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Synthesis and Reactivity of Saturated Hydrocarbon-Bridged Dinuclear Complexes

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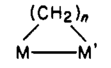
Contents

An intriguing aspect of organometallic chemistry is the fascinating relationship between the chemistry of soluble organometallic compounds and the chemistry of solid metal catalysts. It is hoped that detailed studies of the reactions of organometallic compounds will provide some insight into processes occurring on metal surfaces. The possibility that dinuclear organometallic complexes which have hydrocarbon groups bridging between metal centers might serve as valuable models for hydrocarbon groups bound to metal surfaces is beginning to be actively explored. In fact, there is some hope that a smooth transition from the chemistry of mononuclear compounds to dinuclear compounds to metal clusters to metal surfaces may be found.

The purpose of this review is to discuss the syntheses and reactivities of dinuclear transition-metal complexes which contain saturated hydrocarbon bridges. Two major structural categories will be considered: dinuclear compounds without a metal–metal bond, **1**, and those with a metal–metal bond, **2**. These compounds may be heteronuclear ($M \neq M'$) or homonuclear ($M = M'$). The methylene-bridged, dinuclear compounds ($n = 1$) with metal–metal bonds have been recently reviewed and will not be considered here.[1] Although the extensive review by Lappert et al.[1c] briefly discussed the dinuclear complexes 1 and 2 and a brief review by Moss and Scott of $M–(CH_2)_n–M$ has recently appeared,[1d] we wish to outline recent developments and more fully describe the syntheses and reactivities of these compounds.

$M\text{-}(CH_2)_n\text{-}M'$

1 ($n \geq 1$)



2 ($n \geq 2$)

Interest in these compounds arises from their relationship to potential intermediates in several important catalytic processes. Carbon chain growth in the heterogeneous Fischer–Tropsch reaction has been postulated to occur through combination of a surface-bound methylene with a surface-bound alkyl[2] or through combination of methylene and an olefin.[3] These postulates suggest that related dinuclear compounds might be models for the Fischer–Tropsch reaction. Difficulties in finding homogeneous Fischer–Tropsch catalysts have been attributed to the requirement of more than one metal center for carbon–carbon bond forming processes.[4] The synthesis, insertion reactivity, and thermolysis of dimetallacycloalkyl or α,ω-dimetallaalkyl compounds will be discussed. Olefin insertion reactions with methylene-bridged dinuclear compounds will also be discussed.

Olefin metathesis, another important catalytic process, has been well documented for mononuclear systems.[5a] This review will discuss dinuclear complexes which have recently been observed to undergo olefin metathesis-like reactions.[5b–d] In addition, alkyne polymerization and methylene transfer reactions of methylene-bridged dinuclear compounds will be treated briefly.[6]

I. Dinuclear Compounds without a Metal–Metal Bond

A. The Methylene Bridge

The syntheses and reactivities of methylene-bridged dinuclear compounds without metal–metal bonds will be considered in this section. Most of these compounds contain additional bridging ligands which may increase the stability of the compounds.

The oxidative addition reactions of dihalomethanes and bis[μ-(dimethylphosphonio)dimethanido]digold(I) (**3**) generate A-frame digold(III) compounds **4** which contain a methylene bridge.[7] The remarkably robust organogold compound **4** is stable to 200 °C and is stable in trifluoroacetic acid solution for several days. The structure of **4** was confirmed by X-ray crystallography.

Diiodomethane reacts with $Pd_2(dpm)_3$ (**5**) to generate the A-frame compound **6**, $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$.[8] No

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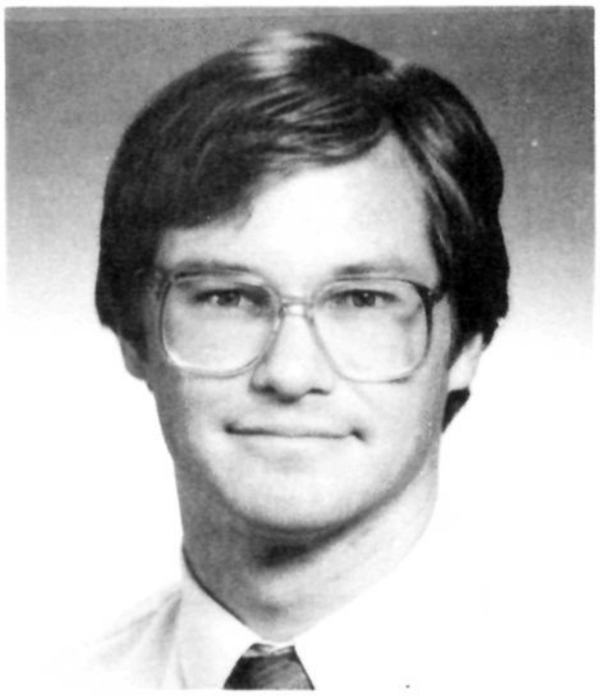
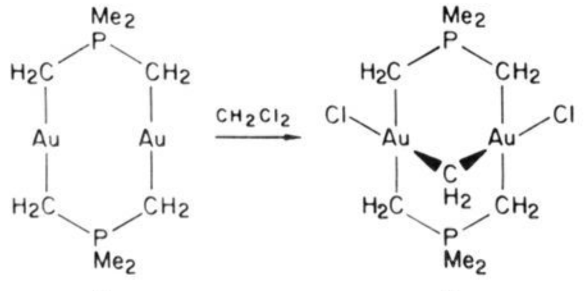
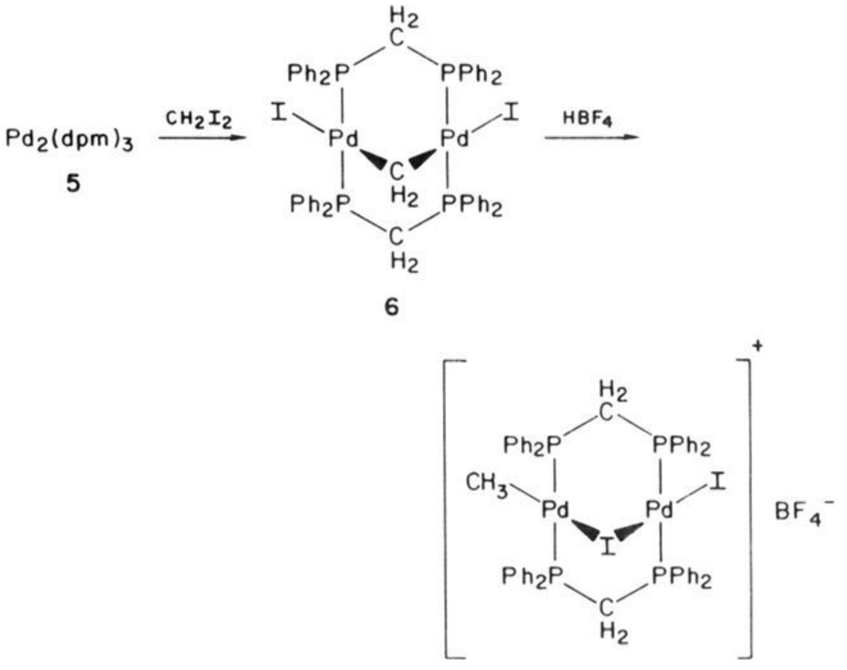


Jay Audett, born in 1956, obtained his B.S. in chemistry at the University of Connecticut, Storrs, during 1978. He received a Ph.D. at the California Institute of Technology, Pasadena, CA, in 1983. His doctoral studies included the formation and rearrangement of Grignard reagents and the oxidation of organometallic substrates. Having completed a year of postdoctoral study at the University of Wisconsin, Madison, he is presently a research chemist with Exxon Chemical Technology in Baton Rouge, LA.



3 4

insertion of carbon monoxide, methyl isocyanide, or sulfur dioxide into the palladium–carbon bond of this air-stable, dipalladium compound was observed. The reaction of **6** with pyridine or methyl isocyanide gives the dicationic substitution product $[Pd_2(dpm)_2(\mu\text{-}CH_2)L_2]^{2+}$ (L = pyridine or methyl isocyanide).

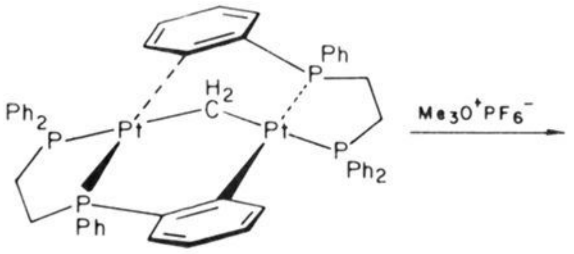


5 6 7

Fluoroboric acid protonates the methylene bridge and yields a brown crystalline methyl compound, **7**, which was characterized by X-ray crystallography. The reverse of this reaction, deprotonation of the cationic methyl complex **7** to regenerate the bridging methylene compound **6**, has not been reported. In the case of another methylene-bridged diplatinum compound **8**, the protonation of the bridging methylene ligand produces methyl complex **9** and has been shown to be reversible.[9] Reaction of the bridging methylene complex **8** with $Me_3O^+PF_6^-$ produces the ethyl analogue **10**.

$[\{Pt\text{-}\mu\text{-}[o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2]\}_2(Me)][I] \underset{HI}{\overset{NaOMe}{\rightleftharpoons}}$

9

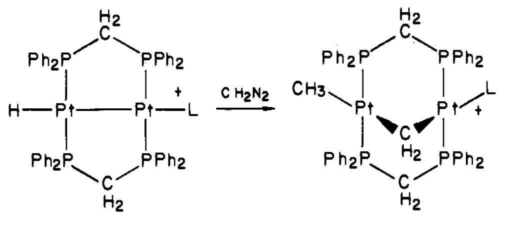


8

$[\{Pt\text{-}\mu\text{-}[o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2]\}_2(Et)][PF_6]$

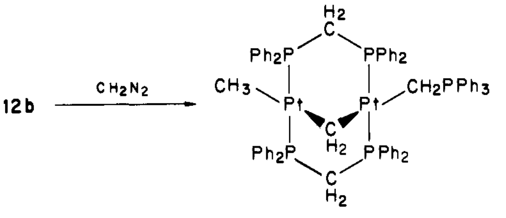
10

Another route to related A-frame structures involves insertion of methylene into a metal–metal bond. Reaction of diazomethane with cationic diplatinum compound **11** results in multiple methylene insertions into the platinum–platinum, platinum–hydrogen, and platinum–phosphorus bonds of the complex.[10] The thermolysis of **12a** does not result in coupling of the methyl and bridging methylene ligands; instead, carbon monoxide and methane are evolved. Coupling of terminal alkyl and bridging methylene groups is thought to be an important carbon–carbon bond-forming process in the Fischer–Tropsch reaction. The absence of any coupling products in the thermolysis of **12a** can be attributed to the trans orientation of the alkyl groups in **12a**. The related triphenylphosphine compound **12b** reacts with excess diazomethane by inserting methylene into the platinum–phosphorous bond which affords triphenylphosphine ylide complex **13**.



11a, L = CO
b, L = PPh3

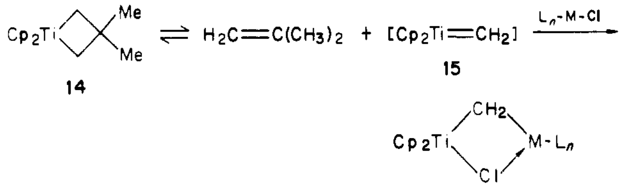
12a, L = CO
b, L = PPh3



13

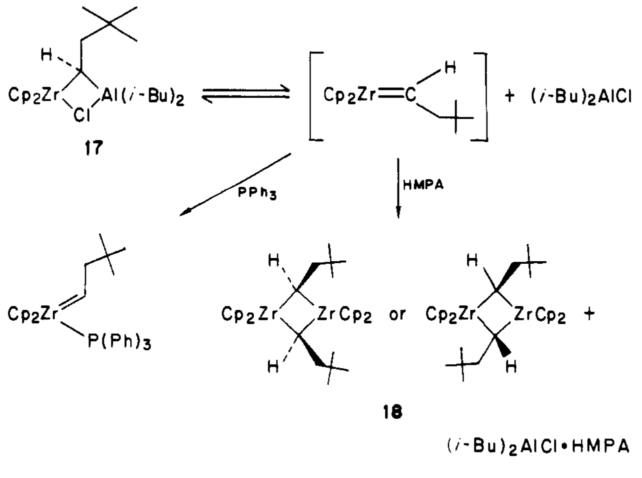
The insertion of diazomethane into the platinum–platinum bond of $Pt_2Cl_2(\mu\text{-dpm})_2$ also produces a μ-methylene derivative.[11] Kinetic studies suggest that the A-frame structures are obtained from electrophilic attack of diazomethane on the metal–metal bond.[12]

Methylene-bridged dinuclear compounds have also been reported for group IV (4^{73}) transition metals. Reactive titanium carbene intermediates 15, generated by thermolysis of metallacyclobutanes 14, react with L_nM–Cl complexes to generate methylene-bridged bimetallic compounds 16.[13] These thermally labile and air-sensitive compounds were characterized by ^1H and ^{13}C NMR. All but the rhodium complex 16c decompose at 25 °C in benzene.

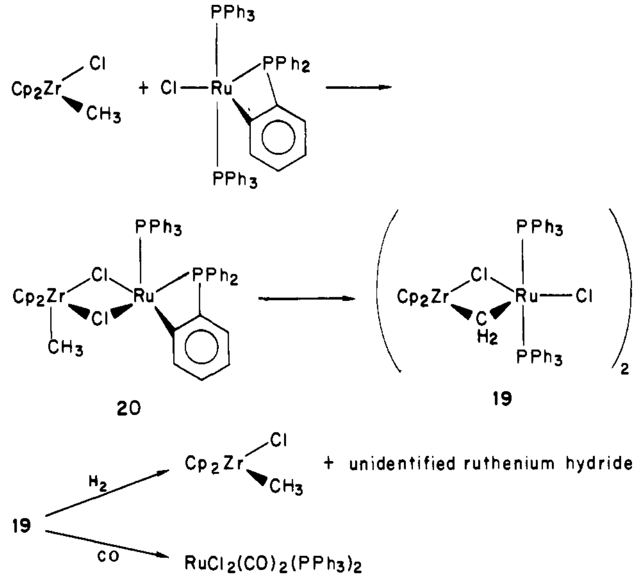


16a, L_n-M-Cl = (η^5-C_5Me_5)$TiCl_2$
b, L_n-M-Cl = (η^5-C_5Me_5)$ZrCl_2$
c, L_n-M-Cl = ½[(COD)RhCl]$_2$
d, L_n-M-Cl = ½[(COD)IrCl]$_2$

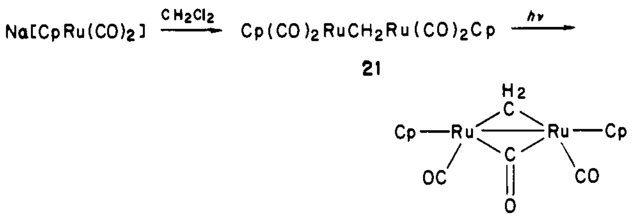
1,3-Dizirconabutanes 18 have been obtained by dimerization of a reactive zirconium carbene intermediate generated by treatment of the zirconium aluminum compound 17 with 1 equiv of HMPA.[14] The proposed intermediate zirconium carbene complex can be trapped by phosphines.



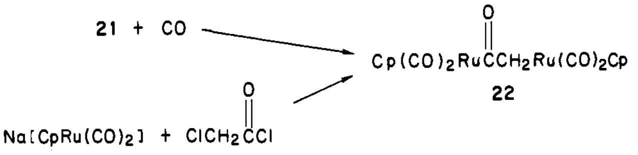
Gervais et al. have reported the formation of a yellow crystalline material in 10% yield which they formulate as the dimeric heteronuclear methylene-bridged complex 19.[15] Dimer 19 was preliminarily characterized by reactions with hydrogen and carbon monoxide. Confirmation of the structural assignment apparently will require crystallography since direct evidence for the bridging methylene ligand was not obtained from ^1H or ^{13}C NMR. An intermediate was detected by ^{31}P NMR and assigned structure 20.



One common feature of these dinuclear compounds is the presence of an additional bridging ligand. $Cp(CO)_2RuCH_2Ru(CO)_2Cp$ (21) is the only example of a μ-methylene complex which lacks a metal–metal bond or an additional bridging ligand.[16] The crystallographically characterized, temperature-sensitive diruthenium complex 21 was prepared from the reaction of methylene chloride and $Na[CpRu(CO)_2]$. Photolysis of the complex results in loss of CO and formation of a ruthenium–ruthenium bond.



Diruthenium μ-methylene compound 21 inserts carbon monoxide at room temperature to produce bridging ketene complex 22.[16] The insertion of carbon monoxide into 21 is much more rapid than into mononuclear $Cp(CO)_2RuR$ compounds. The enhanced reactivity of 21 might be due to relief of steric crowding upon carbon monoxide insertion. The strain in 21 is apparent in the long ruthenium–methylene bonds (2.18 Å) and in the wide ruthenium–methylene–ruthenium angle (123°). 22 can also be prepared from $ClCH_2C(O)Cl$ and $Na[CpRu(CO)_2]$.



Compound 21 reacts with carbon monoxide and

SCHEME I

$$\mathrm{Na[CpFe(CO)_2] + CH_2ICl \rightarrow Cp(CO)_2FeCH_2Cl}$$
$$\mathrm{Na[Mn(CO)_5] + CH_2ICl \rightarrow (CO)_5MnCH_2Cl}$$
$$\mathrm{Na[CpMo(CO)_3] + CH_2ICl \rightarrow Cp(CO)_3MoCH_2Cl}$$
$$\mathrm{Na[CpW(CO)_3] + CH_2ICl \rightarrow Cp(CO)_3WCH_2Cl}$$
$$\mathrm{Na[Re(CO)_5] + ClCH_2OCH_3 \rightarrow (CO)_5ReCH_2Cl}$$

methanol to produce methyl acetate. This is proposed to occur through methanolysis of an unsaturated intermediate which is formed by carbon monoxide insertion into the ruthenium–methylene bond. These results of Lin et al. suggest that metal–metal bonds and other bridging ligands are not essential for μ-methylene complex stability.[16] Similar methylene-bridged organometallic compounds without metal–metal bonds or additional bridging ligands have only been proposed as intermediates.[17] The insertion reactions of **21** with carbenes, methyl isocyanide, and other small molecules should be investigated.

The reactions of chloromethyl transition-metal complexes with transition-metal anions have not been observed to produce heteronuclear methylene-bridged compounds.[18] The syntheses of several chloromethyl compounds are shown (Scheme I). Reaction of diiodomethane with $\mathrm{Na[CpM(CO)_3]}$ (M = W, Mo) affords the unstable iodomethyl compounds $\mathrm{Cp(CO)_3MCH_2I}$ which decompose at room temperature.[18a] A carbon–iodine bond is apparently necessary for the conversion of a dihalomethane and $\mathrm{Na[CpM(CO)_3]}$ (M = Mo, W) to the corresponding haloalkyl derivative. Use of $\mathrm{Cp(CO)_3MoCH_2Cl}$ as a precursor of heteronuclear methylene-bridged compounds was unsuccessful because the molybdenum–carbon bond is more prone to nucleophilic attack than the carbon–chlorine bond.[18a] However, it is still possible that $\mathrm{Cp(CO)_2FeCH_2Cl}$ and $\mathrm{Cp(CO)_3WCH_2Cl}$ might serve as successful precursors of heteronuclear μ-methylene compounds. Lin's work[16] suggests that these compounds should be thermally sensitive.

Chloromethyl pivalate, $\mathrm{(CH_3)_3CCO_2CH_2Cl}$, was successfully used in the synthesis of the metal–metal bonded μ-methylene dimer $\mathrm{[CpFe(CO)_2]_2(\mu\text{-}CH_2)(\mu\text{-}CO)}$[19] but has not yet been used to prepare non-metal–metal bonded bridging methylene complexes.

B. The Ethylene Bridge

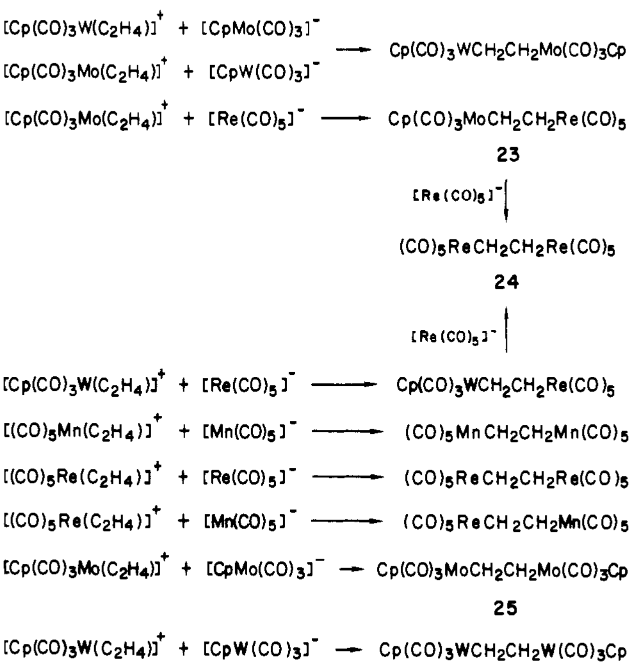
Available strategies for the syntheses of ethylene-bridged dinuclear compounds include (1) reaction of transition metal anions with cationic alkene complexes, (2) insertion of tetrafluoroethylene into metal–metal bonds, (3) reaction of triethylaluminum with $\mathrm{Cp_2ZrCl_2}$, and (4) reactions of transition-metal anions with 1,2-dihaloalkanes.

1. Reactions of Transition-Metal Anions with Cationic Alkene Complexes

Stabilized organic nucleophiles add to alkenes complexed to cationic metal centers to afford neutral metal alkyls.[20]

$$\mathrm{[Cp(CO)_2Fe(C_2H_4)]^+ + R^- \rightarrow Cp(CO)_2FeCH_2CH_2R}$$

SCHEME II

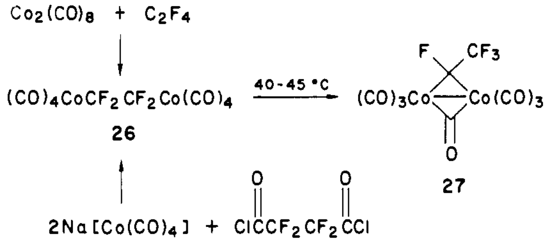


The substitution of a transition-metal anion for the stabilized organic nucleophile has yielded ethylene-bridged homonuclear and heteronuclear compounds from $\mathrm{Cp(CO)_3W(C_2H_4)^+}$, $\mathrm{Cp(CO)_3Mo(C_2H_4)^+}$, $\mathrm{(CO)_5Re(alkene)^+}$, and $\mathrm{(CO)_5Mn(alkene)^+}$ (Scheme II).[21-23] One method of synthesizing dirhenium complex **24** is the nucleophilic displacement of $\mathrm{Cp(CO)_3Mo^-}$ from $\mathrm{Cp(CO)_3MoCH_2CH_2Re(CO)_5}$ (**23**) by $\mathrm{Re(CO)_5^-}$.

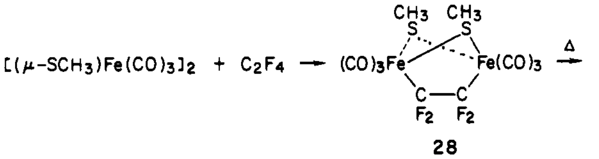
Photolysis or thermolysis of $\mathrm{MCH_2CH_2M}$ compounds such as **24** or **25** results in the evolution of ethylene and formation of metal–metal bonded dimers. The stability of these ethylene-bridged compounds parallels the corresponding metal–carbon bond strengths: rhenium > tungsten > molybdenum. The dimolybdenum compound **25** decomposes at −15 °C while the dirhenium complex **24** is stable at room temperature. A side reaction in this synthetic strategy is nucleophilic attack at the metal rather than at the ethylene ligand. This side reaction is most evident for $\mathrm{Cp(CO)_3Mo(C_2H_4)^+}$ and results in evolution of ethylene and the formation of metal–metal bonded dimers.

2. Tetrafluoroethylene Insertion into Metal–Metal Bonds

The insertion of tetrafluoroethylene into a metal–metal bond was first reported for $\mathrm{Co_2(CO)_8}$ which gave tetrafluoroethylene-bridged dinuclear complex **26**.[24] The product **26** was independently prepared by reaction of the bis acid chloride $\mathrm{ClC(O)CF_2CF_2C(O)Cl}$ with $\mathrm{Co(CO)_4^-}$ followed by decarbonylation.[25] The tetrafluoroethylene-bridged compound **26** rearranges to bridging carbene complex **27** at 40–45 °C, under vacuum.



Ibers et al. studied the insertion of tetrafluoroethylene into an iron–iron bond and noted the rearrangement of **28** to bridging carbene complex **29**.[26] Ibers suggested that this rearrangement proceeds by loss of fluoride to give μ-vinyl-bridged intermediate **30** which then readds fluoride to the terminal vinyl carbon to give the bridging carbene complex **29**. A related μ-vinyl-bridged cation **31** was prepared by fluoride abstraction with $BF_3 \cdot O(CH_3)_2$.



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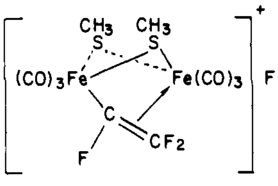

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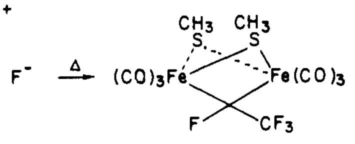

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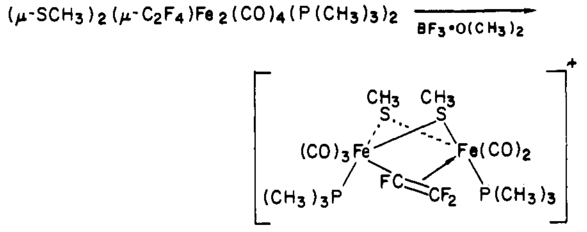

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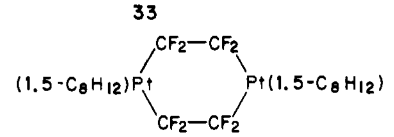
The reaction of tetrafluoroethylene with bis(cycloocta-1,5-diene)platinum affords a 1,4-diplatinacyclohexane complex, **32**.[27] Green et al. speculated that the formation of this compound occurs through dimerization of the 1,3-dipolar intermediate **33**. Another mechanistic possibility involves formation of an intermediate 1,2-diplatinacyclobutane which subsequently inserts tetrafluoroethylene into the platinum–platinum bond to afford the diplatinacyclohexane. In support of this hypothesis, the reaction of $Pd(1,5\text{-}C_8H_{12})_2$ with tetrafluoroethylene produces the 1,2-dipalladacyclobutane complex **34**.[27] The insertion of tetrafluoroethylene into the palladium–palladium bond of **34** was not observed. Green et al. speculate that formation of **34** involves the initial formation of a 1,3-dipolar intermediate which is trapped by the $Pd(1,5\text{-}C_8H_{12})_2$ nucleophile.[27]

$$2[Pt(1,5\text{-}C_8H_{12})_2] \xrightarrow{C_2F_4} \underset{\mathbf{33}}{2[(1,5\text{-}C_8H_{12})\overset{+}{Pt}CF_2CF_2^-]} \longrightarrow$$



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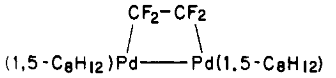

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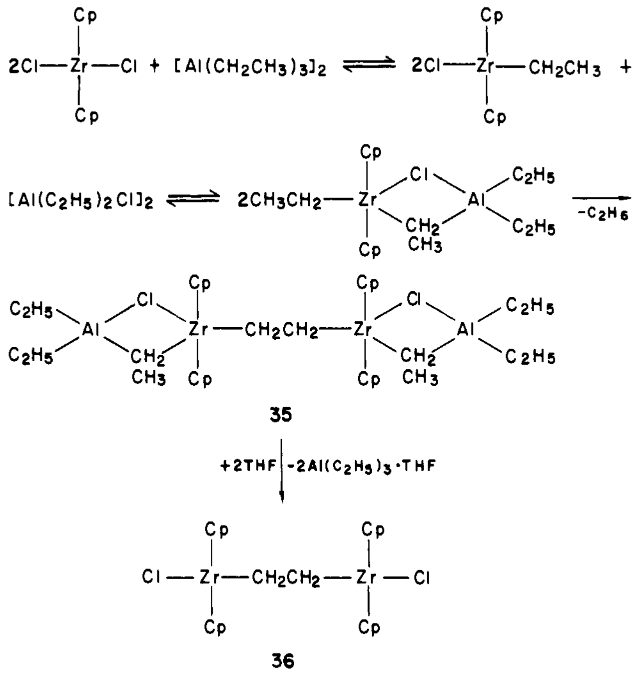
3. *Triethylaluminum and Cp_2ZrCl_2*

One of the compounds obtained from the reaction of Cp_2ZrCl_2 with $AlEt_3$ is the ethylene-bridged dizirconium compound **35**.[28,29] A small Zr–C(1)–C(2) angle of 75.9° and a short zirconium–β-carbon distance of 2.49 Å were found for **35**.[30] The formation of **35** and the related dizirconium compound **36** was suggested to occur as shown in Scheme III.

SCHEME III



Bridging ethylene complex **35** combined with $AlMe_3$ is a very active catalyst for the polymerization of terminal alkenes.[30] Compound **35** has been invoked as a model for an intermediate in the coupling of two Re=CH_2 species.[31]

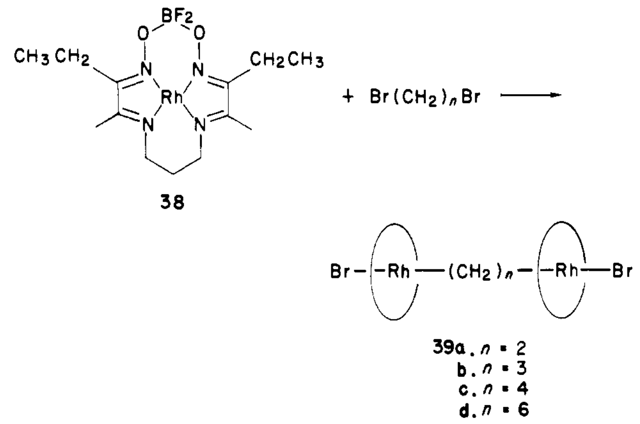
4. *Nucleophilic Substitution Reactions of Transition-Metal Anions and Dihaloethane*

Reactions of 1,2-dihaloethane and transition-metal anions usually give ethylene and metal–metal bonded dimers.[38,40] An exception has been reported in which $Na[CpRu(CO)_2]$ reacts with 1,2-dichloroethane to give the ethylene-bridged diruthenium compound **37**.[16] Photolysis or thermolysis of **37** produces ethylene and $[CpRu(CO)_2]_2$.

$$\underset{\mathbf{37}}{Cp(CO)_2RuCH_2CH_2Ru(CO)_2Cp}$$

Oxidative addition of 1,2-dibromoethane to macrocyclic rhodium(I) compound **38** gave the ethylene-bridged dirhodium complex **39**.[32] No evidence for a monorhodium alkyl intermediate was seen even when ICH_2CH_2Cl was employed. Apparently, the initially formed $Rh\text{–}CH_2CH_2Cl$ species is much more reactive than the starting dihalide. Collman has suggested a cyclic intermediate to explain this neighboring group effect. Reaction of **38** with $Br(CH_2)_nBr$ (n = 3, 4, 6) also gives hydrocarbon-bridged dirhodium complexes.

3,4-Diiron cyclobutenyl complexes and related benzocyclobutenyl complexes in which the two iron centers are linked by a two-carbon bridge have been reported. These 1,2-diiron compounds are unusually stable, probably because elimination would lead to an antiaromatic cyclobutadiene structure. Reaction of $Na[CpFe(CO)_2]$ with *cis*-3,4-dichlorocyclobutene produces the diiron cyclobutenyl complex **40** at low tempera-



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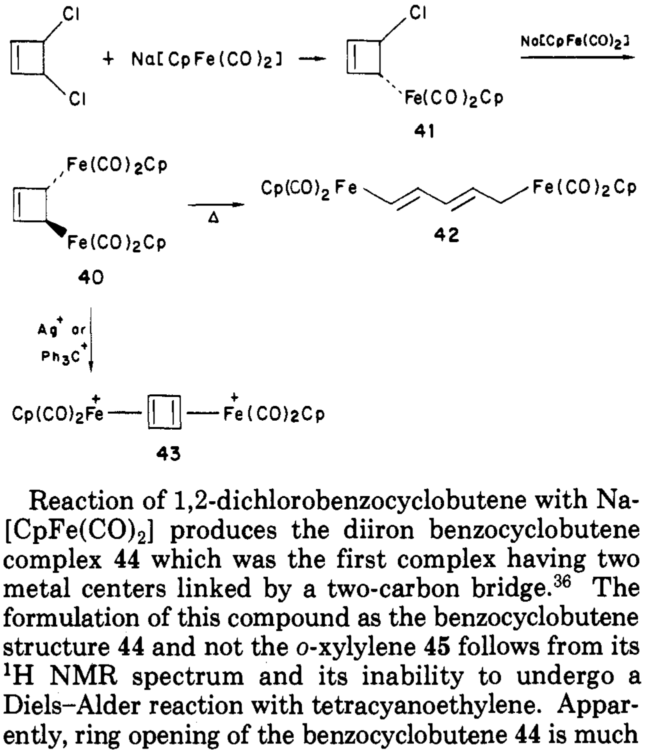
39a, n = 2
b, n = 3
c, n = 4
d, n = 6

ture.[33,34] A trans-monometalated intermediate 41 was isolated. Conversion of 41 to 40 is proposed to occur through S_N2' attack of Na[CpFe(CO)$_2$] at the carbon–carbon double bond from the same side as chlorine.[33,34] It is also possible that iron aids the loss of Cl^- from 41 to form an η^2-cyclobutadiene intermediate that is subsequently attacked by $CpFe(CO)_2^-$ to produce 40. When 40 is refluxed in toluene, cyclobutene ring opening occurs to give 1,4-diiron butadiene complex 42.[35] Oxidation of 40 affords the interesting dinuclear dicationic complex 43.[33]



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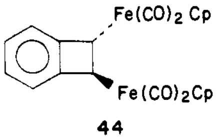
40

42

43

Reaction of 1,2-dichlorobenzocyclobutene with Na[CpFe(CO)$_2$] produces the diiron benzocyclobutene complex 44 which was the first complex having two metal centers linked by a two-carbon bridge.[36] The formulation of this compound as the benzocyclobutene structure 44 and not the o-xylylene 45 follows from its ^{1}H NMR spectrum and its inability to undergo a Diels–Alder reaction with tetracyanoethylene. Apparently, ring opening of the benzocyclobutene 44 is much slower than that of 40 due to the destruction of the benzenoid aromatic system upon ring opening.



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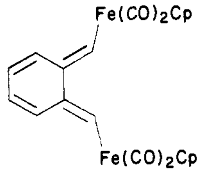

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Giering later studied the mechanism of formation of 44 using trapping experiments and proposed that benzocyclobutadiene was a key intermediate.[37] Benzocyclobutadiene is produced by reduction of the starting dichloride by Na[CpFe(CO)$_2$]. Successive additions of two CpFe(CO)$_2$ radicals to benzocyclobutadiene was proposed to lead to 44.

Attempts to prepare related cyclobutenyl complexes of other metals led only to formation of metal–metal bonded dimers from $CpMo(CO)_3^-$, $CpW(CO)_3^-$, and $Mn(CO)_5^-$.[36]

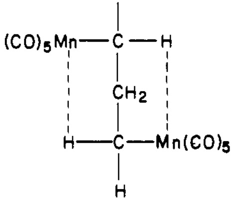
C. The Trimethylene Bridge and Longer Bridges

The syntheses of hydrocarbon bridges with $n \geq 3$ are limited to the reaction of transition-metal anions and dihaloalkanes. The major side reactions include oxidation of the anions affording dimeric coupling products and the conversion of 1,3-dihalopropane to an oxacyclopentylidene ligand.

1. Synthesis

This class of compounds was first synthesized by King in 1963 from the reaction of Na[CpFe(CO)$_2$] with a number of 1,n-dibromoalkanes.[38] Depending upon the choice of dihalide, either a hydrocarbon-bridged dinuclear compound or the oxidative coupling product [CpFe(CO)$_2$]$_2$ was obtained. 1,2-Dibromoethane and 1,4-dichloro-2-butene gave [CpFe(CO)$_2$]$_2$ while $Br(CH_2)_nBr$ (n = 3–6) afforded the desired hydrocarbon-bridged dinuclear compounds, $Cp(CO)_2Fe(CH_2)_nFe(CO)_2Cp$ (n =3–6).[39] The ^{1}H NMR chemical shift difference between the two types of methylene protons in $Cp(CO)_2Fe(CH_2)_3Fe(CO)_2Cp$ is less than 0.2 ppm and was resolved only when 270-MHz NMR became available.[39]

Accounts of this reaction for a variety of other transition-metal anions rapidly followed. The reactions of dibromoalkanes with Na[Mn(CO)$_5$)] gave a more diverse array of products than obtained for Na[CpFe(CO)$_2$].[40] 1,2-Dibromoethane and Na[Mn(CO)$_5$] yielded ethylene and $Mn_2(CO)_{10}$. 1,4-Dibromobutane gave a mixture of $Mn_2(CO)_{10}$ and an unstable product formulated as $(OC)_5Mn(CH_2)_4Mn(CO)_5$. Reaction of 1,3-dibromopropane and Na[Mn(CO)$_5$] gave a product with the formula $Mn_2(CO)_{10}(CH_2)_3$ which was described as structure 46. Long-range interactions of manganese with carbon–hydrogen bonds were invoked to explain the observation of three different ^{1}H NMR chemical shifts for the bridging trimethylene chain. Labeling and model studies later demonstrated that the compound was metal–carbene complex 47.[41] This dimanganese 2-oxacyclopentylidene complex was also synthesized by reaction of $ClCH_2CH_2CH_2C(O)Cl$ and Na[Mn(CO)$_5$]. The mechanism of formation of dinuclear 2-oxacyclopentylidene compounds will be discussed in a following section.



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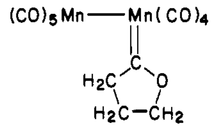

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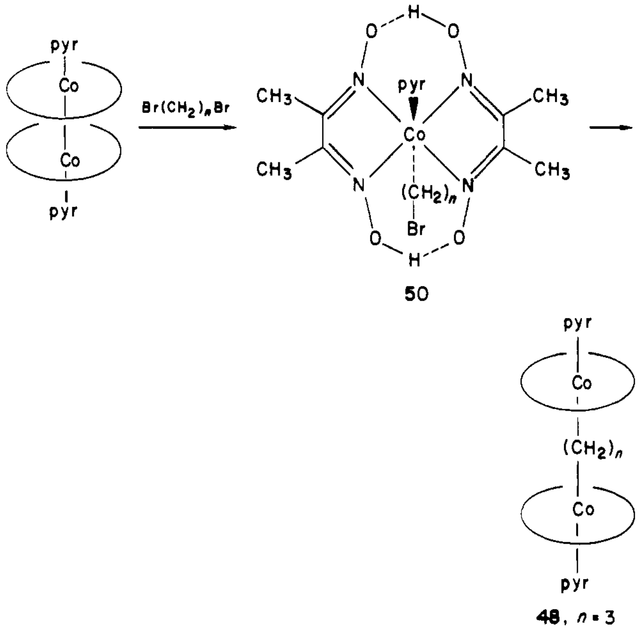
The reaction of $ClC(O)(CF_2)_3C(O)Cl$ and Na[Mn(CO)$_5$] does afford a fluorocarbon-bridged dimanganese complex, $(OC)_5Mn(CF_2)_3Mn(CO)_5$.[40]

The reactions of $CpMo(CO)_3^-$ and $CpW(CO)_3^-$ with 1,*n*-dibromoalkanes (n = 3, 4) resulted in the monosubstituted products $Cp(CO)_3M(CH_2)_nBr$ (M = Mo, W; n = 3, 4).[40] $Cp(CO)_3W(CH_2)_3W(CO)_3Cp$ was later synthesized from $Cp(CO)_3W(CH_2)_3Br$ and $CpW(CO)_3^-$ under more vigorous conditions.[42] $Cp(CO)_3M(CH_2)_4M(CO)_3Cp$ (M = Mo, W) were synthesized from 1,4-diiodobutane and the corresponding transition-metal anion.[42]

Diruthenium and dicobalt compounds with saturated hydrocarbon bridges have been reported. $Na[CpRu(CO)_2]$ reacts with 1,3-dibromopropane or 1,4-dibromobutane affording $Cp(CO)_2Ru(CH_2)_nRu(CO)_2Cp$ (n = 3, 4).[16] Higher yields were obtained by using 1,3-diiodopropane instead of the dibromide.[43] Schrauzer has synthesized cobaloxime dimers **48** and **49** with tri- and tetramethylene bridges from dibromoalkanes.[44] This reaction occurs through a monosubstituted intermediate, **50**, which is obtained in up to 65% yield immediately after the addition of the dibromoalkane. Thermolysis or photolysis of trimethylene compound **48** yielded cyclopropane, while the tetramethylene compound **49** yielded a mixture of butadiene and butenes. Similar chemistry has been reported for the analogous vitamin B_{12s} compounds.[45] The synthesis of polymethylene-bridged macrocyclic dirhodium compounds **39b–d** has been mentioned earlier.



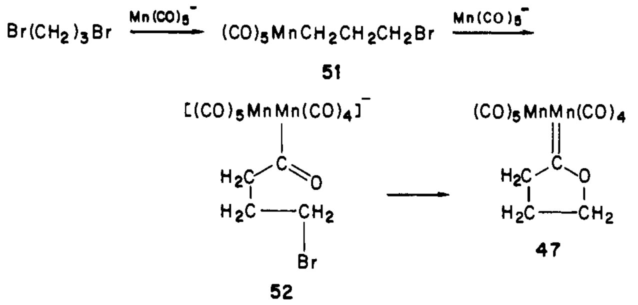
50

48, n = 3
49, n = 4

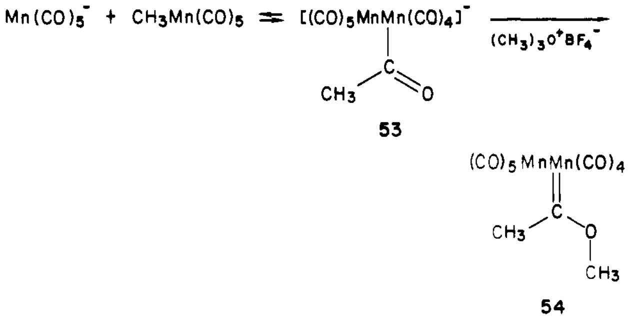
The ability to isolate monometalated intermediates allows the synthesis of heterobimetallic compounds with saturated hydrocarbon bridges. King first attempted this strategy with $Cp(CO)_3Mo(CH_2)_3Br$.[46] Its reaction with the strongly nucleophilic $CpFe(CO)_2^-$ resulted in substitution of both bromide and $CpMo(CO)_3^-$ affording the previously synthesized $Cp(CO)_2Fe(CH_2)_3Fe(CO)_2Cp$. To circumvent displacement of a transition-metal anion in such reactions, the iron compound $Cp(CO)_2Fe(CH_2)_3Br$ was employed since $CpFe(CO)_2^-$ is an extremely poor leaving group.[47] $Cp(CO)_2Fe(CH_2)_3Br$ was synthesized from $Na[CpFe(CO)_2]$ and $Br(CH_2)_3Br$ at −20 °C; the disubstitution product $Cp(CO)_2Fe(CH_2)_3Fe(CO)_2Cp$ is produced only under more vigorous conditions. The less nucleophilic $CpMo(CO)_3^-$ reacted with $Cp(CO)_2Fe(CH_2)_3Br$ to give a low yield of the heterobimetallic compound $Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp$.[47] The reaction of $CpRu(CO)_2^-$ and $Cp(CO)_2Fe(CH_2)_3I$ gives an excellent yield of $Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp$.[43] The success of this synthetic strategy depends upon the choice of halide leaving group, the nucleophilicity of the transition-metal anion, and the choice of transition metal in the metallahalogenoalkane complex. The use of better leaving groups than halides might significantly improve existing synthetic methods.

2. *Formation of 2-Oxacyclopentylidene Products*

As mentioned earlier, the reaction of $NaMn(CO)_5$ with $Br(CH_2)_3Br$ led to the formation of five-membered cyclic carbene complex **47** instead of the expected trimethylene-bridged dimanganese compound.[41] The mechanism proposed for formation of the oxacyclopentylidene involves reaction of an intermediate bromopropyl manganese compound, **51**, with $NaMn(CO)_5$ to give the acyldimanganese anion **52**. Acyl anion **52** is trapped intramolecularly by alkylation of the acyl oxygen by the alkyl bromide.

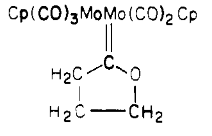


This mechanism is supported by independent studies of the reversible reaction of $NaMn(CO)_5$ with $CH_3Mn(CO)_5$ which produced an equilibrium concentration of the acetyldimanganese anion **53**.[48] The acetyldimanganese anion **53** was O-alkylated by the very reactive methylating reagent $Me_3O^+BF_4^-$ to afford carbene complex **54**. The less reactive alkylating agents CH_3I and dimethyl sulfate did not O-akylate **53** but instead reacted with $Mn(CO)_5^-$ in equilibrium with **53** to give $CH_3Mn(CO)_5$ as the sole product. The intramolecular O-alkylation of intermediate **52** by an alkyl bromide to give oxacyclopentylidene complex **47** probably occurs because formation of five-membered rings by S_N2 processes is extremely favorable.



The competition between formation of trimethylene-bridged bimetallic compounds and formation of oxacyclopentylidene complexes depends on different properties of the transition-metal moieties.

Formation of trimethylene compounds involves nucleophilic attack of a metal anion at an alkyl bromide and is favored for nucleophilic metal anions in the order $CpFe(CO)_2^- > Re(CO)_5^- > CpW(CO)_3^- > CpMo(CO)_3^- \simeq Mn(CO)_5^-$.[49] Formation of an oxacyclopentylidene ligand depends on the ability of a metal alkyl to undergo alkyl to acyl conversion which follows the order $(OC)_5Mn{-}R > Cp(CO)_3Mo{-}R \simeq (OC)_5Re{-}R > Cp(CO)_2Fe{-}R > Cp(CO)_3W{-}R$.[48] For $Mn(CO)_5^-$, the ease of alkyl to acyl conversion and the relatively low nucleophilicity of $Mn(CO)_5^-$ favor oxacyclopentylidene formation. Similarly, $CpMo(CO)_3^-$ reacts with the isolated compounds $Cp(CO)_3Mo(CH_2)_3Br$ to give oxacyclopentylidene complex **55**; this is favored by the ready formation of an acylmolybdenum intermediate.[42] The reaction of $Cp(CO)_3Mo(CH_2)_3Br$ with $CpW(CO)_3^-$ also leads to the formation of an oxacyclopentylidene complex, **56**.[42] In contrast, $CpW(CO)_3^-$ reacts with $Cp(CO)_3W(CH_2)_3Br$ to give a trimethylene-bridged ditungsten complex.[42] The greater nucleophilicity of $CpW(CO)_3^-$ and the diminished facility of alkyl to acyl tungsten conversions both favor nucleophilic displacement of bromide by $CpW(CO)_3^-$ rather than attack of $CpW(CO)_3^-$ at the metal center of $Cp(CO)_3W(CH_2)_3Br$.



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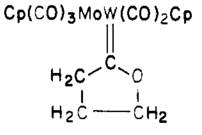

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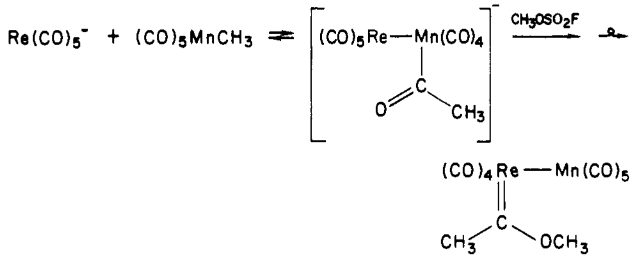
The product obtained from $Cp(CO)_3Mo(CH_2)_3Br$ and $CpW(CO)_3^-$ was expected to have the oxacyclopentylidene ligand bonded to molybdenum; however, the carbene ligand was found by X-ray analysis to be bonded to tungsten in **56**. The initially formed molybdenum carbene complex apparently rearranges via a bridging carbene complex. A similar rearrangement might be involved in the formation of the rhenium–manganese carbene complex **57** in which the carbene ligand has migrated from manganese to rhenium.[48]



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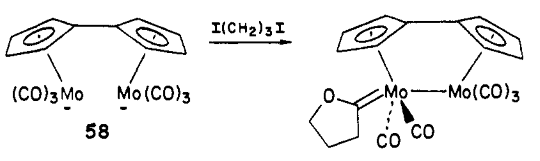
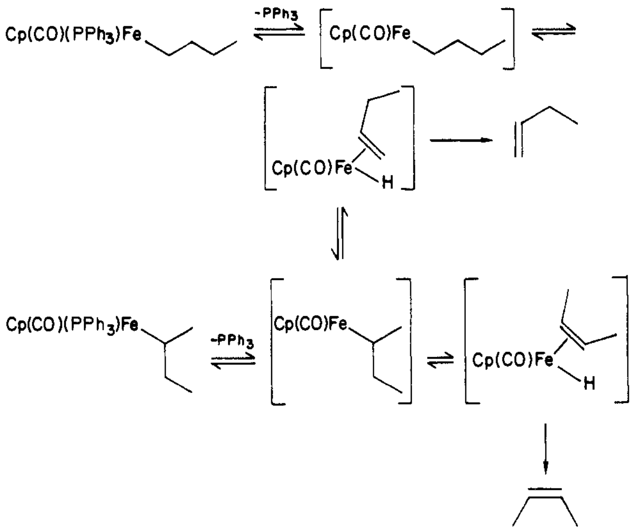
The (η^5:η^5-fulvalene)hexacarbonyldimolybdenum dianion **58** reacts with 1,3-diiodopropane to afford the oxycyclopentylidene complex **59**.[50] Transfer of the carbene ligand between the metal centers was observed as an NMR fluxional process with $\Delta G^{\ddagger} = 18$ kcal mol^{-1}. An intermediate with a bridging carbene and a bridging CO was suggested.



58 59

SCHEME IV



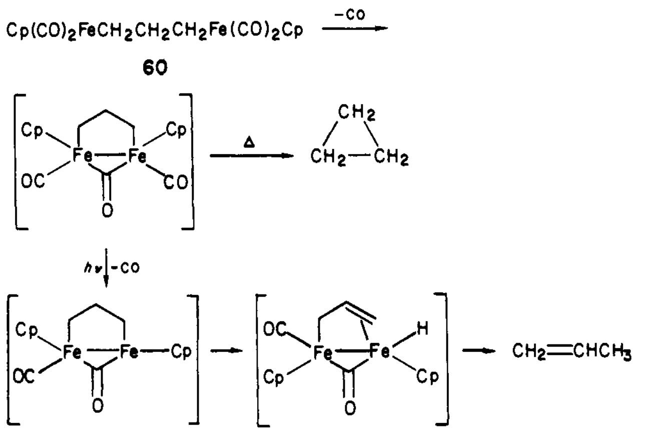
Nucleophiles other than anionic transition-metal complexes have been used to promote oxacyclopentylidene formation. These nucleophiles include iodide,[42,51] cyanide,[42,52] thiophenolate,[42,52] and triphenylphosphine.[52,53] Independent routes to the 2-oxacyclopentylidene ligand which do not involve metallahalogenoalkane intermediates have also been devised.[54]

3. *Reactions of* $M(CH_2)_nM$ *(n > 3) Compounds*

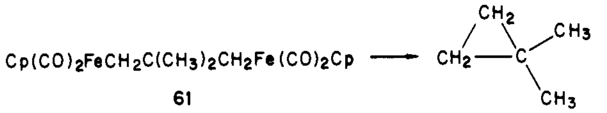
The thermolysis and photolysis of dimetallaalkanes are proposed to proceed by loss of a ligand and formation of an unstable dimetallacycloalkane. In this regard, their chemistry is quite different from that of monometal alkyls. Since a great deal of the chemistry to be discussed here involves $Cp(CO)_2Fe(CH_2)_nFe(CO)_2Cp$ systems, the well-studied chemistry of $Cp(CO)(PPh_3)Fe{-}R$ will be discussed first as background material. Reger has found that the decomposition of $Cp(CO)(PPh_3)Fe{-}R$ in xylene at 61 °C occurs via loss of PPh_3, reversible β-hydride elimination, and dissociation of butenes.[55] In agreement with this mechanism, the same 10.4:1.0:1.2 ratio of 1-butene:*trans*-2-butene:*cis*-2-butene was formed from either *n*-butyl or *sec*-butyl iron compounds and deuterium labels were completely scrambled in the decomposition of $Cp(CO)(PPh_3)FeCH_2CD_2CH_2CH_3$. No *n*-butane or *n*-octane were formed (Scheme IV).

In contrast to this mononuclear chemistry, the thermolysis of diiron trimethylene compound **60** at 125–196 °C in toluene gave a 1:5.3–10.6 ratio of propene:cyclopropane.[43] The carbon–carbon bond formation leading to cyclopropane distinguishes this bimetallic system from decomposition of related mononuclear alkyls. The reaction has been proposed to proceed by loss of CO and formation of a carbonyl-bridged diiron cyclopentane compound which then eliminates cyclopropane.

The photolysis of trimethylene diiron compound **60** gives a much higher ratio of propene:cyclopropane (51:1) than observed in the thermolysis reaction.[43] The reaction is thought to proceed through the same diiron cyclopentane, but photolysis of this intermediate leads to loss of a second CO to give a coordinatively unsaturated intermediate which then undergoes β-hydride elimination leading to propene. When β-hydride elimination was blocked by methyl substitution in **61**, even



photolysis led only to cyclopropane formation.[56]



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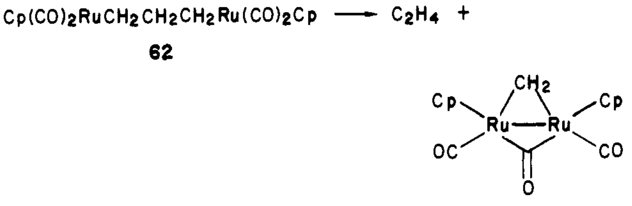
Thermolysis or photolysis of the analogous diruthenium trimethylene compound **62** leads predominantly to propene formation.[43] Apparently, the cleavage of ruthenium–carbon bonds required for cyclopropane formation is retarded by the greater ruthenium–carbon bond strength compared with weaker iron–carbon bonds, and a competing β-hydride elimination dominates the chemistry. In the decomposition of **62**, small amounts of ethylene and methane were also observed.[43] Knox has suggested that these minor products are derived via extrusion of ethylene from a dimetallacyclopentane which produces the bridging methylene complex **63**.



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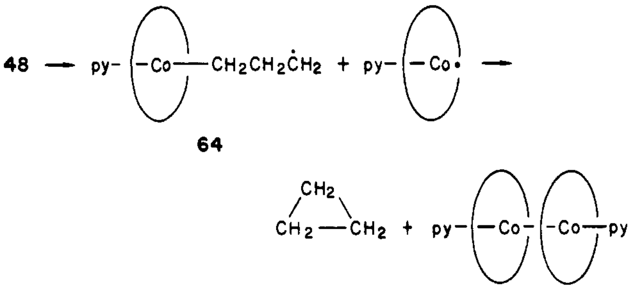
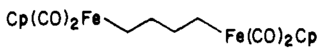
Thermolysis or photolysis of dicobalt trimethylene compound **48** yields only cyclopropane. Schrauzer has suggested direct formation of cyclopropane from **48**.[44] However, since related cobalt alkyls decompose by radical mechanisms, cyclopropane formation may well proceed by cyclization of monocobalt radical **64**. The possibility that $M\text{-}CH_2CH_2CH_2\cdot$ species might be precursors of cyclopropane can now be tested because of the recent syntheses of metallahalogenoalkane complexes such as $Cp(CO)_2Fe(CH_2)_3Br$.



The thermolysis of tetramethylene diiron compound **65** in the solid state gave a 40:12:48 ratio of 1-butene:*trans*-2-butene:*cis*-2-butene.[43] In contrast, thermolysis of the isomeric 1-methyltrimethylene diiron complex **66** gave a 97:3 ratio of *trans*-2-butene:1-butene.[43] These very different product ratios imply that



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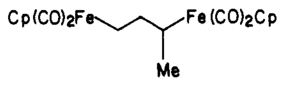

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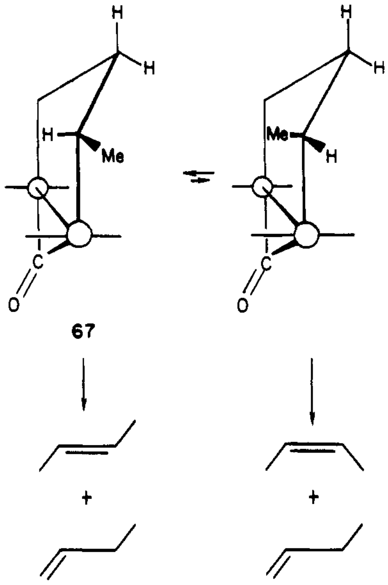
there is no interconversion of **65** and **66** or intermediates derived from them during the thermolysis. This stands in sharp contrast to monometal chemistry and has prompted Knox to suggest that both thermolysis reactions proceed via diiron cycloalkanes of differing ring size. The predominant formation of *trans*-2-butene from **66** was suggested to arise by β-hydride elimination from the more favorable diiron cyclopentane conformer **67** in which the methyl group occupies a pseudoequatorial position. It is not clear why **66** fails to produce methylcyclopropane.



Thermolysis of the tetramethylene diruthenium complex $Cp(CO)_2Ru(CH_2)_4Ru(CO)_2Cp$ gave essentially the same mixture of 1- and 2-butenes as the analogous diiron complex.[43]

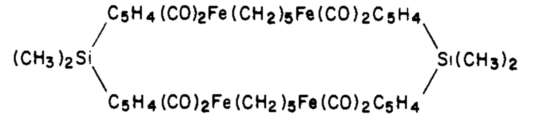
Photolysis of the dimolybdenum tetramethylene complex **68** yields ethylene, butane, and π-allyl complexes, but no butenes.[42] A radical mechanism could readily account for ethylene formation from fragmentation of intermediate molybdenum alkyl radical **69**. The availability of $Cp(CO)_3Mo(CH_2)_4Br$ provides a way of generating radical **69** and testing the proposed pathway to ethylene.

$$\underset{\mathbf{68}}{Cp(CO)_3Mo(CH_2)_4Mo(CO)_3Cp} \longrightarrow \underset{\mathbf{69}}{Cp(CO)_3MoCH_2CH_2CH_2\dot{C}H_2} +$$

$$Cp(CO)_3Mo\cdot \longrightarrow [CpMo(CO)_3]_2 + 2CH_2CH_2$$

Thermolysis and photolysis of tetramethylene dicobalt complex **49** gave 1,3-butadiene and butenes.[44] A β-hydride elimination pathway is most consistent with these results.

There are conflicting reports on the thermolysis of pentamethylene diiron complex $Cp(CO)_2Fe(CH_2)_5Fe(CO)_2Cp$ (**70**). Wegner reported that thermolysis of **70** in Nujol at 150 °C gave an 85% yield of an 87:13 mixture of 1-pentene:2-pentenes and less than 1% pentane.[57] In contrast, Knox reported that solid-state pyrolysis of **70** gave a 70:30 ratio of pentane:1-pentene.[43] The reasons for these differing results are not understood. The macrocyclic complex **71** containing two diiron pentamethylene units produced mostly 1-pentene and less than 1% pentane upon thermolysis in Nujol at 150 °C.[57]



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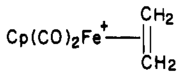

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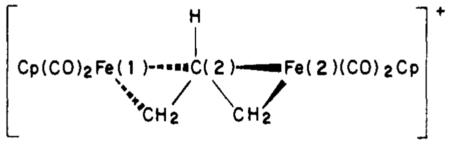
The reactions of dimetallaalkanes with hydride abstracting reagents are potentially very interesting, but only one example has been reported. For the mononuclear system $Cp(CO)_2FeCH_2CH_3$, treatment with $(C_6H_5)_3C^+$ led to hydride abstraction and formation of ethylene complex **72**.[58] Extension of this reaction to the 1,3-diiron propane complex **60** also led to hydride abstraction.[46,59] The X-ray crystal structure of the product **73** indicates that the central electron-deficient carbon atom is stabilized by electron donation from both iron centers which are located above and below the plane of the three-carbon bridge. (Fe_1–C_2 = 2.59 Å; Fe_2–C_2 = 2.72 Å).[60] A related system, **74**, with four iron atoms has been prepared by a totally unrelated route.[61]



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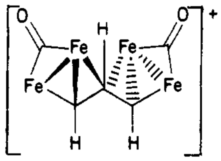


74. Fe≡Cp(CO)Fe

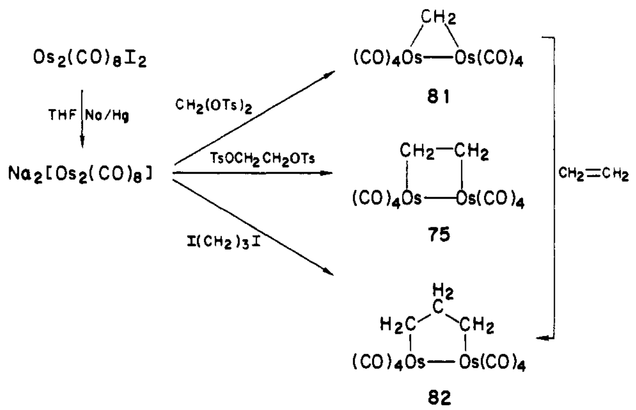
II. Dimetallacycloalkanes

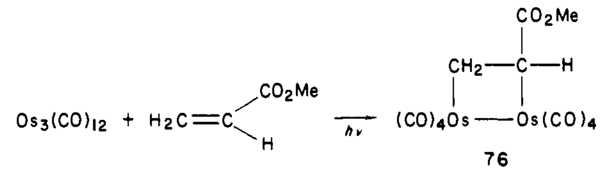
Work on dimetallacycloalkanes has been limited to iron, osmium, and cobalt. The relevance of this chemistry to the Fischer–Tropsch reaction and olefin metathesis, as well as detailed mechanistic work on several interesting cobalt systems will be discussed.

A. Dimetallacyclobutanes

Norton prepared diosmacycloalkanes by the reactions of $CH_2(OTs)_2$, $TsOCH_2CH_2OTs$, or $ICH_2CH_2CH_2I$ with $Na_2[Os_2(CO)_8]$.[5c] X-ray crystallography demonstrated that the four-member ring of the diosmacyclobutane **75** is puckered. A 27° twist about the Os–Os bond avoids eclipsing interactions between the carbon monoxide ligands of the $Os(CO)_4$ units.

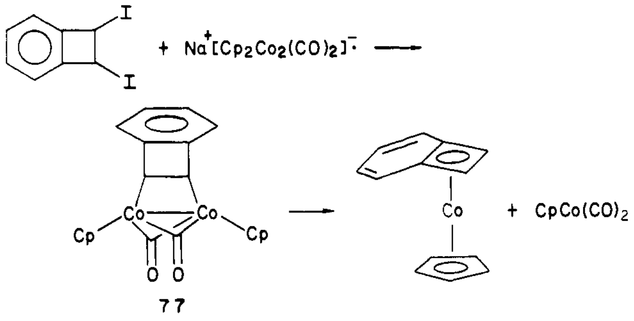
A diosmacyclobutane similar to that reported by Norton has been prepared by an independent route.[62] Takats, Grevels, et al. photolyzed $Os_3(CO)_{12}$ in the presence of methyl acrylate and obtained a mononuclear alkene adduct and diosmacyclobutane **76** (30%). The diosmacyclobutane ring is puckered. A 23° twist about the Os–Os bond again avoids eclipsing interactions of the carbon monoxide ligands.





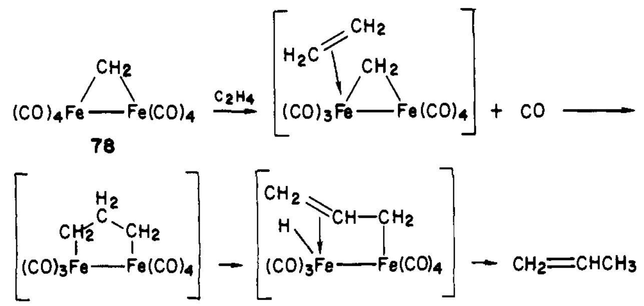
They noted that only mononuclear alkene adducts are obtained in the photolysis of $Ru_3(CO)_{12}$ with alkenes.[62] The difference between $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ is attributed to the metal–metal bond strengths of the intermediate $M_2(CO)_8$ species. The stronger osmium–osmium bond allows for trapping of the $Os_2(CO)_8$ intermediate with alkene while the weaker Ru–Ru bond readily cleaves to $Ru(CO)_4$. They also reported that Norton's diosmacyclobutane **75** was formed by photochemical reaction of $Os_3(CO)_{12}$ with ethylene.

Bergman was unable to synthesize a similar dicobaltacyclobutane from the reaction of 1,2-diiodoethane and $Na[Cp_2Co_2(CO)_2]$.[63] However, the related compound **77** was synthesized from 1,2-diiodo-3,4-benzocyclobutene and $Na[Cp_2Co_2(CO)_2]$.[63] This product decomposed to a mononuclear benzocyclobutadiene complex at room temperature.

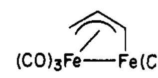


B. Dimetallacyclopentanes

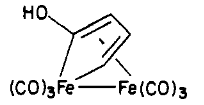
Pettit's report that the reaction of diiron cyclopropane **78** with ethylene affords a 90% yield of propene sparked interest in the syntheses of dimetallacyclopentanes.[64] The diiron cyclopropane **78** was synthesized by the reaction of diiodomethane with $(NEt_4)_2[Fe_2(CO)_8]$.[65,66] The mechanism for propene formation shown below explains inhibition of the reaction by carbon monoxide. A similar reaction between diiron cyclopropane **78** and monosubstituted alkenes



was observed, but no products were seen from reaction with isobutene. The diiron cyclopropane also undergoes alkyne insertion reactions to produce **79** and **80**.[66]



79

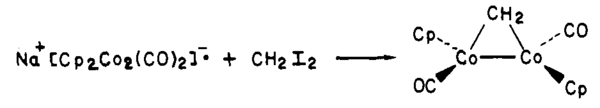


80

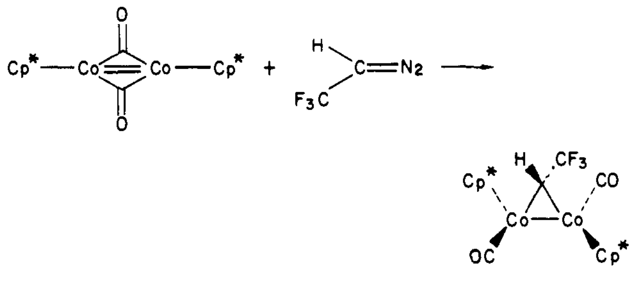
These insertion reactions implicate these compounds as potential models for alkyne polymerization. The related cyclopentadienyl compound $[Cp(CO)Fe]_2(\mu\text{-}CH_2)(\mu\text{-}CO)$ yields some propene upon reaction with ethylene.[56] This ethylene insertion reactivity suggests the intermediacy of diiron cyclopentanes in propene formation.

Norton's reaction[5c] of the diosmacyclopropane **81** and ethylene which affords an isolable diosmacyclopentane, **82**, provides support for the proposed diiron cyclopentane. The thermolysis of this related diosmacyclopentane results in production of ethylene (56%) and propene (21%). The formation of propene from the diosmacyclopentane and proposed diiron cyclopentanes can be explained by β-hydride elimination from the dimetallacyclopentane followed by reductive elimination of propene. The formation of ethylene can be explained if the major degradative pathway involves breakdown of the diosmacyclopentane to ethylene and an observed intermediate diosmacyclopropane. This reactivity pattern is reminiscent of the olefin metathesis reaction and suggests the possibility of dimetallacyclopentane intermediates for some catalytic systems.

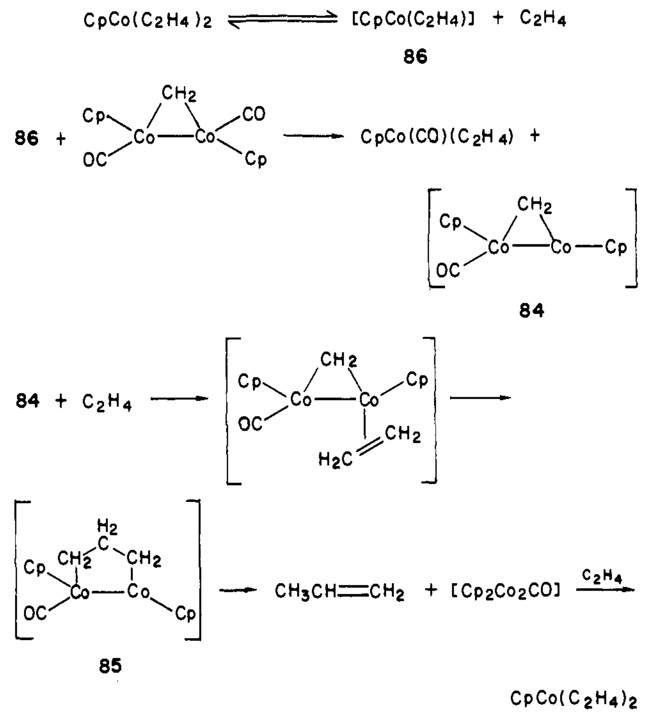
Bergman's group has examined ethylene insertion reactivity in dicobaltacyclopropanes. The reaction of diiodomethane with $Na^+[Cp_2Co_2(CO)_2]^{-\cdot}$ affords the dicobaltacyclopropane compound **83**.[67,68] Another route to dimetallacyclopropanes involves the reaction of diazo compounds with transition-metal dimers.[69]



83

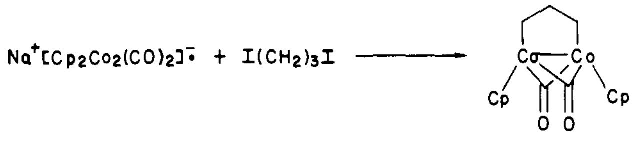


SCHEME V



The reaction of ethylene with the dicobaltacyclopropane **83** produces propene. Attempts to observe a proposed dicobaltacyclopentane intermediate were not successful. It was suggested that propene production requires a coordinatively unsaturated dicobaltacyclopropane, **84**, which reacts with ethylene to give an unsaturated dicobaltacyclopentane, **85**.[67,68] Elimination of propene from **85** is proposed to occur before carbon monoxide recoordinates. The mechanism of propene formation is autocatalytic in coordinatively unsaturated $CpCo(C_2H_4)$ (**86**). The abstraction of carbon monoxide from the dinuclear complex by the autocatalytic reagent **86** gives a coordinatively unsaturated dinuclear complex. Ethylene coordinates and inserts to give a coordinatively unsaturated dicobaltacyclopentane, **85**. β-hydride elimination occurs, and propene is ultimately evolved. Pettit and Bergman both noted carbon monoxide inhibition for their ethylene insertion reactions. One may speculate that the ethylene insertion reaction for Pettit's diiron cyclopropane **78** is autocatalytic in an unsaturated iron monomer (Scheme V).

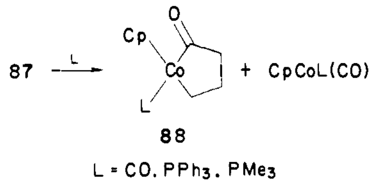
The reaction of 1,3-diiodopropane with $Na^+[Cp_2Co_2(CO)_2]^{-\cdot}$ provides an independent route to the proposed dicobaltacyclopentane intermediate **87**.[63,70]



87

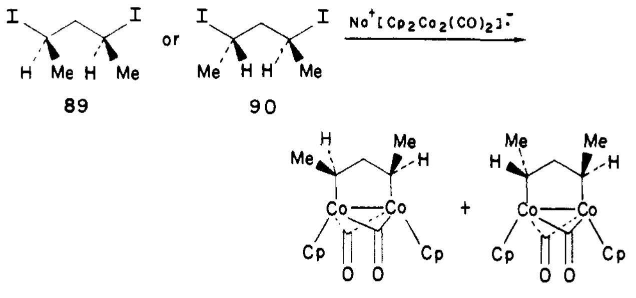
Thermolysis of **87** affords propene (73%) and cyclopropane (17%). This supports the contention that thermolysis of non-metal–metal bonded compounds proceeds with loss of carbon monoxide and formation of a metal–metal bond prior to propene and cyclopropane formation.

Gentle heating of the dicobaltacyclopentane with phosphines or CO produces a mononuclear cobaltacyclopentanone, **88**.[70] Oxidation of the cobaltacyclopentanone with iodine affords cyclobutanone (50%).

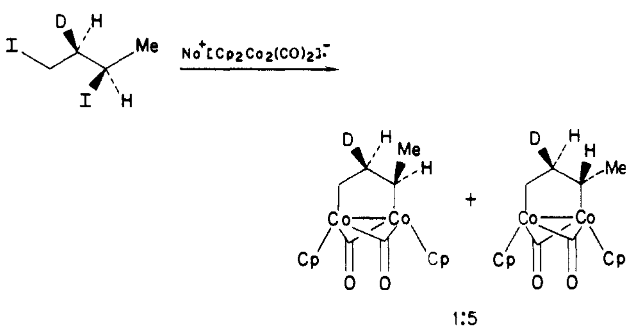


Similar oxidation of the dicobaltacyclopentane **87** gives predominantly cyclopropane (71%) and some propene (9%).

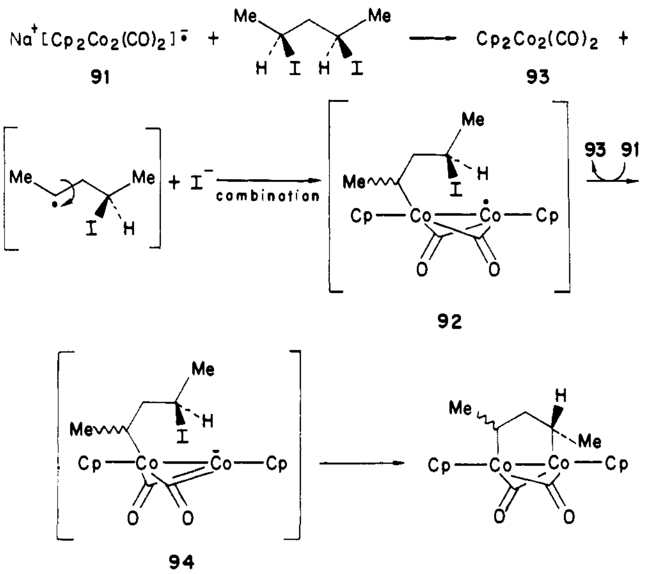
A dicobaltacyclohexane was synthesized from 1,4-diiodobutane and $\mathrm{Na^+[Cp_2Co_2(CO)_2]^{-}\cdot}$ but decomposed at room temperature.



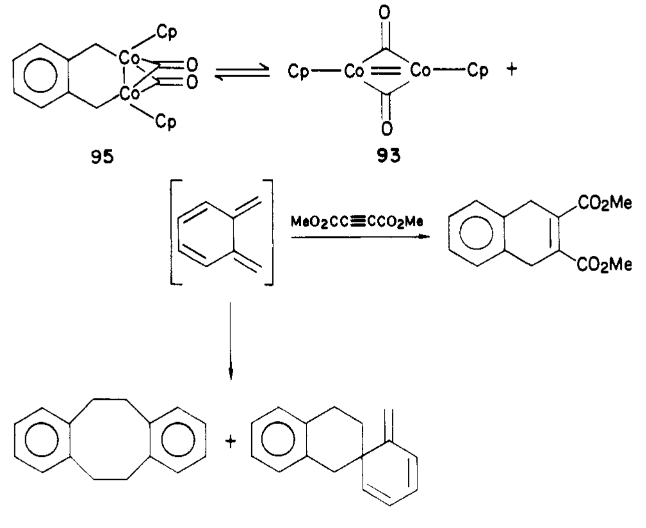
The mechanism for formation of these dicobaltacycloalkanes is addressed in an interesting stereochemical study.[71] The reactions of $\mathrm{Na^+[Cp_2Co_2(CO)_2]^{-}\cdot}$ with stereoisomers of 2,4-diiodopentane show that product formation is stereorandom. The same ratio of product stereoisomers is obtained from either diiodide **89** or **90**. Competition experiments show that a primary iodide is more reactive than a secondary iodide in their reactions with $\mathrm{Na^+[Cp_2Co_2(CO)_2]^{-}\cdot}$. Reaction of deuterium-labeled 1,3-diiodobutane demonstrates that the second bond-forming step (reaction at the secondary center) occurs with predominant inversion of stereochemistry.



This suggests that the stereorandom step is the formation of the first cobalt–carbon bond. Bergman proposes that an initial electron transfer from **91** to the alkyl iodide results in cleavage of the carbon–iodine bond. The resulting organic radical racemizes before bonding to cobalt to produce **92**. Reduction of this intermediate cobalt radical **92** by starting material **91** generates an alkyl dicobalt anion **94** which reacts via intramolecular backside nucleophilic attack of the anionic center on the carbon–iodine bond. Alternatively, the second cobalt–carbon bond-forming step might proceed by an electron-transfer process in which the organic radical is trapped by cobalt before carbon–carbon bond rotation affords a stereorandom process.



The reaction of α,α'-dibromo-*o*-xylene and $\mathrm{Na^+[Cp_2Co_2(CO)_2]^{-}\cdot}$ produces the dicobaltacyclohexene **95** which exhibits an unusual decomposition pathway.[72] Its decomposition involves a reversible dinuclear elimination of *o*-xylylene in a retro-dimetalla Diels–Alder reaction. The *o*-xylylene dimerizes, reacts with dimethylacetylene dicarboxylate in a Diels–Alder reaction, or recombines with the dicobalt compound **93** in a dimetalla-Diels–Alder reaction. This unusual dimetalla Diels–Alder reactivity suggests its extension to other multiple metal–metal bonded compounds for the syntheses of similar dimetallacyclohexenes.



III. Conclusion

In several instances, the chemistry of dinuclear organometallic compounds has been demonstrated to provide a better model for the behavior of heterogeneous catalysts than that provided by mononuclear organometallic compounds. Dinuclear organometallic compounds have the possibility of providing metal–metal interactions present in heterogeneous systems. The contrasting behavior of mononuclear metal alkyls and of dimetallaalkanes is undoubtedly due to such metal–metal interactions. Dinuclear organometallics also have the possibility of having a ligand on one metal react with a ligand on the other metal. This was most clearly demonstrated in the reaction of ethylene with a bridging methylene bimetallic compound to produce propene. The carbon–carbon bond-forming reactivity in the ethylene to propene conversion and the metathesis-like behavior of Norton's diosmacyclopentane demonstrate that dinuclear organometallic compounds serve as reasonable models for several important catalytic processes.

A large number of hydrocarbon-bridged dinuclear complexes have been synthesized since King's initial report of $Cp(CO)_2Fe(CH_2)_nFe(CO)_2Cp$ in 1963, but mechanistic studies of reactions of these compounds are in their infancy. Extensive mechanistic investigations have only been applied to Bergman's dicobaltacycloalkanes. The possible role of radical intermediates in the synthesis and thermolysis of dinuclear compounds needs to be clarified. Do these compounds remain dinuclear throughout these transformations or are mononuclear intermediates involved? Bergman has demonstrated the exchange of cobalt centers in dicobaltacyclopropanes. The use of isotopic labeling, crossover experiments, and other physical organic techniques are appropriate to fully elucidate the reactivity of these compounds.

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