieve a full 18 electron valence shell (<u>8a</u>). An additional resonance structure (<u>8b</u>), however, can also contribute to the bonding.



<u>8a</u>



<u>8b</u>

In this latter representation the acyl is bonded to zirconium by a full covalent zirconium-oxygen bond while interaction with the oxycarbene lone pair completes the valence shell of zirconium. The resultant carbenoid character imparted to the acyl center allows rationalization

of many of the reaction patterns encountered in these systems.

The products obtained upon photolysis or pyrolysis of acyl silanes have been shown to arise via siloxycarbene intermediates.[17,18]

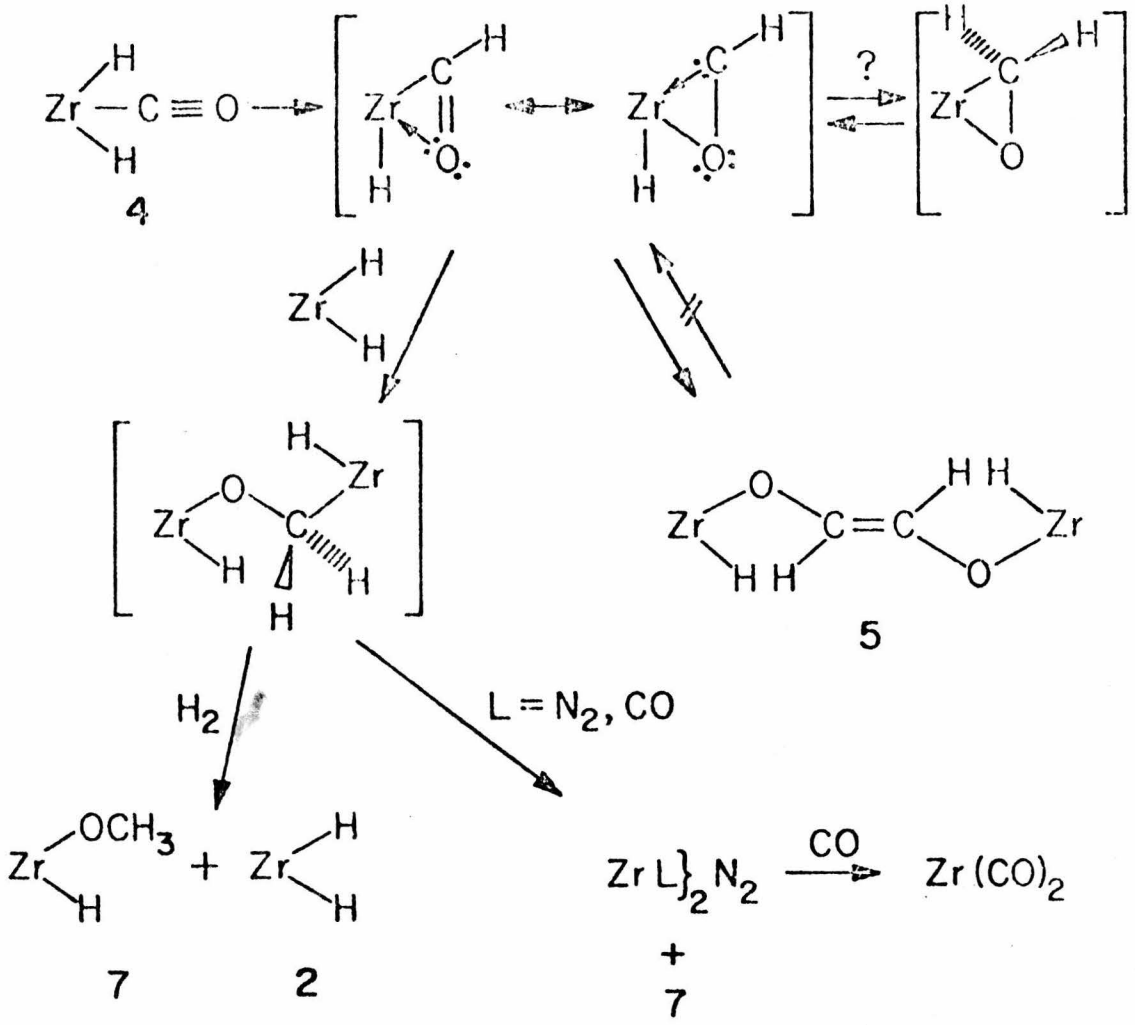
$$Me_3Si\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \xrightarrow{h\nu} Me_3SiO\text{-}\ddot{C}\text{-}CH_3 \xrightarrow{ROH} Me_3SiO\text{-}\overset{OR}{\overset{|}{C}}HCH_3 \qquad (13)$$

$$Me_3Si\text{-}\overset{O}{\overset{\|}{C}}\text{-}CHMe_2 \xrightarrow{200^{o}} Me_3SiO\text{-}\ddot{C}\text{-}CHMe_2 \longrightarrow Me_3SiOCH = CMe_2 \qquad (14)$$

Subsequent reactions of these oxycarbene intermediates include dimerization, insertion into O-H bonds of solvent alcohol and intramolecular insertion into α C-H bonds.[19] The products obtained from reactions of permethylzirconocene acyl and formyl intermediates appear to derive from similar processes.

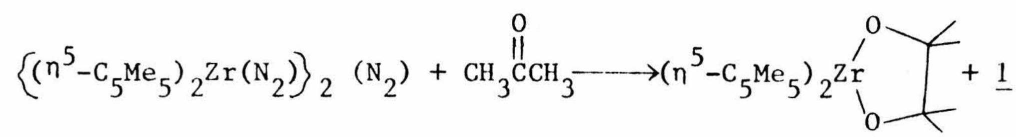
Although the formyl hydride intermediate proposed in Scheme I has not been directly detected, dimerization of an incipient oxymethylene species, $(\eta^5\text{-}C_5Me_5)_2Zr(H)(O\ddot{C}H)$, provides an attractive route to the product, $\{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2$ (μ-OCH=CHO). A <u>trans</u> stereochemistry about the enedioxy bridge would be imposed by the steric bulk of the $(\eta^5\text{-}C_5Me_5)_2ZrH$ units. In the presence of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$, intermolecular insertion of the oxymethylene into a zirconium hydride bond might be expected to complete with dimerization. Subsequent reductive elimination of $(\eta^5\text{-}C_5Me_5)_2\ ZrH(OCH_3)$, induced by H_2 or by good π-acid ligands such as CO or N_2[15] would concurrently yield $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ or $\{(\eta^5\text{-}C_5Me_5)_2ZrL\}_2$ (N_2) (L=CO,N_2),[6,7] respectively (Scheme I).

A competing, reversible intramolecular insertion of the oxymethylene into the remaining zirconium hydride bond of $(\eta^5\text{-}C_5Me_5)_2ZrH$



Scheme I.

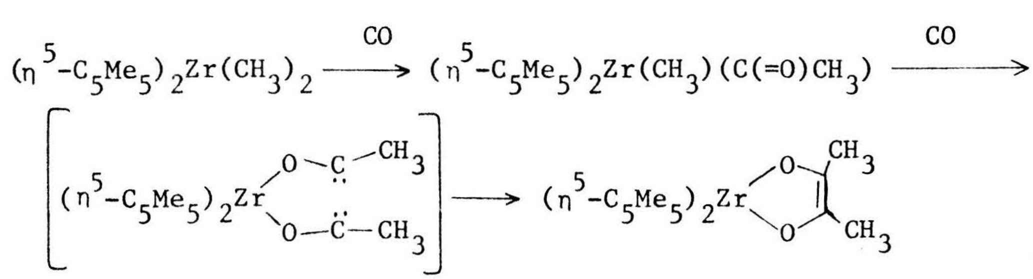
(OCH) to afford a formaldehyde adduct may occur; however, in this system such a pathway appears nonproductive. Attempts to prepare such a formaldehyde adduct by slow addition of 1 equivalent (per Zr) of anhydrous CH_2O to a toluene solution of $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2(N_2)$ (1) led in all cases to a series of complex reactions from which neither 5 nor 7 could be identified. Similarly, the reaction of 1 with 1 equivalent of acetone provided 0.5 equivalent of $(\eta^5\text{-}C_5Me_5)_2$ $\overline{Zr(OC(Me)_2C(Me)_2O)}$ (nmr).



(15)

The reactions of 1 with acetaldehyde or isovaleraldehyde also appear to give products resulting from reductive coupling of the organic carbonyls. These observations contraindicate the intermediacy of free aldehydes or ketones in reaction mixtures derived from CO and hydride or alkyl derivatives of permethyl zirconocene.

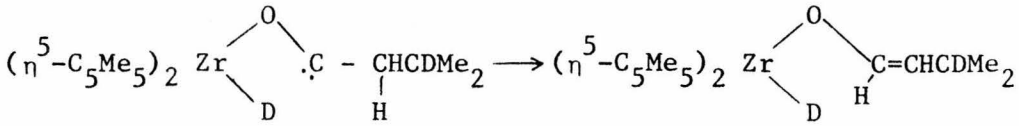
The reactivity of $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)(C(=O)CH_3)$ towards additional carbon monoxide can also be rationalized on the basis of oxycarbenoid character of zirconium acyls. Thus, insertion of CO into the remaining $Zr\text{-}CH_3$ bond provides a bis (acetyl) and, hence, functionally a bis (oxycarbene) complex which need only undergo intramolecular dimerization to provide $(\eta^5\text{-}C_5Me_5)_2$ $\overline{Zr(O(CH_3)C{=}C(CH_3)O)}$.



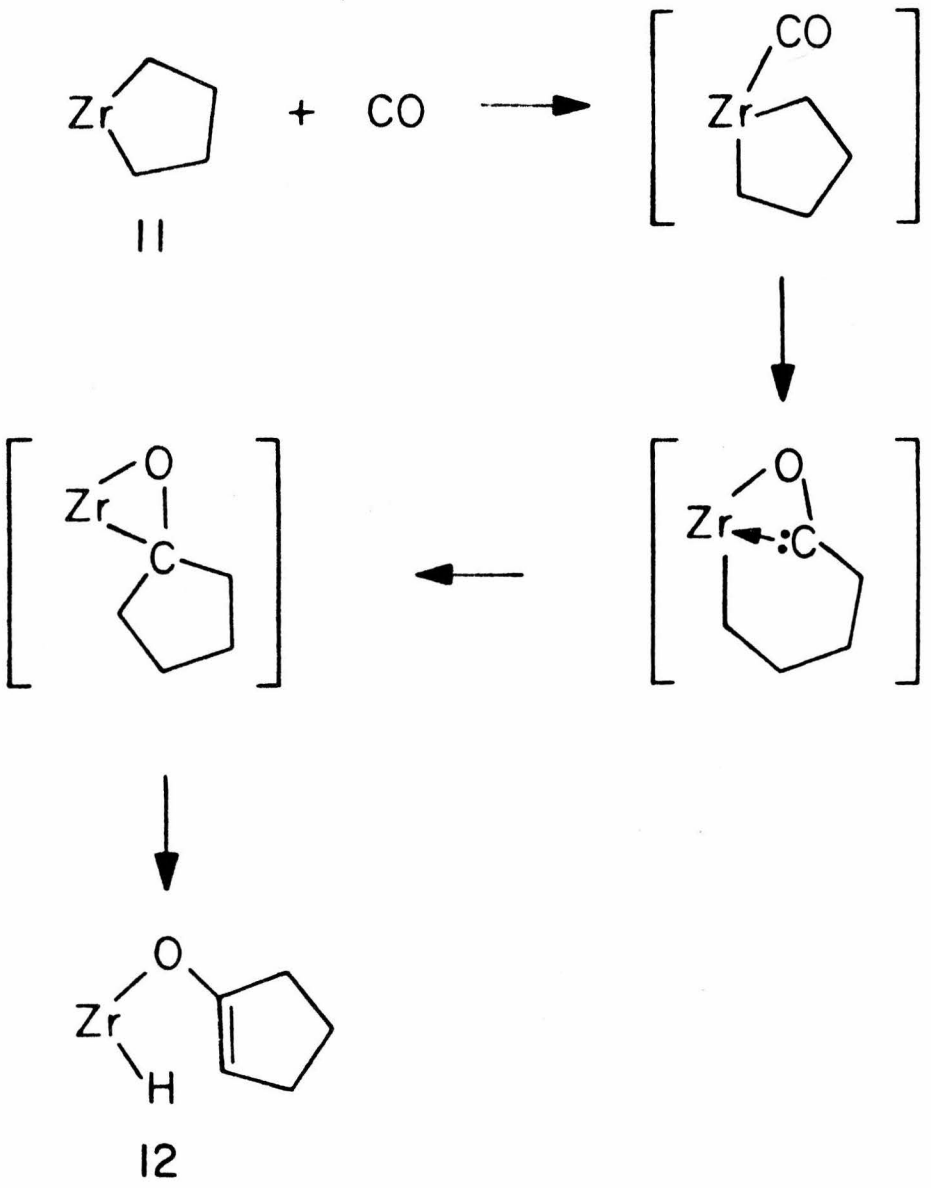
(16)

The reaction of the zirconacyclopentane complex, $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2(CH_2)_2CH_2)$ (11), with carbon monoxide appears to take a somewhat different tack. Unlike $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)_2$, 10 reacts instantaneously with CO at 25°C to yield the enolate hydride compound, 12. Although we have little information about the intermediates in this reaction, the formation of the final product, 12, can be rationalized consistently by assuming that the reaction of 11 with CO proceeds as outlined in Scheme II. Insertion of CO into the zirconacyclopentane ring would generate an acyl which is forced by ring strain to have its acyl carbon adjacent to the remaining zirconium-carbon bond of the metalocycle. This proximity and the incipiency of a five-membered ring may encourage an insertion of the oxycarbene into the Zr-C bond, thus affording a cyclopentanone adduct of permethyl zirconocene. Finally, simple β-hydride abstraction would provide the observed enolate hydride derivative.[20]

The reaction of the isobutyl hydride derivative, $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (13) with carbon monoxide proved to be mechanistically the most transparent of the systems thus far investigated. Rearrangement of the initial, observed product, $(\eta^5\text{-}C_5Me_5)_2Zr(H)(C(=O)CH_2CHMe_2)$ (14) to the enolate hydride, $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH=CHCHMe_2)$ (15) appeared at first to indicate that these oxycarbenoids could undergo insertion into adjacent carbon-hydrogen bonds (eq 17), as is observed for free oxycarbenes.



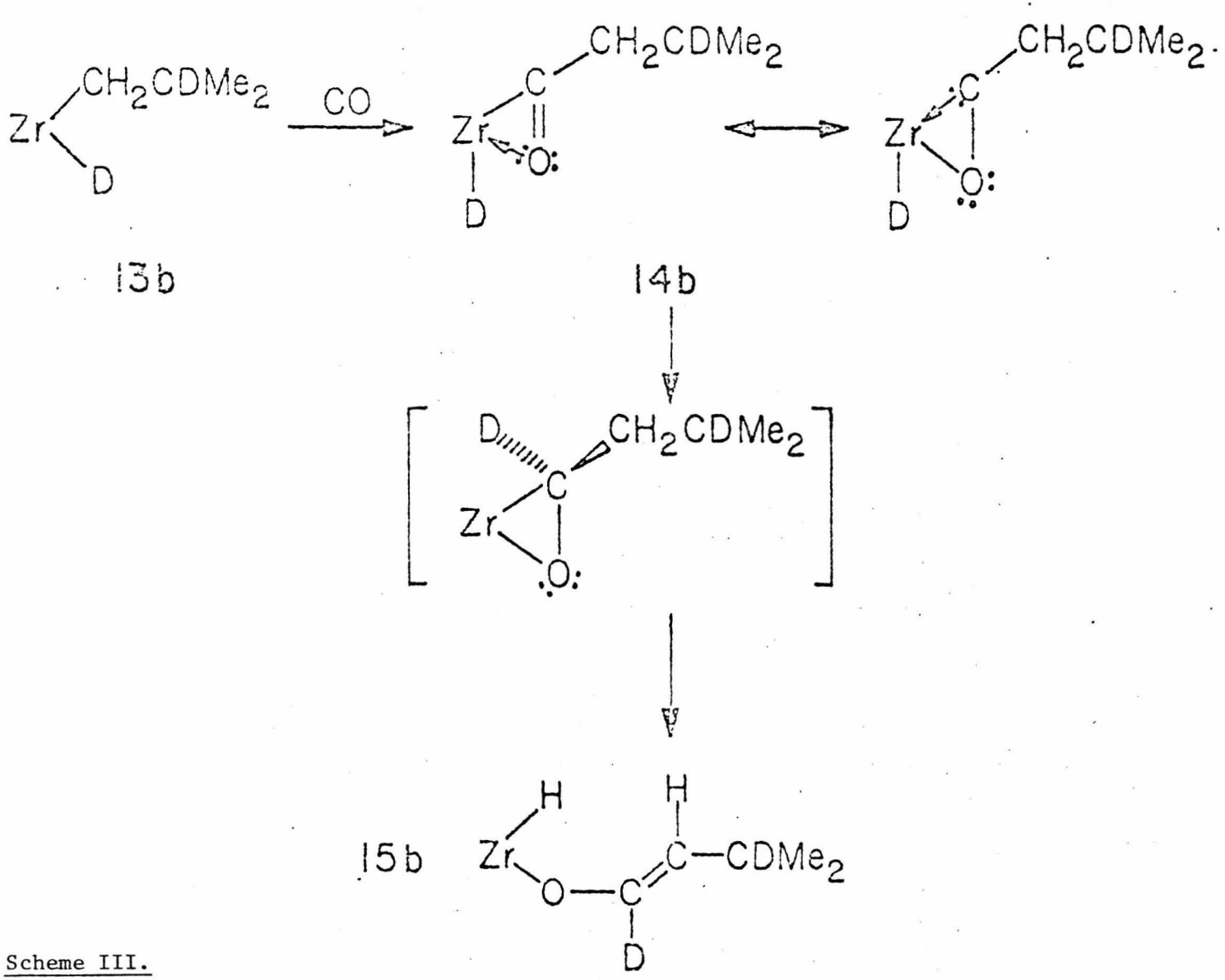
(17)



Scheme II.

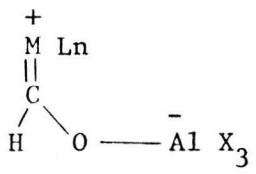
The results of the deuterium labeling studies (eq 12), however, clearly rule out this simple mechanism and suggest instead that outlined in Scheme III. Thus the final location of the deuterium atom which originally resided at zirconium indicates that the oxycarbenoid prefers insertion into Zr-H bonds, reminiscent of the proposed reaction of the oxymethylene species $\left[(\eta^5\text{-}C_5Me_5)_2Zr(H)(O\ddot{C}H)\right]$ with $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (Scheme I). Such insertion provides an aldehyde adduct, which can undergo β-hydride abstraction to afford the enolate hydride 15.

Carbonylation of hydride and alkyl derivatives of permethylzirconocene leads in some instances to products similar to those which might have been expected from more familiar (e.g., Group VIII) organometallic compounds; albeit enolate hydrides, rather than aldehydes or ketones, are produced (12 and 15). In other cases products are derived from coupling of carbonyl carbon atoms (5 and 10). These reaction patterns may be rationalized most simply on the basis of "oxycarbenoid" reactivity imparted to carbon by the unusual mode of coordination of the acyl (or formyl) group to the permethylzirconocene moiety. The reductive coupling of CO is reminiscent of the Fischer-Tropsch synthesis of linear alkanes or alcohols from carbon monoxide and hydrogen,[21,22] and may implicate "side-on" formyl or acyl intermediates in this process. In this context it is interesting to note that homogeneous reduction of CO to produce alcohols or hydrocarbons of carbon number greater than one has thus far only been effected in systems containing either alkyl aluminum hydrides[23] or aluminum trichloride[4], respectively. Both of these reagents (or their degradation products) may function as powerful Lewis acids, suggesting that



Scheme III.

dimerization or insertion of oxycarbene structures such as shown below may mediate these processes.



Facile insertion of CO into zirconium-hydride bonds is certainly indicated in the reaction of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ with carbon monoxide. However, it is important to note that these results do not necessarily require an intramolecular rearrangement of $(\eta^5\text{-}C_5Me_5)_2ZrH_2(CO)$ to $(\eta^5\text{-}C_5Me_5)_2Zr(H)(C(=O)H)$. The very hydridic nature of the hydrogen ligands in these compounds suggests that formyl intermediates may be generated by an alternative mechanism analogous to the reduction of coordinated CO by boron hydrides.[24,25] The observations that $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (2) reacts over several hours at 25° with $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ under H_2 to provide $\{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2(OCH{=}CHO)$ (5) in quantitative yield (eq 18); and that 2 also reacts at about the same rate with thermally non labile $W(CO)_6$ in presence of excess ligand (triphenylphosphine) to give 5 (eq 19), do suggest that 2 can serve to transfer hydride to ligated CO.

$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + (\eta^5\text{-}C_5Me_5)_2Zr(CO)_2 \xrightarrow{H_2} (\eta^5\text{-}C_5Me_5)_2ZrH_2(OCH{=}CHO) \quad (18)$$

$$2(\eta^5\text{-}C_5Me_5)_2ZrH_2 + W(CO_6) \xrightarrow{L} \{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2(OCH{=}CHO) + WL_n \quad (19)$$

Nonetheless, there does not appear to be any compelling reason to

discard intramolecular insertion of CO into Zr-H bonds, especially considering the much greater rate of formation of 5 from $(\eta^5\text{-}C_5Me_5)_2ZrH_2(CO)$ relative to the rates for eqs 18 and 19. Quite possibly, the results of kinetics studies and of attempts to model some of these steps substituting isonitriles for CO will shed more light on these points.

Experimental Section

General Considerations. All manipulations were performed using either glove box or high vacuum line techniques. Solvents were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene".[26] Nmr solvents, toluene-$\underline{d}_8$ and benzene-$\underline{d}_6$ (Stohler, Inc.), were also purified by transfer from "titanocene". Hydrogen and deuterium (MCB) were passed over activated 4 Å molecular sieves and then MnO on vermiculite.[27] Isobutylene and ethylene were distilled from a trap cooled to -78°; carbon monoxide (MCB) was used directly from the cylinder.

^1H nmr spectra were obtained using Varian A60-A, EM-390 and HR-220 spectrometers. ^{13}C nmr spectra were recorded using T-60 (FT) and HR-220 (FT) spectrometers. Infrared spectra were measured on Perkin-Elmer 180 and 457 and on Beckman Ir-12 spectrophotometers.

Several reactions were conducted in sealed nmr tubes and monitored by nmr spectroscopy. A typical example is the reaction of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (2) with CO: ca. 20 mg (0.05 mmol) 2 were transferred to an nmr tube sealed to a groundglass joint and fitted with a teflon needle valve adapter. Toluene-$\underline{d}_8$ (0.3 ml) was distilled into the tube at -78°, one atmosphere CO was introduced and the tube was sealed with a torch.

Procedures (1) $(C_5Me_5)_2Zr(CH_3)_2$. $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ (1.5 g, 5.0 mmol) was slurried in 40 ml diethyl ether at -78°. A portion of 1.84M solution of methyl lithium in diethyl ether (5.4 ml, 9.7 mmol) was added via syringe, and the mixture was allowed to warm to room temperature with stirring. After 3 hr at 25° the solvent was removed in vacuo,

the residue was taken up in 100 ml petroleum ether, the solution was filtered and solvent removed again from the filtrate. White, crystalline material (0.9g, 75% yield) was collected by sublimation (100°, < 10^{-4} torr) of the residue. Calculated for $C_{22}H_{36}Zr$: C 67.50, H 9.20, Zr 93.30; found: C 67.33, H 9.08, Zr 23.52.

(2) $(\eta^5\text{-}C_5Me_5)_2\ Zr(OC(CH_3) = C(CH_3)O)$. A thick walled glass reaction vessel with teflon needle valve was charged with 0.30g (0.75 mmol) 8, 10 ml toluene and 5 mmol (1 atm) CO and heated at 75° with stirring for 24 hr. Solvent was removed in vacuo and the residue was transferred to a sublimator in a glove box. Purple, microcrystalline 10 was collected by sublimation (100°, 10^{-4} torr). Calculated for $C_{24}H_{36}O_2Zr$: C 64.38, H 8.10, Zr 20.37; found: C 64.13, H 7.92, Zr 20.11. Mass spectrum (m/e (rel. intensity)), M^+ (for ^{90}Zr, ^{12}C, ^1H, ^{16}O) 446: 452(6), 451(8), 450(32), 449(10), 448(38), 447(45), 446(100), 403(9), 311(20), 241(8), 223(9), 152(10), 137(10), 119(10), 43(5).

(3) $(\eta^5\text{-}C_5Me_5)_2\ Zr(H)(CH_2CHMe_2)$. An nmr tube was charged with 30 mg of 2, 4 mmol isobutylene, and 0.3 ml benzene-d_6 and sealed. Conversion of 2 to 13 was monitored by ^1H nmr spectrometry and found to be quantitative after a few minutes at 34°. 13 was isolated as follows: To a solution of 0.58 g (1.6 mmol) 2 in 30 ml petroleum ether was admitted 5 mmols isobutylene. After 1 hr stirring at 25°C solvent and excess isobutylene were removed in vacuo leaving 5 ml solution. Slow cooling to -78° provided 0.39 g (58%) yellow, microcrystalline 13 which was collected by filtration at -78° and dried

in vacuo. Calculated for $C_{24}H_{40}Zr$: C 68.66, H 9.61, Zr 21.73; found: C 68.50, H 9.38, Zr 21.42.

$(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ was prepared from $(\eta^5\text{-}C_5Me_5)_2ZrD_2$, obtained via treatment of a petroleum ether slurry of 1 with 1 atm D_2 at 0° for 1 hr, by treatment with excess isobutylene for 4 hr at 0°. 13b was isolated as described above.

(4) $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH{=}CHCHMe_2)$. A solution of 0.21 g (0.5 mmol) 13 in petroleum ether was cooled to -78°, 1 atm CO was admitted and the solution was allowed to warm slowly to room temperature with stirring. Solvent was removed in vacuo to leave an orange oil. Examination of this residue by ^1H nmr indicated 95 mol percent 15 with 5 mol percent $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$.

A diethyl ether solution (15 ml) of 0.14 g of 15 was treated with 0.4 ml 12 M HCl at -78°, and the mixture was stirred as it warmed slowly to room temperature. After 1 hr the volatiles were removed in vacuo at -78°, the solution was warmed, filtered, and the filtrate dried over 4 Å molecular sieves. The remaining organic layer was transferred in vacuo and the volitile fraction analyzed by glc (SE 30 column). Isovaleraldehyde, identified by comparison to an authentic sample, was the only detectable compound other than solvent.

(5) $(\eta^5\text{-}C_5Me_5)_2Zr(OC(Me)_2C(Me)_2O)$. A solution of 0.10 g (0.13 mmol) 1 in 15 ml toluene was prepared in a 25 ml flask fitted with a 10 ml dropping funnel without a pressure equilibrating side arm. The dropping funnel was charged with 0.25 mmol acetone (1 equivalent/Zr) in 3 ml of toluene. The solutions were cooled to -78° and the acetone

solution added slowly, dropwise over a 30 min period. The reaction mixture was allowed to warm slowly to room temperature and stirred for 4 hr. Solvent was removed in vacuo and the remaining oily, red residue was washed with petroleum ether. The white, microcrystalline material that remained was identified as $(\eta^5\text{-}C_5Me_5)_2Zr(OC(Me)_2C(Me)_2O)$ by ^1H nmr (Table I).

The stoichiometry of the reaction was determined as follows: 25 mg 1, 0.03 mmol acetone, 0.3 ml toluene-d_8 and ca. 0.01 mmol TMS were sealed in an nmr tube under N_2. Analysis by ^1H nmr indicated nearly equal amounts of $(\eta^5\text{-}C_5Me_5)_2Zr(OC(Me)_2C(Me)_2O)$ and unreacted 1. There was no evidence of compounds containing hydride or olefinic functionality.

Reactions of acetaldehyde and of isovaleraldehyde with 1 monitored by ^1H nmr as described above give no indication of the formation of enolate hydride compounds (eq 15). Instead, reductive coupling to give products analogous to $(\eta^5\text{-}C_5Me_5)_2\overline{Zr(OC(Me)_2C(Me)_2O)}$ is indicated.

Table I. Proton Nuclear Magnetic Resonance Data

Compound	Solvent			
$(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (2)	benzene-d_6	$C_5(CH_3)_5$	s	2.02 δ
		ZrH_2	s	7.46 δ
$(\eta^5\text{-}C_5Me_5)_2ZrH_2(PF_3)$ (3)	toluene-d_8	$C_5(CH_3)_5$	s	1.77 δ
	-50°	$ZrH_2(PF_3)$	dq	0.55 δ($^2J_{H}{}^{31}{}_{P}$ = 108 Hz, $^3J_{H}{}^{19}{}_{F}$ = 21.5 Hz)
$(\eta^5\text{-}C_5Me_5)_2ZrH_2(CO)$ (4)	toluene-d_8	$C_5(CH_3)_5$	s	1.84 δ
	-64°	$ZrH_2(CO)$	s	1.07 δ
		$ZrH_2(^{13}CO)$	d	1.07 δ($^2J_{H}{}^{13}{}_{C}$ = 25.1 Hz)
$\{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2(OCHCHO)$ (5)	toluene-d_8	$C_5(CH_3)_5$	s	1.94 δ
		$OCH{=}CHO$	s	6.55 δ
		ZrH	s	5.73 δ
		$O^{13}CH{=}^{13}CHO$	10 line AA'XX' pattern	($^1J_{H}{}^{13}{}_{C}$ = 177 Hz, $^1J_{^{13}C^{13}C}$ = 99 Hz, $^2J_{H}{}^{13}{}_{C}$ = 7.5 Hz, $^3J_{HH}$ = 9 Hz)[a]

Table I. (continued)

Compound	Solvent			
$\{(\eta^5\text{-}C_5Me_5)_2ZrI\}_2(OCHCHO)$ (6)	benzene-d_6	$C_5(\underline{CH}_3)_5$	s	1.94 δ
		$OC\underline{H}=C\underline{H}O$	s	6.83 δ
		$O^{13}C\underline{H}=^{13}C\underline{H}O$	10 line AA'XX' pattern ($^1J_{H^{13}C}$ = 180.3 Hz, $^1J_{^{13}C^{13}C}$ = 100 Hz, $^2J_{H^{13}C}$ = 7 Hz, $^3J_{HH}$ = 10Hz)[a]	
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$ (7)	benzene-d_6	$C_5(\underline{CH}_3)_5$	s	1.96 δ
		$Zr\text{-}\underline{H}$	s	5.70 δ
		$OC\underline{H}_3$	s	3.87 δ
$(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)_2$ (8)	benzene-d_6	$C_5(\underline{CH}_3)_5$	s	1.78 δ
		$Zr(\underline{CH}_3)_2$	s	-0.62 δ
$(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)(C(=O)CH_3)$ (9)	benzene-d_6	$C_5(\underline{CH}_3)_5$	s	1.65 δ
		$Zr(\underline{CH}_3)$	s	-0.05 δ
		$Zr(\underline{CH}_3CO)$	s	2.32 δ
$(\eta^5\text{-}C_5Me_5)_2\overline{Zr(O(CH_3)C=C(CH_3)O)}$ (10)	benzene-d_6	$C_5(\underline{CH}_3)_5$	s	1.86 δ
		$O(\underline{CH}_3)C=C(CH_3)O$	s	1.91 δ

Table I. (continued)

Compound	Solvent			
$(\eta^5\text{-}C_5Me_5)_2\overline{Zr(CH_2(CH_2)_2CH_2)}$ (11)	benzene-d_6	$C_5(C\underline{H}_3)_5$	s	1.82 δ
		$C\underline{H}_2(CH_2)_2CH_2$	m	0.50 δ
		$CH_2(C\underline{H}_2)_2CH_2$	m	1.95 δ
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(O\overline{C=CHCH_2CH_2CH_2})$ (12)	benzene-d_6	$C_5(C\underline{H}_3)_5$	s	1.97 δ
		$Zr\underline{H}$	s	6.07 δ
		$OC=C\underline{H}CH_2CH_2CH_2$	m	4.42 δ
		$OC=CHC\underline{H}_2C\underline{H}_2CH_2$	m	2.0-2.5 δ
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (13a)	benzene-d_6	$C_5(C\underline{H}_3)_5$	s	1.93 δ
		$Zr\underline{H}$	s	6.43 δ
		$ZrC\underline{H}_2CH(CH_3)_2$	d	-0.04 δ ($^3J_{H-H}$ = 7 Hz
		$ZrCH_2CH(C\underline{H}_3)_2$	d	1.00 δ ($^3J_{H-H}$ = 6.5 Hz)
$(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ (13b)	benzene-d_6	$ZrC\underline{H}_2CD(CH_3)_2$	s	-0.04 δ
		$ZrCH_2CD(C\underline{H}_3)_2$	s	1.00 δ

Table I. (continued)

Compound	Solvent			
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(C(=O)CH_2CHMe_2)$ (14a)	toluene-d_8	$C_5(CH_3)_5$	s	1.82 δ
	-50°	ZrH	s	3.66 δ
		$C(=O)CH_2CH(CH_3)_2$	d	1.20 δ ($^3J_{H-H}$ = 7 Hz)
		$C(=O)CH_2CH(CH_3)_2$	d	2.54 δ ($^3J_{H-H}$ = 7 Hz)
$(\eta^5\text{-}C_5Me_5)_2Zr(D)(C(=O)CH_2CDMe_2)$ (14b)	toluene-d_8	$C(=O)CH_2CD(CH_3)_2$	s	1.20 δ
	-40°	$C(=O)CH_2CD(CH_3)_2$	s	2.54 δ
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(^{13}C(=O)CH_2CHMe_2)$ (14c)	toluene-d_8	ZrH	d	3.61 δ ($^2J_{^{13}C-H}$ = 9 Hz)
	-40°	$(^{13}C(=O)CH_2CH(CH_3)_2$	d	1.20 δ ($^3J_{H-H}$ = 7 Hz)
		$(^{13}C(=O)CH_2CH(CH_3)_2$	dd	1.18 δ ($^2J_{^{13}C-H}$ = 5 Hz, $^3J_{H-H}$ = 7 Hz)
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH=CHCHMe_2)$ (15a)	benzene-d_6	$C_5(CH_3)_5$	s	1.94 δ
		ZrH	s	6.04 δ
		$OCH=CHCH(CH_3)_2$	d	6.63 δ ($^3J_{H-H}$ = 12 Hz)[a]
		$OCH=CHCH(CH_3)_2$	dd	4.61 δ ($^3J_{H-H}$ = 12 Hz,[a] $^3J_{H-H}$ = 8 Hz)
		$OCH=CHCH(CH_3)_2$	d	1.07 δ ($^3J_{H-H}$ = 6.5 Hz)

Table I. (continued)

Compound	Solvent			
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCD{=}CHCDMe_2)$ (15b)	benzene-d_6	$OCD{=}\underline{C}HCD(CH_3)_2$	s	4.58 δ
		$OCD{=}CHCD(C\underline{H}_3)_2$	s	1.10 δ
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(O^{13}CH{=}CHMe_2)$ (15c)	toluene-d_8	$C_5(C\underline{H}_3)_5$	s	1.90 δ
		$Zr\underline{H}$	s	5.91 δ
		$O^{13}C\underline{H}{=}CHCH(CH_3)_2$	dd	6.53 δ ($^3J_{HH}$ = 12 Hz, $^1J_{^{13}C\text{-}H}$ = 173 Hz)
		$O^{13}CH{=}C\underline{H}CH(CH_3)_2$	m	4.51 δ
		$O^{13}CH{=}CHCH(C\underline{H}_3)_2$	d	1.07 δ ($^3J_{H\text{-}H}$ = 7 Hz)

[a] See note 28.

References and Notes

(1) This chapter is the revised rough draft of a manuscript of the same name co-authored with J.M. Manriquez, R. D. Sanner and J.E. Bercaw and submitted to J. Amer. Chem. Soc.

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(28) Although the magnitudes of the $^{3}J_{HH}$ vinyl couplings for 5 and 6 would appear to indicate cis rather than trans stereochemistry about the olefin, trans is clearly dictated on steric grounds, and is supported by the results of the x-ray structure determination. The 12Hz coupling for 15 is intermediate between typical cis and trans values, but in view of the anomalously small couplings observed for 5 and 6, we have assumed a trans geometry for 15 as well.

Chapter III

Thermal Decomposition of $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ and Reactions with H_2 and Ethylene.

"In case you think this story true,
I merely mention I
Evolved it lately, 'tis a most
Unmitigated misstatement".

R. K.

Introduction

It has commonly been observed that within a homologous series of transition metal cis -dialkyl, -dihydrido and -hydridoalkyl complexes the last is virtually always the least thermally stable.[1] Indeed, the majority of proposed transition metal complexes bearing cis hydride and alkyl ligands are evidenced only by the detection of alkane, presumably generated by reductive elimination from the unstable hydridoalkyl compound. These compounds have frequently been proposed as intermediates in organometallic reactions; in particular, such important processes as catalytic hydrogenation, hydroformylation and olefin isomerization almost certainly proceed by way of hydridoalkyl (or hydrido acyl) intermediates.

Unfortunately, attempts to investigate this important class of compounds both to determine the preferred modes of decomposition and to elucidate possible interactions with molecular hydrogen, olefins, or other donor molecules common to the catalytic systems, have generally been hampered by inability to prepare pure samples. There have been only a few reports of isolable cis-hydridoalkyl complexes. S. Otsuka and co-workers[2-4] have reported the preparation of compounds of the type $(\eta^5\text{-}C_5H_5)_2Mo(H)(R)$ (1) by reaction of $(\eta^5\text{-}C_5H_5)_2MoH_2$ with electron deficient olefins (e.g., dimethyl fumarate, eq 1)

$$(\eta^5\text{-}C_5Me_5)_2MoH_2 + (MeO_2C)(H)C{=}C(H)(CO_2Me) \longrightarrow (\eta^5\text{-}C_5H_5)_2Mo(H)(CH(CO_2Me)CH_2(CO_2Me)) \quad (1)$$

These compounds decompose at 25° to give functionalized alkanes (viz., $CH_2(CO_2Me)CH_2(CO_2Me)$) and a molybdocene polymer. In the presence of excess olefin the organometallic product is the olefin complex, $(\eta^5\text{-}C_5H_5)_2Mo$ (olefin) (eq 2).

$$(\eta^5\text{-}C_5H_5)_2Mo(H)(R) \xrightarrow[25^o]{\text{olefin}} RH + (\eta^5\text{-}C_5H_5)_2Mo \text{ (olefin)} \qquad (2)$$

No dependence, however, of the rate of this reaction on olefin concentration was reported. Dideutero 1, $(\eta^5\text{-}C_5H_5)_2Mo(D)(CH(CO_2Me)CHD(CO_2Me))$, prepared from $(\eta^5\text{-}C_5H_5)_2MoD_2$ and olefin gave primarily the dideutero organic product $CHD(CO_2Me)CHD(CO_2Me)$, indicating a cis elimination.[5]

More recently, J. Norton et al.[6] have reported investigation of the thermal decomposition of cis-$Os(CO)_4(H)(CH_3)$ (2), which at 50° decomposes to give methane according to eq 3.

$$2\ Os(CO)_4(H)(CH_3) \xrightarrow[49^o]{} CH_4 + HOs(CO)_4Os(CO)_4(CH_3) \qquad (3)$$

Kinetics measurements and deuterium labeling studies indicate a rate determining, unimolecular rearrangement of the cis-hydridoalkyl 2 to a mononuclear intermediate, 3, followed by trapping of 3 by excess 2 to generate a binuclear intermediate from which reductive elimination of methane rapidly occurs. In the presence of donor ligands such as $P(C_2H_5)_3$, methane is produced by a mononuclear process apparently as result of phosphine trapping of 3 (eq 4).

$$Os(CO)_4(H)(CH_3) \longrightarrow 3 \xrightarrow{P(C_2H_5)_3} CH_4 + Os(CO)_4(P(C_2H_5)_3) \qquad (4)$$

Norton has suggested that the common intermediate, 3, in these two reactions (eq 3 and 4) might be the five coordinate acetyl hydride complex, $Os(CO)_3(H)(C(=O)CH_3)$, resulting from migration of methyl to coordinated carbon monoxide. The accessibility of a facile process for achieving coordinative unsaturation coupled with the possibility that hydride bridging may be involved in either formation or stabilization of the binuclear intermediate from which reductive elimination most readily occurs have been offered in rationalization of the relative thermal instability of 2 as compared with its dihydrido and dimethyl congeners.

This same relative order of stability is displayed within a homologous series of bis (pentamethylcyclopentadienyl) zirconium (IV) compounds. Thus, while both the dihydrido and dimethyl derivatives of permethylzirconocene are stable indefinitely at 120°, the isobutyl hydride complex, $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (5) decomposes smoothly in solution at 74° providing isobutane quantitatively (nmr). More rapid generation of isobutane is observed upon reaction of 5 with H_2 or with ethylene. The results of kinetics measurements and of deuterium labeling studies of these "reductive elimination" processes are reported in the next section.

Results

The preparation and characterization of 5a by reaction of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (4) with excess isobutylene (eq 5) were described in chapter II of this thesis.

$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 \xrightarrow[25^\circ]{CH_2=CMe_2} (\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2) \qquad (5)$$

The reaction is quantitative (nmr) and apparently completely regioselective. Thus in the preparation of the dideutero complex, $(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ (5b) by the reaction sequence of eq 6 and 7 (cf., Chapter II) there is no indication in the ^{1}H-nmr spectrum of exchange of deuterium with the isobutyl methyl hydrogens as would be expected from reversible formation of $(\eta^5\text{-}C_5Me_5)_2Zr(D)(C(CH_2D)Me_2)$.

$$\left\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\right\}_2(N_2) + 2D_2 \xrightarrow[0^\circ]{} 2(\eta^5\text{-}C_5Me_5)_2ZrD_2 + 3N_2 \qquad (6)$$

$$(\eta^5\text{-}C_5Me_5)_2ZrD_2 \xrightarrow[0^\circ]{CH_2=CMe_2} (\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2) \qquad (7)$$

Reactions involving $(\eta^5\text{-}C_5Me_5)_2ZrD_2$ (4b) must be carried out at low temperature to avoid exchange between the deuteriums on zirconium and the thirty equivalent hydrogens of the two pentamethylcyclopentadienyl rings. Such scrambling is not observed (nmr) for 5b. Erwin and Bercaw[7,8] have made an investigation of the exchange processes encountered with bis(pentamethylcyclopentadienyl) zirconium dihydride and related compounds. Exchange occurs more rapidly between the

hydride positions and hydrogen gas; but, exchange between the hydrides and the hydrogens of the ring methyls is also observed to occur readily at temperatures higher than ca. 50°. The proposed mechanism of these exchange processes is germane to the present discussion and is presented in Scheme I. The key steps include reversible transfer of hydrogen from zirconium to one of the permethylcyclopentadienyl ring carbon atoms (thus effecting a reduction of the formal oxidation state of zirconium from IV to II) and subsequent reversible insertion of zirconium into a carbon-hydrogen bond of a ring methyl group. This exchange process was exploited in the preparation of the perdeuterated compound, $(\eta^5\text{-}C_5(CD_3)_5)_2ZrD_2$ (4c) by repeated exposure of toluene solution of 4 to deuterium gas in a bomb at 80°. $(\eta^5\text{-}C_5(CD_3)_5)_2Zr(D)(CH_2CD(CH_3)_2)$ (5c) was then prepared by reaction of 4c with isobutylene as in eq 7.

The isobutyl hydride complex, 5, is isolated as a pale yellow[9], microcrystalline material. Ir and nmr spectra, analytical data (see Experimental section) and high solubility in hydrocarbon solvents suggest a monomeric, pseudotetrahedral structure as have been encountered with many of these permethylzirconocene derivatives. Thermally, 5 is the most stable transition metal cis-alkyl hydride complex yet reported; however, its solutions are somewhat photosensitive.

When pyrolized in benzene or toluene solution in sealed glass tubes at 74°, 5 quantitatively (nmr) liberates isobutane. Unfortunately, under these conditions the organometallic products appear to undergo further reaction and have not all been identified. However, the rate of disappearance of 5 and the rate of appearance of isobutane

(monitored by ^{1}H-nmr spectroscopy) are in very good agreement, indicating a common rate determining step. The rate law for thermolysis of 5a is:

$$-\frac{d[5a]}{dt} = \frac{d[HC(CH_3)_3]}{dt} = k_{5a}[5a] .$$

At 74° the first order rate constant is, $k_{5a} = (7.2 \pm 0.5) \times 10^{-5}$ sec^{-1}. The activation parameters are: $\Delta H^{\ddagger} = 21$ (±1.0) kcal/mole and $\Delta S^{\ddagger} = -5$ (±0.5) eu. Pyrolysis of $(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ (5b) at 74° occurs with a nearly identical rate, the first order rate constant was measured as $k_{5b} = (7.7 \pm 0.5) \times 10^{-5}$ sec^{-1}. However, the more extensively deuterated compound, $(\eta^5\text{-}C_5(CD_3)_5)_2Zr(D)(CH_2CD(CH_3)_2)$ (5c) decomposed only half as fast, with rate constant $k_{5c} = (3.8 \pm 0.5) \times 10^{-5}$ sec^{-1}.

The determination of the isotopic distribution in the 2-methylpropanes encountered in this study presented some difficulty (cf., Experimental section). However, corrolation of both mass and ir spectral data allows detection of the presence of (conservatively estimated) 5-10% of the specifically labeled d_0, d_1 or d_2 isobutanes.

The 2-methylpropanes resulting from pyrolysis of 5a, 5b and 5c (and from their reactions with H_2, D_2, C_2H_4 and C_2D_4) are given in Table I. Surprisingly, pyrolysis of $(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ (5b) at 74° in toluene-d_8 gives only the monodeuterated alkane, 2-deutero-2-methylpropane. None of the dideuterated alkane (1,2-dideutero-2-methylpropane) which would result from simple reductive elimination--as was reported by S. Otsuka[4] for molybdocene alkylhydride compounds--

was detected. ^{1}H-nmr monitoring of pyrolysis samples at partial completion gives no indication of exchange between the deuteride and the ring methyl hydrogens of unreacted 5b. $(\eta^5\text{-}C_5(CD_3)_5)_2Zr(D)(CH_2CD(CH_3)_2)$ (5c) does, however, give 1,2-dideutero-2-methylpropane when heated at 74° in toluene-d_0. Thermolysis of a 1:1 mixture of 5a and 5c gives only the d_0 and d_2 2-methyl propanes. Thus thermal decomposition of 5 appears to involve intramolecular coupling of the isobutyl fragment with a hydrogen atom from a ring methyl group. Simple coupling of the alkyl and hydride substituents originally cis in the starting material and radical and other bimolecular processes appear to be contraindicated.

These isobutyl hydride complexes react very rapidly in melting toluene with a hydrogen atmosphere to regenerate 4 and produce 2-methylpropane in accord with eq 8.

$$(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2) \xrightarrow[<-80^\circ]{H_2} (\eta^5\text{-}C_5Me_5)_2ZrH_2 + HC(CH_3)_3 \qquad (8)$$

Once again, simple reductive elimination of alkane (followed by trapping of the "zirconocene" thus formed by H_2 to provide 4) is not observed. Instead, the isotopic labeling pattern (Table I) indicates coupling of the isobutyl group only with hydrogen (or deuterium) atoms from the ambient gas. Thus treatment of 5a with D_2 gives only 1-deutero-2-methylpropane, $HC(CH_2D)(CH_3)_2$, while reaction of 5b or 5c with H_2 affords only 2-deutero-2-methylpropane, $DC(CH_3)_3$.

When treated with excess ethylene (a 3:1 molar ratio or higher), 5 reacts over a period of a few hrs at 25° to give isobutanes and the previously characterized zirconocyclopentane[10,11], $(\eta^5\text{-}C_5Me_5)_2$

$\overline{Zr(CH_2(CH_2)_2CH_2}$) (6) (eq 9).

$$(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2) + 2\,CH_2{=}CH_2 \xrightarrow[25^o]{} (\eta^5\text{-}C_5Me_5)_2\overline{Zr(CH_2(CH_2)_2CH_2}) + HC(CH_3)_3 \qquad (9)$$

The alkane resulting from reaction of 5a with only a slight excess over the stoichiometric amount of C_2D_4 consisted of a mixture of d_0 and d_1 2-methylpropanes (Table I). Reaction of 5b or 5c with a larger excess of C_2H_4 on the other hand gave only 2-deutero-2-methylpropane. $(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ (5b) reacts slowly with C_2H_4 at 0^o; ir and nmr spectroscopic examinations of the unreacted 5b at intermediate stages of the reaction indicate progressive replacement of the deuterium on zirconium with hydrogen.

Discussion

Thermolysis of the cis alkyl hydride complex, $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (5a) at 74° in toluene or benzene solution induces quantitative generation of 2-methylpropane. The identification of 2-deutero-2-methylpropane as the only isobutane resulting from pyrolysis of $(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ (5b) is, however, inconsistent with simple, concerted reductive elimination, a process which would give dideutero isobutane as in eq 10.

$$(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2) \not\rightarrow DC(CH_2D)(CH_3)_2 + "(\eta^5\text{-}C_5Me_5)_2Zr" \qquad (10)$$

Homolysis of the zirconium-carbon bond and subsequent abstraction of hydrogen by the isobutyl radical either from solvent or from the organozirconium compounds is also contraindicated. Thus thermal decompositions of 5a in toluene-$\underline{d}_8$ and of 5c in toluene-$\underline{d}_0$ give only $\underline{d}_0$ and $\underline{d}_2$ isobutanes, respectively; ruling out trapping of isobutyl radical by solvent. Moreover, the absence of detectable $\underline{d}_1$-isobutane among the products of thermolysis of a 1:1 mixture of 5a and 5c mitigates against attack of free isobutyl radical on the starting hydridoalkyl complexes or on any of their decomposition products being a major pathway for the decomposition.

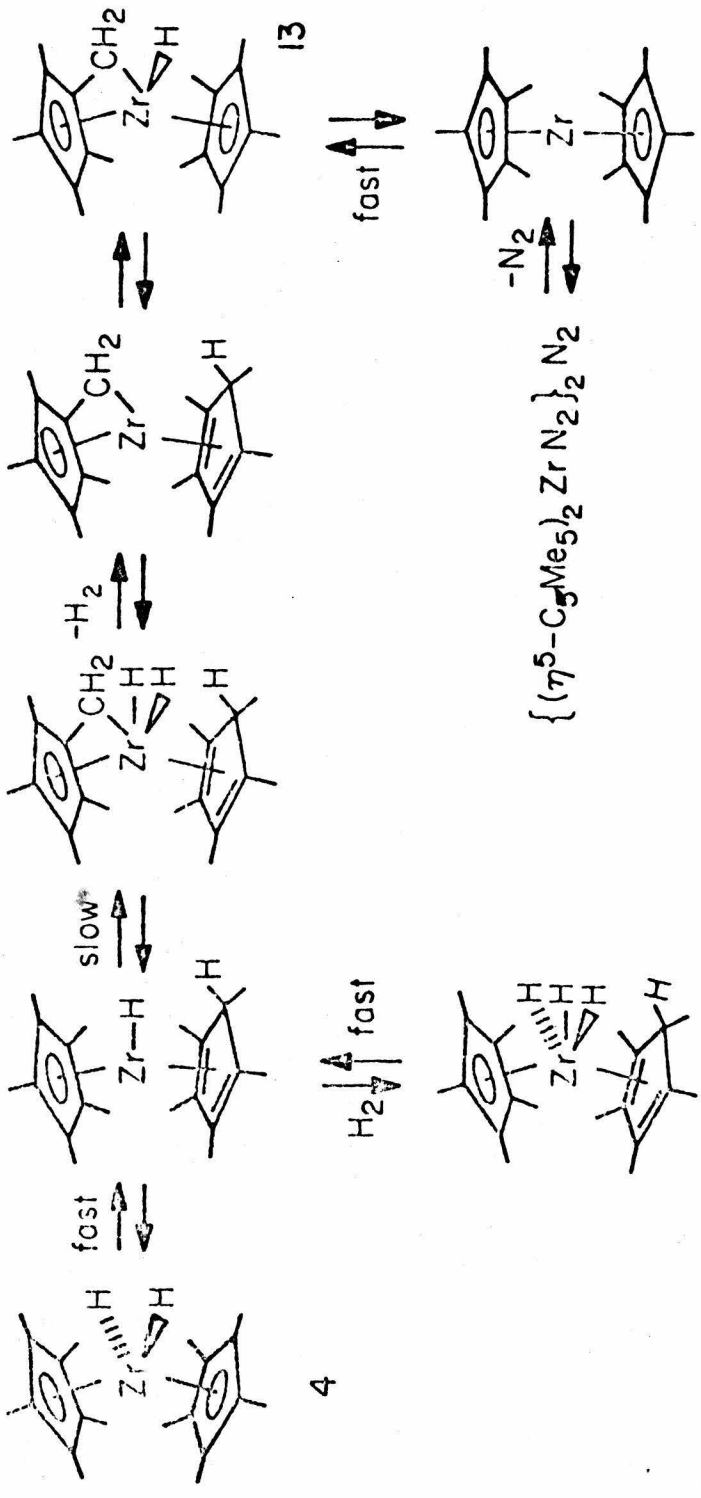
Instead, the observed isotopic selectivity strongly imples an intramolecular process whereby isobutane is generated by coupling of the isobutyl group with a hydrogen from one of the methyls on the pentamethylcyclopentadienyl rings. Such involvement of the hydrogens of the ring methyls is reminiscent of the mechanism proposed for the

exchange between methyl hydrogens of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (4) and deuterium gas[7,8] (Scheme I). Indeed, a very similar mechanistic hypothesis (Scheme II) conveniently accomodates the kinetics and isotopic labeling data for both pyrolysis of 5 and for its reaction with H_2.

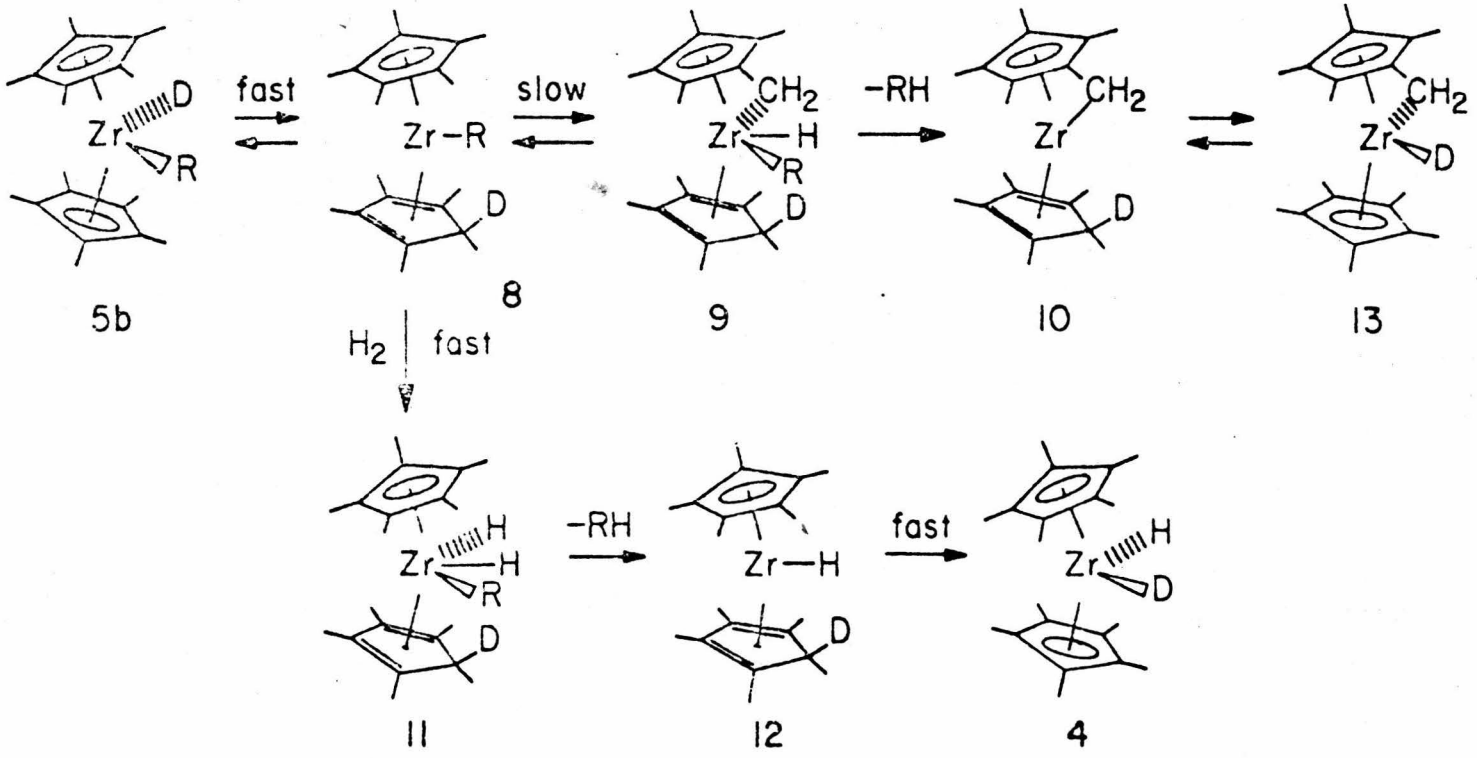
The initial step of Scheme II is a facile and reversible tautomerization of 5 via a zirconium to ring-carbon hydride transfer to provide $(\eta^5\text{-}C_5Me_5)(\text{exo-}\eta^4\text{-}C_5Me_5H)Zr(CH_2CHMe_2)$ (8). Similar metal to cyclopentadienyl ring transfers both of hydride and of alkyl have been observed in the chemistry of bis (cyclopentadienyl) molybdenum and tungsten compounds.[12-13] Subsequent, rate determining, intramolecular insertion of the newly formed zirconium (II) center of 8 into a carbon-hydrogen bond of a ring methyl affords intermediate 9 from which rapid, irreversible elimination of isobutane occurs.

The organozirconium compound, 10, remaining after elimination of isobutane is a tautomer of previously reported $(\eta^5\text{-}C_5(CH_3)_5)(\eta^5\text{-}C_5(CH_3)_4CH_2)ZrH$ (13)[14,15] which is known to decompose in a complicated manner when heated in solution giving products not yet completely characterized but not inconsistent with those observed in pyrolysis of 5.[14] The fact that 13 rather than $(\eta^5\text{-}C_5Me_5)_2Zr$ is formed upon removal of N_2 from the dinitrogen complex $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2(N_2)$ (eq 11) serves as a precedent for the insertion of zirconium into a ring methyl carbon-hydrogen bond postulated in conversion of 8 to 9.

$$\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2(N_2) \longrightarrow 2(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)ZrH + 3N_2 \qquad (11)$$



Scheme I.



Scheme II.

The mechanism of Scheme II accounts for the deuterium distribution found in isobutanes resulting from pyrolysis of 5a, b and c. The observed dependence of the rate of decomposition only on 5 and the small, negative entropy of activation, $\Delta S^{\ddagger} = -5 (\pm 0.5)$ eu. determined for the process are also fully in accord with a rate determining, unimolecular rearrangement of 8 to 9. Moreover, detection of a deuterium isotope effect on the rate only upon deuteration of the ring methyls fits well with this mechanism. The isotope effect, $k_H/k_D = 2$, is admittedly rather small for a primary kinetic isotope effect; however, it is similar to the effect, $k_H/k_D = 1.5$, reported by Norton for the rate of thermal decomposition of cis-$Os(CO)_4(H)(CH_3)$.[6,10]

The reaction of 5 with hydrogen can also be accommodated within the same mechanistic framework (Scheme II). Thus, rearrangement of 5 to 8 provides a zirconium (II) center to which H_2 can oxidatively add. Rapid, irreversible elimination of isobutane from the resulting intermediate, 11, leaves a tautomer of 4, the product actually observed in the reaction.

This mechanism is completely analogous to that proposed for exchange of the ring methyl hydrogens of 4 (Scheme I) and accounts well for the isotopic labeling observed in the isobutanes produced by reaction of 5 with H_2 and D_2. However, an alternate mechanism requiring very rapid exchange between the hydride position of 5 and the H_2 (or D_2) atmosphere has not yet been ruled out. Perhaps investigation of the effect of the quantity of H_2 available on the extent of isotopic selectivity would provide a basis for distinction.

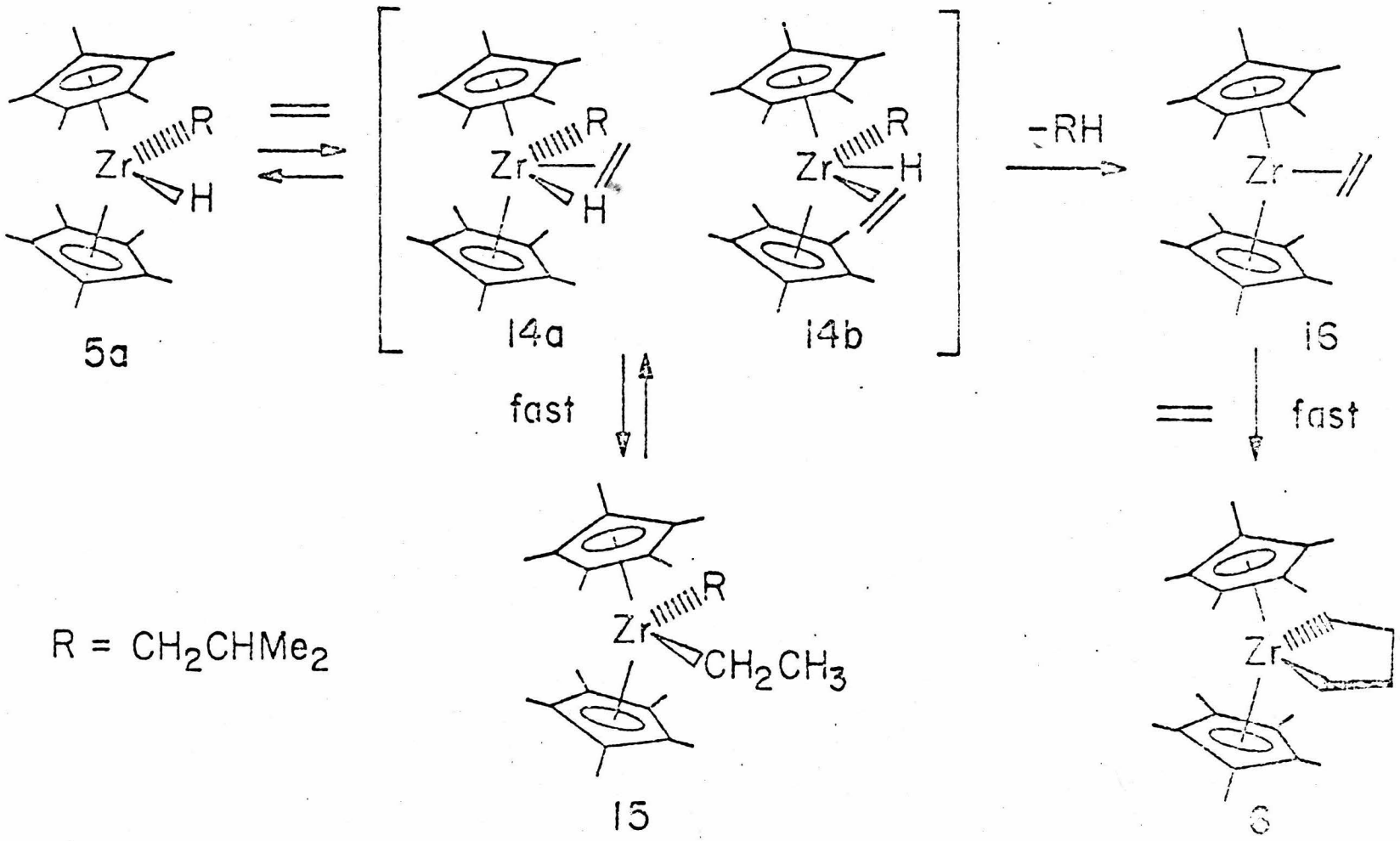
The reaction of 5 with ethylene appears to take a different

course. The generation of both $\underline{d}_0$ and $\underline{d}_1$ isobutanes in the reaction of 5a with only slightly more than 2 molar equivalents of C_2D_4 and the replacement of deuteride by hydrogen observed in the reaction of 5b with excess C_2H_4 at 0^o both indicate some process for exchange between the hydride position of 5 and the hydrogen atoms on the olefin. Reversible insertion of ethylene into the zirconium hydride bond of 5 provides just such a process (Scheme III).

Although β-hydrogen abstraction in the dialkyl complex, $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CH_3)(CH_2CHMe_2)$ (15), postulated as an intermediate in Scheme III could conceivably generate isobutylene and an ethyl hydrido derivative of permethylzirconocene, $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CH_3)$, no evidence of such a reaction (eq 12) is observed.

$$(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CH_3)(CH_2CHMe_2) \not\longrightarrow (\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CH_3) + CH_2{=}CMe_2 \qquad (12)$$

The responsiveness of 5 to steric considerations evidenced by the lack of reaction between 5 and isobutylene makes failure to eliminate the bulkier olefin seem, at first, somewhat surprising. The inability of 5 to react with isobutylene probably reflects the difficulty of getting a relatively bulky, disubstituted olefin into the coordination sphere in order to form an intermediate olefin complex analogous to 14 (Scheme III). However, β-elimination of isobutylene from $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CH_3)(CH_2CHMe_2)$ would presumably require initial formation of just such a complex of a disubstituted olefin and hence might be prevented by the same steric constraints.



Scheme III.

There is, however, no direct evidence of the formation of an ethylene complex such as 14. Other small donor molecules such as $P(CH_3)_3$ and $P(OCH_3)_3$ do not form adducts with 5. Carbon monoxide does react rapidly but gives products resulting from migration of both alkyl and hydride ligands to the carbonyl carbon atom.[6] Nonetheless, it is possible to speculate that perhaps the mode of initial coordination of ethylene to 5--either centrally, between the hydride and alkyl ligands (14a) or to the side, forcing the other two equitorial ligands into closer proximity--could be the factor that distinguishes between the two paths for further reaction.[16]

Clearly, "reductive elimination" in the context of these hydridoalkyl derivatives of permethylzirconocene is a term which covers considerable mechanistic complexity. The existence of different processes for formation of isobutane from $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (5a) induced by thermolysis or by reaction with hydrogen or ethylene may well be of significance with regard to mechanisms of catalytic hydrogenation reactions. It is particularly interesting to note that, while the mechanism of thermal decomposition of 5 is clearly different from those of cis-$Os(CO)_4(H)(CH_3)$ or $(\eta^5\text{-}C_5H_5)_2Mo(H)(CH(CO_2Me)CH_2(CO_2Me))$, the commonly observed relative instability of a hydridoalkyl complex as compared to its dialkyl or dihydrido congeners, is nevertheless clearly maintained.

Experimental Section

General Considerations. All manipulations were carried out using glove box (Vacuum Atmospheres) or high vacuum line techniques. Solvents were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene".[17] Deuterated solvents, toluene-d_8 (Stohler, Inc.) and benzene-d_6 (Aldrich), were also purified by transfer from "titanocene". Hydrogen and deuterium (MCB) were passed through MnO on vermiculite[18] and then over actived 4 Å molecular sieves. Isobutylene and ethylene were passed through a trap at -78°.

^{1}H-nmr spectra were recorded on Varian A60-A, EM-390 and HR-220 spectrometers. Infrared spectra were obtained using Perkin-Elmer 457 and Beckman IR-12 spectrophotometers. Mass spectra were measured on an MS-9 "high resolution" spectrometer.

Kinetics measurements. The thermal decompositions of isobutyl-hydride complexes (5a, b and c) were monitored by ^{1}H nmr. A typical sample was prepared as follows: ca. 20 mg (0.05 mmol) $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (5a) was transferred in a glove box to an nmr tube sealed to a ground glass joint and fitted with a teflon needle-valve adaptor. Benzene-d_6 (0.3 ml) and TMS (0.01 mmol) were vacuum transferred into the tube and it was sealed with a torch. Samples were heated fully immersed in a constant temperature oil bath and ^{1}H-nmr spectra were periodically recorded. Relative concentrations were determined by comparison of integrations of the relavent resonances with that of TMS. The nmr spectra from pyrolysis of 5a gave indication of the formation of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (4) in 50% yield based on 5a along with other resonances indicating formation and transformation of as yet

unidentified compounds.[15]

Plots of the log of the relative concentration of either 5 or isobutane vs. time had identical slopes and were linear for greater than three half-lives. The first order rate constants for decomposition of 5a at 74°, 90° and 105° and for 5b and c at 74° appear in Table III. Activation parameters for pyrolysis of 5a (determined from the Arrhenius-Eyring equation) are: $\Delta H^{\ddagger}$ = 21 (±1.0) kcal/mole and $\Delta S^{\ddagger}$ = -5 (±0.5) eu.

Determination of Isotopic Distribution. The determination of the isotopic labeling of the 2-methylpropanes encountered in this study presented some difficulty. Unfortunately, 2-methylpropane suffers severe fragmentation upon ionization even at very low ionization voltage (5 eV). Therefore the observed parent peaks are only about 5% the intensity of the propyl cation peaks resulting from loss of methyl. Loss of hydrogen (or deuterium) from the tertiary carbon is also a facile process; hence, comparison of the relative intensities of the parent peak and the next two lower m/e peaks gives an indication of the isotopic distribution. Infrared spectroscopy provides a valuable supplement to the mass spectral data. Characteristic ir absorptions of $\underline{d}_0$, $\underline{d}_1$, and $\underline{d}_2$ isobutanes are presented in Table II.

Independently derived samples of $HC(CH_3)_3$ (MCB) and $DC(CH_3)_3$ (prepared by D_2O quenching of $(CH_3)_3CMgCl$) were employed for ir characterization. Spectral samples of $DC(CH_2D)(CH_3)_2$ and $HC(CH_2D)(CH_3)_2$ were derived from reaction of 5b with D_2 and 5c with H_2, respectively.

Typically, the pyrolysis experiments were performed as follows: a thick walled, glass bomb with a teflon valve was charged with 120 mg (0.25 mmol) 5 and solvent, toluene $\underline{d}_0$ or $\underline{d}_8$, introduced by vacuum transfer. After 48 hrs at 74° the bomb was cooled to -78° and isobutane collected by vacuum transfer.

Reactions of 5 with hydrogen (or deuterium) were conducted similarly. The bomb was charged with 80 mg (0.2 mmol) 5 and 3 ml toluene ($\underline{d}_0$ or $\underline{d}_8$); the solution was frozen in liquid nitrogen and 1 atm hydrogen (ca. 2 mmol H_2) admitted. The reaction mixture was allowed to warm to 25° and was then refrozen in liquid nitrogen and H_2 removed in vacuo. The reaction mixture was warmed to -78° and isobutane was collected by vacuum transfer.

For reactions with ethylene, the bomb was charged with 5 (80 mg, 0.2 mmol), 3 ml solvent and ca. 1 mmol C_2H_4. The reaction mixture was stirred at 25° for 4 to 8 hrs and then cooled to -120° in a petroleum ether slush (ca. -120°). Volatiles (excess ethylene) were removed in vacuo, the reaction mixture was warmed to -78° and isobutane was collected by vacuum transfer. Reactions with C_2D_4 were performed analogously except only a slight excess over the stoichiometric requirement of olefin (2 moles C_2D_4/mole Zr) was employed.

Preparation of $(\eta^5\text{-}C_5(CD_3)_5)_2Zr(D)(CH_2CD(CH_3)_2)$ (5c). The preparations of 5a and 5b are described in Chapter II. 5c was prepared from the perdeuterated compound, $(\eta^5\text{-}C_5(CD_3)_5)_2ZrD_2$ generated as follows: a bomb of 1 liter capacity was charged with 800 mg (1 mmole) $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2(N_2)$ dissolved in 10 ml benzene-$\underline{d}_6$. 1 atm H_2 was admitted and the reaction mixture was stirred until the

disappearance of the characteristic red color of the dinitrogen complex signaled complete conversion to 4. The atmosphere was replaced by D_2 and the bomb was heated to 70° for 2 hrs. The atmosphere was replaced with fresh D_2 and the bomb heated 2-4 hrs at 70° for four more cycles. Solvent was removed in vacuo and the residue ($(C_5(CD_3)_5)_2ZrD_2$) was used in reaction with isobutylene at 0° exactly as in the preparation of 5b (Chapter II). It was characterized by its ^1H nmr spectrum: $ZrC\underline{H}_2CD(CH_3)_2$ singlet, -0.04 δ; $ZrCH_2CD(C\underline{H}_3)_2$ singlet, 0.99 δ.

Table I. Isotopic Distribution Data

Pyrolysis:	Solvent	Product
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (5a)	C_7D_8	$HC(CH_3)_3$
$(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ (5b)	C_7D_8	$DC(CH_3)_3$
$(\eta^5\text{-}C_5(CD_3)_5)_2Zr(D)(CH_2CDMe_2)$ (5c)	C_7H_8	$DC(CH_2D)(CH_3)_2$
5a + 5c	C_7H_8	$HC(CH_3)_3 + DC(CH_2D(CH_3)_2$
Reaction with H_2:		
5a	C_6D_6	$HC(CH_3)_3$
5b	C_7D_8	$DC(CH_3)_3$
5c	C_7D_8	$DC(CH_3)_3$
Reaction with D_2:		
5a	C_7H_8	$HC(CH_2D)(CH_3)_2$
5b	C_7D_8	$DC(CH_2D)(CH_3)_2$
Reaction with C_2H_4:		
5a	C_6D_6	$HC(CH_3)_2$
5b	C_7D_8	$DC(CH_3)_3$
Reaction with C_2D_4:		
5a	C_7D_8	$HC(CH_3) + HC(CH_2D)(CH_3)_2$

Table II. Ir Spectra of $\underline{d}_0$, $\underline{d}_1$ and $\underline{d}_2$ Isobutane.

	ν(C-D)	δ(CH_3)	ν(C-C)
$HC(CH_3)_3$		1480s, 1380s, 1335m	1180m
$HC(CH_2D)(CH_3)_2$	2160 m (2180 sh)	1470s, 1385s	1285m, 1155m
$DC(CH_3)_3$	2145m	1475s, 1380s	1235m, 1225m
$DC(CH_2D)(CH_3)_2$	2165m	1470s, 1385s	1295m, 1220m

Table III. Kinetic Data for Thermolytic Decomposition of $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (5a) and Deuterated Analogs, 5b and 5c.

Compound	Temperature	Rate of Decomposition
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (5a)	74°	7.2×10^{-5} s^{-1}
	90°	4.0×10^{-5} s^{-1}
	105°	1.5×10^{-5} s^{-1}
$(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ (5b)	74°	7.7×10^{-5} s^{-1}
$(\eta^5\text{-}C_5(CD_3)_5)_2Zr(D)(CH_2CDMe_2)$ (5c)	74°	3.8×10^{-5} s^{-1}

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(15) Pyrolysis of 5 or of 13[14] for several hours at 70° to 80° results in formation of 4 (ca. 50% yield (nmr) based on starting zirconium complex). The ^{1}H nmr spectra of the remaining compound(s) display several singlets of equal intensity in the region between δ 1.5-2.5 ppm; a feature characteristic of the $C_5(CH_3)_4CH_2$-Zr moiety. Upon longer pyrolysis or at higher temperature further spectral changes indicate reactions of 4 and of the other, unidentified products .

(16) An investigation of reaction of 5 with excess C_2F_4 (5:1 olefin to Zr molar ratio) has been initiated on an "nmr tube" scale. The reaction after several hrs at 25° provides only about 20% the expected isobutane; the isotopic selectivity has not yet been established. A new singlet is observed at 1.80 of proper intensity (20% of starting 5) to represent the permethyl rings of a fluorinated metallocycle analogous to 6 formed in accompaniment with isobutane. The remaining 80% of 5 is converted to a new compound in which the isobutyl moiety is apparently retained. Based on the ^{1}H nmr spectrum (singlet, δ 1.77 (30 H), doublet (J_{HH}=6.5 Hz), δ 1.37 (6H), and doublet (J_{HH}=6.5 Hz), δ 0.72 (2H)) the following structure is proposed:

$(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CHMe_2)(CF_2CF_2H)$. Such a compound is certainly consistent with the mechanism of Scheme III with the provision that this fluorinated analog of 15 is irreversibly formed. An alternate structure analogous to 14 cannot be ruled out, however the relatively slow rate of formation and the thermal stability of this new compound (it is unchanged after 2 hrs at 74°) are not suggestive of a simple adduct. The ^{19}F spectrum indicated only the presence of unreacted C_2F_4. Other resonances, while detectable, were insufficiently well resolved to support any conclusions.

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(18) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, Rev. Sci. Instrum., 33, 491 (1962).