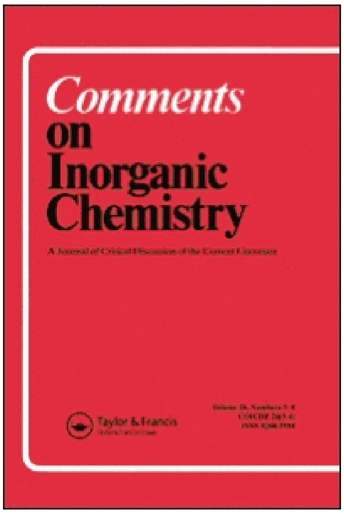


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Metallacycloalkanes As Catalytic Intermediates

R. J. Puddephatt[a]
[a] Department of Chemistry, University of Western Ontario, London, Ontario, Canada

To cite this Article Puddephatt, R. J.(1982) 'Metallacycloalkanes As Catalytic Intermediates', Comments on Inorganic Chemistry, 2: 1, 69 — 95

To link to this Article: DOI: 10.1080/02603598208078110

URL: http://dx.doi.org/10.1080/02603598208078110

Metallacycloalkanes As Catalytic Intermediates

INTRODUCTION

Early developments in organotransition metal chemistry included the synthesis and reactions of hydrido and alkyl derivatives. The insertion of unsaturated reagents into M–C or M–H bonds was shown to be facile in many cases [Eqs. (1) and (2)], and the reaction mechanisms were determined[1–3]:

$$[\mathrm{MnMe(CO)_5}] + \mathrm{CO} \rightleftharpoons [\mathrm{Mn(COMe)(CO)_5}] \qquad (1)$$

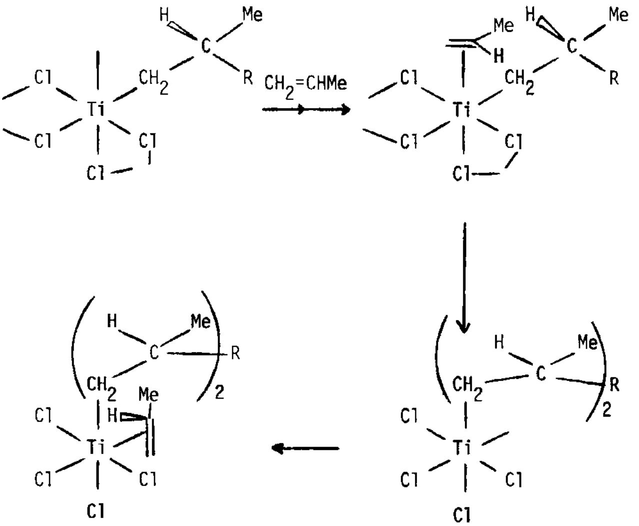
$$\underline{\text{trans}}\text{-}[\mathrm{PtHCl(PEt_3)_2}] + \mathrm{C_2H_4} \rightleftharpoons \underline{\text{trans}}\text{-}[\mathrm{Pt(C_2H_5)Cl(PEt_3)_2}] \qquad (2)$$

These insertion reactions were shown to be significant in several catalytic reactions and it was natural to interpret other, less clearly understood catalytic reactions in terms of similar mechanisms. Some proposed mechanisms for hydrogenation, dimerization and polymerization of alkenes are shown in simplified form in Eqs. (3)–(5)[4–6]:

$$\begin{tikzcd}
{[\mathrm{RhClL_2S}]} \arrow[r, shift left, "\mathrm{H_2}"] & {[\mathrm{RhClH_2L_2S}]} \arrow[l, shift left] \arrow[d, shift left, "\mathrm{RCH{=}CH_2}, -\mathrm{S}"] \\
{[\mathrm{RhClH(CH_2CH_2R)L_2S}]} \arrow[u, "-\mathrm{RCH_2CH_3}"] & {[\mathrm{RhClH_2L_2(RCH{=}CH_2)}]} \arrow[u, shift left] \arrow[l, "\mathrm{S}"']
\end{tikzcd} \qquad (3)$$

Comments Inorg. Chem.
1982, Vol. 2, Nos. 1–2, pp. 69–95
0260-3594/82/0202–0069/$06.50/0

$$\begin{tikzcd}[Rh^{I}Cl_2(C_2H_4)_2]^- \arrow[r, shift left, "H^+Cl^-{,}S"] & \arrow[l, shift left] [EtRh^{III}Cl_3(C_2H_4)S]^- \arrow[d, "S"] \\ [Rh^{I}Cl_2(EtCH{=}CH_2)S]^- \arrow[u, "2\ C_2H_4", "\begin{array}{l}-EtCH{=}CH_2\\ -S\end{array}"'] & [BuRh^{III}Cl_3S_2]^- \arrow[l, "-H^+Cl^-{,}-S"'] \end{tikzcd} \qquad (4)$$



(5)

The hydrogenation reaction of Eq. (3) involves insertion of alkene into a metal–hydrogen bond. This is well established to be a facile process in many model systems as well as in the catalytic systems themselves.[4,7] However, the dimerization and polymerization of alkenes [Eqs. (4) and (5)] require rapid insertion of alkenes into metal–alkyl bonds. These reactions are well established for alkenes and alkynes bearing electronegative substituents or for other particularly activated alkenes,[8] but they do not usually occur with the simple alkenes that are of interest in the catalytic reactions. In the chemistry of the *d*-block elements the best evidence for insertion of simple alkenes into M–C bonds is still indirect and is based on the labeling studies of Eq. (6).[9]

$$\begin{tikzcd}
{[CpCo(CD_3)_2(PPh_3)]} \arrow[r, "-PPh_3", "C_2H_4"'] & {[CpCo(CD_3)_2(C_2H_4)]} \arrow[d] \\
{[CpCo(C_2H_4)(PPh_3)] + CD_3CH{=}CH_2 + CD_3H} & {[CpCo(CD_3)(CH_2CH_2CD_3)]} \arrow[l, "C_2H_4"', "PPh_3"]
\end{tikzcd} \qquad (6)$$

However, direct evidence for insertion into metal–carbon bonds is known for the *f*-block elements [Eq. (7), M = Yb, Lu][10]:

$$(C_5Me_5)_2M(Me)(OEt_2) + CH_2{=}CHMe \longrightarrow (C_5Me_5)_2M(CH_2CHMe_2) \qquad (7)$$

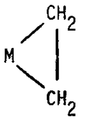
One of the problems in finding good examples for this type of reaction is that the insertion of ethylene, for example, into a methylmetal bond gives a propylmetal group, which will certainly be more reactive than the starting compound since it can undergo β elimination to propene and since the M–Pr bond will almost certainly be weaker than the M–Me bond and hence perhaps more receptive to further insertion reactions. Nevertheless, it is certainly true that insertion of alkenes into M–C bonds is much more difficult in model systems than insertion into M–H bonds, and the chain growth in polymerization or oligomerization of alkenes by the insertion mechanism has therefore been questioned.[11]

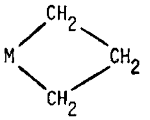
Meanwhile, it has been shown that metallacycloalkanes are often easily formed from alkenes and that C–C bond formation and cleavage can occur particularly easily in many such compounds. Metallacyclobutanes have been known for several years to be intermediates in alkene metathesis reactions,[12] and there has been a great deal of speculative discussion about the possible role of metallacyclobutanes and metallacyclopentanes in many other catalytic reactions. This article will bring together much of the data on model reactions of metallacycloalkanes related to catalysis, and the ensuing debate on catalytic mechanisms will also be summarized.

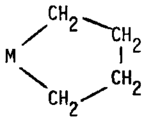
TYPES OF METALLACYCLOALKANES

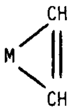
The general types of metallacycloalkanes are shown in Table I. The metallacyclopropane and metallacyclopropene derivatives (I) and (IV) are just alkene and alkyne complexes in disguise and, although arguments can be presented that there is a resemblance between the chemistry

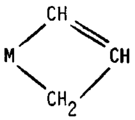
TABLE I
Types of metallacycloalkanes

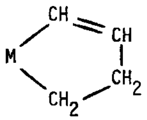

(I)

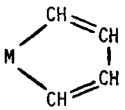

(II)

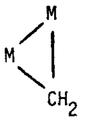

(III)

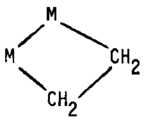

(IV)

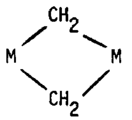

(V)

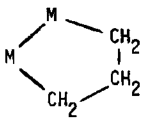

(VI)


(VII)


(VIII)


(IX)


(X)


(XI)

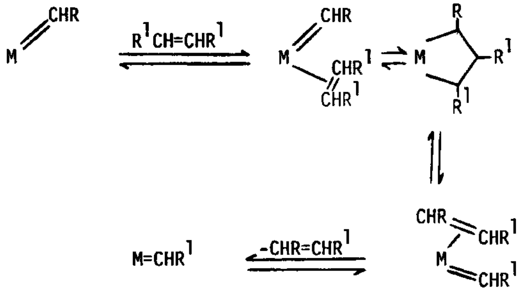
of (I) and metallacyclobutanes (II) and that in some cases the bonding is better described by the canonical forms (I) and (IV), these complexes have been thoroughly studied and reviewed elsewhere and will not be treated here.

Extensions to the simplest metallacyclobutanes and metallacyclopentanes (II) and (III) can be obtained by placing functional groups such as alkyl, halogen or ester groups as substituents on the ring, or of course by changing the metal M, its oxidation state or the other ligands on it. More fundamental changes can be made by introducing unsaturation in the ring as illustrated by the metallacyclobutene, metallacyclopentene and metallacyclopentadiene structures (V)–(VII). In principle, unsaturation could include M–C multiple bonding though known examples are few: of course, the possible number of derivatives increases with increasing ring size.

Finally, it is possible to introduce more than one metal atom in the ring. Examples include the dimetallacyclopropane (VIII), dimetallacyclobutanes (IX and X), and dimetallacyclopentane (XI). Given the possibilities of M–M, M–C and C–C multiple bonding it will be clear that a great number of additional ring types can be built from these, and several examples of such compounds are already known. In ring systems with two or more metal atoms, it is more difficult to separate out alkene and alkyne complexes from other derivatives; for example, (IX) may be considered as an ethylene complex but this is not a particularly useful description.

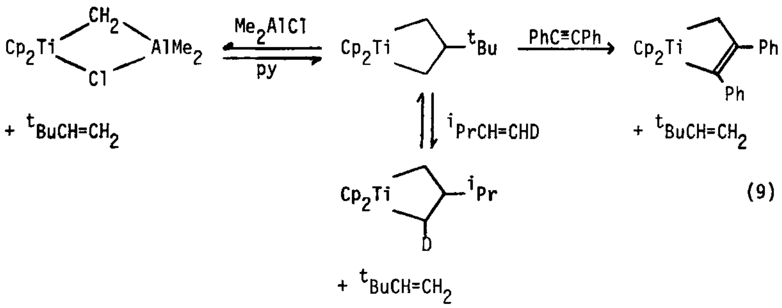
METALLACYCLOBUTANE INTERMEDIATES

Best established are the metallacyclobutane intermediates in alkene metathesis, where the interconversion into alkene–carbene complex intermediates is involved in the propagation steps:



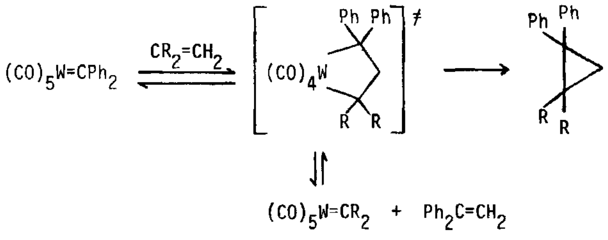
(8)

Evidence for this mechanism has been summarized elsewhere,[12] and only some evidence arising from model reactions involving metallacyclobutanes will be given here. The best model is that based on titanocene derivatives, where the interconversion of carbenelike species with metallacyclobutanes has been demonstrated directly[13]:



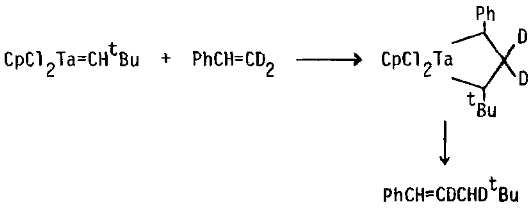
(9)

Another important early demonstration of the involvement of carbene intermediates comes from exchange reactions and cyclopropanation reactions of isolated metal carbene complexes[14]:



(10)

More recent work indicates that metallacyclobutanes may not be involved in these reactions however. Instead a dipolar intermediate is preferred and so the relationship to alkene metathesis is now doubtful.[14] Reactions of tantalum carbene complexes with alkenes give new alkenes, which are probably formed via shortlived tantallacyclobutane intermediates[15]:



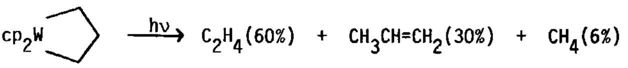
(11)

Here the alkene is formed from the proposed metallacyclobutane by β elimination, but examples are known where metathesis-related reactions occur:

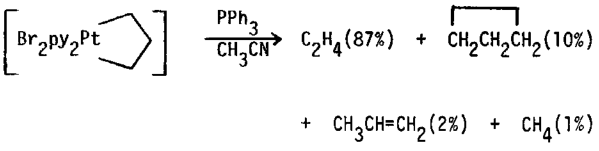
$$(^tBuO)_2Cl(Me_3P)Ta{=}CH^tBu + PhCH{=}CH_2 \longrightarrow {}^tBuCH{=}CH_2(69\%) + \underline{trans}\text{-}PhCH{=}CH^tBu(6\%) \quad (12)$$

These reactions are therefore closely related to those proposed for alkene metathesis, and the compounds are indeed shortlived metathesis catlysts.[15] An oxo(alkylidene)tungsten complex [$W(O)CH\text{-}t\text{-}Bu)Cl_2(PEt_3)$] similarly acts as an efficient metathesis catalyst, although the presumed tungstacyclobutane intermediate was not detected directly.[16]

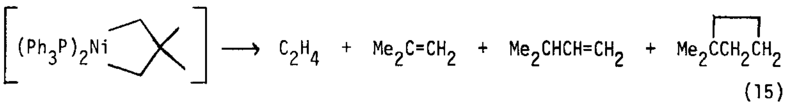
Complementing the above examples, in which the carbene complexes are the best characterized species, are models in which the metallacyclobutanes are characterized but proposed carbene–alkene intermediates are not. Thus either thermolysis or photolysis of isolated metallacyclobutanes can lead to C–C bond cleavage as illustrated in Eqs. (13)–(15)[17–19]:



(13)

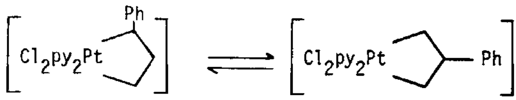


(14)



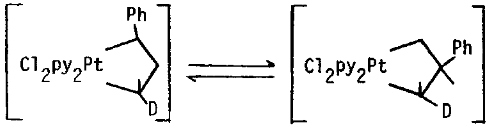
(15)

In addition, skeletal isomerization of platinacyclobutanes can occur easily, as predicted by the methathesis mechanism[19,20]:



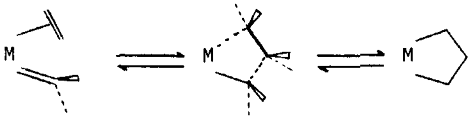
(16)

These reactions occur in a stereospecific manner [Eq. (17)] and it is not certain that carbene–alkene intermediates are involved.[20,21] The evidence concerning this mechanism has been discussed extensively[22]:



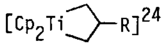
(17)

An interesting problem, as yet unanswered, is whether the more stable species in alkene metathesis systems is the carbene–alkene complex or the metallacyclobutane. The model systems described above suggest that either could be the case, depending on the particular metal complex involved. Recent theoretical studies suggest that in some cases, a nonclassical species intermediate between a metallacyclobutane and carbene–alkene complex might be preferred in some cases[23]:

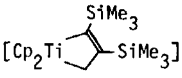


(18)

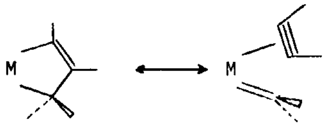
Nonclassical structures were predicted but not observed in the titanacyclobutanes



and many platinacyclobutanes also have almost regular structures with nearly planar PtC_3 rings.[22,25] However, there is evidence for nonclassical structures in titanacyclobutene complexes such as

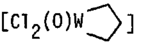


in which bond lengths are interpreted in terms of the resonance forms shown in Eq. (19)[23]:



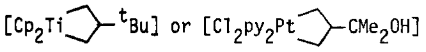
(19)

Calculations also give some support to the proposal that ancillary ligands can have a dominant influence on the reactions of metallacyclobutanes.[15,16] Thus the oxo ligand appears to stabilize metallacyclobutanes with respect to carbene complexes in the model systems, based on calculations on the compounds

$[Cl_2(O)W{=}CH_2]$ and 

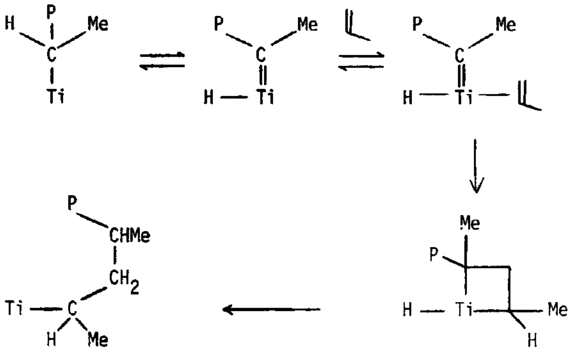
by its ability to π bond with the metal and thus act as an electron donor when required. In the related case with $[Cl_4W{=}CH_2]$, calculations indicate that the carbene complex is more stable than the metallacyclobutane.[26] The practical importance of these findings to alkene metathesis reactivity and selectivity are not yet defined.

The stereochemistry and selectivity in alkene metathesis has often been interpreted in terms of the thermodynamic stability of intermediate metallacyclobutanes which were assumed to be puckered. However, recent structures show that puckering may be very small even when bulky substituents are present,[18,24,25] for example in



and hence these interpretations must be considered doubtful. The barrier to puckering of the metallacyclobutane ring appears to be very low.

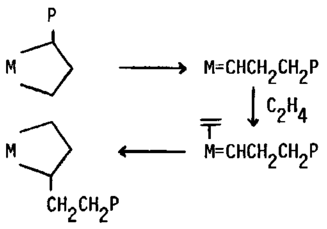
The role of metallacyclobutanes in dimerization and polymerization of alkenes is much more speculative. The mechanism first proposed is shown in Eq. (20), where P = polymer and other ligands on Ti are omitted[11]:



(20)

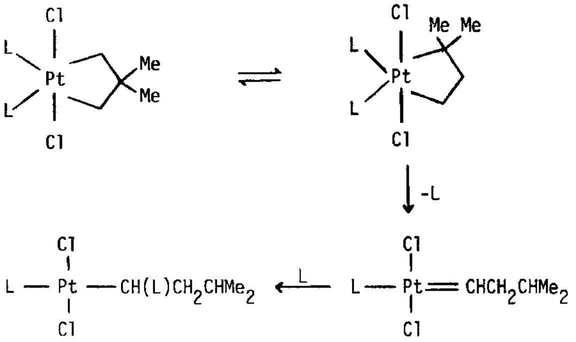
The first step is based on the very easy α elimination from a methyltungsten group in $[Cp_2WMe]^+$ to give $[Cp_2W(CH_2)H]^+$, while the remaining parts are clearly related to the mechanism of alkene metathesis.[27] The insertion of an alkene into a metal–carbon σ bond is avoided in this mechanism.

A similar proposal is shown in Eq. (21); P = polymer chain[27]:



(21)

In this case, the model was the observed decomposition of platinacyclobutanes by α elimination to give carbene complex intermediates, then trapped by reaction with pyridine derivatives [Eq. (22)]; L = 2-methylpyridine[28]:



(22)

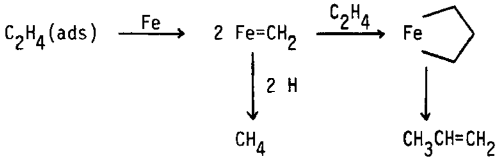
In polymerization it would be necessary for the carbene intermediate to be trapped by the alkene to regenerate the higher metallacyclobutane. It is clear that dimerization or oligomerization of alkenes could occur by this type of mechanism but in no case is there direct evidence for metallacyclobutane intermediates.

Another apparently related reaction is the homologation of alkenes and alkanes on metal surfaces as illustrated by Eqs. (23) and (24):

$$C_2H_4 \xrightarrow[170°C]{Fe} CH_3CH{=}CH_2(70\%) + CH_4(6\%) + \text{butenes}(20\%) \qquad (23)$$

$$n\text{-}C_5H_{12} \xrightarrow[150°C]{W/H_2} CH_4 + C_2H_6(48\%) + C_3H_8(20\%) + n\text{-}C_4H_{10}(24\%) + n\text{-}C_6H_{14}(5\%) \qquad (24)$$

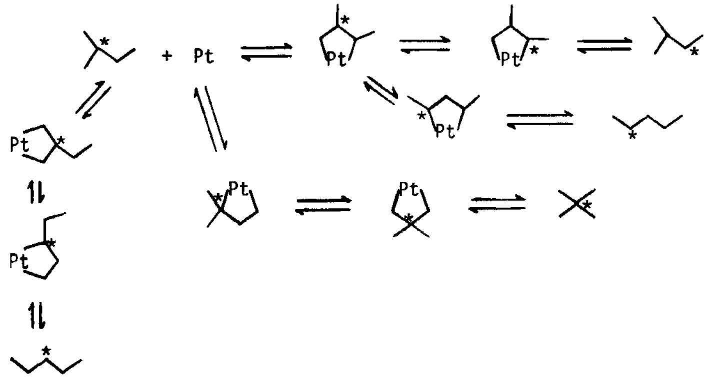
Here the reactions are suggested to occur by dissociative chemisorption of the alkene followed by formation of a metallacyclobutane[29]:



(25)

In order for homologation to occur the metallacyclobutane must decompose by a hydrogen shift to give propene rather than by C–C bond cleavage, but this is a common mode of decomposition of isolated metallacyclobutanes.[22,28] Higher alkenes are formed by reaction of the propene formed initially with a second Fe═CH$_2$ group, and alkanes are formed by hydrogenolysis of similar intermediates if hydrogen is present. It is suggested that similar reactions occur during the Fischer–Tropsch synthesis.

The isomerization of hydrocarbons on platinum catalysts by the bond-shift process has been suggested to occur via metallacyclobutanes according to Eq. (26), * = ^{13}C labeled carbon atom[21,22,30,31].



(26)

Equation (26) shows how ^{13}C labeling studies on the isomerization of isopentane can be explained using this mechanism, but the details of the mechanism on a molecular basis are shown more simply in Figure 1. This shows the proposed mechanism of the neopentane to isopentane isomerization on a platinum catalyst.

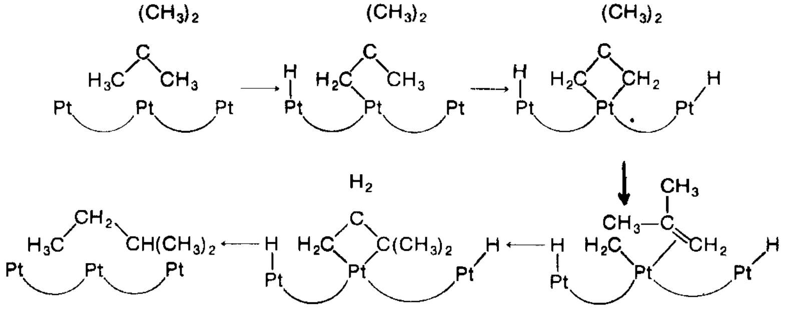
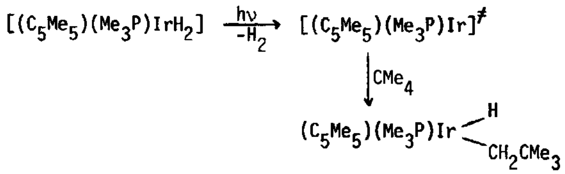
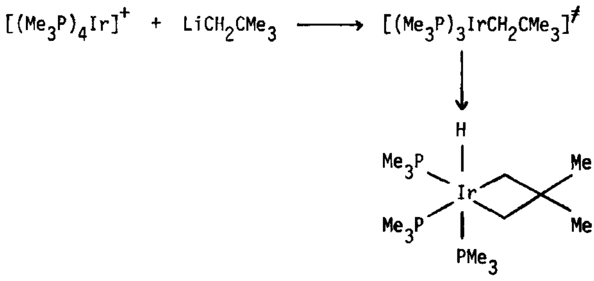


FIGURE 1 Isomerization of isopentane.

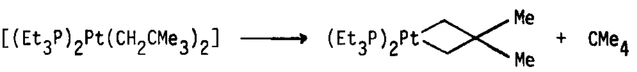
There are now good organometallic precedents for all of the necessary steps in this catalytic cycle. The first steps involve α,γ dimetallation of the alkane, which presumably occurs in a stepwise manner. Good precedents are found in both platinum and iridium chemistry, as illustrated in Eqs. (27)–(29)[32–34]:



(27)



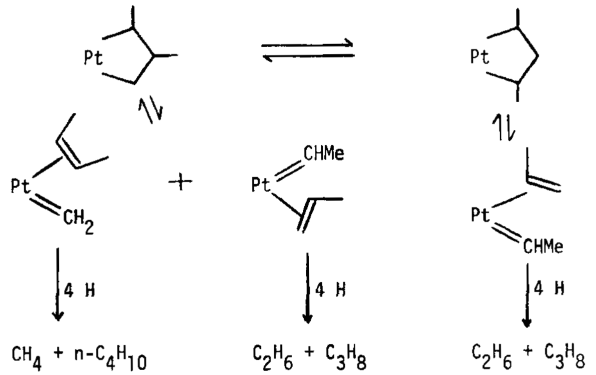
(28)



(29)

The next step in the catalysis involves skeletal isomerization of the platinacyclobutane, a process known to occur readily in model systems, as illustrated in Eqs. (16), (17) and (22). This is the key step at which the bond shift occurs. Finally the alkane is released by hydrogenolysis of the platinacyclobutane, and again the precedent is a good one.[35]

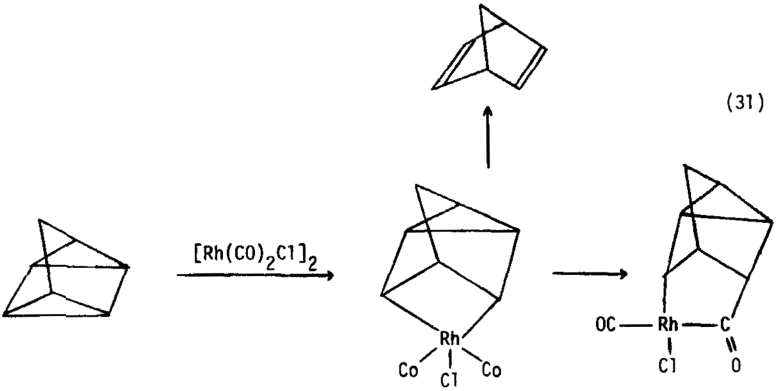
Since it is already established that metallacyclobutanes can decompose by C–C bond cleavage [Eqs. (13)–(15)], the same platinacyclobutane intermediates of Eq. (26) may be invoked to explain the cracking of alkanes according to Eq. (30), taking only one of the proposed platinacyclobutanes as an example:



(30)

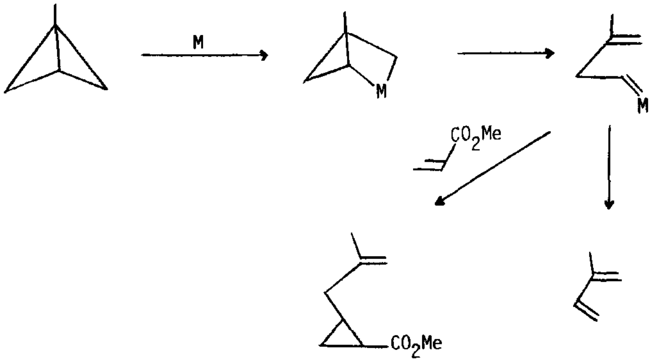
These isomerization and cracking reactions have not been accomplished using homogeneous catalysts although all of the individual steps are known, as described above. This is explicable, since no single metal site could have enough vacant sites to allow all of the steps to occur. On a metal surface, the hydrogen atoms involved in the metallation steps can migrate away from the platinum atom at which the Pt–H bond is initially formed and thus leave a coordination site needed for the next step.

The rearrangement of strained cycloalkanes catalyzed by transition metal complexes is thought to involve metallacyclobutanes in many cases, although the evidence is usually indirect.[36] Perhaps the best example is the rearrangement of quadricyclene to norbornadiene, when a proposed intermediate rhodiacyclobutane was trapped by CO insertion[37]:



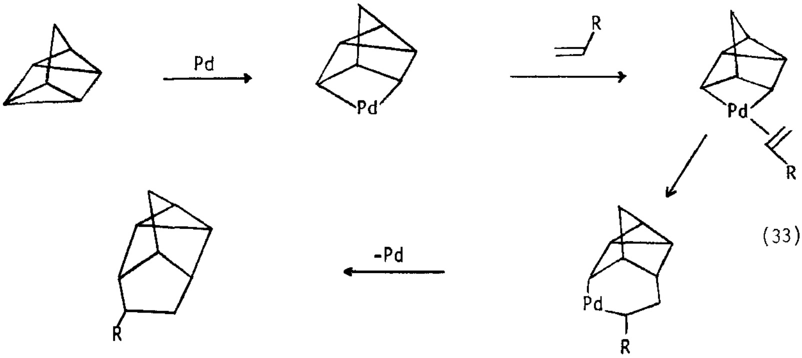
(31)

In bicycloalkanes, the intermediate metallacyclobutanes appear to break down by C–C bond cleavage as in the alkene metathesis mechanism, and the carbene intermediates can sometimes be trapped by added alkene {M = $[RhCl(norbornadiene)]_2$}[38]:



(32)

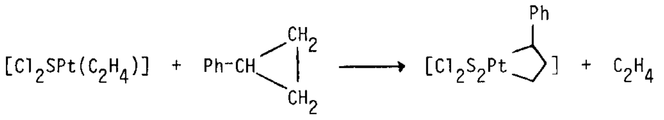
In other cases the alkene may react directly with the metallacyclobutane to give the $[\sigma 2 + \pi 2]$ cycloaddition product of the alkene with cyclopropane [Pd = Pd(o) complex].[39]



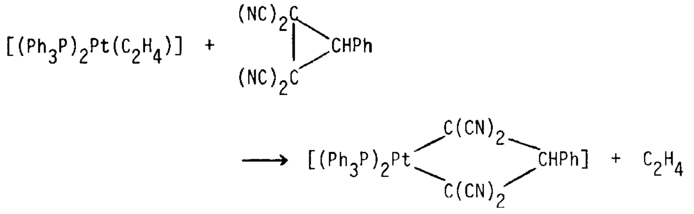
(33)

There are many other examples of similar reactions, and the area has been investigated systematically by organic chemists.[36]

The best model for insertion of a metal into strained C–C bonds of a cyclopropane is in the synthesis of stable platinacyclobutanes by this method (S = solvent)[22,40]:



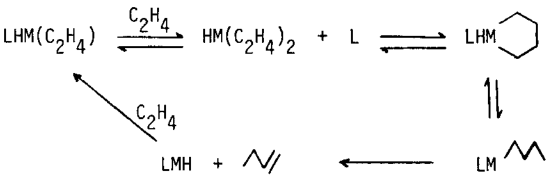
(34)



(35)

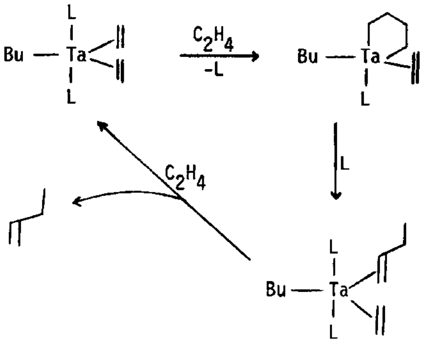
METALLACYCLOPENTANE INTERMEDIATES

The mechanism proposed for dimerization of ethylene to 1-butene using rhodium complex catalysts was shown in Eq. (4) and involves insertion of ethylene into a metal–carbon bond. Because such reactions are rare and because such a mechanism might be expected to be less selective (further insertion of ethylene into Bu–Rh bonds would be expected to some extent), it has been suggested that metallacyclopentane intermediates might be involved instead. A typical mechanism is shown in Eq. (36)[41]:



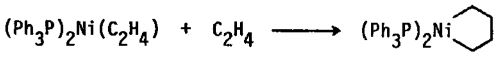
(36)

In this case, the catalyst is a hydridometal complex and the butylmetal derivative is formed in a reductive elimination step. It is also possible that protonation of a metallacyclopentane intermediate could give the butylmetal species.[42] In other cases 1-butene appears to be formed by intramolecular rearrangement of the metallacyclopentane intermediate, without a butylmetal intermediate[42]:

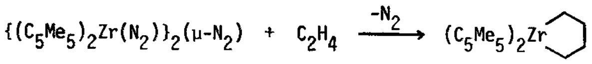


(37)

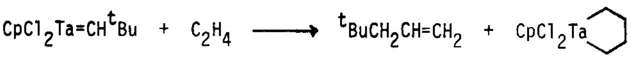
What are the organometallic precedents for these proposed mechanisms? The coupling of two alkenes to give a metallacyclopentane was discovered over 20 years ago.[43] There is now a very large number of examples of such reactions, involving metals from zirconium to platinum and simple alkenes, alkenes with electronegative substituents, dienes, acetylenes and many other unsaturated derivatives. A few examples are shown in Eqs. (38)–(42), but it is not possible to discuss in this review even a minority of the elegant examples known[15,42,44–47]:



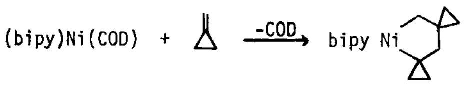
(38)



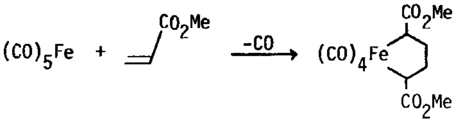
(39)



(40)

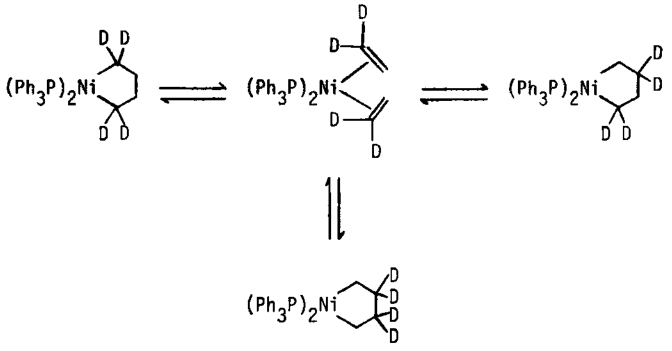


(41)



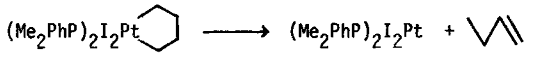
(42)

Labeling studies have shown that the reaction is easily reversible[44]:

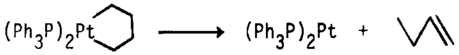


(43)

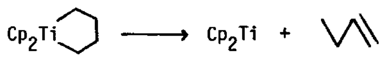
The next stage in the proposed catalytic dimerization of ethylene may involve decomposition of the metallacyclopentane to give 1-butene. Again there are several good models for this reaction as shown in Eqs. (45)–(49):



(44)



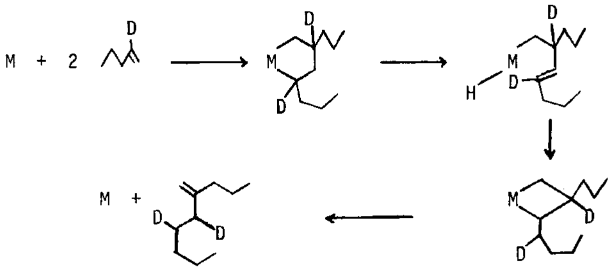
(45)



(46)

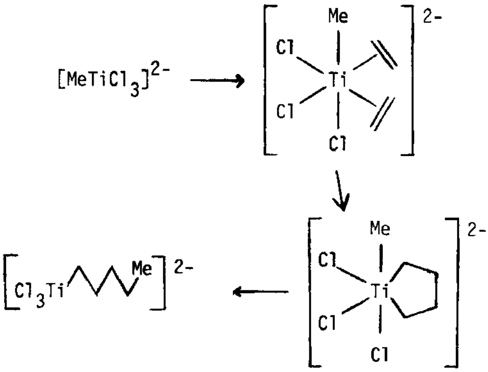
In addition, several of the systems which catalytically dimerize ethylene (and other alkenes) also yield isolable metallacyclopentanes.[15,44] The evidence is thus very powerful for these systems, but it is obviously possible that some dimerization reactions do occur by the original insertion mechanism of Cramer.[5]

Metallacyclopentanes can give not only 1-butene on decomposition, but may also give ethylene or cyclobutane. One catalytic system for dimerization of ethylene to cyclobutane has been developed from this observation.[44] In developing catalysts it is clearly advantageous to be able to predict the mode of decomposition of a metallacyclopentane but this is not always possible.[15,44,48,49] In one case, for example, a metallacyclopentane decomposed by ring contraction to a metallacyclobutane and then by β-elimination-reductive elimination [M = $(C_5Me_5)Cl_2Ta$][15]:



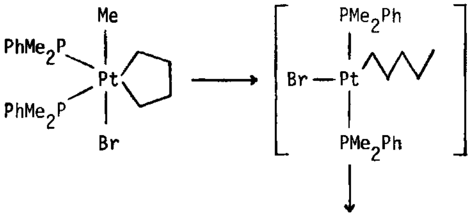
(47)

In an interesting extension of this metallacyclopentane mechanism for alkene dimerization, it has been suggested that alkene polymerization may proceed in an analogous fashion[50]:

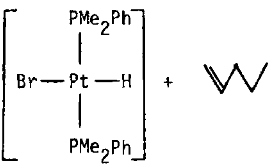


(48)

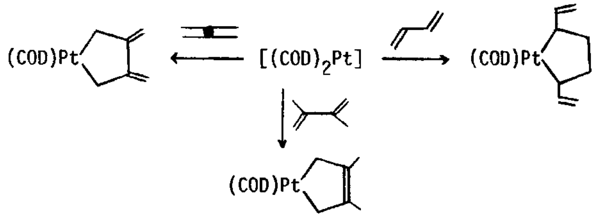
In this case the metallacyclopentane forms as before, but now decomposes by reductive elimination of the growing alkyl chain [Me in Eq. (48)] with one of the M–C bonds of the ring to form the higher alkyltitanium(II) complex. Again there are good organometallic models, though not in titanium chemistry.[48,49] For example, the reaction of Eq. (49) occurs with 97% selectivity and none of the alternative reductive elimination of cyclobutane was observed.[48]



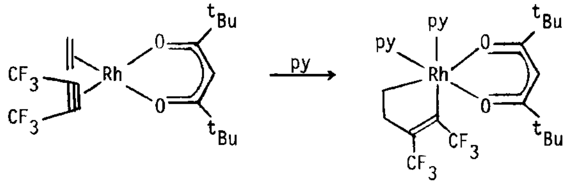
(49)



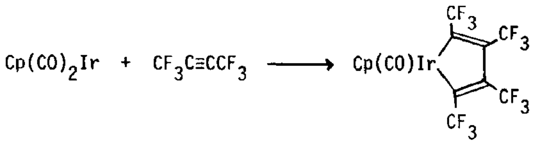
There have been a great number of studies of metallacyclopentanes with unsaturated substituents, of metallacyclopentenes and metallacyclopentadienes. Such compounds are involved in dimerization and trimerization of 1,2- and 1,3-dienes, of cooligomerization of alkenes and alkynes, and of dimerization and trimerization of alkynes respectively.[51] This chemistry is well established and will not be reviewed in detail here. Some examples of the formation of such compounds are shown in Eqs. (50)–(52)[52–54]:



(50)



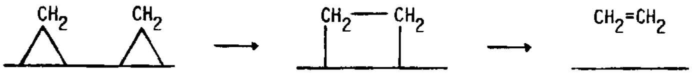
(51)



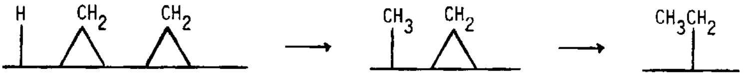
(52)

DIMETALLACYCLOALKANE INTERMEDIATES

Dimetallacyclopropane intermediates are now considered to be important intermediates in the Fischer–Tropsch synthesis. Dissociative chemisorption of carbon monoxide followed by hydrogenation gives the $M_2(\mu\text{-}CH_2)$ fragments on a metal surface. Dimerization or chain growth steps can then occur as shown in Eqs. (53) or (54), where the solid line represents the metal surface[55]:

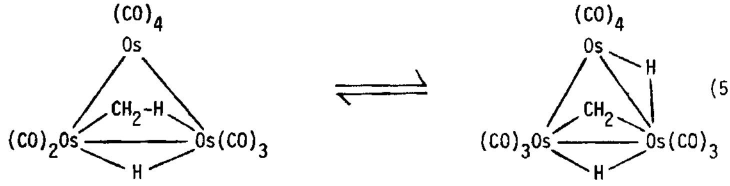


(53)



(54)

Evidence for the reduction of carbide is found in the oxidation of $[Fe_4(C)(CO)_{12}]^{2-}$ in the presence of hydrogen to give $[HFe_4(\eta^2\text{-}CH)(CO)_{12}]$, with a sideways bound methylidyne ligand.[56] Evidence for the reduction of a μ-methylene group to methyl is best seen in the triosmium complexes of Eq. (55)[57]:

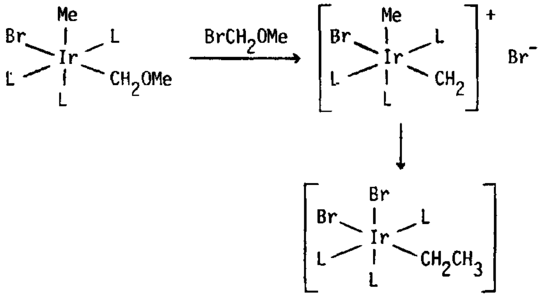


(55)

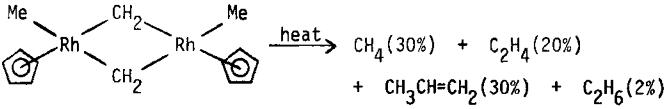
The reaction of Eq. (55) is rapid and reversible, and the unsymmetrical μ-methyl group is now well established. Similar reactions have been found in other complexes.[57–58]

Another possible route to the μ-methylene or dimetallacyclopropane complexes in the Fischer–Tropsch synthesis is by reduction of coordinated CO. This has been achieved in the reduction of $[Os_3(CO)_{12}]$ to $[Os_3(CO)_{11}(\mu\text{-}CH_2)]$ in a stepwise manner.[59]

The migration of methyl groups to methylene groups gives the next stage in the proposed mechanism. There are good models in both mononuclear compounds with terminal methylene groups and in binuclear compounds with dimetallacyclopropane rings as shown in Eqs. (56) and (57)[60]:

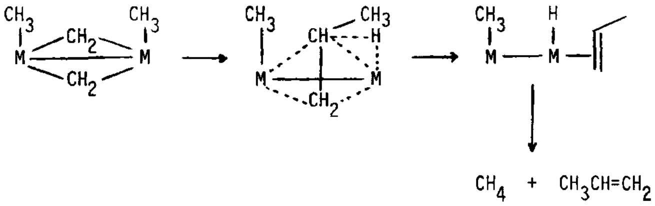


(56)



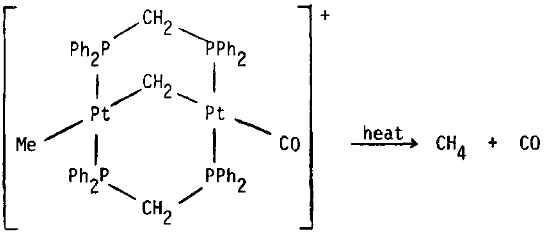
(57)

The formation of propene in Eq. (57) is considered to occur as in Eq. (58):



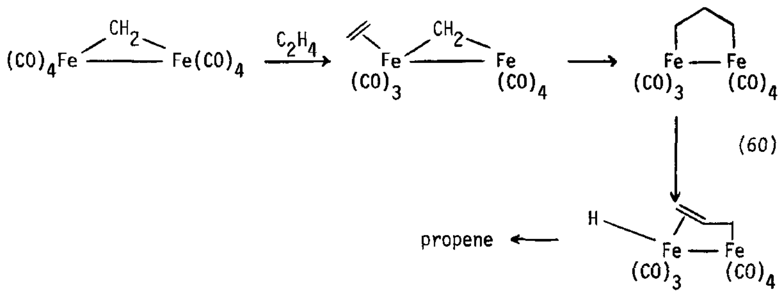
(58)

However, in cases where the methyl and methylene groups are mutually *trans* it seems that coupling cannot occur easily[61]:

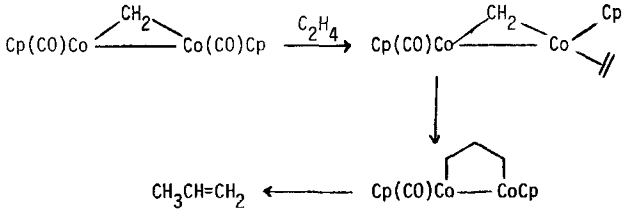


(59)

Another propagation mode could involve coupling of μ-methylene groups with ethylene, and again there are good models to demonstrate the feasibility of this mechanism[62]:

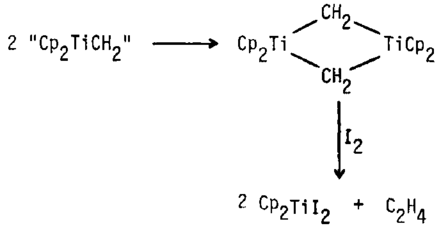


(60)



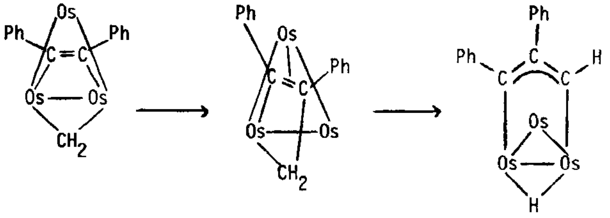
(61)

In both cases dimetallacyclopentane intermediates are thought to be involved, and the mechanisms are probably more complex than shown.[62] The ethylene needed for this reaction would probably be formed by coupling of methylene fragments in the Fischer–Tropsch synthesis. Such reactions are known to occur and intermediate dimetallacyclobutanes may be involved:



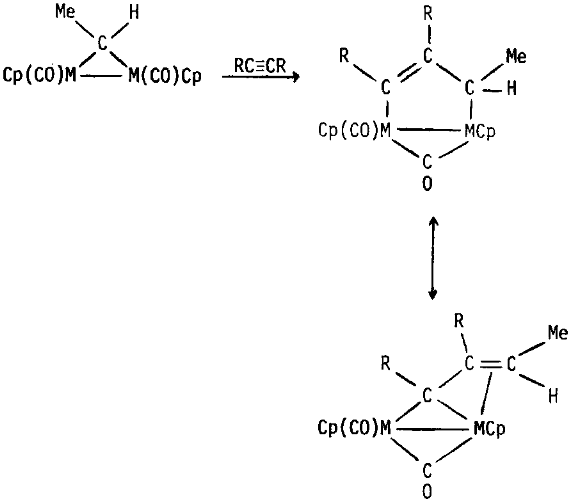
(62)

The nature of the reactions involved on surfaces may be analogous to the coupling of diphenylacetylene with a μ-methylene group in $[Os_3(CO)_9(C_2Ph_2)(CH_2)]$ (CO groups omitted)[63]:



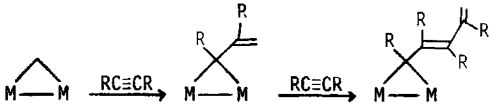
(63)

The insertion of alkynes into μ-methylene groups gives a possible mechanism for polymerization of alkynes (M = Fe, Ru)[64]:



(64)

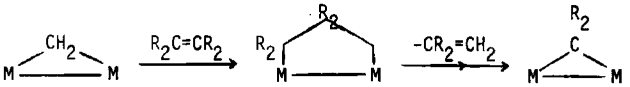
The proposed polymerization mechanism is then given by Eq. (65):



(65)

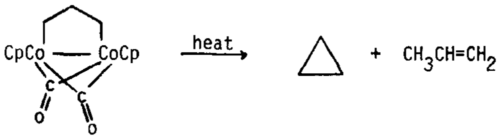
Polymerization of alkynes can actually be carried out using a similar binuclear tungsten complex.[65]

It should also be apparent that the reaction of alkenes with μ-methylene complexes could give a basis for alkene metathesis[64,66]:



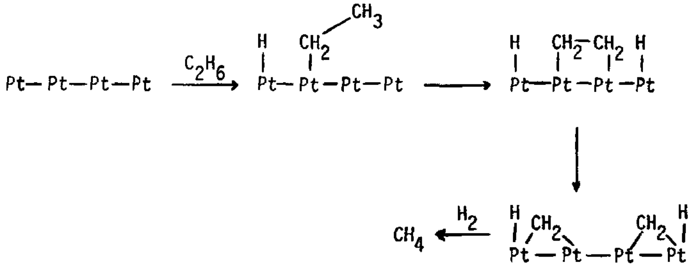
(66)

So far the precedents for this sequence are less promising. For example, an isolated dimetallacyclopentane gave propene and cyclopropane on thermolysis[67]:



(67)

Dimetallacyclopropanes and dimetallacyclobutanes may be invoked to explain the cleavage of C–C bonds of alkanes over metal surfaces such as platinum[30]:



(68)

As in Figure 1, activation of C–H bonds of the alkane gives the metallacycle and then the C–C bond cleavage occurs within the metallacycle.

CONCLUSIONS

As can be seen from the above discussion, it is very fashionable to propose metallacycloalkanes as intermediates in catalysis. In some cases, as in alkene metathesis or in some alkene dimerization reactions, the evidence is very strong. In other cases, the proposals are based largely on model systems which can only indicate that the mechanism is chemically reasonable. The mechanistic proposals are then best regarded as constructive speculation, and as such they have already sparked the rapid development of this area of organometallic chemistry. Whether the present view that metallacycles may be key intermediates in a very wide range of catalytic reactions is a valid one will be the subject of intense research over the next few years. It should be an interesting period.

R. J. PUDDEPHATT
Department of Chemistry,
University of Western Ontario,
London, Ontario,
Canada N6A 5B7

References

1. J. P. Collman and L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry* (University Science Books, Mill Valley, California, 1980).
2. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley, New York, 1980).
3. J. K. Kochi, *Organometallic Mechanisms and Catalysis* (Academic, New York, 1978).
4. J. Halpern, T. Okamoto and A. Zakhariev, J. Mol. Catal. **2,** 65 (1978). J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, J. Chem. Soc. **1966,** A, 1711 (1966).
5. R. Cramer, J. Am. Chem. Soc. **87,** 4717 (1965).
6. P. Cossee, J. Catal. **3,** 80 (1964). E. J. Arlman and P. Cossee, J. Catal. **3,** 99 (1964).
7. D. L. Thorn and R. Hoffman, J. Am. Chem. Soc. **100,** 2079 (1978).
8. H. C. Clark and R. J. Puddephatt, Inorg. Chem. **10,** 18 (1971). A. Johnson and R. J. Puddephatt, J. Chem. Soc. Dalton Trans. **1977,** 1384 (1977); **1978,** 980 (1978).
9. E. R. Evitt and R. G. Bergman, J. Am. Chem. Soc. **102,** 7003 (1980).
10. P. L. Watson, J. Am. Chem. Soc. **104,** 337 (1982).
11. K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green and R. Mahtab, J. Chem. Soc. Chem. Commun. **1978,** 604 (1978).
12. R. H. Grubbs, Prog. Inorg. Chem. **24,** 1 (1978). N. Calderon, J. P. Lawrence and E. A. Ofstead, Adv. Organomet. Chem. **17,** 449 (1979).
13. F. N. Tebbe, G. W. Parshall and D. W. Ovenall, J. Am. Chem. Soc. **101,** 5074 (1979). F. N. Tebbe, G. W. Parshall and G. S. Reddy, J. Am. Chem. Soc. **100,** 3611 (1978). T. R. Howard, J. B. Lee and R. H. Grubbs, J. Am. Chem. Soc. **102,** 6878 (1980).
14. C. P. Casey and T. J. Burkhardt, J. Am. Chem. Soc. **96,** 7808 (1974). C. P. Casey, S. W. Polichnowski, A. J. Shusterman and C. R. Jones, *ibid.* **101,** 7282 (1979). J. Levisalles, H. Rudler, D. Villemin, J. Daran, Y. Jeannin and L. Martin, J. Organomet. Chem. **155,** C1 (1978).
15. R. R. Schrock, Acc. Chem. Res. **1979,** 98 (2979). S. J. McLain, C. D. Wood and R. R. Schrock, J. Am. Chem. Soc. **99,** 3519 (1977); **101,** 4558 (1979). C. D. Wood, S. J. McLain and R. R. Schrock, *ibid.* **101,** 3210 (1979). S. M. Rocklage, J. D. Fellman, G. A. Rupprecht, L. W. Messerle and R. R. Schrock, *ibid.* **103,** 1440 (1981). S. J. McLain, J. Sancho and R. R. Schrock, *ibid.* **102,** 5610 (1980).
16. J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert and W. J. Youngs, J. Am. Chem. Soc. **102,** 4515 (1980).
17. M. Ephritikhine and M. L. H. Green, J. Chem. Soc. Chem. Commun. **1976,** 926 (1976).

18. D. C. L. Perkins, R. J. Puddephatt and C. F. H. Tipper, J. Organomet. Chem. **186,** 419 (1980). D. C. L. Perkins, R. J. Puddephatt, M. C. Rendle and C. F. H. Tipper, *ibid.* **195,** 105 (1980). R. J. Klingler, J. C. Huffman and J. K. Kochi, *ibid.* **206,** C7 (1981).
19. R. J. Al-Essa, R. J. Puddephatt, D. C. L. Perkins, M. C. Rendle and C. F. H. Tipper, J. Chem. Soc. Dalton Trans. **1981,** 1738 (1981).
20. R. J. Puddephatt, M. A. Quyser and C. F. H. Tipper, J. Chem. Soc. Chem. Commun. **1976,** 626 (1976). R. J. Al-Essa, R. J. Puddephatt, C. F. H. Tipper and P. J. Thompson, J. Organomet. Chem. **157,** C40 (1978). R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser and C. F. H. Tipper, J. Am. Chem. Soc. **101,** 364 (1979).
21. C. P. Casey, D. M. Scheck and A. J. Shusterman, J. Am. Chem. Soc. **101,** 4233 (1979). R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser and C. F. H. Tipper, Inorg. Chim. Acta. **34,** L187 (1979). R. J. Al-Essa, R. J. Puddephatt, P. J. Thompson and C. F. H. Tipper, J. Am. Chem. Soc. **102,** 7546 (1980).
22. R. J. Puddephatt, Co-ord. Chem. Rev. **33,** 149 (1980).
23. O. Eisenstein, R. Hoffman and A. R. Rossi, J. Am. Chem. Soc. **103,** 5582 (1981). R. J. McKinney, T. H. Tulip, D. L. Thorn, T. S. Coolbaugh and F. N. Tebbe, *ibid.* **103,** 5584 (1981).
24. J. B. Lee, G. J. Gajda, W. P. Schaefer, T. R. Howard, T. Ikariya, D. A. Straus and R. H. Grubbs, J. Am. Chem. Soc. **103,** 7358 (1981).
25. J. A. Ibers and N. Jones, personal communication.
26. A. K. Rappé and W. A. Goddard III, J. Am. Chem. Soc. **104,** 448 (1982); **104,** 297 (1982).
27. N. J. Cooper and M. L. H. Green, J. Chem. Soc. Dalton Trans. **1979,** 1121 (1979).
28. R. J. Al-Essa and R. J. Puddephatt, J. Chem. Soc. Chem. Commun. **1980,** 45 (1980). S. M. Ling and R. J. Puddephatt, *ibid.* **1982,** 412 (1982).
29. C. O'Donohoe, J. K. A. Clarke and J. J. Rooney, J. Chem. Soc. Chem. Commun. **1979,** 648 (1979); J. Chem. Soc. Faraday I **76,** 345 (1980). F. Hugues, B. Besson and J. M. Basset, J. Chem. Soc. Chem. Commun. **1980,** 719 (1980).
30. G. W. Parshall, T. Herskovitz, F. N. Tebbe, A. D. English and J. V. Zeile, Fund. Res. Homog. Catal. **3,** 95 (1979). G. W. Parshall, *Homogeneous Catalysis* (Wiley, New York, 1980).
31. F. Garin and F. G. Gault, J. Am. Chem. Soc. **97,** 4466 (1975). A. O'Cinneide and F. G. Gault, J. Catal. **37,** 311 (1975). F. G. Gault, Gazz. Chim. Ital. **109,** 255 (1979).
32. A. H. Janowicz and R. G. Bergman, J. Am. Chem. Soc. **104,** 352 (1982).
33. T. H. Tulip and D. L. Thorn, J. Am. Chem. Soc. **103,** 2448 (1981).
34. P. Foley and G. M. Whitesides, J. Am. Chem. Soc. **101,** 2732 (1979). P. Foley, R. DiCosimo and G. M. Whitesides, **102,** 6713 (1980).
35. W. J. Irwin and F. J. McQuillin, Tetrahedron Lett. **1968,** 1937 (1968).
36. K. C. Bishop III, Chem. Rev. **76,** 461 (1976).
37. L. Cassar and J. Halpern, J. Chem. Soc. Chem. Commun. **1971,** 1082 (1971).
38. P. G. Gassman and R. R. Reitz, J. Organomet. Chem. **52,** C51 (1973).
39. K. Itoh, Fund. Res. Homog. Catal. **3,** 865 (1979).
40. R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser and C. F. H. Tipper, J. Organomet. Chem. **150,** 295 (1978).
41. R. Barone, M. Chanon and M. L. H. Green, J. Organomet. Chem. **185,** 85 (1980).
42. J. D. Fellmann, R. R. Schrock and G. A. Rupprecht, J. Am. Chem. Soc. **103,** 5752 (1981).
43. K. F. Watterson and G. Wilkinson, Chem. Ind. **1960,** 1358 (1960). T. A. Manuel, S. L. Stafford and F. G. A. Stone, J. Am. Chem. Soc. **83,** 249 (1961).
44. R. H. Grubbs and A. Miyashita, J. Am. Chem. Soc. **100,** 1300 (1978); **100,** 7416

(1978). J. Chem. Soc. Chem. Commun. **1977,** 864 (1977). R. H. Grubbs, A. Miyashita, M. Liu and P. Burk, J. Am. Chem. Soc. **100,** 2418 (1978).

45. J. M. Manriquez, D. R. McAlister, R. D. Sanner and J. E. Bercaw, J. Am. Chem. Soc. **100,** 2716 (1978).
46. P. Binger, M. Cetinkaya, M. J. Doyle, A. Germer and U. Schuchardt, Fund. Res. Homog. Catal. **3,** 271 (1979).
47. C. Krüger and Y-H. Tsay, Cryst. Struct. Commun. **5,** 215 (1976).
48. M. P. Brown, A. Hollings, K. J. Houston and R. J. Puddephatt, J. Chem. Soc. Dalton Trans. **1976,** 786 (1976). A. K. Cheetham, R. J. Puddephatt, A. Zalkin, D. H. Templeton and L. K. Templeton, Inorg. Chem. **15,** 2997 (1976). D. C. L. Perkins, R. J. Puddephatt and C. F. H. Tipper, J. Organomet. Chem. **191,** 481 (1980).
49. J. X. McDermott, J. F. White and G. M. Whitesides, J. Am. Chem. Soc. **98,** 6521 (1976). J. X. McDermott, M. E. Wilson and G. M. Whitesides, *ibid.* **98,** 6529 (1976). G. B. Young and G. M. Whitesides, *ibid.* **100,** 5808 (1978).
50. R. J. McKinney, J. Chem. Soc. Chem. Commun. **1980,** 490 (1980).
51. P. W. Jolly and G. Wilke, *The Organic Chemistry of Nickel,* Vols. 1 and 2 (Academic, New York, 1974, 1975).
52. F. G. A. Stone, J. Organomet. Chem. **100,** 257 (1975). F. G. A. Stone, Accounts Chem. Res. **14,** 318 (1981).
53. C. E. Dean, R. D. W. Kemmitt, D. R. Russell and M. D. Schilling, J. Organomet. Chem. **187,** C1 (1980).
54. P. A. Corrigan and R. S. Dickson, Austral. J. Chem. **32,** 2147 (1979).
55. R. C. Brady III and R. Pettit, J. Am. Chem. Soc. **102,** 6181 (1980); **103,** 1287 (1981).
56. E. L. Muetterties, ***Reactivity of Metal–Metal Bonds,*** ACS Symposium Series, Vol. 155, 1981, p. 273. M. Tachikawa and E. L. Muetterties, J. Am. Chem. Soc. **102,** 4541 (1980). E. L. Muetterties, Catal. Rev. Sci. Eng. **23,** 69 (1981).
57. R. B. Calvert and J. R. Shapley, J. Am. Chem. Soc. **99,** 5225 (1977); **100,** 6544 and 7726 (1978).
58. G. M. Dawkins, M. Green, A. G. Orpen and F. G. A. Stone, J. Chem. Soc. Chem. Commun. **1982,** 41 (1982). M. Green, D. R. Hankey, M. Murray, A. G. Orpen and F. G. A. Stone, *ibid.* **1981,** 689 (1981).
59. G. R. Steinmetz and G. L. Geoffroy, J. Am. Chem. Soc. **103,** 1278 (1981).
60. D. L. Thorn and T. H. Tulip, J. Am. Chem. Soc. **103,** 5984 (1981). K. Isobe, D. G. Andrews, B. E. Mann and P. M. Maitlis, J. Chem. Soc. Chem. Commun. **1981,** 809 (1981).
61. K. A. Azam, A. A. Frew, B. R. Lloyd, Lj. Manojlovic-Muir, K. W. Muir and R. J. Puddephatt, *J. Chem. Soc. Chem. Commun.,* **1982,** 614 (1982).
62. C. E. Sumner Jr., P. E. Riley, R. E. Davis and R. Pettit, J. Am. Chem. Soc. **102,** 1752 (1980). K. H. Theopald and R. G. Bergman, *ibid.* **103,** 2489 (1981). K. C. Ott and R. H. Grubbs, *ibid.* **103,** 5922 (1981).
63. A. D. Clauss, J. R. Shapley and S. R. Wilson, J. Am. Chem. Soc. **103,** 7387 (1981).
64. A. F. Dyke, S. R. Finnimore, S. A. R. Knox, P. J. Naish, A. G. Orpen, G. H. Riding and G. E. Taylor, ***Reactivity of Metal–Metal Bonds,*** ACS Symposium Series, Vol. 155, 1981, p. 259.
65. J. Levisalles, F. Rose-Munch, H. Rudler, J. C. Daran, Y. Dromzee and Y. Jeannin, J. Chem. Soc. Chem. Commun. **1981,** 152 (1981), *ibid.* **1981,** 1055, 1057 (1981).
66. J. Levisalles, H. Rudler, F. Dahan and Y. Jeannin, J. Organomet. Chem. **188,** 193 (1980). F. Garnier, P. Krausz and J. E. Dubois, *ibid.* **170,** 195 (1979).
67. K. H. Theopald and R. G. Bergman, J. Am. Chem. Soc. **102,** 5694 (1980).