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The Organometallic Chemistry of Alkanes

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Contents

I. Introduction

A general class of problem that has continued to attract the attention of inorganic chemists over many years is the coordination and activation of the small molecules of nature by transition-metal complexes. Considerable advances were made in the 1960s and 1970s in understanding how substrates such as H_2, CO, CO_2, R_3SiH, alkyl halides, and olefins can be activated in this way.[1] In each case, catalytic processes,[2] some of considerable commercial importance, have been developed that rely on these initial activation steps. Perhaps the most challenging substrates in this area of chemistry are N_2 and alkanes, both of which are notoriously unreactive. The great importance of both substrates has encouraged study of their behavior with transition-metal complexes. Advances in our understanding of the nitrogen fixation problem[3] during the 1960s and 1970s were not matched by corresponding advances in the alkane area until recently. Only now has a sufficient body of work emerged from which general principles can be drawn.

Robert H. Crabtree was born in London in 1948. He worked with M. L. H. Green at Oxford, obtaining the B.A. in 1970, and with J. Chatt on nitrogen fixation for a D. Phil. at Sussex University in 1973. With H. Felkin at the CNRS, Gif, he was a postdoctoral worker and then Attache de Recherche, looking at H_2 activation by rhodium and iridium compounds. In 1977 he moved to Yale and started work on the alkane problem in the spring of 1978. He received the Corday–Morgan Medal of the Royal Society of Chemistry in 1984, and is now Professor of Chemistry at Yale.

Parts of the area have been included in a number of previous reviews,[4] for example by Parshall[5] and by Muetterties;[6] Shilov[7] has written an interesting monograph. Other areas of transition-metal chemistry are also relevant to this problem, and useful reviews are available, for example, by Bruce[8] on cyclometalation, by Brookhart and Green[9] on C–H···M-bridged species, and by Muetterties[10] and by Somorjai[11] on surface chemistry.

In this review we hope to cover the organometallic chemistry of alkanes. This means that the very important and interesting work on alkane chemistry involving high-valent metal complexes will not be covered in detail. Fortunately there is an excellent recent monograph on this area.[12] C–H activation in substrates other than alkanes (e.g., arenes, phosphines) is only considered to the extent that it can teach us something about the alkane problem itself. The literature is covered up to the beginning of 1985, but some later papers have been included.

II. The Chemical Properties of Alkanes

We shall cover in this section only those properties directly relevant to the alkane activation problem. More detailed discussions are available in the literature.[13]

The unreactive character of unstrained alkanes largely resides in the unavailability both of lone pairs and of empty orbitals. This in turn is a reflection of the fact that carbon and hydrogen both belong to the

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small group of elements that have a number of valence electrons equal to the number of valence orbitals available. The strong bonding between C and H (dissociation energy 90–110 kcal mol^{-1}) means that the HOMO's are deep lying σ bonding orbitals and the LUMO's are high lying σ^* levels, neither easily accessible to an attacking reagent. The low polarity of the C–H bond is also a factor in the unreactivity of alkanes, but the case of fluorocarbons, rivals of alkanes in low reactivity, but having polar bonds, shows that the unavailability of orbitals is the more important factor. It might be argued that H_2 should also be unreactive on these criteria. This is a significant point because many metal complexes are known to activate H_2; we will consider this question of the analogy between C–H and H–H activation below (section IIIE). The tetrahedral disposition of bonds to carbon also places a steric inhibition on those reagents (X in eq 1) which attack the alkane C–H bond, since forming incipient bonds to both C and H involves steric interference between X and the other groups on carbon. Being more accessible, the C–H bonds of alkanes are generally more susceptible to attack than are the C–C bonds. An incoming reagent has the choice of (i) donating electron density to the C–H σ^* orbital, (ii) of abstracting C–H σ-bonding electrons, or (iii) of doing both at once. Strategy i seems to be the least successful approach because nucleophiles do not react with alkanes. Strategy ii is adopted by a variety of electrophilic reagents such as Lewis acids. Strategy iii seems to be the most successful. It appears to be the one adopted by radicals, by carbenes, by metal surfaces, and by the low-valent metal complexes that constitute the chief object of this review. It is likely that for metal complexes, electron withdrawal from the σ orbital is as important or more important than is donation into the σ^*. This is in contrast[3] to the related case of N_2, where the π^* orbitals are the most available for an attacking metal. Nucleophilic metal fragments alone are capable of binding N_2 and mediating subsequent reduction to NH_3. We will see that both nucleophilic and electrophilic metal centers can attack alkanes.

(1)

The second strategy is typified by electrophilic attack on the C–H bond. This occurs in strong acids such as $AlCl_3$,[14] H_2SO_4, HF, and super acids in general[15] and on the acidic sites of certain aluminosilicates and related metal oxides. Since branched alkanes are thermodynamically more stable than linear alkanes, catalytic conversion to the branched isomers is possible. This reaction constitutes an important part of the upgrading of petroleum hydrocarbons, since branched alkanes are more useful in fuels. The intermediates are carbonium ions, which are well-known to undergo facile carbon skeletal rearrangement reactions.[15] A typical example of this reaction is the conversion of any of a variety of $C_{10}H_{16}$ hydrocarbons to adamantane with $AlCl_3$. The reaction is probably initiated by X^- abstraction from an RX (X = halogen) impurity present in the alkane, or by $AlCl_3$ hydrolysis to give free H^+, followed by electrophilic attack on the alkane to give a carbocation which can rearrange to give the thermodynamic mixture of alkanes. Strategy iii is adopted by carbenes, which react not only with C–H bonds of alkanes but also C–Hal, Si–H, N–H, and O–H bonds of various substrates. Singlet methylene shows very little distinction between the various types (primary, secondary, and tertiary) of C–H bond. Hoffman[16] has suggested a reaction trajectory for $CH_4 + CH_2 \rightarrow C_2H_6$ in which initial electrophilic attack by the empty p orbital of singlet CH_2 on the C–H bond is followed by migration of the H on to the CH_2 group. Intramolecular insertions seem to favor those C–H bonds that can achieve a triangular transition state, as we shall see is also true for transition-metal complexes. There seems to be an analogy between the way that the diamagnetic singlet carbenes insert into C–H bonds and the same reaction for diamagnetic low-valent metal species. Both are ligand deficient, both have an empty orbital and a lone pair, and in both cases direct insertion of both nucleophilic as well as electrophilic CR_2 and ML_n fragments into alkane C–H bonds has been found. Paramagnetic triplet carbenes, on the other hand, react via H atom abstraction[17] and radical recombination, like the paramagnetic high oxidation state metal oxo complexes mentioned in section V.

Strained hydrocarbons can also react in ways not available to their unstrained analogues. Cyclopropane is a typical example in which relief of strain drives ring opening.[7,13] Br_2, HBr, and H_2SO_4 react as shown in eq 2–4. In each case the reaction is probably initiated by electrophilic attack on one of the strained C–C bonds.

$$C_3H_6 + Br_2 \rightarrow Br(CH_2)_3Br \qquad (2)$$

$$C_3H_6 + HBr \rightarrow H(CH_2)_3Br \qquad (3)$$

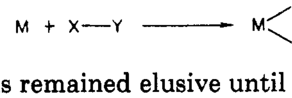
$$C_3H_6 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } H_2SO_4} H(CH_2)_3OH \qquad (4)$$

Before 1980, the vast majority of alkane reactions with transition-metal complexes involved strained alkanes; these are dealt with in section IIIJ.

III. Reactions with Low-Valent Metal Complexes

A. Early Work

During the 1960s interest in the alkane activation problem grew as a consequence of several related developments. The "oxidative addition" reaction was recognized,[1] in which low-valent metal complexes were shown to insert into a variety of X–Y bonds (XY = H_2, HCl, MeI, Cl_2, R_3Si–H) (eq 5). The oxidative addition of C–H bonds remained elusive until the discovery of cyclometalation[8] provided a rich source of such reactions. It was the existance of cyclometalation that offered the most direct indication that alkane activation might be possible. This reaction is simply an intramolecular oxidative addition of a ligand C–H bond to the metal (eq 6). This was first explicitly observed[18]



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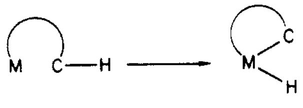
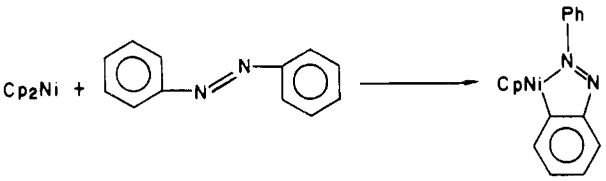


(6)

for the aryl C–H bonds of azobenzene (1963) (eq 7), but the earlier (1960) catalytic synthesis[19] of indazolones from azobenzene and CO must also involve the same reaction (eq 8).



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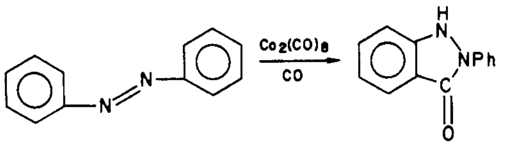
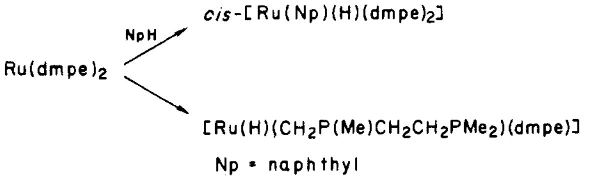


(8)

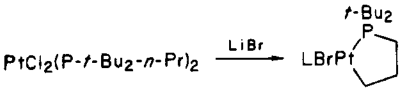
The first example of the cyclometalation of sp^3 C–H bonds came from Chatt and Davidson's[20] 1965 study of "Ru(dmpe)$_2$" (dmpe = $Me_2PCH_2CH_2PMe_2$). They found not only that this complex spontaneously cyclometalates at the phosphorus methyl groups but also that the system reacts with free naphthalene to give *cis*-[Ru(Np)(H)dmpe$_2$] (Np = 2-naphthyl) (eq 9). This



(9)

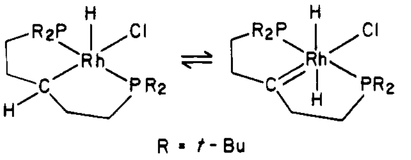
was the first explicit connection between the inter- and intramolecular varieties of C–H bond breaking by transition-metal complexes. This classic paper is also of interest in that the chemistry was worked out almost entirely on the basis of isotopic labeling, IR spectroscopy, and dipole moments, with NMR studies playing a very minor role.

Shaw[21] showed that severe steric congestion in a complex strongly accelerates cyclometalation even of sp^3 C–H bonds (eq 10). This finding will be seen to



(10)

have important implications for the alkane problem in that steric effects appear to influence the choice between alkane activation and cyclometalation (section III I. Recently, cyclometalation has been used to form unusual types of alkylidene complex in the conformationally restricted backbone of certain diphosphines (eq 11).[22]

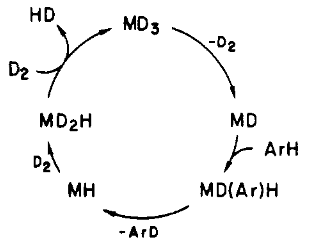


(11)

R = *t*-Bu

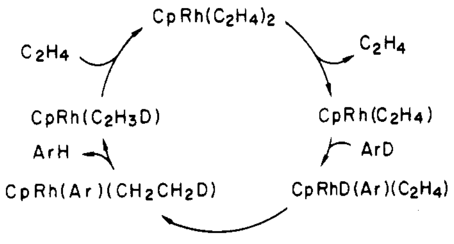
The first steps in the problem of intermolecular C–H activation date from the 1960s. As Halpern[23] remarked at a Faraday Society Discussion in 1968: "the development of successful approaches to the activation of carbon–hydrogen bonds, particularly in saturated hydrocarbons, remains to be achieved and presently constitutes one of the most important and challenging problems in this whole field [of homogeneous catalysis]". In a preparative paper on the rhenium polyhydrides dating from 1969, Chatt and Coffey[24] briefly noted catalytic H/D exchange between $ReH_7(PPh_3)_2$ and C_6D_6. During the same period, Garnett and Hodges[25] and also Shilov et al.[26] started reporting their studies on arene and alkane reactions with the $PtCl_4^{2-}$ system. These electrophilic processes are reviewed in section IIID.

At the same time, the du Pont group entered the area with Tebbe and Parshall's[27] study on H/D exchange in arenes catalyzed by Cp_2NbH_3 and $TaH_5(dmpe)_2$. They proposed that H_2 is lost from these complexes and the coordinatively unsaturated intermediates insert into an arene C–H bond. In accord with this mechanism, deuterium incorporation occurred stepwise, with one exchange per catalytic event (eq 12). The platinum



(12)

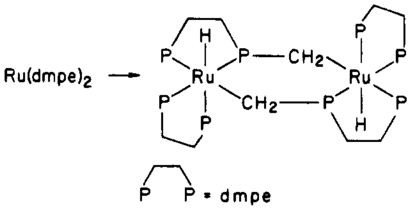
metals also give similar chemistry, $CpRh(C_2H_4)_2$ reacts with C_6D_6 above 115°, leading to D incorporation into the C_2H_4 and Cp ligands.[5b] Ethylene dissociation is implicated as the first step; the subsequent chemistry probably occurs by the general mechanism shown in eq 13.



(13)

Ar = C_6D_5 or $C_5H_4Rh(C_2H_4)_2$

From 1974, the M(O)-alkylphosphine chemistry initiated by Chatt and Davidson[20] a decade earlier came in for detailed reexamination by several groups. Cotton[28a] showed crystallographically that the cyclometalated form of "Ru(dmpe)$_2$" is in fact a dimer of the type shown in eq 14. Both Muetterties[29] and



(14)

P⌒P = dmpe

Schmidbaur[30] attempted to make "Fe(PMe$_3$)$_4$" but found that this species can only be obtained in the cyclometalated form [HFe(η^2-CH_2PMe_2)(PMe$_3$)$_3$]. This was a disappointing finding for workers who were thinking about in the alkane problem because it suggested that even PMe$_3$ is able to cyclometalate. Although cyclometalation had frustrated many efforts to activate alkanes, it might have been hoped that PMe$_3$ would be free of this complication. As will be seen later, the balance between cyclometalation and alkane activation can be altered by moving to different metal systems, but at the time the prospects for a solution based on metal phosphine complexes certainly looked as dark as they had ever been.

In 1978, Tolman, Ittel, and Jesson[31] looked at the "$M(dmpe)_2$" systems for all three members of the iron triad. They found that the complexes originally considered[32] to be $M(dmpe)_2$ (M = Fe and Ru) were in fact the five-coordinate $[((dmpe)_2M)_2(\mu\text{-dmpe})]$ containing a bridging bidentate dmpe group. Exchange with other arenes was studied and Chatt's suggestion that the reaction goes via the unstable $M(dmpe)_2$ fragment was confirmed. The nucleophilic character of "$M(dmpe)_2$" was identified as being an important factor favoring the oxidative addition of C–H bonds to the metal. We will see later that while this is true for such activated substrates as arenes, for alkanes themselves such high nucleophilicity (low ionization potential) is not necessarily required (eq 15–18).

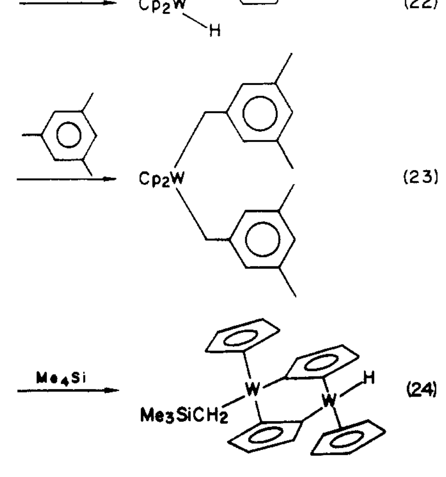
$$\mathrm{Fe(Np)(H)dmpe_2} \xrightarrow{\mathrm{C_6D_6}} \mathrm{Fe(C_6D_5)(D)dmpe_2} \quad (15)$$

$$\mathrm{Fe(Np)(H)dmpe_2} \xrightarrow{\mathrm{PhMe}} \mathrm{Fe(}m\text{- and }p\text{-tolyl)(H)dmpe_2} \quad (16)$$

$$\mathrm{Fe(Np)(H)dmpe_2} \xrightarrow{\mathrm{PhOMe}} \mathrm{Fe(}m\text{- and }p\text{-anisyl)(H)dmpe_2} + \mathrm{Fe(OPh)(Me)dmpe_2} \quad (17)$$

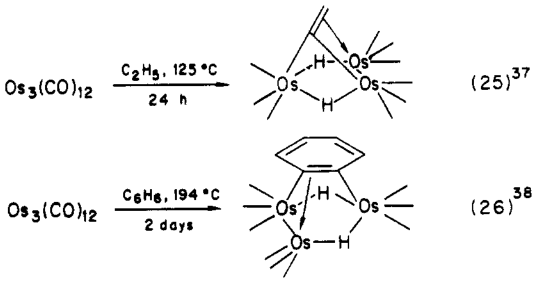
$$\mathrm{Fe(Np)(H)dmpe_2} \xrightarrow{\mathrm{PhCHO}} \mathrm{Fe(COPh)(H)(dmpe)_2} \quad (18)$$

Green[33] made important early contributions in this area by discovering the photoextrusion of H_2 from a metal dihydride, Cp_2WH_2. He used this reaction to activate C–H bonds in a number of molecules[34] (see eq 19–24). The more activated substrates gave the simple oxidative addition product. Even such a weakly activated molecule as Me_4Si also reacted, but in this case in a more complicated way than before. Note that if the substrate is too unreactive to react at all, the complex reacts with itself instead. This result could be taken to suggest the unpleasant possibility that all attempts to activate alkanes might be doomed to failure through deactivation by such a self-reaction, except perhaps if a vanishingly small concentration of metal complex were used. This work came very close to the heart of the problem and the photoextrusion of hydrogen was to play an important role in subsequent alkane chemistry (section IIIF).



Other reasons for pessimism were discussed.[35] For example, the fact that $Pt(PPh_3)_2(Me)(H)$ undergoes intramolecular decomposition to methane even at −25 °C shows that this reaction both has a low activation energy and is thermodynamically favorable. Therefore, the addition of CH_4 to $[Pt(PPh_3)_2]$ is precluded on thermodynamic rather than kinetic grounds. From this second conclusion and the fact that few mononuclear alkyl hydride complexes are stable, it was suggested that unless some special circumstances were encountered, simple oxidative addition was not a promising approach to alkane activation in general. We will see later how this problem has been circumvented in two different ways: trapping an initially formed unstable adduct by subsequent thermodynamically favorable steps and by using photochemistry, or the reductive elimination of an alkane from a preexisting alkyl hydride complex, to gain access to metal species which are thermodynamically much more unstable than is $[Pt(PPh_3)_2]$.

During this period, cluster complexes received serious consideration as alkane activation catalysts. A contemporary view of the problem is provided by a 1978 conference contribution.[36] Certainly, clusters are known to give intermolecular C–H activation reactions, but only with activated substrates. Some early examples were the reaction of cyclooctene with $M_3(CO)_{12}$ (M = Ru or Os) to give $[M_3H_2(C_8H_{12})(CO)_9]$ and of ethylene and benzene with $Os_3(CO)_{12}$ to give the products[37,38] shown in eq 25 and 26. Rather vigorous reaction conditions were required. Cluster complexes have not figured prominantly in alkane chemistry perhaps in part because these complexes are commonly stabilized by CO groups; these tend to bind too strongly for alkanes to be able to compete successfully for any active sites opened up by thermolysis or other means. Thermal cluster fragmentation might well generate suitable mononuclear units, but no case is yet known.



Apart from the "oxidative addition" mechanism, there is a second well-established way in which transition-metal species can react with hydrocarbons: electrophilic aromatic substitution. The earliest case seems to be the reaction of $AuCl_3$ with arenes reported by Kharasch[39] in 1931. This may well also go by arene precoordination

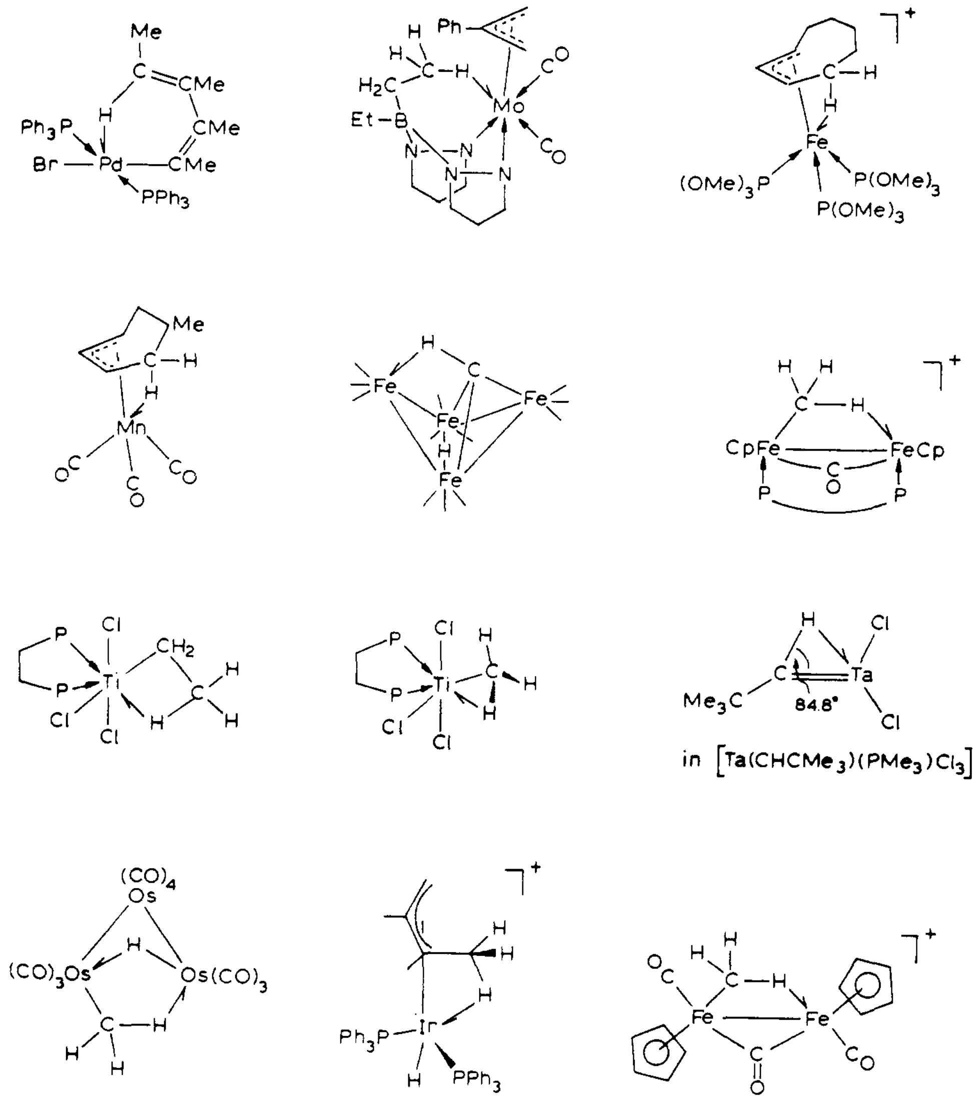
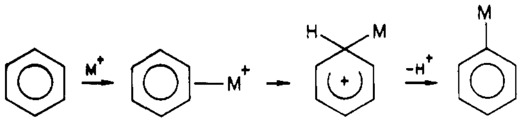


Figure 1. Some examples of complexes containing C–H···M bridges[9] (taken from ref 9 with permission). Copyright 1983 by Elsevier.

as shown in eq 27. Mercury(II), lead(IV), and thallium(III) also undergo this type of reaction.[40]



(27)

B. Complexes Containing C–H···M Bridges

Complexes of this type have been known for more than a decade.[28b,c] They are important because they represent a plausible intermediate stage on the way to oxidative addition of C–H bonds to a metal complex. Regarding them in this light can give us information about the approach to the transition state for the C–H + M reaction. A large number of examples of C–H···M bridges have now been described in a variety of complexes (Figure 1). In each case, the ML_n fragment would have 16 valence electrons or less if it did not have the C–H···M bridge; no 18-electron case is known. The bridging can therefore be seen as a way for the metal to become coordinatively saturated. In the absence of any suitable lone pairs, the C–H bonding pair is donated to the metal in a two-electron, three-center bond. Some degree of d_π–σ^* back-donation may be involved. Cotton[28b] estimated the strength of the interaction as being about 17–20 kcal mol^{-1} by NMR measurements on $[(\eta^3\text{-allyl})H(CO)_2\ (Et_2Bpz_2)Mo]$, which bridges via a methylene group of an ethyl substituent.

Brookhart and Green[9] have comprehensively reviewed the field very recently and have drawn attention to its relation to C–H bond activation, we shall therefore not cover it in detail here. They have also coined the useful term "agostic" to describe such interactions. Crabtree, Lavin, and Holt[41] were interested to see whether the structural data on these complexes could be used to throw some light on the C–H + M → C–M–H reaction trajectory, by using the method pioneered by Bürgi and Dunitz.[42] In this approach, the structures of the C–H···M fragment are compared to see if the system undergoes any systematic changes as the C–H to metal separation, r_{bp}, changes (r_{bp} is a measure of the C–H to metal distance). The trends shown by the data suggest that the C–H bond is not significantly lengthened until the C–H bond approaches very close to the metal. This implies a late transition state. The second feature of interest is that the M–H–C angle at H, 130° (not 180°) at large r_{bp}, falls rapidly as r_{bp} decreases. This implies that at the transition state (which probably has a short r_{bp}) considerable steric interference between the ligands on the metal and the substituents at the carbon of the C–H bond are to be expected. A

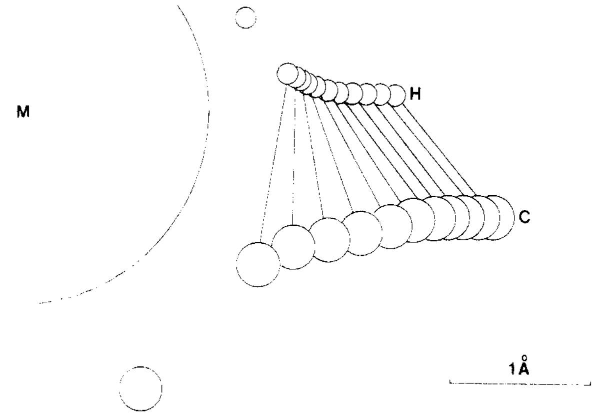


Figure 2. The reaction trajectory for C–H + M = C–M–H deduced from the structures of some of the complexes shown in Figure 1 (see ref 41 for details). The isolated circles are the final positions of C and H in the product alkyl hydride (taken from ref 41 with permission).

pictorial representation of the reaction profile is shown in Figure 2. Experimental evidence for the occurrence of steric effects in alkane activation systems will be discussed in section IIIF. This work has also contributed to an understanding of the factors that decide whether any given system will undergo cyclometalation or activate alkanes instead (see section IIII).

A useful comparison with H_2 can be made at this point. Just as the C–H···M system appears to be an intermediate stage on the way to C–M–H, complexes containing the M(η^2-H_2) group have recently been described.[41b,43,44] There is some evidence[41b] that these, too, are intermediates in the oxidative addition of H_2. In both of the cases M(H_2) and M(HC), the coordinated X–H ligand (X = C or H) seems to be more easily deprotonated than does free X–H; this may throw on the mechanism of heterolytic activation of H_2 and of alkanes.

Valuable theoretical insights into these questions has been provided by Saillard and Hoffmann.[43b] Interaction of H_2 and CH_4 with metal surfaces was also considered in their paper.

C. Alkane Complexes

The existence of C–H···M bridges suggests that it should be possible to have an isolable metal complex of an intact alkane, perhaps chelating via two or three C–H bonds. This would be analogous to the known cases[41b,43] of complexes containing an intact H_2 molecule: e.g., $[(\eta^2\text{-}H_2)W(CO)_3(PCy_3)_2]$. The closest approach to date has been the demonstration[44] that a variety of unsaturated metal carbonyl fragments such as $Cr(CO)_5$ in an alkane matrix give UV–visible spectroscopic evidence for interaction with the matrix material.

D. Electrophilic Systems for Alkane Activation

In 1967, Garnett and Hodges[25] showed that $PtCl_4^{2-}$ catalyzes H/D exchange between arenes and the D_2O/CH_3COOD solvent medium. In 1969 Shilov[45] reported that the reaction was also successful in the case of alkanes. This was a striking and important observation. These authors proposed that homogeneous platinum(II) complexes were responsible for the catalysis, because under conditions in which visible precipitation of metallic Pt took place, the reaction rate fell. The exchange is suppressed by chloride ion, which led to the suggestion that $[PtCl_3(solv)]^-$ and $[PtCl_2(solv)_2]$ are more active species than $PtCl_4^{2-}$ itself. $[Pt(H_2O)_4]^{2+}$ was shown to react more slowly than $PtCl_2$. A whole variety of Pt(II) complexes, even Pt(acac)$_2$ are also active.[7] The order of reactivity of C–H bonds in different substrates is primary > secondary > tertiary, unlike the usual order in the case of radical or electrophilic reactions. Hindered methyl groups react slowly, however. Steric effects such as these are also found in many other systems (section IIIF). Arenes are more reactive than alkanes, but not by much; once again this is observed in other systems (section IIIF).

Unexpectedly, detailed kinetic analysis shows the exchange is multiple. That is to say that more than one hydrogen/deuterium exchange occurs for each contact of the hydrocarbon with the catalyst. For alkanes which can give olefins, one could argue that olefins are intermediates, but multiple exchange occurs even with methane, and so the intermediacy of species containing a Pt=CH_2 group was suggested.[7] Ethane preferentially undergoes multiple exchange at one methyl group before the other. This is difficult to understand, and to account for this, it is necessary to propose that α-elimination of the ethylplatinum group occurs preferentially to β-elimination, contrary to what is usually observed in solution (e.g., the $CpRh(C_2H_4)_2$ system described above). This property of the catalyst is the one most reminiscent of heterogeneous catalysts which also tend to give multiple exchange.[46,47]

Garnett and Hodges[48] not only observed H/D exchange in their early work on arenes but also, in the presence of H_2PtCl_6, chlorination of the arene with concomitant reduction of Pt(IV) to Pt(II) and catalyzed by Pt(II). In 1972, Shilov[49] showed that alkanes could also be chlorinated in the same way. Linear alkanes tend to substitute at the methyl groups. For example, propane gave 3:1 *n*-PrCl/*i*-PrCl. When run in CF_3CO_2H, trifluoroacetate esters are also formed. In the case of cyclohexanes, the major products are arenes, presumably formed by dehydrochlorination of the intermediates. This system has also been made catalytic with Cu^{2+} and air, and up to five catalytic cycles of oxidation were observed.[50] A related catalyst[51] deposited on silica proved to be 10^5 more active than the well-known $CuCl_2$ catalyst for methane chlorination. In general, the selectivity and rate patterns observed in the chlorination chemistry resembles those previously seen in the H/D exchange work.[52] This led to the suggestion that the initial step of both reactions is the same and that the intermediate alkylplatinum species could go on to either product according to the exact conditions.[53] In particular, the RCl is believed to arise from oxidation of Pt(II)–R to Pt(IV)–R by the excess Pt(IV).

Much more recently, aryl complexes[54] of the type $[ArPtCl_4L]^-$ have been isolated from the reactions of ArH with H_2PtCl_6 (e.g., Ar = 2-napthyl; L = NH_3), and the kinetics of the formation reaction studied.[55] A methylplatinum species has even been detected by ^1H NMR in the reaction products[56] of CH_4 and H_2PtCl_6. For the process involving alkanes and Pt(II), Shilov believes that the C–H bond adds to the metal via a classical oxidative addition but that H^+ is rapidly lost from the $Pt^{IV}(R)(H)$ product species to give a Pt(II) alkyl, which is responsible for the chemistry observed; this is essentially equivalent to an electrophilic attack on an alkane. The reactions involving arenes may well involve classical electrophilic aromatic substitution.

In an interesting recent development, Shilov and Shulpin found that irradiation of $PtCl_6^{2-}$ and hexane in AcOH or CF_3CO_2H–H_2O gives a platinum(II) complex of 1-hexene: $[(olefin)PtCl_2]_2$ (**1**).[57] The hypothesis is that **1** is formed by β-elimination in a σ-alkyl Pt(IV) complex. This contrasts with the α-elimination invoked to account for isotopic exchange. The same reaction was attempted with Me_2CO, which lacks β-hydrogens. After the addition of ammonia to stabilize the product, $NH_4[MeCOCH_2PtCl_4(NH_3)]$ was isolated. The photoplatination of toluene gave an exactly analogous *p*-tolyl product. The proposed mechanism for all these reactions involves generation of an active site at Pt(IV) by photoextrusion of Cl^- followed by electrophilic attack on the substrate. Interestingly the ρ^+ value for the reaction with substituted arenes, 1.5, is the same as that for the Ag^+-catalyzed rearrangement of strained-ring compounds (see section IIIJ), also an electrophilic process.

Schwartz[58a] has described some very interesting alkane activation reactions that appear to go by an electrophilic mechanism and so these are best considered in this section. In this work, $Rh(allyl)_3$ is supported on silica, most plausibly as $[Si]$–$ORh(allyl)_2$, which on hydrogenation is believed to give $[Si]$–ORh(allyl)H. At 100 °C D_2/n-C_4H_{10} exchange reactions occur. It was suggested that this may involve hydride abstraction from the alkane by an electrophilic Rh(III). $^{13}CH_4$ reacted with the supported system to give, on protonolysis, butane having a 70% incorporation of ^{13}C.[58b] This was ascribed to coupling of the original allyl ligand with a Rh–$^{13}CH_3$ group. If the intermediate is chlorinated rather than protonated, then $^{13}CH_3Cl$ is obtained. The supported system also catalyzed the CH_4–Cl_2 reaction. The catalyst seems to be relatively stable, and many turnovers are observed. Understandably, characterization of these surface-bound species is not easy, but these new materials are of considerable interest. The reactions observed are quite different from those seen on a classical Rh/SiO_2 heterogeneous catalyst.

The well-known $CoOAc_3/O_2$ system (see section VB) for alkane oxidation and (in the presence of a Cl· donor) chlorination may be mechanistically closely related to those described above, at least to the extent that the initial C–H bond breaking may occur by electrophilic attack (eq 28).

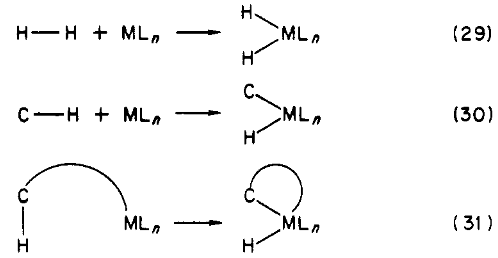
$$\text{C–H} + \text{Co(III)} \rightarrow \text{C–Co(III)}^- + \text{H}^+ \qquad (28)$$

Rosan[59a] has shown that $S_8[AsF_6]_2$, $S_{19}[HS_2O_7]_2$, and $Se_4[HS_2O_7]_2$ react with alkanes in SO_2 solution, presumably below room temperature. In the case of the reaction of S_8^{2+} with CH_4, CH_3SH was detected among the products. Electron transfer is proposed as the first step. Reactions of such cations with Nujol was briefly reported as early as 1969 by Gillespie and Pez;[59b] other related reports are extant.[59c]

E. Thermodynamic Considerations

Before moving further it would be useful to consider the thermodynamic limitations on alkane activation in general. It is important to discuss at this stage just what reactions of alkanes we wish to bring about. Two types of reaction are of interest. The first type involves reaction of an alkane with a metal complex to generate a new metal complex containing an alkane derived fragment, (i.e., a stoichiometric reaction). The second type involves using a metal complex to catalyze some rearrangement or other reaction of the alkane itself.

The most straightforward example of the stoichiometric type would be an oxidative addition of an alkane C–H bond to metal to give an alkyl hydride in analogy to the corresponding reaction of H_2 and to cyclometalation (eq 29–31) Virtually all the known examples of alkyl hydride complexes readily lose alkane. This suggested to several workers (among whom I include myself) that the direct oxidative addition would not prove possible.[35] In fact, important recent work has shown that this direct reaction can occur (see section IIIF below) and so we must examine the assumptions more critically. With hindsight, we can now see that the alkyl hydride product will be stable to loss of alkane if the resulting metal fragment is sufficiently unstable. Norton[60] had pointed this out, although not in connection with alkane activation, during his studies on the complexes *cis*-$OsMe_2(CO)_4$, $OsMeH(CO)_4$, and $OsH_2(CO)_4$. Here the $Os(CO)_4$ fragment is particularly unstable, and this is enough to prevent the classical direct reductive eliminations from occurring. Indeed, if $Os(CO)_4$ did not so easily trimerize to the very stable $Os_3(CO)_{12}$, there can be little doubt that it would activate methane.



(29)

$$\text{H–H} + \text{ML}_n \longrightarrow \text{H}_2\text{ML}_n$$

(30)

$$\text{C–H} + \text{ML}_n \longrightarrow (\text{C})(\text{H})\text{ML}_n$$

(31)

To put it another way, a major reason why alkane activation is observed so rarely is not any great kinetic barrier to the process, but that the alkyl hydride is usually thermodynamically unstable with respect to alkane elimination. The low kinetic barrier and the thermodynamic preference for RH + M rather than R–M–H is most clearly shown by the fact that alkyl hydride complexes commonly lose alkane by reductive elimination under mild conditions. An early idea was that donor ligands could drive the alkane reaction by thermodynamically stabilizing the adduct, which has a higher formal oxidation state than the starting complex. In fact, alkane C–H addition is probably not very oxidizing,[61] and experiment (see section IIIF) shows that strongly electron donor ligands are not required for the observation of a stable adduct. Halpern[62] has been closely associated with the development of these ideas and has published an important short review[62c] very recently. Briefly, he argues that M–C and M–H bond strengths for late d-block transition-metal alkyl and metal hydride complexes probably usually have the following approximate values: ca. 25 kcal/mol for M–C and ca. 60 kcal/mol for M–H. On the basis of these values, H_2 addition would be expected to be exothermic, but alkane C–H addition to be endothermic. M–C bond strengths are as yet only available for a relatively restricted range of complexes,[62] and higher values may be found in the future, especially for sterically uncongested second and third row complexes.

This weakness of the M–C compared to the M–H bond may be due to steric effects. Halpern[62c] has shown that the Co–R bond strength in complexes of the type $RCo(dmg)_2L$ (dmg = dimethylglyoximato-) depends on the size of the axial base L. Structural studies show the dmg groups are subject to sterically induced distortions which are probably responsible for the observed lengthening of the Co–C bond for bulky L groups.

Another factor that may be important in certain cases is the mutual influence of the ligands present. For example, the apparent M–H bond strength must be affected by cis or trans bond-weakening effects on the other ligands present, due to the hydride group; the effects due to a methyl group might well differ in magnitude.

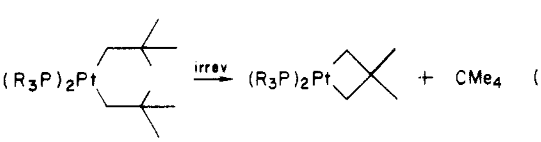
We can now identify the weakness of the M–C bond as the factor that makes the addition of the alkane C–H bond generally endothermic, when the addition of H_2 to the same system is often exothermic.[62c] For f block,[62d] and perhaps early d-block elements, M–C bond strengths are probably higher than for the later d block. We suggest that some of the extra stability of M–C bonds with early metals may arise from C–H···M bridges, in principle possible for all f-block complexes, because 18-electron-rule limitations do not apply.

M–C bonds strengths are notably high for gas-phase species such as $[M-R]^+$, as high or higher than the corresponding $[M-H]^+$ species (see section IVB). This helps to account for the great readiness which with these species break both C–H and C–C bonds of alkanes. The greater M–C bond strength in these cases may be due to the polarization of the methyl group by the metal ion, to the absence of steric effects,[62] and possibly to the formation of C–H···M bridged structures in these alkyls.

Clearly, eq 32 has a ΔH close to zero. An interesting

$$R\text{-}H + M\text{-}R' \rightarrow M\text{-}R + R'\text{-}H \qquad (32)$$

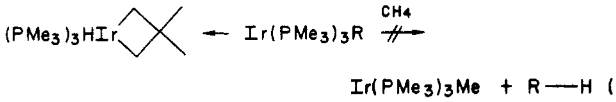
observation by Ibers and Whitesides[63a] is relevant here. They found that eq 33 proceeds only in the forward direction but that the reverse reaction is undetectable under the same conditions. According to the argument



(33)

R = C_2H_5

presented above, there seems at first sight to be no reason why the reverse reaction (which would, of course, be an example of alkane activation) does not occur. Whitesides successfully argued that there should be no particular strain in the metalacyclic product; he also suggested that entropic factors should not be sufficiently unfavorable to account for the observed failure to react. It seems reasonable to say that an important factor in this case is the fact that steric congestion greatly favors cyclometalation (as was discussed in section IIIA; see also section IIII) (eq 34) and that this, in addition to the entropic factor (chelate effect), may be sufficient to account for the observation of eq 33. It



(34)

R = neopentyl

might be thought that $Ir(PMe_3)_3(CH_2CMe_3)$ would be a better candidate for, say, methane activation than the Pt complex of eq 33. Certainly, thermodynamically this would almost certainly be favorable, but attempts to prepare this complex lead to metallacycle formation.[63b] This shows how cyclometalation can deactivate a potential alkane activation system (see also section IIII).

The catalytic reactions are easier to analyze thermodynamically in the sense that the relevant thermodynamic data are accurately known for the organic reagents and products and we do not have to be concerned with M–H and M–C bond strengths which are still not as well determined as one would wish. One very simple approach to functionalizing alkanes (see section IIIF) is to dehydrogenate them to alkenes. Since the chemistry of the latter is very rich, we have in principle a two-step route to any of a large variety of functionalized products. Unfortunately the reaction of eq 35

$$CH_3\text{—}CH_3 \rightarrow CH_2\text{=}CH_2 + H_2 \qquad (35)$$

is thermodynamically unfavorable at moderate temperatures (<ca. 200 °C), as is obvious from the fact that the reverse reaction, olefin hydrogenation, proceeds essentially to completion under ambient conditions (1 atm of H_2, 25 °C); ΔH(hydrogenation) is of the order of 30–32 kcal mol^{-1} for most alkenes. Clearly, the hydrogen from the alkane has to be transferred to some hydrogen acceptor with a ΔH above 30 kcal mol^{-1}. Reaction with oxygen to give water might be an ideal solution to the problem, except that the majority of organometallic species are air sensitive. Olefins are satisfactory from the thermodynamic point of view, and we introduced t-BuCH=CH_2 (tbe) for this purpose (eq 36). Apart from other virtues, this olefin has an ex-

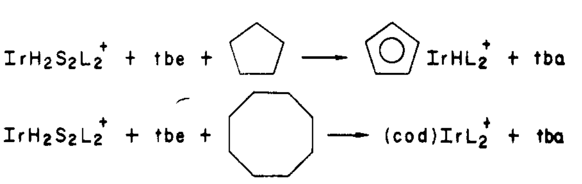
$$\text{alkane} + \underset{\text{tbe}}{t\text{-BuCH=CH}_2} \rightarrow \text{alkene} + \underset{\text{tba}}{t\text{-BuCH}_2\text{CH}_3} \qquad (36)$$

ceptionally high heat of hydrogenation (33 kcal mol^{-1})[64] which makes it unusually well suited for this application. The reactions can be catalyzed by a number of transition-metal complexes (section IIIF), and they proceed best in neat alkane as solvent. As will be seen in section IIIF cyclooctane gives exceptionally good results in catalytic dehydrogenation. As a result of medium ring conformational effects, this alkane has an unusually low heat of dehydrogenation (+23.5 kcal mol^{-1}).[65] The formation of aromatic compounds by multiple dehydrogenation steps confers an additional driving force on the overall process, although a hydrogen acceptor is still needed, even for the dehydrogenation of cyclohexane to benzene.

Electrophilic C–H activation of R–H by M^+ to give $M\text{-}R^+$ and a proton or $M\text{-}H^+$ and the R^+ ion has been suggested as the mechanism for the reactions of section IIID. It is also a well known pathway for H_2 activation.[62c] It avoids some of the thermodynamic limitations of the direct oxidative addition in that a base can help drive the process. It can also occur when oxidative addition is not possible. A plausible pathway for such electrophilic processes is binding of the C–H or H–H bond to the metal to form an "agostic" system. These are thought to be subject to deprotonation,[9,41b] perhaps because the partial electron donation from the X–H bond to the metal leaves the H with δ^+ character.

F. Alkane Activation by Oxidative Addition

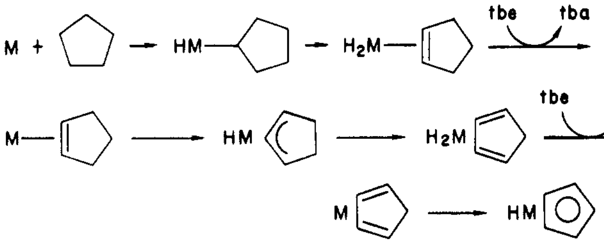
In 1979, Crabtree, Mihelcic, and Quirk[66] reported the dehydrogenation of a number of alkanes by $[IrH_2(Me_2CO)_2L_2]BF_4$ (**2**, L = PPh_3) and *tert*-butylethylene (tbe) in chlorinated solvents (eq 37a and 37b). They proposed that the initial step is oxidative addition of an alkane C–H bond to the metal. Previous model studies on olefins as substrates had identified this iridium acetone complex as particularly active in olefin dehydrogenation. The role of the tbe is in part kinetic, to dehydrogenate, and so activate **2**, and in part thermodynamic, to provide additional driving force for the overall reaction. The rationale for this approach was the belief that any intermediate alkyl hydride formed by oxidative addition would be unstable and would need to be trapped by subsequent β-elimination to give the corresponding olefin. The resulting metal dihydride would then be dehydrogenated by the tbe and the cycle could continue until a stable product had been formed. In support of these ideas, some of the proposed intermediates were prepared independently and observed directly (eq 38).[67] In order to be able to effect these multiple dehydrogenation steps, *multiple* coordinative unsaturation is required at the metal. A 16-electron ML_n fragment would give an 18-electron $(R)(H)ML_n$ species in which subsequent trapping by β-elimination would not be possible. **2** has a dihydride unit that can be removed by tbe, as well as two labile acetone ligands, so that it is a masked form of the 12-electron species "IrL_2^+". More recently it has been shown that the same system is accessible, though less efficiently, from $[IrH(\eta^5\text{-}C_6H_7)L_2]^+$, $[Ir(diene)H_2L_2]^+$, and $[Ir(\eta^4\text{-}naphthalene)L_2]^+$, by loss of C_6H_6, alkene, or naphthalene, respectively.[68] Tbe is one of the very few olefins that is an effective hydrogen acceptor, and it was only discovered after an extensive search. It is successful probably because it lacks allylic C–H bonds, which if cleaved by the metal would lead to an allyl complex and so block the active sites on the metal. Tbe is also sufficiently bulky so it does not bind strongly (ethylene is an ineffective hydrogen acceptor, for example), and we had previously found tbe to be the olefin most rapidly hydrogenated by the related hydrogenation system: $[Ir(cod)PCy_3(py)]BF_4/H_2/CH_2Cl_2$.[69] Arylalkenes are ineffective hydrogen acceptors because they undergo an unusual rearrangement;[70] e.g., styrene gives $[(\eta^6\text{-}PhEt)IrL_2]$ (eq 39).



(37a)

(37b)

S = Me_2CO; L = PPh_3; tbe = *t*-BuCH=CH$_2$; tba = *t* BuEt



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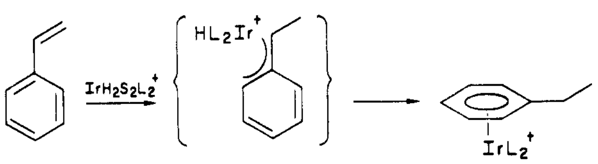
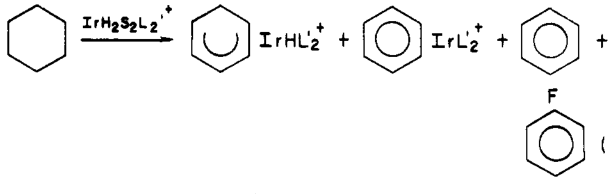


(39)

As we shall see in section IIIL, the presence of metallic surfaces formed by decomposition of the metal complex needs to be excluded before such a system can be considered to be homogeneous. The presence of metal (colloidal or bulk) was excluded in this case on the basis of a variety of tests, including light-scattering studies, and by conducting the reaction in the presence of metallic mercury (see section IIIL), among others.[67] Radical intermediates were considered unlikely because no dicyclopentyl nor cyclopentyl chloride was formed, as might have been expected by dimerization or Cl atom abstraction from the solvent. Carbocationic intermediates were excluded because the tbe exclusively gave tba and no Wagner–Meerwein rearrangement products such as would have been expected if carbocations were involved. Finally, the observed selectivities of such systems (e.g., eq 43) are not consonant with electrophilic attack. The system is closely related to a hydrogenation catalyst[69] that is known to proceed via the standard Wilkinson-type[71] hydrogenation cycle and so the "retro-hydrogenation" mechanism shown above was proposed.

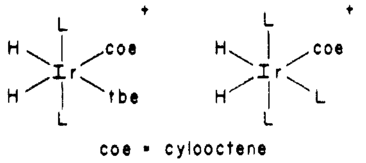
Although cyclooctane and cycloheptane also react (to give $[Ir(cod)L_2]^+$ (cod = 1,5-cyclooctadiene) and $[Ir(\eta^5\text{-}C_7H_9)HL_2]^+$), cyclohexane did not. Examination of the products from the cyclohexane reaction showed that complexes of the type $[(IrHL_2)_2(\mu\text{-}Cl)_3]^+$ were formed (they were also formed in small amounts even in the successful alkane reactions), and this in turn suggested that the chlorinated solvent had led to complete deactivation of the metal complex in the case of the more slowly reacting cyclohexane. On moving to cyclohexane as "solvent" this deactivation pathway is avoided and now cyclohexane reacts, ultimately to give free benzene, although only in stoichiometric amounts (eq 40). A new and slower deactivation pathway now appears to take over: P–C hydrogenolysis.[73] This accounts for the appearance of fluorobenzene (derived from $(p\text{-}FC_6H_4)_3P$) in the products. We will return to this process in discussing the kinetic problems of alkane activation (section IIII).



(40)

L' = (*p* -FC_6H_4)$_3$P

These systems are not catalytic perhaps because they involve multiple dehydrogenations. The structures shown below illustrate this point for cyclooctane.

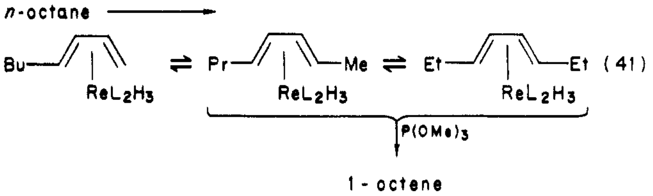


The "IrL_2^+" system in principle allows tbe to bind and dehydrogenate the metal via the olefin dihydride intermediate shown, and the cyclooctene can go on to give 1,5-cyclooctadiene (cod) which binds so strongly it is not released. In an "IrL_3^+" system, in contrast, the corresponding intermediate, shown above, is 18-electron, and cyclooctene (coe) now needs to dissociate to allow the tbe to bind and dehydrogenate the catalyst. This in turn implies that the final product will be coe, not cod, and the reaction may be catalytic not simply stoichiometric. Felkin[74] had previously observed catalytic alkene formation from what he believes is a 14-electron "ReH_3L_2" fragment (see below), which would be consistent with this view. $[IrH_2(CF_3CO_2)L_2]$, a neutral alkane-soluble system which probably also gives a 14-electron fragment, "$IrL_2(OCOCF_3)$", is much more satisfactory.[75b] Up to 28 turnovers of coe can be obtained in this system (L = PCy_3) at 20 °C under photolysis, but since ca. 70% of the catalyst is recovered at the end of the reaction, a much larger number of cycles are in principle possible. Linear alkanes are also dehydrogenated, but less efficiently and to a mixture of alkenes, mostly internal. The arylphosphine catalysts seem to be more liable to P–C cleavage than the cyclohexylphosphine systems, but some P–C cleavage occurs even here. In an attempt to avoid phosphine-containing systems, $[(dct)IrCl]_2$ (dct = *sym*-dibenzocyclooctatetraene) was studied, but only traces of cyclooctane dehydrogenation were observed.[75c]

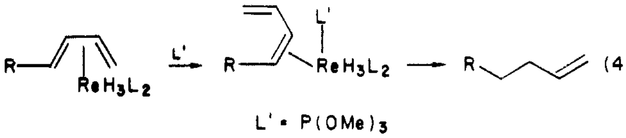
In the photolytic systems, catalytic olefin production is observed even in the absence of tbe, if N_2 is passed through the solution to remove the H_2 that is formed. In this case, the light itself provides the thermodynamic driving force to dehydrogenate the alkane.[75b]

Felkin et al.[76] were able to apply the same type of *tert*-butylethylene chemistry discussed above to the case of $ReH_7(PPh_3)_2$. While cyclopentane gave the type of product that had previously been observed for iridium, the C_6–C_8 cycloalkanes gave free olefin for the first time.[74] Initially this was obtained only in stoichiometric amounts, but later improvements of the experimental conditions (lowering the concentration of the complex) gave up to 9 turnovers of cyclooctene at 80 °C and 1.6 turnovers even at 30 °C.[77] The homogeneity of the catalyst was confirmed, and a mechanism proposed in which the olefin dissociates after two C–H bond breaking steps have occurred. The H_2 abstracted from the alkane and now bound to the metal is then removed by tbe, and the cycle can continue.

A particularly interesting result[78] was obtained with the linear C_5–C_8 alkanes which each gave rapidly interconverting mixtures of all possible 1,3-diene complexes. For octane, the three possible isomers are all formed in a 2:2:1 ratio (eq 41). Remarkably, on heating with excess $P(OMe)_3$, the corresponding 1-alkenes were formed in 95% yield and 98% selectivity. Clearly the $P(OMe)_3$ induces selective hydrogenation of the diene. The most reasonable explanation seems to be that $P(OMe)_3$ selectively displaces the terminal double bond of the terminal diene complex and two hydrogen atoms bound to Re are transferred to the 3,4-C=C group because it is also still bound to the metal; the equilibrium is then drained off through this reactive isomer (eq 42).



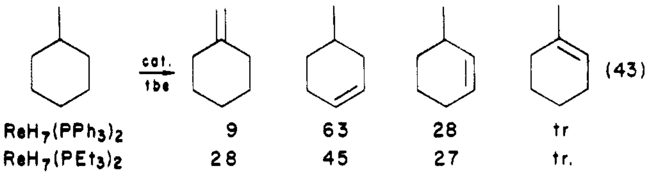
(41)



(42)

Other polyhydrides were also investigated and IrH_5L_2 and RuH_4L_3 (L = $(p\text{-}FC_6H_4)_3P$) shown to be active for the conversion of cyclooctane and tbe to cyclooctene at 150 °C; 40–70 catalytic turnovers were observed over several days. Mercury did not inhibit the reactions.[79]

Useful information was obtained on the selectivity of the rhenium system by studying[77] the dehydrogenation of methylcyclohexane (eq 43). Only traces of the most stable product olefin 1-methylcyclohexene were observed. Instead, products arise from attack at the methyl group and the unhindered 3- and 4-positions of the ring. The reaction appears to be selective for initial attack at the least hindered C–H bonds, followed by β-elimination. Neither carbonium ion nor radical mechanisms can be invoked to explain these results. The direct insertion of the metal into the alkane C–H bond, with the severe steric requirements of that process (see section IIIB), is almost certainly involved.



(43)

Caulton et al.[80a] showed that photolysis (366 nm) of ReH_5L_3 (L = PMe_2Ph) liberates L rather than H_2, and in the presence of tbe as hydrogen acceptor, they found that cyclopentane could be dehydrogenated to give $CpReH_2L_2$.

It is not yet known what step in the catalytic systems discussed above is turnover limiting. Trapping of the initial alkyl hydride by β-elimination is a possible candidate. This would explain why cyclooctane is dehydrogenated faster than cyclohexane; the MCCH unit in a metal cyclohexyl system is rigidly noncoplanar, while the cyclooctyl could more easily attain the coplanarity required for β-elimination.[80b,66] All of the systems discussed up to now in this section are believed to operate via the direct insertion of the metal into a alkane C–H bond. The presumed initial adduct was never observed, however, because the high degree of coordinative unsaturation at the metal encouraged further dehydrogenation.

In 1982, a particularly important development was the discovery by three groups of two different but related methods of generating fragments sufficiently reactive to attack solvent alkane C–H bonds and give a stable alkyl hydride product. The intermediates are

TABLE I. Relative Rates of Reaction of $Cp^*M(PMe_3)H_2$ with Various Hydrocarbons on Photolysis[a]

hydrocarbon	rel rate/C–H bond M = Ir	 M = Rh
benzene	4.0	19.5
cyclopropane	2.65	10.64
n-hexane	*b*	2.7[c]
	b	0.2[d]
cyclopentane	1.6	1.1
neopentane	1.14	
cyclohexane	1.0	1.0
cyclodecane	0.23	
cyclooctane	0.09	

[a] $Cp^* = C_5Me_5$. Data on a per hydrogen basis from ref 81 and 84b. [b] Primary to secondary attack ratio is 2.7:1 on a per hydrogen basis. [c] Primary. [d] Secondary.

presumably 16-electron, but it has not yet proved possible to observe or characterize them directly. This was particularly significant because it allowed the critical first step in alkane activation to be studied in detail. It also demonstrated the unanticipated stability of the alkyl hydride adduct.[81,82]

$$Cp^*Ir(PMe_3)H_2 \xrightarrow[\text{R–H}]{h\nu} Cp^*Ir(PMe_3)(R)(H) \quad (44)$$

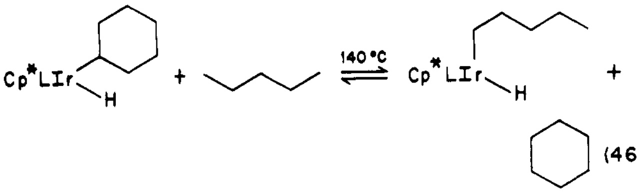
$$Cp^*Ir(CO)_2 \xrightarrow[\text{R–H}]{h\nu} Cp^*Ir(CO)(R)(H) \quad (45)$$

$$Cp^* = C_5Me_5$$

The first of these reports was by Janowicz and Bergman,[81] who showed that photolysis of Cp^*IrLH_2 ($Cp^* = C_5Me_5$, L = PMe_3) in a wide variety of alkanes gives the corresponding alkyl hydride adducts with extrusion of H_2. These adducts eliminate alkane thermally at 110 °C and allow exchange with other alkanes. This demonstrates that the reaction is also possible via thermally generated intermediates. Significantly, competitive cyclometalation of the PPh_3 analogue was observed, but the corresponding PMe_3 complex gave only alkane activation (see also section IIII for a fuller discussion of the question of alkane activation versus cyclometalation). The cyclohexyl hydride has now been structurally characterized.[83]

Photolysis in C_6D_6 gave only $Cp^*Ir(L)D(C_6D_5)$ and H_2, with no H/D exchange. This rules out photoextrusion of H atoms, for example. Radical mechanisms are also ruled out by the observed attack at the ring C–H bonds as well as at the substituent methyl groups in *p*-xylene; essentially only benzylic attack is expected for radicals. The relative rates of attack at different types of C–H bond were determined (Table I). Alkanes and arenes differ suprisingly little. It is interesting to see that cyclooctane, which is so reactive in the catalytic dehydrogenation systems, is one of the least reactive substrates here; steric factors may be involved since "$Cp^*Ir(PMe_3)$" is probably a more sterically congested system than "$M(PPh_3)_2$".

A mixture of neopentane and cyclohexane-d_{12} gave less than 10% crossover, as expected for a direct insertion of a photogenerated "Cp^*IrL". The isotope effect deduced from these results is $k_H/k_D = 1.38$ which is consistent with the proposed mechanism. Propane gives both primary and secondary insertion products; the statistically corrected relative reactivity is 1.5:1 for attack at a primary over a secondary C–H. Heating the mixed primary and secondary products from pentane at 110 °C leads to rearrangement to give the thermodynamically more stable *n*-pentyl hydride complex. The alkyl hydride complexes tended to lose alkane when attempts were made to functionalize them with a variety of reagents, but treatment with bromoform gave the stable alkyl bromo analogues. The neopentyl complex reacted with $HgCl_2$ with transalkylation to give the functionalized derivative $t\text{-}BuCH_2HgCl$. As mentioned above,[84] it has been shown that an equilibrium between different alkyl hydrides and their corresponding alkanes can be established thermally. From the equilibrium constants and the known C–H bond energies it is possible to infer that the primary M–C bond in the *n*-pentane adduct is 5.5 kcal/mol stronger than the secondary M–C bond in the cyclohexane adduct (eq 46). This suggested that a hydrido methyl complex might be particularly stable, and so perhaps accessible via a thermal exchange reaction. A direct photolytic reaction in the presence of methane, which gave a methyl hydride adduct in Graham's system (see below), proved unsuccessful here, but heating the cyclohexyl hydride at 150 °C with 20 atm of CH_4 in cyclooctane gave the methyl hydride, the "thermodynamic sink" in the system.[84a]



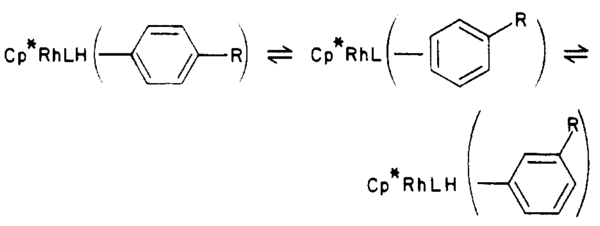
(46)

Cp^*IrL also reacts with C_2H_4 to give $Cp^*IrL(CH_2{=}CH_2)$ and $Cp^*IrL(CH{=}CH_2)H$.[83] Surprisingly, the ethylene complex does not rearrange to the vinyl hydride under the reaction conditions and so is not an intermediate in the formation of the latter. Faller and Felkin[79] have also reported direct vinyl C–H bond activation in tbe by $IrH_5(PPr_3)_2$ in an H/D exchange experiment in C_6D_6: *trans*-*t*-BuCH=CHD was the major product. The thermodynamic advantages of arene activation probably also apply to the vinyl case, and the process may be important in olefin reactions in general.

In an independent study, Hoyano and Graham[82] photolyzed $Cp^*Ir(CO)_2$ in neopentane to give the neopentyl hydride $Cp^*Ir(CO)(R)(H)$ with loss of CO. This in turn could be converted to the alkyl chloro complex with CCl_4. Methane was also shown to react,[85] in the first instance by using 8 atm of CH_4 over a perfluorohexane solution of the dicarbonyl. The same reaction was also observed for the unsubstituted cyclopentadienyl complex $CpIr(CO)_2$.

Graham, Rest[86] et al. have more recently reported CH_4 activation at 12 K by irradiation of $IrCp^*(CO)_2$ in a CH_4 matrix. This demonstrates how low the kinetic barrier to alkane activation must be in this system.

Jones and Feher[87a] studied a related rhodium complex $Cp^*Rh(PMe_3)H_2$ and found that photolysis gave insertion into both arene and alkane C–H bonds. In the arene case, they noted an unusual 1,2-rearrangement in the product which they ascribed to the intermediacy of an η^2-arene species (eq 47). In the case of *n*-propane, they found that at −55 °C irradiation in the liquid alkane gave the *n*-propyl hydride, which decomposed at −15 °C unless converted to the corresponding bromide with bromoform. The exclusive formation of



(47)

the *n*-propyl species suggests that exchange is probably occurring as in the iridium system, but at a temperature over 150 °C lower in this more labile rhodium case. A fuller study by the same authors concluded that arene activation may occur via prior η^2-coordination. A free energy diagram for alkane vs. arene activation was derived from kinetics and equilibrium studies. The Rh–Ph bond was shown to be 12.5 ± 1 kcal mol^{-1} more stable than the Rh–Me bond in the $Cp^*Rh(PMe_3)R(H)$ system.[87b]

Bergman et al.[84b] have also studied this system. They find that it has greater selectivity between different types of C–H bonds than does the Ir analogue (Table I). Direct bromination of the alkyl hydride complexes led to the formation of free alkyl bromide in 70–85% yield. An interesting thermal rearrangement of the cyclopropyl hydride to the rhodacyclobutane was observed.[83] Unexpectedly, the rearrangement occurs even in benzene, which suggests that free "Cp*RhL" is not formed because C_6H_6 would be expected to trap this intermediate. An $[\eta^3\text{-CpRhL}(C_3H_7)H]$ may be involved.

Hoffmann et al.[43b] have suggested that C–H addition to square-planar ML_4 is favored by folding back two trans L groups and that this may be the reason why the isolobal CpML fragments are so reactive.

Kaska[88] has dehydrochlorinated the five-coordinate cyclometalated Rh(III) hydrido–chloro complex $Rh((t\text{-}Bu_2PCH_2)_2C_6H_3)HCl$ with $NaN(SiMe_3)_2$. In cyclohexane, one of the products formed is identified as the five-coordinate cyclohexyl hydride; this is unexpected because such a species might have been anticipated to β-eliminate to give cyclohexene and the corresponding dihydride.

Bergman et al.[83] have recently been able to generate the transient "$CpReL_2$" (L = PMe_3) by irradiation of $CpReL_3$. Significantly, only methane, cyclopropane, and primary alkane C–H bonds will add to these more bulky rhenium bis(phosphine) systems. In cyclohexane, cyclometalation of L is observed. The more bulky pentamethylcyclopentadienyl analogue directly attacks methane and cyclopropane, but not n-hexane or cyclohexane, where cyclometalation occurs. The cyclometalated species are not inert, but give back the reactive transients on heating; these can be trapped with C_6H_6 or CH_4.

These results require us to abandon the earlier view that alkane activation by oxidative addition to give an alkyl hydride complex should be thermodynamically unfavorable and not be observed. In the case of the alkane dehydrogenation chemistry, only a small equilibrium concentration of alkyl hydride is required, because the subsequent thermodynamically favorable steps should trap even a small equilibrium concentration. In the second approach described above, in contrast, the metal fragment is generated as a high-energy species, either photochemically or thermally; given a sufficiently unstable metal fragment, formation of the alkyl hydride can now become thermodynamically favorable. We should also consider the possibility that metal–carbon bonds in some of the species involved in the successful alkane activation systems are stronger than those in stable complexes for which measurements are available. We emphasize that the successful systems are sterically uncongested, a situation most likely to lead to the formation of strong M–C bonds.[62] Addition of R—H across a C=C double bond or coupling of two R—H fragments to give R—R has not yet been observed in these systems, but it appears possible in principle.

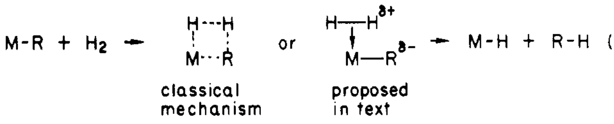
G. Alkane Activation by a Four-Center Mechanism

A different approach to making a reaction with alkane C–H bonds thermodynamically favorable is to choose a metal that is known to form alkyls with strong M–C bonds. Main-group and early d-block alkyls (e.g., $AlEt_3$, $D(\text{M–C}) = 66$ kcal mol^{-1}; $TaMe_5$, $D(\text{M–C}) = 64$ kcal mol^{-1})[89] and probably also lanthanide and actinide alkyls fall into this class.

Watson[90] was the first to observe alkane activation among this group of metals. She used $^{13}CH_4$ to follow the exchange reaction of eq 48. Such reactions are

$$Cp^*_2LuCH_3 + {}^{13}CH_4 \rightarrow Cp^*_2Lu^{13}CH_3 + CH_4 \qquad (48)$$

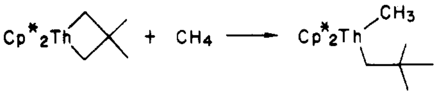
usually assumed to take place via a four-center transition state, as is common for these elements, rather than the oxidative addition pathway favored by the late d-block elements. Just as we suggested above that a molecular hydrogen, $M(\eta^2\text{-}H_2)$, complex might be an intermediate in heterolytic H_2 and C–H activation in the late d-block metals, a similar intermediate looks very reasonable here. For methane activation, a methane complex containing a C–H···M bond and, for H_2 activation, a dihydrogen complex seem to have all the requisite properties. The formation of such complexes requires Lewis acidity but not back-donation from the metal. The removal of electrons from the H–H or C–H bonds gives the H δ^+ character, making it liable to deprotonation,[9,41b] and the Ln–R groups can be considered as strong bases suitable for such a deprotonation (eq 49). Another significant feature of organo



(49)

f-element chemistry is that although the metal can be sterically coordinatively saturated, it can virtually never be electronically coordinatively saturated in the sense that the inert-gas configuration is never attained. The restrictions imposed on organo d-element chemistry by the existence of the 18-electron rule are therefore lifted for these elements.

More recently, Marks et al.[91] have reported a productive methane reaction with a $(C_5Me_5)_2Th$ metallacycle (eq 50). That this reaction goes in the forward direction, rather than the reverse, is perhaps a reflection of the fact that M–C bond strengths are greater for methyl



(50)

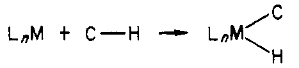
than for primary alkyls and also that the steric congestion decreases on going to the product.[91b] Careful thermochemical work leads to D(Th–alkyl) values of 70–80 kcal/mol, much larger than for the d block.[62e]

H. Other Systems

The electrochemical reduction of $Rh(dpe)_2^+$ in the presence of deuteriated alkane has been reported[92] to give $RhD(dpe)_2$. It is proposed that a $Rh(dpe)_2$ radical is formed, which abstracts D from alkanes. The reaction may in reality be more complicated than this, however, because one would not normally expect the Rh–H bond dissociation energy of $RhH(dpe)_2$ to exceed that of an alkane C–H bond; this would of course be necessary for the direct abstraction to be thermodynamically possible.

I. Kinetic Considerations

Why was it that the alkane activation reactions of sections IIIF and IIIG took so long to be discovered, given the long-standing interest in the area? It certainly was *not* the existence of any large intrinsic kinetic barrier to the reaction



$$L_nM + C{-}H \rightarrow L_nM{<}^{C}_{H} \qquad (51)$$

This is demonstrated most dramatically by the remarkable observation of photoactivation of methane by $Cp^*Ir(CO)_2$ at 12 K[86] and by the relatively small kinetic selectivity between different types of C–H bonds that is usually observed in the successful alkane activation systems.[84] Even before these recent discoveries it was clear that alkyl hydride complexes tend to decompose rapidly to alkane, suggesting the reverse reaction (alkane activation) would have no very great kinetic barrier.[35]

As we saw in section IIIA the problem had consistently been that the metal tended to activate C–H bonds in its own ligands by cyclometalation.[8] This is presumably due to the entropic advantage to be gained in an intramolecular reaction (the chelate effect) and also the high thermodynamic stability of the cycloadduct. In looking at the successful reactions of sections IIIF and IIIG, it is easy to overlook the reaction that ought to have taken place but did not, as illustrated by Sherlock Holmes' celebrated remark[93] about the incident of the dog in the nighttime. As a reviewer aptly put it in reviewing our initial paper on the subject: "why is it that all other systems cyclometalate and do not react with alkanes, but this one does not cyclometalate and does react with alkanes." This is, in the view of the present author, one of the important remaining problems in alkane activation. Fortunately, promising working hypotheses are emerging from recent studies, which we shall now describe.

Up to 1982, one might have argued that cyclometalation was occurring in competition with alkane activation, but that it was reversible and was therefore not observed in the ultimate thermodynamic products, such as $[CpIrHL_2]$ or $[CpReH_2L_2]$. Recent studies[72] have shown that there is in fact very little D incorporation into the PPh_3 groups in the dehydrogenation of cyclohexane-d_{12}, suggesting that cyclometalation is slow. For the alkane/$h\nu$/Cp^*IrLH_2 and related systems, however, the only product is the alkyl hydride where L = PMe_3, but cyclometalation does occur for PPh_3.[81,83] As shown by Muetterties,[29] PMe_3 can cyclometalate, so why does it not do so here?

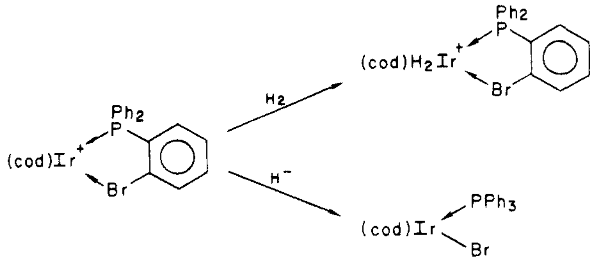
Two lines of approach give us some clues. Jones and Feher[94] extended the alkyl chain (R) of the phosphine groups in $[Cp^*RhH_2(PMe_2R)]$ until, for R = n-Pr, cyclometalation becomes competitive with alkane activation. Kinetic and equilibrium studies showed that while alkane activation is kinetically favored, cyclometalation is the thermodynamically preferred pathway. This is a very important first step toward an understanding of this problem. We still need to understand the physical origin of the higher barrier for cyclometalation in the Rh system and why cyclometalation is the kinetically favored path in so many other systems. Our results[41] on the C–H + M reaction trajectory, mentioned in section IIIB, suggest a possible physical origin for the higher kinetic barrier for cyclometalation. This study helps to establish the widely held view[43b] that the transition state for C–H activation is triangular. It is therefore more easily accessible for an intramolecular reaction with free alkane, than for an intermolecular reaction with a phosphine C–H bond, because excessive strain is involved in adopting a conformation which yields a triangular transition state. If the alkyl chain on the phosphine is long enough (e.g., n-Pr) to allow a C–H bond of the terminal methyl group to adopt this conformation, the cyclometalation is favored.

As discussed in section IIIA, cyclometalation in phosphines is strongly driven by steric congestion,[21] no doubt because the degree of congestion falls in the approach to the transition state. This is because the bulky groups on phosphorus tend to bend away from the metal as the much less bulky group, which contains the C–H bond to be broken, approaches the metal. For alkane activation, in contrast, the degree of congestion rises in the transition state, because an external substrate molecule has to approach the metal, and so a high degree of congestion at the metal suppresses rather than encourages the alkane reaction. We[41] therefore proposed (and others[62c,63a] have made related suggestions) that the balance between alkane activation and cyclometalation is decided by two factors. First, the conformational effect which favors alkane activation over cyclometalation, and second, steric congestion which favors cyclometalation over alkane activation. In systems having a "normal" degree of steric congestion (e.g., "Cp_2W", $Ir(PPh_3)_3Me$, or $[Ir(PMe_2Ph)_4]^+$)[95] cyclometalation is favored. It is notable that both our own system and Felkin's are of the "ML_2" type and therefore unusually sterically uncongested. These activate alkanes even when L = PPh_3. The "Cp^*ML" systems, being more congested, cyclometalate where L = PPh_3 but not where L = PMe_3. "Cp_2W", being more congested still, does not activate alkanes at all. Bergman[83] has recently studied "Cp^*ReL_2"; in line with these arguments, cyclometalation is competitive with alkane activation in this system even for L = PMe_3.

Given that cyclometalation can be eliminated as a deactivation pathway by moving to sterically uncongested systems, what other deactivation reactions can limit catalyst turnover? Notable among these is P–C cleavage, which probably occurs by a direct oxidative addition as discussed by Hoffman.[96] Equation 40 shows a case where it has been observed in an alkane activation system; we have subsequently seen similar chemistry for the catalytic system based on $[IrH_2(CF_3CO_2)L_2]$. A recent review by Garrou[73] considers this reaction in detail.

Degradation of phosphines has tended to limit the range of application of homogeneous catalysis to problems of commercial significance. Alkane activation provides a searching test of the stability of the catalyst, because of the unreactivity of the alkane. An important item on the agenda of homogeneous catalysis over the next few years will be the solution to this problem. Can new types of degradation-resistant phosphines be synthesized, or will we be forced to move away from phosphines to some more resistant class of ligands. Several candidate ligands (e.g., $C_6F_5PMe_2$,[75a,80c] PMe_nAd_{3-n},[80c] $PMe_n(CH_2Ad)_{3-n}$,[80c] and $P(OCH_2)_3CR$[80c] (Ad = 1-adamantyl)) have been unsuccessful, either because of facile P–C cleavage or solubility problems. Advances in this area could have significant commercial impact. Also relevant to the question of catalyst degradation is the Shilov[49–57] system (see section IIID). Here the ligands are usually Cl^-, H_2O, and acetate, all relatively robust in character. This suggests the general solution of using simpler complexes even if more forcing conditions are then required for reactivity. There is an analogy here with the very robust classical heterogeneous catalysts, which can be regarded as metal atoms having other metal atoms or the support oxide ions as ligands.

Other deactivation pathways occur in alkane activation systems. Our own early work was carried out in halogenated solvents such as $ClCH_2CH_2Cl$.[66] We were surprised the metal was not completely deactivated by attack of solvent C–H and C–Cl bonds. Some insight into this problem was obtained when it was found that halocarbons coordinate to the iridium cation to give complexes such as $[IrH_2(IMe)_2L_2]BF_4$.[97] These seem to be the first crystallographically characterized halocarbon complexes. It was also shown[97b,98] that the cationic complex $[(cod)Ir(PPh_2\textit{o}\text{-}C_6H_4\textit{B}r)]^+$ "oxidatively" adds H_2 at −80 °C but fails to attack the coordinated C–Br bond even at 100 °C. In contrast, HCO_2^- adds H^- to the same complex; C–Br cleavage then occurs at once at 25 °C to give the neutral complex $[(cod)Ir(PPh_3)Br]$ as final product (eq 52). This suggests that it is the positive charge on the metal in $[IrH_2(Me_2CO)_2(PPh_3)_2]^+$ that protects it from reacting with C–Cl bonds of the solvent.



(52)

Selectivity in the alkane activation reactions of sections IIIF and IIIG seems to be determined largely by steric effects. The suggestion that the high steric sensitivity of the reaction originates from a proposed side-on transition state was discussed in section IIIB. Steric effects may also be responsible[62b] for the greater M–C bond strengths of primary over secondary metal alkyls. These, in turn, determine the position of equilibrium in the alkane exchange reactions[85,88] of eq 46, which are under thermodynamic control.

The fact that C–H activation is so much more common for arenes than for alkanes may either be due to arene precoordination[87] (contrary views[62c] have been expressed, however) or simply to the fact that M–R bonds seem to be much stronger when R = aryl than when R = alkyl. To the extent that this effect appears in the transition state, the reaction will be accelerated. More importantly, many more activations will be thermodynamically favorable for the arene than for the alkane case. Where a system activates both alkanes and arenes, no very large kinetic preferences have been seen.[84] The reason for the greater strength of M–Ar over M–alkyl probably resides in the π-bonding possible in the aryl case and in the greater electronegativity of the aryl compared with the alkyl group.

The wide range of types of metal complex that insert into alkane C–H bonds is an interesting feature of the results reported in section IIIG: nucleophilic (Cp^*MLH_2), electrophilic ($[IrH_2(Me_2CO)_2L_2]^+$), and borderline (ReH_7L_2, $CpIr(CO)_2$) complexes all appear to react by oxidative addition. This suggests that the ability to activate alkanes may prove to be a much more common property of transition-metal complexes than has generally been thought. The alkane reaction has been found so rarely, not because of any kinetic problem with the oxidative addition itself, but because the deactivating side reactions discussed above tend to divert the metal from reaction with the alkane. If these are suppressed, then the alkane reaction may become the expected process for an unsaturated transition-metal fragment, although thermodynamic factors may prevent an alkyl hydride complex from being the stable ultimate product.

We may summarize the requirements for an ML_n system to be able to bring about the alkane activation reactions of sections IIIF and IIIG as follows: (A) The system must be coordinatively unsaturated or, for dehydrogenation and other catalytic reactions, have the potential for multiple coordinative unsaturation. (B) The second-row and especially the third-row metals are preferred because of their strong M–C and M–H bonds. Early d-block and f-block metals may also be advantageous because of their strong M–C bonds. (C) The ML_n system must be sterically uncongested. (D) The ligands L should be sufficiently cyclometalation resistant to prevent this deactivation reaction. (E) As well as the empty orbital specified in A above, a filled orbital is required to interact with the C–H σ^* orbital. (F) Precoordination of the alkane may be desirable. Keeping the alkane concentration high, as neat solvent, for example, is clearly advantageous.

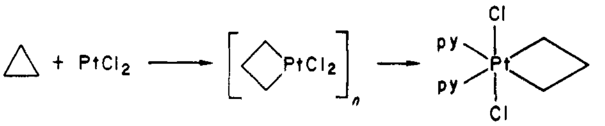
J. C–C Bond Breaking in Ligands and Strained Alkanes

C–C bond breaking in alkanes is of interest because this reaction can lead to skeletal rearrangement or cracking. Such processes are important in petroleum refining, for example, because branched alkanes are more useful fuels than are linear ones. Industrially, much of this chemistry is based on Lewis acids, but transition metals have been implicated in some heterogeneous skeletal rearrangement reactions of alkanes.

In the homogeneous realm, only very recently have C–C bonds in unstrained alkanes been activated and then only by an indirect method.[99] Previously, all reports had dealt either with highly strained alkanes or with cycloinsertion (eq 53), the analogue in C–C activation of cyclometalation in C–H activation chemistry. Gas-phase studies involving C–C cleavage are discussed in section IV.

(53)

The first example of a reaction of a strained alkane (indeed of an alkane of any type) with a metal complex dates from Tipper's[100] 1955 report of the reaction between $PtCl_2$ and cyclopropane to give a product formulated as $[PtCl_2{\cdot}C_3H_6]_2$ (eq 54). The platinacyclobutane structure was only elucidated in 1961 by Chatt,[101] using a combination of NMR and IR studies on the bis(pyridine) adduct. Mason[102] also confirmed the structure crystallographically. Chatt[101] had shown that a further reaction takes place with refluxing benzene to give a product later characterized crystallographically as **3**.[103] This reaction has only recently been adequately explained in mechanistic terms (eq 56).



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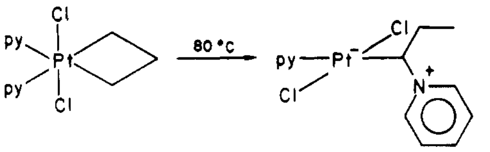

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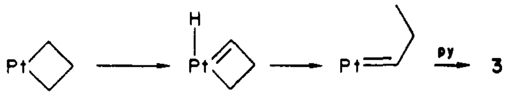

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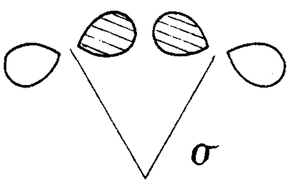
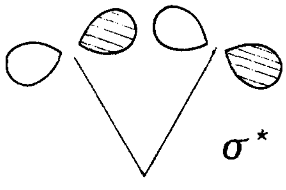
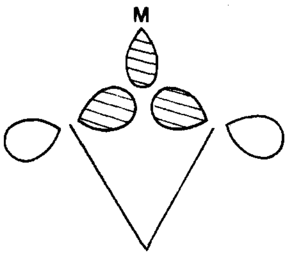
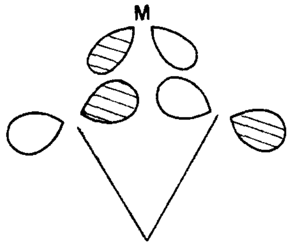
The Walsh[105] model of cyclopropane adequately accounts for the high reactivity of this alkane. The HOMO and LUMO are shown below.



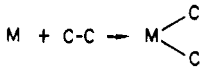


This allows interaction with both the metal d_σ and d_π orbitals.



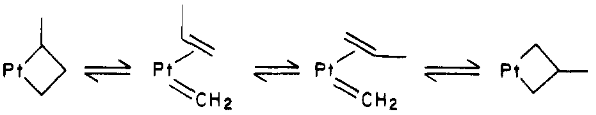


The rarity of alkane C–C bond activation arises in part from the fact that two relatively weak M–C bonds are formed in the process, and so the overall process is usually endothermic (eq 57). One way for this to become thermodynamically feasible is to arrange for a compensating relief of strain on going to the product. This is essentially the reason that cyclopropanes and, to a much smaller extent, cyclobutanes are so reactive. That this is not the universal outcome of cyclopropane reactions is shown by the fact that Bergman's C–H activation chemistry (section IIIF) was first discovered with cyclopropane, a case in which precedent would have suggested that C–C not C–H bond breaking would occur. More recently, Bergman[83] has reported the rearrangement of the initial C–H activation product of cyclopropane reaction with $Cp^*Rh(PMe_3)H_2$. The final product is a C–C cleaved metallacycle which appears to be formed without alkane dissociation from rhodium. This gives us a clue as to the type of metal fragment likely to attack C–C bonds in cyclopropane. Since the σ^* orbital is relatively high and inaccessible, electrophilic metals, like $PtCl_2$, are kinetically more likely to attack the C–C bond than nucleophilic ones, like "Cp*IrL". In accord with this view, McQuillin[106] found that the presence of electron-withdrawing groups on the cyclopropane suppresses the C–C activation reaction.



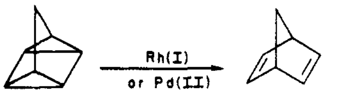
$$M + C\text{-}C \rightarrow M{<}^{C}_{C} \qquad (57)$$

Structurally, the platinacyclobutane shows a large distortion in which the two C–C bonds are unequal: 1.48 (9) and 1.82 (9) Å for $[PtCl_2py_2(CH_2)_3]$. Carried to an extreme, this distortion would produce a carbene–olefin complex (eq 58). The facile rearrangements of these platinacycles at 60 °C have been attributed to such a transformation.[107]



(58)

Since 1967, reactions between metal complexes and a large number of strained alkanes have been reported,[108] for example, quadricyclane to norbornadiene (eq 59).[109] Halpern[110] was able to show that when $[Rh(CO)_2Cl]_2$ was used, one of the organometallic intermediates in the rearrangement undergoes CO insertion and can be trapped (eq 60). Alternatively, if not trapped, it could undergo a retro-oxidative coupling reaction to give norbornadiene directly.



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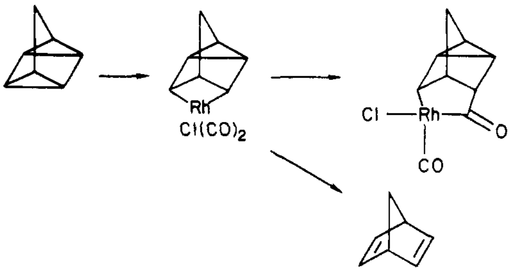
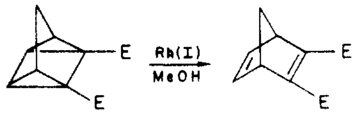


(60)

Hogeveen[111] has provided evidence that the $AgClO_4$-catalyzed version of the reaction does not go via the same type of mechanisms implicated for Rh(I). The facile reduction or hydrolysis of $AgClO_4$ to give traces of acid may have been responsible for some of the chemistry observed in such studies. Whether H^+ or Ag^+ is the active species, however, these reactions seem to go via ionic mechanisms as suggested by the following trapping experiments.



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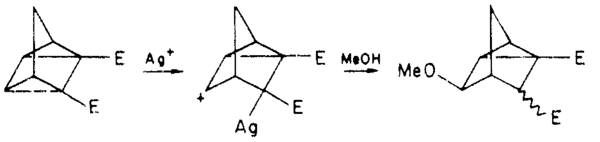
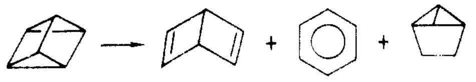


(62)

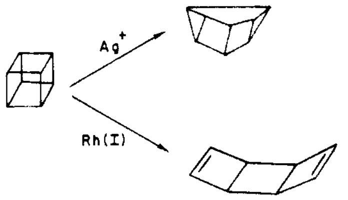
E = CO_2R

Kinetic studies also suggested that a preequilibrium was important in the Rh(I) case. An edge-bound Rh–cyclopropane complex was suggested, but ester groups can also act as ligands[112] and so this possibility cannot be excluded.

The closely allied rearrangement of prismanes to Dewar benzenes is also known (eq 63).[113] A wide variety of products can be formed, depending on conditions.


(63)

Rearrangements of cubanes can give two different types of products, depending on the mechanism adopted.[114] The ionic mechanism, with Ag^+ catalysis, gives cuneane and the retro-oxidative coupling route, with Rh(I), gives tricyclooctadiene (eq 64). Palladium(II) can give either product, depending on conditions. The Ag^+-catalyzed version of the reaction is far more sensitive to substituents ($\rho^* = -1.5$) than is the Rh(I) version ($\rho^* = -0.5$), because the former involves ionic intermediates.[115] Once again a trapping experiment with $[Rh(CO)_2Cl]_2$ led to isolation of a stable insertion product (eq 65).[116] The following rearrangement is catalyzed by Vaska's complex (eq 66). The bis(cyclopropane) is said to form an edge-bound chelating cyclopropane complex with Ziese's salt; a metallacycle of some sort is much more likely.[117] Bicyclo[2.1.0]pentanes are rearranged to cyclopentenes by Rh(I) but not by silver ion (eq 67).[118,119] Bicyclo[3.1.0]hexanes and bicyclo[4.1.0]heptanes behave similarly.[108]



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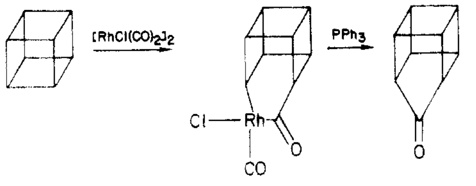

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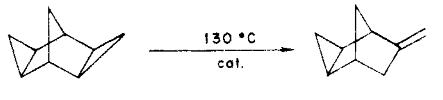

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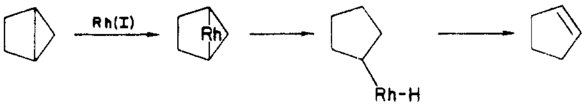
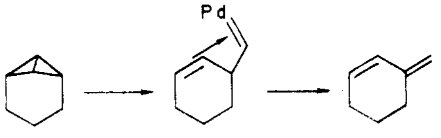


(67)

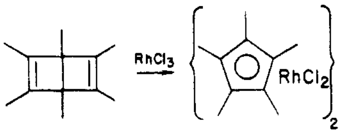
The rearrangement of the bicyclobutanes has been extensively studied. Four different reaction paths have been proposed to account for the complexity of the products formed.[120] Carbene intermediates have been proposed; free carbenes have been formed from diazoalkanes in the presence of the transition-metal catalysts and have been shown to give a similar product distribution. As early as 1972, NMR studies led Dauben[121] to suggest that an organometallic intermediate he observed in the rearrangement of 4 is the alkylidene–olefin complex 5. An excellent review of this area by Bishop[108] is available.



4 5

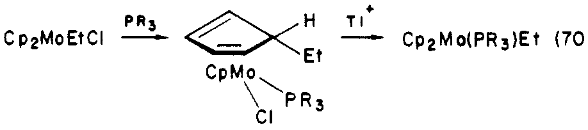
(68)

Very many examples of C–C bond cleavage in ligands is also known. We will only discuss here those cases most relevant to the alkane problem. Maitlis[122] showed how a pentamethylcyclopentadienyl complex could be formed from hexamethyl-Dewar benzene (eq 69).



(69)

Green[123] observed a most interesting reversible rearrangement in which an ethyl group migrates reversibly to and from a cyclopentadienyl ring (eq 70). More recently a related observation has emerged from studies in metal atom chemistry (eq 71).[124] Eilbracht[125] has perhaps studied these types of reactions in most detail (eq 72).



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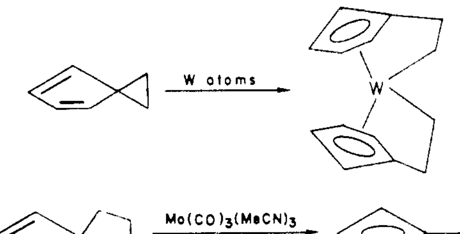
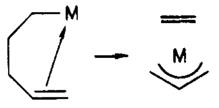


(71)

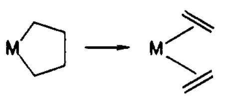
(72)

Rearrangements of pentenylnickel complexes to allylmetal ethylene complexes have also been proposed[126] to account for certain skeletal rearrangements of dienes catalyzed by nickel complexes (eq 73). Grubbs[127]



(73)

showed how metallacyclopentanes and -hexanes decompose with C–C bond fission (eq 74 and 75). Both α- and β-cleavage were shown to be operating. β-C–H bond cleavage would have been favored if the β-C–H bonds were accessible to the metal, but in their absence C–C bond breaking takes place instead.



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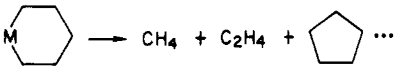
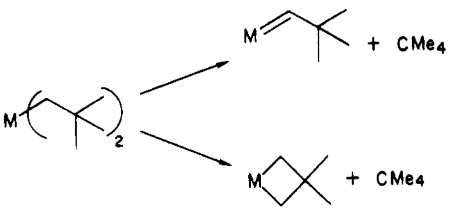


(75)

Formation and cleavage of C–C bonds is slow but can occur in alkylaluminum compounds (eq 76). This is

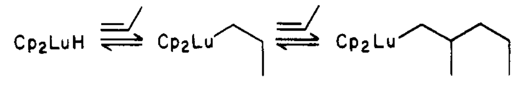
$$Al(CH_2CMe_3)_3 \rightarrow Al(CH_2CMe_3)_2Me + Me_2C{=}CH_2 \quad (76)$$

a reflection of the fact that Al–C bond energies are comparable with those for Al–H. A d-block transition metal would tend to break C–H, not C–C bonds,[63] because the M–C bonds are weaker in this case[62] (eq 77).



(77)

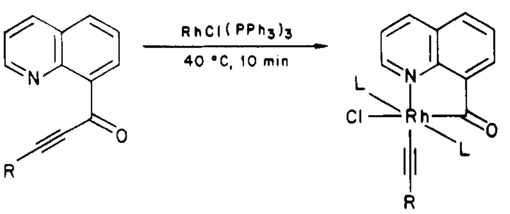
Watson[128] made the very interesting observation that lutetium, an f-block transition metal, readily makes and breaks C–C bonds in coordinated alkyl ligands (eq 78).



(78)

This is relevant to the mechanism of Ziegler–Natta polymerization,[129] which is most commonly catalyzed by the early d-block metals. M–C bond strengths for f-block and early d-block transition elements may be higher than for the later d block.

Suggs[130a] has reported on a very interesting case of C–C cleavage in the late transition metals. Here an sp^2–sp C–C bond is cleaved in a situation where this bond is held close to the metal by a quinoline group and there are no C–H bonds available (eq 79). An intermolecular version of this reaction occurs at elevated temperatures.[131] More recently, 8-quinolinyl alkyl ketones have been shown to undergo C–C cleavage at 25–90 °C on reaction with $[Rh(C_2H_4)_2Cl]_2$ (eq 80).[130b] Labeling studies showed that concomitant C–H activation was not involved. Addition of PPh_3 caused reductive elimination to give the starting ketone.



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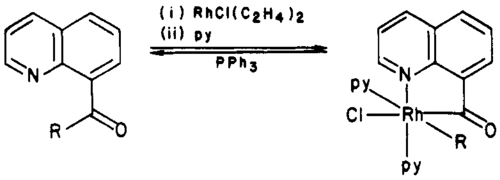
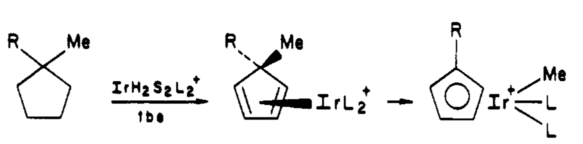


(80)

Flood[132] has observed cyclobutane ring C–C bond cleavage in (1-methylcyclobutyl)methylplatinum(II) complexes, a reaction which is facilitated both by ring strain and by the chelate effect.

K. C–C Bond Breaking in Unstrained Alkanes

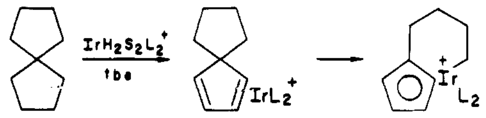
Very recently, Crabtree and Dion[99] have reported a reaction sequence which leads to indirect C–C bond cleavage in an unstrained alkane by combining the alkane dehydrogenation reactions discussed in section IIIF with the alkyl migration reactions discussed above (eq 70).



(81)

S = Me$_2$CO; L = PPh$_3$; R = Me or Et; tbe = t-BuCH=CH$_2$

Where R = Et, the methyl group prefers to go endo to the metal, and this is the group that preferentially migrates. In the case of diethylcyclopentane, C–H activation occurs at the diene stage, in preference to C–C bond cleavage, by cyclometalation of a PPh$_3$ group. By tying back the alkyl groups as a spiroalkane, C–C bond cleavage once more takes over (eq 82).[133] Thermodynamically, C–H cleavage is still preferred and C–C bond cleavage is only possible because of the simultaneous formation of the aromatic ring, which must add 25 kcal/mol of extra stability to the product. Kinetically, the reaction appears to be slower than C–H activation and higher temperatures are needed (150 °C) than is the case for C–H activation in an analogous system (cyclopentadiene gives CpIrHL$_2^+$ below 0 °C). This is consistent with the fact[60] that a metal dimethyl complex is usually much stabler to reductive elimination than is a methyl hydride, because reductive elimination is simply the reverse of the corresponding activation reaction. The hydrogen atom, bonding as it does via a 1s orbital, can presumably more easily migrate and eliminate that can two methyl groups where rehybridization at each carbon must be required in the transition state (eq 83 and 84).



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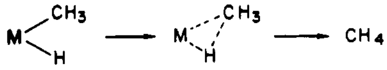

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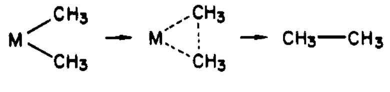
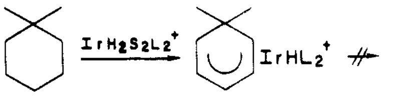


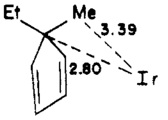
(84)

As in the case of catalytic alkane dehydrogenation, here too, multiple sites of coordinative unsaturation are required to activate C–C bonds by this type of route, because the 1,1-dialkyl diene intermediate complex must have an electron count of 16 or less. In case of dimethylcyclohexane, the corresponding intermediate, now 18-electron does not undergo C–C cleavage (eq 85).[99]



(85)

In the case of the intermediate $Ir(C_5H_4(Me)(Et))L_2^+$ a crystal structure[133] shows that the carbon–carbon bond between the quaternary carbon and the endo methyl group is well within the sum of the van der Waals radii from the metal and may be interacting with it to some extent. This might be considered as an example of an "agostic" C–C bond, but further comparative data will be required before a decision can be made.



6

The activation of C–C bonds in unstrained alkanes by a d-block transition-metal complex may *require* C–H activation to precede C–C breaking. It is likely that if any metal complex is able to accomplish this reaction directly, it will contain an f-block or early d-block element, because, as mentioned above, these have the strongest M–C bonds.[89]

L. Alkane Activation by Metal Surfaces and the Question of Catalyst Homogeneity

Alkane reactions with metal surfaces is a vast area, far too large to do more than mention here.[11] Nevertheless these reactions undoubtedly involve organometallic intermediates, albeit surface bound. The existence of such reactions was also one of the chief motivating factors that led to the search for homogeneous alkane chemistry. Yet the existence of such facile alkane reactions on metal surfaces also means that it is prudent to check the homogeneity of any ostensibly "homogeneous" catalyst for alkane reactions or risk misinterpreting one's work. This is also a problem in other areas of homogeneous catalysis but does not yet seem to have been fully recognized. The novelty and interest of a homogeneous catalyst for alkane conversion diminishes if it is later shown that the reaction is proceeding by well-known chemistry on metal surfaces formed in the partial decomposition of the metal complex involved. The problem is most grave for systems involving platinum, because this is one of metals most active in heterogeneous reactions and one of the metals that most readily precipitates from its compounds.

It is not surprising that a clean metal surface should be so reactive. It has a closely spaced set of unoccupied potential binding sites, each of which is a highly coordinatively unsaturated metal. Nickel film, for example, is known to catalyze H/D exchange between D_2 and alkanes at −50 °C.[134] Dehydrogenation, dehydrocyclization,[135] and isomerization[136] reactions have all been known for many years, especially on the platinum group metals. Structural data at the molecular level on the nature of the organometallic intermediates is beginning to be obtained.[11] The structures are often reminiscent of those known in discrete cluster complexes.[10] In particular, bridging alkylidenes and alkylidynes seem to be present and may play a significant role. Mechanistic details at the molecular level are elusive because the systems are much harder to study than are reactions of complexes in solution.

In order to discover whether the active species in a "homogeneous" catalyst is really a metal surface, it might be thought that a simple visual check for any dark precipitated metal would be satisfactory. Unfortunately, this is not so because the metal surfaces may all be present in the colloidal form (particulate metal in a stable suspension where $r = 10–10^3$ Å). When this happens, the appearance of the "solution" can easily give the deceptive impression of a soluble system. Highly catalytically active preparations of colloidal platinum metals can be light yellow, and be stable to precipitation of metal in visible form. Colloidal preparations can also pass through micropore filters and survive centrifugation. In short, a catalyst may appear to be a clear stable solution, but still owe all of its activity to the present of metal surfaces.

Maitlis[137] has suggested a filtration method to characterize catalyst homogeneity, but this is likely to be satisfactory only in cases where bulk metal is precipitated. Collman[138] has covalently bound substrates to polystyrene, arguing that only homogeneous catalysts can penetrate the pores. Although the polymer will probably exclude bulk precipitated metal, colloidal preparations can contain particles of small radius (10–80 Å is common), small enough to enter into the pores of most polymers. Anton and Crabtree[139] have used a combination of physical methods such as light scattering, chemical selectivity tests such as $ArNO_2$ hydrogenation, and selective poisons such as *sym*-dibenzocyclooctatetraene (which poisons homogeneous catalysts) and metallic mercury (which poisons heterogeneous catalysts). The latter, originally suggested by Whitesides,[140] is probably the quickest and easiest method. It relies on the long-established fact[141] that Hg atoms can be absorbed on to bulk metallic catalysts and poison them. Experimentally, a variety of homogeneous catalysts are unaffected.[139] By these criteria, even well-known "homogeneous" catalysts, such as the McQuillin[142] system for nitroalkane reduction, are in fact preparations of colloidal metal. As in all mechanistic studies, reliance on a single method or lack of rigor in the design and interpretation of the experiments can give misleading results. These methods have as yet been applied to very few alkane conversion catalysts, and further work in this area is desirable.

IV. Alkane Reactions with Metal Atoms and Ions

A. Reactions in Matrices and by Metal Vapor Synthesis

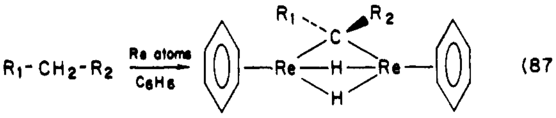
The use of metal atoms as synthetic reagents in inorganic chemistry is a relatively recent development. In this technique, metal vapor is cocondensed at a cold surface with ligand vapor. On warming, metal complexes, as well as free metal, are isolated. Usually metal–metal recombination tends to predominate over metal–ligand recombination unless the ligand rapidly forms strong bonds to M. Alkanes are not usually very effective ligands. Klabunde[143] was the first to describe an alkane reaction from a metal atom reaction of this sort. He found that codeposition of Ni atoms and pentane leads to a solid product containing nickel, carbon, and hydrogen in the ratio 2–5:1:2. Hydrogenation or hydrolysis produced C_1–C_5 alkanes, so the alkane framework had undergone cracking, reminiscent of the well-known heterogeneous cracking processes on nickel. Klabunde suggested that surface reactions on nickel crystallites were responsible for the chemistry observed. Skell[144] found that Zr atoms codeposited with neopentane gave a residue which on deuteriolysis gave t-$BuCH_2D$ and polydeuterated C_2–C_4 hydrocarbons. He suggested that the C_5 product arises from a neopentylzirconium species. These results illustrate a difficult mechanistic problem common to many of the atom condensation experiments. In some of the homogeneous chemistry described in previous sections, we saw that special care had to be taken to exclude the possibility that metal surfaces were mediating the alkane chemistry observed. In metal vapor synthesis work, bulk metal is often present in the matrix and so the same problem recurs. Radiation from the furnace may also give photochemical reactions. Characterization of the matrix species that are undergoing reaction by physical methods is therefore desirable to help characterize the reaction mechanistically. Pearson[145] used Mössbauer spectroscopy to try to do this in the case of an Fe–CH_4 matrix. He suggested that although isolated iron atoms do not react, iron dimers do so to give a product showing Fe–H bands in the IR.

The photoexcitation of metal atoms has been a rich source of reactive excited state species capable of giving reactions with alkanes. As early as 1929, Taylor and Hill showed that mercury vapor can act as a photosensitizer for alkane reactions in the gas phase. This was developed by Steacie,[147] who showed that the $^3P_1$ excited state of atomic Hg abstracts an H atom from an alkane RH. Both H_2 and R_2 are formed by recombination reactions, although at 400 °C the R· radical can also undergo thermal rearrangements with C–C cleavage.

Billups[148] showed in 1980 that photoexcitation of Fe atoms in a methane matrix led to a reaction for the product of which he suggested the structure $HFeCH_3$. Ozin[149] looked at this reaction in more detail and found that the reaction can be reversed by subsequent photolysis at a different wavelength (eq 86). Photoexcited

$$\mathrm{Fe} + \mathrm{CH_4} \underset{400\ \mathrm{nm}}{\overset{300\ \mathrm{nm}}{\rightleftharpoons}} \mathrm{H{-}Fe{-}CH_3} \qquad (86)$$

Cu(^{2}P) was also found to react with methane in a matrix at 12 K. The initial photoadduct, proposed as $HCuCH_3$ on IR and ESR evidence, subsequently decomposed photolytically to CuH and CuMe.[150] Clearly, as discussed in section IIII, the kinetic barrier for C–H activation is low. It is interesting that the initial alkyl hydride adduct appears to be thermally stable. Probably the very low steric congestion of the system allows the M–C bond in the adduct to be sufficiently strong to make MeMH system thermodynamically stable with respect to CH_4 + M. The entropic advantage to dissociation is, of course, much less at 12 K than at room temperature. Green et al.[151,152] have approached this problem by cocondensing metal atoms with an alkane/ligand mixture. For the first time in metal atom work, this has allowed the isolation of crystalline organometallic species in two cases, shown in eq 87 and 88. The bridging carbene product is of particular



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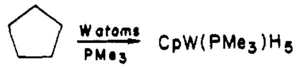


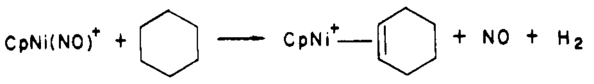
(88)[152]

significance because alkanes can, it is believed, chemisorb on metal surfaces in the form of bridging alkylidenes and alkynes[10,11] (see section IIIL). The activation of alkane C–H bonds in the presence of arene C–H bonds is presumably possible because the arene cannot give a bridging carbene, the thermodynamic sink for the system.

These types of reactions are likely to be quite general. More recently, Green and O'Hare[15] have shown that osmium atoms react with isobutane and benzene to give $[(C_6H_6)_3(\mu_2\text{-}H)_3Os_3[(CH_2)_3CH]]$ in which the trimethylenemethyl group is bonded to each metal in the cluster. This is also a rare example of a non-carbonyl cluster complex.

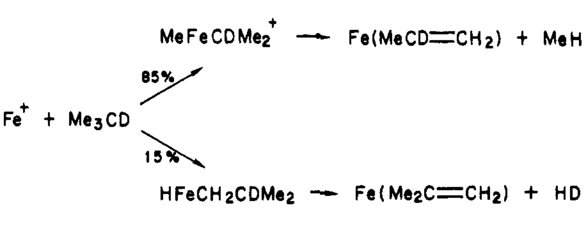
B. Reactions with Metal Ions in the Gas Phase

Alkanes also react with simple or complex metal ions in the gas phase. This can be conveniently studied by ion beam mass spectroscopy or by ion cyclotron resonance.[153] In such cases only products still carrying charge are observed and only their mass and, in a CID[155] experiment, their fragmentation patterns are known. Their structures can be inferred only indirectly from this evidence. Müller and Goll[154] appear to have been the first to report the formation of organometallic species from alkanes in this way (1973).



(89)

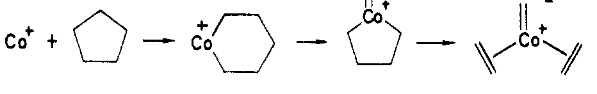
It can be seen that this reaction involves a metal–ligand fragment, rather than a bare metal ion. More recently, Ridge[155] found that naked Fe^+ ion could not only break C–H but also C–C bonds in n-butane and isobutane (eq 90). A concerted oxidative addition was proposed in



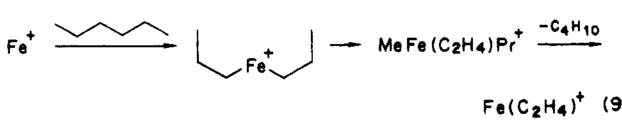
(90)

each case, followed by loss of methane or H_2. While the C–H bond breaking is analogous to the solution results of section IIIF, direct alkane C–C bond breaking is unknown in homogeneous systems (but see sections IIIJ and IIIK). This important difference can be understood in terms of the M–CH_3^+ bond strength, which has been measured by Beauchamp[156] for the case of iron to be 69 ± 5 kcal mol^{-1}. This is greater than the corresponding Fe–H^+ bond strength of only 58 ± 5 kcal mol^{-1}. In contrast, the values for such metal complexes as $L_nFe–CH_3$ and $L_nFe–H$ probably lie around 30 and 55 kcal mol^{-1}, respectively. The extra stabilization of the $Fe–CH_3^+$ bond compared to the $L_nFe–CH_3$ probably arises from steric and agostic effects, and the polarization of the CH_3 group by the bare Fe^+ ion. These are lost on adding the n L groups to $Fe–CH_3^+$ to give $L_nFe–CH_3^+$. The alkane C–C bond breaking can be seen to have a *greater* thermodynamic driving force than C–H bond breaking in the case of Fe^+.

In the case of reaction of M^+ (M = Fe, Co, Ni) with n-butane, $M(C_2H_4)^+$ is an important product. The central, weakest 2,3 C–C bond of the molecule is therefore readily and preferentially cleaved in spite of its being sterically hindered. Cr^+ does only this but Fe^+, Co^+, and Ni^+ also give some 1,2 C–C cleavage.[155,157a] Fe^+ reacts with the C_5 and C_6 cycloalkanes exclusively by C–H bond cleavage to give the $Fe(cycloalkene)^+$ adduct. The C_8 and C_9 cycloalkanes give exclusive C–C bond breaking; in the C_8 case the major product appears to be $Fe(1\text{-hexene})^+$ and C_2H_4. The C_7 and C_{10}–C_{12} cases give both types of products.[157b] It is notable that these M^+ reactions are so facile, perhaps even more facile than the corresponding reaction for the atoms M. It may be that M^+ is able to polarize the alkane substrate and therefore activate it more easily. It is also true that alkanes tend to be activated by electrophiles rather than by nucleophiles; electron withdrawal from the C–H σ bonds seems to be a key factor. Beauchamp et al.[158] studied Co^+ + isobutane in an ion beam apparatus connected to a mass spectrometer. They were able to observe very similar chemistry to that seen by Ridge but were also able to obtain both dissociation energies and ionization potentials for $Co–CH_3^+$ and $Co–H^+$, which allowed them to compare the bond strengths of the cationic species with their neutral analogues. The results were $D^0(Co^+–H) = 52 \pm 4$ and $D^0(Co^+–Me) = 61 \pm 4$ kcal mol^{-1} and $D^0(Co–H) = 39 \pm 6$ and $D^0(Co–Me) = 41 \pm 10$ kcal mol^{-1}. The important conclusion from this result is that while the Co^+ reacts exothermically with both alkane C–H and C–C bonds, the latter are preferred thermodynamically. For the neutral atom, it is probable that neither reaction is exothermic, nor is one particularly favored over the other. Co^+ reacts with C_3–C_6 cycloalkanes almost exclusively by C–C cleavage reactions to give metallacycles which themselves decompose largely by C–C cleavage pathways.[159] Just one proposed pathway involving cyclopentane is shown in eq 91. The same sorts of reaction occur with Fe^+ and C_8–C_9 cycloalkanes, but for C_5–C_6, dehydrogenation takes place, rather than C–C cleavage.[155] An analogous reaction in the case of linear alkanes is β-methyl transfer; this is also observed[156b] (compare eq 78), e.g., eq 92.



(91)



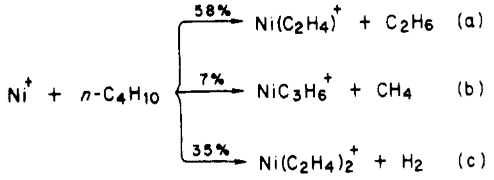
(92)

In some cases processes that would be endothermic for the ground-state ion are observed, suggesting that the metal ions involved are in excited electronic states. A reaction of this type is shown in eq 93, and ^4D, ^4G,

$$(Cr^+)^* + CH_4 \rightarrow Cr{=}CH_2 + H_2 \qquad (93)$$

or ^4P excited states of Cr^+ seem to be implicated.[160] Ridge[155] has also observed interesting ligand effects. For example, while Co^+ reacts with alkanes, Co_2^+ does not. The addition of CO to give $Co_2(CO)^+$ restores activity.

Ni^+ reacts[161] with n-butane as shown in eq 94. n-Butane-*1,1,1,4,4,4*-d_6 gives only D_2 so 2,3 C–C bond cleavage, followed by β-elimination, was proposed for route c. Once again, the bis(olefin) structure of the product was suggested on the basis of circumstantial evidence.



(94)

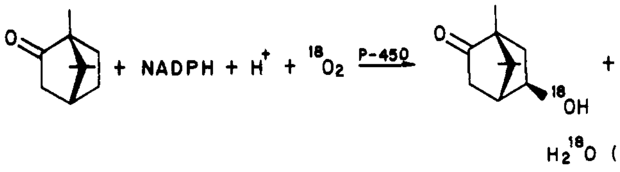
The important conclusions of these studies are that the high M–C bond strengths allow facile C–C bond cleavage for the bare ions, but not apparently for the metal–ligand fragments, and that the multiple coordinative unsaturation of these species leads to multiple C–H and C–C bond-breaking steps. This second feature has some analogy in the multiple-bond-breaking steps observed in solution studies of species with multiple coordinative unsaturation (see sections IIIF and IIIJ). Even C–C bond breaking appears to be kinetically facile as the initial step. This is not so for metal complexes, as discussed in sections IIIK and IIIJ, presumably because of the steric congestion of the L_nM^+ compared to the bare metal ion.

V. Alkane Activation by High-Valent Metal Complexes

In discussing this topic we are venturing beyond the strict bounds of the organometallic chemistry of alkanes as currently known. In doing so, we intend to suggest that true organometallic species should be accessible in this way and to show how these radical-based systems differ from the ones discussed up to now. We can do no more than touch upon this important and interesting aspect of alkane activation in this review.

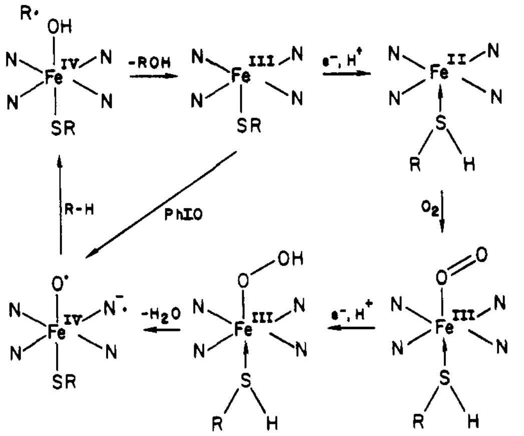
A. Enzymatic Alkane Activation

Much of the significance of this area comes from the fact that alkane activation in natural systems relies on this chemistry for the hydroxylation of hydrocarbons. This hydroxylation renders them more soluble and so more easily excreted. The natural cytochrome[162] P-450 reduces dioxygen to 1 equiv of water and 1 equiv of an active oxo fragment that is capable of transfer to the substrate. The reaction occurs at an iron porphyrin (heme), which is the prosthetic group of the enzyme. Cytochrome P-450 is itself a component of a variety of monooxygenases (so called because only one atom of oxygen in O_2 is transferred to the substrate) which occur in the mammalian liver and in some bacteria. Camphor 5-oxygenase from *Pseudomonas putida* is perhaps the most fully studied; it catalyzes the transformation of eq 95, where the oxygen is labelled to show where it



(95)

ends up in the products.[12,163] Apart form the P-450 component, two-electron-transfer proteins, a flavoprotein, and a diiron–sulfur protein, putidaredoxin, are also present in the enzyme complex. The NADPH reduces the flavoprotein, which in turn reduces the putidaredoxin, which reduces the heme–O_2 system. The fifth ligand for the heme group appears to be a cysteinyl (RS–) group.[164] It is interesting that a system sufficiently strongly oxidizing to attack alkanes has as a ligand an RS^- group which is normally so easily oxidized. The Fe(II) heme is believed to coordinate O_2 much as does hemoglobin, but that reduction and loss of 1 equiv of water leads to what may be an "Fe(V)" oxo or more likely an Fe(IV) oxo with the extra electron in the porphyrin π^* system. This has radical character on oxygen and abstracts an H· from the alkane to give an Fe(III)–OH and R·. It only requires OH· transfer from iron to R· to complete the process (eq 96). It has also been found possible to short-circuit O_2 activation by use of an O-transfer reagent such as PhIO.[12,163]



(96)

It is important to note that the high selectivity of this process is determined by conformational effects in the enzyme–substrate complex, not the intrinsic, rather unselective character of the chemistry itself. It is for this reason that free OH· radicals are not employed by the natural system. With Fe–O· the radical center can be held in the precise position which will best achieve the desired results. Model systems may well be developed in the future to emulate the selectivity of the natural system. Successful C—H activation requires that the bond dissociation energy of the C—H bond to be cleaved is less than that of the O—H bond formed after H· abstraction by the M=O group; kinetic barriers for such reactions tend to be low.

B. Alkane Activation with O_2 and H_2O_2 as Oxidant

The first inorganic system capable of hydroxylating alkanes was Fenton's reagent,[165] Fe^{2+} and aqueous H_2O_2, discovered in 1897. This is believed to operate via a free radical chain decomposition process of the H_2O_2 in which the active principle is OH· radical. The fact that the O–H bond dissociation energy of water (110 kcal mol) exceeds the usual C–H bond dissociation energies of alkanes (<100 kcal mol) means that H· abstraction from the latter by OH· can occur. In view of more recent developments, however (see eq 97–101), the presence of some sort of iron oxo species cannot be excluded. In practice much of the oxidizing power of the H_2O_2 is lost via reactions such as eq 97 and 101, and Fenton's reagent has no synthetic value.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (97)$$

$$\cdot OH + R\text{–}H \rightarrow R\cdot + H_2O \quad (98)$$

$$R\cdot + \cdot OH \rightarrow ROH \quad (99)$$

$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O \quad (100)$$

$$HO_2\cdot + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2 \quad (101)$$

In 1954, Udenfriend[166] devised a simple monoxygenase model system using O_2, Fe(II), EDTA, and ascorbic acid as the reducing agent. This is capable of hydroxylating arenes and, as shown in 1964, alkanes.[167] Other similar systems have been reported since.[168] Hamilton suggested that OH· radical was not the active species but that some sort of metal oxo species was involved. Perhaps one of the most interesting systems using O_2 is due to Mimoun.[169] Hydrazobenzene is the reducing agent and $FeCl_2$ the catalyst; hydroxylation of cyclohexane and adamantane are observed.

The very high oxidizing power of $Co(OAc)_3$ has long been recognized (1931).[170] More recently,[171] the system $CoOAc_2/O_2$ has been shown to have similar properties, including the ability to oxidize alkanes. At 100–120 °C, this system gives acetic acid from butane and adipic acid from cyclohexane (eq 102); the latter is industrially important in the manufacture of nylon.[172] No deuterium isotope effect was observed and primary C–H bonds were not particularly reactive, which led to the initial proposal that electron transfer from R–H to Co(III) was involved (eq 103–107). Direct electrophilic attack at an alkane C–H bond, analogous to the mechanism proposed for the Shilov chemistry discussed in section IIID, has also been suggested for this type of reaction (eq 108 and 109).[173] This is perhaps more likely and implies that organometallic intermediates, albeit evanescent, are involved. The presence of Cl· donors such as Cl_3CCO_2H can lead to chlorinated products, with the unusual selectivity pattern shown in eq 110.[174] A very interesting system, recently described by Barton and Motherwell,[175] consists of iron powder

(102)

$$RH + Co(III) \rightarrow RH^{+}\cdot + Co(II) \quad (103)$$

$$RH^{+}\cdot \rightarrow R\cdot + H^+ \quad (104)$$

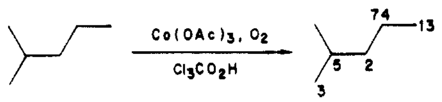
$$R\cdot \xrightarrow{Co(III)} R^+ \rightarrow \text{products} \quad (105)$$

$$R\cdot \xrightarrow{O_2} RO_2\cdot \rightarrow \text{products} \quad (106)$$

$$Co(II) \xrightarrow{O_2} Co(III) \quad (107)$$

$$C\text{–}H + Co(III) \rightarrow C\text{–}Co(III)^- + H^+ \quad (108)$$

$$C\text{–}Co(III) \rightarrow C\cdot + Co(II) \quad (109)$$



(110)

selectivity for chlorination (%) shown

in pyridine–AcOH–H_2O. This mixture catalyzes the oxygenation of alkanes by O_2, but the observed preference for methylene over methyl or methine attack on methylcyclohexane is unexpected. The authors find that the major products are ketones, but that they are formed not by oxidation of the corresponding alcohols but by a direct and nonradical route. They suggest that an organometallic intermediate, an iron alkylidene complex, may be involved.

C. Alkane Activation with Other Oxidizing Agents

Important recent advances in chemical model systems date from the work of Groves[176] and of Chang[177] (1979) and of Hill[178] (1980). Groves found that in CH_2Cl_2, Fe(TPP)Cl catalyzes alkane hydroxylation by PhIO. The radical character of the process was suggested by the 12:1 ratio for tertiary:secondary products from adamantane. The catalysts were not stable, however, and deactivation occurs in part by attack of the porphyrin ligand. Chang's[177] initial report concerned hydroxylation of the alkyl chain of a "strapped" iron porphyrin with PhIO. Hill[178] showed that Mn(TPP)X (X = Cl, Br, I, N_3) gave similar chemistry with cyclohexane and PhIO. He also noted the formation of R–X and R–R among the products, consistent with X· abstraction by R· and dimerization of R·, respectively. The neophyl radical rearrangement is observed in the oxidation of *t*-BuPh. As was seen in section IIIF, deactivation processes seem to lead to inactive species especially when the substrates are alkanes rather than more reactive species such as olefins or arenes.

$$\mathrm{PhCMe_3} \xrightarrow{-\mathrm{H}\cdot} \mathrm{PhCMe_2CH_2}\cdot \longrightarrow \mathrm{PhCH_2\dot{C}Me_2} \xrightarrow{+\mathrm{X}\cdot} \mathrm{PhCH_2CXMe_2} \quad (111)$$

Chromium porphinates were studied by Groves,[179] and ESR evidence for the intermediacy of a Cr(V)–oxo species was presented. In contrast, an Fe(IV)–porphyrin radical cation structure was preferred for the "Fe(V)–oxo" species implicated in the iron porphyrin work.[180] In line with the proposed H· abstraction mechanism, k_H/k_D for cyclohexane hydroxylation was found to be 13.[181] Evidence has been presented for similar chemistry going on in the natural P-450 system.[182] No organometallic intermediates have yet been implicated.

Suslick[183] has shown that by substituting the manganese–porphyrin system with bulky groups at the meso position, a greater degree of selectivity can be achieved for alkane hydroxylation at unhindered C–H bonds using *t*-BuOOH as the oxidant. For *n*-heptane, the usual MnTPP catalyst gives only 3% primary alcohol, but with 2,4,6-triphenylphenyl groups present at the meso positions, 26% of the primary alcohols were obtained. Better results might be possible using shape selective clay minerals as supports.

Other related studies have also been reported,[184] in particular, Tabushi[185] has observed P-450 type O_2 activation using H_2/colloidal Pt as the reducing agent.

Radical pathways for alkane activation may not be limited to first-row porphyrin complexes, and it seems likely that in the future, isolable organometallic species will be formed by reactions such as are described in this section. This will be of considerable interest in its own right and may have important implications for the chemical transformation of alkanes.

VI. Future Prospects and Conclusion

Alkane C–H and C–C bonds have now been activated but much remains to be done. We need to look for ways of using these reactions to do further chemistry. Catalytic reactions offer an exciting prospect, for which we require more robust catalysts. The search for these will teach us much about deactivation reactions in homogeneous catalysis in general. The difficult problem of catalytically functionalizing alkanes in new ways, and mechanistic questions, such as the details of the photoinduced reactions of metal hydrides and carbonyls, and the homogeneity of catalysts will continue to attract attention.

A likely trend in the next few years will be the application of what we have learned with alkanes to the problem of selective functionalization of C–H and C–C bonds in organic compounds in general, perhaps steered by directing effects of existing functionality. In view of the wide importance of C–H and C–C bonds to chemistry as a whole, we can look forward to these problems continuing to stimulate new work for many years to come.

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