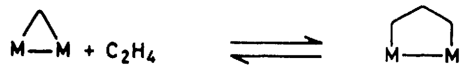
Organic Chemistry of Dinuclear Metal Centres. Part 5.[1] Generation of Hydrocarbons from Methylene Chains linking Two Metal Centres. Evidence for a Dimetallacycle Intermediate

Michael Cooke, Nigel J. Forrow, and Selby A. R. Knox *
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The hydrocarbon products of the thermal and photochemical decompositions of the complexes $[(\eta\text{-}C_5H_5)(CO)_2M^1\{\mu\text{-}(CH_2)_n\}M^2(CO)_2(\eta\text{-}C_5H_5)]$ ($M^1 = M^2 = Fe$, n = 3—5; $M^1 = M^2 = Ru$, n = 3 or 4; $M^1 = Fe$, $M^2 = Ru$, n = 3) have been determined and the results interpreted in terms of a transient dimetallacycle which undergoes decomposition *via* β-elimination and reductive elimination processes. Decomposition of the compounds containing three-carbon bridges yields cyclopropane and propene in a ratio strongly dependent upon the identity of the metal atoms and the conditions, factors which are rationalised by the proposed mechanism. But-1-ene, and *cis*- and *trans*-but-2-ene are obtained from the decomposition of complexes containing four-carbon chains, but only but-1-ene and *trans*-but-2-ene are produced from the thermolysis of $[(\eta\text{-}C_5H_5)(CO)_2Fe\{\mu\text{-}CH(Me)CH_2CH_2\}Fe(CO)_2(\eta\text{-}C_5H_5)]$. This is attributed to a methyl-substituted dimetallacyclopentane intermediate adopting for steric reasons a conformation which does not allow the formation of *cis*-but-2-ene. The low proportion of but-1-ene can also be traced to crowding in the dimetallacyle. Pentane is preferentially evolved from $[(\eta\text{-}C_5H_5)(CO)_2Fe\{\mu\text{-}(CH_2)_5\}Fe(CO)_2(\eta\text{-}C_5H_5)]$, with smaller amounts of pent-1-ene, and *cis*- and *trans*-pent-2-ene, interpreted as due to a predominantly radical mechanism for the decomposition of this compound. The organometallic products of the decompositions are the dimers $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Fe or Ru) and, where appropriate, those of the subsequent photolysis of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$. Carbon–carbon bond fission occurs on heating $[(\eta\text{-}C_5H_5)(CO)_2Ru\{\mu\text{-}(CH_2)_3\}Ru(CO)_2(\eta\text{-}C_5H_5)]$ with Me_3NO in tetrahydrofuran, giving a low yield of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$.

Metallacyclobutane rings (1) are now fairly common in organometallic complexes and are accepted as intermediates in the transition-metal catalysed metathesis of olefins; it has been suggested [2,3] that they are involved in the carbon chain growth of the Fischer–Tropsch synthesis. The possibility that a dimetallacyclopentane (2) takes part in these important processes has also been considered.[3-5] Such a unit was invoked to explain the formation of propene when the μ-CH_2 complexes (3a) [6] and (3b) [7] are treated with ethylene, and (2b) obtained independently as a stable complex does evolve propene on heating.[8] The confirmation of this (3) ⟶ (2) ring expansion reaction was very recently obtained, when ethylene was observed to interact with (3c) to give the diosmacyclopentane (2c).[9] Although (2c) decomposed to give propene, as required in a model for Fischer–Tropsch carbon chain growth, ethylene was also liberated and (3c) regenerated, modelling an olefin metathesis step at a dinuclear metal centre.

(1)



(3a) M = $Fe(CO)_4$ (2a)
(3b) M = $Co(CO)(\eta\text{-}C_5H_5)$ (2b)
(3c) M = $Os(CO)_4$ (2c)

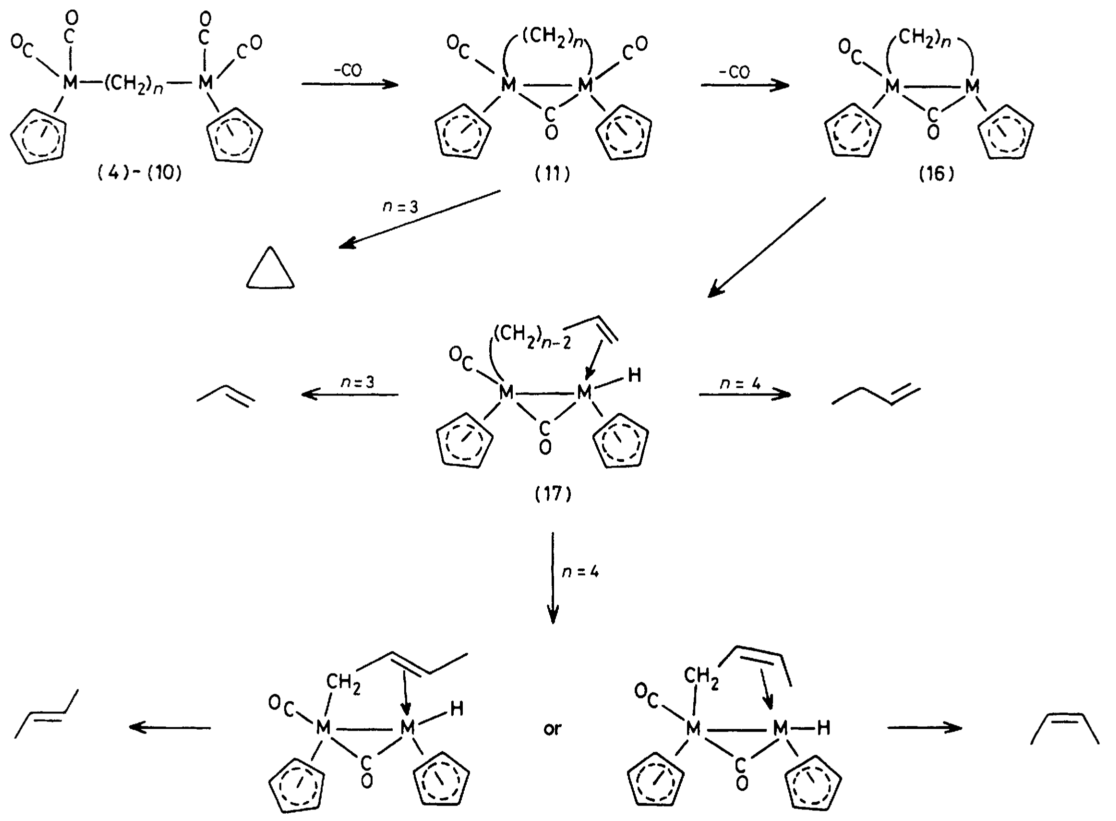
We have also explored this system, with results described herein. Some known and new compounds (4)—(10), which comprise C_3—C_5 hydrocarbons disubstituted by $M(CO)_2(\eta\text{-}C_5H_5)$ (M = Fe or Ru) groups, have been subjected to thermolysis and photolysis in an attempt to effect cyclisation to a complex of form (11) through CO loss and metal–metal bond formation (Scheme). When n = 1, (11) exists for both iron and ruthenium, *i.e.* complexes (12) [10] and (13).[11] However, decomposition of (4)—(10) resulted in the elimination of the hydrocarbon chain, but as hydrocarbons which are consistent with the intermediacy of the desired, but unstable, dimetallacycles. The interconvertibility of (2) and (3) for ruthenium is also indicated. A preliminary account of this work has appeared.[12]

Results and Discussion

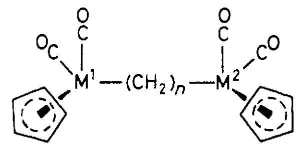
Synthesis of Metal Complexes.—The complexes $[(\eta\text{-}C_5H_5)(CO)_2Fe\{\mu\text{-}(CH_2)_n\}Fe(CO)_2(\eta\text{-}C_5H_5)]$ (4)—(6) were readily prepared in 35—45% yield, by an adaptation of the literature method,[13] from $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ and the appropriate α,ω-dibromoalkane. Reaction times were normally 45 min at room temperature, whereas the preparation of the new complex $[(\eta\text{-}C_5H_5)(CO)_2Fe\{\mu\text{-}CH(Me)CH_2CH_2\}Fe(CO)_2(\eta\text{-}C_5H_5)]$ (7) required stirring the anion with 1,3-dibromobutane for 2 h. A lower yield (22%) of (7) was obtained as substitution of bromine at a secondary carbon atom was required. In fact, attempts using less nucleophilic $[Ru(CO)_2(\eta\text{-}C_5H_5)]^-$ to prepare the analogous diruthenium complex $[(\eta\text{-}C_5H_5)(CO)_2Ru\{\mu\text{-}CH(Me)CH_2CH_2\}Ru(CO)_2(\eta\text{-}C_5H_5)]$ were unsuccessful and resulted only in the isolation of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, $[Hg\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$,[14] and a yellow oil believed to be $[Ru\{CH_2CH_2CH(Me)I\}(CO)_2(\eta\text{-}C_5H_5)]$.

The synthesis of the new complexes $[(\eta\text{-}C_5H_5)(CO)_2Ru\{\mu\text{-}(CH_2)_n\}Ru(CO)_2(\eta\text{-}C_5H_5)]$ (8), (9) was accomplished in good yield by the same method used for the compounds (4)—(7), except that an α,ω-di-iodoalkane was required. Stirring $Na[Ru(CO)_2(\eta\text{-}C_5H_5)]$ with an α,ω-dibromoalkane gave the desired product in only *ca.* 10% yield as an inseparable mixture with the mercury compound $[Hg\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$.

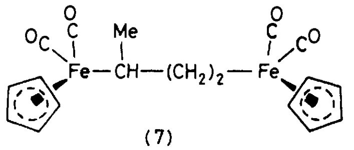
Reaction of the anion $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ with 1,3-di-



Scheme.



(4) $M^1 = M^2 = Fe$, $n = 3$
(5) $M^1 = M^2 = Fe$, $n = 4$
(6) $M^1 = M^2 = Fe$, $n = 5$
(8) $M^1 = M^2 = Ru$, $n = 3$
(9) $M^1 = M^2 = Ru$, $n = 4$
(10) $M^1 = Fe$, $M^2 = Ru$, $n = 3$



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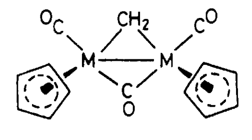


(12) M = Fe
(13) M = Ru

iodopropane in 1 : 1.5 molar ratio resulted in the isolation of $[Fe\{(CH_2)_3I\}(CO)_2(\eta\text{-}C_5H_5)]$ as a yellow oil in low yield. Moss[15] has recently prepared the chloro- and bromo-analogues in high yields by performing the reaction between the iron anion and the appropriate 1,3-dihalogenopropane at −20 °C. Reaction of the bromo-compound with $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ gave $[(\eta\text{-}C_5H_5)(CO)_2Fe\{\mu\text{-}(CH_2)_3\}Mo(CO)_3(\eta\text{-}C_5H_5)]$ in 18% yield. Similarly, we have found that stirring the iodo-complex with the anion $[Ru(CO)_2(\eta\text{-}C_5H_5)]^-$ gives an 87% yield of $[(\eta\text{-}C_5H_5)(CO)_2Fe\{\mu\text{-}(CH_2)_3\}Ru(CO)_2(\eta\text{-}C_5H_5)]$ (10).

Characterisation of the new compounds was by analysis, i.r., ^1H and ^{13}C n.m.r., and mass spectra (see Experimental section) and revealed no remarkable features.

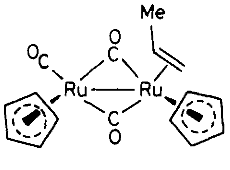
Decomposition of Metal Complexes.—All attempts at obtaining a stable dimetallacycle of the form (11) through thermolysis or photolysis of the complexes (4)—(10) were unsuccessful. Di-iron complexes (4)—(7) gave $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in high yield, heating the iron–ruthenium complex (10) likewise gave a mixture of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, while the diruthenium complexes (8) and (9) produced $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$. Photolysis of (8), however, yielded a mixture of ruthenium compounds: $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (27%), $[Ru_4(CO)_4(\eta\text{-}C_5H_5)_4]$ (25%),[16] $[Ru_4(CO)_6(\mu\text{-}\sigma{:}\eta^5\text{-}C_5H_4)_2(\eta\text{-}C_5H_5)_2]$ (20%), $[Ru_2(CO)_4(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)\}]$ (4%),[17] the propene complex $[Ru_2(CO)_3(C_2H_3Me)(\eta\text{-}C_5H_5)_2]$ (14) (2%),[18] and a trace of the μ-alkylidyne complex $[Ru_3(CO)_3(\mu_3\text{-}CEt)(\eta\text{-}C_5H_5)_3]$ (15). Although it appears that the decomposition of (8) is more complicated than that of the iron analogue (4), in fact the second, third, and fourth compounds listed are known products of the photolysis of the first.[19] We therefore conclude that $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ is the initial product of photolysing (8), and that this reacts further to give these species. Both (14) and (15), containing a C_3 ligand, clearly derive directly from the trimethylene complex (8) and their formation will be discussed later in conjunction with the proposed mechanism of decomposition. High-yield routes to both (14)[19] and (15)[20] are known.

The fate of the methylene chains was investigated in order

Table 1. Decompositions of trimethylene compounds [a]

Compound	T/°C or u.v.	Ratio propene : cyclopropane
(4) [b]	u.v.	$(51 \pm 9) : 1$ [c]
(4)	125—193	$1 : (2.3 \pm 0.3)$ [d]
(4) [b]	125—196	1 : 10.6—5.3
(8) [b]	u.v.	100% propene
(8)	158	84 : 1
(8) [b]	174	30 : 1
(10)	190	1 : 1.3

[a] In the solid state for 2 h unless otherwise stated. [b] In toluene. [c] Independent of reaction time (0.5—12 h) or concentration (0.0003—0.016 mol dm^{-3}). [d] Independent of reaction time (75 min—5 h) or quantity (50—250 mg).



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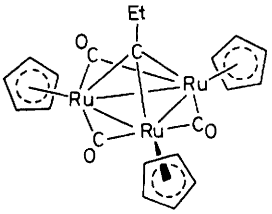


(15)

to shed light on the decomposition pathway. Compounds were heated both in the solid state and in toluene solution, and subjected to u.v. irradiation in toluene, the evolved hydrocarbons being analysed by gas–liquid chromatography.

Trimethylene Complexes.—The results of the decomposition experiments are summarised in Table 1. The C_3 chains are evolved overwhelmingly as propene and cyclopropane, with traces of methane, ethylene, and ethane (<1% combined). Control experiments on the thermal decomposition of $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ both in the solid state and in toluene yielded no C_1—C_3 hydrocarbons, but photolysis of $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in toluene did give the C_1 and C_2 gases, revealing that it is not possible to conclude that they derive from rupture of the trimethylene unit when (4), (8), and (10) are photolysed. The propene : cyclopropane ratio varies considerably, and three major influences may be identified.

(*a*) *The nature of the metal.* Iron favours cyclopropane formation more strongly than ruthenium. This is seen in the photolyses of (4) and (8), which give a propene : cyclopropane ratio of *ca.* 50 : 1 and 100% propene, respectively, but better in the solid state thermolyses of (4), (8), and (10). Heating (4) to decomposition releases, contrary to photolysis, a preponderance of cyclopropane over propene of 2.4 : 1. The diruthenium complex (8), on the other hand, ejects mainly propene, in 84 : 1 ratio with cyclopropane. The perhaps naive expectation that the iron–ruthenium complex (10) would fall between favouring cyclopropane, as with (4), or propene, as with (8), was actually observed; the propene : cyclopropane ratio was 1 : 1.3.

(*b*) *Photolysis or thermolysis.* Propene formation is favoured by photolysis rather than thermolysis, seen when toluene solutions of (4) and (8) are either irradiated or heated. For (4), a propene : cyclopropane ratio of 50 : 1 on photolysis turns around to a ratio of *ca.* 1 : 11 on heating at 125 °C. This ratio fell gradually to *ca.* 1 : 5 on raising the thermolysis temperature to 196 °C, a trend for which we have been unable to provide a satisfactory explanation. The transformation is less dramatic for (8); only propene is formed on photolysis but heating at 174 °C yields about 3% of cyclopropane.

Table 2. Decompositions of tetramethylene compounds *

Compd.	T/°C	Ratio but-2-ene : but-1-ene	Ratio *cis* : *trans* but-2-ene
(5)	118—196	$(1.5 \pm 0.4) : 1$	$(4.3 \pm 1.0) : 1$
(9)	205	1.5 : 1	4.4 : 1
(7)	125—145	$(31.4 \pm 0.1) : 1$	100% *trans*

* In the solid state for 2.5 h.

(*c*) *The presence or absence of solvent.* When heated in solution in toluene both (4) and (8) provide a larger proportion of cyclopropane than when heated in the solid state. This is the least significant factor of the three.

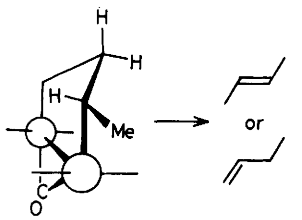
Tetramethylene Complexes.—The thermolyses of the solid tetramethylene complexes (5) and (9) gave but-1-ene, and *cis*- and *trans*-but-2-ene almost exclusively (Table 2), with traces of methane, ethylene, ethane, propene, and cyclopropane. Moreover, the ratios but-1-ene : but-2-ene and *cis* : *trans* but-2-ene are essentially independent of the nature of the metal.

Compound (7), a methyl-substituted trimethylene species, also yields only butenes on thermolysis, but now but-2-ene is very strongly favoured. Even more striking is that only *trans*-but-2-ene is produced, a result with important mechanistic implications, discussed below.

Pentamethylene Complexes.—Thermolysis of (6) in the solid state for 2 h gave only the C_5 hydrocarbons pentane, pent-1-ene, *cis*-pent-2-ene, and *trans*-pent-2-ene in 70 : 30 : 1 : 3 ratio.

Mechanism of Decomposition.—The preferential formation of pentane from (6) is evidence of a radical mechanism for the decomposition of this compound. Iron–carbon bond fission followed by hydrogen abstraction or hydrogen loss accounts for the observed products. No propane or butane was evolved from the C_3- and C_4-bridged complexes, however, and this leads us to a non-radical mechanism for the decomposition of these. In addition, the generation of cyclopropane from the trimethylene complexes strongly suggests that they decompose *via* an unstable dimetallacyclopentane in view of the fact that the dicobaltacyclopentane complex $[(\eta\text{-}C_5H_5)(CO)\overline{Co\{\mu\text{-}(CH_2)_3\}Co}(CO)(\eta\text{-}C_5H_5)]$ evolves cyclopropane (in 1 : 4 ratio with propene) on heating.[8] A pathway for cyclopropane and propene production from this dicobalt complex has been indicated [7] and is extended in the Scheme to complexes (4)—(10). It envisages the initial formation of a dimetallacycle (11), which for $n = 3$ undergoes reductive elimination to produce cyclopropane. Reductive elimination from a dinuclear metal centre is known (see, for example, refs. 21 and 22), but not when the coupling is of two alkyl groups. However, there is precedent for the creation of cyclic hydrocarbons through carbon–carbon bond formation at a dinuclear metal centre; treatment of $[(\eta\text{-}C_5H_5)\overline{Cr\{\mu\text{-}(CH)_8\}Cr}(\eta\text{-}C_5H_5)]$ with CO releases cyclo-octatetraene,[23] while heating or bromination of $[(CO)_2\overline{Co\{\mu\text{-}(CH)_{6-n}(CBu^t)_n\}Co}(CO)_2]$ ($n = 2$ or 3)[24] yields arenes.[25] The ease with which carbon–carbon bond formation processes can occur at a dinuclear metal centre is becoming increasingly apparent.[18,26]

Loss of CO from (11) is proposed, resulting in the formation of co-ordinatively unsaturated (16), whose vacant site allows β-elimination to proceed to give (17). Propene or but-1-ene may be generated from (17) by conventional mononuclear



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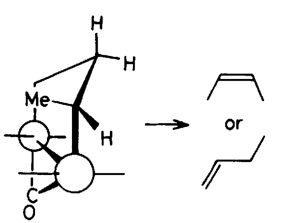

(19)

reductive elimination, after hydride migration from one metal centre to the other, but the formation of but-2-enes requires an isomerisation of the hydrocarbon chain of (17; $n = 4$) for which there is ample precedent in organometallic chemistry.

The strong tendencies towards propene formation when trimethylene complexes are photolysed, and towards cyclopropane when the metal is iron rather than ruthenium, are readily rationalised in terms of the Scheme. Photolysis will favour the dissociation of CO and creation of the vacant site in (16) required for the β-elimination which precedes propene formation. The stronger metal–carbon bonds of a second-row transition element would also restrict the reductive elimination of cyclopropane from the diruthenium centre compared with the iron–ruthenium and di-iron centres derived from (10) and (4) respectively. The metal–metal distance in (11) would also be a factor in controlling dinuclear reductive elimination, with carbon–carbon bond formation expected to be favoured at the dimetal centre in the order di-iron > iron–ruthenium > diruthenium, as observed.

The tendency towards cyclopropane formation when (4) and (8) are heated in toluene solution, as opposed to in the solid state, must be rationalised in terms of the Scheme as due to a repression of β-elimination. This could be a consequence of toluene blocking the vacant site.

Very strong evidence in support of the intermediacy of a dimetallacycle is found in the high but-2-ene : but-1-ene ratio and selective formation of *trans*-but-2-ene when the μ-$CH(Me)CH_2CH_2$ complex (7) is thermolysed. If a molecular model of (11; $n = 3$) is constructed it is apparent that the conformation of the dimetallacyclopentane ring allows two orientations for an α-methyl substituent. These are depicted as (18) and (19). In (18) the methyl group lies nearly parallel to the metal–metal axis, between the terminal η-C_5H_5 and CO, whereas in (19) it is nearly perpendicular to it and interacts sterically to a much greater extent with these ligands. We have reported in an earlier part [27] of this series that in μ-CHMe complexes of types (12) and (13) the methyl exclusively adopts an *anti* configuration with respect to a pair of *cis* cyclopentadienyls, emphasising the importance of steric factors. The arrangement (18) is therefore expected to be strongly favoured. β-Elimination must be preceded by the dissociation of CO to produce a vacant site, and when this occurs for (18) at the metal adjacent to the methyl group the transfer of the central *endo*-hydrogen of the ring to the metal centre will create a *trans* carbon skeleton, leading to *trans*-but-2-ene. A similar sequence for (19) would generate *cis*-but-2-ene. The 100% selectivity for *trans*-but-2-ene consequently indicates that form (18) is actually adopted to the exclusion of (19). The loss of CO from the other metal atom will induce β-elimination at that site and for (18) [and (19)] lead to the evolution of but-1-ene. This is not a favoured product (but-2-ene : but-1-ene *ca.* 30 : 1) and again we find an explanation in the steric pressures within (18); CO is expected to be lost more readily from the metal atom adjacent to the sterically demanding methyl substituent.

The formation of the propene complex (14), and the product of its decomposition (15),[19] in the photolysis of (8) can be traced to the intermediate (17). Migration of hydride from one metal centre of (17) to the other, followed by reductive elimination and retention of olefin co-ordination, then CO uptake, would provide (14).

The evolution of small amounts of ethylene on heating (8) is consistent with the formation of (13), more so since thermolysis of (13) is known [20] to afford methane, another low-yield product. Moreover, when the trimethylene (8) is heated in tetrahydrofuran (thf) at reflux in the presence of Me_3NO, a reagent often used smoothly to remove metal-bound CO (as CO_2), a 0.4% yield of complex (13) was actually isolated. This suggests that the (2) ⟶ (3) transformation can occur for ruthenium, but is an unfavourable process. The reverse, a (3) ⟶ (2) ring expansion, appears more easy; it is implicated in the production of propene when (13) is treated with ethylene.[20]

Conclusions

Investigation of the decomposition of three- and four-carbon chain systems linking two metal centres has provided strong evidence for the intermediacy of a dimetallacycle in the production of hydrocarbons. With five-carbon chains this process appears to be less significant, a radical mechanism being the dominant process. The identity of the hydrocarbons evolved has indicated that carbon–carbon bond fission plays only a trivial role in the decomposition of the dimetallacycle. This lends support to the suggestions of the involvement [3] of a dimetallacyclopentane in the carbon chain growth of the Fischer–Tropsch synthesis, but not to its involvement [4,5] in olefin metathesis.

Experimental

The majority of techniques and instrumentation were as described in Part 1 [17] of this series. Photolyses were performed on toluene solutions of complexes, in silica flasks, using a 250-W mercury lamp. Thermolyses were performed in sealed, evacuated glass tubes of *ca.* 5 cm³ volume. G.l.c. analysis of hydrocarbon products was carried out on a Pye Series 104 instrument, employing a 2-m 80—100 mesh Chromosorb 102 column, operating at 130—190 °C.

Preparations.—[(η-C_5H_5)$(CO)_2$Fe{μ-$(CH_2)_n$}Fe$(CO)_2$(η-C_5H_5)] (4)—(6). These known compounds were prepared by an adaptation of the literature method.[13] The sodium salt of the anion [Fe$(CO)_2$(η-C_5H_5)]$^-$ was stirred with the appropriate α,ω-dibromoalkane for 45 min at room temperature. Purification was by chromatography on alumina columns. Elution with hexane gave yellow bands which afforded orange crystals of (4)—(6) in 35—45% yields.

[(η-C_5H_5)$(CO)_2$Fe{μ-$CH(Me)CH_2CH_2$}Fe$(CO)_2$(η-C_5H_5)] (7). A thf (100 cm³) solution of [$Fe_2(CO)_4$(η-C_5H_5)$_2$] (3.0 g, 8.47 mmol) was reduced to Na[Fe$(CO)_2$(η-C_5H_5)] by stirring over a 1% sodium amalgam for 1 h. Treatment of the anion with 1,3-dibromobutane (1.83 g, 8.47 mmol) and stirring for 2 h gave a yellow-brown solution. The reaction mixture was evaporated to dryness and a filtered diethyl ether solution of the brown residue was chromatographed on alumina. Elution with hexane–diethyl ether (9 : 1) gave a yellow band from which was obtained 0.69 g (22%) of orange crystalline complex (7), m.p. 84—87 °C {Found: C, 52.4; H, 4.7%; *M*, 186 [Fe$(C_5H_5)_2^+$]. $C_{18}H_{18}Fe_2O_4$ requires C, 52.7; H, 4.4%; *M*, 410}; ν(CO) (in hexane) 2 009vs, 2 003vs, and 1 955vs cm^{-1}; ^{1}H n.m.r. (in $CDCl_3$), δ 4.70 (s, 10 H, 2 C_5H_5), 2.48 (br, 1 H, CH), 1.63 (m, 4 H, CH_2CH_2), and 1.36 (d, $J = 6$ Hz, 3 H, Me).

[(η-C_5H_5)$(CO)_2$Ru{μ-$(CH_2)_3$}Ru$(CO)_2$(η-C_5H_5)] (8). A yellow solution of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.8 g, 1.80 mmol) in thf (60 cm^3) was reduced to $Na[Ru(CO)_2(\eta\text{-}C_5H_5)]$ by stirring for 1 h over a 1% sodium amalgam. Addition of 1,3-di-iodopropane (0.53 g, 1.80 mmol) resulted in an immediate colour change from dark grey to yellow-brown. After stirring for 45 min, evaporation of the solvent and chromatography on Florisil, eluting with hexane–diethyl ether (19 : 1), gave a yellow band from which was obtained 0.663 g (76%) of pale yellow crystalline complex (8), m.p. 84—87 °C {Found: C, 42.1; H, 3.5%; *M*, 445 $[Ru_2(CO)_4(C_5H_5)_2{}^+]$. $C_{17}H_{16}O_4Ru_2$ requires C, 42.0; H, 3.3%; *M*, 487}; ν(CO) (in hexane) 2 017vs and 1 957vs cm^{-1}; ^1H n.m.r. (in $CDCl_3$), δ 5.30 (s, 10 H, 2 C_5H_5) and 1.72 (br, 6 H, 3 CH_2); ^{13}C n.m.r. (in $CDCl_3$), δ (p.p.m.) 28.7 (β-CH_2), 49.1 (α-CH_2), 87.5 (C_5H_5), and 201.6 (CO).

Further elution with hexane–diethyl ether (1 : 1) gave 71 mg (10%) of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, identified by i.r.

$[(\eta\text{-}C_5H_5)(CO)_2Ru\{\mu\text{-}(CH_2)_4\}Ru(CO)_2(\eta\text{-}C_5H_5)]$ (9). A thf solution of $Na[Ru(CO)_2(\eta\text{-}C_5H_5)]$ was prepared from $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.5 g, 1.1 mmol) as above. Addition of 1,4-di-iodobutane (0.349 g, 1.1 mmol) gave an immediate colour change to yellow-brown. Chromatography on Florisil, eluting with hexane–diethyl ether (19 : 1), gave a yellow band which afforded 259 mg (46%) of pale yellow crystalline complex (9), m.p. 130—132 °C {Found: C, 43.1; H, 3.4%; *M*, 445 $[Ru_2(CO)_4(C_5H_5)_2{}^+]$. $C_{18}H_{18}O_4Ru_2$ requires C, 43.2; H, 3.7%; *M*, 501}; ν(CO) (in hexane) 2 022vs and 1 958vs cm^{-1}; ^1H n.m.r. (in $CDCl_3$), δ 5.20 (s, 10 H, 2 C_5H_5) and 1.63 (br, 8 H, 4 CH_2); ^{13}C n.m.r. (in $CDCl_3$), δ (p.p.m.) −3.3 (β-CH_2), 45.2 (α-CH_2), 88.6 (C_5H_5), and 202.5 (CO).

$[(\eta\text{-}C_5H_5)(CO)_2Fe\{\mu\text{-}(CH_2)_3\}Ru(CO)_2(\eta\text{-}C_5H_5)]$ (10). A thf solution of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ prepared from $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.646 g, 1.8 mmol) was added dropwise to 1,3-di-iodopropane (1.08 g, 3.6 mmol). The resulting mixture was stirred for 1 h. Removal of the solvent and chromatography on alumina, eluting with hexane, gave a yellow band which afforded 170 mg (14%) of oily $[Fe\{(CH_2)_3I\}(CO)_2(\eta\text{-}C_5H_5)]$ [ν(CO) (in hexane) 2 013vs and 1 960vs cm^{-1}; ^1H n.m.r. (in $CDCl_3$), δ 4.72 (s, 5 H, C_5H_5), 3.20 (t, 2 H, CH_2I), and 2.20—1.13 (m, 4 H, 2 CH_2)]. Further elution with diethyl ether developed a brown band from which was obtained 270 mg (42%) of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$. A mixture of $[Fe\{(CH_2)_3I\}(CO)_2(\eta\text{-}C_5H_5)]$ (170 mg, 0.25 mmol) and $Na[Ru(CO)_2(\eta\text{-}C_5H_5)]$, prepared from $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (150 mg, 0.34 mmol) in thf, was stirred for 1 h. Evaporation of the solvent, followed by chromatography on Florisil, gave a yellow band with hexane. This contained 187 mg (87%) of yellow crystalline complex (10), m.p. 85—86 °C (Found: C, 46.3; H, 3.7%; *M*, 441. $C_{17}H_{16}FeO_4Ru$ requires C, 46.3; H, 3.6%; *M*, 441); ν(CO) (in hexane) 2 021vs, 2 010vs, and 1 957vs cm^{-1}; ^1H n.m.r. (in $CDCl_3$), δ 5.3 (s, 5 H, Ru–C_5H_5), 4.7 (s, 5 H, Fe–C_5H_5), and 1.22—1.72 (m, 6 H, 3 CH_2); ^{13}C n.m.r. (in $CDCl_3$), δ (p.p.m.) 216.8 (Fe–CO), 201.5 (Ru–CO), 87.5 (Ru–C_5H_5), 84.2 (Fe–C_5H_5), 47.7 (Fe–CH_2), 46.4 (Ru–CH_2), and 6.7 (β-CH_2).

Organometallic Products of the Decompositions of Complexes (4)—(10).—Thermolysis of the di-iron complexes (4)—(7) and diruthenium complexes (8) and (9) produced $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ respectively in near 100% yield, while a mixture of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ was obtained from heating the iron–ruthenium complex (10). The dimers were purified by chromatography and identified by i.r. spectroscopy. Photolysis of the di-iron complex (4) afforded a near quantitative yield of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$, but u.v. irradiation of a toluene (100 cm^3) solution of the diruthenium complex (8) (500 mg, 1.03 mmol) for 4.5 h gave a mixture of compounds. Evaporation of the solvent and chromatography on alumina, eluting with dichloromethane–hexane (1 : 1), gave two yellow bands. The first afforded 113 mg (27%) of orange crystalline $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and the second 10 mg (2%) of the known propene complex $[Ru_2(CO)_3(C_2H_3Me)(\eta\text{-}C_5H_5)_2]$ (14) [18] as an orange powder, identified by i.r. and mass spectra. Further elution with dichloromethane–hexane (7 : 3) developed a third yellow band, which yielded 30 mg (4%) of yellow crystalline $[Ru_2(CO)_4(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4Ru(CO)_2(\eta\text{-}C_5H_5)\}]$,[17] together with a fourth broad yellow band which afforded 93 mg (20%) of bright yellow powdery $[Ru_4(CO)_6(\mu\text{-}\sigma{:}\eta^5\text{-}C_5H_4)_2(\eta\text{-}C_5H_5)_2]$,[19] each also identified by i.r. and mass spectra. A faint orange band and a purple band were eluted with 1 : 9 and 1 : 4 acetone–dichloromethane mixtures respectively. The former yielded a trace of the μ-alkylidyne complex $[Ru_3(CO)_3(\mu_3\text{-}CEt)(\eta\text{-}C_5H_5)_3]$ (15),[19] sufficient for i.r. and mass spectroscopic identification, and the latter gave 100 mg (25%) of purple crystalline $[Ru_4(CO)_4(\eta\text{-}C_5H_5)_4]$,[16] identified by i.r.

Reaction of $[(\eta\text{-}C_5H_5)(CO)_2Ru\{\mu\text{-}(CH_2)_3\}Ru(CO)_2(\eta\text{-}C_5H_5)]$ (8) *with* Me_3NO.—A solution of (8) (319 mg, 0.66 mmol) and Me_3NO (73 mg, 0.66 mmol) in thf (100 cm^3) was heated at reflux for 2 h. Evaporation of the solvent and chromatography on alumina, eluting with hexane–diethyl ether (9 : 1), gave a single yellow band which afforded 93 mg of (8). No further bands were visible but a fraction eluted with dichloromethane–hexane (1 : 1) gave 1.2 mg (0.4%) of yellow crystalline $[Ru_2(\mu\text{-}CO)(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$,[11] characterised by ^1H n.m.r., i.r. and mass spectroscopy.

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