

Homogeneous Catalytic Activation of C-H Bonds

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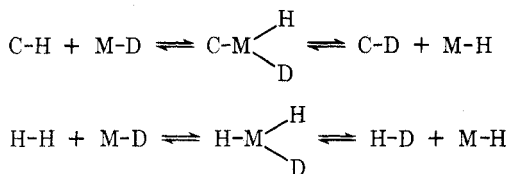
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Very recently it has become apparent that some soluble transition-metal complexes can activate the C-H bonds of hydrocarbons in much the same way that the H-H bond of hydrogen is activated in catalytic hydrogenation reactions. This discovery points the way to a new type of homogeneous catalysis for reactions such as aromatic substitution¹ and opens some interesting opportunities for applications in synthesis.

The classical methods for substitution of arenes and alkanes involve attack of the hydrocarbon by a highly reactive reagent. The role of the catalyst has been to make the attacking reagent more reactive. In halogenation, for example, the catalyst generally promotes dissociation of the X-X bond, either by heterolytic cleavage to produce a highly reactive species with characteristics approaching those of X⁺ or by homolytic cleavage to give a X· species. In either case, it is the halogen reagent that is activated rather than the hydrocarbon.

Recent work in several laboratories has shown that the C-H bonds in benzene are activated toward processes such as H-D exchange, by a variety of transition-metal complexes including high-valent species such as Ta^VH₃(C₅H₅)₂, low-valent species like Ru⁰-(dmpe)₂ (dmpe = (CH₃)₂PCH₂CH₂P(CH₃)₂), and electrophiles (Pd²⁺ and Pt²⁺). The activation is generally agreed to involve cleavage of a C-H bond by the metal and formation of a C-M bond. The C-M bond then undergoes reaction with a reagent such as D₂ or Cl₂. The process is similar to the metal-catalyzed activation of H₂ as illustrated by H-D exchange with a metal deuteride



Although many of the studies of hydrocarbon activation involve the trivial reaction of hydrogen-deuterium exchange, more substantial synthetic applications are emerging. As described below, C-H activation can be utilized to introduce substituents such as -Al(C₂H₅)₂ directly onto an aromatic ring. Chelate effects can produce specific ortho substitution in aromatic rings, while enhanced steric effects can direct substituents into meta and para positions.

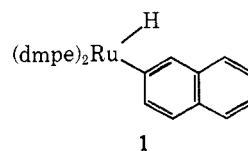
This Account relates several lines of research in our laboratories which bear on the problem of how a metal atom interacts with a C-H bond, either aromatic or aliphatic.

Background

To put the situation in its proper context, the activation of benzene C-H bonds by heterogeneous catalysts has been known for almost 40 years. Farkas and Farkas² discovered that a platinum film catalyzes the exchange between gaseous benzene and D₂ even at room temperature. Subsequent work has provided a reasonable picture of the mechanism.^{3,4} As discussed later, there seems to be a close analogy between the processes occurring at the active sites of a metal surface and those occurring at the central metal atom in soluble complex.

The first observation of interaction between benzene and a soluble transition-metal compound was made by Chatt and Davidson.⁵ They found that a reduction product of RuCl₂(dmpe)₂ reacts with benzene, naphthalene, and other aromatic hydrocarbons to give arylruthenium hydride complexes such as 1.⁶

Catalytic activation of aromatic C-H bonds by soluble species was discovered by Garnett and coworkers



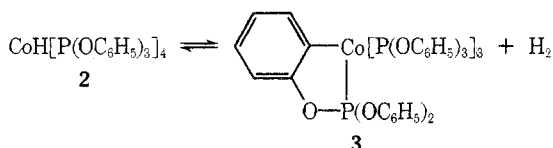
George W. Parshall was born in Minnesota in 1929. He received his B.S. degree from the University of Minnesota and his Ph.D. from the University of Illinois. He is Research Supervisor in the Central Research Department, Du Pont Experimental Station, in Wilmington, Del. His major research interests are in homogeneous catalysis and in synthetic applications of organometallic compounds.

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 (2) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 33, 827 (1937).
 (3) J. R. Anderson and C. Kemball, *Advan. Catal.*, 9, 51 (1957).
 (4) J. L. Garnett, *Catal. Rev.*, 5, 229 (1971).
 (5) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).
 (6) S. D. Ibeke, B. T. Kilbourn, U. A. Raeburn, and D. R. Russell, *J. Chem. Soc. A*, 1118 (1971).

ers.⁴ Benzene and substituted benzenes react with D₂O in acetic acid in the presence of [PtCl₄]²⁻ salts to produce deuterated benzenes. Although the catalyst appears to be soluble in the medium, the exchange resembles the heterogeneous catalytic exchange in two respects: (1) multiple exchange occurs, i.e. statistical analysis shows that more than one exchange occurs per catalytic event; (2) exchange also takes place in the side chains of alkylbenzenes. This observation of alkyl C-H exchange has led to the discovery of alkane activation by this catalytic system.^{7,8}

Initial Studies

Much of the impetus for study of benzene C-H activation came from our studies of intramolecular aromatic substitution⁹ in which a transition-metal atom reacts with an ortho aryl C-H bond of a donor ligand to form a metal-carbon bond. A typical example involves the interconversion of **2** and **3**. This transformation was first postulated¹⁰ on the basis of selective ortho deuteration of the phenoxy groups of **2** by exposure to deuterium gas in solution at 100°. The ortho-bonded complex **3** has now been isolated.¹¹ Interestingly, its conversion to the Co-D analog of **2** by treatment with D₂ is accompanied by extensive ortho deuteration even under conditions in which **2** does not react with D₂ at a significant rate.



The occurrence of such intramolecular reactions raised the question as to whether or not similar reactions might not occur with benzene itself. Initial tests showed that two polyhydride complexes, TaH₃(C₅H₅)₂ and IrH₅[P(CH₃)₃]₂, do indeed catalyze the exchange of benzene with D₂. When benzene solutions of these complexes are heated with deuterium in a sealed tube, H₂ and HD appear in the gas phase. Deuterium is statistically exchanged with both benzene and ligand C-H and with M-H as well.¹²

Polyhydride Catalysts

Subsequent studies of the benzene-D₂ reaction have shown catalysis by polyhydride complexes of transition metals with odd numbers of valence electrons. Perhaps, because of the nature of our synthesis programs, greatest activity has been found for group V hydrides such as NbH₃(C₅H₅)₂¹³ and TaH₅(dmpe)₂.¹⁴ The latter has produced the fastest C₆H₆-D₂ exchange rates that we have yet observed with a soluble catalyst. Rhenium polyhydrides such as ReH₅[P(C₆H₅)₃]₃, which have been reported to ex-

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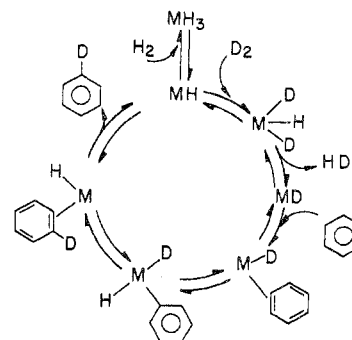


Figure 1. Proposed scheme for exchange between benzene and D₂ catalyzed by metal polyhydrides.

change Re-H with C₆D₆,¹⁵ also catalyze exchange between benzene and deuterium. Complexes such as [NbH(μ-C₅H₄)(C₅H₅)₂] and TaH(PR₃)(C₅H₅)₂, which give rise to trihydrides on treatment with hydrogen, also catalyze exchange.

These metal hydride catalyzed exchanges have several features in common.^{16,17} (1) Only aryl C-H bonds exchange. In contrast to Pt metal or [PtCl₄]²⁻ catalysis, no deuterium enters the methyl groups of toluene or xylene. (2) Exchange occurs stepwise, one C-H bond at a time, again in contrast to the heterogeneous and [PtCl₄]²⁻-catalyzed reactions. (3) Little deuteration occurs ortho to bulky groups such as CH₃ or CF₃. (4) A deuterium isotope effect, *k_H/k_D*, of 2-3 suggests some degree of C-H bond breaking in the rate-determining step.

Reactions of substituted benzenes with deuterium in the presence of the polyhydride complexes are generally favored by electron-withdrawing substituents. The usual rate sequence is C₆H₅F ~ C₆H₅CF₃ > C₆H₆ > C₆H₅OCH₃ ~ C₆H₅CH₃ in competitive experiments, quite similar to that expected for a nucleophilic reaction. However, the range of rates is quite small, less than a factor of 10. In fact, with TaH₃(C₅H₅)₂ and TaH₃(C₅H₄CH₃)₂, there is no significant rate difference among the various monosubstituted benzenes. (*p*-Xylene is much slower, presumably because all the aryl hydrogens are ortho to methyl groups.)

The mechanism shown in Figure 1 has been proposed¹⁶ to account for these results as well as other experimental data such as the position of deuterium substitution. A key intermediate in this scheme is a coordinatively unsaturated metal hydride formed by dissociation of H₂ from a trihydride species. (Other ligands have been neglected for simplicity and generality.) This monohydride (MH) is capable of exchange with D₂ as shown in the clockwise sequence and can coordinate a benzene molecule as illustrated with the analogous monodeuteride (MD). The coordinated benzene is proposed to transfer a hydrogen to the metal with simultaneous formation of a C-M bond, a formal oxidative addition to the metal atom. Reversal of the oxidative addition and dissociation of the deuterated benzene complete the catalytic cycle.

Although there is no direct experimental evidence for coordination of benzene to the metal in our system, sound precedent for both arene coordination

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and oxidative addition of a C-H bond exists in the reaction of benzene with a ruthenium(0) complex⁵ described previously. More recently Green¹⁸ and Brintzinger¹⁹ have observed an irreversible addition of a benzene C-H bond to transient $M(C_5H_5)_2$ derivatives of molybdenum and tungsten, closely analogous to our proposed $MH(C_5H_5)_2$ catalysts based on niobium and tantalum.

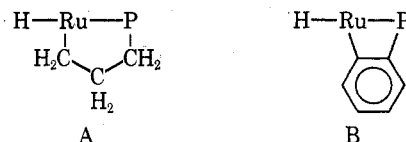
The assumption of benzene coordination permits one to account for the small or nonexistent substituent effects observed in the exchange reactions of substituted benzenes if one assumes that oxidative addition and coordination are both rate-limiting factors and have opposing substituent effects. In the case of the niobium compounds which catalyze exchange preferentially with negatively substituted benzenes, oxidative addition is assumed to be rate controlling (consistent with the observed isotope effect, $k_H/k_D = 2.3$). Hence, for this series of catalysts, oxidative addition has some of the characteristics of a nucleophilic reaction.

Monohydride System. Recently it has been observed¹⁷ that the monohydride, $RuHCl(PPh_3)_3$, catalyzes the exchange between benzene and deuterium gas under vigorous conditions. Although many aspects of this reaction remain unexplored, there are some interesting differences between this system and the polyhydride systems discussed above. When triphenylphosphine is added to the benzene- D_2 exchange reactions, it undergoes extensive deuterium substitution. With $RuHCl(PPh_3)_3$ as the catalyst, the deuterium appears exclusively in the ortho positions,¹⁰ but with $TaH_5(dmpe)_2$, all the deuterium substitution occurs in the meta and para positions.¹⁷ The difference seems to be that, with the ruthenium compound, exchange occurs by a conventional ortho-metalation mechanism while the tantalum compound effects exchange without coordination of the triphenylphosphine phosphorus to the metal. In effect, the latter catalyst treats triphenylphosphine as a $(C_6H_5)_2P$ -substituted benzene in which $(C_6H_5)_2P$ - is an inert but bulky substituent which directs exchange away from the ortho positions.

The differences between the two types of catalysts may possibly extend to the intimate interaction of the metal with the aryl C-H bond in the oxidative addition process. In the reaction of $(C_6H_5)_2P(CH_2)_nCH_3$ compounds with D_2 catalyzed by $RuHCl(PPh_3)_3$, alkyl as well as aryl C-H bonds undergo exchange. With the ruthenium catalyst, the methyl C-H bonds of $(C_6H_5)_2PCH_2CH_2CH_3$ are activated even at 20°. The exchange rates of methyl and ortho hydrogens (after statistical adjustment) are equivalent, and both exchanges show the same activation energy, *ca.* 6 kcal/mol, over a 140° range. Some deuteration of the methylene groups also occurs at temperatures above 100°, with α deuteration ($E_{act} = ca. 13$ kcal/mol) favored over β deuteration.

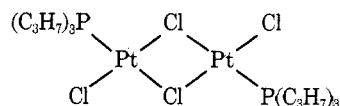
In the $RuHCl(PPh_3)_3$ -catalyzed exchanges, oxidative addition to a coordinatively unsaturated ruthenium(II) species seems a likely mechanism for C-H bond activation. In comparing ortho aryl *vs.* γ meth-

yl exchange it should be noted that the methyl group reaction involves an unstrained five-membered ring (A) while ortho exchange requires a relatively strained four-membered ring (B). For comparison of



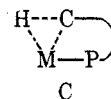
ring size effects, exchange of $(C_6H_5)_2POC_6H_5$ with deuterium was carried out in the presence of $RuHCl(PPh_3)_3$. Ortho deuteration of the phenoxy group (involving a five-membered ring intermediate) was at least 50 times as fast as in the P-bonded phenyl.

The ring size effect is similar to that reported²⁰ elsewhere for the deuteration of tri-*n*-propylphosphine in the complex



When this substance was treated with $CH_3COOD-D_2O$, deuterium was incorporated exclusively into the methyl groups, consistent with a five-membered ring intermediate as in A above. Such cyclic intermediates have been isolated in reactions of $PtCl_2(PR_3)_2$ complexes.²¹ No α - CH_2 deuteration has been noted in the platinum complexes, although metalation of C-H bonds α to phosphorus has been observed in $Ru(dmpe)_2$ ^{5,22} and in $IrH_5(PMe_3)_2$.¹⁶

In the γ deuteration catalyzed by the Ru and Pt complexes, precoordination of the γ carbon to the metal does not seem to be required for C-H bond cleavage. A reasonable transition state is represented by C. This configuration resembles the C-H/metal



interaction detected in pyrazolylborate complexes of molybdenum by spectroscopic²³ and crystallographic^{24,25} techniques.

Nonhydridic Catalysts

In the previous exchange studies from our laboratory, gaseous deuterium has been the source of labeled hydrogen and the catalysts have usually been metal hydrides. Now benzene activation has been detected with catalysts which contain no M-H bonds.

When a solution of ethylbis(π -cyclopentadienyl)-(ethylene)niobium (4) in benzene- d_6 is heated for extended periods, substantial amounts of deuterium (up to d_9) appear in the ethyl and ethylene ligands of the recovered complex.²⁶ This result is attributed to exchange between C_6D_6 and a transient species,

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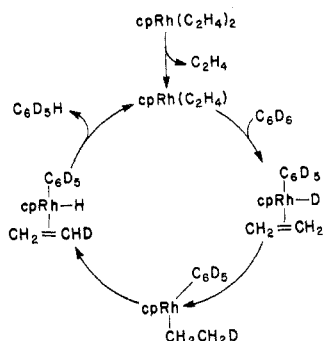
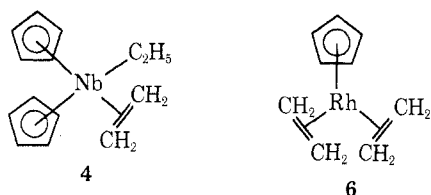


Figure 2. Mechanism for exchange between benzene- d_6 and coordinated ethylene.

$\text{NbH}(\text{C}_5\text{H}_5)_2$ (5), by the mechanism of Figure 1. The monohydride (5), which has been proposed¹³ as an intermediate in many reactions of $\text{NbH}_3(\text{C}_5\text{H}_5)_2$, may be formed by dissociation of two molecules of ethylene from 4. [Dissociation of one ethylene to give $\text{NbH}(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_5)_2$ has been observed.] If the ethylene dissociation is reversible, addition of C_2H_4 to $\text{NbD}(\text{C}_5\text{H}_5)_2$ provides a ready route to the observed incorporation of deuterium.



The path for C_6D_6 -ligand exchange is less obvious for the rhodium complex 6 which reacts with benzene- d_6 at 130° to introduce deuterium into both the ethylene and cyclopentadienyl ligands.²⁷ Several other arenes, including pyridine- d_5 , toluene- d_8 , and nitrobenzene- d_5 , also participate in this reaction as deuterium donors. The rate sequence is $\text{C}_6\text{D}_6 \sim \text{C}_5\text{D}_5\text{N} > \text{C}_6\text{D}_5\text{NO}_2 > \text{C}_6\text{D}_5\text{CD}_3$. With pyridine- d_5 , deuterium enters the ethylene ligands, but little appears on the cyclopentadienyl ligands of the recovered complex.

Substitution of ^1H onto the deuteriobenzene is statistically random, consistent with one exchange per productive collision of arene and 6. This behavior is in contrast to the multiple exchange encountered on the surface of metal films. The implication is that the arene activation is a homogeneous process. The solutions remain clear during the reaction. The absence of methyl C-D exchange in toluene- d_8 experiments also tends to exclude heterogeneous catalysis by metallic rhodium, which would be very active in this reaction.²⁸

Another significant observation is that the exchange between C_6D_6 and 6 is repressed by the presence of C_2H_4 or C_2D_4 . Similarly the intramolecular exchange between ethylenic and cyclopentadienyl C-H bonds in $\text{Rh}(\text{C}_2\text{D}_4)_2(\text{C}_5\text{H}_5)$ is inhibited by C_2D_4 . Significantly the exchange occurs only at temperatures above 115° , at which point ethylene dissociates from 6.²⁹

A mechanistic scheme to account for exchange be-

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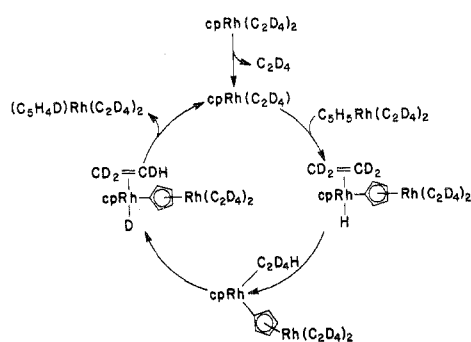
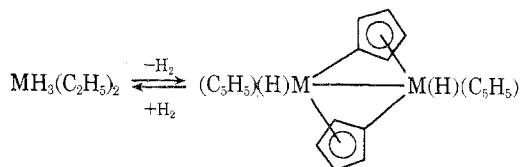


Figure 3. Proposed mechanism for H-D exchange between coordinated ethylene and cyclopentadienide ligands.

tween C_6D_6 and coordinated ethylene is shown in Figure 2. Ethylene dissociation from 6 generates a coordinatively unsaturated species which provides entry to the catalytic cycle. Oxidative addition³⁰ of a C-D bond to the coordinatively unsaturated $\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_5)$ species generates a phenylrhodium deuteride. Addition of the Rh-D bond to ethylene followed by elimination of Rh-H accomplishes exchange by a well-established pathway.³¹

A strictly analogous scheme (Figure 3) can account for exchange of hydrogen and deuterium between the ethylene and cyclopentadienide ligands. In this speculative proposal, the cyclopentadienylrhodium complex is considered to behave as an arene. A cyclopentadienyl C-H bond of one molecule of complex is oxidatively added to the $\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_5)$ species generated by dissociation of ethylene from a second. Thus, the apparently intramolecular exchange may occur by a bimolecular mechanism. This point has not been confirmed by kinetic studies, but intermolecular exchange between $\text{Rh}(\text{C}_2\text{D}_4)_2(\text{C}_5\text{H}_5)$ and $\text{Rh}(\text{C}_5\text{H}_5)(1,5\text{-cyclooctadiene})$ has been observed, consistent with this mechanism.

A similar oxidative addition of a cyclopentadienyl C-H bond to the metal atom of a second molecule of complex is believed to occur in the dimerization of dicyclopentadienyl complexes of niobium and tantalum.^{13,32}



Such phenomena abound in the "titanocene" system³³ and considerably complicate the study of nitrogen fixation³⁴ by cyclopentadienyl complexes of titanium.

If the reaction schemes of Figures 2 and 3 are confirmed, a very satisfying unity of mechanism between the group V and group VIII metal catalyzed reactions will have been demonstrated. In addition, the mecha-

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(31) (a) R. Cramer, *Accounts Chem. Res.*, 1, 186 (1968); (b) C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972)

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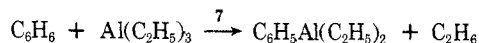
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nism of Figure 2 permits catalytic exchange between different arenes *via* an ethylene ligand of the rhodium complex. Exchange between C_6D_6 and fluorobenzenes does indeed occur at 128° in the presence of 6.¹⁷

Application to Synthesis

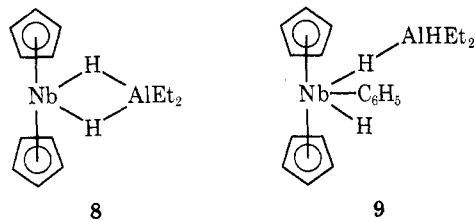
Although H-D exchange is a convenient tool for detecting potentially useful catalytic species, it is not generally a synthetically useful reaction in itself. An extension of the chemistry described above into synthetically useful substitution reactions has been developed by Dr. Tebbe.²⁶

The reaction of $NbH_3(C_5H_5)_2$ (7) with triethylaluminum in benzene at elevated temperatures, in contrast to that at room temperature,³⁵ produces diethylphenylaluminum. This condensation reaction of



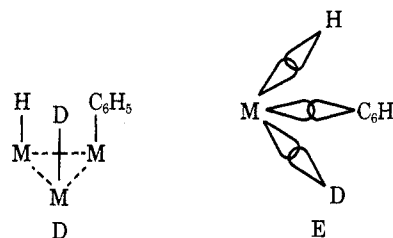
benzene and an alkylaluminum compound appears to be the first aromatic substitution other than HD exchange catalyzed by the transition-metal polyhydrides. Although it is possible that the catalysis occurs simply by a strong base mechanism,³⁶ it seems more likely to involve intermediates similar to those involved in H-D exchange.

The reaction of $NbH_3(C_5H_5)_2$ with $Al(C_2H_5)_3$ at room temperature³⁵ proceeds with evolution of ethane to give the hydride-bridged species 8. Oxidative addition of a benzene C-H bond to 8 has the potential to generate 9, which, in turn, can give $C_6H_5Al(C_2H_5)_2$ by a number of paths.



Relation to Heterogeneous Catalysis

The reactions of aromatic hydrocarbons described here, like the arene⁴ and alkane^{7,8} reactions catalyzed by $PtCl_4^{2-}$, show many similarities to those produced by metal films and supported metal catalysts. It is very tempting to propose that the intermediate species on a metal surface are similar to those involved in catalysis by soluble species. It is usually assumed that the three essential "sites" for exchange of arene C-H are disposed on three separate metal atoms as in D. In contrast, we propose that the exchange "sites" for a homogeneous catalyst are simply three adjacent orbitals on a single metal atom (E). In the metallic surface (D), the catalytically active metal atoms are bonded to "ligand" metal atoms. In

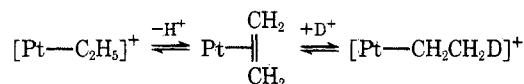


the soluble complex (E), hydrocarbon or tertiary phosphine ligands create the proper steric and electronic environment for catalytic activity.

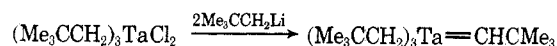
One of the most interesting problems in aromatic hydrocarbon activation is study of the interrelation between the homogeneous and heterogeneous catalysts.³⁷ While it may be difficult to determine whether or not monoatomic sites analogous to E exist on a heterogeneous surface, the information may be quite rewarding. Similarly, development of soluble metal clusters with trimetallic sites like D may greatly increase the scope of hydrocarbon activation reactions accessible through homogeneous catalysis.

Saturated Hydrocarbons

One of the most dramatic developments in hydrocarbon activation has been the report by Shilov⁷ that methane and ethane undergo exchange with D^+ in the presence of $PtCl_4^{2-}$. Given the observation that metal complexes can break C-H bonds in aliphatic ligands as described above, it is perhaps not surprising that alkanes also react. With ethane, exchange is proposed to proceed *via* ethyl and ethylene complexes.



An analogous mechanism for methane exchange requires a relatively unprecedented $Pt=CH_2$ intermediate in place of the ethylene complex. Support for the existence of such species now comes from the work of R. R. Schrock in our laboratories who has isolated and fully characterized a simple alkylidene complex.



Confirmation of the existence of such a multiply bonded species (frequently postulated in mechanisms of heterogeneous catalysis) helps to rationalize the phenomenon of multiple exchange encountered in Shilov's system and in CH_4-D_2 exchange catalyzed by metallic films. If two hydrogens are removed from CH_4 in its interaction with a metal such as Pt, products such as CH_2D_2 are not unexpected. Taken together, the results of Shilov and of Schrock support the proposal that homogeneous and heterogeneous C-H bond activation mechanisms are similar.

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