

RECENT ADVANCES IN THE CHEMISTRY OF
PENTAMETHYLCYCLOPENTADIENYL
COMPLEXES OF ZIRCONIUM AND
TANTALUM

by

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ABSTRACT

The recent literature concerning pentamethylcyclopentadienyl (C_5Me_5) complexes of zirconium and tantalum has been reviewed. The major aspect of the work that is discussed here is the reactivity of these transition metal complexes with small molecules. Also included, where possible is a comparison of the reactivity of C_5Me_5 complexes with the reactivity of C_5H_5 complexes. In the first section zirconium complexes of dinitrogen are discussed followed by reductive elimination of alkanes from zirconium compounds (both C_5Me_5 and C_5H_5 complexes). Finally, the reduction of carbon monoxide and nitrile compounds by zirconium complexes is reviewed. In the second section the synthesis and reactivity of tantalum olefin and metallacyclopentane complexes are covered. Discussion of why C_5Me_5 complexes of tantalum are longer lived catalysts in the dimerization of α -olefins than the C_5H_5 analogs follows. Finally, the details of the reduction of carbon monoxide by a tantalum complex are mentioned.

INTRODUCTION

Synthesis and study of complexes of the cyclopentadienyl anion have been one of the major areas of organometallic research since the discovery of ferrocene (Cp_2Fe) in 1952.¹ The Cp (Cp = Cyclopentadienyl) ligand was shown to form very strong bonds with transition metals, opening an extensive area of organometallic research.

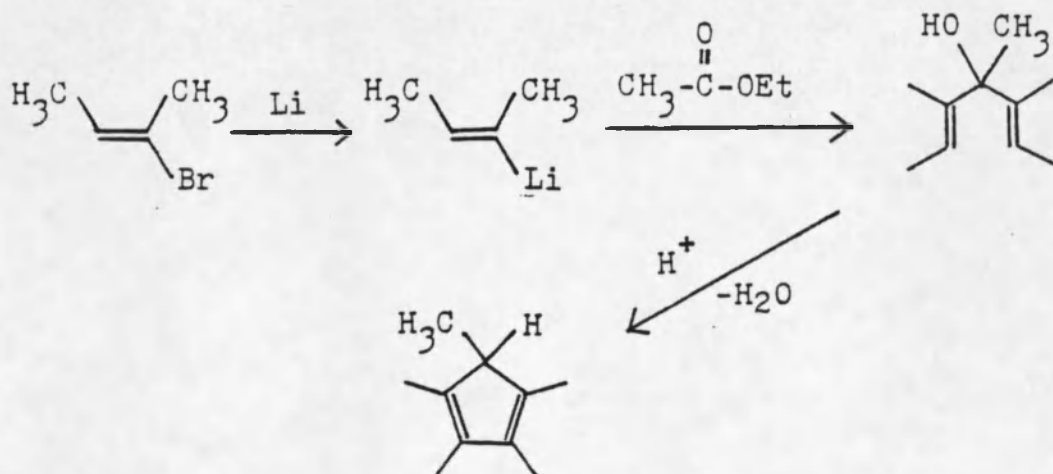
It was early thought that if the cyclopentadienyl ligand could be substituted at all five hydrogens that this should result in substantial changes in the properties of the complexes containing these ligands. To this end several substituted systems were synthesized: pentachlorocyclopentadienide,² pentacyanocyclopentadienide,³ pentaacetylcyclopentadienide,⁴ and pentamethylcyclopentadienide.⁵ Complexes of the pentamethylcyclopentadienide have been the most extensively studied probably due to the high crystallizability and greater stability of compounds formed with this ligand.^{5,6}

Several reviews concerning use of this ligand in middle and late transition metal complexes have appeared.⁷ However, in recent years a great deal of work has appeared concerning early transition metal complexes of the $\eta^5\text{-C}_5\text{Me}_5$ ligand, especially with zirconium and tantalum.

The purpose of this paper is to review the new work. Included, where possible will be a comparison of the reactions of these complexes with those of their C_5H_5 analogs.

Pentamethylcyclopentadiene

Although several synthetic routes to pentamethylcyclopentadiene have appeared in the literature,^{8,9} a convenient method for large-scale preparation of the ligand has only recently been reported by Bercaw and Threlkel.⁵ The outline of the synthesis is shown in Scheme 1. Cis-2-bromo-2-butene was synthesized by bromination of trans-2-butene followed by dehydrohalogenation of the product 2,3-dibromobutane. In situ treatment of 2-butenyllithium (prepared by reaction of the 2-bromo-2-butene with lithium wire) with 0.5 molar equivalents of ethylacetate afforded di-s-2-butenyl methylcarbinol. Treatment of the alcohol with acid produced a carbonium ion which underwent electrocyclic ring closure⁸ followed by deprotonation to give neutral pentamethylcyclopentadiene. The pentamethylcyclopentadienide anion was generated by treatment of the neutral diene with butyl lithium.



Scheme 1

ZIRCONIUM COMPLEXES

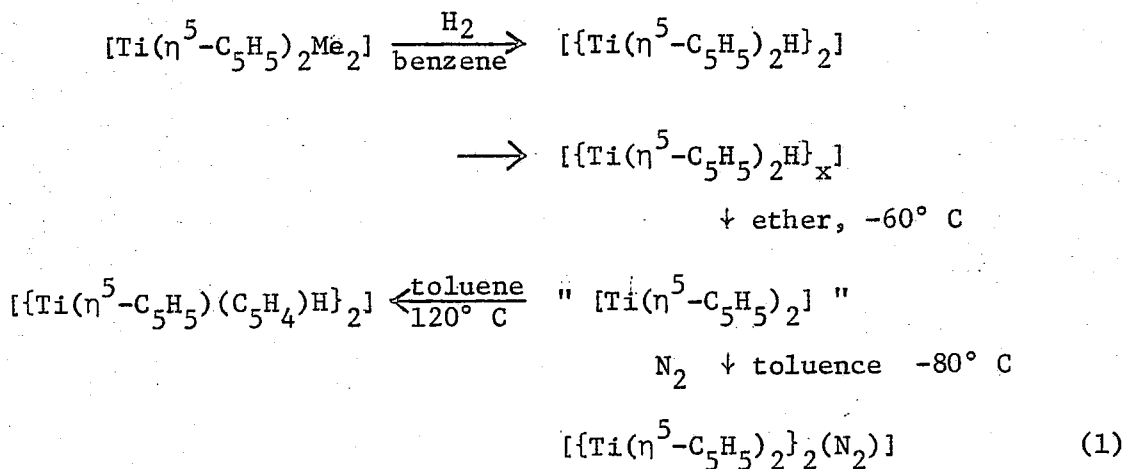
In recent years the study of zirconium complexes of $\eta^5\text{-C}_5\text{H}_5$ has resulted in the discovery of a number of useful reactions such as hydrozirconation,¹⁰ cross-coupling of alkenes,¹¹ reduction of CO¹² and conjugate addition of an alkenyl unit to enones.¹³ Some of these reactions will be discussed later in connection with $\eta^5\text{-C}_5\text{Me}_5$ complexes. In contrast to the $\eta^5\text{-C}_5\text{H}_5$ compounds, the $\eta^5\text{-C}_5\text{Me}_5$ systems were first studied in detail because of their relationship to nitrogen fixation.

Complexes of Dinitrogen

Dinitrogen complexes of zirconium and titanium have been known since the early seventies, and due to its importance, this area has been covered in several reviews.¹⁴ As an introduction to the chemistry of C_5Me_5 complexes of zirconium, a few of the reactions with titanium and zirconium will be mentioned here.

Shilov et al. reported that the dimer $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}\}_2]$ reacted with P_R^iMgCl in Et_2O in the presence of dinitrogen to give $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{P}_R^i)\}_2(\text{N}_2)]$.¹⁵ Complex 1 was subsequently reported to react further with P_R^iMgCl to give $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\}_2(\text{N}_2)\text{MgCl}]$.¹⁶ Titanium (III) complexes of the type $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{R}]$ ($\text{R} = \text{Ph}$; o-, m- or p- $\text{CH}_3\text{C}_6\text{H}_4$; 2, 6- $\text{Me}_2\text{C}_6\text{H}_3$; 2, 4, 6- $\text{Me}_3\text{C}_6\text{H}_2$; CH_2Ph ; or C_6F_5) reacted with dinitrogen in toluene to give $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{R}\}_2(\text{N}_2)]$.¹⁶

In addition Brintzinger et al, have shown that hydrogenation of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Me}_2]$ in benzene gave a polymeric hydride complex which upon standing in ether lost dihydrogen to give " $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2]$ " (titanocene) which in turn reacted rapidly with dinitrogen (eq. 1).¹⁷ Complexes of stoichiometry $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\}_2(\text{N}_2)]$ were readily generated from " $[\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}]$ " and dinitrogen. In addition Pez has

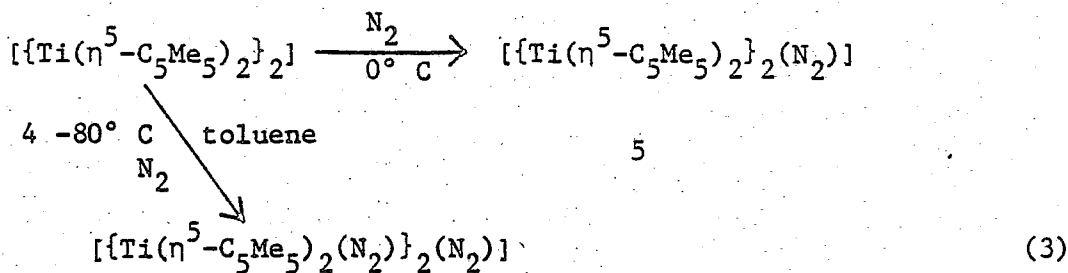
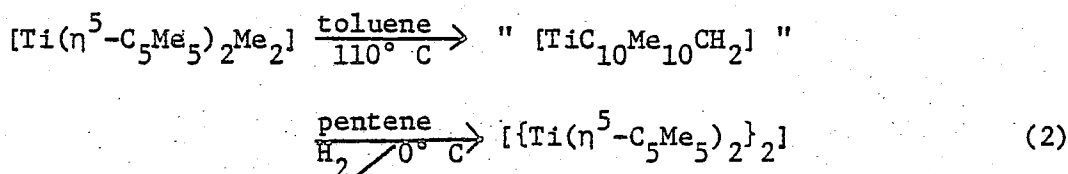


x is the unknown number > 2.

isolated and characterized by X-ray crystallography the compound $[(\eta^5\text{-C}_5\text{H}_5)_2\text{-Ti}-\mu-(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{-Ti}(\eta^5\text{-C}_5\text{H}_5)]$, which, at least empirically, closely resembled the "titanocene" discussed above.¹⁸ This dinuclear complex also reacted with dinitrogen to give

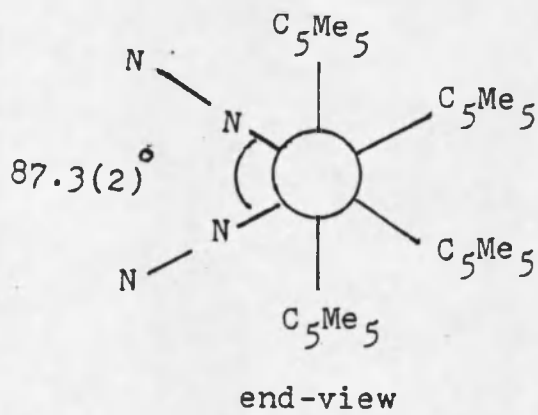
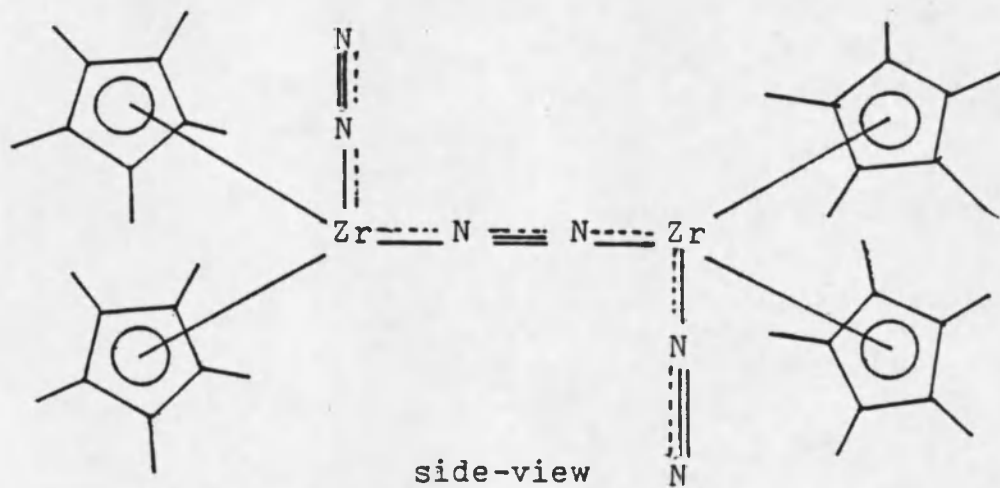
$[\{\text{Ti}_2(\text{C}_5\text{H}_5)_3(\text{C}_5\text{H}_4)\}_2(\text{N}_2)]$ which appeared to have a dinitrogen group bridging two metal dimer units. The complication of the titanium system were reduced by substitution of C_5H_5 with C_5Me_5 . This produced more stable compounds which have been studied in an analogous manner to C_5H_5 complexes.

Thus the analogue of titanocene with (C_5Me_5) ligands 4 has been prepared (eq. 2), and complex 4 was observed to react with dinitrogen in two distinct stages (eq. 2).¹⁹ The ^{15}N NMR spectrum of complex 5 showed a singlet and two doublets; this pattern was originally interpreted as a mixture of complexes with end-on and side-on dinitrogen. However, subsequent experiments indicated that the formulation of 5 was probably incorrect and that it should instead be $[\{Ti(\eta^5-C_5Me_5)_2 \cdot (N_2)\}_2 - (N_2)]$ which is analogous to its better characterized zirconium analogue as shown below. The suggested bonding scheme for these compounds resembles that already developed for similar binuclear systems.²⁰



The dominant interactions are evidently between occupied titanium d-orbitals and the vacant π^* dinitrogen orbital and also between vacant titanium d-orbital and the filled π dinitrogen orbital.²⁰

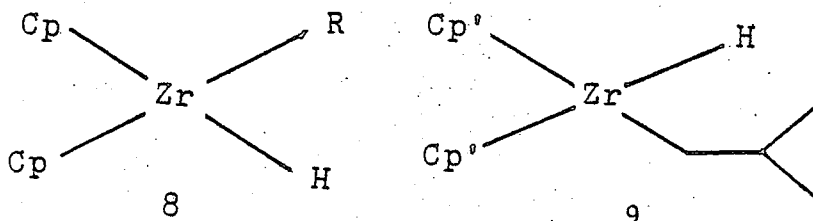
The zirconium analog $[\{Zr(\eta^5-C_5Me_5)_2(N_2)\}_2(N_2)]$ of the above Ti complex was prepared by treatment of $Zr(\eta^5-C_5Me_5)_2Cl_2$ with Na/Hg amalgam under the N_2 atmosphere. The structure of this compound has



been determined by X-ray diffraction, and there are two terminal dinitrogen ligands and one bridging dinitrogen ligand present in the molecule.²¹

Reductive Elimination of Alkanes from
Zirconium Alkyl Hydrides

In recent years zirconium complexes containing zirconium-carbon bonds have been more intensely studied, and one of the clearest examples of the difference in reactivity for complexes of C_5Me_5 vs complexes of C_5H_5 is seen in the behavior of their alkyl hydrido zirconium compounds of the two ligands. Schwartz²² has reported synthesis and reactivity of the Cp (Cp = C_5H_5) complex 8, while Bercaw²³ has studied the synthesis and reactivity of the C_5Me_5 (Cp' = C_5Me_5) complex 9.

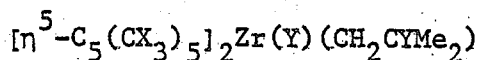


At room temperature 8 (R = $-CH_2-C_6H_{11}$) decomposes over several days to give methylcyclohexane in 60% yield.²² The decomposition mechanism was not simple reductive elimination since decomposition of 8- d_2 gave a mixture of d_0 , d_1 , and d_2 methylcyclohexane. Under 1 atm of H_2 rapid decomposition of 8 to give methylcyclohexane occurred, and experiments using labeled species caused Schwartz to suggest the mechanism

shown in Scheme 2 where H_2 attacks 8 in a heterolytic fashion followed by reaction of H^+ with 10 to give the final product.

The initial step would be reductive elimination of hydride with a ring carbon to give 10 which could oxidatively add either to H_2 or to a ring methyl in the thermal decomposition as shown. This step would be followed by irreversible reductive elimination of alkane and regeneration of a 16 electron complex.

In contrast the C_5Me_5 substituted complex 9 was quite stable at room temperature and had to be heated to $75^\circ C$ to induce decomposition giving isobutane quantitatively.^{23,24} After subjecting species 9_{a-c} to thermal decomposition and to reaction with hydrogen, Bercaw suggested



9

a X = Y = H

b X = H; Y = D

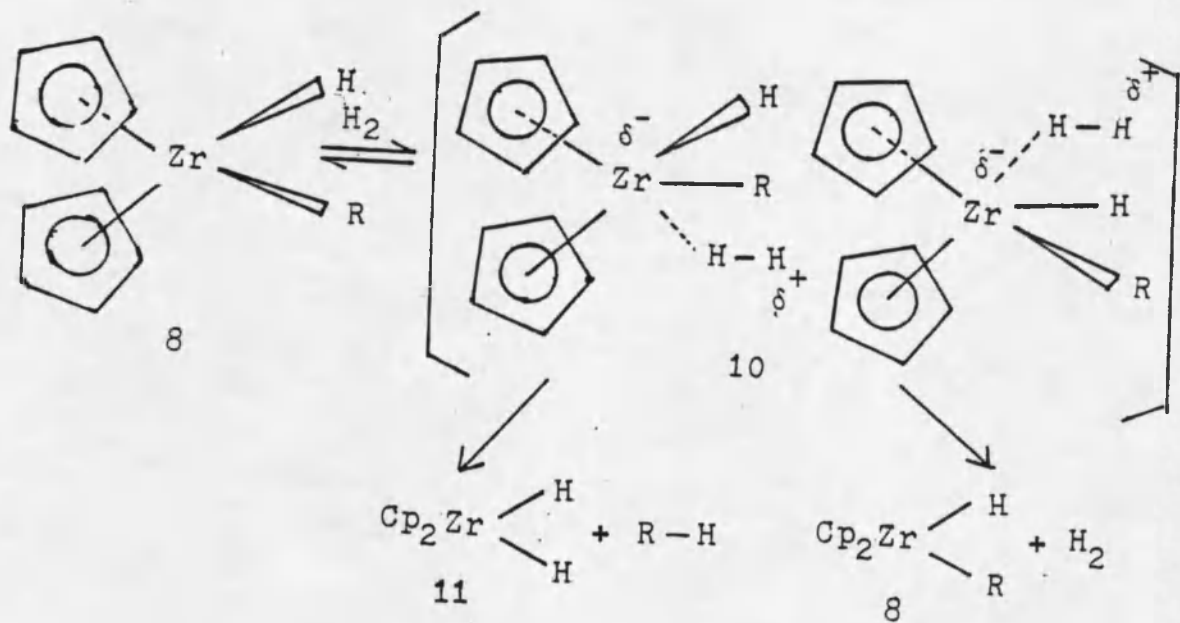
c X = Y = D

the mechanism shown in Scheme 3. This is a major departure from the interactions put forth for the C_5H_5 compound especially in that the ring methyls are implicated in the reaction.

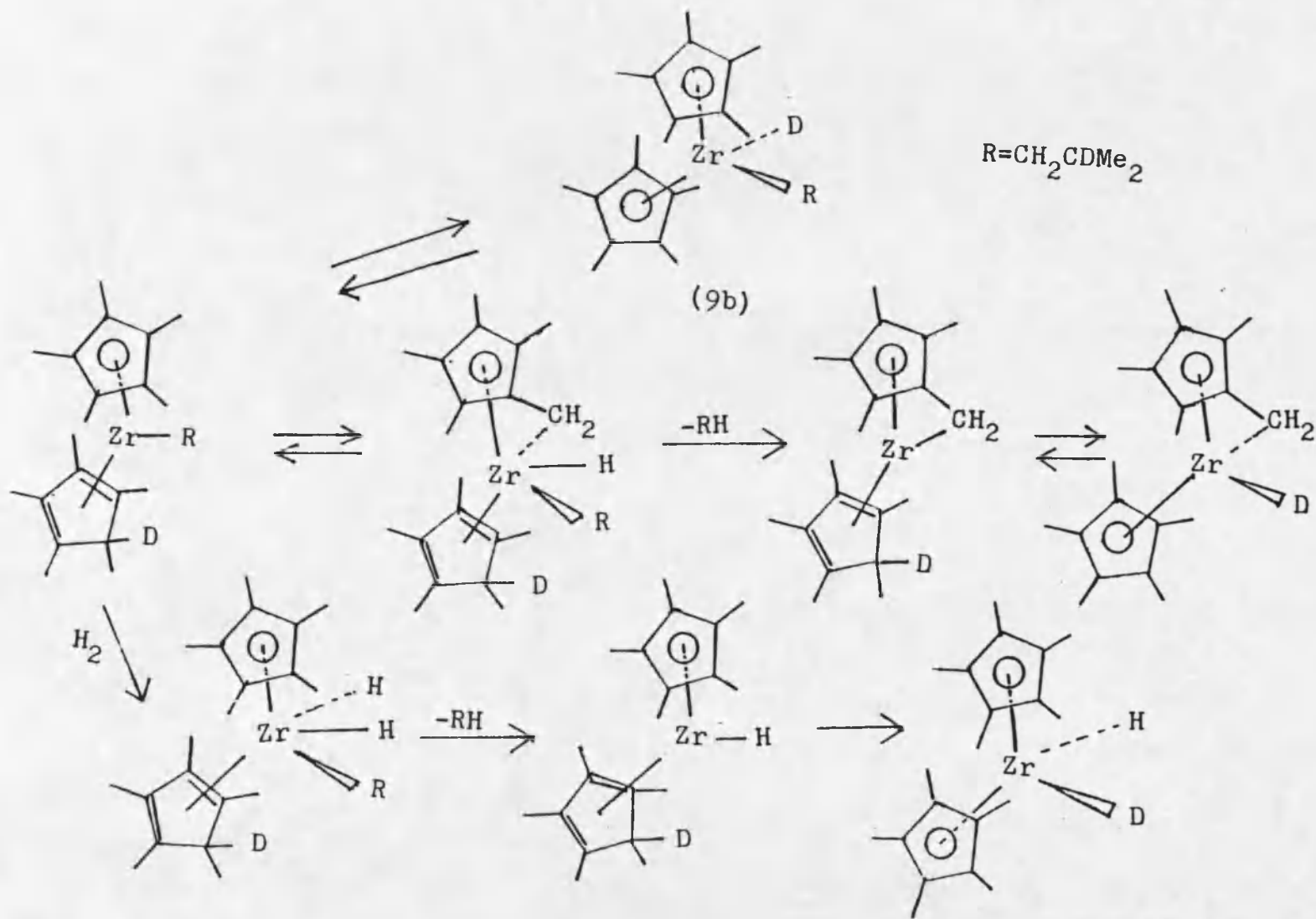
Reduction of Small Molecules by Zr Complexes

Co

Due to its direct relation to the Fischer Tropsch reaction and other catalytic reactions, the interaction of small molecules such as carbon monoxide with transition metal complexes is one of the processes



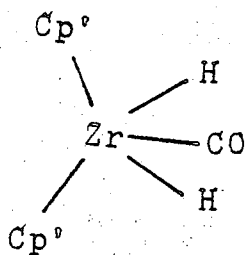
Scheme 2



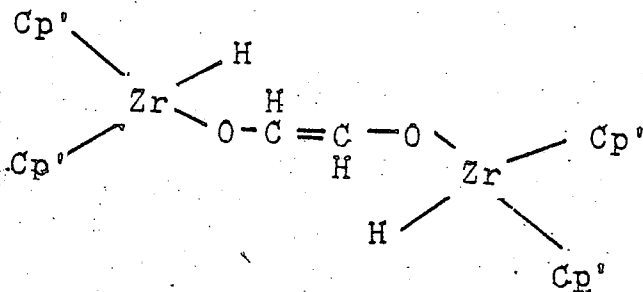
Scheme 3

undergoing intense investigation at the present time. Bercaw has recently shown that a number of the bis $(C_5Me_5)_2$ zirconium derivatives interact with carbon monoxide resulting in reduction of this molecule in a manner not observed for later transition metals.^{12,25}

Reaction of bis(pentamethyl) zirconium dihydride with CO at less than $-50^\circ C$ resulted in coordination of CO to form the 18-electron complex 12. Warming a solution of 12 above $-50^\circ C$ caused formation of dimer 13. However, if 12 was allowed to warm in the presence of H_2 and $(C_5Me_5)_2 ZrH_2$, a mixture of the dihydride 13, and $(C_5Me_5)_2 ZrH(OCH_3)_2$ 14 was recovered. Slowly bleeding CO into a solution of $(C_5Me_5)_2 ZrH_2$ at $25^\circ C$ lead to isolation of 14 only. Bercaw and co-workers have ex-



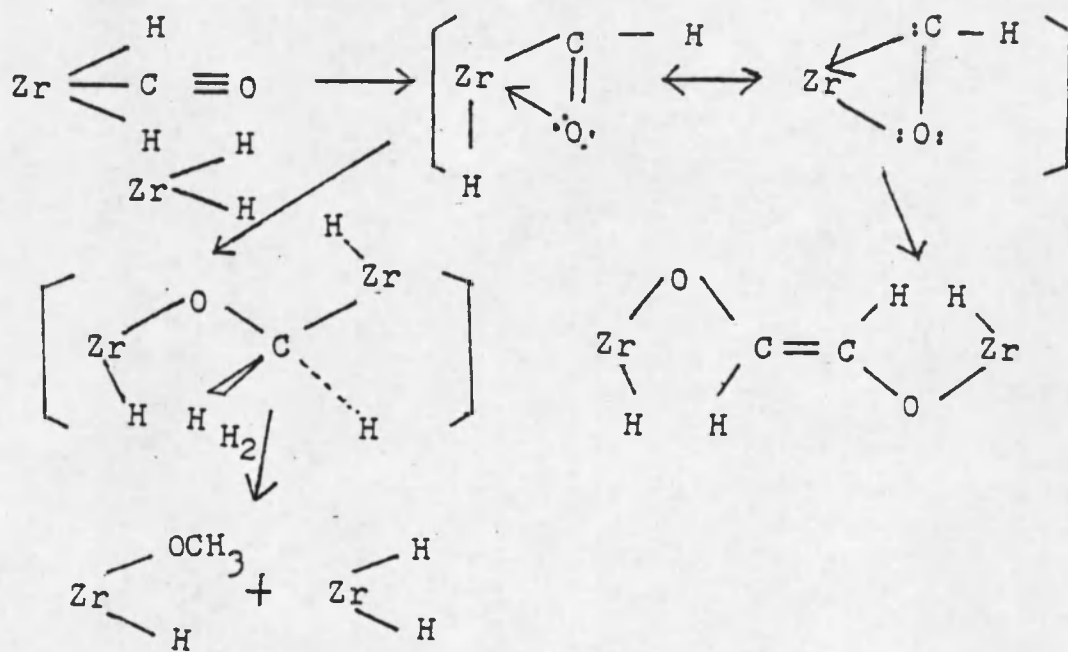
12



13

plained the above result by the reaction Scheme 4. The proposal of an oxycarbene species has precedence in work with silane compounds.²⁶ The oxycarbene species could dimerize to give 13 or insert into the zirconium hydride bond followed by addition of H_2 to give 14 and the dihydrido species.

In addition Bercaw and co-workers have synthesized three zirconium alkyls and studied their reaction with carbon monoxide.²⁵

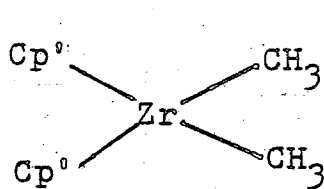


14

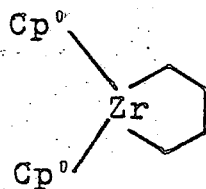
Scheme 4

Interaction of 15 with CO initially gave the acyl complex

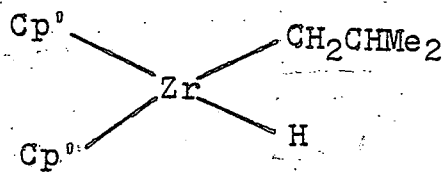
$(C_5Me_5)_2Zr(CH_3)(COCH_3)$ in exact parallel to the $(C_5H_5)_2Zr(CH_3)_2$ species.²⁵ However, continued reaction of 15 with CO leads to isolation



15



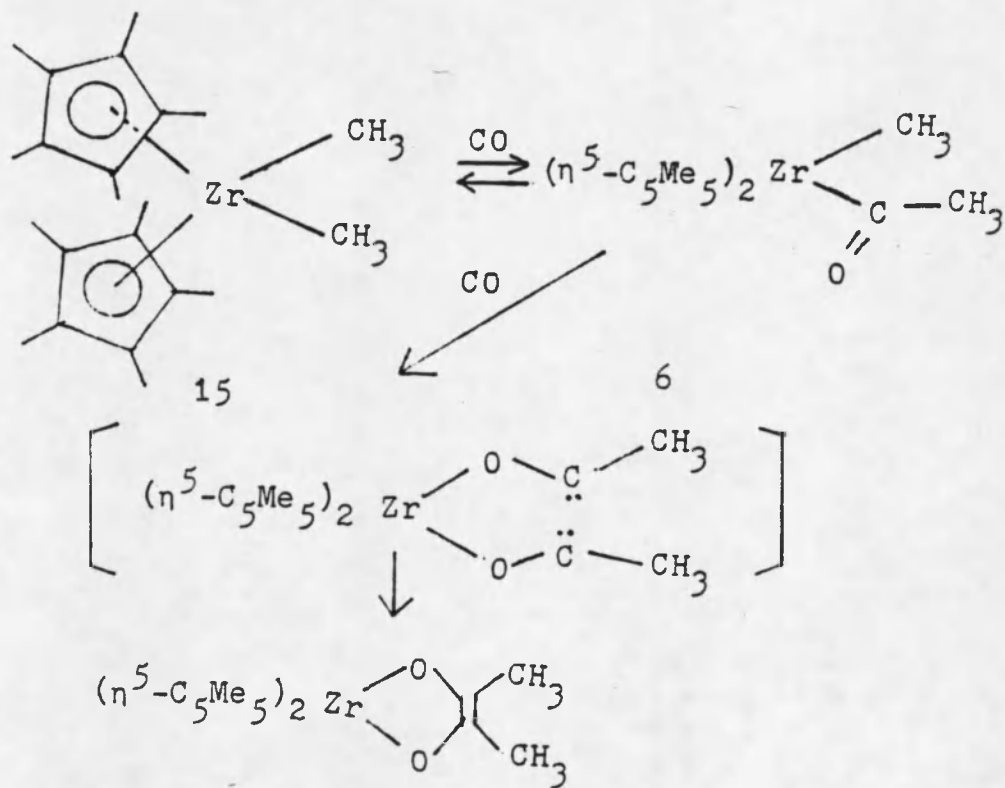
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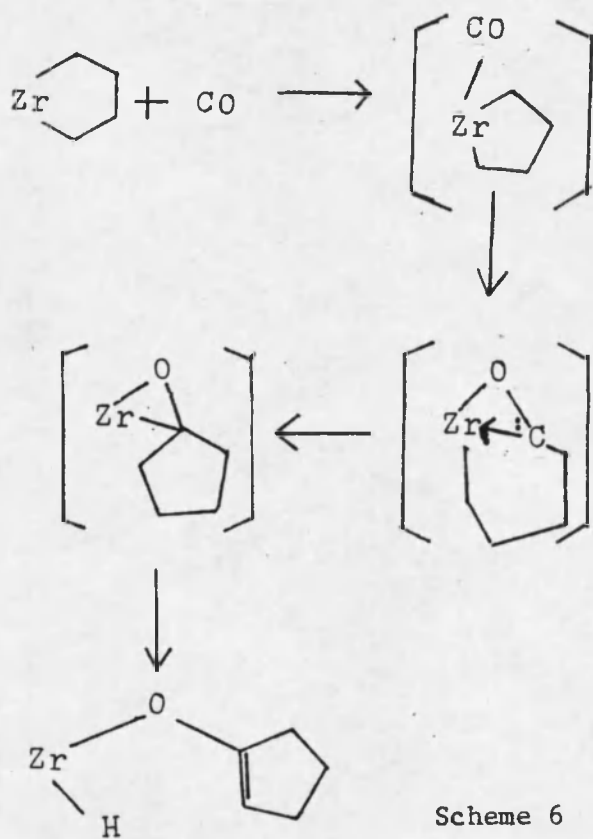
17

of 6 as shown in Scheme 5, whereas $(C_5H_5)_2Zr(CH_3)_2$ ²⁷ gives rise to several products via a complicated reaction. As is shown, a C_5Me_5 bis-oxycarbene species was proposed to undergo intramolecular dimerization to give the final product.

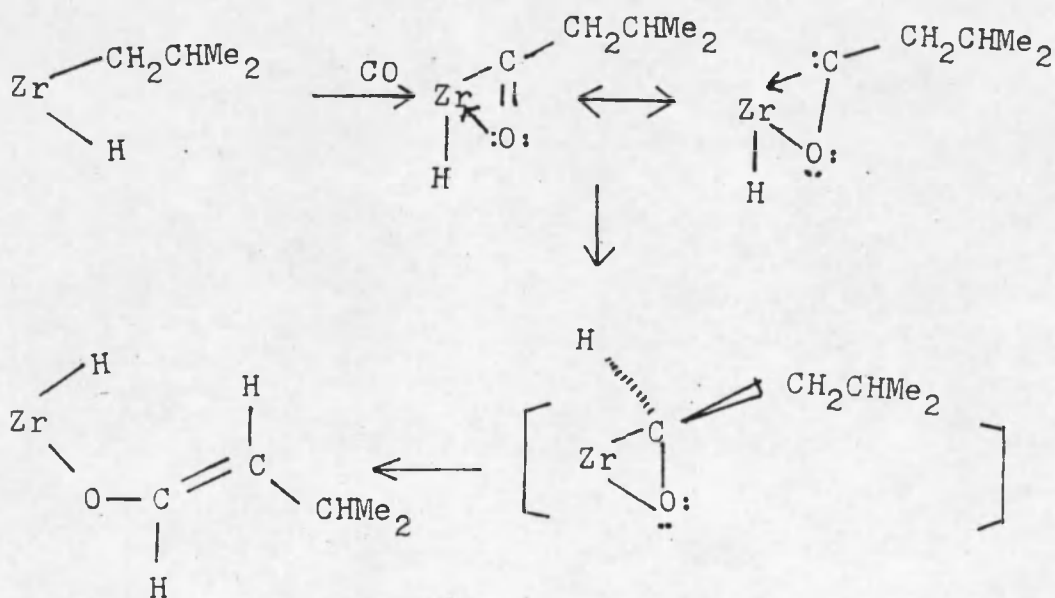
The reaction of 16 and 17 with CO are depicted in Schemes 6 and 7. They were similar, one involving hydrogen transfer to the oxycarbene and the other carbon transfer; both are followed by β -hydride elimination to give the final product. With the metallacycle 16 CO probably initially attached at a less sterically hindered "outside" position. Bercaw indicated that these results could implicate "side on" coordination of formyl and acyl moieties in the Fischer Tropsch synthesis of linear alkanes. It is of interest that alcohols and hydrocarbons other than methane were formed in this process only when Lewis acids were added. Bercaw has proposed that these could in fact be involved in the stabilization of the oxycarbenoid species.



Scheme 5

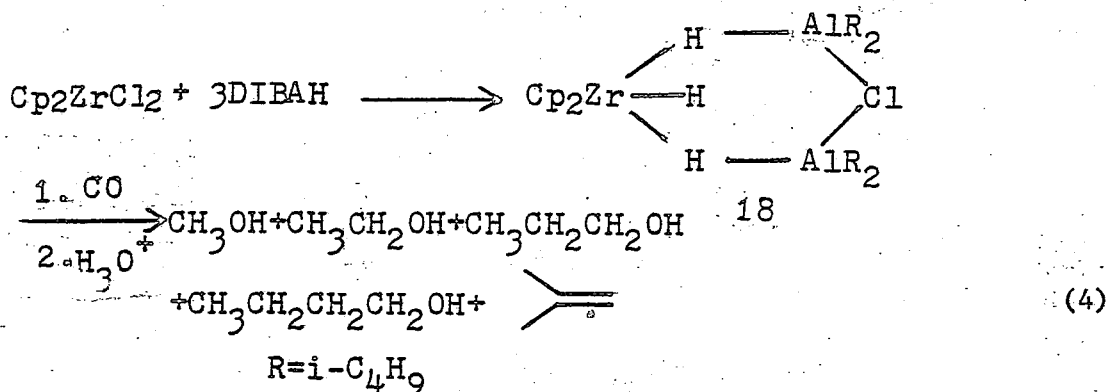


Scheme 6



Scheme 7

In light of this suggestion the recent findings by Schwartz on the reaction of $\eta^5\text{-C}_5\text{H}_5$ zirconium complexes with CO in the presence of Lewis acid²⁸ are of interest. Schwartz found first of all that treatment of Cp_2ZrCl_2 in benzene with $(i\text{-Bu}_2\text{-AlH})$ leads to formation of 18. The benzene solution absorbs CO at room temperature to give a golden

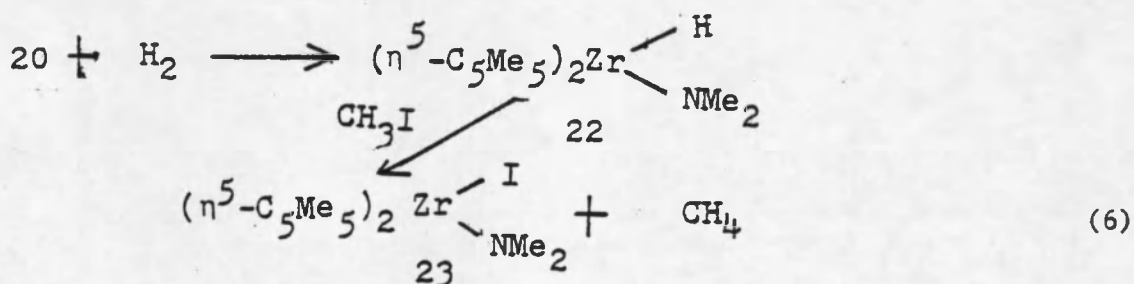
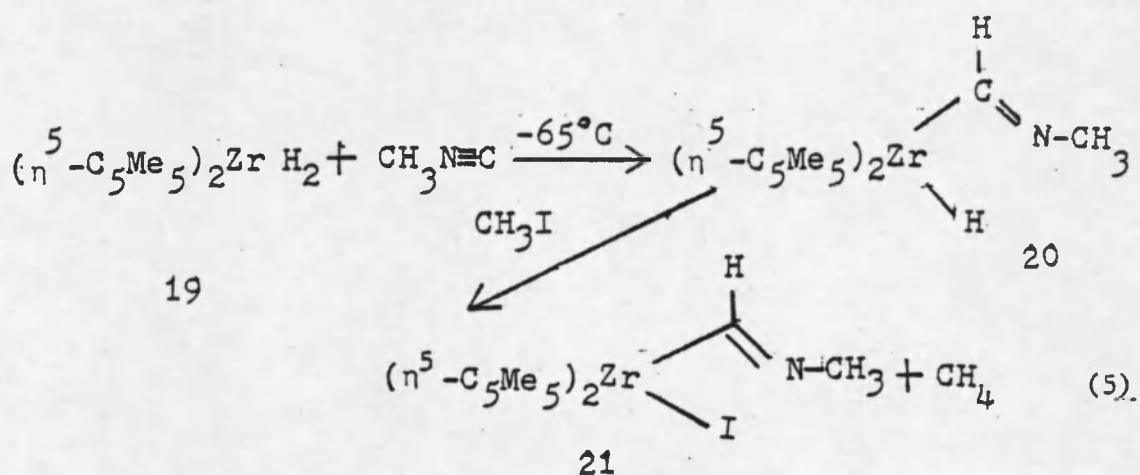


solution followed by precipitation of the Cp_2ZrCl_2 starting material. The golden yellow solution was a complex mixture of aluminum alkyls. Treatment of the oily product of CO absorption with $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ yielded, methanol, ethanol, propanol, and 1-butanol, with an indication of 1-pentanol.

R - C \equiv N

In addition to carbon monoxide reduction, Bercaw has recently shown that the isoelectronic isonitriles were also reduced by $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$.²⁹ This fact lent further support to the proposal of migratory insertion of CO into a Zr-H bond during the reduction process as shown in Scheme 4.

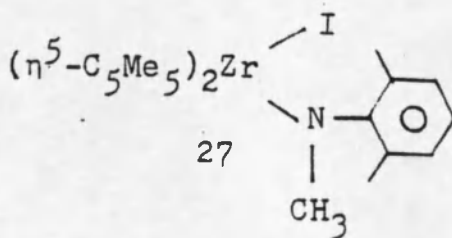
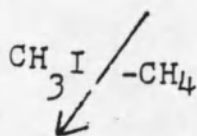
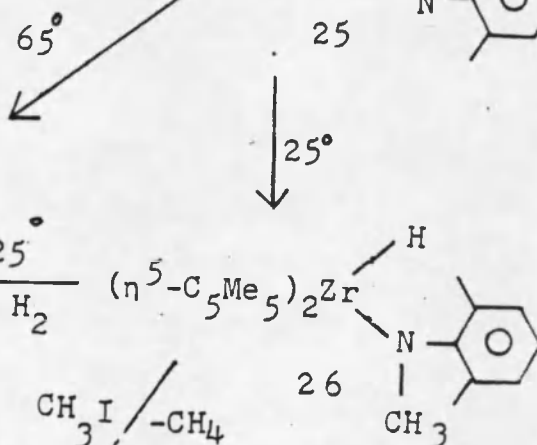
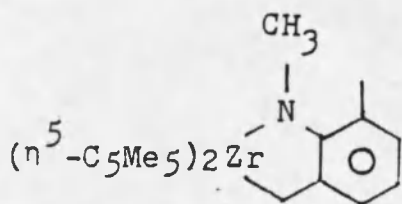
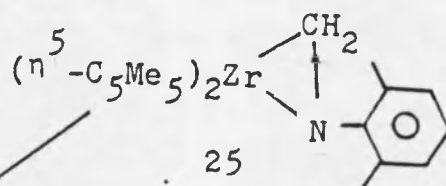
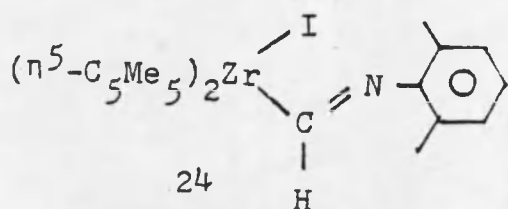
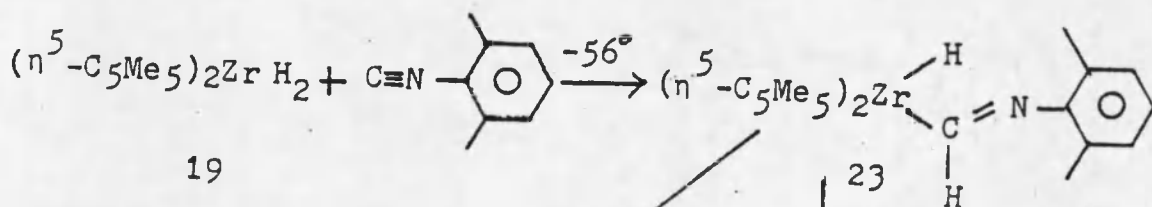
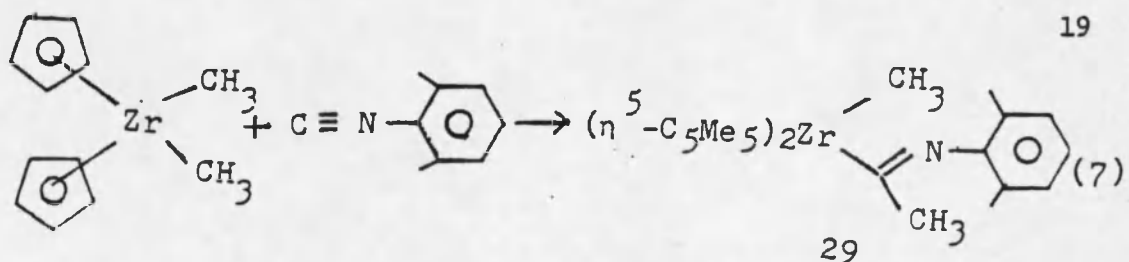
Bercaw's group reported that methyl isocyanide reacted rapidly with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ at -65°C to give formimidoyl complex 20 which could be stabilized by conversion to the iodo derivative using CH_3I (eq. 5). Reaction of 20 with H_2 lead to further reduction of the carbon-nitrogen bond and isolation of the amido complex 22 which was also stabilized using CH_3I .



Reaction of 2,6-dimethylphenyl isocyanide with the dihydride complex led to isolation of methylene imine adduct 25 which probably arose through rearrangement of the formimidoyl hydride intermediate

(Scheme 8). Heating of 25 at 65° C or treatment with H₂ (catalytic) resulted in isolation of the zirconacycle 28. The hydrogen catalyzed reaction evidently involved an amido hydride intermediate as shown by trapping of the iodo derivative in the presence of CH₃I (Scheme 8).

Finally, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)_2$ was allowed to react with 2,6-dimethylphenyl isocyanide. In this case insertion again occurred, and the acetimidoyl methyl complex 29 was formed in greater than 95% yield.



Scheme 8

TANTALUM COMPLEXES

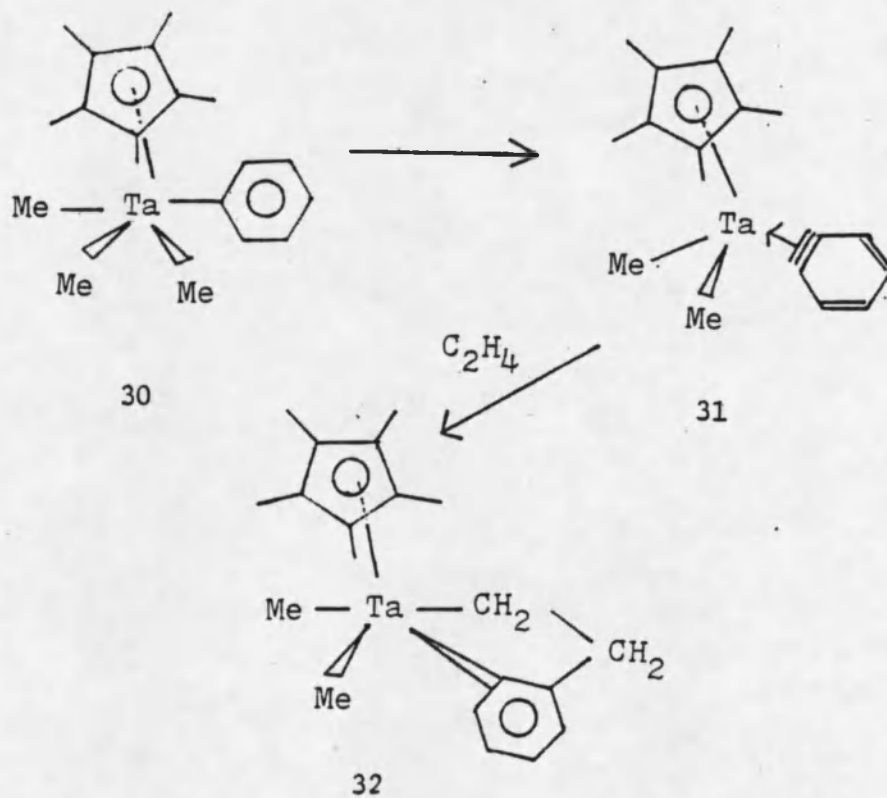
This section covers recent discoveries in the area of pentamethylcyclopentadienyl tantalum complexes. Initially, there is a short section on synthesis of a stable tantalum benzyne complex followed by a discussion of tantalum olefin complexes and finally the reduction of CO using a tantalum compound.

A Tantalum Benzyne Complex

Using the $\eta^5\text{-C}_5\text{Me}_5$ ligand with tantalum has resulted in the isolation of the first reported benzyne complex. Reaction of phenyl lithium with $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3\text{Cl}$ at -78°C in ether produced after workup yellow, crystalline complex 30.³⁰ Heating the sigma bonded phenyl species at 120°C for 30 minutes resulted in loss of methane and an 80% isolated yield of the benzyne complex 31. The metal bonded carbon atoms of the benzyne ligand appeared at 230.5 ppm downfield from TMS in the ^{13}C NMR spectrum. Finally, reaction of 31 with ethylene resulted in formation of the metallocyclopentene complex 32 (see Scheme 9).

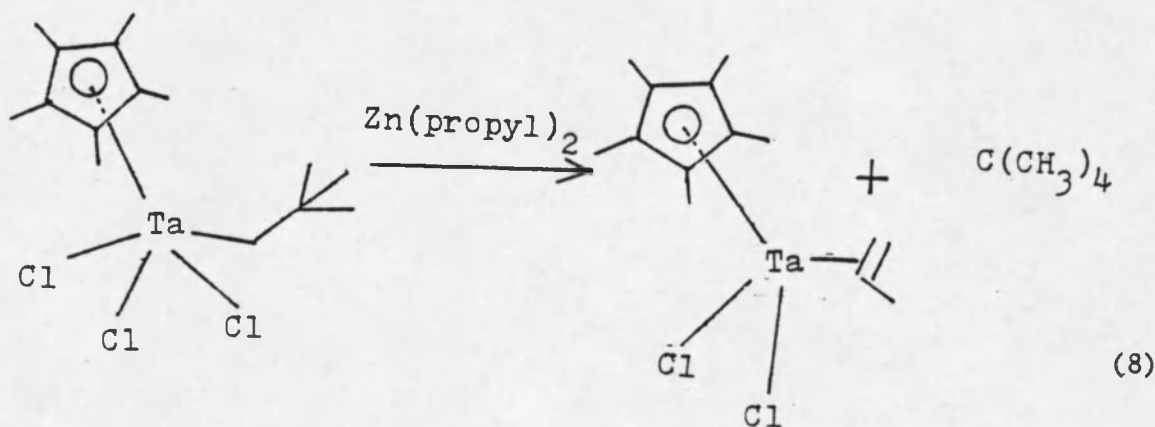
Tantalum Olefin Complexes

Another clear example of the greater stability of C_5Me_5 complexes as compared to C_5H_5 complexes has been shown in the attempted syntheses of their Ta(III) olefin complexes. Thus $\text{C}_5\text{Me}_5\text{TaCl}_2$ (olefin) complexes were stable and could be isolated, whereas the corresponding C_5H_5 tantalum compounds have not been observed.³¹



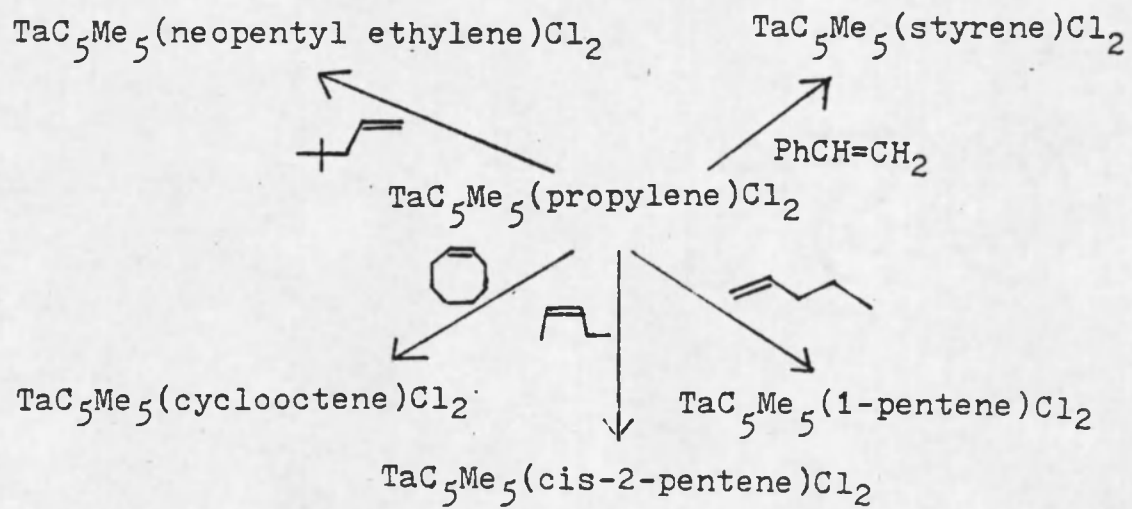
Scheme 9

The reaction of ZnPr_2 with $\text{TaC}_5\text{Me}_5(\text{CH}_2\text{CMe}_3)\text{Cl}_3$ ³¹ resulted in loss of neopentane and isolation of $\text{TaC}_5\text{Me}_5(\text{propylene})\text{Cl}_2$. The ethylene compound was formed in a similar manner. Other olefin complexes



were synthesized by an "exchange" reaction as shown in Scheme 10. All the olefin complexes were sensitive to oxygen and moisture but were stable, crystalline compounds under an inert atmosphere at room temperature. Through variable temperature ^1H NMR Schrock was able to measure a $\Delta G^\ddagger = 9.3 \pm 0.3$ Kcal/mol for rotation of the ethylene ligand about the metal-ethylene bond.

All attempts to prepare the analogous $\eta^5\text{-C}_5\text{H}_5$ compounds failed. Schrock felt that possibly two factors were involved: bimolecular decomposition pathways were not sterically blocked in $\eta^5\text{-C}_5\text{H}_5$ compounds, and/or cleavage of cyclopentadienyl carbon-hydrogen bonds were involved in the decomposition process.



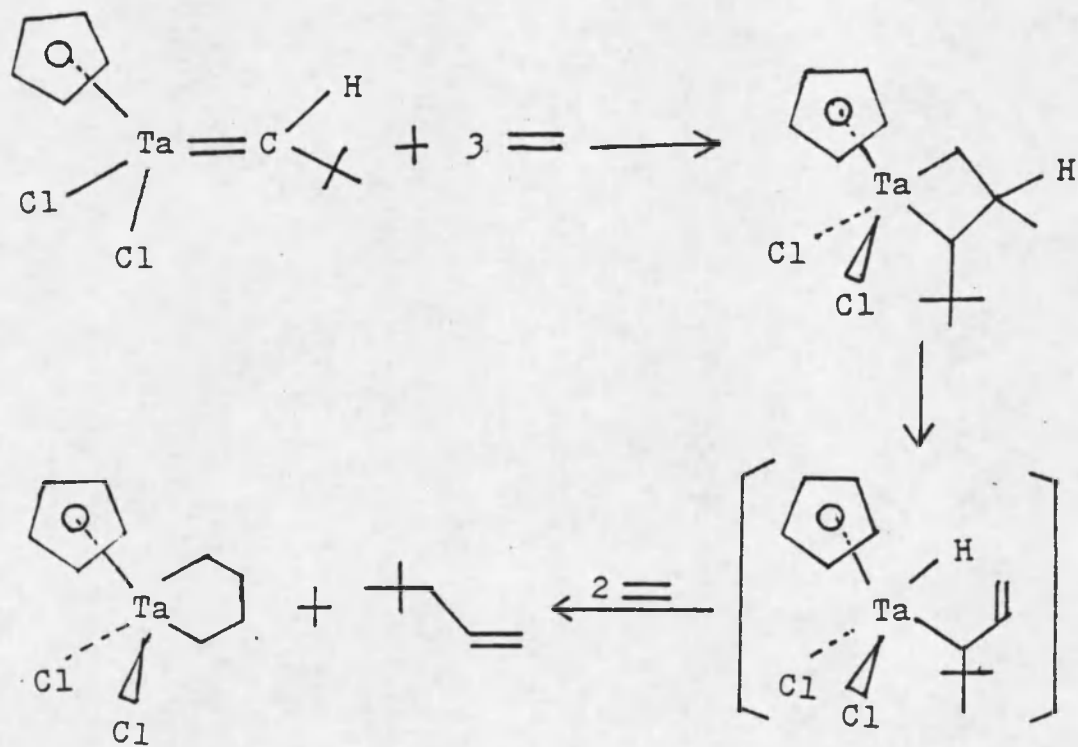
Scheme 10

Tantalum-Metallacyclopentane Complexes

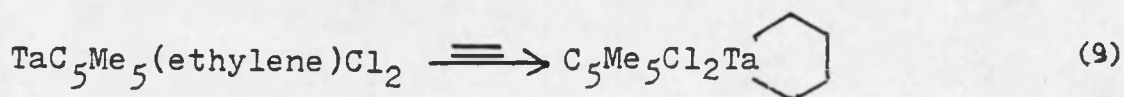
Intimately related to the olefin complexes are the $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{Me}_5$ tantalum metallacyclopentane complexes,³¹ which catalytically dimerize α -olefins.³² The $\eta^5\text{-C}_5\text{H}_5$ metallacyclopentane complexes were prepared by the reaction of the carbene complex $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ with acyclic α -olefins in pentane at 25° C.³¹ The reaction probable proceeds through a metallacyclobutane intermediate as shown for ethylene in Scheme 11.

Both the ethylene and propylene metallacycle were isolated and characterized but were unstable unless kept cold (-30° C) under N_2 . The structures of these complexes were proved by ^1H and ^{13}C NMR data. High yields of the expected organic products (91% $\text{Me}_3\text{CCH}_2\text{-CH}=\text{CH}_2$ from the ethylene reaction and 86% $\text{Me}_3\text{CCH}_2\text{-C}(\text{Me})=\text{CH}_2$ from the propylene reaction) were obtained.

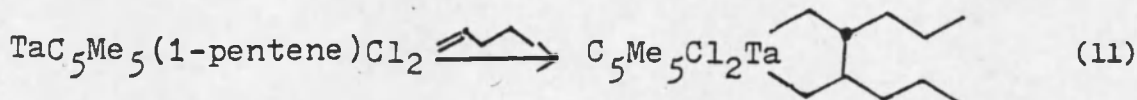
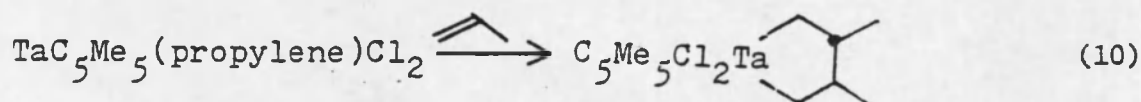
In contrast to the above carbene complex-olefin reaction, the $\eta^5\text{-C}_5\text{Me}_5$ complexes could be made from the stable $\eta^5\text{-C}_5\text{Me}_5\text{ TaCl}_2(\text{olefin})$ complexes.³¹ Thus $\text{TaC}_5\text{Me}_5\text{Cl}_2(\text{ethylene})$ reacted rapidly at -35° C with excess ethylene to give the metallacyclopentane complex 33. In a similar manner the propylene and 1-pentene complexes react with propene and 1-pentene, respectively, to give the corresponding metallacyclopentane shown below. More substituted olefins do not form metallacyclopentane complexes. For instance addition of cis-2-pentene to $\text{C}_5\text{Me}_5\text{ TaCl}_2(\text{cis-2-pentene})$ gave no evidence for formation of a metallacycle derivative (cis- ^1H NMR).



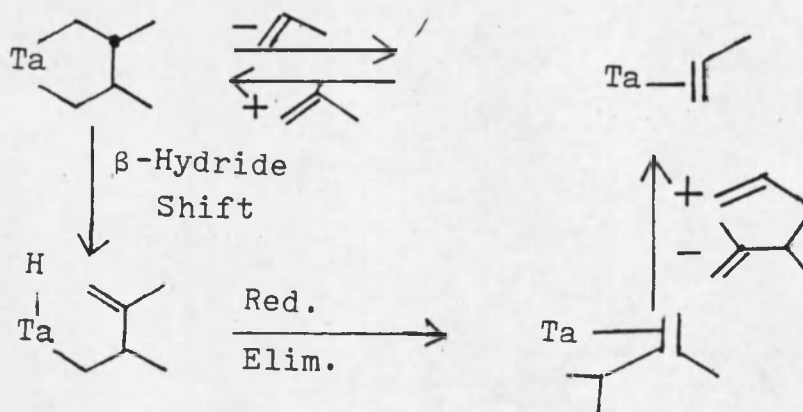
Scheme 11



33



All of the metallacycle tantalum complexes ($\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{Me}_5$) decompose rapidly in the absence of excess olefin.³¹ The $\eta^5\text{-C}_5\text{Me}_5$ ethylene metallacycle 33 was stable under 1 atm of ethylene. However, the substituted metallacycles decompose even in a closed system. For this reason, Schrock suggested two modes of decomposition: one involving cleavage of the β , β' carbon atom with concomitant loss of 1 mole of olefin and one involving β -hydride shift, reductive elimination and replacement of the new olefin with excess olefin present in solution. Both processes are depicted in Scheme 12 with the propylene metallacycle. The second mechanism was supported by isolation of 0.5 mole per Ta of 2,3-dimethyl-1-butene, the expected new olefin, from the decomposition of the propylene metallacycle complex. The $\eta^5\text{-C}_5\text{H}_5$ substituted propylene metallacycle also decomposed to give 2,3-dimethyl-1-butene; however, its rate of decomposition was twice that of the $\eta^5\text{-C}_5\text{Me}_5$ complex. Also, no propylene complex was formed due to the instability of these systems as earlier mentioned.

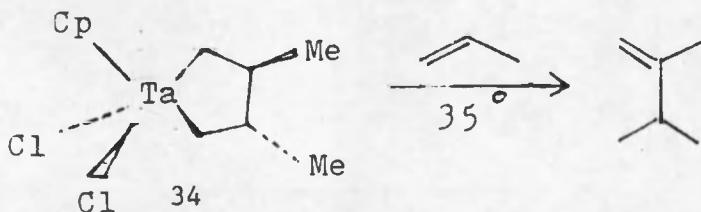


Scheme 12

Catalytic Dimerization of α -Olefins

While working on the olefin and metallacyclopentane tantalum complexes, Schrock and co-workers discovered that these complexes can catalytically dimerize monosubstituted α -olefins.³³ Of importance to this work is the fact the $\eta^5\text{-C}_5\text{Me}_5$ substituted system was indefinitely active³² while the $\eta^5\text{-C}_5\text{H}_5$ substituted system³³ was short lived.

When the metallacycle, $\text{CpCl}_2\text{Ta} \overbrace{\text{CH}_2\text{CH}(\text{Me})\text{CH}(\text{Me})\text{CH}_2}^{\text{metallacyclopentane}}$ 34, was heated (35° C) in the presence of propylene that 2,3-dimethyl-1-butene was formed catalytically. The rate of formation of 2,3-dimethyl-1-butene in the catalytic reaction was approximately equal to the rate of stoichiometric decomposition of 34 to give a 93% yield of .



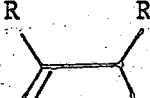
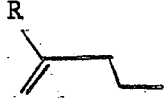
(12)

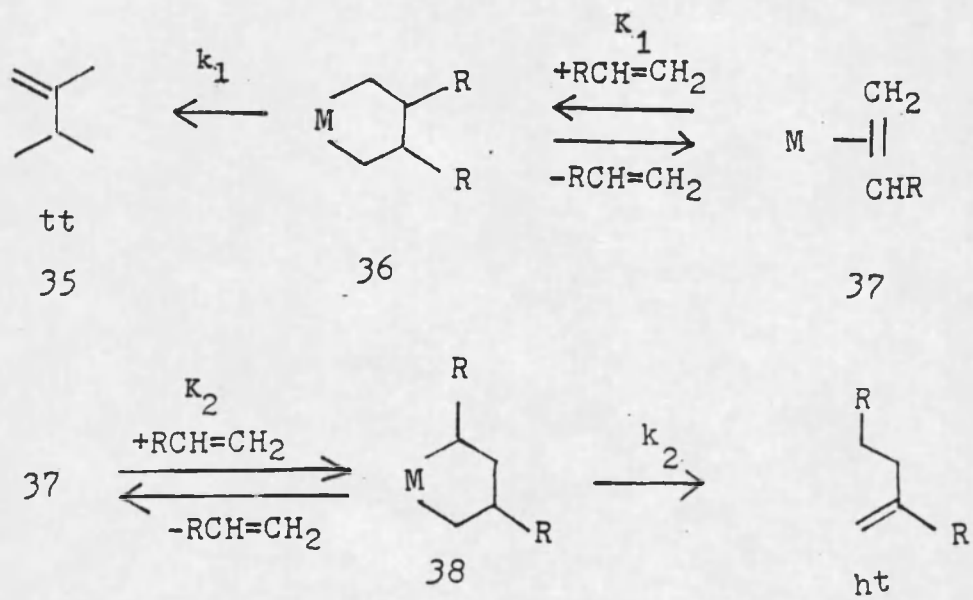
2,3-dimethyl-1-butene. "Head to tail" and "tail to tail" dimers were formed from the catalytic dimerization of α -olefins using the $\eta^5\text{-C}_5\text{Me}_5\text{Cl}_2\text{Ta}(\text{olefin})$ system as shown in Table 1. The ht dimers were thought to arise from the α , β' metallacyclopentane 38 and the tt dimers from the β , β' metallacyclopentane intermediate as shown in Scheme 13. Evidently as R became larger K_2 became dominant over K_1 (and/or k_2 over k_1). The intimate details of the mechanism were studied using 1-pentane-2-d.

With 1-pentane-2-d a substantial deuterium isotope effect ($k_{\text{H}}/k_{\text{D}} = 3.3$) was observed for the formation of the tt dimer 35 which is consistent with formation of a butenyl hydride followed by reductive elimination (eq. 1, Scheme 14). Schrock pointed out, however, that deuterium labeling in the minor isomer 41 indicated that a ring contraction mechanism (Scheme 15) was possible. This mechanism would also fit the deuterium labeling observed in the major isomer (eq. 2, Scheme 14). Schrock showed that this mechanism was dominant by codimerization of propylene and 1-pentene-2-d, which gave products 43b and 44b, as expected for the ring contraction mechanism, rather than 43c and 44c, the products from the reductive elimination pathway.

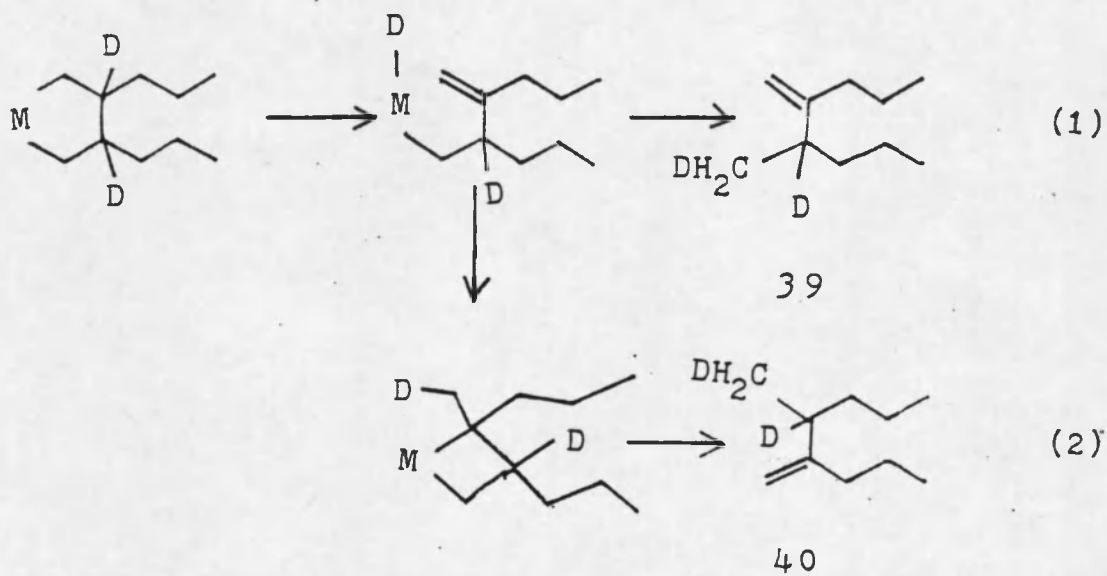
The real usefulness of the dimerization catalyst comes about because of the presence of the C_5Me_5 ligand. With the C_5H_5 ligand only 20 turnovers in the catalytic system were observed whereas with the C_5Me_5 substituted system as many as 1258 mol of dimer per mole of catalyst was observed. As alluded to earlier this phenomenon can probably

Table 1. Four Catalytic Dimerizations at 50° C in Toluene

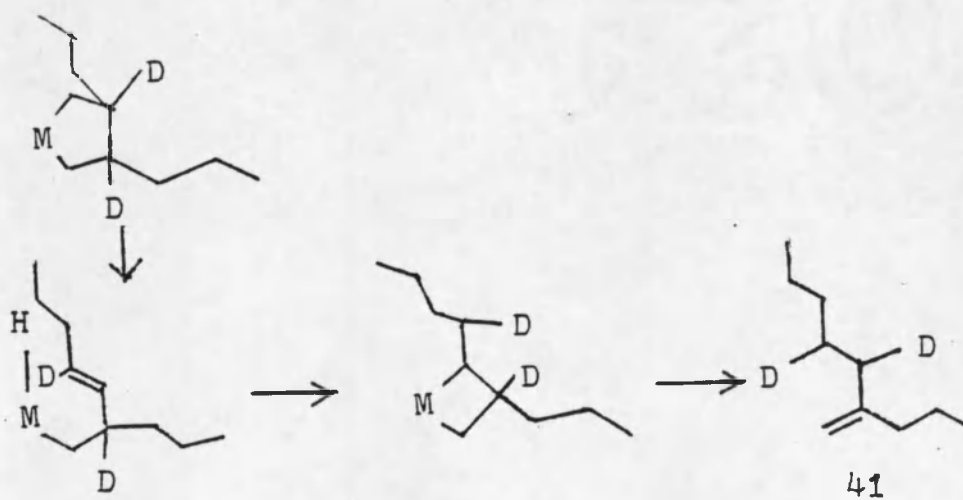
Olefin	 (%) (tt)	 R (%) (ht)
$\text{CH}_2 = \text{CHMe}$	98	2
$\text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{Me}$	88	12
$\text{CH}_2 = \text{CHCH}_2\text{CHMe}_2$	61	39
$\text{CH}_2 = \text{CHCH}_2\text{-CMe}_3$	0	100



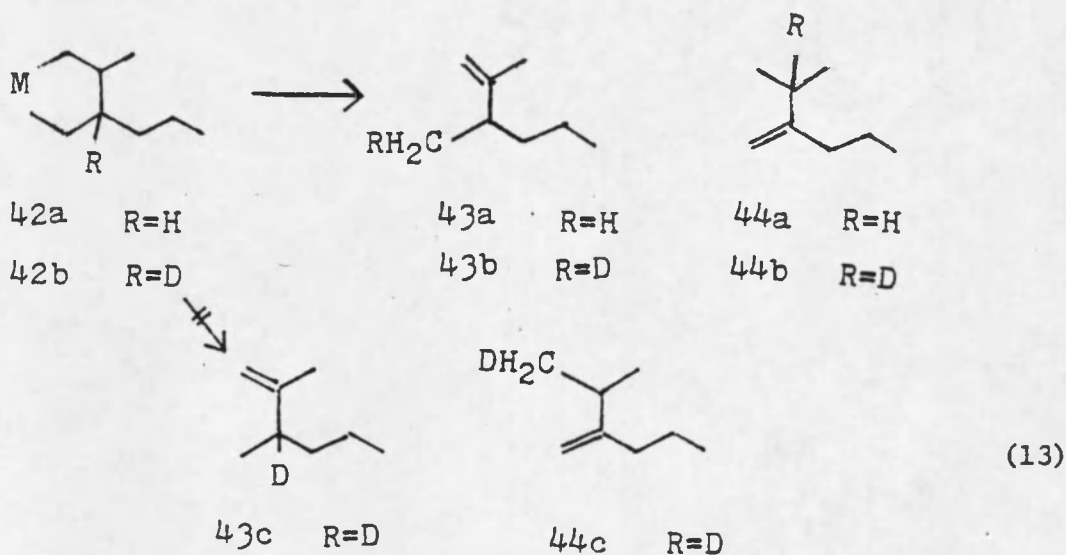
Scheme 13



Scheme 14



Scheme 15



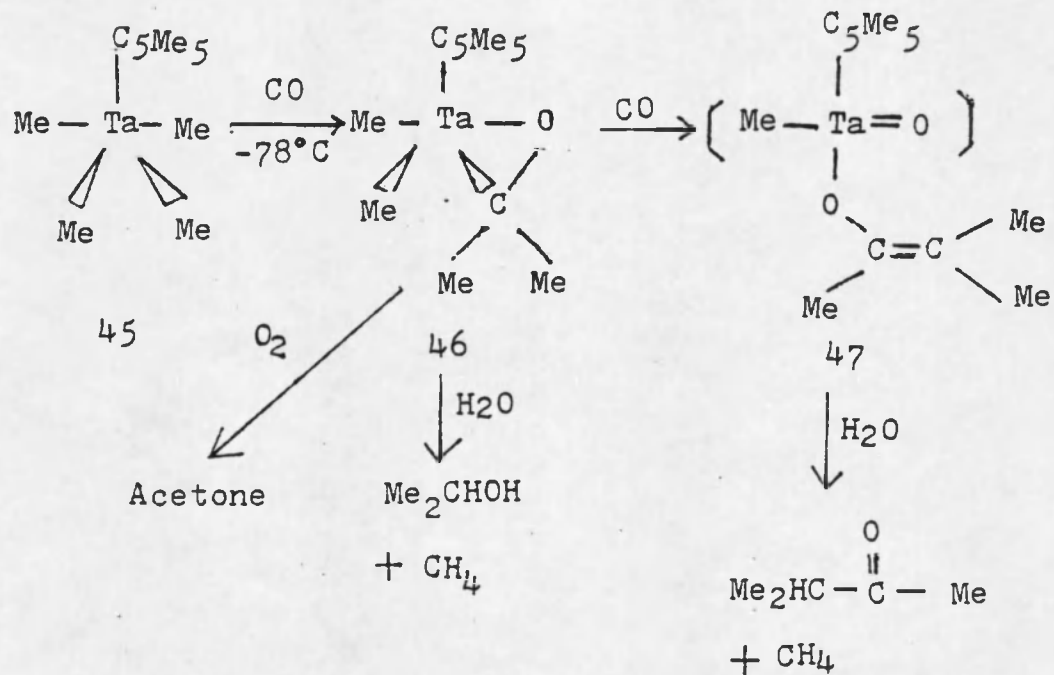
be traced to the different stability of olefin complexes in the two systems.

Reaction of a Tantalum Complex with CO

$\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_4$ also reduced carbon monoxide,³⁴ but no comparison with a $\eta^5\text{-C}_5\text{H}_5$ derivative can be made.

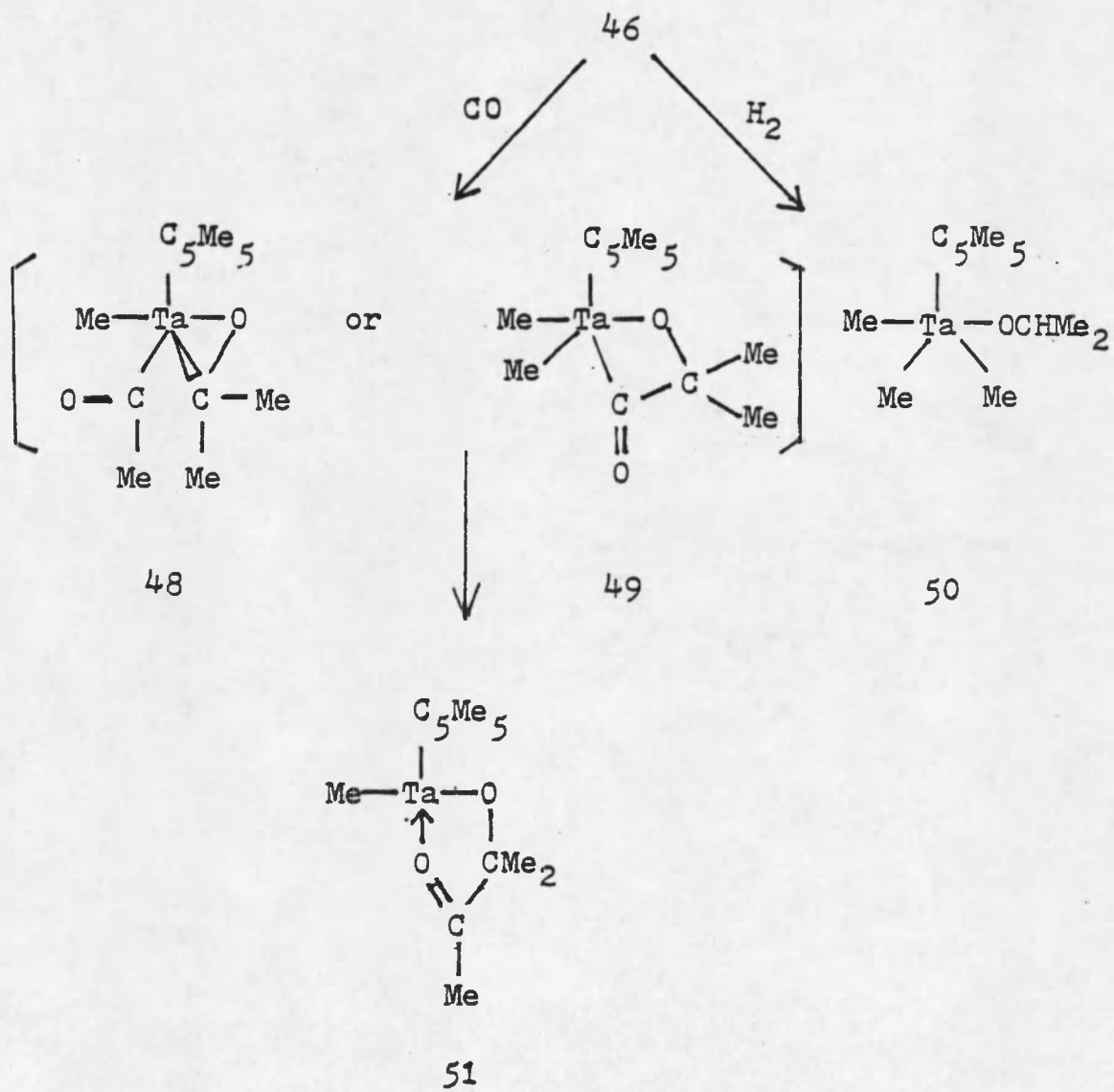
Schrock and co-workers have reported that $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_4$ 45 reacted first with one mole and then two moles of CO to give 46 and 47, respectively (Scheme 16). The identification of 46 and 47 was accomplished using ^1H and ^{13}C NMR spectroscopy.

As shown in Scheme 16 treatment of 46 with O_2 gave acetone whereas treatment with water produced 2-propanol. In a similar manner hydrolysis of 47 with H_2/HCl led to isolation of methyl isopropyl ketone, probably via the enol.



Scheme 16

Schrock proposed that reaction of the " η^2 -acetone" complex 46 with additional CO probably proceeded through intermediate 48 or 49 (Scheme 17). Intermediate 49 was favored because treatment of 46 with H_2 resulted in cleavage of the acetone carbon-tantalum bond rather than a methyl tantalum bond. In any case either of the two intermediates, 48 or 49 (which were considered to be oxycarbenes in line with earlier proposals by Bercaw),²⁵ could couple intramolecularly to a methyl group to give 51 followed by rearrangement to give 47.



Scheme 17

CONCLUSION

Several reasons are mentioned in the literature as to why early transition metal complexes of C_5H_5 react differently from those of C_5Me_5 : (1) slowing of binuclear decomposition pathways and (2) elimination of reaction with hydrogens attached to the C_5H_5 ring. Although the proof is indirect, the observation that the $\eta^5-C_5Me_5$ tantalum olefin complexes are much longer lived catalysts than the $\eta^5-C_5H_5$ tantalum metallacycles for the dimerization of α -olefins could support these suppositions. The greater thermal stability of the $\eta^5-C_5Me_5$ complexes could be related to the hindering of decomposition pathways. However, one should also note that in several reactions involving zirconium complexes, the hydrogens on the ring methyls (C_5Me_5) participate, indicating that new pathways of reaction are present in C_5Me_5 systems.

Finally, these complexes are very useful in the study of the interaction of early transition metal complexes with small molecules. This is especially true with important reactions such as fixation of nitrogen and Fischer Tropsch reduction of carbon monoxide. From the current rate of publication in this area of research, it is apparent that the study of complexes of pentamethylcyclopentadiene, especially of the early transition metals, is well underway and is opening new avenues of thought in transition metal organometallic chemistry.

LIST OF REFERENCES

1. Kealy, T. J. and P. L. Pauson. *Nature (London)*, 168, 1039 (1951).
2. McBee, E. T. and D. K. Smith. *J. Am. Chem. Soc.*, 77, 389 (1955).
3. Webster, O. W. *J. Am. Chem. Soc.*, 88, 4055 (1966).
4. Vries, L. de. *J. Org. Chem.*, 25, 1838 (1960).
5. Threlkel, R. S. and J. E. Bercaw. *J. Organomet. Chem.*, 136, 1 (1977).
6. Fischer, E. O. and R. Röhrscheid, *2. Naturforsch. Teil B*, 17, 483 (1962).
7. King, R. B. *Coord. Chem. Rev.*, 20, 155 (1976).
8. Campbell, P. H., N. W. K. Chiu, K. Deugan, I. J. Miller and T. S. Sorenson. *J. Am. Chem. Soc.*, 98, 8351 (1976).
9. Feitler, D. and G. M. Whitesides. *Inorg. Chem.*, 15, 466 (1976).
10. Gell, K. I. and J. Schwartz. *J. Am. Chem. Soc.*, 100, 3246 (1978).
11. Negishi, E., N. Okukado, A. O. King, D. E. Van Horn and B. I. Spiegel. *J. Am. Chem. Soc.*, 100, 2256 (1978).
12. McAlister, D. R., D. K. Erwin, and J. E. Bercaw. *J. Am. Chem. Soc.*, 100, 5966 (1978).
13. Shoer, L. I. and J. Schwartz. *J. Am. Chem. Soc.*, 99, 5831 (1977).
14. Wailles, P. C., R. S. P. Coutts and H. Weigold. *The Organometallic Chemistry of Titanium, Zirconium and Hafnium*. Academic Press, New York, N. Y., 249 (1974); Chatt, J., J. R. Dilworth and R. L. Richards. *Chem. Rev.*, 78, 589 (1978).
15. Shilov, A. E., A. K. Shilova, E. F. Kuashina and T. A. Vorontsova. *J. Chem. Soc. Chem. Commun.*, 1590 (1971).
16. Teuben, J. H. and H. J. de Liefde Meyer. *J. Organomet. Chem.*, 46, 313 (1972); Teuben, J. H. *J. Organomet. Chem.*, 57, 159 (1973).

17. Bercaw, J. E., R. H. Marvich, L. G. Bell and H. H. Brintzinger. J. Am. Chem. Soc., 94, 1219 (1972).
18. Pez, G. P. J. Am. Chem. Soc., 98, 8072 (1976).
19. Bercaw, J. E. J. Am. Chem. Soc., 96, 5087 (1974).
20. Sanner, R. D., D. M. Duggan, T. C. McKenzie, R. E. Marsh and J. E. Bercaw. J. Am. Chem. Soc., 98, 8358 (1976).
21. Manriquez, J. M., R. D. Sanner, R. E. Marsh and J. E. Bercaw. J. Am. Chem. Soc., 98, 8351 (1976).
22. Gell, K. I. and J. Schwartz. J. Am. Chem. Soc., 100, 3246 (1978).
23. McAlister, D. R., D. K. Erwin and J. E. Bercaw. J. Am. Chem. Soc., 100, 5966 (1978).
24. Molecular Weight Determined Cryoscopically for 82.4 mg of 9 a/g of C_6H_6 : 460 ± 30 (calcd 420).
25. Manriquez, J. M., D. R. McAlister, R. D. Sanner and J. E. Bercaw. J. Am. Chem. Soc., 100, 2716 (1978).
26. Bassindale, A. R., A. G. Brook and J. Harris. J. Organomet. Chem., 90, C6 (1975); Yates, P. Pure Appl. Chem., 16, 93 (1968).
27. Fachinelfi, G., C. Floriani, F. Marchetti and S. Merlino. J. Chem. Soc., Chem. Commun., 522 (1976).
28. Shoer, L. I. and J. Schwartz. J. Am. Chem. Soc., 5831 (1977).
29. Bercaw, J. E. and Peter T. Wolezanski. J. Am. Chem. Soc., 101, 6450 (1979).
30. McLain, S. J., R. R. Schrock, D. R. Sharp, M. R. Churchill and W. J. Yonngs. J. Am. Chem. Soc., 101, 263 (1979).
31. McLain, S. J., C. D. Wood and R. R. Schrock. J. Am. Chem. Soc., 101, 4558 (1979).
32. McLain, S. J., J. Sancho, R. R. Schrock. J. Am. Chem. Soc., 101, 5451 (1979).
33. McLain, S. J. and R. R. Schrock. J. Am. Chem. Soc., 100, 1315 (1978).
34. Wood, C. D., R. R. Schrock. J. Am. Chem. Soc., 101, 5421 (1979).

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