Coordination Chemistry Reviews, 60 (1984) 171–190
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

μ(α,ω)-ALKANEDIYL COMPLEXES OF TRANSITION METALS

JOHN R. MOSS * and LOUISE G. SCOTT

Department of Inorganic Chemistry, University of Cape Town, Rondebosch 7700 (Republic of South Africa)

(Received 23 March 1984)

CONTENTS

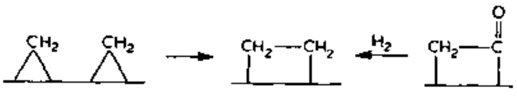
A. INTRODUCTION

$\mu(\alpha,\omega)$-Alkanediyl complexes are binuclear metal complexes of general formula $L_xM{-}(CH_2)_n{-}M'L'_y$ ($n \geqslant 2$) in which the metal centres are bonded to the two terminal carbons of an alkyl chain. Two types of $\mu(\alpha,\omega)$-alkanediyl complexes are known, (**I**) without a metal–metal bond and (**II**) with a metal–metal bond (Fig. 1). Compounds of type (**II**) are called dimetallocycloalkanes and those of type (**I**) have been termed polymethylene bridged compounds.

The $-(CH_2)_n-$ bridge is the formal extension of a methylene bridge, and $\mu(\alpha,\omega)$-alkanediyl species, like methylene bridged species [1], are of interest as possible models for surface intermediates in various metal-catalysed reactions. In the Fischer–Tropsch reaction, for example, an ethanediyl bridged intermediate **1** has been implicated to account for the formation of ethylene [2]. Such an intermediate could be formed by dimerization of

(I) (II)

Fig. 1. Two types of $\mu(\alpha,\omega)$-alkanediyl complexes.

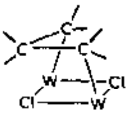


1

Scheme 1

surface methylene groups [2b] or by reduction of a CH_2CO bridge on the metal surface [2a] (Scheme 1).

Alkanediyl intermediates could be postulated for other metal-catalysed reactions involving the formation or rearrangement of hydrocarbons, such as the Ziegler–Natta polymerization of ethylene [3] and platinum-catalysed hydrocarbon rearrangement [4]. Dimetallocycloalkanes have been implicated in several catalytic reactions such as olefin metathesis [5] and alkene dimerization [6]. An example is the proposed formation of a ditungsten–cyclopentane intermediate **2** in the photoinduced metathesis of *cis-* and *trans-* RCH=CHMe catalysed by $W(CO)_6/CCl_4$ [5].

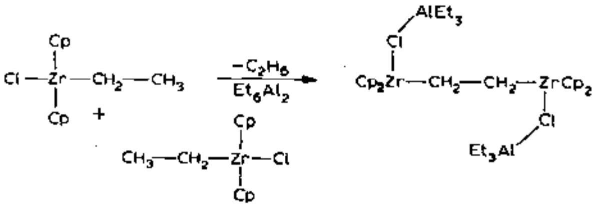


2

Discrete $\mu(\alpha,\omega)$-alkanediyl bridged complexes could serve as useful models for such intermediates and as such their structure, stability and reactivity are of interest. This paper reviews the preparative routes to, and properties of, transition metal $\mu(\alpha,\omega)$-alkanediyl complexes of both types, according to the transition metal groups in the periodic table.

B. TITANIUM GROUP

Kaminsky and Sinn [7] have isolated the type-(**I**) μ(1,2)-ethanediyl dizirconium compound **4** from the reaction of $[(\eta^5\text{-}C_5H_5)_2ZrCl_2]$ and triethylalane. The initial product is $[(\eta^5\text{-}C_5H_5)_2ClZrEt]$, compound **3** which combines by intermolecular β-hydrogen transfer and elimination of ethane to form **4** [8].



3 4

(1)

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

The similar compound $[Et_2Al\text{-}(\mu\text{-}Cl)_2\text{-}Zr(\eta^5\text{-}C_5H_5)_2]_2\{\mu\text{-}(CH_2)_2\}$, **5**, is formed in a parallel reaction from compound **3**, while a third dimethylene bridged species $[(\eta^5\text{-}C_5H_5)_2ZrCl]_2\{\mu\text{-}(CH_2)_2\}$, **6**, is obtained from compound **4** by treatment with THF. Compound **3** also reacts with triethylalane to form a mixed metal compound $[(\eta^5\text{-}C_5H_5)_2ClZr(CH_2CH_2)AlEt_2]$, **7**, the acidic β-hydrogen cleaving an Al–Et bond to eliminate ethane [7].

These 1,2-ethanediyl bridged species are observed intermediates in a side reaction which occurs during homogeneous Ziegler–Natta polymerization of α-olefins catalysed by bis-(cyclopentadienyl)-zirconium(IV) compounds, and are themselves of interest as potential homogeneous catalysts for this reaction [3]. Compound **4** reacts with α-olefins and 1,3-dienes on addition of excess trimethyl- or triethylalane, especially in the presence of water. Dechlorination occurs, presumably with the formation of aluminoxanes, to give an extremely active halogen-free homogeneous catalyst for polymerization of α-olefins, particularly ethylene [9].

The structural study of compound **4** [9] confirms that there is a $-(CH_2)_2-$ bridge between non-bonded zirconium atoms. The C–C bond distance in the bridge is close to that in ethane (1.53 Å). An anomalous feature of this structure is the small Zr–C–C bond angle (76°). Other structurally characterized (α,ω)-alkanediyl bridged compounds show much larger M–C–C bond angles. For example, the Re–C–C angle in $[(CO)_5Re]_2\{\mu\text{-}(CH_2)_2\}$ is 121° [20]. The Zr–β-carbon distance in compound **4** is only slightly greater than the Zr–α-carbon bond distance. This suggests that the bonding of the $-(CH_2)_2-$ bridge is intermediate between a σ and an $\eta^2(C_2H_4)$-type interaction (Fig. 2).

Despite predictions of inherent instability for a (1,2)-ethanediyl bridged species [10], the dizirconium compounds **4**–**6** are thermally stable, up to 96, 110 and 180 °C, respectively [7]. This is in contrast to the ethyl compound $[(\eta^5\text{-}C_5H_5)ClZrEt]$ which decomposes above 0 °C via β-hydrogen elimination [11]. Considering the observed proximity of the β-carbons to the metal atoms in compound **4**, the resistance to decomposition via β-elimination is surprising. This resistance could be accounted for, in part, by steric factors; steric crowding in the transition state for β-elimination (compound **8**) would

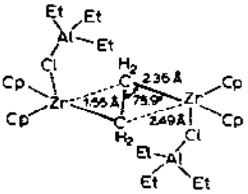
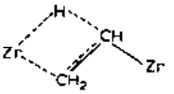


Fig. 2. Molecular structure of $[Et_3Al(\mu\text{-}Cl)Zr(\eta^5\text{-}C_5H_5)]_2\{\mu\text{-}(CH_2)_2\}$.

disfavour decomposition by this route



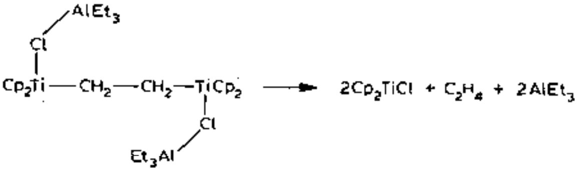
8

This steric effect has been observed for certain zirconium alkyl compounds; e.g., the bulky $[Zr(\eta^5\text{-}C_5H_5)_2Bu^n\{CH(SiMe_3)_2\}]$ is reluctant to undergo β-elimination, yielding n-butane on thermolysis at 150 °C, whereas $[Zr(\eta^5\text{-}C_5H_5)_2Bu^n_2]$ decomposes at room temperature with the loss of 1-butene [12].

These $-(CH_2)_2-$ bridged compounds decompose on addition of HCl with elimination of the dimethylene bridge as ethane [7].

The analogous titanium ethanediyl bridged compounds $[Et_3Al(\mu\text{-}Cl)Ti(\eta^5\text{-}C_5H_5)_2]_2\{\mu\text{-}(CH_2)_2\}$, compound **9**, and $[(\eta^5\text{-}C_5H_5)_2ClTi(CH_2)_2AlEt_3]$, have been detected spectroscopically during the reaction of $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$ with $AlEt_3$ [3]. However, these titanium(IV) compounds could not be isolated owing to the ease of reduction of titanium(IV) to the trivalent state

(2)



9

C. CHROMIUM GROUP

Beck and Olgemöller [13,14] have prepared (1,2)-ethanediyl bridged complexes of molybdenum and tungsten, **11–13**, e.g. by nucleophilic addition of the metal anion to the ethylene complex cation **10**

$$[Cp(CO)_3M(C_2H_4)]^+ + [Cp(CO)_3M']^- \rightarrow [Cp(CO)_3M(CH_2)_2M'(CO)_3Cp]$$

10

11 M = M′ = Mo

12 M = M′ = W

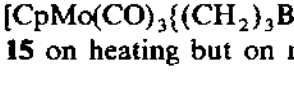
13 M = Mo, M′ = W

(3)

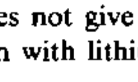
These compounds have low solubility and are readily isolated from solution at low temperatures. They are, however, unstable in solution, decomposing spontaneously at ambient temperatures. The mixed metal compound **13** decomposes to the (1,2)-ethanediyl tungsten compound **12** and $[CpMo(CO)_3]_2$ with evolution of ethylene. Compound **11** is unstable even in the solid state above −20 °C, while compound **12** is stable at 20 °C [14]. The higher stability of the tungsten compound is attributed [14] to the greater strength of the tungsten–carbon bond than the Mo–C bond [15]. This trend is also observed in the mixed metal compounds $[Cp(CO)_3M(CH_2CH_2)Re(CO)_5]$ (M = Mo,W) [14]. $[Cp(CO)_3Mo(CH_2CH_2)Re(CO)_5]$ decomposes above −15 °C, while $[Cp(CO)_3W(CH_2CH_2)Re(CO)_5]$ is stable at 20 °C. The rhenium–carbon σ-bond is known to be particularly strong [16]; the difference in the stability of these compounds can thus be attributed to the differing strengths of the Mo–C and W–C bonds.

The triphenylphosphine-substituted tungsten compound $[CpW(CO)_2(PPh_3)]_2\{\mu\text{-}(CH_2)_2\}$ is produced in the reaction of $[CpW(CO)_2(PPh_3)]^-$ with $[CpW(CO)_2(PPh_3)(C_2H_4)]^+$ [13]. The IR and ^{1}H-NMR data for this compound indicate a trans arrangement of CO groups in the tetragonal pyramidal configuration of ligands around the metal atom (Cp at the apical position) (Fig. 3) [17]. This compound is extremely sensitive to light and decomposes rapidly with evolution of ethylene in solution at room temperature.

Longer chain (α,ω)-alkanediyl bridged molybdenum and tungsten compounds are also known. The stable compound $[CpMo(CO)_3]_2\{\mu\text{-}(CH_2)_4\}$, **14**, (decomposition above 150 °C) is obtained from the reaction of $[CpMo(CO)_3]^-$ with $I(CH_2)_4I$ [18]. The analogous reaction of the metal anion with $I(CH_2)_3I$ results in the substitution of only one halide atom, giving $[CpMo(CO)_3\{(CH_2)_3I\}]$, which will react further on heating to give the 2-oxacyclopentylidene complex, **15** [18].



14



15

Reactions of $[CpMo(CO)_3]^-$ with $Br(CH_2)_nBr$ (n = 3,4) also produce the monohaloalkyl compounds $[CpMo(CO)_3\{(CH_2)_nBr\}]$ (n = 3,4) [19]. $[CpMo(CO)_3\{(CH_2)_3Br\}]$ does not give the bromo analogue of compound **15** on heating but on reaction with lithium iodide does yield **15** [19]. King

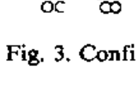


Fig. 3. Configuration of ligands at the metal centres in $[CpW(CO)_2(PPh_3)]_2\{\mu\text{-}(CH_2)_2\}$.

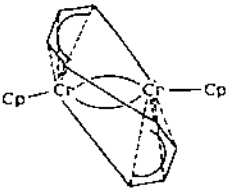
and Bisnette [20] have isolated the perfluoro (1,3)-propanediyl bridged species $[Cp(CO)_3Mo]_2\{\mu\text{-}(CF_2)_3\}$ by thermolysis of $[Cp(CO)_3Mo\{CO(CF_2)_3CO\}Mo(CO)_3Cp]$. This diacyl compound is formed in the reaction of $[CpMo(CO)_3]^-$ with $ClCO(CF_2)_3COCl$.

$[CpMo(CO)_3]_2\{\mu\text{-}(CH_2)_{10}\}$ has been reported [21], as the product of the reaction of $[CpMo(CO)_3]^-$ with $[CpMo(CO)_3\{(CH_2)_{10}X\}]$ (X = halogen).

The mixed metal compound $[Cp(CO)_3Mo\{\mu\text{-}(CH_2)_3\}Fe(CO)_2Cp]$ is formed on addition of $[CpMo(CO)_3]^-$ to $[CpFe(CO)_2\{(CH_2)_3Br\}]$ [22]. However, in the reaction of $[CpMo(CO)_3\{(CH_2)_nBr\}]$ ($n = 3,4$) with $[CpFe(CO)_2]^-$ both the bromine atom and the $CpMo(CO)_3$ group are replaced by $[CpFe(CO)_2]^-$ to give $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 3,4$) [19].

Contrary to previous observations [19], the reaction of $[CpW(CO)_3]^-$ with $Br(CH_2)_3Br$ does produce the propanediyl bridged species $[CpW(CO)_3]_2\{\mu\text{-}(CH_2)_3\}$, though only in small yield, after prolonged heating (J.R. Moss and L.G. Scott, unpublished results, 1983). This compound is thermally stable, decomposing above 160 °C. The fact that the reaction of $Br(CH_2)_3Br$ with $[CpW(CO)_3]^-$ produces some of the μ(1,3)-propanediyl species, whilst that with $[CpMo(CO)_3]^-$ gives only the monohaloalkyl compound, is accounted for by the greater nucleophilicity of the tungsten anion [23].

No polymethylene bridged chromium compounds have been prepared, although compounds with unsaturated hydrocarbon bridges between chromium atoms are known, e.g. $[(CpCr)_2(\mu\text{-}C_8H_8)]$ **16** [24].



16

D. MANGANESE GROUP

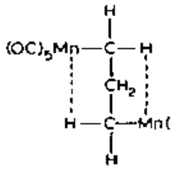
The reaction of $[Mn(CO)_5]^-$ with 1,3-dibromopropane or $ClCO(CH_2)_3Cl$ yields a yellow crystalline compound which was originally thought [25] to be the μ(1,3)-propanediyl species, $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_3\}$. To explain the ^{1}H-NMR spectrum of this compound, which shows three CH_2 proton signals, the unusual structure **17** with manganese–hydrogen bonding was proposed [25]. Casey [26] subsequently showed, by means of deuterium labelling and exchange experiments, that this compound is in fact the cyclic carbene species **18**.

From observations made by King [25] it appears that the reaction of

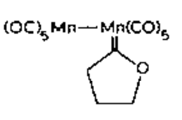
$[Mn(CO)_5]^-$ with 1,4-dibromobutane yields the analogous six-membered cyclic carbene species, and possibly some of the $-(CH_2)_4-$ bridged compound. These products could not be separated from $Mn_2(CO)_{10}$ also produced in the reaction.

The only bridged manganese compound isolated is the perfluoro propanediyl bridged derivative $[(CO)_5Mn]_2\{\mu\text{-}(CF_2)_3\}$ [25]. This is readily obtained by thermal decarbonylation of the perfluoroacyl compound $[(CO)_5Mn\{CO(CF_2)_3OC\}Mn(CO)_5]$ which is produced in the reaction of $[Mn(CO)_5]^-$ with perfluoroglutaryl dichloride. The ^{19}F-NMR spectrum of this compound exhibits two resonances in a 2 : 1 ratio, as expected, for the perfluoroalkyl bridge.

The attempt [19] to prepare a mixed metal manganese compound by addition of $[Mn(CO)_5]^-$ to $[CpMo(CO)_3\{(CH_2)_3Br\}]$ leads only to the cyclic carbene compound **18**.



17



18

The only other alkanediyl bridged metal compound of this group known is the μ(1,2)-ethanediyl rhenium species $[(CO)_5Re(CH_2CH_2)Re(CO)_5]$, **20** [13]. This has been prepared by two routes: (i) addition of two equivalents of $[Re(CO)_5]^-$ to $[Cp(CO)_3M(C_2H_4]^+$ (M = Mo or W) [13], and (ii) reaction of $[Re(CO)_5]^-$ with $[(CO)_5Re(C_2H_4)]^+$ [27] (Scheme 2).

(i) $[Cp(CO)_3M(C_2H_4)]^+ + [Re(CO)_5]^- \rightarrow [Cp(CO)_3M(CH_2CH_2)Re(CO)_5]$
19a M = Mo **19b** M = W
$\downarrow [Re(CO)_5]^-$
(ii) $[(CO)_5Re(C_2H_4)]^+ + [Re(CO)_5]^- \rightarrow [(CO)_5Re]_2\{\mu\text{-}(CH_2)_2\}$
20

Scheme 2

The mixed metal intermediates **19a** and **19b** have been isolated at low temperature.

$[(CO)_5Re]_2\{\mu\text{-}(CH_2)_2\}$ is considerably more stable than the μ(1,2)-ethanediyl molybdenum and tungsten compounds discussed previously; it is stable in solution at 20 °C and in the solid form decomposes with elimination of ethylene at 138 °C [14]. This is reasonable since rhenium alkyls are known to be particularly stable [16].

In compound **20**, the $Re(CO)_5$ groups are trans with respect to the C–C bond of the $-(CH_2)_2-$ bridge with Re–C–C angles of 121°. The three equatorial carbonyl ligands on each Re atom are approximately in the plane of the bridge carbons. The C–C bond of the bridge is considerably shorter than that in ethane (1.53 Å) (Fig. 4) [14]. In the mass spectrum of **20**, peaks of equal intensity for the ions $[(CO)_9Re_2(C_2H_4)]^+$ and $[Re_2(CO)_{10}]^+$ are observed, indicating competitive loss of CO and C_2H_4.

E. IRON GROUP

The compounds $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 3$–6), prepared by King [28] from $[Cp(CO)_2Fe]^-$ and $Br(CH_2)_nBr$, were the first alkanediyl bridged species of type (I) known. These compounds have also been synthesised by other routes, e.g. the addition of $[Cp(CO)_2Fe]^-$ to the monohaloalkyl compounds $[Cp(CO)_2M\{(CH_2)_nBr\}]$ (M = Mo or W; $n = 3,4$) [19] or $[Cp(CO)_2Fe\{(CH_2)_nBr\}]$ ($n = 3$–5) [22] and photochemical decarbonylation of the diacyl species $[Cp(CO)_2Fe\{CO(CH_2)_4CO\}Fe(CO)_2Cp]$ to give $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_4\}$ [29]. The perfluoroalkyl compound $[Cp(CO)_2Fe]_2\{\mu\text{-}(CF_2)_3\}$ has similarly been prepared by photolysis of $[Cp(CO)_2Fe\{CO(CF_2)_3CO\}Fe(CO)_2Cp]$ [20].

The structural study of the propanediyl and butanediyl bridged compounds [30] confirms that the Fe atoms are linked by a $-(CH_2)_n-$ chain with the carbons of the α-methylene groups σ-bonded to the iron atoms ($Fe-CH_2$ = 2.08 Å) as postulated by King [28]. A constant C–C bond distance of 1.55 Å and C–C–C bond angle of 111° are observed in the alkanediyl bridges (Fig. 5). ^{1}H-NMR (270 MHz) and $^{13}C\{^1H\}$NMR spectra are consistent with the crystallographic results, each showing two resonances for the methylene groups in the bridges [30].

Recently, the compounds $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 7$–12) have been synthesised from $[Cp(CO)_2Fe]^-$ and $Br(CH_2)_nBr$ to extend the existing series (J.R. Moss and L.G. Scott, unpublished results, 1983). The compounds

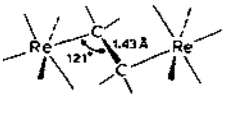


Fig. 4. Structure of $[(CO)_5Re]_2\{\mu\text{-}(CH_2)_2\}$.

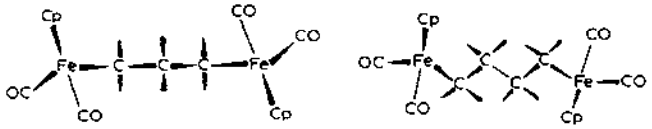
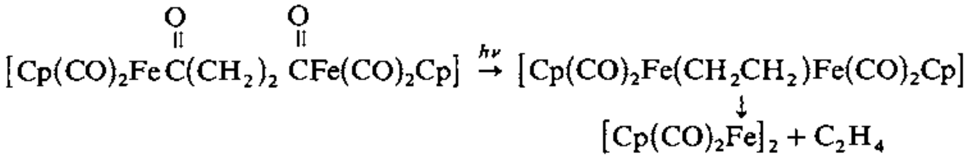


Fig. 5. Structures of $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_3\}$ (left) and $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_4\}$ (right).

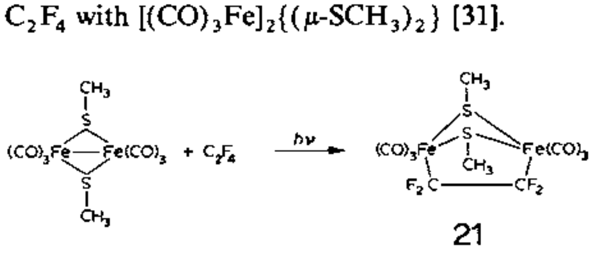
$[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 3$–12) are all thermally stable in the solid state; decomposition points as determined by differential scanning calorimetry (DSC) (J.R. Moss, L.G. Scott, M.E. Brown and K. Hindson, unpublished results, 1984) are in the range 179–190 °C for $n = 4$–12 and 158 °C for $n = 3$. However, these compounds are light sensitive and decompose rapidly in solution at room temperature. Attempts to prepare the ethanediyl bridged compound have failed. The reaction of $[Cp(CO)_2Fe]^-$ with 1,2-dibromo or diiodo-ethane produces only the dimer $[Cp(CO)_2Fe]_2$ [19], and the desired product cannot be detected even at low temperature (J.R. Moss and L.G. Scott, unpublished results, 1983). Similarly, reaction of $[CpFe(CO)_2]^-$ with $[CpFe(CO)_2(C_2H_4)]^+$ gave only $[CpFe(CO)_2]_2$. Pettit and co-workers [29] have attempted to isolate $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_2\}$ by photochemical decarbonylation of $[Cp(CO)_2Fe\{CO(CH_2)_2CO\}Fe(CO)_2Cp]$. The organometallic product is again $[Cp(CO)_2Fe]_2$ but the production of ethylene during the reaction suggests that the (1,2)-ethanediyl bridged species is formed and under the reaction conditions decomposes with elimination of ethylene to $[Cp(CO)_2Fe]_2$ as follows



$$\begin{aligned}[]
[\mathrm{Cp(CO)_2Fe}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{(CH_2)_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Fe(CO)_2Cp}] &\xrightarrow{h\nu} [\mathrm{Cp(CO)_2Fe(CH_2CH_2)Fe(CO)_2Cp}]\\
&\qquad\qquad\qquad\downarrow\\
&\qquad\quad [\mathrm{Cp(CO)_2Fe}]_2 + \mathrm{C_2H_4}
\end{aligned} \qquad (4)$$

This reaction has a precedent among known dimethylene bridged species. The analogous compounds $[Cp(CO)_3M]_2\{\mu\text{-}(CH_2)_2\}$ (M = Mo, W) decompose with evolution of ethylene to the corresponding dimer [13].

The only known two-carbon bridged iron compound is the perfluoroethanediyl bridged species **21**, isolated from the photoinduced reaction of C_2F_4 with $[(CO)_3Fe]_2\{(\mu\text{-}SCH_3)_2\}$ [31].

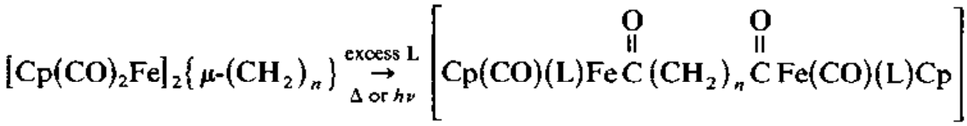


21 (5)

In this compound the iron atoms are held in a cis arrangement with respect to the C–C bond in the C_2F_4 bridge by the bridging methylthiolato groups. The C_2F_4 group bridges the non-bonded iron atoms through two σ-C–Fe bonds (2.02 Å) with the C–C bond parallel to the Fe–Fe axis. The trimethyl phosphine-substituted compound $[(CO)_2(PMe_3)Fe]_2\{\mu\text{-}(CF_2)_2\}$

$\{(\mu\text{-}SCH_3)_2\}$ has also been isolated by addition of PMe_3 to compound **21** in solution. These C_2F_4 bridged compounds are stable in the solid form but rearrange readily in solution to the $>CFCF_3$ carbene bridged species [31].

The alkanediyl bridged iron compounds, $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\}$ (n = 3–12) undergo various reactions which are well known for mononuclear alkyl compounds. The photo- or thermally-induced reaction with CO or phosphine leads to CO insertion into the Fe–C bonds to form the diacyl species, **22** [21,29 and J.R. Moss and L.G. Scott, unpublished results, 1983]



$$[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\} \xrightarrow[\Delta \text{ or } h\nu]{\text{excess L}} \left[Cp(CO)(L)Fe\overset{O}{\overset{\|}{C}}(CH_2)_n\overset{O}{\overset{\|}{C}}Fe(CO)(L)Cp\right]$$

22 $(n = 3,4,7)$

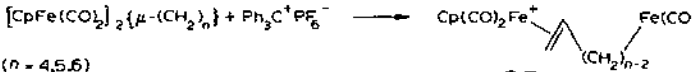
(6)

L = CO, PPh_3

For $n = 3$ and 4 the reaction with excess PPh_3 produces a mixture of the mono- and diacyl compounds in the ratio 3 : 1 and 1 : 3, respectively. This could be attributed to steric crowding in the diphosphine-substituted products, particularly for the propanediyl bridged species (J.R. Moss and L.G. Scott, unpublished results).

The CO insertion is reversible; e.g., photolysis of the diacyl species $[Cp(CO)_2Fe\{CO(CH_2)_4CO\}Fe(CO)_2Cp]$ produces $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_4\}$ in 40% yield [29].

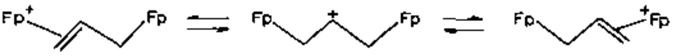
As observed with mononuclear iron alkyl compounds [32], β-hydride abstraction from the alkanediyl bridge in $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\}$ (n = 4–6) leads to formation of a cationic olefin species (J.W. Johnson and J.R. Moss, unpublished results, 1983). These cationic species are assigned structure **23**, in which one iron atom is π-bonded and the other σ-bonded to the alkenyl chain, on the basis of ^{1}H-NMR data



23

(7)

The analogous reaction of $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_3\}$ produces a symmetrical cationic complex $[Cp(CO)_2Fe(CH_2CHCH_2)Fe(CO)_2Cp]^+$ [19,33]. This was first thought [19] to be a carbonium ion complex **25** which exists in dynamic equilibrium with the stable olefinic complexes **24** and **26** (Scheme 3)



24 25 26

Scheme 3

Subsequent dynamic ^{1}H-NMR studies have revealed that the compound is fluxional rather than in dynamic equilibrium [34]. The crystallographic study of the cation [33] suggests that the positive charge is isolated on the β-carbon and is stabilized by weak Fe–CH interactions. The cation is approximately symmetric, with Fe–CH separations of 2.59 and 2.72 Å, and Fe–CH_2–CH bond angles of 91° and 98°, respectively (Fig. 6). The fluxional behaviour is attributed to the restricted rotation about the CH_2–CH bonds in solution [33,35].

Several workers have studied the thermal and photochemical decomposition of the compounds $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 3$–6), both in solution and in the solid state [29,36,37 and J.R. Moss, L.G. Scott, M.E. Brown and K.E. Hindson, unpublished results, 1983]. The decomposition gives $[Cp(CO)_2Fe]_2$ with loss of the alkanediyl bridge as alkane, alk-1-ene or cis- or trans-alk-2-ene. There is a general trend of an increasing proportion of alkane produced with increasing length of the alkanediyl chain (J.R. Moss, L.G. Scott, M.E. Brown and K.E. Hindson, unpublished results). For example, thermolysis and photolysis of $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_3\}$ yields cyclopropane and propene but no propane [29,37] and $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_4\}$ evolves mainly butenes on decomposition, with a trace of butane [29,37]. However, a substantial proportion of pentane is produced on decomposition of the pentanediyl bridged compound [37]. The ratio of products is also dependent on the conditions under which the compound is decomposed, e.g. in solution or solid state.

Pettit and co-workers [29] and Knox and co-workers [37] have proposed a mechanism involving β-hydride elimination or reductive elimination from a dimetallocycle **27** to account for the decomposition products of $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 3,4$) (Scheme 4).

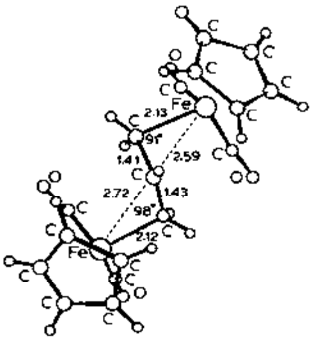
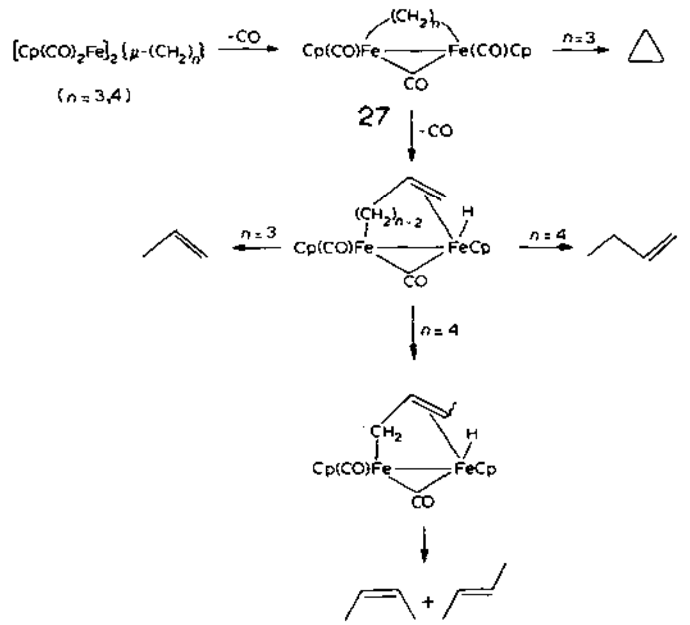


Fig. 6. Molecular structure of the cation $\{[Cp(CO)_2Fe(CH_2CHCH_2)Fe(CO)_2Cp]\}^+$.



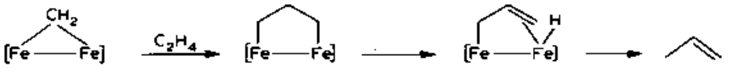
Scheme 4

In this mechanism, the alkenes are formed by β-hydride abstraction followed by hydride migration and reductive elimination from the dimetallocycloalkane. The reductive elimination of but-1-ene or cis- or trans-but-2-ene is clearly more favourable than a second β-hydride elimination step as no 1,4-butadiene is observed. With increasing length of the alkanediyl chain, decomposition via a dimetallocyclic intermediate may be expected to become less favourable, owing to the lower stability of the larger ring dimetallocyclic intermediates. This could account for the observed trend of increasing alkane to alkene ratio with increasing n in $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$. The formation of alkane from these compounds is attributed to decomposition via a radical mechanism involving Fe–C bond fission followed by hydrogen abstraction.

Knox and co-workers [37] have also studied the thermal decomposition of the analogous ruthenium compounds $[Cp(CO)_2Ru]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 3,4$) and the mixed metal compound $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$. These compounds are prepared by addition of $[CpRu(CO)_2]^-$ to $X(CH_2)_nX$ (X = I, Br) [37,38] and $[Cp(CO)_2Fe\{(CH_2)_3I\}]$, respectively. A comparison of the decompositions of the propanediyl bridged iron and ruthenium compounds reveals that the nature of the metal affects the ratio of the organic decomposition products, propene and cyclopropane. The mixed metal compound shows a product ratio intermediate between those of $[Cp(CO)_2Fe]_2\{\mu\text{-}(CH_2)_3\}$ and $[Cp(CO)_2Ru]_2\{\mu\text{-}(CH_2)_3\}$, as would be expected. Wreford and co-workers [38] have observed the production of $Cp(CO)_2RuH$ and $Cp(CO)_2Ru(\eta\text{-}C_3H_5)$ in equimolar ratio on photolysis of $[Cp(CO)_2Ru]_2\{\mu\text{-}(CH_2)_3\}$. This clearly provides evidence for the role of β-hydride elimination in the decomposition of this μ(1,3)-propanediyl species.

Wreford and co-workers [38] have also synthesised the (1,2)-ethanediyl bridged ruthenium compound from 1,2-dichloroethane and $[Cp(CO)_2Ru]^-$. Thermolysis and photolysis of $[Cp(CO)_2Ru]_2\{\mu\text{-}(CH_2)_2\}$ produces ethylene.

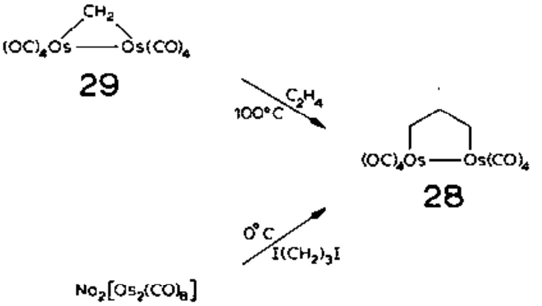
A mechanism involving β-hydride elimination from a dimetallocycle has also been postulated to account for the formation of propene in the reaction of the methylene bridged iron compounds $[(CO)_3Fe]_2(\mu\text{-}CO)_2(\mu\text{-}CH_2)$ and $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ with ethylene [39] (Scheme 5).



([Fe–Fe] = $[Cp(CO)Fe]_2(\mu\text{-}CO)$ or $[(CO)_3Fe]_2(\mu\text{-}CO)_2$)

Scheme 5

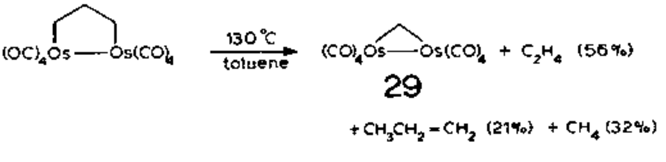
The reaction of $[Fe_2(CO)_8]^{2-}$ with 1,3-diiodopropane also produces propane, presumably via formation of a diferracyclopentane intermediate. The recent isolation [40] of the diosmacyclopentane **28** from the analogous reactions of $[(CO)_4Os]_2\{\mu\text{-}(CH_2)\}$ and $[Os_2(CO)_8]^{2-}$ provides direct evidence in support of this mechanism.



(8)

(9)

Reaction (8) is reversible; heating compound 28 in toluene solution to 130 °C produces compound **29** and a mixture of organic products



(10)

The formation of propene on decomposition of compound **28** provides

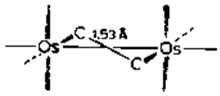
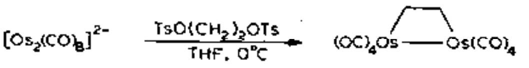


Fig. 7. Molecular structure of compound **30** showing the bent diosmacyclobutane ring.

further support for the mechanism of Pettit and Knox (see Scheme 4).

The diosmacyclobutane **30** was also prepared from the reaction of $[Os_2(CO)_8]^{2-}$ and $TsO(CH_2)_2OTs$



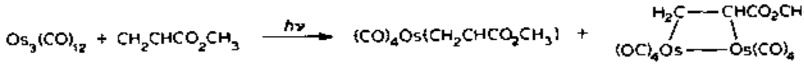
30

(11)

(OTs = p-toluenesulphonyl group)

The crystallographic study of compound **30** reveals that the cyclobutane ring is bent and the Os–C–C angles are slightly compressed (105°) so that the $Os(CO)_4$ units are twisted out of the unfavourable eclipsed arrangement (by 27°). The $-(CH_2)_2-$ bridge is σ-bonded to the Os atoms (Os–C = 2.22 Å) and the C–C bond in the bridge is the length of a normal single bond (Fig. 7).

The substituted diosmacyclobutane **31** has also been reported recently [41] as a product of the photochemical reaction of $Os_3(CO)_{12}$ with methylacrylate



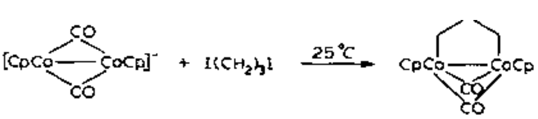
31

(12)

The structure of compound **31** closely resembles that of compound **30**. The four-membered ring is also puckered and the twist angle about the Os–Os bond is similar to that in **30** (21°).

F. COBALT GROUP

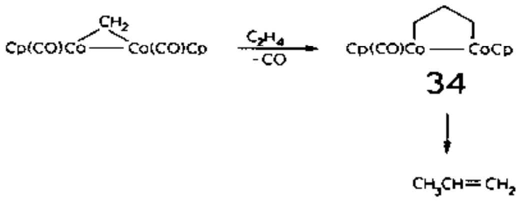
The first type-(**II**) (α,ω)-alkanediyl bridged compound (with a metal–metal bond) reported was the five-membered ring metallocycle containing two cobalt atoms, **33**, which is obtained by dialkylation of $[(CpCo)_2(\mu\text{-}CO)_2]^-$, **32**, with 1,3-diiodopropane [42]



32 **33**

(13)

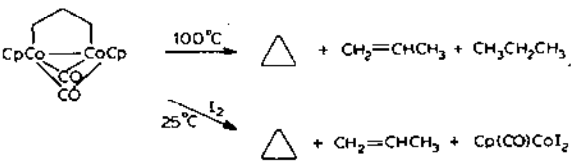
It is not possible to isolate compound **33** from the reaction of the methylene bridged dimer $[Cp(CO)Co]_2(\mu\text{-}CH_2)$ with C_2H_4 although a coordinatively unsaturated dimetallocyclopentane intermediate, **34**, has been implicated to explain the formation of propene in this reaction [43]



34

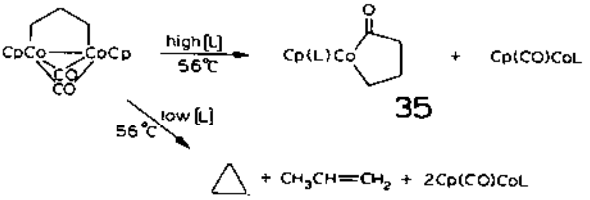
(14)

Compound **33** is considerably more stable than acyclic dialkyl cobalt species; e.g., the dimethyl compound $[CpCoMe]_2(\mu\text{-}CO)_2$ decomposes in solution at room temperature, whereas compound **33** only undergoes slow thermolysis in benzene at 100 °C. Such resistance to decomposition by β-elimination has also been observed for mononuclear five-membered metallocycles [44]. The decomposition of compound **33** in solution produces propene (73%), cyclopropane (18%) and propane (1%) with $CpCO(CO)_2$ and $Cp_4Co_4(CO)_2$ as the main organometallic products [43]. Labelling experiments indicate that the decomposition process is predominantly intramolecular. In the presence of I_2, reductive elimination of cyclopropane is favoured and decomposition produces mainly cyclopropane (71%) propene (9%) and the diiodide $[Cp(CO)CoI_2]$ [42] (Scheme 6)



Scheme 6

Theopold and Bergman [45] have investigated the reaction of the metallocycle **33** with CO and phosphines. At high concentrations of ligand, the reaction occurs rapidly at 56 °C, producing the mononuclear metallocycle **35** and Cp(CO)CoL. Lowering the ligand concentration causes a decrease in the reaction rate and increasing amounts of cyclopropane and propane are produced (Scheme 7)

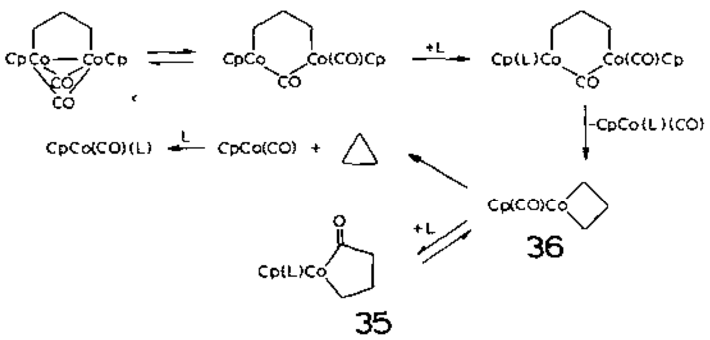


35

$L = CO, PPh_3, PMe_3$

Scheme 7

To explain these observations, a mechanism was postulated [45] in which a ligand-independent route to cyclopropane competes with ligand attack on a metallocyclobutane intermediate **36** to form cobalt cyclopentanone, **35** (Scheme 8)



Parallel reactions involving the migration of an alkyl group from one metal to the other are known for dialkyl dicobalt systems, e.g. the generation of acetone from $[(CpCoMe)_2\{\mu\text{-}(CO)_2\}]$ via a mononuclear dimethyl cobalt intermediate [46]. Reactions of both systems lead to the formation of new carbon–carbon bonds. The structure of compound **33** has been reported recently (Fig. 8) [45]. The two Co–C bond lengths and Co–Co–C bond angles for the propanediyl bridge are the same (Co–C = 2.04 Å, Co–Co–C = 94.5°). However, the bridge is not symmetrical; the C_1–C_2 bond is longer than the C_2–C_3 bond and the Co–C_1–C_2 angle greater than the Co–C_3–C_2 angle. The dihedral angle for the five-membered ring Co–C_1–C_2–C_3 is 32.9°. The CO ligands are bent slightly towards the propanediyl bridge.

Theopold and Bergman also report [45] the synthesis of the six-membered metallocycle **37** by reaction of $I(CH_2)_4I$ with $[(CpCo)_2(\mu\text{-}CO)_2]^-$. This compound is considerably less stable than **33**, decomposing rapidly at room temperature in solution. In the solid state compound **37** decomposes above 100 °C whereas compound **33** is stable up to 170 °C. Treatment of $[(CpCo)_2(\mu\text{-}CO)_2]^-$ with 1,2-diiodoethane does not yield the four-membered

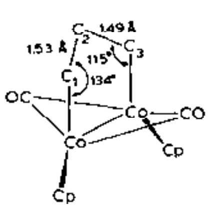
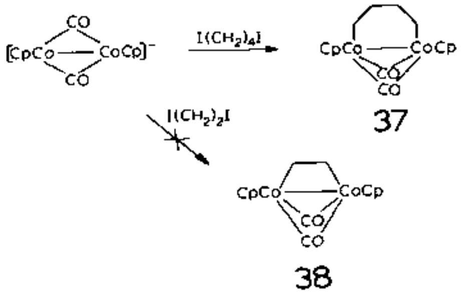


Fig. 8. Molecular structure of compound **33**.

metallocycle **38**



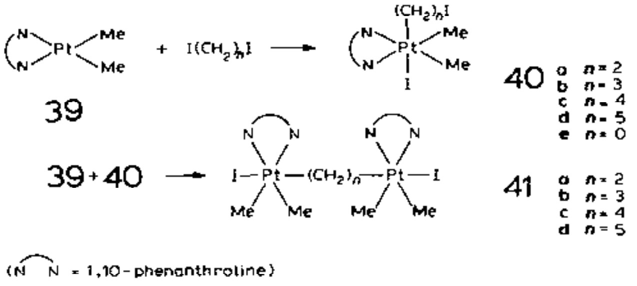
(15)

The only type (I) (α,ω)-alkanediyl bridged cobalt compounds known are the perfluoroalkyl derivatives $[(CO)_4Co(CF_2)_nCo(CO)_4]$ ($n = 2,3$) [46,48] and $K_6[(NC)_5Co(CF_2)_2Co(CN)_5]$ [49]. $[(CO)_4Co(CF_2)_2Co(CO)_4]$ [47] and $[(NC)_5Co(CF_2)_2Co(CN)_5]^{6-}$ [49] are produced by reaction of C_2F_4 with $Co_2(CO)_8$ and $[(CN)_5Co]^{3-}$, respectively. $[(CO)_4Co]_2\{\mu\text{-}(CF_2)_4\}$ is formed by addition of $[(CO)_4Co]^-$ to $ClCO(CF_2)_4COCl$ [48].

No alkanediyl bridged rhodium or iridium compounds are known.

G. NICKEL GROUP

Monaghan and Puddephatt have recently reported the synthesis of the alkanediyl bridged platinum complexes **41a–d** by oxidative addition of $I(CH_2)_nI$ ($n = 2$–5) to dimethyl(1,10-phenanthroline)platinum(II), **39** [50].



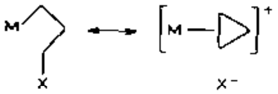
(16)

(17)

Scheme 9

The reactions of compound **39** with $I(CH_2)_nI$ ($n = 3$–5) produce mixtures of compounds **40** and **41**, but with a large excess of $I(CH_2)_nI$ compound **40** is the only product (reaction (16)) and this can be isolated and reacted with compound **39** to give the bridged compound **41** in high yield (reaction (17)). The reaction with $I(CH_2)_2I$ produces a mixture of **41a**, ethylene, and **40e** (rather than **40a**). The ^1H-NMR and $^{13}C\{^1H\}$NMR spectra of **41d** show three resonances, two with ^{195}Pt coupling for the hydrogen and carbon nuclei in the $-(CH_2)_5-$ chain, respectively, as expected for a (1,5)-pentanediyl bridge between two Pt atoms. The low solubility of the compounds with $n = 2$–4 prevents NMR study.

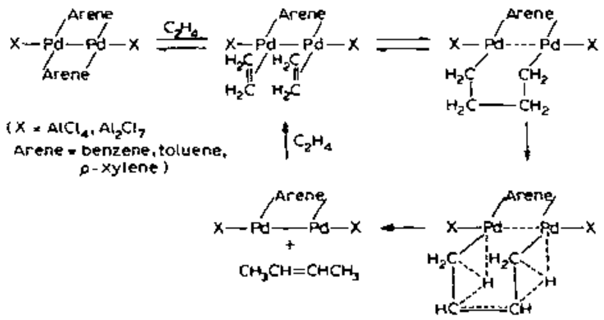
Investigation of the kinetics of reactions (16) and (17) reveals that the rates of these reactions follow the order $n = 2 \gg 3 > 4 \simeq 5$. A small neighbouring atom effect by the metal atom on the C–X bond in $M(CH_2)_nX$ is observed for $n = 3$–5; the C–X bond is activated to further oxidative addition. For example, the second-order rate constant for reaction of compound **39** with compound **40c** is three times greater than that for the reaction of compound **39** with $I(CH_2)_3I$. This may be attributed to a lowering of the energy of the transition state of the reaction, by combinations of the resonance terms



(18)

which would facilitate halide displacement.

Palladium (α,ω)-alkanediyl bridged species have been implicated as intermediates in the catalytic dimerization of ethylene by bis(η-arene)dipalladium, **42**, but have not been isolated [51] (Scheme 9)



These Pd(II) complexes also catalyse the dimerization of propene.

REFERENCES

1 W.A. Herrman, Pure Appl. Chem., 54 (1982) 65; Angew. Chem. Int. Ed. Engl., 21 (1982) 117.

2 (a) C. Masters, Adv. Organomet. Chem., 17 (1979) 61.
(b) R.C. Brady and R. Pettit, J. Am. Chem. Soc., 102 (1980) 6181.

3 H. Sinn and W. Kaminsky, Adv. Organomet. Chem., 18 (1980) 99.

4 G.A. Samorjai and S.M. Davis, Platinum Met. Rev., 27 (1983) 54.

5 F. Garnier, P. Krausz and J.-E. Dubois, J. Organomet. Chem., 170 (1979) 195.
6 P. Pertici and G. Vitulli, Tetrahedron Lett., 21 (1979) 1897.
7 W. Kaminsky and H. Sinn, Justus Liebigs Ann. Chem., (1975) 424.
8 H. Sinn and E. Kolk, J. Organomet. Chem., 6 (1966) 373.
9 W. Kaminsky, J. Kopf, H. Sinn and H.-J. Vollmer, Angew. Chem. Int. Ed. Engl., 15 (1976) 629.
10 J.E. Ellis, J. Organomet. Chem., 86 (1975) 1.
11 H. Sinn and G. Oppermann, Angew. Chem. Int. Ed. Engl., 5 (1966) 962.
12 J.L. Atwood, G.K. Barker, J. Holton, W.E. Hunter, M.F. Lappert and R. Pearce, J. Am. Chem. Soc., 99 (1977) 6645.
13 W. Beck and B. Olgemöller, J. Organomet. Chem., 127 (1977) C45.
14 W. Beck and B. Olgemöller, Chem. Ber., 114 (1981) 867.
15 F.A. Adedeji, J.A. Connor, H.A. Skinner, L. Galyer and G. Wilkinson, J. Chem. Soc. Chem. Commun., (1976) 159.
16 H.C. Lewis, Jr. and B.N. Storhoff, J. Organomet. Chem., 43 (1972) 1.
17 (a) J.W. Faller and A.S. Anderson, J. Am. Chem. Soc., 91 (1969) 1550.
(b) A.R. Manning, J. Chem. Soc. A, (1967) 1984.
18 N.A. Bailey, P.L. Chell, A. Mukhopadhyay, H.E. Tabbron and M.J. Winter, J. Chem. Soc. Chem. Commun., (1982) 215.
19 R.B. King and M.B. Bisnette, J. Organomet. Chem., 7 (1967) 311.
20 R.B. King and M.B. Bisnette, J. Organomet. Chem., 2 (1964) 15.
21 W. Herrmann and G. Kriechbaum, unpublished results, quoted in W.A. Herrmann, Adv. Organomet. Chem., 20 (1982) 159.
22 J.R. Moss, J. Organomet. Chem., 231 (1982) 229.
23 R.E. Dessy, R.L. Pohl and R.B. King, J. Am. Chem. Soc., 88 (1966) 5121.
24 W. Geibel, G. Wilke, R. Goddard, C. Krüger and R. Mynott, J. Organomet. Chem., 160 (1978) 139.
25 R.B. King, Inorg. Chem., 85 (1963) 1922.
26 C.P. Casey, J. Chem. Soc. Chem. Commun., (1970) 1220.
27 K. Raab, B. Olgemöller, K. Schloler and W. Beck, J. Organomet. Chem., 214 (1981) 81.
28 R.B. King, Inorg. Chem., 85 (1963) 531.
29 S.C. Kao, C.H. Thiel and R. Pettit, Organometallics, 2 (1983) 914.
30 L. Pope, P. Sommerville, M. Laing, K.J. Hindson and J.R. Moss, J. Organomet. Chem., 112 (1976) 309.
31 J.J. Bennet, R. Mathieu, R. Poilblanc and J.A. Ibers, J. Am. Chem. Soc., 101 (1979) 7487.
32 M.L.H. Green and P.L.I. Nagy, J. Organomet. Chem., 1 (1963) 58.
33 M. Laing, J.R. Moss and J.W. Johnson, J. Chem. Soc. Chem. Commun., (1977) 656.
34 R.C. Kerber, W.P. Giering, J. Bauch, P. Waterman and E.-Hua Chou, J. Organomet. Chem., 120 (1976) C31.
35 G.E. Jackson, J.R. Moss and L.G. Scott, S. Afr. J. Chem., 36 (1982) 69.
36 P.A. Wegner and G.P. Sterling, J. Organomet. Chem., 167 (1978) C31.
37 M. Cooke, N.J. Forrow and S.A.R. Knox, J. Organomet. Chem., 222 (1981) C21 and J. Chem. Soc. Dalton Trans., (1983) 2435.
38 Y.C. Lin, J.C. Calabrese and S.S. Wreford, J. Am. Chem. Soc., 105 (1983) 1679.
39 C.E. Sumner, Jr., P.E. Riley, R.E. Davis and R. Pettit, J. Am. Chem. Soc., 102 (1980) 1752.
40 K.M. Motyl, J.R. Norton, C.K. Schauer and O.P. Anderson, J. Am. Chem. Soc., 104 (1982) 7325.
41 M.R. Burke, J. Takats, F.W. Grevels and J.G.A. Reuvers, J. Am. Chem. Soc., 105 (1983) 4092.

42 K.H. Theopold and R.G. Bergman, J. Am. Chem. Soc., 102 (1980) 5694.
43 K.H. Theopold and R.G. Bergman, J. Am. Chem. Soc., 103 (1981) 2489.
44 J.X. McDermott, J.F. White and G.M. Whitesides, J. Am. Chem. Soc., 95 (1973) 4451.
45 K.H. Theopold and R.G. Bergman, Organometallics, 1 (1982) 1571.
46 N.E. Shore, C. Ilenda and R.G. Bergman, J. Am. Chem. Soc., 98 (1976) 7436.
47 (a) H.H. Hoehn, L. Prall, K.F. Watterson and G. Wilkinson, J. Chem. Soc., (1961) 2738.
(b) B.L. Booth, R.N. Haszeldine and P.R. Mitchell, J. Chem. Soc. A, (1969) 691.
48 B.L. Booth, R.N. Haszeldine and T. Inglis, J. Chem. Soc. Dalton Trans., (1975) 1449.
49 M.J. Mays and G. Wilkinson, Nature, 203 (1964) 1167.
50 P.K. Monaghan and R.J. Puddephatt, Inorg. Chim. Acta, 76 (1983) L237.
51 P. Pertici and G. Vitulli, Tetrahedron Lett., 21 (1979) 1897.