

Activation of C–H Bonds by Metal Complexes

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Contents

I. Introduction	2879	B. Alkane Oxidation by Metal Ions	2908
II. Cleavage of the C–H Bond	2881	C. Oxidation by Metal Oxo Complexes	2909
A. "Inertness" of Alkanes	2881	1. Oxygenation of Alkanes with Derivatives of Cr(VI) and Mn(VII)	2909
B. Splitting of the C–H Bonds by Compounds Other than Metal Complexes	2881	2. Oxygenation by Ruthenium(IV) and Other Complexes	2910
1. Transformations That Do Not Involve Metals or Their Compounds	2881	3. Alkane Functionalization under the Action of Polyoxometalates	2911
2. Reactions Promoted by Metals or Their Oxides	2883	D. Oxygenation by Peroxo Complexes	2911
C. Reactions of C–H Compounds with Metal Complexes: An Historical Survey	2884	V. Oxygenation of Hydrocarbons by Molecular Oxygen and Oxygen-Atom Donors	2912
D. Three Types of the C–H Bond Cleavage Promoted by Metal Complexes	2884	A. Traditional Chain Autoxidation of Alkanes	2912
1. Classification Based on the Mechanism	2884	B. Novel Low-Temperature Processes of Hydrocarbon Oxidation	2912
2. Mechanisms of the C–H Bond Activation	2885	1. Oxidation of Alkanes	2912
III. Activation of Hydrocarbons by Low-Valent Metal Complexes	2886	2. Oxygenation of Aromatic Compounds	2913
A. Formation of σ -Organyl Hydride Complexes	2886	C. Coupled Oxidation of Alkanes. Gif Systems	2914
1. Cyclometalation	2886	D. Aerobic Photooxygenation of Alkanes	2914
2. Intermolecular Oxidative Addition	2886	E. Oxidations by Peroxides	2916
3. Some Special Cases	2888	1. Oxidations with Hydrogen Peroxide	2916
B. Functionalization of Hydrocarbons in Solutions	2890	2. Oxidations by Alkyl Hydroperoxides	2918
1. H–D Exchange	2890	F. Oxygenation by Other Oxygen Atom Donors	2919
2. Dehydrogenation of Alkanes or Alkyl Groups	2890	VI. Biological Oxidation and Its Chemical Models	2919
3. Carbonylation of C–H Compounds	2892	A. Hydrocarbon Oxygenations by Cytochrome P450 and Its Chemical Models	2919
4. Introduction of Other Functional Groups into Organic Molecules	2893	1. Mechanism of Oxidation Catalyzed by Cytochrome P450	2920
C. Reactions with Metal Atoms and Ions	2893	2. Modeling Oxidation Catalyzed by Cytochrome P450	2921
1. Reactions with Metal Atoms at Low Temperature	2893	B. Methane Monooxygenase and Other Non-Heme Iron-Containing Oxygenases	2921
2. Processes in the Gas Phase	2894	1. Methane Monooxygenase	2921
D. Mechanism of the Oxidative Addition of C–H Compounds	2895	2. Iron-Containing Oxygenases	2922
1. H–H and C–H Groups as Ligands in Metal Complexes	2895	3. Chemical Models	2922
2. Thermodynamics of Oxidative Addition	2898	C. Enzymes Containing Other Metals and Their Models	2923
3. Quantum-Chemical Consideration of Hydrocarbon Oxidative Addition	2898	1. Copper-Containing Enzymes	2923
E. Activation of Alkanes by Platinum Complexes	2900	2. Enzymes Containing Vanadium, Molybdenum, and Manganese	2923
1. H–D Exchange Catalyzed by Pt(II) Complexes	2900	VII. Conclusions	2923
2. Oxidation of Alkanes and Alkyl Groups	2901	VIII. Acknowledgments	2923
3. Mechanistic Consideration of Alkane Activation Reactions	2901	IX. References	2923
IV. Reactions with High-Valent Metal Complexes	2903		
A. Electrophilic Metalation of C–H Compounds	2903		
1. Metalation of Aromatic Compounds	2903		
2. Metalation of Alkanes and Alkyl Groups	2906		
3. Cases of Problematic Mechanistic Interpretation	2907		

I. Introduction

Hydrocarbons, especially saturated hydrocarbons (alkanes), are the main constituents of oil and natural gas, the feedstocks for chemical industry. Therefore, it is obvious that transformations of saturated, as well as aromatic, olefinic, and acetylenic hydrocarbons constitute an extremely important field of

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contemporary chemistry. Development of this area is necessary in order to discover fundamentally new routes from hydrocarbons to more valuable products, such as alcohols, ketones, acids, and peroxides. In addition, new types of hydrocarbon transformations could help reduce petroleum pollution and other important environmental problems. Finally, the well-known inertness of saturated hydrocarbons

makes their chemical transformation challenging from a basic science viewpoint. Only in recent decades has the vigorous development of metal-complex catalysis expanded our knowledge of unsaturated hydrocarbon transformations and opened the door to alkane transformations. The transformation of hydrocarbons (both saturated and unsaturated) through the action of metal complexes seems to be a very promising field, particularly when the complexes act as catalysts. Indeed, in contrast to almost all the presently employed processes, reactions of hydrocarbons with metal complexes occur at low temperatures and can be selective.

When we refer to “the activation” of a molecule, we mean that the reactivity of this molecule increases due to some action. What then is “the activation of an ordinary σ -bond”? It is reasonable to propose that to activate a σ -bond such as C–H bond is to increase the reactivity of this bond toward a reagent. As a consequence, the bond is capable of splitting to produce two particles in place of the one initial species. In many cases, this rupture of a saturated bond is implied when the term “activation” is used. Nevertheless, the splitting of the bond is actually a consequence of its activation, and it would be more correct to refer specifically to the “splitting of the C–H bond” in these situations. The main result of “activation” of a C–H bond is the replacement of the strong C–H bond with a weaker, more readily functionalized bond. The activation of an unsaturated species can be induced by coordination of a particle to the unsaturated bond, following which the bond may undergo addition or rupture. For example, olefin and arene π -bonds can be activated by π -complexation. Saturated compounds do not have this advantage, examples of coordination between some particles and saturated hydrocarbons have been demonstrated recently. In the present review, we will consider all the processes by which metal complexes split the C–H bonds in hydrocarbons, as well as the problem of coordinating alkanes or alkyl groups in organic compounds with metal complexes. This latter problem becomes important when we discuss the possible mechanisms of C–H bond splitting, because such alkane–metal adducts can lie on the reaction coordinate.

Section II of this review is devoted to some general problems, while section III presents a review of hydrocarbon activation by low oxidation state metal complexes. These reactions often proceed as typical oxidative additions. The final part of section III concerns reactions of hydrocarbons with platinum compounds. Despite the fact that the activation of alkanes by platinum(II) salts was historically the first “true” (*vide infra*) metal complex activation of saturated hydrocarbons, its mechanism is still somewhat unclear. However, since platinum(II) complexes exhibit both nucleophilic and electrophilic properties in reactions with C–H compounds, the discussion of their mechanisms is a good bridge to the discussion of hydrocarbon reactions with high-valent metal compounds (section IV). Metal complexes in both low and high oxidation states are known to promote oxidation of hydrocarbons by molecular oxygen, peroxides, and other oxygen atom donors. Such oxygenation processes are briefly discussed in section V.

Finally, major advances in understanding the mechanism of biological hydrocarbon oxidation by atmospheric oxygen have been achieved recently. In particular, the studies of hydrocarbon oxidations catalyzed by enzymatic models are progressing rapidly. It is becoming clear that the active centers which interact with the C–H bond in the hydrocarbon include high-valent derivatives of a metal, usually iron. This review would not be comprehensive without a discussion of this topic. Section VI gives only a very brief survey of this interesting and important field of bioinorganic chemistry.

Several books¹ and many reviews² have appeared recently, which are wholly or partly devoted to metal complex activation of C–H bonds. Reviews and books devoted to more narrow topics will be cited later. Consequently, the present article emphasizes works published during the last decade. Due to the number of such papers, we cite reviews rather than original publications in some cases. This review covers studies which appeared up to early 1997.

II. Cleavage of the C–H Bond

This section is devoted to some general problems. First the inertness of saturated hydrocarbons toward typical chemical reagents is discussed, and then some recent reactions of alkanes and aromatic hydrocarbons with reagents that are not metal complexes are briefly described. After that a historical review of the activation of hydrocarbons by metal complexes is given and these reactions are divided into three types.

A. "Inertness" of Alkanes

The well-known chemical inertness of alkanes is reflected in one of their old names, "paraffins", from the Latin *parum affinis* (without affinity). Alkanes may be called the "noble gases of organic chemistry"; however, this comparison is not fully accurate. Indeed, whereas noble gases do not react easily with any usual compound, there is at least one well-known substance which "activates" paraffins very readily. This substance is the oxygen in air. Alkanes undergo deep oxidation, or burning, in air to produce thermodynamically stable products: water and carbon dioxide. However, it should be emphasized that alkanes are absolutely inert toward air at room temperature in the absence of a catalyst. Furthermore some active reagents, such as atoms, free radicals, and carbenes, can react with saturated hydrocarbons at room temperature and below. Finally, alkanes are easily transformed under elevated (>1000 °C) temperatures in the absence of other reagents. Some important reactions of alkanes have been developed, for example their autooxidation by molecular oxygen at elevated temperatures which involves a radical chain mechanism. However, this reaction, as well as many other alkane reactions, is characterized by a lack of selectivity. This is because radical reactions give rise to the formation of many products, and all possible isomers may be obtained. Burning is an exception, in that this process can be very selective, producing solely carbon dioxide. However, while combustion is an important source of energy, it is useless from the viewpoint of the synthesis of organic materials.

What alkanes are extremely inert toward are "normal" (i.e., not very reactive) reagents in reactions that proceed more or less selectively. In many respects, alkanes, especially the lower ones (methane, ethane), are similar to molecular hydrogen. Indeed, like alkanes, dihydrogen is inert toward molecular oxygen at ambient temperatures, but can be burned in air to produce thermodynamically stable water. The values of the C–H and H–H dissociation energies for methane and dihydrogen molecules are almost exactly equal (104 kcal mol⁻¹). Like methane, dihydrogen is relatively unreactive with many reagents. Ethylene, acetylene, and benzene, which have stronger C–H bonds (106, 120, and 109 kcal mol⁻¹, respectively) than methane, are known to exhibit much higher reactivities. The inertness of methane and dihydrogen is due to the fact that both are completely saturated compounds, which contain neither π - nor n -electrons. Conversely, the π - and n -electrons of unsaturated hydrocarbons allow most of their reactions to proceed by addition, followed in some cases by elimination.

B. Splitting of the C–H Bonds by Compounds Other than Metal Complexes

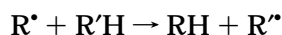
Although alkanes are undoubtedly much less reactive than other organic compounds including unsaturated hydrocarbons, the number of known alkane reactions is large. In this section we will briefly survey the main types of hydrocarbon transformations that occur without the participation of metal complexes. These reactions are presented for comparison to the metal complex activation reactions.

1. Transformations That Do Not Involve Metals or Their Compounds

Heating alkanes³ at temperatures of 900–2000 °C gives rise to the intermediate formation of radicals and carbenes. For example, ethane, ethylene, acetylene, and elemental carbon are produced by the pyrolysis of methane. Cracking higher alkanes gives a wider range of products. Analogous transformations of alkanes may be induced by light irradiation under ambient temperature.⁴ When irradiated with light at $\lambda = 121.6$ nm methane (which absorbs light at $\lambda < 143$ nm) decomposes to generate the species: ¹CH₂, ³CH₂, H[•], CH[•], H₂, from which the stable products HC≡CH, CH₂=CH₂, C₂H₆, and CH₃C≡CH are formed. Likewise, radiolysis of methane produces ethane, ethylene, and higher hydrocarbons. These reactions proceed because atoms and free radicals are very reactive toward all organic substances including saturated hydrocarbons.

The reactions of alkanes with atoms and radicals are stages of the various chain–radical processes, and occur both in the gas phase⁵ and in solutions.^{1c,6} Some of these reactions have been mentioned earlier (for example, see refs 7a–c). Interactions of hydrocarbons with ions in the gas phase are also known (for an example, with Si⁺, see ref 7d). For example, the phenylium ion formed from 1,4-T₂-benzene reacts with methane and other lower alkanes to give tritiated alkylbenzene.^{7e} Also, a carbon atom inserts into the C–H bond of methane to produce a species which is transformed into ethylene and some other hydrocarbons.^{7f} However, the most usual reaction of

alkanes and other C–H compounds with atoms and free radicals is the hydrogen atom abstraction:



The activation energy of this reaction is usually low. When a branched alkane is used as the substrate, a radical attacks its C–H bonds in accordance with "normal" selectivity, i.e., the reactivity of the C–H bonds decreases in the following order: tertiary > secondary > primary (or using another notation $3^{\circ} > 2^{\circ} > 1^{\circ}$). It is interesting that unsaturated hydrocarbons and even alkanes are capable of forming weak complexes with various radicals.⁸ A theoretical consideration of the model system $H_2NO\cdots HCH_3$ (by the INDO UHF method) showed that the stabilization energy of this complex is $<1 \text{ kcal mol}^{-1}$ at the equilibrium distance $r(O\cdots H) \cong 2 \text{ \AA}$. It is reasonable to suggest that complexes of this type are intermediate species in alkane reactions with radicals.

Halogenation and especially chlorination of alkanes is a very important process in that it gives halogenated alkyls.⁹ If the temperature is high during radical-chain chlorination of methane and the time of contact between the hydrocarbon and the chlorine is short, large amounts of ethane or ethylene and hydrogen (Benson's process^{9a,d}) are obtained in addition to chlorinated hydrocarbons. For example, the ethylene, propylene, and acetylene content reaches 77% at 1273 K. Chlorine atoms can be also generated at ambient temperature by light irradiation of molecular chlorine mixed with a hydrocarbon.^{9e} This photochlorination of alkanes also occurs if solutions of metal chlorides (for example, $AuCl_4^-$ or $PtCl_6^{2-}$; see refs 9f and g) are used. The related process hydrogen abstraction by photoexcited ketones and other organic compounds also has been investigated thoroughly.¹⁰ The alkyl radicals which are formed can react with molecular oxygen which is present in the solution. If dioxygen is replaced with carbon monoxide, carbonylation of the alkane occurs to produce an aldehyde or ketone.^{10f} A theoretical study of this H-abstraction from aliphatic alcohols was carried out.¹¹ Carbene species react with alkanes to give a variety of products.¹²

Singlet state species, such as an oxygen atom or carbene, are known to insert into the C–H bond of an alkane, whereas the same species in a triplet state will react with an alkane in a manner similar to that of a free radical. This is because the insertion of a triplet species is spin-forbidden.^{12e} Investigation of the reactions of singlet state oxygen $O(^1D_2)$ with alkanes in the gas phase has revealed that two distinct pathways exist for these reactions. These pathways were interpreted as an insertion into a C–H bond and a H-atom abstraction to form an OH radical. The insertion component dominates for small molecules (CH_4 , C_2H_6) with strong C–H bonds, while the abstraction component is the dominant mechanism for larger molecules [C_3H_8 , $C(CH_3)_4$] with stronger steric hindrances and weaker C–H bonds. An insertion mechanism was confirmed for the interaction of singlet state oxygen with methane by *ab initio* theoretical calculations.^{12f} The minimum energy path for this reaction was found to be an almost collinear approach of the $O(^1D)$ to one of the

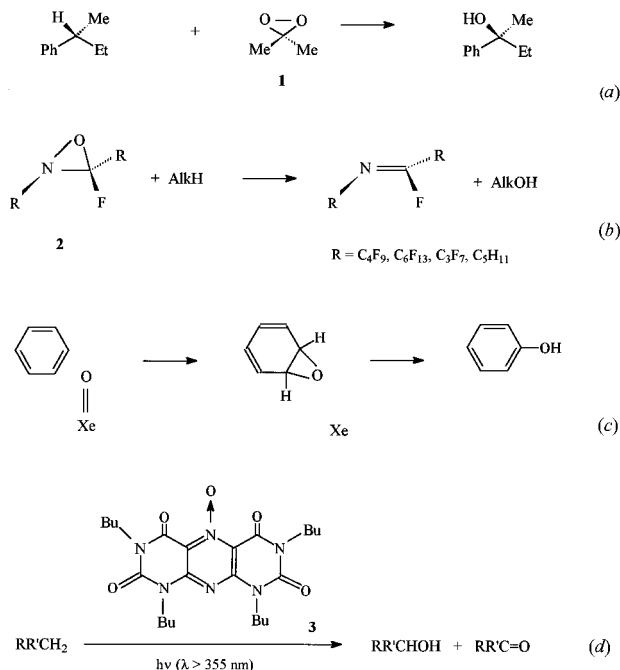
hydrogen atoms on methane. When the oxygen and hydrogen atoms reached a distance of 1.66 Å, the oxygen atom migrated off-axis. This competition between insertion and H-atom abstraction has also been proposed to occur in the enzymatic, and model enzymatic, reactions of metal-bound oxygen atoms ("oxenes") with alkanes.

The complete oxidation of alkanes by burning them into air to form water and carbon dioxide is an extremely important source of energy.^{13a} Partial oxidation of saturated hydrocarbons is also possible and produces various organic substances, e.g., alcohols and ketones or aldehydes.^{13b–e} Thus, methane oxidation in the gas phase at $\sim 670 \text{ K}$ and a pressure of 5–10 MPa gives methanol and formaldehyde. Since both products are much more reactive than the original hydrocarbon, the yield of alcohol and aldehyde is only a few percent. The reaction proceeds as a radical chain process.^{13d,f} A number of other examples of partial oxidation reactions have been reported, and several are listed here. Cycloalkanes are oxidized in a radiofrequency plasma to give mixtures of the corresponding cycloalkanones and cycloalkanols.^{13g} The reactions of $O(3P)$ atoms with benzene derivatives at $\sim 300 \text{ K}$ yield substituted phenols as the main products.^{13h} Liquid-phase oxidation of butane is a commercial method of acetic acid production. Alkylarenes can be oxidized with molecular oxygen at 70–140 °C if Br^- and tertiary ammonium salts are present in the solution.¹⁴ Photosensitized oxidation of hydrocarbons by oxygen or air gives alkyl hydroperoxides, ketones, and alcohols. Anthraquinone, cyanonaphthalenes, and some other compounds are widely used as the sensitizers in these reactions.¹⁵

Careful investigation of the reaction of ozone with C–H compounds (including alkanes) showed that hydride abstraction and the concerted insertion of ozone into a C–H bond are the reaction pathways which are most consistent with the kinetic data^{16a} (see also ref 16b). Ozone is also a promoter of arene nitration with nitrogen oxides,^{16c} and NO_2 reacts with adamantane in the presence of ozone to give nitration or nitroxylation products.^{16d}

New, efficient reagents, such as dimethyldioxirane and its fluorinated derivative, have been described for oxyfunctionalization of C–H compounds (for example, see ref 17a–c and references therein). Dimethyldioxirane (**1** in Scheme 1a) hydroxylates^{17a} (–)-2-phenylbutane to yield only (–)-2-phenylbutan-2-ol with complete retention of configuration and no loss of optical purity. This stereospecificity rules out a radical-chain oxidation mechanism. Perfluoro-dialkyloxaziridines (**2** in Scheme 1b) are also mild, selective reagents for the introduction of an OH group into alkanes.^{17d} Oxygen-containing derivatives of xenon (which may be generated by dissolution of XeO_3 or XeF_2 in water or aqueous acetonitrile) oxidize benzene, cyclohexane^{17e} and even methane.^{17f} Hydroxyl radicals are apparently the active species in these oxygenations; however, direct arene epoxidation in the initial stage of the mechanism can not be ruled out. Path c in Scheme 1 depicts this arene oxidation,^{17e} which is analogous to the crucial step proposed for arene hydroxylation by cytochrome P450 in living cells (*vide infra*). MO calculations of alkane

Scheme 1



oxidation by a model singlet atom donor (water oxide, $\text{H}_2\text{O}-\text{O}$) suggest the following mechanism.^{17g} The electrophilic oxygen approaches the hydrocarbon to form a carbon–oxygen σ -bond. This is followed by a concerted hydrogen migration to an adjacent oxygen's lone pair of electrons to give the alcohol insertion product. The activation barriers for oxygen atom insertion into the weakest C–H bond were calculated for methane (10.7), ethane (8.2), propane (3.9), butane (4.8), isobutane (4.5), and methanol (3.3 kcal mol^{−1}).

In aqueous solution at 100 °C, the radical ion $\text{SO}_4^{\cdot-}$, which is generated from $\text{S}_2\text{O}_8^{2-}$, abstracts a hydrogen atom from methane and ethane to generate radicals of the type Alk^\cdot . These radicals react with $\text{SO}_4^{\cdot-}$ to form AlkOSO_3^- . If the reaction is carried out in a carbon monoxide atmosphere, AlkCOOH can be obtained.^{17h} In a similar manner, the photooxygenation of alkanes by heterocyclic *N*-oxides (path d in Scheme 1) begins with a hydrogen abstraction from the alkane.¹⁷ⁱ Other free-radical processes which alkanes undergo include their oxidation by aromatic peracids^{17j} and the substitution of chlorine atoms on vinyl and aryl chlorides by alkanes.^{17k} Methane also reacts with sulfur at 700–1600 K to produce CS_2 , C_2 -hydrocarbons, propene, and aliphatic, cyclic and aromatic thiols by a radical process.^{17l}

When alkanes, including methane, are dissolved in superacids they are transformed into various products.^{18a–c} Novel aprotic organic superacids of the type $\text{RCOX}\cdot 2\text{AlX}_3$, where R = alkyl, aryl; X = Br, Cl and $\text{CBr}_4\cdot n\text{AlBr}_3$, where $n = 1$ or 2 have recently been described. These superacids are highly active toward alkanes (for example, see ref 18d). In protic media, the first step of the reaction is protonation of the alkane, which in the case of methane forms the methonium ion, CH_5^+ . The ground state of this ion has C_s symmetry and it may be regarded as a complex of a CH_3^+ cation with a H_2 molecule (the H–H distance has been found to be 0.936 Å which suggests formation of a bond). The ground-state energy is only slightly different (~ 1 kcal mol^{−1}) than

that of the excited state which has C_{4v} symmetry. Two transition states which have different symmetries are even closer in energy to the ground state.^{18e} This finding corresponds to extremely fast hydrogen atom movements in CH_5^+ and other similar carbonium ions; therefore, fast isomerization, or epimerization, of alkane molecules is expected to proceed in superacid solutions. Further support for this conclusion comes from *ab initio* calculations which have shown that triprotonated methane CH_7^{3+} resides at a minimum on its potential energy surface, although its deprotonation is highly exothermic.^{18f}

Electrophiles formed in superacid media are able to attack alkanes primarily via electrophilic addition to a C–H bond. For example, Olah *et al.* observed O atom insertion during the reaction of hydrogen peroxide with methane in Magic Acid at temperatures above 0 °C. This reaction produced methanol with a very high selectivity (>95%).^{18g} The particle $(\text{OH})^+$, which can be considered to be a protonated oxygen atom in the singlet state, is apparently the active species in the reaction. The methyl alcohol which is formed in this reaction is immediately protonated to the methyloxonium ion (CH_3OH_2^+), and this prevents further oxidation. Another example of an electrophilic reaction in a superacid is the protium–deuterium exchange which is observed for isobutane in $\text{DF}-\text{SbF}_5$.^{18h} The aprotic organic superacid $\text{CBr}_4\cdot 2\text{AlBr}_3$ also catalyzes the reaction of adamantane with CO in the presence of methylcyclopentane to produce 1-adamantanecarbaldehyde.¹⁸ⁱ The methylcyclopentane in this reaction acts as a source of hydride ion. Likewise, sulfuric acid can induce carbonylation of iso- and cycloalkanes.^{18j} Strong acids promote the electrophilic hydroxylation of aromatics, and sodium perborate–trifluoromethanesulfonic acid has been found to be a versatile reagent for the monohydroxylation of arenes to phenols.^{18k} Finally, *ab initio* MO theory recently has been applied to investigate the reactions of the electrophiles NO^+ and NOH^{2+} with methane.^{18l}

2. Reactions Promoted by Metals or Their Oxides

Transformations of hydrocarbons which are promoted by solid metals and their oxides play a very important role in chemical industry. Heterogeneous metal-containing catalysts are widely employed for oxidation, dehydrogenation, cracking, isomerization, and many other processes which are performed on saturated as well as aromatic hydrocarbons (for example, see reviews 19a–c). Usually such reactions occur only at high temperatures (>200 °C).

Metal oxides (Cr_2O_3 , Al_2O_3 , NiO , etc.) catalyze H–D exchange between alkanes and D_2 , as well as between alkanes and deuterated alkanes. Metal surfaces are also capable of inducing isotope exchange, although aromatic and alkylaromatic hydrocarbons are more reactive than alkanes. The highest reactivities are exhibited by arene hydrogens in *meta* and *para* positions, while the low reactivity of *ortho*-hydrogens is due to steric restrictions. In alkyl aromatics, the most reactive side-chain hydrogens are those in benzylic positions. Other types of heterogeneous metal catalysts which have been employed in recent years to activate hydrocarbons include metal clusters,^{19d} suspended metal catalysts,^{19e} metal mem-

branes,^{19f} and supported metals.^{19g} Also, the perspective homologation of olefins and acetylene with methane on transition metals has been demonstrated.^{19h}

Both metals and metal oxides catalyze either deep oxidation (to produce carbon dioxide and water) or selective partial oxidation (to afford alcohols, ketones, and carboxylic acids, as well as "synthesis gas", i.e., $\text{CO} + \text{H}_2$) of hydrocarbons with molecular oxygen (for example, see ref 20). In addition to insertion of an oxygen atom into a hydrocarbon molecule, heterogeneous metal catalysts can also promote oxidative condensation, or coupling, of methane. A great number of papers have been devoted to this process (see refs 21a and b). Methane can also be cocondensed with some compounds in the presence of heterogeneous catalysts and molecular oxygen (Khcheyan's reaction^{21c}). Thus, oxidative coupling of methane and acetonitrile gives propionitrile and acrylonitrile. Styrene may be obtained from methane and toluene, in addition to some other compounds.^{21d-f} This reaction is thought to proceed by a multistage mechanism which includes free radicals. Finally, isobutane^{21g} and cyclohexane^{21h} are oxidized to their corresponding hydroperoxides when irradiated with green or blue light in the presence of O_2 and a zeolite.

C. Reactions of C–H Compounds with Metal Complexes: An Historical Survey

The first metal-containing systems which were capable of reacting with hydrocarbons and other C–H compounds, such as Fenton's reagent (hydroxylation) and mercury salts (direct mercuration), were discovered as early as the end of nineteenth century. During the 1930s, the electrophilic auration of arenes was described,^{22a} a radical-chain autooxidation of hydrocarbons initiated by metal derivatives was developed,^{22b} and a method for the metal–oxo complex-promoted oxidation of alkenes and arenes by hydrogen peroxide was proposed.^{22c} A second spurt in pioneering research occurred in this field in the 1960s. Reactions involving the cyclometalation (i.e., the cleavage of a C–H bond in a metal-coordinated phosphine or amine ligand) of aromatic^{22d} and sp^3 -hybridized carbon atoms^{22e} were found. It was demonstrated that palladium(II) derivatives induce the oxidative coupling of arenes^{22f} and the arylation of alkenes (the Fujiwara reaction),^{22g} while platinum(II) salts catalyze H–D exchange between benzene and D_2O .^{22h} In 1969 the first activation reactions of C–H bonds in alkanes were discovered.²²ⁱ It was found that (i) platinum(II) salts catalyze the H–D exchange between methane or its analogs and D_2O at 100 °C, and (ii) the complex $\text{CoH}_3(\text{PPh}_3)_3$ induces the deuteration of methane by D_2 at room temperature. It has now become evident that organometallic derivatives are formed as intermediates in all these instances. In the 1970s it was shown that alkanes are oxidized by platinum(IV),^{23a} palladium(II),^{23b} ruthenium(IV),^{23c} and cobalt(III)^{23d,e} compounds and that complexes of iridium(III)^{23f} and titanium(II)^{23g} catalyze the H–D exchange. The next decade was marked by vigorous development of the activation of alkanes and arenes by low-valent metal complexes. These reactions proceed via an oxidative addition mechanism to form either alkyl and aryl derivatives of metals or alkenes.^{23h-n}

In contrast to the numerous publications devoted to C–H bond activation by low-valent metal complexes, far fewer examples of C–H bond activation bond by high oxidation state metal complexes are known which proceed by formation of organometallic compounds. For example, the ion PtCl_6^{2-} metalates arenes in a manner similar to palladium(II). However, σ -aryl complexes of Pt(IV) are stable compounds and have been isolated,^{24a} while σ -aryl complexes of palladium(II) are not stable and continue to react. The PtCl_6^{2-} ion easily platinates arenes when irradiated with light^{24b} or γ -irradiation.^{24c} This platination is the first example of a photoelectrophilic substitution on an arene. Another example of C–H bond activation by a high-valent metal complex is provided by the exchange reaction between a methyltitanium σ -complex and $^{13}\text{CH}_4$.^{24d}

At the end of the 1980s, the intensity of investigations into C–H bond activation by low-valent metal complexes began to diminish and interest gradually shifted to the oxidation of hydrocarbons by high-valent metal–oxo compounds and oxygen. Currently, attention is being focused on biological and biomimetic oxidations. Cytochrome P450 model studies were propelled by the use of iodosyl benzene as an oxygen atom donor in catalytic oxidation reactions and by the use of metalloporphyrins as models for the active center of the enzyme (for one of the pioneering papers see ref 24e). The more recent Gif systems used for the selective oxidation of alkanes are of considerable interest because the reasons for their unusual selectivity and their mechanisms remain somewhat mysterious. The Gif systems consist of oxygen, an iron complex, a reductant, a carboxylic acid, and pyridine.^{24f}

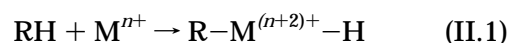
D. Three Types of the C–H Bond Cleavage Promoted by Metal Complexes

In the Introduction, we discussed the term "activation" when applied to saturated compounds and concluded that the cleavage of an ordinary bond (e.g., C–H) can result from such activation. In many cases we might consider the activation and splitting as synonymous.

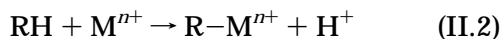
1. Classification Based on the Mechanism

We propose to divide all the C–H bond splitting reactions which are promoted by metal complexes into three groups based on their mechanisms.

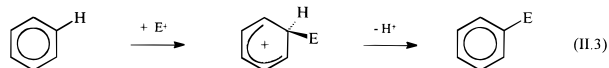
a. "True" Activation: When σ -Organyl Derivatives Are Formed. The first group, that of "true" activation, consists of all processes where an organometallic derivative, i.e., a compound containing an M–C σ -bond (M = metal),^{1b} is formed as an intermediate or as the final product. The σ -ligand in the resulting compound is an organyl group, i.e., alkyl, aryl, vinyl, acyl, etc., which is bound to the metal via a carbon atom. This M–C σ -bond can be cleaved, and in catalytic processes the dissociation of this bond is inevitable. The cleavage of the C–H bond by direct participation of a transition metal ion proceeds via an oxidative addition mechanism



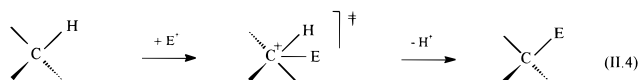
or an electrophilic substitution mechanism



Metals in low and high oxidation states undergo oxidative addition and are discussed in section III, while high oxidation state metals take part in electrophilic substitutions and are dealt with in section IV. Electrophilic metalation of an aromatic nucleus is an example of the latter reaction and proceeds in two stages. The electrophilic species first adds to the arene with the formation of a Wheland intermediate:



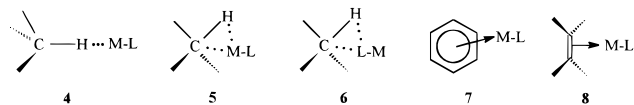
An analogous intermediate might be formed during the interaction of a saturated hydrocarbon with an electrophilic metal-containing species, but should be much less stable:



not surprisingly, the reactivities of arenes and alkanes in electrophilic substitution reactions are different, with the former being much more active. Consequently, the oxidative addition mechanism which characterizes the interaction of both saturated and aromatic hydrocarbons with low oxidation state metal complexes is in principle the same. Therefore, the reactivities of arenes and alkanes in this reaction usually do not differ dramatically.

As we have shown, reactions in our first classification group involve “true” metal complex activation of the C–H bond. We call this type of activation “true” because it is only in this case that the closest contact between a metal ion and the C–H bond (i.e., a normal σ -bond between M and C) is realized. In the “true” activation, a C–H-containing compound enters the coordination sphere of the metal complex in the form of a σ -organyl ligand.

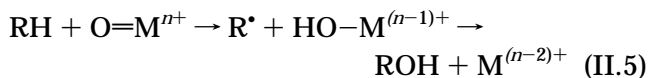
Very weak alkane or alkyl adducts, in which the C–H bond is directly coordinated to the metal (**4** and **5**) or its ligands (**6**), do not necessarily lead to subsequent cleavage of the C–H bond. However, compounds like **4–6** may be intermediate species lying on the reaction coordinate which leads to σ -organyl products. These intermediates are analo-



gous in some respects to the much more stable π -complexes (e.g., **7** and **8**) which are formed by unsaturated hydrocarbons. This coordination of the metal complex to the C–H bond may be referred to as preactivation of the compound's C–H.

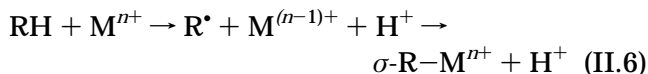
b. Second Type: When There Is No Direct Contact between the Metal and the C–H Bond. In the second group, we include reactions in which a metal complex cleaves a C–H bond but no σ -C–M bond is directly generated at any stage. The function of the metal complex in these reactions usually consists of abstracting an electron or a hydrogen atom from the hydrocarbon, RH. The radical ions $\text{RH}^{\cdot+}$ or radicals R^{\cdot} which are formed then interact with other

species, such as molecular oxygen which is present in the solution or one of the ligands on the metal complex. For example, in the hydroxylation of an alkane by an oxo complex of a high-valent metal, an alkyl radical is generated and subsequently reacts with a hydroxy ligand on the metal:



In this reaction the metal–oxo complex is an oxidant of the type CrO_4^{2-} or MnO_4^- or an oxoferryl species. For example, it could be one of the states of the cytochrome P450 enzyme which contains the $\text{P}^+\text{Fe}^{\text{V}}=\text{O}$ species.

It should be noted that some reactions which proceed via radical intermediates can result in the formation of alkyl σ -complexes and thus should be assigned to the first classification category. For example, such a reaction could proceed by the mechanism



However, since the alkyl σ -derivative is frequently unstable, it is usually difficult to demonstrate its intermediate formation. The mediated (i.e., without metal contact) splitting of the C–H bond in a hydrocarbon, RH, by a complex also can be effected by a *molecular* mechanism. In this mechanism, RH is in direct contact with only a ligand of the complex.

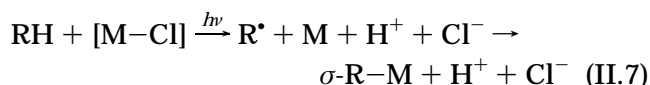
In addition to activating a hydrocarbon, the metal complex sometimes is capable of simultaneously activating another reactant. Thus, for example, the active center of cytochrome P450 initially transforms an oxygen molecule to a reactive state, in which one of the two oxygen atoms is coordinated to the iron center, to form an oxo ligand. This same active center then activates a hydrocarbon molecule with the participation of the oxo ligand.

c. Third Type: When a Metal Complex Promotes the Formation of a Reactive Species Which then Attacks the C–H Bond. Whereas the reactions included in the second group require direct contact between a molecule of the C–H compound and the metal complex (albeit via the ligand), complexes belonging to the third type initially activate some other reactant (e.g., O_2 or H_2O_2) to form a reactive species which then attacks the hydrocarbon molecule. The reactive species is usually a radical, such as a hydroxyl radical, which attacks the hydrocarbon independent of any participation of the metal complex. The oxidation of alkanes by Fenton's reagent is an example of such a process.

2. Mechanisms of the C–H Bond Activation

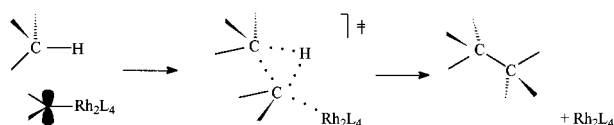
Naturally, the classification scheme described above is a rather approximate division of all the known reactions in accordance with their mechanisms. Nevertheless, the unambiguous assignment of a process to a particular type requires a detailed knowledge of the reaction mechanism. For example, the process shown earlier in eq II.6 could proceed with participation of the ligands of the metal complex. Another example is given by the photochemical

reaction depicted in eq II.7.^{24b,c} Although the first step of its mechanism suggests that it belongs to the third type, the reaction possibly forms a σ -organyl-metal derivative and thus belongs to the first type:



A final example is provided by the insertion of a carbene into a C–H bond,^{25a,b} in which a rhodium complex may be assumed to decompose the diazoacetoacetate to generate a free carbene species. If this were so, the reaction should be attributed to the third type. However, the mechanism is apparently not so simple and includes the formation of a rhodium carbene complex. Overlap of the metal carbene's p-orbital with the σ -orbital of the reacting C–H bond initiates C–C and C–H bond formation accompanied by dissociation of the carbene from the metal (Scheme 2).^{25a} This reaction therefore is of the second type.

Scheme 2



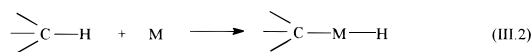
Unfortunately, many processes' mechanisms have not yet been elucidated even broadly.

III. Activation of Hydrocarbons by Low-Valent Metal Complexes

Although processes involving the oxidative addition of molecular hydrogen to metal complexes, in accordance with the equation



have been known since the 1960s, numerous reactions of hydrocarbon oxidative addition were discovered and investigated in detail only in recent years. Such transformations may be schematically depicted as follows:



In some cases the intermediate organyl hydride complexes cannot be isolated, although the evidence of their formation is obtained. In the present section we will consider activation of hydrocarbons via oxidative addition as well as some other reactions in which low-valent metal complexes participate.

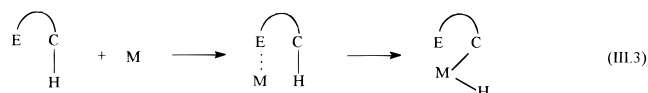
A. Formation of σ -Organyl Hydride Complexes

Reactions which proceed in accordance with the formal eq III.2 result in an increase in the oxidation state of the metal center. Thus, the metal's oxidation state is two units higher in the organyl hydride complex than it was in the initial metal compound. Alkanes, arenes, alkenes, and monosubstituted acetylenes all undergo this oxidative addition processes. The reactions frequently occur in solution at room temperature, although sometimes heating is required, and certain reactions are stimulated by irradiation. Either heat or light is essential for the

abstraction of several ligands from the initial complex to form a coordinatively unsaturated species capable of oxidatively adding the C–H compound.

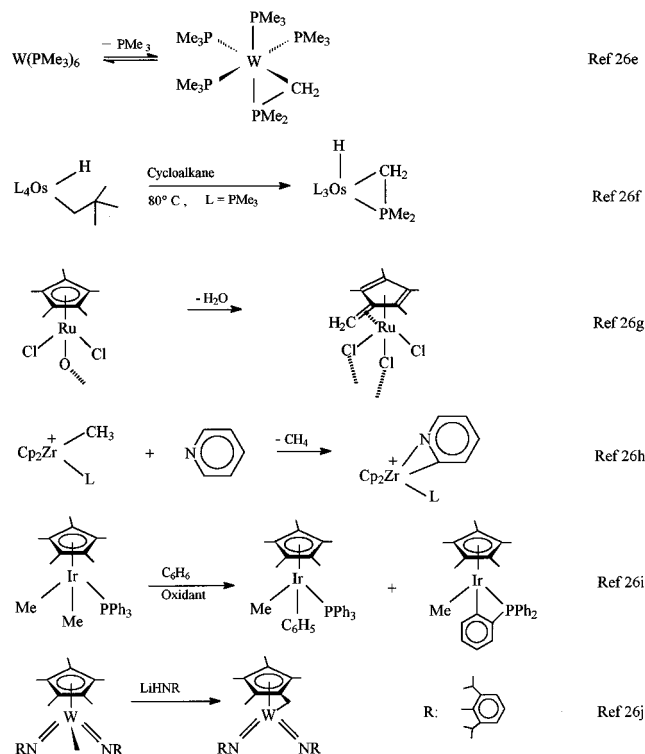
1. Cyclometalation

The *intramolecular* cleavage of a C–H bond occurs much more easily than *intermolecular* activation and gives rise to a more stable σ -organyl hydride complex. The schematic equation of this cyclometalation is depicted as follows:



Here E is a donor atom, such as N, P, or As. Many reviews^{26a-d} and even a book^{1d} have been devoted to the cyclometalation reaction; therefore, we will give only a few examples of the cyclometalation of sp^3 - and sp^2 -C–H bonds; it should be noted that not all the cyclometalation reactions shown in Scheme 3 proceed via an oxidative addition mechanism.

Scheme 3



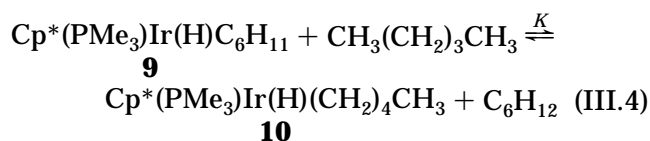
2. Intermolecular Oxidative Addition

In many cases, the σ -organyl complexes formed from the oxidative addition^{27a} of alkanes, arenes, alkenes, and monosubstituted acetylenes are fairly stable and can be isolated. For example, upon heating or photolysis, the complexes Cp_2WH_2 , Cp_2WCO , and Cp_2WHCH_3 give rise to a coordinatively unsaturated tungstocene species, Cp_2W , which readily combines with aromatic or alkylaromatic hydrocarbons.²³ⁿ The products obtained from the reaction with toluene are $\text{Cp}_2\text{W}(\text{H})\text{C}_6\text{H}_4\text{CH}_3$ and $\text{Cp}_2\text{W}(\text{CH}_2\text{-Ph})\text{C}_6\text{H}_4\text{CH}_3$. In forming these products, the tungsten inserted into both a C–H bond in the aromatic ring and a C–H bond at the sp^3 -hybridized carbon

atom. However, cyclohexane and neopentane do not give rise to insertion products under similar conditions.

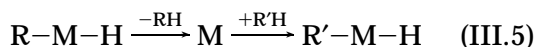
The oxidative addition of alkanes to form alkyl hydride complexes was first definitively demonstrated by Bergman in studies using iridium complexes. The iridium dihydride derivative $\text{Cp}^*\text{Ir}(\text{H})_2\text{PMe}_3$ (Cp^* = pentamethylcyclopentadienyl) was irradiated in a cyclohexane or neopentane solution, to produce the complexes $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{C}_6\text{H}_{11})$ and $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})\text{CH}_2\text{CMe}_3$ in a satisfactory yield.^{27b} Other saturated hydrocarbons and benzene also readily added to this iridium complex. The resulting alkyl hydride complexes were converted into the more stable derivatives, $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Br})\text{R}$, by treatment with CHBr_3 at -60°C . Irradiation of $\text{Cp}^*\text{Ir}(\text{H})_2\text{PMe}_3$ in a $\text{CMe}_4 + \text{C}_6\text{D}_{12}$ mixture led to the formation of $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})\text{CH}_2\text{CMe}_3$ and $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{D})\text{C}_6\text{D}_{11}$ with very small admixtures of cross-addition products. An analogous reaction of alkanes with the complex $\text{Cp}^*\text{Rh}(\text{H})_2\text{PMe}_3$ took place upon irradiation at temperatures below -30°C .^{27c} Both substrate and positional selectivities proved to be much higher for the rhodium complex than for the iridium complex.

When the cyclohexyliridium hydride complex **9** or the *n*-pentyliridium hydride derivative **10** was heated for 50 h at 140°C in a mixture of 91.5% cyclohexane and 8.5% *n*-pentane, the following equilibrium was established:



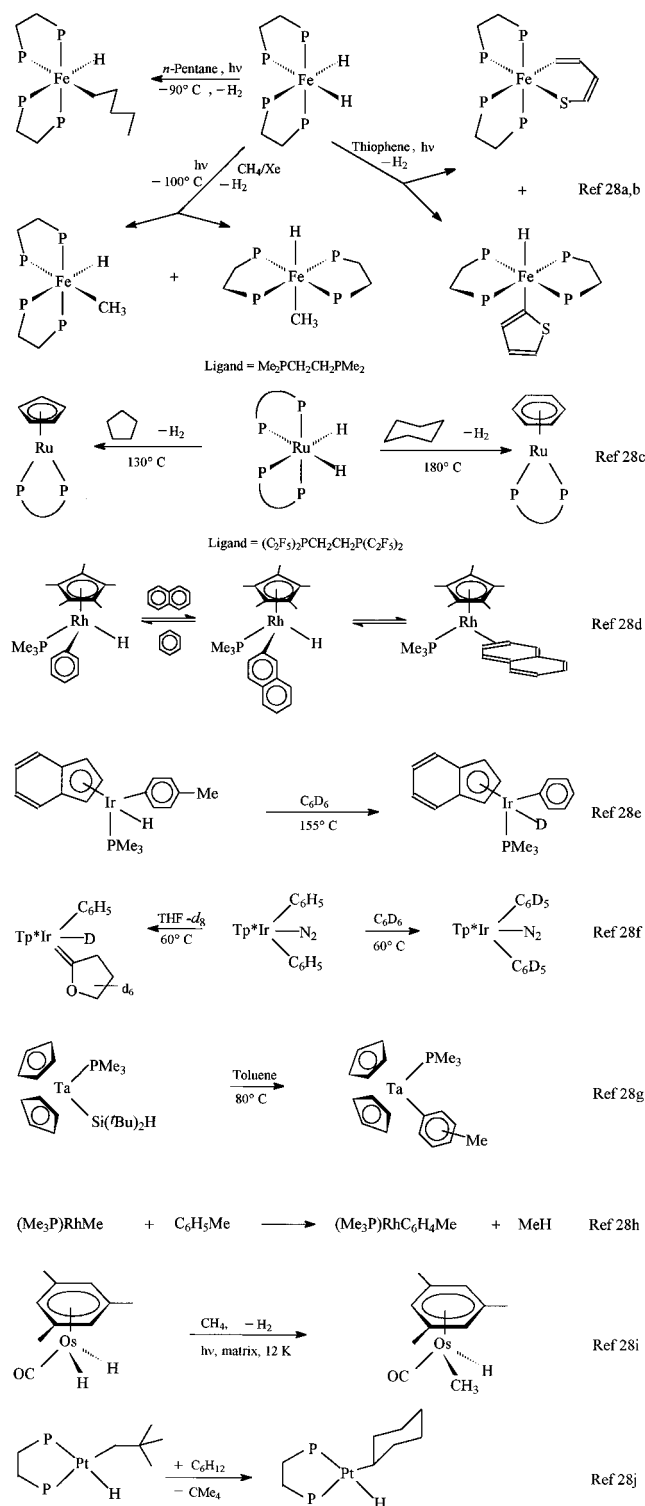
The ratio of **10:9** was 1.0 ± 0.1 . Hence $K = [\text{10}]/[\text{C}_6\text{H}_{12}]/[\text{9}]/[\textit{n}\text{-C}_5\text{H}_{12}] = 10.6$, which corresponds to $\Delta G^\circ = -2.0 \text{ kcal mol}^{-1}$. It has been suggested that the entropy changes in the reaction are small. Assuming that the CH_2 and CH_3 bond energies in cyclohexane and *n*-pentane are 94.5 and 98 kcal mol^{-1} , respectively, we find that the energy of the M–C bond in complex **10** is higher than in complex **9** by 5.5 kcal mol^{-1} . It follows that the methyliridium hydride complex $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})\text{CH}_3$ should also be thermodynamically very stable and this found to be the case. The desired methyliridium hydride complex was obtained in 58% yield upon heating a solution of complex **9** in cyclooctane in the presence of methane.^{27c}

In addition to the reactions just discussed, a large number of reactions are known which form a coordinatively unsaturated species by elimination of molecular hydrogen or an RH molecule ($\text{R} = \text{alkyl, aryl, etc.}$). These species can then react according to eq III.5, and several examples are demonstrated in Scheme 4. Both R and R' are H, alkyl, aryl, etc. Analogous reactions of iron and iridium complexes with thiophene give rise to both C–H and C–S insertion products.^{28a,b,k}



A coordinatively unsaturated species capable of adding RH can be also generated by the extrusion of neutral ligands such as phosphines (Scheme 5), carbon monoxide (Scheme 6), and olefin as well as

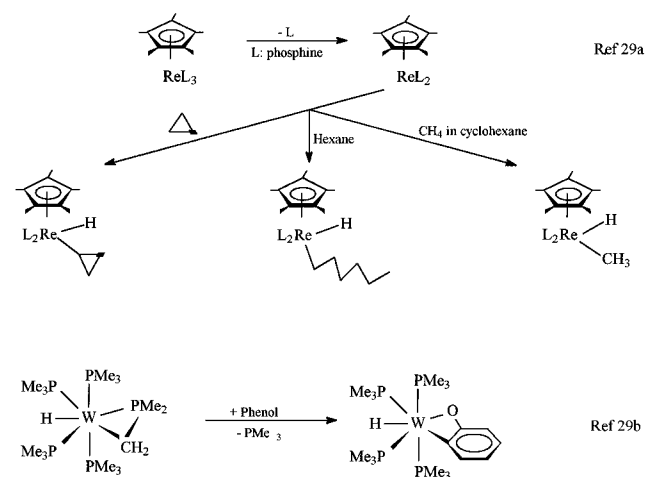
Scheme 4



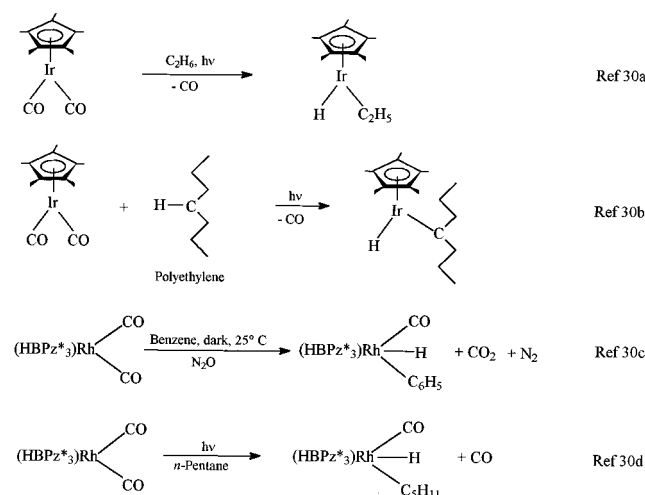
some other ligands (Scheme 7). Some examples of the oxidative addition of a Si–H bond, which is similar to the C–H bond in many respects,^{31g} also are shown in these schemes.

It is interesting that thermal and photochemical activation sometimes can result in the formation of different products. For example, heating a solution of the ethylenerrhodium carbonyl complex $\text{RhHBPz}^*_3\text{-(CO)(C}_2\text{H}_4)$ ($\text{Pz}^* = 3,5\text{-dimethylpyrazole}$) in benzene entails the elimination of the ethylene π -ligand and formation of a phenylrhodium hydride complex (**11** in Scheme 8).^{32a} However, irradiation of this solution causes the hydride ligand to add to the ethylene

Scheme 5



Scheme 6



molecule, rather than the metal atom, which results in the appearance of an σ -ethyl group in complex **12**.^{32b} In some cases, a coordinatively unsaturated species followed by an oxidative addition product can be formed via rearrangement of the complex without elimination of any particles. For example, the olefin complex **13** can be converted into the π -allyl hydride derivative **14** in Scheme 8^{32c} in this manner.

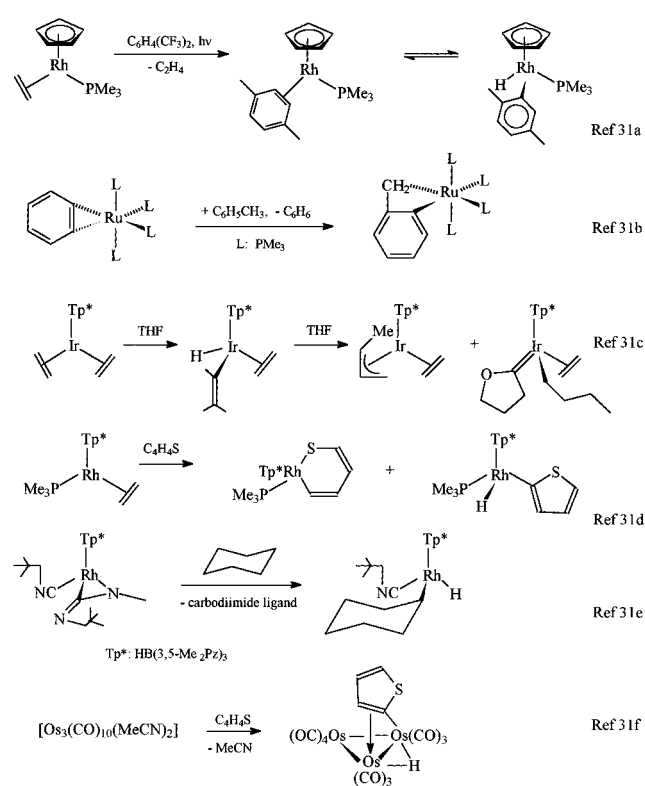
Transition metal complexes readily cleave the C–H bonds in ethylenes (Scheme 9) and acetylenes (Scheme 10), in addition to the C–H bonds in arenes and alkanes which were described above.

3. Some Special Cases

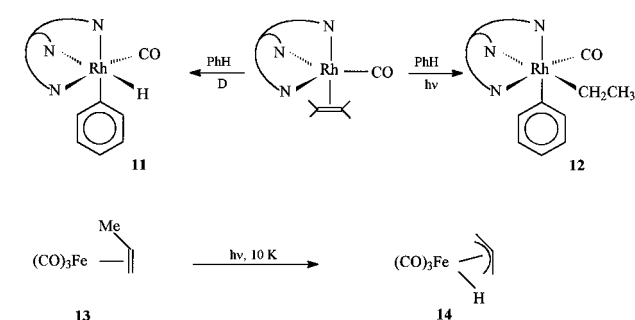
Some examples of oxidative addition coupled with other transformations were mentioned in the previous section. In this section we discuss other oxidative addition reactions which are rather complicated and do not lead to the formation of organyl hydrides.

When a cyclohexane solution of neopentylthorium complex **15** (Scheme 11) is heated, one of the ligands is eliminated and the remaining alkyl group is cyclometalated.^{35a} The resulting metallacycle **16** then intermolecularly metalates tetramethylsilane. The reaction does not stop at compound **17**, however, and the cyclometalated silyl complex **18** can be obtained. It is interesting that even methane is readily activated by this thorium complex. It should be noted that thorium formally is not a low-valent

Scheme 7



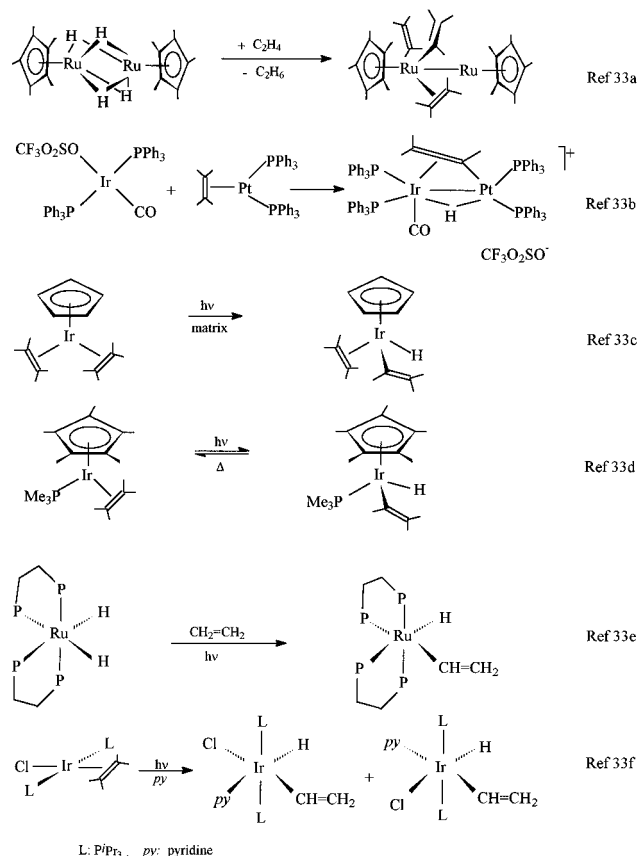
Scheme 8



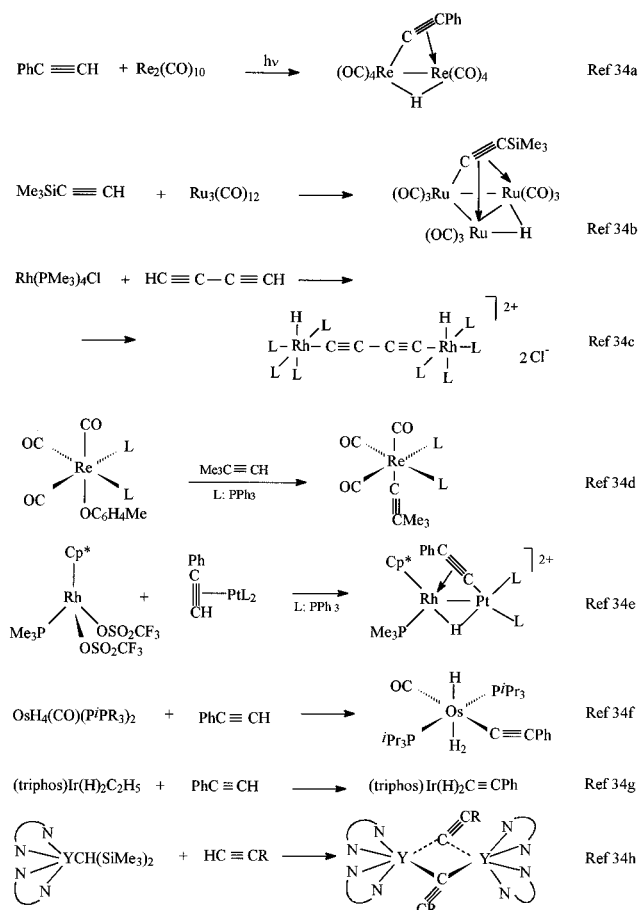
ion in these reactions. The hydrogen atom from the alkane cannot add directly to the metal ion but must add to a ligand instead. This can also be seen in the related example shown for complex **19** (Scheme 11). Heating a solution of **19** and methane in deuterated cyclohexane leads to replacement of the CD₃ group by a methyl from the methane and also yields CD₃H.^{35b} Species **20** is assumed to be an intermediate in this process. The reaction of the tantalum hexamethylbenzene complex **21** with deuterated 3,3-dimethylbutyne-1 also proceeds as an intramolecular oxidative addition and gives rise to the σ -organyl complex **22** (Scheme 11).^{35c}

Rhodium(II) porphyrin complexes were observed to react with the C–H bonds of alkylbenzenes and even methane (Scheme 12).^{35d–g} In this case components of the C–H bond added simultaneously to two species of the activating complex. The authors proposed that the crucial step in the reaction is the attack of metal-centered radicals on the C–H compound. The formation of a transition state that contains two PorRh[•] units and methane could occur in a single step (mechanism A in Scheme 12) or through a series of bimolecular steps involving an intermediate (mechanism B).

Scheme 9

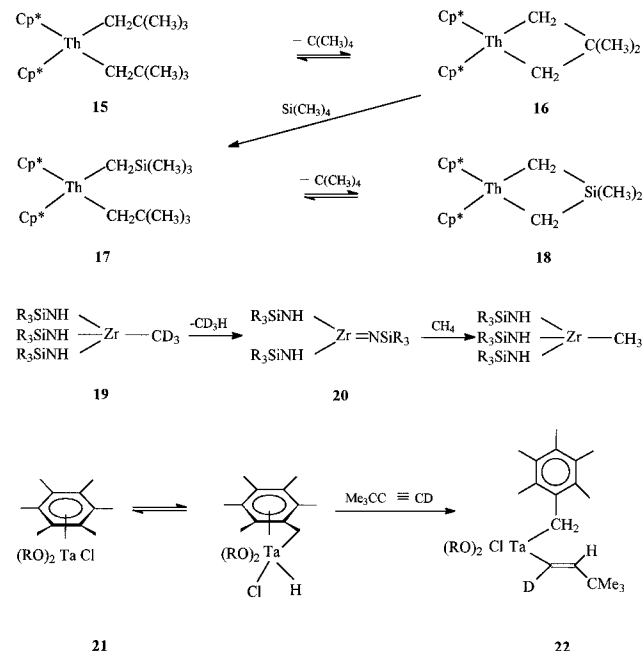


Scheme 10

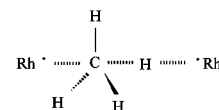


A complex $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{CH}_3)^+$ reacts at low temperature with an alkane, RH , to yield the σ -alkyl

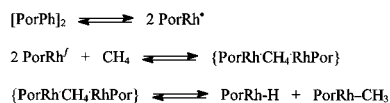
Scheme 11



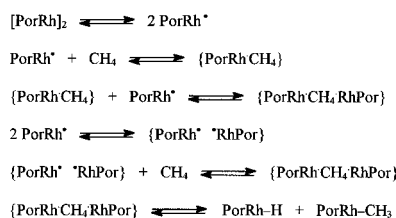
Scheme 12



Mechanism A:



Mechanism B:



derivative $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{R})^+$ and methane.^{35h,i} Two different mechanisms were proposed for this metathesis: (a) formation of a four-center adduct between the methyl complex and RH (for such a mechanism see section IV.A.2 below); and (b) oxidative addition followed by the reductive elimination of a methane molecule.

Recent theoretical calculations support a low-energy oxidative addition mechanism.^{35j} Reaction of the unsolvated cationic complex $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{CH}_3)^+$ with pentane, cyclohexane, or benzene in the gas phase also gives $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{R})^+$ as the product. However, a mechanistic investigation of this process by electrospray tandem spectrometry has demonstrated that neither the oxidative addition-elimination mechanism nor the concerted σ -bond metathesis mechanism is operative. Instead, the authors pro-

posed a dissociative elimination–addition mechanism which proceeds through a series of 16-electron Ir(III) intermediates.^{35k}

Various other examples of the activation of C–H bonds by conventional, low-valent metal complexes have been recently described.^{35l–v} Not all of these reactions proceed via an unambiguous, simple oxidative addition mechanism.

The reactions of alkanes bearing electron-withdrawing substituents with electrophilic oxidizing reagents are more difficult than the analogous reactions with unsubstituted alkanes. For example, permanganate ion in a solution of aqueous trifluoroacetic acid reacts with alkanes but does not oxidize nitroethane. Thus, the reactions of alkanes with strong oxidants in organic solvents can be stopped at the initial step by incorporating a polar functional into the alkane molecule. In contrast, C–H oxidative addition reactions with low-valent electron-donor metal complexes are facilitated by electron-withdrawing substituents which stabilize the resulting higher oxidation state product. Examples of this reaction include the oxidative addition of acetonitrile,^{36a} nitromethane,^{36b} and acetone^{36c} to complexes of iridium, palladium, and gold, respectively.

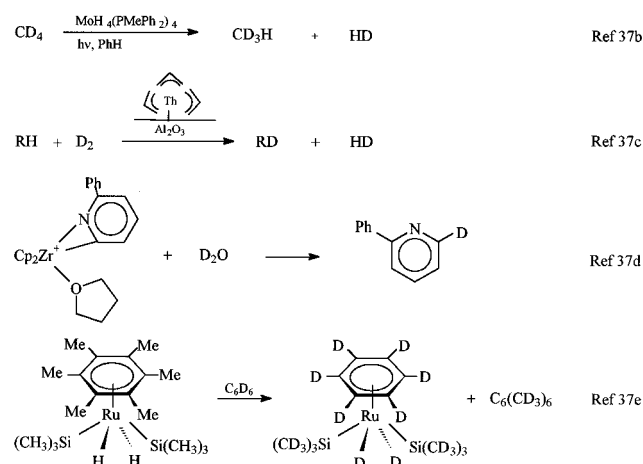
B. Functionalization of Hydrocarbons in Solutions

Metal complexes induce a whole series of reactions in which hydrocarbon hydrogen atoms are replaced by atoms of other elements. These reactions are frequently catalyzed by the metal complex. A considerable proportion of the processes initially proceed by an oxidative addition mechanism. This first stage forms an alkyl hydride complex which undergoes further transformations. The resulting reaction may be a H–D exchange, dehydrogenation of an alkane or alkyl group, or the introduction of a functional group into a C–H compound. The epimerization of secondary alcohols catalyzed by rhenium alkoxide complexes proceeds via this C–H bond activation, such that the first step of the reaction is a hydrogen atom migration from the alcohol to the metal ion.^{37a}

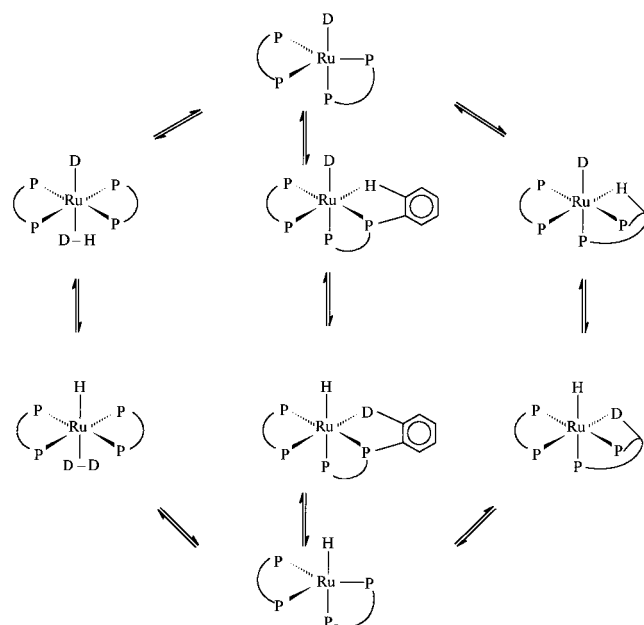
1. H–D Exchange

Many works devoted to isotope exchange have appeared in recent decades. This exchange may occur between an alkane or arene and molecular deuterium, between deuterated and undeuterated hydrocarbons, or between a hydrocarbon and another deuterated inorganic (e.g., water) or organic substance. Two different groups within the same molecule also can exchange their hydrogen and deuterium atoms. Some examples of all these reactions are shown in Scheme 13. NMR studies showed that the hydrogen in the five-coordinate ruthenium complex $[\text{RuH}(\text{dppb})_2]\text{PF}_6$ exchanged among the terminal hydride, the agostic hydrogen, and a noncoordinating methylene hydrogen of the 1,4-bis(diphenylphosphino)butane ligand (dppb).^{37f} When the partially deuterated ligand $\text{Ph}_2\text{P}(\text{CD}_2)_4\text{PPh}_2$ was used and the reaction was carried out at high temperature, hydrogen scrambling between the *ortho* hydrogens on the phenyl groups, all the methylene hydrogens, and the terminal hydride was observed in this complex. Deuterium incorporation took place at the *ortho*

Scheme 13



Scheme 14



From ref 37f, copyright 1994 American Chemical Society.

positions and all the methylene positions on the diphosphine ligand when the complex was in contact with D_2 in solution. The relative abundance of deuterium incorporated at each site was $\beta\text{-CH}_2 > \alpha\text{-CH}_2 > o\text{-CH}$. The proposed mechanism for the deuterium incorporation and the hydrogen scrambling is depicted in Scheme 14.

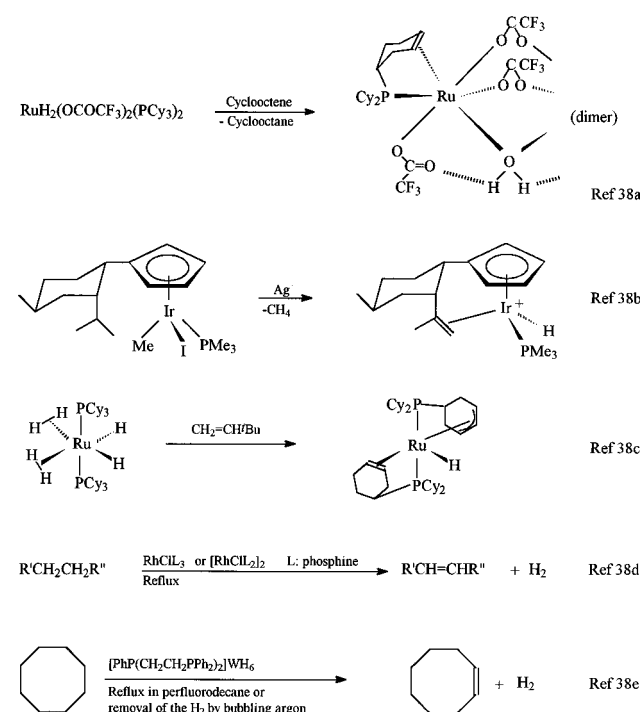
The complex $\text{MnH}_3(\text{dmpe})_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] activates aromatic and benzylic C–H bonds under both thermal and photochemical conditions. This activation can be observed through the intermolecular H–D exchange with C_6D_6 and D_2 ^{37g} which the hydride manganese complex catalyzes (86 °C, 20 h). Data for this reaction are shown in Table 1. Electron-deficient ruthenium(II) porphyrins also catalyze H–D exchange into methane and benzene and into toluene both the benzyl and aryl positions.^{37h}

2. Dehydrogenation of Alkanes or Alkyl Groups

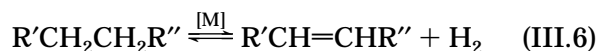
The intramolecular dehydrogenation of alkyl groups in σ -alkyl metal complexes is well known to produce chelated π -olefin complexes (see examples in Scheme

Table 1. H–D Exchange Catalyzed by $\text{MnH}_3(\text{dmpe})_2$ (From Ref 37g. Copyright 1992 American Chemical Society)

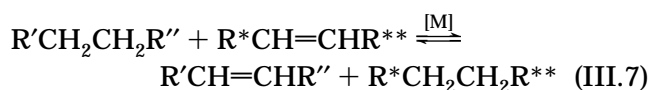
substrate	in C_6D_6 , turnovers (aliph)	exchange with D_2 in neat substrate	
		turnovers (arom)	selectivity (arom/aliph)
toluene	11.9	70.0	5.9
<i>m</i> -xylene	29.8	24.7	0.8
mesitylene	48.0	0	0
anisole	3.0	8.0	2.6

Scheme 15

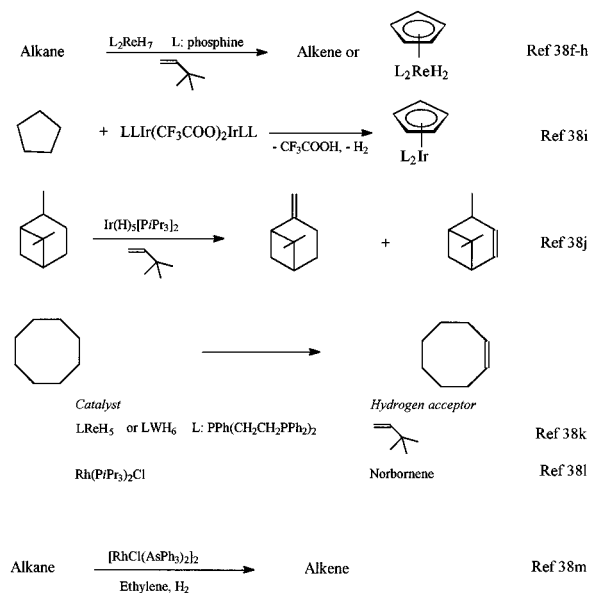
15). Various transition metal complexes readily abstract hydrogen atoms from C–H compounds to produce π -olefin derivatives. Cyclopentane yields a π -cyclopentadienyl ligand, and cyclohexane forms a π -benzene complex in this manner). If the π -complex formed by this dehydrogenation process is relatively unstable, the π -ligand dissociates and the reaction becomes catalytic with respect to metal complex:



Thermally induced reactions of this type are shown in Schemes 15 and 16. Continuous removal of the molecular hydrogen evolved through the reflux process displaces the equilibrium III.6 toward the olefin (Fujii–Saito method^{38d}). Hydrogen evolved in the course of the dehydrogenation also can be efficiently removed by carrying out the reaction in refluxing perfluorodecane or by bubbling argon through the reaction mixture (Aoki–Crabtree methods^{38e}). The equilibrium may be also shifted to the right by adding a molecular hydrogen acceptor, such as an olefin or carbonyl compound:



Indeed, if 3,3-dimethylbutene is present in the reac-

Scheme 16**Table 2. Product Distribution (%) for Isopropylcyclohexane Dehydrogenation by Different Catalytic Systems (From Ref 38o. Copyright 1992 American Chemical Society)**

catalyst system	products ^a		
$\text{RhL}_3\text{Cl} - \text{H}_2$	20	30	50
$\text{RhL}_2\text{Cl}(\text{CO}) - h\nu$	20	27	54
$\text{RhL}_2\text{Cl}(\text{P}i\text{Pr}_3) - \text{H}_2$	27	11	63

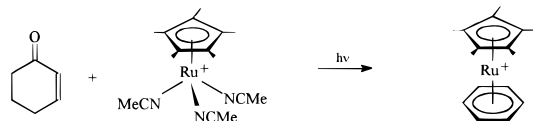
^a Values were obtained by extrapolation to initial time.

tion mixture (Crabtree–Felkin system) the turnover number is noticeably increased (Scheme 16).

Efficient, low-temperature dehydrogenation of alkanes catalyzed by $\text{Rh}(\text{PMe}_3)_2\text{Cl}(\text{CO})$ proceeds under a high-pressure dihydrogen atmosphere.³⁸ⁿ Norbornene has been used as a hydrogen acceptor in this reaction. Under 1000 psi of dihydrogen at 60 °C for 25 h, a cyclooctane solution of the complex and norbornene yielded 560 turnovers of cyclooctene and norbornane. It is noteworthy that at 100 °C a similar solution afforded 950 turnovers in 15 min. Even greater activities were obtained at much lower hydrogen pressures when other complexes containing the RhL_2Cl fragment were used, such as $\text{RhL}_2\text{Cl}(\text{P}i\text{Pr}_3)$ and $[\text{RhL}_2\text{Cl}]_2$ (L: PMe_3).^{38o} The selectivities obtained for isopropylcyclohexane dehydrogenation catalyzed by three different systems are summarized in Table 2. The thermal system involving $\text{RhL}_2\text{Cl}(\text{P}i\text{Pr}_3) - \text{H}_2$ afforded a higher ratio of 4- to 3-isopropylcyclohexene, which has been attributed to participation of an intermediate such as $\text{RhLCl}(\text{P}i\text{Pr}_3)$. This species could be more sensitive to steric factors than the alternative RhL_2Cl fragment. The authors proposed that the role of the dihydrogen was to add to the four-coordinate rhodium centers, giving octahedral dihydride complexes which then lose L' , or dissociate in the case of $[\text{RhL}_2\text{Cl}]_2$. The resulting intermediate, $\text{H}_2\text{RhL}_2\text{Cl}$, then hydrogenates a sacrificial olefin to generate the active species RhL_2Cl . A related series of olefin-containing complexes, RhCl -

$(\text{CH}_2=\text{CH}_2)(\text{PMe}_3)_2$, catalyzed hydrogen transfer from cycloalkanes to ethylene under ethylene pressure at temperatures over 170 °C. At 230 °C, ethylene inserted into cycloalkane C–H bonds to produce ethylcycloalkanes.^{38p} Interestingly, uranium hydrogen sponge could be used as a hydrogen acceptor in these reactions.^{38q} Finally, an iridium complex, $\text{IrClH}_2(\text{PPr}_3)_2$, also catalyzed the dehydrogenation of alkanes to alkenes at 150 °C.^{38r}

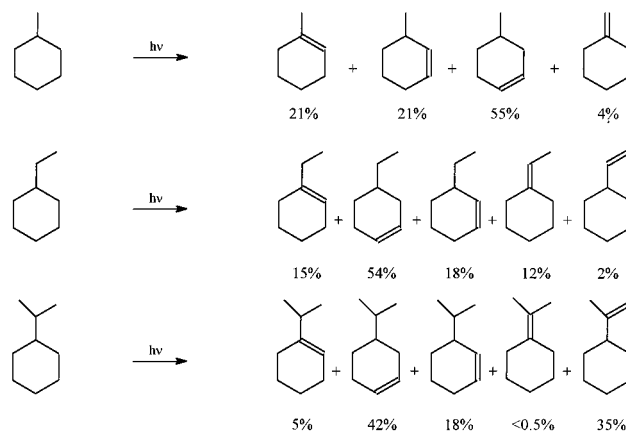
Numerous publications devoted to photochemical, metal-induced dehydrogenations of C–H compounds have appeared during the last decade. For example, irradiation of a solution of 2-cyclohexen-1-one and the complex $\text{Cp}^*\text{Ru}(\text{MeCN})_3\text{PF}_6$ in methylene chloride, for 3 h under the full light of a high-pressure mercury lamp, led to the formation of $\text{Cp}^*\text{Ru}(\pi\text{-C}_6\text{H}_6)\text{PF}_6$ with a yield of 40% based on Ru. Under analogous conditions, an acetonitrile ruthenium complex reacted with cyclohexene and even cyclohexane to produce the corresponding π -benzene derivative (yield ~10%).^{39a}



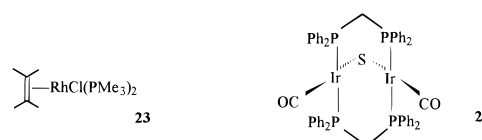
Complexes of rhodium and iridium are known to be the most effective photocatalysts for alkane dehydrogenation and have been investigated thoroughly. The full-light irradiation of a solution of $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ in cyclohexane at room temperature by a mercury high-pressure lamp, induces the formation of cyclohexene (138 mol per 1 mol of the catalyst after 16.5 h) and molecular hydrogen.^{39b,c} In addition, a small amount of benzene (3 mol) is detected. Analogously, the dehydrogenation of *n*-hexane affords a mixture of hexenes (155 mol per 1 mol of the catalyst after 27 h). The ratio 1:2:3-isomers of hexene is 1:79:20, while the *cis/trans* ratio for 2-hexene is 1:3. Once the olefins are formed, they isomerize rapidly under the reaction conditions, with the double bond migrating along the hydrocarbon chain. As a result of this isomerization, the ratio of 1-hexene:2-hexene gradually decreases. This reaction is reversible under the conditions described; however, if dinitrogen is bubbled through the reaction solution during irradiation, the dihydrogen which is formed is removed and the rate of the photodehydrogenation is increased.

The dehydrogenation of alkylcyclohexanes which is photocatalyzed by complex $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ affords mixtures of products (see Scheme 17^{39d,e}). The mechanism proposed for this reaction includes oxidative addition of an alkane to the species $\text{RhCl}(\text{PMe}_3)_2$, followed by elimination of hydrogen from the β -position on the alkyl chain of the resulting alkylhydride derivative.^{39e,f} Photodehydrogenation of alkanes is usually carried out using the alkane as a solvent, however bulky hydrocarbons like 2,2,5,5-tetramethylhexane and 1,3,5-tri-*tert*-butylbenzene may be employed as inert solvents.^{39g} Naturally, the rate of photodehydrogenation depends dramatically on the wavelength of light used to stimulate the reaction.^{39h} UV light has been used in almost all cases, but complexes **23**³⁹ⁱ and **24**^{39j,k} do catalyze the dehydro-

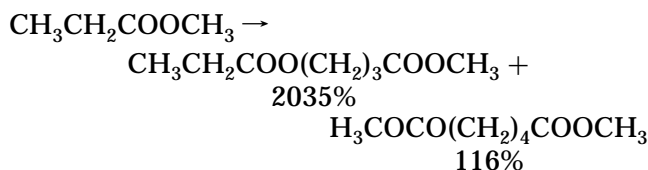
Scheme 17



genation of alkanes under irradiation with visible light ($\lambda > 375$ nm for **23** and $\lambda > 450$ nm for **24**).

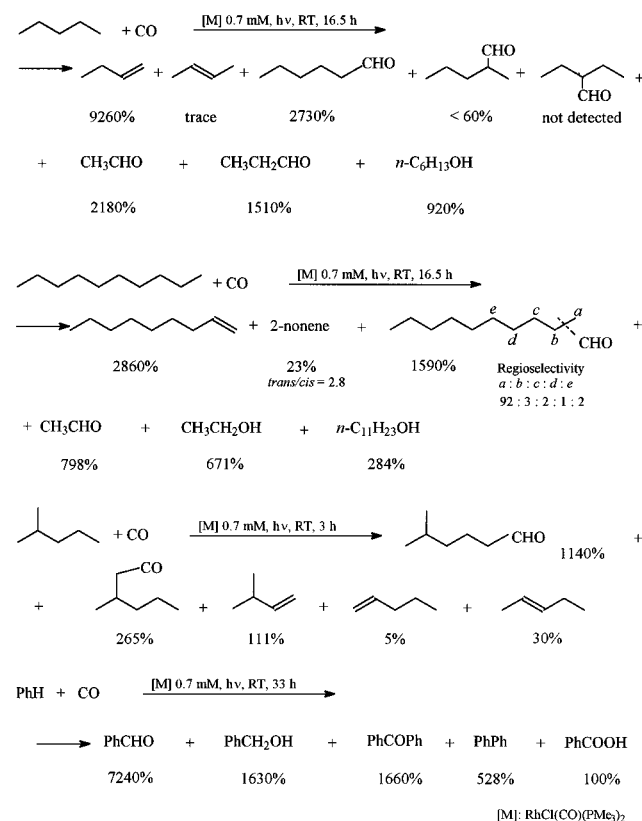
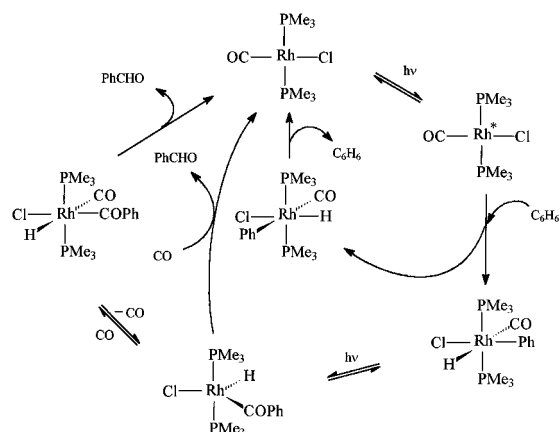


In addition to olefins, carbonyl compounds can be used as hydrogen acceptors in light-induced alkane dehydrogenations. Thus, complex $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ catalyzes the reduction of aldehydes to their corresponding alcohols at room temperature in the presence of cyclooctane.^{39l} Like alkanes, some organic compounds containing alkyl groups can be dehydrogenated photocatalytically. For example, irradiation of methylpropionate in the presence of $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ gives rise to the formation of dimeric products (yields are based on Rh):^{39m}

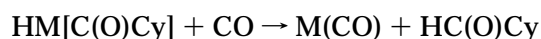
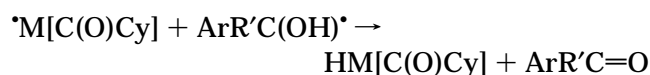
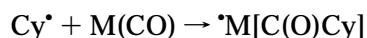
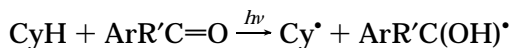


3. Carbonylation of C–H Compounds

A few examples of the metal-catalyzed substitution of a hydrogen atom in an alkane or arene by a functional group have been reported. These are mainly carbonylation reactions. Complex $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$, which was successfully used for dehydrogenation of alkanes, also turned out to be an efficient catalyst for photochemically introducing a CO group into alkanes and arenes. Scheme 18 shows the products of the carbonylation of *n*-pentane, *n*-decane, and 2-methylpentane, as well as benzene (yields are given based on Rh).^{40a} The isomeric ratio of the tolualdehydes formed during the carboxylation of toluene was *ortho:meta:para* = 0.2:1. The yield of phenylacetaldehyde was only about 1% that of tolualdehyde. Competition reactions revealed the following reactivity order: benzene > cyclohexane > pentane \approx decane > cyclooctane. The mechanism proposed by Goldman *et al.* for the photocarbonylation of benzene is presented in Scheme 19^{40b} (also see refs 40c–e). Photochemical cyclohexane carbonylation was found to be cocatalyzed by d⁸ transition metal carbonyls and aromatic ketones and alde-

Scheme 18**Scheme 19**

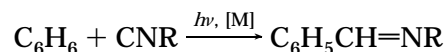
hydrides.^{40f} The following mechanism has been suggested for this reaction:



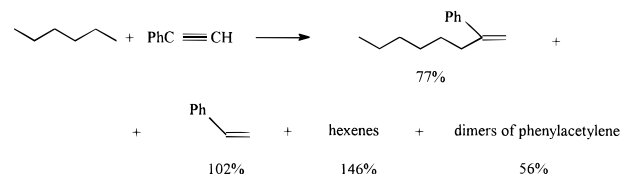
4. Introduction of Other Functional Groups into Organic Molecules

Transition metal complexes provide the possibility of catalytically inserting various functional groups into C–H bonds. For example, $\text{RhX}[\text{P}(\text{Pr})_3]_2(\text{CNR})$

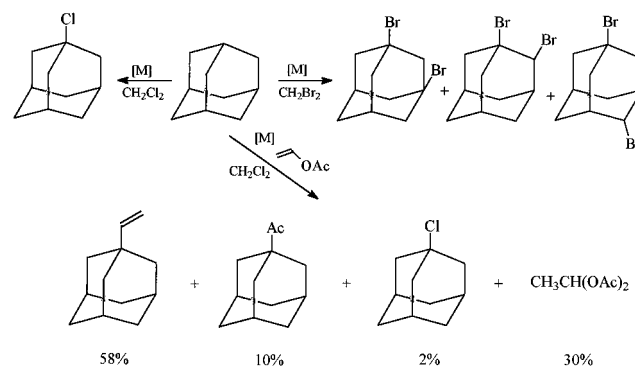
(X = Cl, I; R = neopentyl, 2,6-xylyl) catalyzes isocyanide insertion into aromatic C–H bonds:^{41a,b}



The reaction of aromatic and aliphatic C–H bonds with terminal alkynes gives 1,1-disubstituted ethenes when photocatalyzed by $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$.^{41c,d} Thus, the reaction of hexane with phenylacetylene affords the following products (yields are based on Rh):^{41c}



Intramolecular hydroacylation of unsaturated aldehydes is catalyzed by $\text{Co}_2(\text{N}_2)(\text{PPh}_3)_6$ and some other transition metal complexes. The proposed mechanism for this reaction includes the cleavage of aldehyde C–H bond as a crucial step.^{41e,f} Rhodium complexes, particularly $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, induce functionalization of adamantane as shown in Scheme 20.^{41g} Aromatic hydrocarbons can be functionalized

Scheme 20

by $(\text{CO})_5\text{MnBcat}$ (catalyst $\text{O}_2\text{C}_6\text{H}_4$),^{41h} while ruthenium carbonyl hydride complexes catalyze the addition of olefins to the *ortho* C–H bonds of aromatic ketones with a high degree of efficiency and selectivity.⁴¹ⁱ Finally, activation of an α -C–H bond in the coordinated Et_2O of $[\text{Cp}^*\text{W}(\text{CO})_3(\text{OEt}_2)]^+$ by a phosphine, PR_3 , to yield $[\text{CH}_3(\text{EtO})\text{CH}(\text{PR}_3)]^+$ has been described.^{41j}

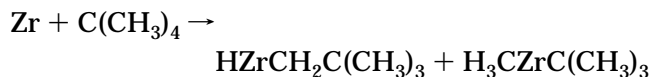
C. Reactions with Metal Atoms and Ions

Although the reactions of naked metal atoms with hydrocarbons in the gas phase and at low temperatures are very different from the chemistry of metal complexes in solutions, it is reasonable to briefly discuss these gas-phase reactions. This is because the reactions' mechanisms may be very similar, even though their experimental details are very different. In both cases the crucial step in the process is usually an oxidative addition of the C–H bond to the metal atom or low-valent metal center.

1. Reactions with Metal Atoms at Low Temperature

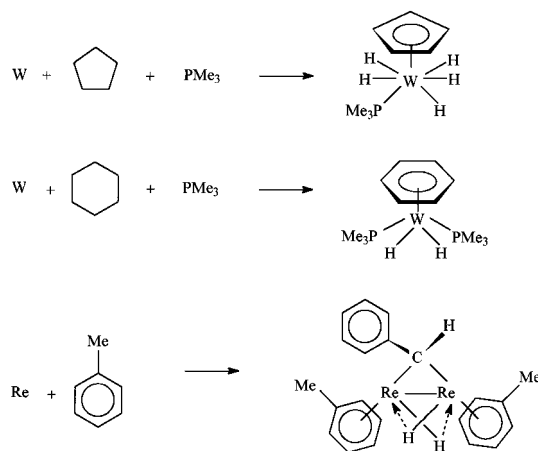
Metals are well known to react with alkanes at high temperatures. For example, at temperatures $>1600^\circ\text{C}$, tungsten interacts with methane to pro-

duce W_2C , WC , and H_2 .^{42a} Recently, however, numerous reactions of metal atoms with hydrocarbons also have been discovered at very low temperatures.^{42b,c} For example, a method of cocondensing metal atoms with various compounds has been used to investigate the reaction of zirconium atoms with isobutane and neopentane at 77 K.^{42d} The zirconium atoms insert into both C–H and C–C bonds:



Likewise, the reaction of Fe_2 dimers with methane in a matrix at 77 K gives rise to the species $H-FeFe-CH_3$ or $FeFe-CH_3$.^{42e} The C–H bonds in alkanes are cleaved analogously by nickel clusters.^{42f} Methane activation also has been detected during the cocondensation of methane with aluminum atoms at 10 K.^{42g} It is interesting that under the same conditions, atoms of Mg, Ti, Cr, Fe, Ga, Pd, and some other metals do not react with methane. Various organometallic compounds can be prepared by the cocondensation of transition metals with some other hydrocarbons (for examples, see Scheme 21).^{42h,i}

Scheme 21



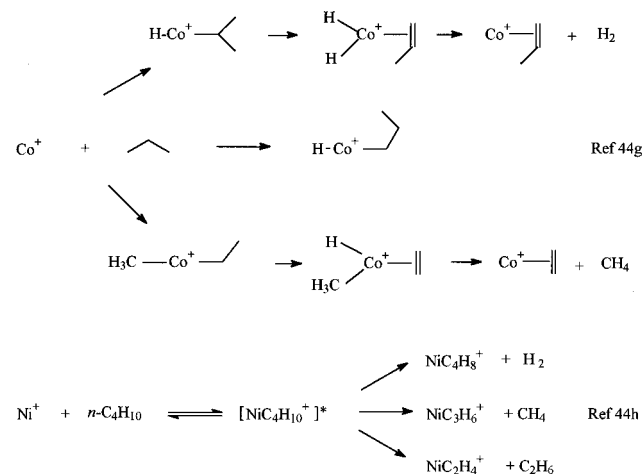
When metal atoms in their ground state do not react with alkanes at low temperature, an active species can be generated by photoexcitation of the metal atoms. The excited atoms which are formed are capable of inserting into the C–H bonds of alkanes (see refs 42j–l). Irradiated ($\lambda < 360$ nm) iron atoms react with methane to produce CH_3FeH . Likewise, excited atoms of Mn, Co, Cu, Zn, Ag, and Au also can insert into the C–H bond of methane. However, atoms of Ca, Ti, Cr, and Ni are inactive in this reaction.^{42m} Photoexcited particles Cu and Cu_2 can activate methane.⁴²ⁿ An investigation of the reactions of excited gallium atoms with methane in Ar, Kr, and neat CH_4 matrices has shown that $HGaCH_3$ is the only photoreaction product.^{42o} Theoretical investigations of these reactions of photoexcited metal atoms with alkanes have been carried out.^{42p–r}

2. Processes in the Gas Phase

a. Reactions with Metal Ions. Metal ions are well known to react with hydrocarbons, particularly

alkanes, in the gas phase (see refs 43a–j). Oxidative addition of C–H (and C–C) bonds occurs in the first step of the process. The alkyl hydride or dialkyl derivatives thus formed undergo further transformations. “Naked” metal ions (for example, Co^+ , Fe^+ , Cr^+ , Ti^+ , and V^+) react with alkanes, alkanes bearing functional substituents, and silanes.^{44a–f} Some reactions of this type are shown in Scheme 22. Gas-phase

Scheme 22



Methane oligomerization:



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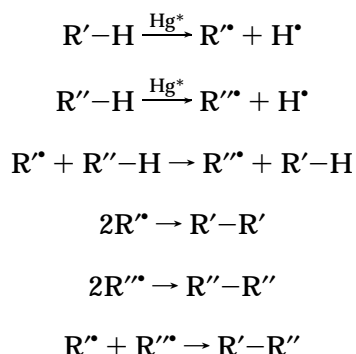
reactions of metal cluster ions (for example, $MgFe^+$; ref 44j) oxometal cations (e.g., CoO^+ , ScO^+ , FeO^+ ; refs 44k–o) and positively or even negatively charged complex ions [for instance, $Co_4(CO)_n^+$; ref 44p, and $(OC)_2Fe^-$; ref 44q] with various hydrocarbons in the gas phase have been described. Numerous other examples can be found in recent publications.^{44r–z}

b. Reactions with Photoexcited Atoms. Vapors of mercury, cadmium, and zinc are known to sensitize photochemical alkane transformations.^{45a,b} Thus, irradiation of propane with light of $\lambda = 307.6$ nm at 633 K and pressure 67–40000 Pa in the presence of zinc vapor gives rise to the formation of hydrogen, methane, ethylene, and dimethylbutane.^{45a} The first step in the reaction is a hydrogen atom transfer from alkane to excited zinc atom:

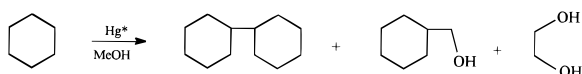


Preparative-scale alkane functionalization by mercury-photosensitized C–H bond activation has been recently developed (the Crabtree reaction).^{45c–j} Mercury absorbs 254-nm light to generate a 3P_1 excited state, which homolyzes a substrate C–H bond with a $3^\circ > 2^\circ > 1^\circ$ selectivity. Radical disproportionation can produce an alkene, but this intermediate is recycled back into the radical pool via H-atom attack. This recycling is beneficial both in terms of yield and selectivity. The reaction ultimately yields alkane dimers and cross-dehydrodimerization products with

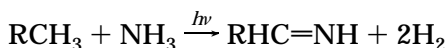
various C–H compounds:



For example, the interaction between cyclohexane and methanol proceeds according to the equation:^{45d}



When a mixture of alkane, ammonia, and a trace of mercury vapor was exposed to UV light, an oligomeric, high-boiling liquid containing C, H, and N was formed.^{45h} The authors proposed that the reaction produced imines:



Here R = H and CH₃. The analogous dehydrodimerization of aromatic substrates proceeded with the formation of an organometallic exciplex, ³[Hg(η²-C₆H₆)].⁴⁵ⁱ

D. Mechanism of the Oxidative Addition of C–H Compounds

Many papers devoted to the theoretical aspects of C–H bond activation, and especially to the oxidative addition of C–H compounds to metal complexes, have been published in recent decades. Some of their results are already summarized in reviews.^{46a–c}

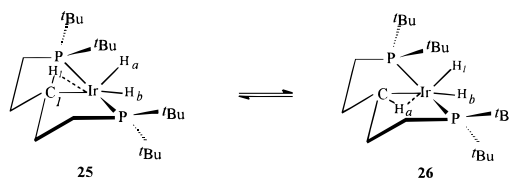
1. H–H and C–H Groups as Ligands in Metal Complexes

In many cases, reactions between metal complexes and organic substrates begin with the coordination of these reactants. Many of the most common substances employed in catalytic processes, such as olefins, acetylenes, and carbon monoxide, are capable of forming rather stable complexes with transition metals due to their π- and n-electrons. On the contrary, the formation of any complexes of saturated hydrocarbons is still difficult to imagine from a classical viewpoint due to their lack of π- or n-electrons. Fairly stable complexes of molecular hydrogen recently have been prepared and thoroughly investigated (see ref 47). On the basis of these known species, one can foresee the possible existence of alkane complexes. However, since saturated hydrocarbons are extremely weak electron donors and poor electron acceptors, one can postulate that alkane–metal adducts should be extremely unstable. Indeed, a quantum-chemical calculation for one of the simplest metal-free systems, CH₄–O₂, showed that if the C–H σ-bond is located along the axis of an oxygen p orbital such that the O⋯H distance is 2.05 Å, a minimum appears on the potential curve which

corresponds to a bond energy of ~0.5 kcal mol^{–1} (see ref 8). In addition, an INDO calculation on another model system, CH₃H⋯ONH₂, showed that the stabilization energy for an O⋯H distance of ~2.0 Å cannot exceed 1 kcal mol^{–1}.

a. “Agostic” Bonds. Numerous complexes having an intermolecular bond between a metal atom and a ligand C–H group have been discovered in recent decades. These have been observed by X-ray diffraction and confirmed by IR and NMR spectroscopy.^{47a,48a,b} The bonds formed by saturated hydrocarbon fragments, especially methyl groups, are of particular interest. It has been suggested that such a bond be referred to as “agostic” and be designated by a half arrow: C–H→M. Thus, the term “agostic” bond refers to the case where a hydrogen atom is simultaneously covalently bound to a carbon and transition metal atom by a three-centered two-electron bond. When an agostic bond is formed, the C–H bond usually lengthens by 5–10%, except when it is formed from a C(sp³)–H fragment, in which case virtually no increase in length is observed. An agostic M–H bond is also somewhat longer (by 15–20%) than the usual metal–hydride bond. The M–C bond length is always appreciably smaller than the sum of the van der Waals radii of M and C.

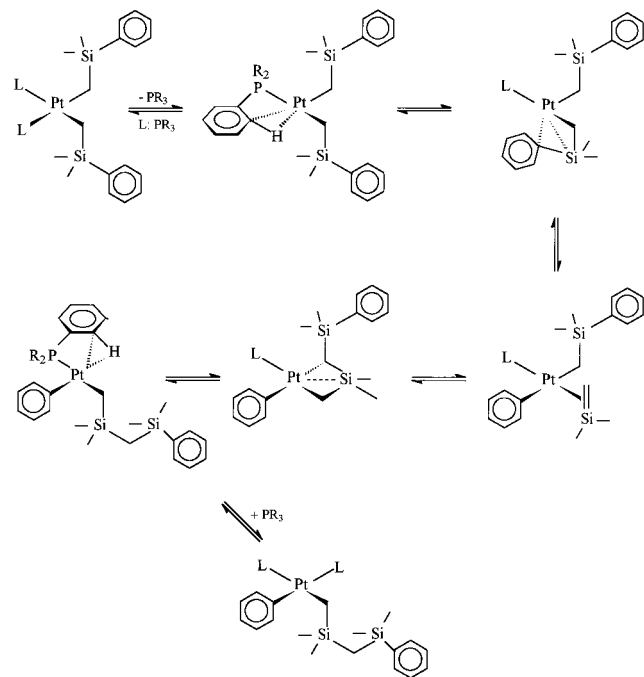
The appearance of an agostic bond is reflected in its NMR spectrum, which shows an upfield shift of both the ¹H and ¹³C signals, and in its IR spectrum, where the stretching vibration frequency of the C–H bond decreases to 2700–2350 cm^{–1}. These spectral changes suggest that a C–H→M agostic bond is on the reaction pathway between a C–H + M system and the alkyl hydride derivative C–M–H. In the last few years, compounds containing agostic bonds have been proposed as intermediates in reactions involving C–H bond activation. Thus, the thermolytic rearrangement of *cis*-bis(silylmethyl)platinum(II) complexes is proposed to occur by a mechanism which involves preliminary dissociation of one Pt–P bond, which is compensated for by an agostic interaction between the coordinatively unsaturated metal and a phosphine substituent (Scheme 23).^{48c} Similarly, the ¹³C NMR equivalence of the tertiary butyl groups' quaternary carbons in an iridium complex indicates dynamic motion of the metalated C–H bond and/or exchange of the agostic hydrogen atom. It has been proposed that the slow exchange in the equilibrium **25** ⇌ **26** occurs by the agostic atom H₁ moving to the iridium atom while one of the iridium hydrogen atoms moves to C₁.^{48d}



Theoretical investigations of complexes containing agostic bonds have been carried out.^{48e–h}

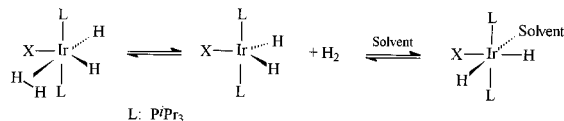
b. Formation of Unstable Adducts between Alkanes and Metal Complexes. “Alkane σ-Complexes”. Dissolution of chromium tris(acetylacetonate) in 1-chlorobutane entails a paramagnetic shift of the ¹³C NMR signals of the solvent.^{49a} It is

Scheme 23



From ref 48c. Copyright 1994 American Chemical Society.

Scheme 24



From ref 49e. Copyright 1996 American Chemical Society.

interesting that the $\Delta\delta$ shift diminishes with each successive carbon along the chain until it again increases for the terminal CH_3 group. The ratio of the $\Delta\delta$ s are $\text{C}(1):\text{C}(2):\text{C}(3):\text{C}(4) = 1.00:0.30:0.14:0.62$. These results indicate that there is a transfer of electron spin density from the complex to the methyl group of the chlorobutane which is coordinated to it. Since the complex is coordinatively saturated, the interaction apparently takes place by outer-sphere coordination at the complex's acetylacetonate ligand. Acetylacetonate complexes of chromium(III) and iron(III) also induce chemical shift changes in the ^{13}C NMR spectra of various alkanes.^{49b} Furthermore, application of the NMR method led to the detection of short-lived adducts of bis[hydrotris(pyrazolyl)-borato]cobalt with alkanes in solution.^{49c,d}

It has been shown^{49e} that solid samples of the complex $\text{IrXH}_2(\text{H}_2)(\text{P}'\text{Pr}_3)_2$ which are dissolved in hydrocarbons liberate hydrogen. The equilibrium shown in Scheme 24 has been proposed for this reaction. The values of ΔH and ΔS which were determined for the chloride and bromide analogs were higher in alkane solvents than in toluene (Table 3). On the basis of these results it has been concluded that Cl and Br complexes lose an H_2 molecule with little or no complexation of the alkane and that solvent coordination to the resulting five-coordinate complex occurs in toluene solution. The low values obtained for the iodo complex's thermodynamic parameters indicate that this five-coordinate complex adds a solvent molecule to produce the adduct $\text{IrH}_2(\text{P}'\text{Pr}_3)_2(\text{Alkane})$.

Table 3. Thermodynamic Parameters for the Loss of H_2 from $\text{IrXH}_2(\text{H}_2)(\text{P}'\text{Pr}_3)_2$ (See Scheme 24) (From Ref 49e. Copyright 1996 American Chemical Society)

X	solvent	ΔH (kcal mol ⁻¹)	ΔS (eu)
Cl	toluene- <i>d</i> ₈	8.6	15
	methylcyclohexane- <i>d</i> ₁₄	12.4	35
	<i>n</i> -hexane- <i>d</i> ₁₄	12.3	36
Br	toluene- <i>d</i> ₈	8.0	10
	methylcyclohexane- <i>d</i> ₁₄	12.1	31
	<i>n</i> -hexane- <i>d</i> ₁₄	12.0	32
I	toluene- <i>d</i> ₈	<i>a</i>	<i>a</i>
	methylcyclohexane- <i>d</i> ₁₄	10.5	22
	<i>n</i> -hexane- <i>d</i> ₁₄	10.2	22

^a Equilibrium shifted too far toward $\text{IrH}_2(\text{H}_2)(\text{P}'\text{Pr}_3)_2$ for accurate determination of the equilibrium constants.

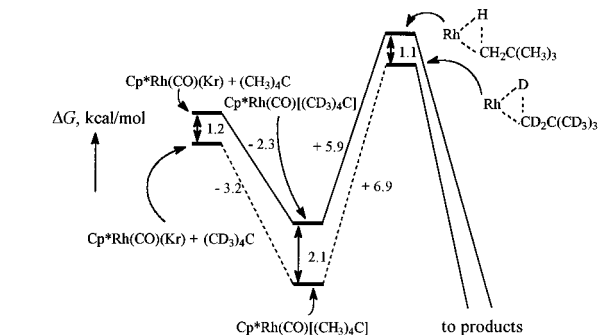
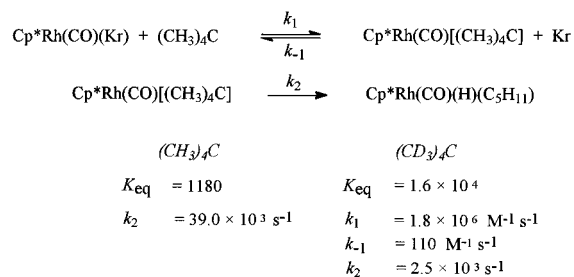


Figure 1. Activation of $(\text{CH}_3)_4\text{C}$ and $(\text{CD}_3)_4\text{C}$ by $\text{Cp}^*\text{Rh}(\text{CO})_2$ in liquid Kr at 165 K. (From ref 50c. Copyright 1994 American Chemical Society).

The adducts of alkanes with various metal complexes which are formed at low temperature can be detected by IR spectroscopy.^{50a} EPR spectroscopy also has revealed that the RhH_2 molecule is strongly complexed to methane in argon matrices at 4 K.^{50b} An investigation^{50c} of the photoinitiated reaction of $\text{Cp}^*\text{Rh}(\text{CO})_2$ with neopentane and neopentane-*d*₁₂ in liquid krypton by low-temperature IR flash kinetic spectroscopy gave results that are consistent with a preequilibrium mechanism. According to this mechanism, an initial transient krypton complex $\text{Cp}^*\text{Rh}(\text{CO})(\text{Kr})$ is in rapid equilibrium with a transient alkane complex $\text{Cp}^*\text{Rh}(\text{CO})(\text{Me}_4\text{C})$. The alkane in the latter complex inserts Rh to form a neopentyl hydride via a unimolecular step. It is interesting that the rhodium is bound to $(\text{CD}_3)_4\text{C}$ an order of magnitude more strongly than to $(\text{CH}_3)_4\text{C}$ (Figure 1). The detection of transient alkane complexes in solution by laser flash photolysis also has been described recently.^{50d}

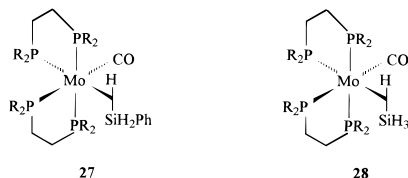
When cobalt atoms, diazomethane, and dihydrogen are cocondensed with argon onto a rhodium-plated copper surface at 12 K, their reaction proceeds spontaneously to yield methane and MeCoH . Wavelength-dependent photolysis of this reaction provided evidence for the formation of a cobalt-methane complex.^{50e} Similarly, $(\text{alkane})\text{M}(\text{CO})_5$ intermediates

were predominantly produced after flash photolysis of the carbonyls $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) in alkane solution. It has been proposed that the alkane is coordinated to the metal in these intermediates via a C–H \cdots M agostic interaction.^{51a,b} Nanosecond and microsecond transient absorption spectroscopy performed during the photolysis of $(\eta^2\text{-dfepe})\text{Cr}(\text{CO})_4$ [$\text{dfepe} = (\text{C}_2\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_2\text{F}_5)_2$] in hexane and cyclohexane indicated that alkane complexes of the type $(\eta^2\text{-dfepe})\text{Cr}(\text{CO})_3(\text{alkane})$ and $(\eta^1\text{-dfepe})\text{Cr}(\text{CO})_4(\text{alkane})$ were formed.^{51c} The rearrangement of a related silane complex $\text{CpMn}(\text{CO})_2(\text{HSiEt}_3)$ also has been studied by photoacoustic calorimetry.^{51d} See very recent publication.^{51e}

It has been established that methane inhibits the free-radical chain autooxidation of dialkylcadmium^{52a} and the reaction of butyllithium with butyl iodide.^{52b} In the latter reaction, the authors proposed that this effect is due to the coordination of methane to the alkyllithium to form a reaction or prereaction complex. A kinetic investigation^{52c,d} of the reductive elimination of methane from the complex $\text{Cp}^*_2\text{W}(\text{CH}_3)\text{H}$ or $\text{Cp}_2\text{W}(\text{CH}_3)\text{H}$ led to the proposal of an intermediate methane “ σ -complex”, that is, a complex with η^2 -coordination of the C–H σ -bond (see ref 47d). The existence of an analogous intermediate has been postulated in the elimination reaction of CH_4 from a methylrhenium hydride derivative.^{52e}

η^2 -Alkane complexes have also been detected in the gas phase. A time-resolved IR spectroscopic study of the interaction of a range of open-chain and cyclic alkanes with the 16-electron species $\text{W}(\text{CO})_5$ showed that reversible complexes formed with all the unsubstituted alkanes except methane.^{52f} The equilibrium constant at 300 K increased as the number of carbon numbers increased, and ranged from 610 atm^{-1} in ethane to 5200 atm^{-1} in *n*-hexane, and from 1300 atm^{-1} in cyclopropane to 7300 atm^{-1} in cyclohexane. Binding energies were in the $7\text{--}11 \text{ kcal mol}^{-1}$ range, and again increased with the size of the alkane. A $[\text{Mn}, \text{C}_6, \text{O}_5, \text{H}_4]^+$ ion was observed by high-pressure mass spectrometry when $\text{Mn}_2(\text{CO})_{10}$ was used as the precursor and methane as the chemical ionization agent.^{52g} The authors proposed that this ion is a $(\text{OC})_5\text{Mn}^+/\text{CH}_4$ complex formed in the high-pressure ion source by the interaction of $(\text{OC})_5\text{Mn}^+$ and methane.

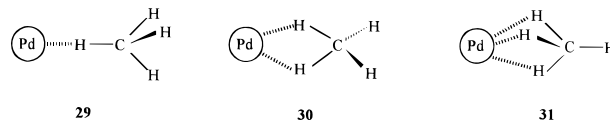
Recently the η^2 -coordination of Si–H in complexes **27**^{53a} and **28**^{53b} and C–H bonds of the *meso*-octa-ethyltetraoxaporphyrinogen^{53c} has been confirmed by X-ray analysis.



A transient “carbon–hydrogen σ -bond complex” has been proposed^{53d} to occur during equilibration between the diastereomeric chiral rhenium alkene complexes of $[\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHR})]^+$.

c. Quantum-Chemical Calculations for Alkane Complexes. The coordination of alkanes to metal atoms, ions, and complexes has attracted the attention of theoretical chemists. It has been sug-

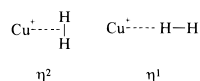
gested that the interaction of saturated C–H bonds with transition metals is due to overlap of the diffuse outer orbitals of the transition metal with the localized orbitals of the saturated bond.^{54a,b} The simplest system used to model the interaction of a C–H bond with an unoccupied, diffuse metal orbital is a methane molecule coordinated to a palladium atom. A nonempirical SCF MO calculation has been carried out for this system.^{54c} Three possible symmetrical structures, each of which differs in the number of hydrogen atoms directly coordinated to the palladium atom, were examined. Two of the structures had C_{3v} symmetry (**29** and **31**), while the third structure had C_{2v} symmetry (**30**).



The calculated $\text{CH}_4\cdots\text{Pd}$ bond energies decrease according to the sequence **29** > **30** > **31**, although they are similar for all three structures (8.4 and $7.3 \text{ kcal mol}^{-1}$ for **29** and **31**, respectively). Coordination of the methane leads to a slight transfer of electron density, mainly from its hydrogen atoms, to the $5s$ and $5p$ orbitals of palladium. This donor–acceptor mechanism entails some redistribution of electron density in the individual AOs of both components. Thus, the electron density in the $4d_z^2$ AO of the palladium atom decreases in all three structures. Although there is a simultaneous increase of electron density in the $5s$, $5p_x$, and $5p_y$ AOs, the effective negative charge on palladium increases overall. Changes in the populations of the methane AOs are much smaller, but show that the electron density also is transferred to some extent by a dative mechanism. Since the methane molecule is oriented toward the palladium atom via three hydrogen atoms in structure **31** (the equilibrium $\text{Pd}\cdots\text{H}$ distance in **31** is 2.2 \AA vs 1.7 \AA in **29**), the primary dative transfer of electron density from the palladium to the carbon atom is most clearly expressed by this structure. It is interesting that the bond energy in the $\text{Pd}\cdots\text{H}_2$ system, when calculated by the same method, is almost twice as high as the bond energy in the methane complex. This is because the donor–acceptor transfer in the alkane complex is much smaller than in the dihydrogen complex. However, since the HOMO energy for methane is higher than for hydrogen (the ionization potentials are 12.7 and 15.4 eV , respectively), methane should be the better electron donor. One can therefore conclude that the interaction is determined by the overlap of the corresponding orbitals and not by the difference between energy levels.

The nonempirical MO method has been also used to calculate the complexation of copper(I) ion to molecules of hydrogen, methane and ethane.^{54d} The potential surfaces for the addition reactions of H_2 , CH_4 , and C_2H_6 are of bonding character from infinity up to the equilibrium state. There is only one minimum on these surfaces, and it corresponds to the complexes $\text{Cu}^+\cdots\text{H}_2$ (energy of complexation $\sim 17 \text{ kcal mol}^{-1}$), $\text{Cu}^+\cdots\text{CH}_4$ ($\sim 10 \text{ kcal mol}^{-1}$) and $\text{Cu}^+\cdots\text{C}_2\text{H}_6$ ($\sim 13 \text{ kcal mol}^{-1}$). The H_2 molecule is coordinated more strongly to the central Cu^+ ion by an η^2 -mode than

by an η^1 -mode. In fact, the η^1 -complex lies 3.7 kcal mol⁻¹ higher in energy and transforms into the η^2 -configuration without any barrier.



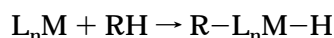
As with structure **31**, tridentate coordination of a methane molecule to a Cu⁺ ion is more advantageous. The bidentate and monodentate coordination structures (analogous to structures **30** and **29**) are situated 3–4 kcal mol⁻¹ higher than the tridentate configuration. These differences are small and Cu⁺ may migrate around the CH₄ molecule at low temperatures such as all the possible modes of coordination alternate. It is important to note that the geometric parameters of CH₄ change negligibly when it coordinates to Cu⁺, thus making it impossible that the Cu⁺ ion could rupture a C–H bond in the methane. All the Cu⁺ complexes are stable with respect to monomolecular decay and can exist in the gas phase or in matrices of inert gases.

Methane adducts of the pyramidal complexes M(NH₂)(=NH)₂ where M = Nb, Ta, and M(=NH)₃, where M = Mo, W, have appreciable binding enthalpies (~11–16 kcal mol⁻¹) as determined by *ab initio* calculations^{54e} (however, see ref 54f). Planar imido complexes (NH₂)₂M=NH, where M = Ti, Zr, and (HO)₂Ti=NH have much smaller binding enthalpies. The calculations showed a significant covalent contribution to the bonding between the substrate and the formally d⁰ complexes. Upon coordination, there is weakening of the methane C–H bond, a charge transfer from methane to the metal, and an increased C^{δ-}–H^{δ+} polarization. All of these effects indicate that the adduct has a role in the all-important C–H scission step which follows.

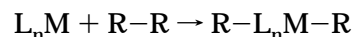
Recently, high accuracy calculations were used to explore possible molecular precursor complexes in the reaction between methane and a selected set of second-row transition metal complexes.^{54g} These showed that the electronic structure requirements are quite different when forming a strong precursor or obtaining a low barrier for the oxidative addition reaction. A ground state singlet is important for the formation of a strong precursor and the precursor binding energy will be larger if the complex does not have any π -acid ligands. For example, the precursor binding for complex RhH(CO) (10.8 kcal mol⁻¹) is smaller than the precursor binding for complex RhH(NH₃) (14.5 kcal mol⁻¹). A low barrier for the oxidative addition reaction with methane requires that the reactant be in a low-lying triplet state. For example, the complexes RhCl(CO) and RuH₂, which are ground-state triplets, could be used as reactants. Finally, an *ab initio* study^{54h} demonstrated that the complexes *cis*-Mo(CO)(PH₃)₄(HSiH₃) (compare to structure **28**) and CpMn(CO)₂(HSiR₃) can be regarded as pseudooctahedral d⁶-ML₆, which defines a particularly stable class of complexes.

2. Thermodynamics of Oxidative Addition

An estimation^{55a} of the heat of oxidative addition via the mechanism



demonstrated that this reaction is usually endothermic with $\Delta H \approx +10$ kcal mol⁻¹. Oxidative addition with cleavage of the C–C bond via the mechanism



should be thermodynamically even less favorable. The above considerations refer to complexes of the first series of transition metals, as the alkyl–metal bonds may be stronger in the case of heavy metals. However, the $D(\text{M}-\text{CH}_3)$ values for the M⁺–CH₃ ions in the gas phase do not support this trend when passing from light to heavy metals within a given Group. The calculated^{55b} values $D(\text{Pt}-\text{C}) = 36$ kcal mol⁻¹ and $D(\text{Pt}-\text{H}) = 60$ kcal mol⁻¹ make it possible to estimate the enthalpies of the oxidative addition of dihydrogen (–16 kcal mol⁻¹; exothermic reaction), the CH₃–H bond of methane (+9 kcal mol⁻¹; endothermic reaction), and the CH₃–CH₃ bond of ethane (+19 kcal mol⁻¹; strongly endothermic reaction) to Pt(PH₃)₂. The rate of addition of methane to Cp*IrCO depends only very slightly on temperature.^{55c} Also, the nature of the ligand L has little influence on the reactivities of the Cp*IrL complexes with alkanes, and this can indicate that the activation barrier is low.

The energy of the oxidative addition of hydrocarbons RH to complexes L_nM is determined by the equation^{55d}

$$E_{\text{M}-\text{R}} + E_{\text{M}-\text{H}} - E_{\text{R}-\text{H}} \approx E_{\text{M}-\text{M}}$$

and hence can be estimated from $E_{\text{M}-\text{M}}$. The highest value of $E_{\text{M}-\text{M}}$ has been obtained for platinum. Furthermore, the $E_{\text{M}-\text{M}}$ values show that reactions involving group VIII and I transition metals are energetically favorable. Other thermodynamic aspects of alkane oxidative addition to complexes of rhodium, iridium and some other metals have been discussed.^{55e–j} Our consideration of the thermodynamics of oxidative addition will be continued in the next section on quantum-chemical calculations.

3. Quantum-Chemical Consideration of Hydrocarbon Oxidative Addition

Both the oxidative addition of saturated H–H or C–H bonds to metals and the reductive elimination of RH from metal complexes have been investigated by quantum-chemical methods.^{56a–u} We will begin our discussion of oxidative addition with the simplest saturated molecule, namely H₂.^{56a} During oxidative addition, the bonding σ -orbitals of hydrogen interact with the unoccupied acceptor orbital of the complex while the hydrogen's antibonding σ^* -orbital interacts with the complex's occupied donor orbital. This interaction produces four new orbitals for the hydride derivative. Electrons fill the two low-lying orbitals, one of which is symmetric and the other anti-symmetric relative to their 2-fold axis or the mirror symmetry plane. The M–H bond represents a symmetrical combination, thus electron transfer from the occupied $\sigma_g(\text{H}_2)$ -orbital to ML_n weakens the H–H bond and strengthens the M–H bond. The electron transfer in the opposite direction, namely “donor orbital $\rightarrow \sigma_u^*$ ”, also weakens the H–H bond and strengthens the M–H bond.

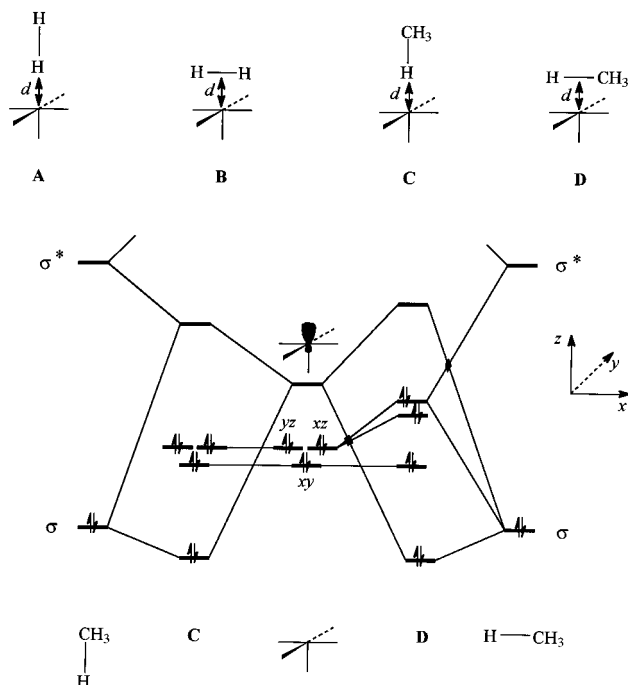


Figure 2. Oxidative addition of the methane molecule to fragment $\text{Cr}(\text{CO})_5$. (From ref 56a. Copyright 1984 American Chemical Society).

One can assume that the occupied a_1 -orbitals and the three degenerate t_2 -orbitals of methane correspond to the σ_g -orbital of the hydrogen molecule. Since the energy of the t_2 -orbital is 2 eV greater than the energy of the $\sigma_g(\text{H}_2)$ -orbitals, the methane molecule is a somewhat stronger donor. The total energy of the system $\text{H}_2 \cdots \text{Cr}(\text{CO})_5$ has been calculated by the extended Hückel method.^{56a} The interaction energy is negative for both the perpendicular orientation (structure A in Figure 2) and the parallel orientation (structure B) of the H_2 molecule approaching the C_{4v} symmetry $\text{Cr}(\text{CO})_5$ fragment. However, the energy of the system has a much more distinct minimum for the parallel approach of H_2 .

When H_2 is replaced by CH_4 , the perpendicular approach curve (structure C) retains its form but the parallel approach (structure D) becomes extremely unfavorable. This is because, with CH_4 , the donor d_{xz} -orbital is lowered for C, while the energies of both the d_{xz} - and d_{yz} -orbitals increase for D (Figure 2). If the methane molecule approaches $\text{Cr}(\text{CO})_5$ in such a way that the $\text{H}-\text{CH}_3$ axis forms an angle θ with the height of the pyramid, then the structure is stable for $d(\text{M}-\text{H}) = 2.0 \text{ \AA}$ and $\theta \leq 130^\circ$. However, the perpendicular orientation ($\theta = 180^\circ$) remains the most favorable. Additional reactions involving the oxidative addition of dihydrogen and methane to the $\text{Rh}(\text{CO})_4^+$ fragment, the corresponding isolobal complex $\text{CpRh}(\text{CO})$, and to the metallic surfaces of nickel and titanium have also been analyzed.^{56a}

Theoretical studies^{56b} of the complete reaction profile for the dehydrogenation of methane by gaseous iridium ions have shown that three salient factors are responsible for the high reactivity of these ions. These are the ability of Ir^+ to change spin easily, the strength of the $\text{Ir}-\text{C}$ and $\text{Ir}-\text{H}$ bonds, and the ability of Ir^+ to form up to four covalent bonds. Iridium is unique in that all three characteristics are the strongest for this ion. The reaction steps for the

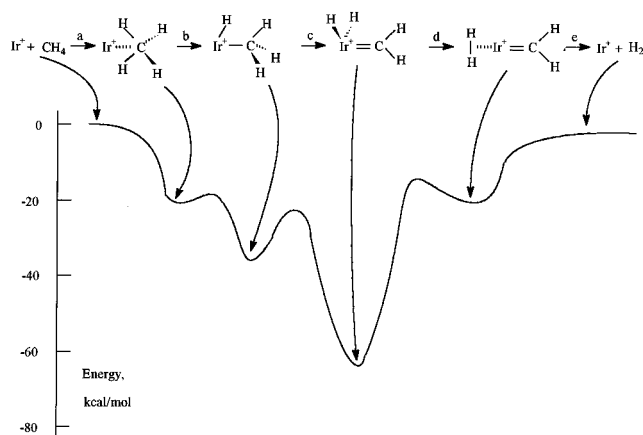
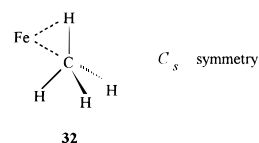


Figure 3. Dehydrogenation of methane by ions Ir^+ . (From ref 56b. Copyright 1994 American Chemical Society).

dehydrogenation (Figure 3) are as follows: (a) initial formation of an η^2 -molecular complex, $\text{Ir}(\text{CH}_4)^+$; (b) oxidative addition of a single C–H bond to form the hydridomethyliridium complex, $\text{Ir}(\text{H})(\text{CH}_3)^+$; (c) insertion into a second C–H bond to form the pyramidal dihydridomethylideneiridium complex, $\text{Ir}(\text{H})_2(\text{CH}_2)^+$; (d) coupling of the $\text{H}-\text{H}$ bond to form the planar (dihydrogen)methylideneiridium complex, $\text{Ir}(\text{H}_2)(\text{CH}_2)^+$; and (e) elimination of H_2 .

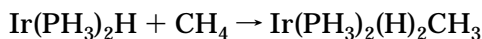
There is a global minimum ($\sim 63 \text{ kcal mol}^{-1}$) for the singlet $\text{Ir}(\text{H})_2(\text{CH}_2)^+$ structure, which plays an important role in the activation. The overall exothermicity of the reaction is calculated to be 3 kcal mol^{-1} . On the basis of these calculations, the authors suggest that solution-phase analogues also may activate methane. However, in order to obtain a solution-phase complex which reacts analogously to the gas-phase iridium ion, it is necessary to remove two electrons. This suggests that Re^+ in the form of the complex XReL_3 , may mimic gas phase Ir^+ .

Oxidative addition reactions between methane and all of the second-row transition metals from yttrium to palladium have been carried out.^{56c} The lowest barrier for to C–H insertion was found for rhodium, while palladium has the lowest methane elimination barrier. The formation of complexes $[\text{CH}_4-\text{Fe}]^q$ ($q = +1, 0, -1$) and the oxidative addition of methane to these Fe^q was studied using the MINDO/SR-UHF method.^{56d} The potential energy curves for the oxidative addition were calculated for a C_s symmetry (structure 32). These potential energy curves showed

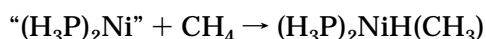


that both the formation of the alkane complexes and the oxidative addition are favored as the system became negatively charged. This suggests that an electronic transfer from the metal to the methane molecule promotes C–H bond activation. An increase in the p character of the metal center also favors the C–H bond splitting.

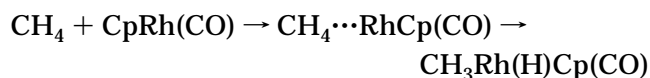
When an $\eta^2\text{-C-H}$ coordinated adduct $\text{X}(\text{PH}_3)_2\text{-Ir} \cdots \text{HCH}_3$ is formed, considerable weakening of the coordinated methane C–H bond occurs.^{56e} The calculated enthalpy for the reaction



is $-12.8 \text{ kcal mol}^{-1}$. Restricted Hartree-Fock *ab initio* calculations^{56f} for the reaction



showed that the oxidative addition is endothermic by $7.0 \text{ kcal mol}^{-1}$ and that the planar *trans* product is more stable than the *cis* isomer by $3.4 \text{ kcal mol}^{-1}$. Calculations^{56g} for the reaction



which were carried out using the MP2 technique, predicted that the intermediate alkane complex is stabilized by $14.8 \text{ kcal mol}^{-1}$. They also predicted that a transition state lies $4.1 \text{ kcal mol}^{-1}$ higher than this intermediate and that the reaction is exothermic ($30.6 \text{ kcal mol}^{-1}$).

The effects of ligands on C–H bond activation by transition metal complexes have been discussed. It has been suggested^{56h} that hydride and lone-pair ligands with minimal π -bonding should be an optimal combination for the reaction between methane and model Rh(I) and Ru(II) complexes. For example, it should be advantageous to have methyl and lone-pair ligands interact with as little covalent bonding as possible. methane activation by a Ru(II) complex has not yet been accomplished experimentally, however, it is predicted that halide ligands and strongly π -bonding lone-pair ligands should be avoided. One ligand is needed to improve the exothermicity of the reaction of Rh^+ with methane, and the position of this ligand is critical.⁵⁶ⁱ Covalent ligand effects have been evaluated for the oxidative addition of methane to second-row transition metal complexes.^{56j}

Adducts of the complexes $\text{M}(\text{=NH})_2(\text{NH}_2)$ ($\text{M} = \text{V}$, Nb , and Ta) with methane have been considered above (see ref 54e). A theoretical study of methane activation by these complexes demonstrated that an activation pathway involving C–H addition across the metal–amido bond (σ -bond metathesis) is disfavored relative to a pathway involving C–H addition across the metal–imido bond ($[2_\sigma + 2_\pi]$ addition).^{56k} A comparison of the activation of a C–H bond vs a Si–H bond has been carried out. This showed that C–H bond activation by $\text{RhCl}(\text{PH}_3)_2$ passes through an $\eta^2\text{-CH}_4$ adduct and a three-centered transition state, while the analogous Si–H bond activation is downhill in energy and the $\eta^2\text{-SiH}_4$ complex is a transition state for the intramolecular rearrangement of two silyl hydride complexes.^{56l} It is also noteworthy, that while reactions of C–H and C–C bonds with $\text{Pt}(\text{PH}_3)_2$ are characterized as typical oxidative additions, the Si–H and Si–Si reactions with the same platinum complex are considered to be covalent bond rearrangements rather than oxidative additions.^{56m} The barriers for insertion of different transition metals into C–C bonds have been found to be $14\text{--}20 \text{ kcal mol}^{-1}$ higher than the barriers for C–H insertions.⁵⁶ⁿ Calculations for the activation of the C–H bond in ethylene by second-row transition metal atoms showed that the oxidative addition barrier is lowest for the atoms to the right. For example, there is no barrier for rhodium, and the

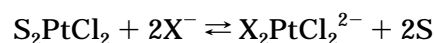
barrier for palladium is almost zero.^{56o} An *ab initio* MO study also was carried out on the mechanism of activation of C–H, H–H, N–H, O–H, and Si–H bonds by transient species $\text{CpRh}(\text{CO})$.^{56p} Finally, theoretical investigations of alkane activation by tris(imido) complexes,^{56q} $\text{RhCl}(\text{CO})(\text{PH}_3)_2$,^{56r} palladium clusters,^{56s} and bare metal ions^{56t–v} have been published recently.

E. Activation of Alkanes by Platinum Complexes

The reactions of alkanes with platinum(II) complexes were the first examples of “true” homogeneous activation of saturated hydrocarbons in solution. These reactions are described in detail in refs 1a,i and 2b,o. It is important to note that complexes of Pt(II) exhibit both nucleophilic and electrophilic properties, therefore, they do not react with alkanes via a typical oxidative addition mechanism, nor can they be regarded as typical oxidants.

1. H–D Exchange Catalyzed by Pt(II) Complexes

When methane or another alkane is heated to $\sim 100^\circ\text{C}$ in a sealed tube containing a solution of PtCl_4^{2-} in a D_2O – CD_3COOD mixture, the hydrogen atoms in the alkane are replaced by deuterium.²²ⁱ The process also occurs in pure D_2O , but the addition of acetic acid increases the rate of reaction by a factor of 30. When anions X^- are added to the system, new complexes are formed via the reaction



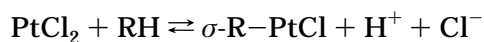
and these also catalyze the H–D exchange in cyclohexane. The following sequence has been established for the platinum(II) ligands on the rate of the H–D exchange: $\text{PPh}_3 \cong \text{py} < \text{DMSO} < \text{CN}^- < \text{NO}_2^- < \text{NH}_3 < \text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- \cong \text{H}_2\text{O}$.

This sequence is the opposite of what would be expected on the basis of the *trans* effect of the corresponding ligands. Therefore, the alkanes cannot be considered to be nucleophiles substituting the platinum ligands in a classic manner. The rate constants for the H–D exchange reaction catalyzed by platinum(II) are described satisfactorily by the two-parameter equation

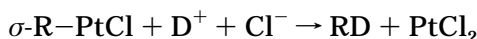
$$\log(k/k_0) = \rho^* \sigma^* + n\psi \quad (\text{III.8})$$

where σ^* is the Taft constant which takes into account the polar influence, ψ is the parameter which characterizes the conjugation of the substituent α to the H atom with the reaction center, and n is the number of substituents. The value $\rho^* = -1.4$ which is obtained for the platinum complex indicates that it has moderately electrophilic properties. Unbranched alkanes are the most reactive in the H–D exchange reaction. Branched hydrocarbons show a “reverse” reactivity sequence, i.e., $1^\circ > 2^\circ > 3^\circ$, in the H–D exchange reaction. Evidently this is due to the strong influence of steric factors. The low rate of H–D exchange in the methyl and methylene groups which adjoin the *tert*-butyl groups of 2,2-dimethylpropane and 2,2-dimethylbutane can be explained in the same way. Likewise, in 2-alkylindanes, deuterium atoms are predominantly ex-

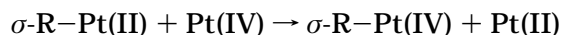
platinum(II) complex on the hydrocarbon molecule, RH. This results in the formation of an alkylplatinum(II) σ -complex:^{1a,i,2o}



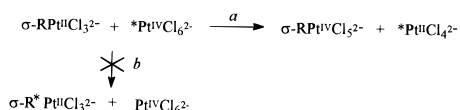
In the absence of platinum(IV), the alkylplatinum σ -derivative undergoes electrophilic attack by a D^+ ion:



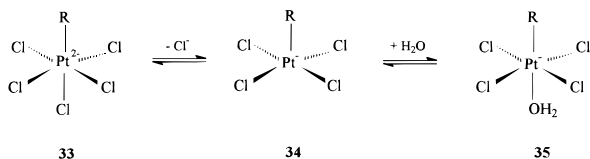
However, if a platinum(IV) derivative is present in the system, it interacts with the platinum(II) σ -complex and converts it into an alkylplatinum(IV) σ -complex:



Recent experiments with isotopically enriched ^{195}Pt complexes demonstrated^{61a,b} that this oxidation process (at least in the case when $\text{R} = \text{CH}_2\text{CH}_2\text{OH}$) involves electron transfer, rather than alkyl transfer (step *a* rather than *b*):



The σ -alkylplatinum(IV) complex reacts with nucleophiles H_2O and Cl^- to afford an alcohol ROH and an alkyl chloride RCl, respectively. Complexes **33** and **35** ($\text{R} = \text{CH}_3$ or $\text{CH}_2\text{CH}_2\text{OH}$) have been shown^{61b} to exist in equilibrium with a constant $K = 0.9$ M at 25 °C in aqueous solutions containing excess chloride. This rapid dissociative exchange of ligand the *trans* to the alkyl substituent was proposed to occur via the five-coordinate intermediate **34**:



The following rate law has been established for the nucleophilic displacement of Pt(II) by water and chloride:

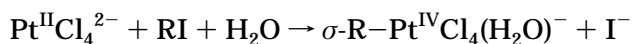
$$-\frac{d[\mathbf{33} + \mathbf{35}]}{dt} = k_{\text{obs}} [\mathbf{33} + \mathbf{35}]$$

$$k_{\text{obs}} = \frac{k_1[\text{Cl}^-] + k_2[\text{H}_2\text{O}]}{1 + K^{-1}[\text{Cl}^-]}$$

The authors proposed an $\text{S}_{\text{N}}2$ mechanism for the formation of the final oxidation products.

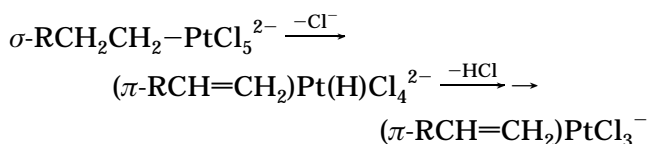
Complexes of types **33** or **35** can be easily prepared by the method initially described in ref 61c. According to this method, the chloride complex $\text{Pt}^{\text{II}}\text{Cl}_4^{2-}$ is reacted with an alkyl iodide at room temperature in aqueous solution to produce a σ -alkylplatinum(IV)

complex. Methyl,^{61c} ethyl,^{61d,e} and acetyl^{61f} complexes of Pt(IV) have been prepared by this method. An interesting feature of the reaction is that the sixth coordination site in the octahedral product is occupied by water, while the I^- ion is bound to another platinum(II) complex (PtI_2 and analogous products are formed and precipitate):



The acetyl complex turned out to be the most stable, which is apparently due to the absence of β -hydrogens in its alkyl chain.^{61d,e} Indeed, the σ -ethyl derivative readily decomposed to produce a π -ethylene complex of Pt(II) in addition to the usual alcohol and alkyl chloride products. The reaction between PtCl_4^{2-} and *n*-hexyl iodide also produced a (1-hexene)platinum(II) π -complex.^{61e} Another method for forming σ -alkyl complexes of platinum(IV) is the reaction of PtCl_6^{2-} with certain alkyl derivatives of non-transition metals. For example, PtCl_6^{2-} reacts slowly^{61g} with $(\text{CH}_3)_4\text{Sn}$ in CD_3COOD at room temperature to form $\sigma\text{-CH}_3\text{-PtCl}_5^{2-}$. The reaction is accelerated by the addition of PtCl_4^{2-} and is of first order with respect to platinum(II). In the absence of PtCl_6^{2-} , tetramethyltin reacts with Na_2PtCl_4 in aqueous acetone to also form a methylplatinum(IV) complex. The precipitation of metallic platinum is observed in this reaction, which partly proceeds by an oxidative addition of the $\text{Me}_3\text{Sn-Me}$ bond to platinum(II). As in the case of the alkyl iodides, one component adds to the platinum(II) ion, while the other is bound to and reduces another platinum species. Both these tetramethyltin reactions model the interaction of the Pt(IV) + Pt(II) system with saturated hydrocarbons to a certain extent. The cleavage of the Sn-CH_3 bond by the PtCl_6^{2-} complex is accelerated by irradiation.^{61g} The formation of a $\sigma\text{-C}_2\text{H}_5\text{-PtCl}_5^{2-}$ complex has been observed by ^1H NMR in the photochemical $(\text{CH}_3)_2(\text{CH}_2\text{CH}_3)_2\text{Sn}$ reaction in CD_3COOD . Light apparently accelerates the conversion of this σ -ethyl complex into a π -ethylene complex.^{61g}

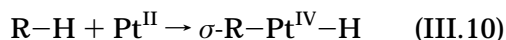
It can be concluded that reactions which form platinum(IV) alkyl derivatives, in which the alkyl fragment contains a β -hydrogen, ultimately lead to π -olefin complexes of platinum(II). These reactions include the interactions of platinum chlorides with alkyl iodides and alkyl derivatives of tin, as well as the thermal and photochemical dehydrogenation of *n*-hexane by PtCl_6^{2-} . One possible mechanism for the *n*-hexane dehydrogenation is the formation of a σ -hexyl complex of platinum(IV) and its subsequent transformation into π -olefin complex of platinum(II) via a β -hydrogen elimination:^{57c}



The intimate mechanism of this reaction deserves special attention not only because it was the first example of alkane activation by a metal complex but also because the activation of alkanes by platinum(II) complexes remains unique in many respects. For

example, the reaction takes place in a neutral water solution with conventional chloride ligands on the metal, yet coordinatively unsaturated species are formed without any special action, such as irradiation, being taken. A number of works therefore have been directed to the elucidation of the interaction between the alkane and the platinum(II) complex. Platinum(II) complexes are unique in that they exhibit both nucleophilic and electrophilic properties (for example, see the investigation of cyclometalation by of some transition metal complexes^{62a}).

Two main mechanisms may be proposed for the first step of the alkane interaction with platinum(II) complexes: (1) oxidative addition



followed by reversible proton elimination; and (2) electrophilic substitution with simultaneous proton abstraction. The oxidative addition mechanism was originally proposed²²ⁱ because of the lack of a strong rate dependence on polar factors and on the acidity of the medium. Later, however, the electrophilic substitution mechanism also was proposed. Recently, the oxidative addition mechanism was confirmed by investigations into the decomposition and protonolysis of alkylplatinum complexes, which are the reverse of alkane activation.

There are two routes which operate in the decomposition of the dimethylplatinum(IV) complex $Cs_2Pt(CH_3)_2Cl_4$.^{62b} The first route leads to chloride-induced reductive elimination and produces methyl chloride and methane. The second route leads to the formation of ethane. There is strong kinetic evidence that the ethane is produced by the decomposition of an ethylhydridoplatinum(IV) complex formed from the initial dimethylplatinum(IV) complex. In D_2O-DCI , the ethane which is formed contains several D atoms and has practically the same multiple exchange parameter and distribution as does an ethane which has undergone platinum(II)-catalyzed H–D exchange with D_2O . Moreover, ethyl chloride is formed competitively with H–D exchange in the presence of platinum(IV). From the principle of microscopic reversibility it follows that the same ethylhydridoplatinum(IV) complex is the intermediate in the reaction of ethane with platinum(II).

Important results were obtained by Labinger and Bercaw^{62c} in the investigation of the protonolysis mechanism of several alkylplatinum(II) complexes at low temperatures. These reactions are important because they could model the microscopic reverse of C–H activation by platinum(II) complexes. Alkylhydridoplatinum(IV) complexes were observed as intermediates in certain cases, such as when the complex $(tmeda)Pt(CH_2Ph)Cl$ or $(tmeda)PtMe_2$ ($tmeda = N,N,N,N$ -tetramethylenediamine) was treated with HCl in CD_2Cl_2 or CD_3OD , respectively. In some cases H–D exchange took place between the methyl groups on platinum and the, CD_3OD prior to methane loss. On the basis of the kinetic results, a common mechanism was proposed to operate in all the reactions: (1) protonation of Pt(II) to generate an alkylhydridoplatinum(IV) intermediate, (2) dissociation of solvent or chloride to generate a cationic, five-coordinate platinum(IV) species, (3) reductive C–H bond formation, producing a platinum(II) alkane

σ -complex, and (4) loss of the alkane either through an associative or dissociative substitution pathway.

These results implicate the presence of both alkane σ -complexes and alkylhydridoplatinum(IV) complexes as intermediates in the Pt(II)-induced C–H activation reactions. Thus, the first step in the alkane activation reaction is formation of a σ -complex with the alkane, which then undergoes oxidative addition to produce an alkylhydrido complex. Reversible interconversion of these intermediates, together with reversible deprotonation of the alkylhydridoplatinum(IV) complexes, leads to multiple H–D exchange with the solvent.

Recently, it has been shown^{62d} that heating a solution of $[(tmeda)Pt(CH_3)(NC_5F_5)]^+$ in pentafluoropyridine under 30 atm of $^{13}CH_4$ at 85 °C gives rise to the slow growth of a Pt– $^{13}CH_3$ resonance in the ^{13}C NMR spectrum due to methyl exchange. The reaction is accompanied by the formation of CH_4 and by deposition of metallic platinum, which is associated with the C–H activation process. The authors note a very close similarity between this reaction and the activation of alkane C–H bonds observed^{35h,i} with $[Cp^*Ir(PMe_3)(CH_3)(ClCH_2Cl)]^+$ and $Cp^*Ir(PMe_3)(CH_3)(Otf)$ (also see ref 35k). When both Ir(III) and Pt(II) participate in the C–H activation process, a σ -bond metathesis mechanism cannot be excluded^{62d} as an alternative to oxidative addition (however, see ref 35j).

Earlier, a few other possible mechanisms have been also suggested on the basis of quantum-chemical calculations for the interaction between Pt(II) and the alkane C–H bond.^{62e–l}

IV. Reactions with High-Valent Metal Complexes

Reactions of hydrocarbons and other C–H-containing compounds with complexes of metals in high oxidation state may involve direct metalation (with or without subsequent decomposition of the σ -organyl complex formed). Part A of this section is devoted to reactions which lead to isolable or detectable organometallic compounds. However, many known processes of hydrocarbon oxidation by high-valent metal complexes either do not involve σ -organyl derivatives at all or the formation of such intermediates is only suspected. High-valent metal intermediates have been proposed to take part in certain biological oxidation processes (see section VI). The design of ligands for oxidizing complexes and biomimetic chemistry is a very important problem in this field of chemistry.^{63a}

A. Electrophilic Metalation of C–H Compounds

1. Metalation of Aromatic Compounds

Reactions involving the electrophilic substitution of hydrogen in arenes are known both for non-transition metals [Hg(II), Tl(III), Pb(IV)] and transition metals [Au(III), Pd(II), Pt(IV), Rh(III)]. All these reactions apparently proceed through intermediate formation of Wheland complexes. Some parameters for these reactions are summarized in Table 4.^{1f}

a. Reactions of Aromatics with Palladium(II) Compounds. Despite the numerous works devoted to the oxidation of aromatics by palladium(II) com-

Table 4. Metalation of Arenes by Nontransition and Transition Metal Compounds

parameter		Hg(II)	Tl(III)	Pb(IV)	Au(III)	Pd(II)	Pt(IV)
$\rho(\sigma)$?	-12.8	?	?	?	-3.0
$\rho^+(\sigma^+)$		-6.3	-6.9 ^a -7.4 ^a -8.3 ^a	-9	?	-0.4 ^a -0.7 ^a -1.4 ^a	-1.5
k_H/k_D	benzene	5.6	4.3		?	4.5 ^a 5.1 ^a	3.0
	toluene	7.0	5.0		?	3.5	2.3
	anisole	?	?	4.5	?	?	?
$S_f = \log(I_p^{Me}/I_m^{Me})$		1.3	1.5 ^a 1.8 ^a	1.7 ^a 2.0 ^a	?	-0.03	1.2
ortho-meta-para-isomerization		yes	yes	?	?	no	yes
transmetalation		yes	yes	?	?	yes	yes
acceleration by light		yes	?	?	?	no	yes

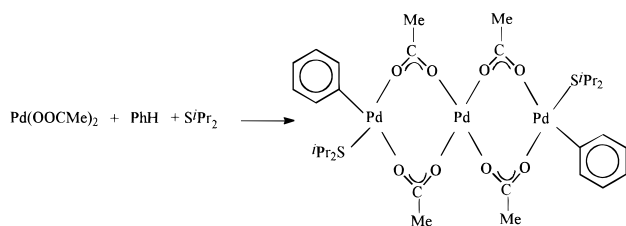
^a The data given are from different works.

pounds, the mechanism of these processes is still not clear. There are three main types of reactions.

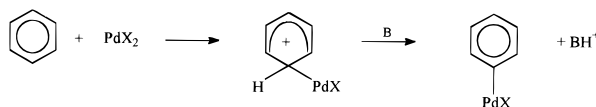
i. *Oxidative Coupling of Aromatic Nuclei (the van Helden Reaction^{22f})*



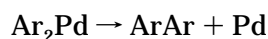
The mechanism of this process has been investigated.^{63b-d} The reaction exhibits the features of electrophilic substitution, such that electron-releasing substituents in the aromatic nucleus accelerate the metalation. Usually σ -aryl complexes of palladium(II) are not stable and cannot be isolated. However, dialkyl sulfides stabilize the complexes which then can be isolated as yellow crystals.^{63e,f}



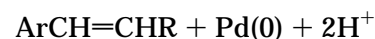
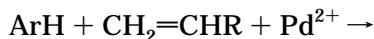
The kinetics of the oxidative coupling of benzene which is induced by $\text{PdCl}_2\text{-NaOAc}$ in acetic acid follows the equation: $w = k[\text{Pd(II)}][\text{C}_6\text{H}_6]$. Sodium acetate is a necessary reagent even though it is not reflected in the equation. The first step in the oxidative coupling mechanism is proposed to be an electrophilic substitution of a proton by the palladium. The acetate resides in the coordination sphere of the palladium, and its role apparently is to facilitate the proton abstraction. The reaction appears to be irreversible since there is no H-D exchange with the solvent.



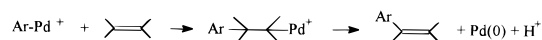
The reaction then is assumed to proceed by disproportionation, followed by biaryl formation:



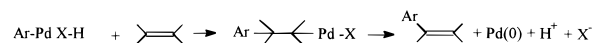
ii. *Oxidative Coupling of Arenes and Olefins (the Fujiwara Reaction^{22g})*



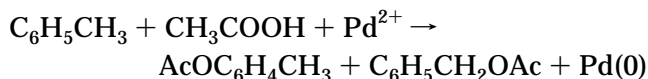
The first step of this reaction is palladation of the arene. Olefin insertion into the Ar-Pd bond is then possible (for example, see ref 63g,h):



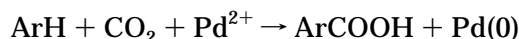
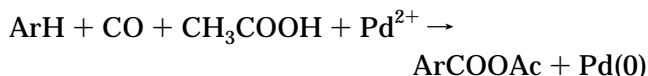
An alternative mechanism involves the formation of an aryl hydride intermediate, followed by insertion of the olefin into the Ar-Pd bond as before



iii. *Acetoxylation⁶³ⁱ*



iv. *Carbonylation by Carbon Monoxide^{63j,k} or by Carbon Dioxide^{63j-1}*



Fujiwara *et al.* (see refs 63j,k) have shown that analogous alkanes, including methane, can be carboxylated with CO or CO₂ by palladium and/or copper catalysts (and also by S₂O₈²⁻) in trifluoroacetic acid (*vide infra*).

The addition of an oxidizing reagent makes reactions i-iv catalytic with respect to palladium(II). In addition, palladium compounds catalyze many other reactions involving C-H bond activation. For example, benzaldehyde and benzoic acid can be produced by the partial oxidation of toluene. This reaction is carried out in a gas-phase fuel cell using palladium black as the anode.^{63m} The authors proposed that a π -allyl-benzyl-Pd²⁺ complex was formed as the reactive intermediate. Recently, Pd(II)-catalyzed acetoxylation of arenes with iodosyl acetate also has been described.⁶³ⁿ

b. Thermal and Photoinduced Reactions of Arenes with PtCl₆²⁻ To Afford Stable σ -Aryl Complexes of Pt(IV). Heating a solution of H₂PtCl₆ and an aromatic compound ArH in either CF₃-

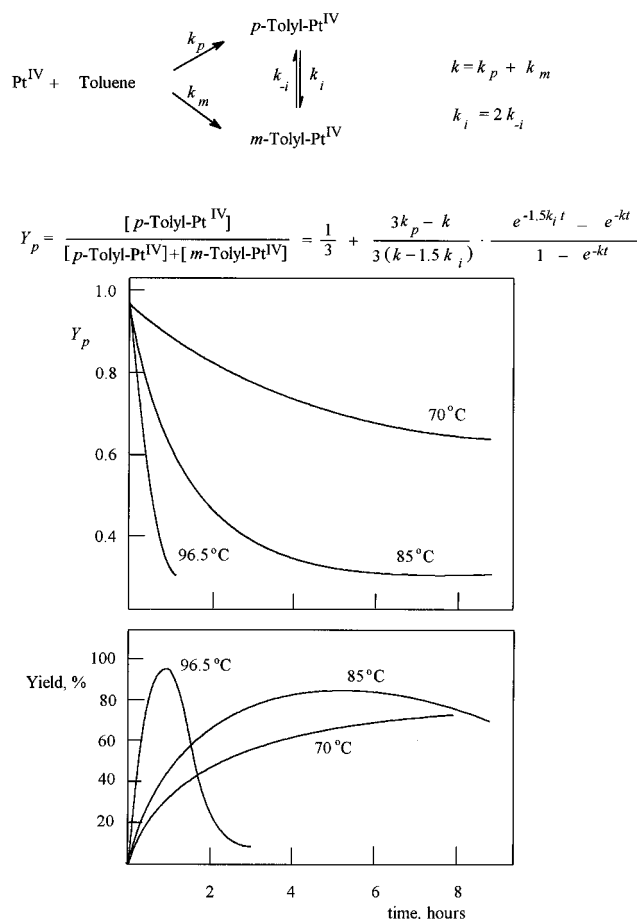
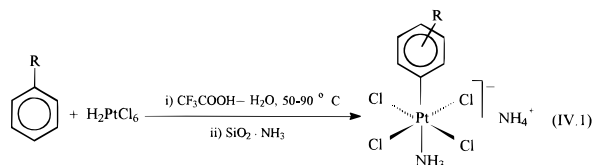


Figure 4. The reaction of H_2PtCl_6 with toluene in $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ to afford a σ -tolyl complex of platinum(IV). Accumulation and decomposition of the σ -tolyl complex (the yield of *para* + *meta* isomers is given at the bottom) and *para*–*meta* isomerization of this complex (Y_p is the content of *para* isomer in the *para* + *meta* mixture). (From refs 64a,e.)

$\text{COOH}-\text{H}_2\text{O}$ mixture or in CH_3COOH leads to the formation of relatively stable σ -aryl complexes of platinum(IV) in yields up to 95%. These complexes can be isolated in the form of anionic adducts with ammonia after chromatographing them on silica gel containing ammonia.^{24a,64a–c}



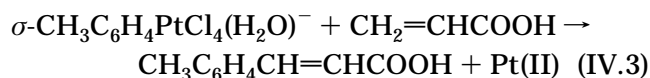
The final complexes have been characterized by X-ray diffraction and by ^{195}Pt NMR spectroscopy. Before their isolation as ammonia adducts, the complexes apparently exist as $\sigma\text{-ArPtCl}_5^{2-}$ and $\sigma\text{-ArPtCl}_4(\text{H}_2\text{O})^-$. On prolonged heating, these complexes decompose^{64d} to produce biaryls, chlorinated arenes, and platinum(II) derivatives. Formation of the σ -tolyl complex of platinum(IV) is accompanied by its *para*–*meta* isomerization.^{64a,e} If the initial substitution takes place mainly in the *para* position ($\sim 90\%$) in toluene, then the statistical distribution *meta*:*para* = 2:1 is gradually attained (Figure 4). The substituent does not occupy the *ortho* position for steric reasons. The relative amount of the *para* isomer Y_p can be calcu-

lated from the equation shown in Figure 4. The activation energies of both the formation and the *para*–*meta* isomerization are $\sim 25 \text{ kcal mol}^{-1}$. Competing reactions established^{64a} that the reaction relative rates (given in parentheses) for arenes $\text{C}_6\text{H}_5\text{X}$ decrease in the following sequence for substituents X: OH (16), OCH_3 (8.5), CH_3 (3), C_2H_5 (2.7), OC_6H_5 (2.0), $\text{CH}(\text{CH}_3)_2$ (1.9), H (1.0), C_6H_5 (0.9), F (0.3), COCH_3 (0.1), COOH (0.09), Cl (0.08), NO_2 (0.04). The logarithms of these values correlate with the Hammett constant σ and the Brown constant σ^+ , with parameters $\rho = -3.0$ and $\rho^+ = -1.5$, respectively. The kinetic isotope effect for the reaction is small, and is ~ 3 for benzene and ~ 2.3 for toluene.

A study of the decomposition products from the *meta* and *para* isomers of the σ -tolylplatinum(IV) complex, formed in the reaction between H_2PtCl_6 and toluene in aqueous trifluoroacetic acid, showed that a large amount of unexpected 2,3'- and 2,4'-bitolyls are formed isomers after a long induction period along with the expected 3,3'-, 4,4'-, and 3,4'-bitolyl.^{64f} These products, in which substituents are found *ortho* to the methyl group, are apparently formed by interaction of the *meta*- and *para*-platinated toluenes with free toluene which is present in solution. Indeed, if toluene is removed from the reaction mixture when the concentration of the σ -tolylplatinum(IV) complex is close to a maximum ($\sim 90\%$ yield), the rate of decomposition of this complex diminishes.^{64g} Analogously, the decomposition of a σ -methoxyphenyl complex of platinum(IV) affords 4,4'-dimethoxydiphenyl and, after an induction period, 2,4'-dimethoxydiphenyl.^{64h} The platinum(IV)-containing fragment can be easily transferred from one arene to another. For example, transmetalation occurs when a solution of the σ -tolyl complex of platinum(IV) is heated in aqueous trifluoroacetic acid with an excess of anisole or ethylbenzene.^{64g}



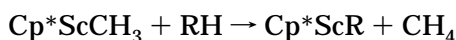
Upon prolonged heating with anisole, the σ -tolyl complex decomposes mainly to isomers of dimethoxybiphenyl and to lesser amounts of ditolyl and tolyl-methoxyphenyl. Likewise, heating a solution of the σ -tolyl complex with acrylic acid yields the product of olefin arylation:



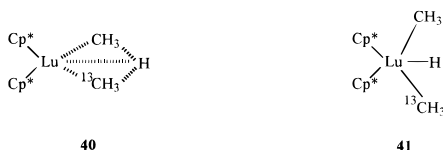
The proposed^{64a,e} mechanism for the reaction of PtCl_6^{2-} and arene which affords *para* and *meta* isomers of a σ -arylplatinum(IV) complex (**39_p** and **39_m**; Scheme 25) involves the formation of a weak π -areneplatinum(IV) complex **36** which is transformed into an intermediate Wheland-type complex. Isomerization of the Wheland complexes **37_p** and **37_m** may proceed through transition state **38**, or may arise from at least partial reversibility of the formation of **37**. The transarylation mentioned above (eq IV.2) may also be due to the reversibility of the Wheland complex formation.

Heating a solution of an aromatic compound (for example, benzene or toluene) with Na_2PtCl_4 in aqueous trifluoroacetic acid affords a σ -aryl complex of platinum(II) which is much less stable than the

complex and RH ($^{13}\text{CH}_4$, arenes, alkynes) gives a σ -organyl derivative of scandium:^{67a}

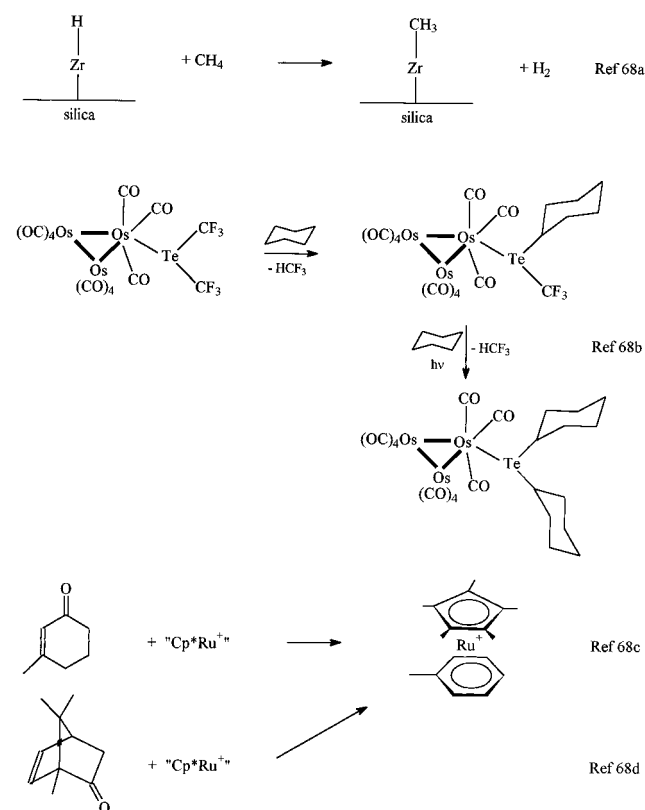


The exchange reaction of methane with a lutetium complex apparently proceeds via the transition state **40** rather than via an oxidative addition involving intermediate **41**.



Quantum-chemical calculations have been carried out for the mechanism involving *inter alia* a four-electron four-center transition state of type **40**.^{67b–d} The barrier for methane exchange was calculated^{67c} to be 28.0 kcal mol^{−1} for the reaction $\text{Cl}_2\text{ScCH}_3 + \text{CH}_4$ and 61.7 kcal mol^{−1} for $\text{Cl}_2\text{AlCH}_3 + \text{CH}_4$. Some examples of other reactions between alkanes and electrophilic metal complexes are shown in Scheme 26. The electrophilic “Cp*Ru⁺” fragment generated

Scheme 26

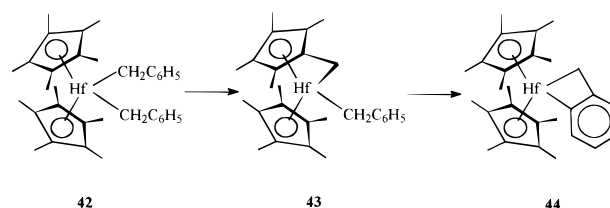


by protonation of $[\text{Cp}^*\text{Ru}(\text{OMe})_2]$ with $\text{CF}_3\text{SO}_3\text{H}$ is capable of activating the bonds C–H, C–O, and C–C in various organic compounds. Light (λ 180–360 nm) irradiation of an aqueous solution of C_2 – C_7 alkane and mercury(II) sulfate in air gave rise to alkane oxidation products, predominantly carbon dioxide.^{68e} The authors tentatively assumed that the key step in the reaction is the interaction of the hydrocarbon with the photoexcited Hg(II) species, which is believed to occur via electrophilic substitution. The alkyl mercury derivative thus formed then can be

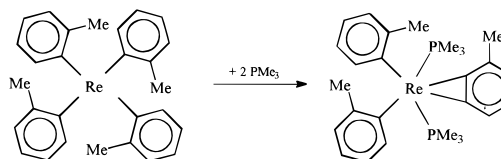
photolyzed to produce Hg(I) and R[•] radicals which further react with molecular oxygen. However, an alternative reaction mechanism could be proposed. A novel mode of electrophilic activation of aliphatic C–H bonds, also has been reported. This reaction is induced by Zr(IV) porphyrin complexes and achieved through the use of lithium, sodium, or potassium hydrides.^{68f}

3. Cases of Problematic Mechanistic Interpretation

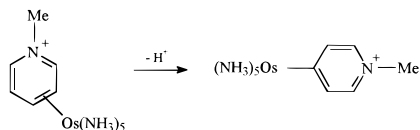
In recent years, numerous cases of C–H bond activation have been discovered, for which the reaction mechanism cannot be definitely attributed to either a typical oxidative addition to a nucleophilic metal center or to an electrophilic substitution at an electron-deficient metal ion. In some cases the mechanism is not clear at all. The intramolecular activation of a C–D bond in benzene-*d*₆ by the complex $(\text{Me}_3\text{P})_2\text{Pt}(\text{CH}_2\text{CMe}_3)(\text{SO}_3\text{CF}_3)$ apparently begins with the formation of a coordinatively unsaturated species, $[(\text{PMe}_3)_2\text{Pt}(\text{CH}_2\text{CMe}_3)]^+$, which then reacts with benzene-*d*₆ to form an arylplatinum hydride complex via oxidative addition.^{69a} The final product $(\text{Me}_3\text{P})_2\text{Pt}(\text{C}_6\text{D}_5)(\text{SO}_3\text{CF}_3)$ is formed following the elimination of CH_2DCMe_3 . However, the authors do not rule out the possibility that the positively charged platinum species carries out an electrophilic attack on the benzene ring. Another example is the thermolysis of complex **42** in benzene-*d*₆, which leads to the intramolecular metalation product **44**.^{69b} This reaction takes place in several steps and the intermediate complex **43** has been isolated. The introduction of several substituents onto the benzene ring has virtually no effect on the rate of metalation. Therefore, the authors believe that the transformation **43** → **44** occurs via four-membered transition state rather than as a typical electrophilic metalation by the Hf(IV) ion.



In yet another example, the mechanism of the reaction between tetraarylrhenium and phosphines is not completely clear:^{69c}

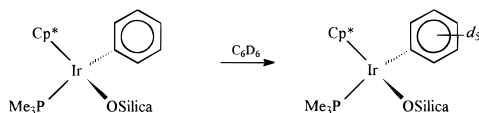


According to the authors' proposal, one step of the reaction is an oxidative addition of an *ortho*-C–H bond by the metal atom. Also the reduction of the complex $(\text{NH}_3)_5\text{Os}(\text{trifluoromethanesulfonate})$ with cobaltocene in the presence of *N*-methylpyridinium forms a π -complex which rearranges into a σ -aryl complex of osmium(II).^{69d}

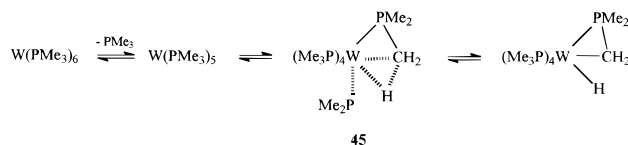


The mechanism of this C–H bond activation is unknown although the reaction may proceed by an oxidative addition.

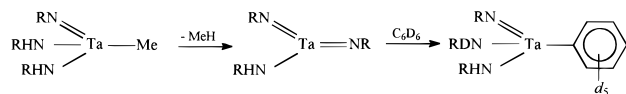
The interaction between the complex $\text{Cp}^*\text{Ir}(\text{CH}_3)_2$ (DMSO) and an arene $\text{C}_6\text{H}_5\text{X}$ leads to the formation of a σ -aryl derivative $\text{Cp}^*\text{Ir}(\text{CH}_3)(\text{C}_6\text{H}_4\text{X})$ (DMSO) and evolution of methane.^{69e} The rate of metalation decreases in the following sequence for X: $\text{I} > \text{NO}_2 > \text{CF}_3 > \text{CN} > \text{COOCH}_3 > \text{COCH}_3 > \text{Br} > \text{H} > \text{OCH}_3 > \text{Cl} > \text{F} > \text{NH}_2$. The metal atom substitutes only at *meta* and *para* positions on the benzene ring. In the case of $\text{X} = \text{NH}_2$, only the *meta* isomer is formed. The authors propose that the reaction proceeds by an arene replacing the DMSO ligand followed by subsequent oxidative addition of the C–H bond to iridium to produce an iridium(IV) derivative. This derivative then reductively eliminates methane and adds DMSO to give the final product. A synchronous elimination of methane and addition of the arene cannot be ruled out however. An iridium pentamethylcyclopentadienyl complex which is related to the iridium complexes that activate alkanes via typical oxidative addition, also reacts^{69f} with arenes, albeit by an unknown mechanism unknown:



A mechanism was proposed for the formation of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ from $\text{W}(\text{PMe}_3)_6$ which involved a concerted C–H bond metalation via the intermediate or transition state **45**. However, this mechanism has been discounted due to the lack of an observable kinetic isotope effect.^{69g}



The formation of oxametallacycles in the reactions of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ with phenols does not proceed via oxidative addition of the OH group to the tungsten center. Instead, it proceeds by a direct reaction at the W–C bond of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$.^{69g} The reaction between a tantalum complex and benzene forms an initial complex which is thermolyzed to produce an electrophilic three-coordinate imido intermediate. This intermediate then is capable of metalating benzene (R: tBu_3Si).^{69h}

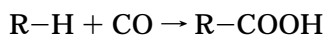


Finally, it has been concluded that the interaction of an analogous vanadium complex with hydrocar-

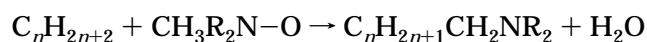
bons does not occur by a simple σ -bond metathesis mechanism.⁶⁹ⁱ

B. Alkane Oxidation by Metal Ions

Saturated hydrocarbons can be oxidized by some transition metal complexes in concentrated sulfuric acid. The acid enhances the oxidative properties of the complexes to such an extent that their reaction with alkanes becomes possible even at room temperature (see earlier refs 1c and 70a,b). Trifluoroacetic acid also has been used as a solvent for effective alkane oxidations.⁷¹ Solutions of palladium(II), platinum(III), manganese(III), or mercury(II) derivatives as well as some other compounds such as hydrogen peroxide, ammonium persulfate, nitric acid, and even concentrated sulfuric acid itself, can be used as oxidants. In the case of metal-free oxidants, the active species are apparently electrophiles such as NO_2^+ or SO_3H^+ . Hydrocarbons also can be carbonylated and aminomethylated by carbon monoxide and *tert*-methylamine *N*-oxides in the presence of palladium(II) and/or Cu(II).^{63j,k,71g-i}



(R: CH_3 , C_2H_5 , C_3H_7 etc.)



The oxidation of alkanes and benzene by polyvanadate in CF_3COOH to produce alkyl or phenyl trifluoroacetates and ketones is stimulated by light.^{71j} In fact, the alkane and benzene reactions virtually do not proceed in the absence of light. On the other hand, ethylbenzene and toluene are rapidly oxidized in the dark, even at 10 °C.

The following common features have been identified for oxidations in sulfuric acid:^{70b}

i. All the reactions follow a second-order kinetic equation $-\text{d}[\text{RH}]/\text{d}t = k_2[\text{RH}][\text{M}^{2+}]$. The only exception is found with manganese(III) complexes, which form an active radical species during an alkane-independent manganese complex decomposition.

ii. The cleavage of the C–H bond takes place at the rate-determining step of the reaction. The kinetic isotope effect (KIE) is $\sim 2.0 \pm 0.2$ for almost all the systems investigated and is the same for the cleavage of both tertiary and secondary C–H bonds. However, the KIE values are higher (4 ± 1) for CrO_3 , MnO_3 , and O_3 . It is interesting that for these oxidants the rate of the oxidation decreases with decreasing C–H bond energies: $\text{C}_3 > \text{C}_4 > \text{C}_6 > \text{C}_5 > \text{C}_7 > \text{C}_8$.

iii. In all cases, the selectivity for the rupture of the C–H bond decreases according to the sequence: tertiary > secondary > primary. However, the selectivity parameter is different for different reagents, such that the $3^\circ:2^\circ$ and $2^\circ:1^\circ$ ratios decrease in the sequence: $\text{Hg(II)} > \text{Pt(III)} > \text{H}_3\text{SO}_4^+ > \text{NO}_2^+ > \text{Pd(II)} > \text{S}_2\text{O}_8^{2-} \approx \text{Mn(III)}$. The $3^\circ:2^\circ$ ratio is 3000 for the most selective system, $\text{Hg}^{\text{II}}\text{--H}_2\text{SO}_4$, and only 12 for the system exhibiting the poorest selectivity, $\text{Mn}^{\text{III}}\text{--H}_2\text{SO}_4$.

iv. For alkanes containing *tert*-C–H bonds, the oxidation rate increases according to the sequence: $\text{Me}_3\text{C-H} < \text{Me}_2\text{EtC-H} < \text{MeEt}_2\text{C-H} < \text{Et}_3\text{C-H}$. For all systems of the type $\text{Mn}^+\text{--H}_2\text{SO}_4$, the rates obey the Taft equation

$$\log k = \text{const} + \rho^* \sum \sigma^* + \delta \sum E_S^0$$

with the ρ^* value ranging from -3 to -1 . This is typical for abstraction of a hydrogen atom.

v. The rate of the reaction increases exponentially with an increase in the Hammett acidity function

$$\log k = \text{const} - mH_0$$

This shows that protonation is a mode of activation for the species reacting with the alkanes.

vi. Bases can participate in the oxidation process. For example, in the NO_2^+ –aqueous H_2SO_4 system the rate dependence passes through a maximum at a H_2SO_4 concentration of 92–94%.

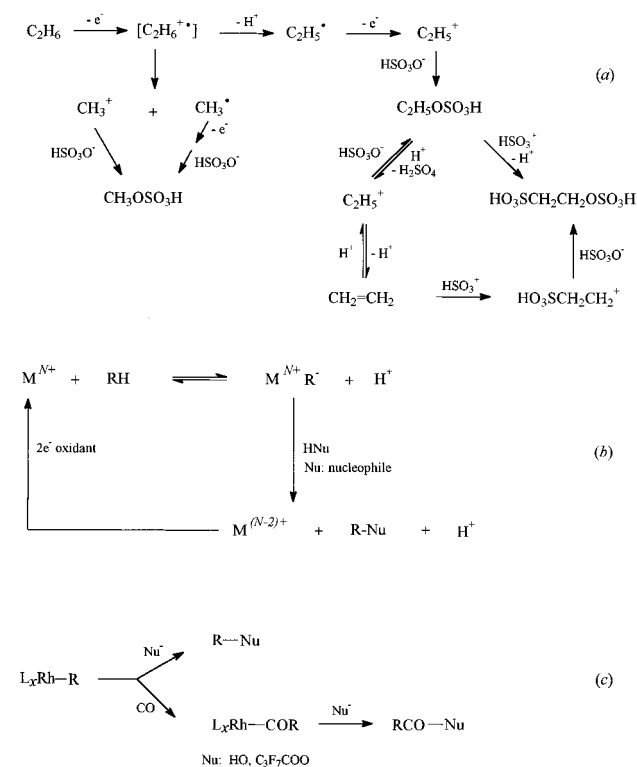
Periana *et al.*^{72a} reported selective catalytic oxidation of methane by sulfuric acid to produce methyl bisulfate at 180 °C. The reaction was catalyzed by mercuric ions, and sulfur dioxide was produced through sulfuric acid reduction. At a methane conversion of 50%, an 85% selectivity was observed for methyl bisulfate. The major side product of this reaction was carbon dioxide, and the mercury turnover efficiency was 10^{-3} s^{-1} . The Hg^{2+} ion reacts with methane as an electrophile and substitutes for a proton. This initially produces an intermediate methylated mercury complex, $\text{CH}_3\text{HgOSO}_3\text{H}$. The complex is formed in an appreciable steady-state concentration and was observed directly by ^{13}C and ^{199}Hg NMR spectroscopy. Under the reaction conditions methyl mercuric bisulfate decomposed to produce methyl bisulfate, $\text{CH}_3\text{OSO}_3\text{H}$, and the reduced mercurous species, Hg_2^{2+} . The catalytic cycle was completed by the reoxidation of Hg_2^{2+} with H_2SO_4 to regenerate Hg^{2+} along with SO_2 and H_2O :



Incorporation of D into the methane was observed in the presence of D_2SO_4 and mercuric salts under the reaction conditions. An independent reaction of specially prepared methyl mercuric bisulfate confirmed that protolysis of this species occurred at 180 °C, thus confirming the mechanism for the isotope exchange.

A variety of oxidants, such as $\text{S}_2\text{O}_8^{2-}$, Ce(IV) , Pd(II) , and Hg(II) have been employed by Sen *et al.*^{72b} The main product of the methane oxidation in 98% sulfuric acid was $\text{CH}_3\text{OSO}_3\text{H}$, while for ethane, the observed products were $\text{CH}_3\text{OSO}_3\text{H}$ and $\text{HO}_3\text{SCH}_2\text{CH}_2\text{OSO}_3\text{H}$. The proposed reaction steps are shown in Scheme 27a. A remarkable similarity has been observed in the rate constants for methane and methanol under the action of the platinum(II) ion, such that the ratio of the oxidation rate constants for methane versus methanol is 0.17. The methyl group of ethanol was oxidized to produce 1,2-ethanediol as the predominant product. An electrophilic pathway for the activation of C–H compounds is presented in Scheme 27b.^{72b} Complex RhCl_3 catalyzed the direct formation of methanol and acetic acid from methane, CO and O_2 in a mixture of perfluorobutyric acid and water.^{72c} At 80–85 °C the turnover rate was $\sim 2.9 \text{ h}^{-1}$ based on Rh. Ethane was more reactive, and under similar conditions gave ethanol, acetic acid and methanol (rate $\sim 7.5 \text{ h}^{-1}$). The

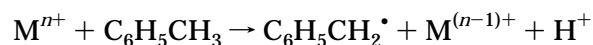
Scheme 27



From refs 72b,c. Copyright 1994, 1996 American Chemical Society.

latter product arose from a C–C bond cleavage. It is interesting that for both methane and ethane, the product alcohols are less reactive than the starting alkanes. The authors assumed that the ratio of alcohol to the corresponding carboxylic acid is a function of the relative rates of nucleophilic attack versus CO insertion into a Rh–alkyl bond (see Scheme 27c).

Arylalkanes can react with electrophilic oxidants^{73a} to produce alkyl radicals via simultaneous electron transfer and deprotonation:

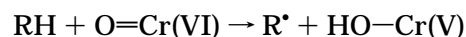


The first step of the reaction may involve the formation of a radical cation,^{73b} and this route is typical of arenes which possess low ionization potentials, $<8 \text{ eV}$.

C. Oxidation by Metal Oxo Complexes

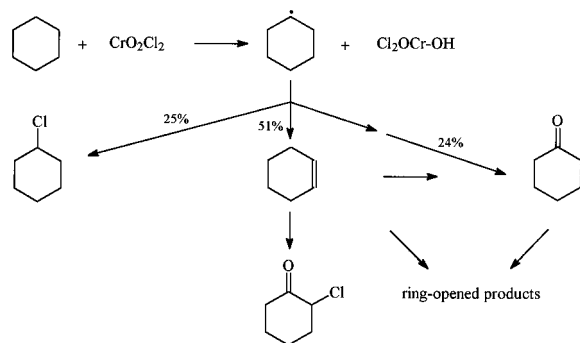
1. Oxygenation of Alkanes with Derivatives of Cr(VI) and Mn(VII)

Chromium(VI) oxo derivatives are strong oxidants which are also used as catalysts in organic synthesis.^{74a} The reaction of alkanes with chromium(VI) oxo compounds apparently takes place with the intermediate formation of radicals:



However, not all the radicals formed are liberated in the solution, since the oxidation of (+)-3-methylheptane by chromic acid involves the formation of (+)-3-methyl-3-heptanol with 70–85% retention of configuration. Normal selectivity has been observed in the hydroxylation of branched alkanes. Chromyl

Scheme 28

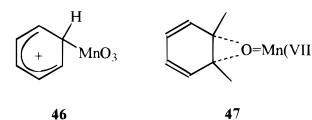


From ref 74b. Copyright 1994 American Chemical Society.

chloride, CrO_2Cl_2 , reacted^{74b} with cyclohexane to give a dark precipitate along with chlorocyclohexane and a small amount of cyclohexene. Hydrolysis of the precipitate yielded cyclohexanone and chlorocyclohexanone. Cyclohexene also was readily oxidized by the chromium compound to give mostly ring-opened products with some 2-chlorocyclohexanone and cyclohexanone (Scheme 28). This reaction proceeds via an initial hydrogen-atom transfer from cyclohexane to the Cr(VI) . The cyclohexyl radical then is rapidly trapped by a chromium species via one of three pathways: (a) chlorine-atom abstraction, (b) formation of a C–O bond, or (c) transfer of a second hydrogen atom. A correlation has been found between O–H bond strength and the hydrogen atom transfer rate.

The addition of ruthenium(IV) or iridium(IV) chloride complexes to the alkane oxidation reaction increased the rate of the chloroalkane formation.^{74c} The selectivity of the oxidation was different for ruthenium(IV) ($1^\circ:2^\circ:3^\circ = 1:100:1000$) that it was for iridium(IV) ($1:30:250$); and the primary C–H bond was more reactive in the latter case. One possible cause for the greater oxidizing capacity of the chromium(VI) compounds in the presence of Ru(IV) or Ir(IV) is the formation of a mixed complex such as $[\text{Cl}_4\text{RuOCrO}_3]^{3-}$. The addition of strong acids also accelerated the reaction and gave rise to protonated species, such as $\text{O}=\text{Cr}(\text{OH})_3^+$ and HCrO_3^+ . The rate of oxidation is proportional to the acidity of the medium. Furthermore, the oxidation of alkanes and of aromatic alkyl-substituted compounds by oxo derivatives of chromium(VI) was greatly accelerated by light irradiation.^{74d–h} Acetic acid, acetonitrile, and methylene chloride have been used as solvents, and the products were an alcohol and a carbonyl compound. The reaction apparently begins with the abstraction of a hydrogen atom from the C–H bond by an excited species of the oxo complex. The logarithms of the relative rate constants for the oxidation of substituted toluenes $\text{XC}_6\text{H}_4\text{CH}_3$ by CrO_3 in acetic acid both in the dark and under light ($\lambda > 300 \text{ nm}$), correlate with the Brown constants σ^+ of the substituents X.^{74f} It is interesting that in both the dark and light reactions the points corresponding to the substituent $p\text{-OCH}_3$ do not lie on the straight line. The chromium trioxide–3,5-dimethylpyrazole complex has been found to be a mild and selective reagent for the oxidation of cyclopropyl hydrocarbons, and the reaction proceeds in the dark at -20°C .⁷⁴ⁱ

Permanganate also oxidizes alkanes at room temperature in trifluoroacetic acid solution,^{75a} and the MnO_3^+ cation is apparently the active species. The selectivity of this reaction is $1^\circ:2^\circ:3^\circ = 1:60:2100$. In $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ solution the active species may be MnO_4^- , HMnO_4 , or $\text{O}_3\text{MnOCOCF}_3$.^{75b} The oxidation of benzene proceeds via either cation **46** or oxenoid **47**.

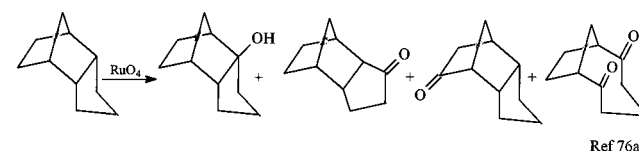


Aqueous solutions of permanganate oxidize methane at $40-100^\circ\text{C}$ and produce carbon dioxide as the sole product.^{75c} In addition, potassium permanganate–triethylamine is a convenient reagent for the oxidation of benzylic methyl, methylene, and methine groups.^{75d}

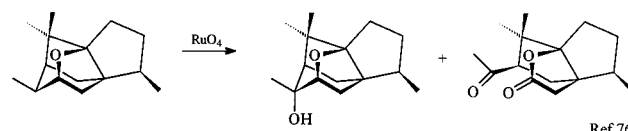
2. Oxygenation by Ruthenium(IV) and Other Complexes

Ruthenium tetroxide, which is formed from $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ or other ruthenium derivatives and sodium periodate oxidize saturated hydrocarbons (Scheme 29).^{76a–e} Ruthenium trichloride catalyzes the oxida-

Scheme 29

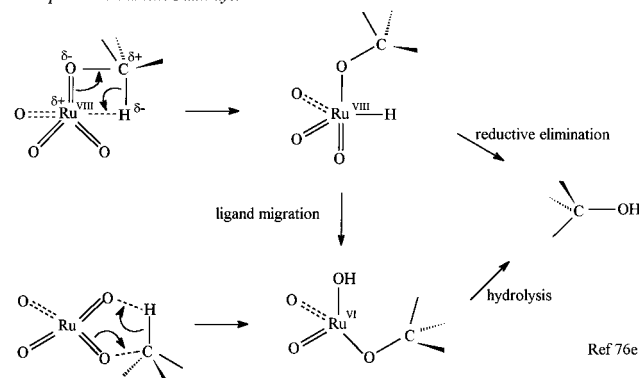


Ref 76a



Ref 76e

Proposed Mechanistic Pathways:



Ref 76e

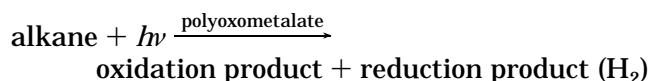
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tion of 2-methylnaphthalene to 2-methylnaphthoquinone with ammonium dichromate.^{76f} Cyclohexane, adamantane, *n*-hexane, toluene, and ethylbenzene can be oxidized at room temperature by barium ruthenate.^{76g} Complexes of ruthenium-containing chelating ligands, as well as some other ligands, effectively oxidize alkanes both in the dark and under light irradiation.^{77a–g} In the presence of 2,2'-bipyridine, barium ruthenate generates a highly reactive ruthenium–oxo system that is capable of oxidizing ethane and propane at room temperature.^{77h} Like-

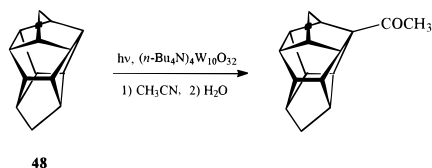
wise, a ruthenium(VI) complex containing two oxo ligands oxidizes alkyl chains in alkyl aromatics,^{77j} and molybdenum(VI) dioxo complexes oxidize arylalkanes either thermally or under UV irradiation.^{77j} More recently, a novel oxidizing reagent based on potassium ferrate(VI) has been described.^{77k} This potassium ferrate, when used in conjunction with an appropriate heterogeneous catalyst such as K10 montmorillonite clay is a strong oxidant which produces cycloalkanols and cycloalkanones from cycloalkanes, and benzyl alcohol and benzaldehyde from toluene. A theoretical study has demonstrated that the enthalpies for the reactions of transition metal oxo complexes with aliphatic alcohols follows the order:^{77l} OH hydrogen abstraction > CH hydrogen abstraction > CH bond addition > OH bond addition. Thus, since an OH group is not initially present, the oxidation of hydrocarbons by a (μ -oxo)manganese complex, $[\text{L}_2\text{Mn}(\mu\text{-O})\text{MnL}_2](\text{PF}_6)_3$ ($\text{L} = 1,10\text{-phenanthroline}$) proceeds via a hydrogen atom abstraction.^{77m}

3. Alkane Functionalization under the Action of Polyoxometalates

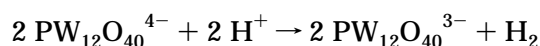
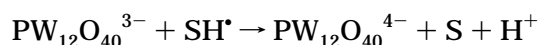
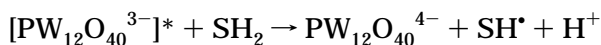
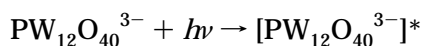
Hill and co-workers^{78a–g} irradiated an air-free solution of alkane, polyoxometalates, and metallic platinum in acetonitrile with light. This reaction gave a variety of oxidation and reduction products, as shown in the following equation:



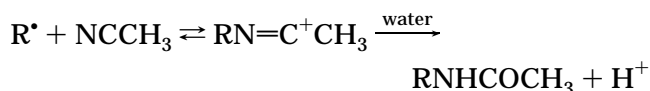
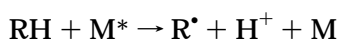
The oxidation products were alkenes, *N*-alkylacetamides, alkyl methyl ketones, and dialkyls. Thus, hydrocarbon **48** was acetylated by this method:



The following sequence of steps has been proposed. First, the photoexcited polyoxometalate species M^* abstracts hydrogen atoms from the SH_2 substrate. The reduced form of the metalate then transforms the H^+ ions into molecular hydrogen:



Alkane derivatives may be formed according to the following scheme:

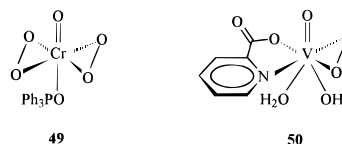


The relative rate constants for linear $\text{C}_5\text{--C}_9$ alkanes correlate with their ionization potentials.

Semiempirical ASED–MO calculations have been carried out for the photodimerization of cyclohexene and methane by decatungstate anions.^{78h} The hydrogen abstraction activation energies calculated for C–H bonds in methane are higher than in cyclohexene, but they are still low enough that methane dimerization should be looked for in future experiments.

D. Oxygenation by Peroxo Complexes

The peroxo complexes of many transition metals^{79a–e} are capable of oxidizing various organic compounds, including alkanes and aromatic hydrocarbons. Thus, the peroxochromium complex **49** stoichiometrically oxygenated cyclohexane.^{79f} For example, the interaction of **49** with cyclohexane in a 1:1 $\text{CH}_2\text{Cl}_2\text{--Me}_3\text{COH}$ mixture at room temperature gave 9.3% of cyclohexanol and 1.6% of cyclohexanone based on chromium.



Mimoun's^{80a} vanadium complex **50**, which contains picolinate (pic), is an effective oxidizing reagent and is capable of oxygenating both alkanes and arenes.^{80a–e} For example, benzene was oxidized by this complex to produce phenol along with dioxygen. The reaction is a radical–chain process,^{80c} where initiation produces a radical anion of the peroxovanadium complex as the actual oxidant. In the propagation steps, this species reacts with either the original peroxo complex to give dioxygen or with the aromatic hydrocarbon to form phenols.^{80c} Likewise, the oxidation of cyclohexane in acetonitrile afforded cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone in about a 2:1:1 ratio. Both the alkane and arene reactions were accelerated upon irradiation with visible and, especially with UV light.^{80e} When a solution of $[(\text{BuOO})\text{Pd}(\text{OCOCH}_3)]_4$ and cyclohexane in methylene chloride was exposed to the light of a high-pressure mercury lamp in a glass vessel ($\lambda > 310 \text{ nm}$), cyclohexanol and cyclohexanone were detected in the reaction mixture.^{80f} The oxidation of alkanes by $[(\text{BuOO})\text{Pd}(\text{OCOCF}_3)]_4$ occurred in a benzene solution both in the dark and under light irradiation. It is interesting that the dark reaction produced a significant amount of cyclohexyl hydroperoxide in addition to the cyclohexanol and cyclohexanone.^{80f}

There is evidence that metal peroxo complexes also can oxidize alkanes by a nonradical mechanism. Peroxo complexes which are formed by the reaction of hydrogen peroxide with high-valent metal compounds in acid solution, can react with alkanes, such as cyclohexane, to produce alcohols and ketones. This reaction does not seem to depend on free radicals. Particularly convincing results are reported in refs 80g,h. For example, the peroxovanadium complex produced by the reaction of $\text{VO}(\text{acac})_2$ or KVO_3 with H_2O_2 , reacted with cyclohexane in acetic acid to form cyclohexanol and cyclohexanone. The evidence is against this reaction occurring by a free radical mechanism. For example, the reaction was

not inhibited by typical chain reactions inhibitors. Also, neither the reaction rate nor the yield of cyclohexanol was influenced by the addition of isopropyl alcohol or carbon tetrachloride, both of which would have been readily attacked by free radicals if they were present. The reaction was much faster in trifluoroacetic acid than in acetic acid, and in CF_3COOH it produced cyclohexanol and cyclohexyl trifluoroacetate but not cyclohexanone. The conversion of the hydrocarbon reached 5–8% in acetic acid with a 10-fold excess of hydrogen peroxide, and 95–98% in trifluoroacetic acid with only a 4–5-fold excess of H_2O_2 . Ozone was detected when hydrogen peroxide was decomposed without substrate in the presence of acid. The O_3 which was formed in CF_3COOH comprised 10–15% of all the gaseous products formed. This formation of ozone shows that the oxygen atom is easily transferred from the peroxo ligand of the active species to even such weak acceptors as another peroxo ligand. Apparently, the C–H bond in an alkane is a sufficiently strong acceptor to insert an O atom and form an alcohol. These reaction systems therefore appear to be similar to superacid solutions, where hydrogen peroxide and ozone react with alkanes by inserting oxygen atoms into C–H bonds in a nonradical fashion. Peroxo derivatives of transition metals are intermediates in the oxidations of organic compounds by hydrogen peroxide or alkyl hydroperoxides which are catalyzed by various metal complexes. Such processes, which involve the formation of free radicals, will be discussed in the following section.

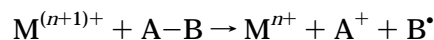
V. Oxygenation of Hydrocarbons by Molecular Oxygen and Oxygen-Atom Donors

The oxidation of hydrocarbons with molecular oxygen as well as with oxygen-atom donors such as hydrogen peroxide and alkyl hydroperoxides, is a very important field. Many industrial processes are based on these reactions.^{1f,1,2w,81} There have been a number of publications which have dealt with this problem and we will discuss it only briefly here.

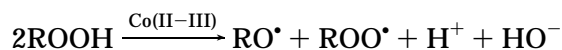
A. Traditional Chain Autoxidation of Alkanes

Higher alkanes and alkyl aromatic hydrocarbons can be oxidized by heating them under oxygen at rather high (usually above 100 °C) temperatures. This reaction proceeds after a long induction period, which can be reduced or eliminated by adding a free radical donor. The formation of oxygen-containing products from hydrocarbons and molecular oxygen is always a thermodynamically allowed process, due to the high exothermicity of oxidation reactions. However, this same exothermicity usually makes these processes unselective. The main problem becomes how to prevent various parallel and consecutive oxidation reactions which produce numerous byproducts. Destruction of the carbon chain is one possible route in the oxidation.^{82a} The autoxidation of saturated hydrocarbons or their fragments occurs as a chain process with the participation of free radicals. Azobis(isobutyronitrile) is frequently used as chains initiator.^{82b–d} Any additive which can react with the free radicals formed in such a process to form stable adducts instead will inhibit the oxida-

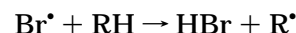
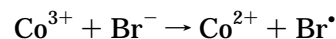
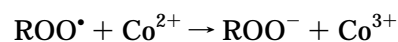
tion.^{82e} Ions of transition metals, either homogeneous or supported on polymers,^{82f} also effectively catalyze the autoxidation. The role of the metal ion M^{n+} is to produce free radicals upon reacting with a molecule A–B:



In accordance to these equations, each metal ion can alternately increase or decrease its oxidation state to produce a large number of free radicals; thus, it plays the role of a catalyst. A transition metal ion can also react with hydroperoxides formed in the course of the oxidation to produce new free radicals, for example:



Alkylaromatic hydrocarbons are easily oxidized by dioxygen in the presence of cobalt and bromine ions.^{83a–d} The catalytic effect of these ions is due to their participation in the chain-propagation step:



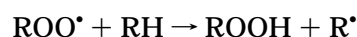
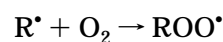
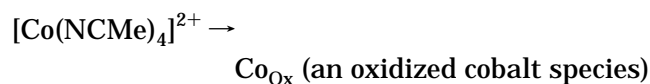
In recent years, many investigations of hydrocarbon autoxidation have been carried out (for example, see refs 84a–c).

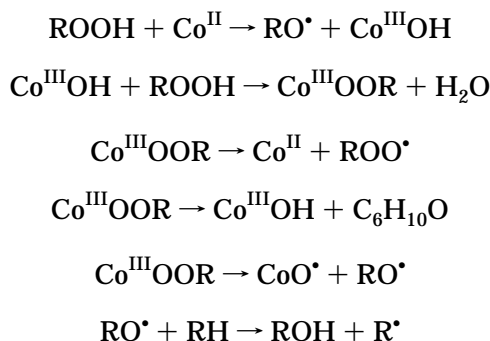
B. Novel Low-Temperature Processes of Hydrocarbon Oxidation

Some recently described reactions between hydrocarbons and molecular oxygen will be briefly considered here. These processes are often radical-chain autoxidations, but in some cases the reaction mechanisms of are not clear.

1. Oxidation of Alkanes

A weakly solvated complex containing acetonitrile, $[\text{Co}(\text{NCMe})_4](\text{PF}_6)_2$, catalyzes the air oxidation of cyclohexane and adamantane at 75 °C.^{85a} The commercial catalyst for cyclohexane oxidation does not function under these conditions. The metal ions function both as an initiator and as a hydroperoxide decomposition catalyst, and the following steps have been proposed for the oxidation reaction:

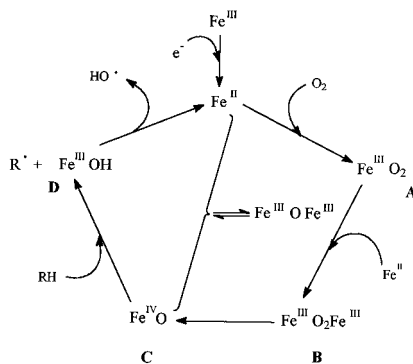




Cobalt chloride in diglyme is a useful catalyst for benzylic^{85b} and allylic^{85c} oxidations under mild conditions. Likewise, ethylbenzene is slowly oxidized by air in the presence of a catalytic amount of chromium trioxide MeCN.^{85d} Complexes of Fe(III) and Co(II) with dipyrindyl- and acetylacetonate-functionalized polymers, showed a high degree of activity and selectivity in the oxidation of ethylbenzene by oxygen.^{85e} An oxidation of alkanes by molecular oxygen, which is catalyzed by *N*-hydroxyphthalimide combined with transition metal salts or Co(acac)_{*n*} (*n* = 2, 3), has been recently described.^{85f,g}

Halogenated metalloporphyrins are effective catalysts for the selective air oxidation of light alkanes.⁸⁶ The postulated mechanism (Scheme 30)^{86c} is similar

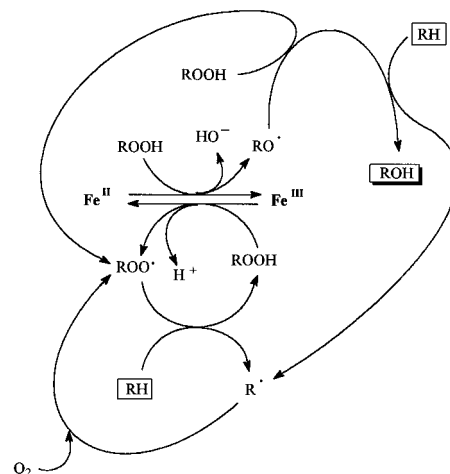
Scheme 30



to those proposed for biological oxidations by cytochrome P450 and methanemonooxygenase, *vide infra*. It involves the reduction of Fe(III), followed by the addition of dioxygen to produce dioxo species **A**. Species **A** then reacts with a second molecule of catalyst (intermediate **B**) to give two molecules of the monooxo complex **C**, which is capable of oxidizing the alkane. Species **C** abstracts a hydrogen atom from the alkane to generate an alkyl radical and the hydroxy derivative **D**. However, there is an alternative mechanism which does not include an Fe^{II}–O₂ species and instead assumes that the reaction proceeds by a conventional radical–chain autoxidation mechanism,^{86g} as shown in Scheme 31. Half-metallated iron(III) porphyrin dimers also catalyze the hydroxylation of cyclohexane with molecular oxygen under mild conditions.^{86h}

Heteropolyanions have been shown to effectively catalyze the oxidation of alkanes into their corresponding alcohols and ketones.⁸⁷ Thus, [PW₉O₃₇]-[Fe₂Ni(OAc)₃]¹⁰⁻ catalyzes^{87a} the transformation of adamantane into 1-adamantanol (76%), 2-adamantanol (12%), and 2-adamantanone (12%) with total of 25 turnovers and a 29% conversion. The mixed-

Scheme 31

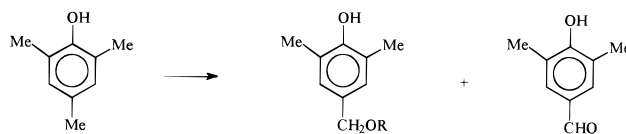


addenda heteropolyanion [PV₂Mo₁₀O₄₀]⁵⁻ catalyzes aerobic, oxidative dehydrogenation of α-terpinene to *p*-cumene.^{87c} Transition metal-substituted Keggin-type polyoxomolybdates also have been shown to catalyze the autoxidation of cumene or cyclohexene to yield alkyl hydroperoxides which epoxidize alkenes.^{87d} In addition, alkylbenzenes and alkanes can be oxygenated by dioxygen when ammonium molybdovanadophosphate is used as a catalyst.^{87e}

A Ru^{III}–EDTA system catalyzes the oxidation of cyclohexane by molecular oxygen.^{88a,b} In the presence of manganese(II) acetate and molecular oxygen, alkenes and active methylene compounds react to yield cyclic peroxides.^{88c,d} α-Substituted cycloalkanones are oxidized to oxo acids by a copper(II) nitrate–dioxygen–acetic acid–water system:^{89a}

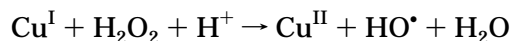
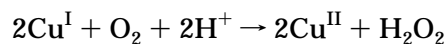


Copper(II) chloride, in combination with acetoxime, catalyzes the oxidation of a methyl group in 2,4,6-trimethylphenol when the reaction is carried out in alcohols, ROH, at ambient temperature:^{89b}



2. Oxygenation of Aromatic Compounds

Copper(I) chloride promotes the molecular oxygen oxidation of benzene to phenols.^{90a} The active species is proposed to be a hydroxyl radical generated in the following manner:



Analogously, benzene is oxidized in the presence of silica-supported palladium catalysts under ambient conditions to give phenol, benzoquinone, hydroquinone, and catechol.^{90b} The palladium chloride which is used to prepare the catalyst is believed to be converted into metallic palladium. A synthesis of

Table 5. The Nomenclature of Gif Systems (From Ref 91a. Copyright 1992 American Chemical Society)

system	catalyst	electron source	oxidant
Gif ^{III}	Fe(II)	Fe (metal)	O ₂
Gif ^{IV}	Fe(II)	Zn (metal)	O ₂
GO (Gif-Orsay)	Fe(II)	cathode	O ₂
GoAgg ^I	Fe(II)		KO ₂ /Ar
GoAgg ^{II}	Fe(III)		H ₂ O ₂
GoAgg ^{III}	Fe(III)/picolinic acid		H ₂ O ₂
GoChAgg	Cu(II)		H ₂ O ₂
Cu ⁰ /O ₂	Cu(I)?	Cu(0)	O ₂

phenol from benzene and molecular oxygen via the direct activation of a C–H bond by the catalytic system Pd(OAc)₂–phenanthroline in the presence of carbon monoxide has been described.^{90c,d} The proposed mechanism includes electrophilic attack of an active palladium-containing species on benzene to produce a σ -phenyl complex of palladium(II). This is followed by the subsequent activation of dioxygen by a Pd–phen–CO complex to form a Pd–OPh complex, which reacts with acetic acid to yield phenol.

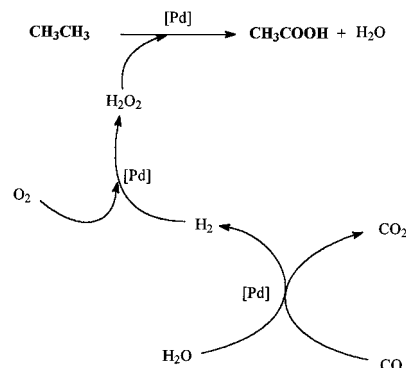
C. Coupled Oxidation of Alkanes. Gif Systems

Some enzymes can oxygenate a saturated or aromatic C–H bond using molecular oxygen, only if a reducing reagent converts the second oxygen atom from O₂ into a water molecule. Many analogous chemical systems are known which oxidize hydrocarbons by dioxygen in the presence of a reducing reagent.

Since 1983, Barton and co-workers^{24d} have developed a family of systems for oxidation and oxidative functionalization of alkanes under mild conditions. These systems exhibit “unusual” selectivities (see reviews,^{91a,b} some recent publications,^{91c–s} and papers on these systems by other authors⁹²). These oxidations occur in pyridine in the presence of an organic acid and are catalyzed by transition metal complexes (mainly iron). If dioxygen is used as the oxidizing reagent, a reductant must also take part in the reaction. The first such system was invented in Gif-sur-Yvette,^{24d} thus their name: Gif systems. Gif systems with geographically based names are described in Table 5. All Gif systems have the same chemical peculiarities: (i) the major products of the reaction are ketones, and alcohols are not reaction intermediates; (ii) the presence of an excess of some easily oxidizable compound (e.g., alcohols, aldehydes) does not significantly suppress the alkane oxidation; (iii) the selectivity of oxidation for branched hydrocarbons is secondary > tertiary > primary; (iv) secondary alkyl free radicals are not reaction intermediates; (v) olefins are not epoxidized; and (vi) the addition of trapping reagents can divert the reaction to form monosubstituted alkyl derivatives instead of ketones. For example, in the presence of CBrCl₃, alkyl bromides are formed in quantitative yield.

It should be noted that despite of numerous works devoted to Gif systems, their mechanism is not completely clear.

A whole series of other systems are known which oxygenate organic substrates using oxygen in a process which is coupled to the oxidation of a low-valent metal derivative. However, these reactions do

Scheme 32

From ref 93a. Copyright 1992 American Chemical Society.

not exhibit the peculiarities of the Gif systems mentioned above. For example, the hydroxylation of alkanes by oxygen in the presence of SnCl₂ in acetonitrile at room temperature occurs with a selectivity of 1°:2°:3° = 1:5.1:12.5. It has been established that the interaction of dioxygen with SnCl₂ involves a branched chain mechanism in which hydroxyl radicals are formed and react with saturated hydrocarbons. Nevertheless, all oxidations of alkanes which are coupled with the oxidation of metal compounds can be considered in some respects as models of biological monooxygenase-type oxidations (see section VI). A heterogeneous, formal analog of alkane monooxygenase has been described.^{93a} The system involves a metal catalyst (palladium) and a coreductant (carbon monoxide) and transforms ethane into acetic acid at temperature <100 °C. The proposed mechanism is shown in Scheme 32.

In some cases, hydrocarbon oxidation in the presence of a reducing agent does not require a transition metal catalyst. For example, a carbon whisker cathode was found to actively oxidize toluene into benzaldehyde and benzyl alcohol in a H₂–O₂ fuel cell reaction.^{93b} Also, the electrolysis of water at room temperature, caused the epoxidation of 1-hexene and the hydroxylation of benzene to phenol and hydroquinone, to occur simultaneously on the anode and cathode, respectively.^{93c} Examples of oxidations by dioxygen in the presence of various reducing agents, which are catalyzed by transition metal complexes, are given in Table 6.

D. Aerobic Photooxygenation of Alkanes

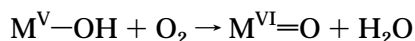
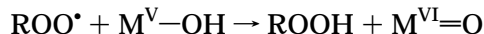
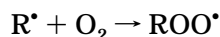
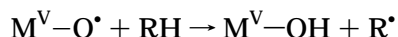
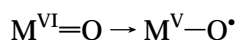
In 1989, a few groups simultaneously described the aerobic oxygenation of alkanes and arylalkanes in solutions containing catalytic amounts of metal oxo complexes under light irradiation. These complexes were heteropolymetalates in methylene chloride,^{95a} acetic acid, alcohols, acetone, or acetonitrile,^{95b,c} and polyoxotungstate W₁₀O₃₂^{4–} in acetonitrile^{95d,e} or water.^{95f} Other oxo compounds which also catalyze alkane photooxygenation include K₂Cr₂O₇ in a two-phase water–1,2-dichloroethane system,^{96a} CrO₃ in acetonitrile,^{95d} (nBu₄N)₂Cr₂O₇, (nBu₄N)₂Cr₃O₁₀ and (nBu₄N)Cr₄O₁₃ in methylene chloride,^{96b} and UO₂Cl₂ in acetic acid or acetonitrile.^{96c} The photooxygenation of alkanes catalyzed by molybdenum or tungsten carbonyl apparently begins with the transformation of a carbonyl complex into an active oxo species.^{96d,e} Some other chromium and vanadium complexes also

Table 6. Oxidation of Hydrocarbons by Dioxygen in the Presence of Reducing Agents

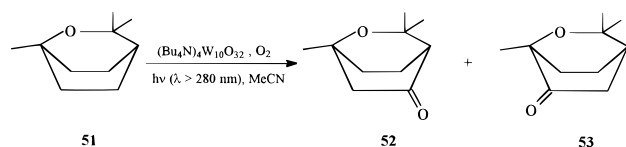
substrates	products	reducing agent	catalyst	ref
alkanes	alcohol + ketone	Zn powder	EuCl ₃	94a
cyclohexane	cyclohexanol + cyclohexanone	Zn powder	SmCl ₃	94b
cyclohexane	cyclohexanol + cyclohexanone	aldehyde	metalloporphyrins	94c
alkanes	alcohol + ketone	heptanal	Fe	94d
benzene	phenol	crotonaldehyde	VO(1,3-diketonato) ₂	94e
arenes	phenols	hydroquinones	catecholatoiron complex	94f
benzene	phenol	H ₂	Pd–Ti silicalites	94g
hexane	hexanols			
alkanes	alcohols	Zn powder	[{Fe(HBpz ₃)(hfacac)} ₂ O]	94h
arenes	phenols			
alkanes	alcohol + ketone	acetaldehyde	Cu(OH) ₂	94i
alkanes	alcohols	hydrazobenzene	Fepy ₄ Cl ₂	94j
arenes	phenols	Fe	Fe(II)	94k
cyclohexane	cyclohexanol + cyclohexanone	Zn powder	Fe(II) on silica gel	94l

have been reported to catalyze alkane photooxidation.^{96f–i}

The mechanism of aerobic alkane photooxidation catalyzed by metal oxo complexes includes the formation of a photoexcited species which is capable of abstracting a hydrogen atom from an alkane. The alkyl radical thus formed rapidly adds a molecule of oxygen. The resulting species eventually forms an alkyl hydroperoxide which decomposes to produce a ketone and an alcohol.



Oxidation photocatalyzed by polyoxometalates has been used to functionalize cycloalkanes^{96j} as well as the ubiquitous natural product 1,8-cineole (structure **51**).^{96k} The photooxygenation of **51** gave a mixture of ketones and alcohols which were subsequently transformed by pyridinium chlorochromate into 5- and 6-keto derivatives in the ratio **52**:**53** = 2.5:1. A laser flash photolysis study of the mechanism has been carried out for the decatungstate anion catalyzed reaction.^{96l}



Iron(III) chloride has been found to be an efficient photocatalyst for alkane oxidation with atmospheric oxygen.⁹⁷ The kinetics of the cyclohexane photooxidation in the presence of a catalytic amount of FeCl₃, as well as some other compounds (*vide infra*), are shown in Figure 5.^{97g} As with the reaction catalyzed by oxometalates, the first step of this process is apparently the photoexcitation of the iron chloride species to stimulate homolysis of the Fe–Cl bond.^{97h} The chlorine radical (either free or trapped in the solvent cage) then attacks the alkane. This results in an iron(II) derivative which can be oxidized either by molecular oxygen or by an alkylperoxo radical

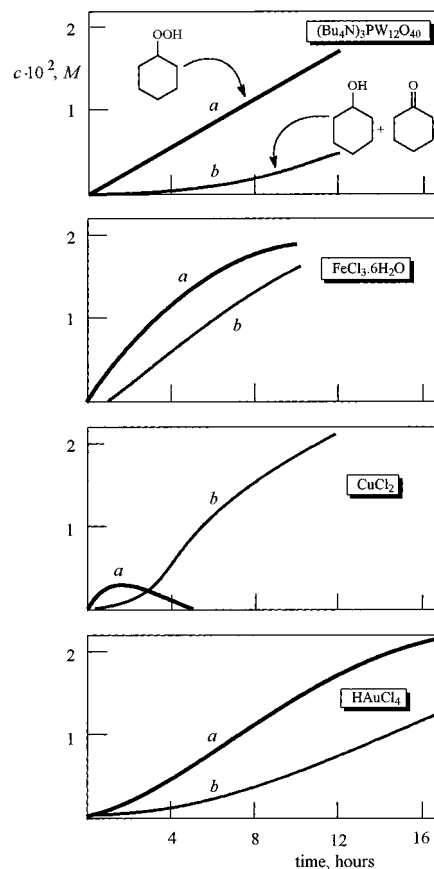


Figure 5. Kinetics of the aerobic photooxygenation of cyclohexane (0.46 M) in the presence of various catalysts (5×10^{-4} M) in MeCN under full light irradiation with a street luminescent lamp (250 W) at 10 °C to produce cyclohexyl hydroperoxide (a) and a mixture (sum) of cyclohexanol and cyclohexanone (b). (From ref 97g.)

(Scheme 33). One possible pathway to the alkyl hydroperoxide formation may involve electron transfer $Cl-Fe^{III}$ and reorganization of bonds within a six-membered structure (**A** or **B**, Scheme 33). Other transition metal chlorides, for example CuCl₂ (refs 97d,g and 98a,b), AuCl₄[−] (refs 97g and 98c,d) (see Figure 5), PtCl₆^{2−} (refs 97d and 98d,e), and CrCl₃ (ref 98f) also photocatalyze the aerobic oxygenation of alkanes in acetonitrile, methylene chloride, or acetic acid. However, the reaction mechanisms in these cases seem to be different from that postulated for the FeCl₃-catalyzed process,^{97h} and apparently involve low-valent species. These species may add an oxygen molecule to produce metal peroxo radicals and peroxo complexes. Such a mechanism has been

Table 7. Oxidation of Alkanes and Arylalkanes with Hydrogen Peroxide Catalyzed by Metal Complexes

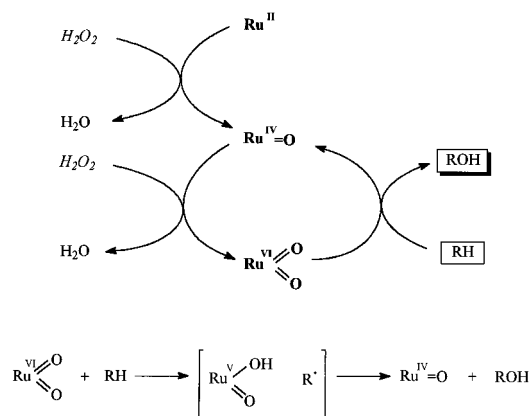
substrates	products	solvent	catalyst	ref
methane	methanol + formaldehyde	H ₂ O	<i>cis</i> -[Ru(dmp) ₂ S ₂](PF ₆) ₂ ^a	104a
alkanes	alcohols + ketones	MeCN	<i>cis</i> -[Ru(dmp) ₂ S ₂](PF ₆) ₂ ^a	104b
cycloalkanes	alcohols + ketones	H ₂ O (microemulsion)	iron salts	104c
alkyl aromatics	ketones + alcohols	MeCN	polyoxometalates	104d
alkyl aromatics	ketones + alcohols	various	H ₃ PV ₂ Mo ₁₀ O ₄₀	104e
alkanes	alkyl esters	CF ₃ COOH	Rh salts	104f
alkanes	trifluoroacetates	CF ₃ COOH	RuCl ₃	104g
alkanes	ketones + alcohols	H ₂ O–CH ₂ Cl ₂	CrO ₃ or (Bu ₃ SnO) ₂ CrO ₂	104h,i
alkanes	alkyl hydroperoxides	MeCN	Pd(OCOCF ₃) ₂	105a
			CrO ₃	
			FeSO ₄	
			LMnCl ^b + imidazole	
alkanes	alkyl hydroperoxides	MeCN	ⁿ Bu ₄ NVO ₃ + pyrazine-2-carboxylic acid	105a–k
methane	methyl hydroperoxide (+ formaldehyde + formic acid)	MeCN	ⁿ Bu ₄ NVO ₃ + pyrazine-2-carboxylic acid	105k
		H ₂ O		
cyclohexene	cyclohexenyl hydroperoxide	MeCN	ⁿ Bu ₄ NVO ₃ + pyrazine-2-carboxylic acid	105j
<i>n</i> -hexane	hexanols + hexanones	MeOH	zeolite TS-1	105l,m
cyclohexane	cyclohexanol + cyclohexanone	acetone	Ti silicate	105n
cyclohexane	cyclohexanol + cyclohexanone	MeCN	peroxide adduct of Fe(III)	105o
cyclohexane ^c	cyclohexanol	MeOH–CH ₂ Cl ₂	iron porphyrinate	105p

^a dmp = 2,9-dimethyl-1,10-phenanthroline, S = H₂O or MeCN. ^b L = tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrinate.
^c Competitive reaction with cyclooctene in the presence of H₂¹⁸O.

Table 8. Oxidation of Aromatic Compounds with Hydrogen Peroxide Catalyzed by Metal Complexes

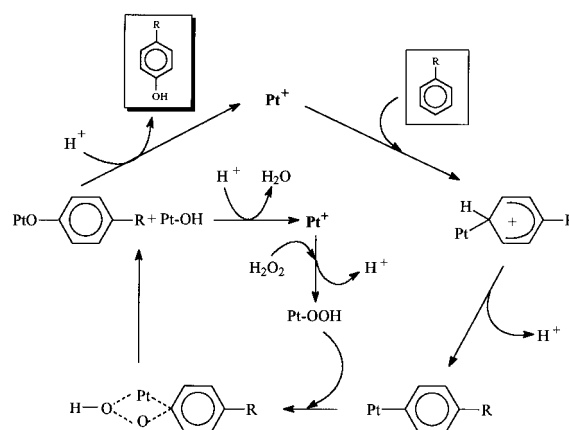
substrates	products	solvent	catalyst	ref
arenes	phenols	isopropyl alcohol	(P-P)Pt(CF ₃)X ^a	106a
benzene	phenol	MeCN	iron salts	106b
arenes	phenols	MeCN	VO(O ₂)(Pic)(H ₂ O) ₂ ^b	106c
methylnaphthalene	naphthoquinones	CH ₃ COOH	CH ₃ ReO ₃	106d
phenol	hydroquinone + catechol		Ti silicalite	106e
phenol	hydroquinone + catechol	<i>t</i> -BuOH	metallo-silicalite xerogels	106f
arenes	phenols	triphasic	Ti silicate molecular sieve	106g
phenol	catechol + hydroquinone + benzoquinone	water	Fe(II) 1,10-phenanthroline	106h
benzene	hydroxylation products		hexagonal silicas	106i

^a P-P = tetraaryldiphosphine, X = OH, OPh. ^b Pic = picolinic acid anion.

Scheme 34

From ref 104b. Copyright 1994 American Chemical Society.

assumed for cytochrome P450 and its models (see section VI) (Scheme 34).^{104b} Meanwhile, the mechanism proposed for the hydroxylation of aromatics catalyzed by cationic complexes of platinum(II) involves an electrophilic metalation of the aromatic ring to yield platinum-aryl intermediates followed by oxygen transfer from a platinum-hydroperoxy species (Scheme 35).^{106a} Finally, the oxidation^{106c} of aromatic compounds by hydrogen peroxide which is catalyzed by the peroxovanadium complex VO(O₂)(Pic)(H₂O)₂ is proposed to occur via direct oxygenation of the

Scheme 35

From ref 106a. Copyright 1992 American Chemical Society.

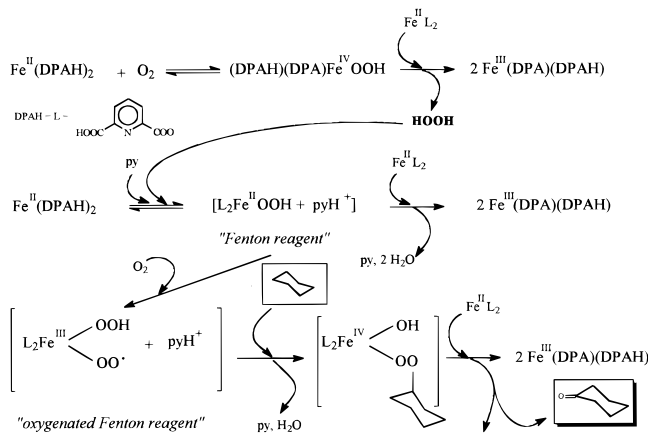
arene by this complex. The active complex then is restored by reaction with H₂O₂.

Recently, a highly efficient alkane oxidation has been described^{105a–k} for the “O₂–H₂O₂–vanadium complex–pyrazine-2-carboxylic acid” reagent (for examples of this reaction, see Table 7). The reagent also oxygenates arenes to phenols,^{105b,d} and alcohols to ketones,^{105d} and hydroperoxidizes the allylic position in olefins.^{105j} At low temperatures in acetonitrile or water, the predominant alkane oxidation product is the corresponding alkyl hydroperoxide; alcohols

and ketones or aldehydes are formed simultaneously in smaller amounts, and the hydroperoxide is then slowly decomposes to produce the corresponding ketone and alcohol. The amounts of alkyl hydroperoxide, alcohol and alkanone in the reaction mixture were estimated by comparing gas chromatographic analyses of the solution before and after its reduction with triphenylphosphine. This method allows the determination of alkyl hydroperoxides present in the solution together with the original H_2O_2 and alcohol and alkanone (see refs 97e–h, 99b, 100a, 101c,d, and 105a–k). Direct measurements of the peak intensities corresponding to ROOH were also made.^{105h} It has been demonstrated^{105k} that atmospheric oxygen takes part in this reaction, since the oxygenation does not proceed in the absence of air. The cyclohexane oxidation under an $^{18}\text{O}_2$ atmosphere unambiguously showed a high degree of ^{18}O incorporation into the oxygenated products. Thus it may be concluded that in alkane oxidation, hydrogen peroxide plays the role of a promoter while atmospheric oxygen is the true oxidant. The oxidation of *n*-heptane by the " O_2 – H_2O_2 –vanadium complex–pyrazine-2-carboxylic acid" reagent exhibits^{105h} low selectivity, C(1):C(2):C(3):C(4) \approx 1:4:4:4. This selectivity is close to that found for the oxidation of *n*-heptane by H_2O_2 in MeCN under UV irradiation (1.0:3.4:3.2:3.0). The selectivities of the reactions with branched alkanes such as 2- and 3-methylhexane and *cis*- and *trans*-decalin are also very similar to those observed for alkane with hydrogen peroxide under UV irradiation.¹⁰⁵ⁱ However, the product distributions for oxidations of *cis*-decalin by the " O_2 – H_2O_2 –vanadium complex–pyrazine-2-carboxylic acid" reagent^{105i,j} are different than those obtained with Mimoun's complex.^{80a} The vanadium-based reagent also readily oxidizes methane, ethane, propane, *n*-butane, and isobutane in acetonitrile solution.^{105g,k} In addition to alkyl hydroperoxides, which are the primary oxidation products, alcohols, aldehydes or ketones, and carboxylic acids are obtained with high total turnover numbers (420 for methane and 2130 for ethane at 75 °C after 4 h) and H_2O_2 efficiencies. It has been proposed^{105a–k} that the first step in an oxidation by " O_2 – H_2O_2 – VO_3^- –pyrazine-2-carboxylic acid" is the very efficient generation of HO^\bullet radicals. These radicals abstract a hydrogen atom from the alkane, RH, to generate the alkyl radical, R^\bullet , which reacts rapidly with an O_2 molecule to give the peroxy radical, ROO^\bullet . This radical is then transformed simultaneously into three products: an alkyl hydroperoxide, a ketones and an alcohol. The relative amounts of the latter two products increased at higher reaction temperatures.

It is noteworthy that alkane oxidations with H_2O_2 or ROOH in air, when catalyzed by various metal complexes^{105a} including $\text{Pd}(\text{OCOCF}_3)_2$, CrO_3 , FeSO_4 , and PorphMnCl , often give varying amounts of alkyl hydroperoxides which can be easily detected by GC. If alkyl hydroperoxides are present, the intensities of the alcohol and ketone peaks differ significantly for the samples before and after their reduction with triphenylphosphine. In many publications, however, only the yields of ketones and alcohols are given, even though these stable products can be formed in the chromatograph from the corresponding alkyl hydroperoxide.

Scheme 36



From refs 103f, 107e. Copyright 1996, 1994 American Chemical Society.

Sawyer, Sobkowiak and their co-workers have developed the iron-, cobalt-, and copper-induced activation of hydrogen peroxide (along with dioxygen) for oxidation of organic substances, especially alkanes.^{103e,f,107} The main feature of these reactions is their predominant formation of ketones from cycloalkanes. The ketonization is carried out in a pyridine–acetic acid solution and so is relevant to the oxidation by Gif-type systems (*vide supra*). Thus, it has been found that the combination of $\text{Fe}(\text{DPAH})_2$ ($\text{DPAH}_2 = 2,6$ -dicarboxypyridine) and dioxygen in a pyridine–acetic acid (2:1) mixture results in rapid autoxidation to produce hydrogen peroxide and $\text{Fe}(\text{DPA})(\text{DPAH})$. The hydrogen peroxide thus formed reacts with an excess of the starting iron(II) compound to yield "a Fenton reagent", $[(\text{DPAH})_2\text{FeOOH} + \text{pyH}^+]$. This species adds dioxygen and then attacks a cyclohexane molecule to produce cyclohexanone as shown in Scheme 36.

2. Oxidations by Alkyl Hydroperoxides

Examples of recent works devoted to alkane oxidation catalyzed by various metal complexes are given in Table 9. It has been shown^{110c} that $\text{VO}(\text{acac})_2$ is initially transformed by an alkyl hydroperoxide into the alkylperoxo complex $\text{VO}(\text{acac})_2\text{OOR}$ and the alkoxo complex $\text{VO}(\text{acac})_2\text{OR}$. These complexes decompose to yield $\text{VO}(\text{OR})_3$ and two other vanadium(V) species which have been identified as an alkylperoxo complex (I) and an alkoxo complex (II). Complex I does not react directly with cyclohexane, but produces the free radical ROO^\bullet instead. This peroxy radical then initiates oxidation of the cyclohexane. Complex $[\text{Fe}(\text{PMA})]^{2+}$ also efficiently catalyzes the oxidation of alkanes with tBuOOH in acetonitrile at room temperature.^{110d} The mechanism proposed by the authors for this reaction involves the formation of free alkyl radicals and their subsequent reaction with molecular oxygen (Scheme 37). The CyOO^\bullet radical may be involved in a Russell-type termination^{110e} which produces cyclohexanol and cyclohexanone in equal amounts, along with molecular oxygen:

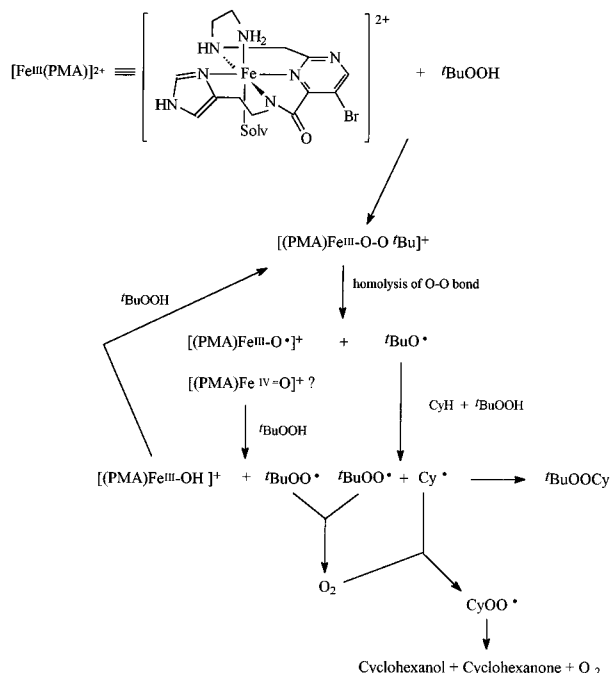


It is possible that the CyOO^\bullet radical also is transformed in the course of the reaction into CyOOH or

Table 9. Oxidation of Alkanes with Alkyl Hydroperoxides Catalyzed by Metal Complexes

ROOH	alkane	products	solvent	catalyst	ref
^t BuOOH	cyclohexane, etc.	ketones + alcohols	MeCN	[Mn(bipy) ₃](BF ₄) ₂ , etc.	108a
^t BuOOH	ethane	ethanol	MeCN	Mn ₄ O ₂ (O ₂ CPh) ₇ (bipy) ₂ , etc.	108b
^t BuOOH ^a	cycloalkanes	ketones + alcohols	benzene	Mn ²⁺ -exchanged clay catalyst	108c
^t BuOOH	cyclohexane	cyclohexanone + cyclohexanol	CH ₂ Cl ₂	[RuLO ₂ (CF ₃ CO ₂)]ClO ₄ ^b	109a
^t BuOOH CumOOH ^c	alkanes	ketones + alcohols	benzene	RuCl ₂ (PPh ₃) ₃	109b
^t BuOOH	alkanes	ketones	H ₂ O-CH ₂ Cl ₂	K ₅ [Ru(H ₂ O)PW ₁₁ O ₃₉]	109c
^t BuOOH	cyclohexane	cyclohexanone + cyclohexanol	CH ₂ Cl ₂	Co(III) complexes	109d
^t BuOOH CumOOH ^c	cyclohexane	cyclohexanone + cyclohexanol + ^t BuOOcy	MeCN	Fe(TPA) ^d	109e
^t BuOOH ^a	benzylic C–H	ketones	various	CrO ₃	110a
^t BuOOH	benzylic C–H	alcohols + ketones + peroxides		VAPO-5	110b

^a 70% aqueous *tert*-butyl hydroperoxide. ^b L = *N,N,N'*-trimethyl-1,4,7-triazacyclononane. ^c Cum = cumyl. ^d TPA = tris(2-pyridylmethyl)amine.

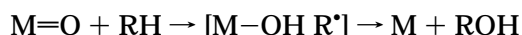
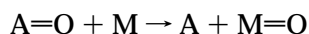
Scheme 37

From ref 110d. Copyright 1996 American Chemical Society.

CyOO[•]Bu which then decomposes in the GC to yield approximately equal amounts of cyclohexanol and cyclohexanone (*vide supra*, and, e.g., refs 105a–k).

F. Oxygenation by Other Oxygen Atom Donors

In recent decades, some additional oxygen-containing oxidizing reagents have been used in hydrocarbon oxygenations catalyzed by transition metal complexes. It is assumed¹¹¹ that these oxidizing reagents, A=O, transfer an oxygen atom to a metal–complex catalyst, M, thus forming a high-valent oxo complex. This complex then is capable of oxidizing the alkane, RH, for example, via the “oxygen rebound” radical mechanism:

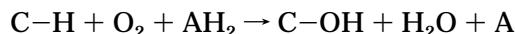


Examples of hydrocarbon oxidations by oxygen atom donors which are catalyzed by metal complexes are presented in Table 10. Other recent publications

have been devoted to hydrocarbon oxidation by dioxygen and oxygen-containing oxidants catalyzed by complexes of chromium,^{114c} rhenium,^{114d–f} iron,^{114g–j} ruthenium,^{114k–n} copper,^{114o} palladium,^{114p} vanadium,^{114q–s} titanium^{114t} and metal-substituted polyoxometalates.^{114u,v} It should be emphasized that when the metal–complex catalyst is a metalloporphyrin (or even any other complex), the reaction can be considered to be a model for biological hydrocarbon oxidation (see next section VI).

VI. Biological Oxidation and Its Chemical Models

Organic compounds, including alkanes and arenes, can be surprisingly easily oxidized by dioxygen in the cells of bacteria, plants, insects, fish, and mammals, including man. The group of enzymes, called monooxygenases, which catalyze the hydroxylation of C–H compounds by molecular oxygen can induce the insertion of only one oxygen atom from O₂ into the C–H bond, while the second oxygen atom is reduced to form water:



The hydrogen donor AH₂ can be NADH, NADPH, the ascorbate anion, and other biological reductants. In virtually all biological oxidations of hydrocarbons, hydroxylation is preceded by the activation of oxygen on the metalloenzyme. The creation of chemical models of the enzymatic oxidation of alkanes and arenes makes it possible not only to understand its mechanisms better, but also to develop what are likely to be fundamentally new processes for the conversion of hydrocarbon raw materials. Many books¹¹⁵ and reviews¹¹⁶ have been devoted to enzymatic oxidations and processes that more or less closely model these oxidations (other reviews will be cited below). Only a brief survey of the most recent data for biological C–H activation and hydrocarbon oxidation will be presented in this review. Somewhat unexpectedly, important and profound analogies exist between chemical activation by metal complexes and biological C–H oxidation.

A. Hydrocarbon Oxygenations by Cytochrome P450 and Its Chemical Models

Cytochrome P450 is a widely distributed enzyme in nature. It is a monooxygenase and is especially

Table 10. Oxidation of Hydrocarbons with Oxygen Atom Donors Catalyzed by Metal Complexes

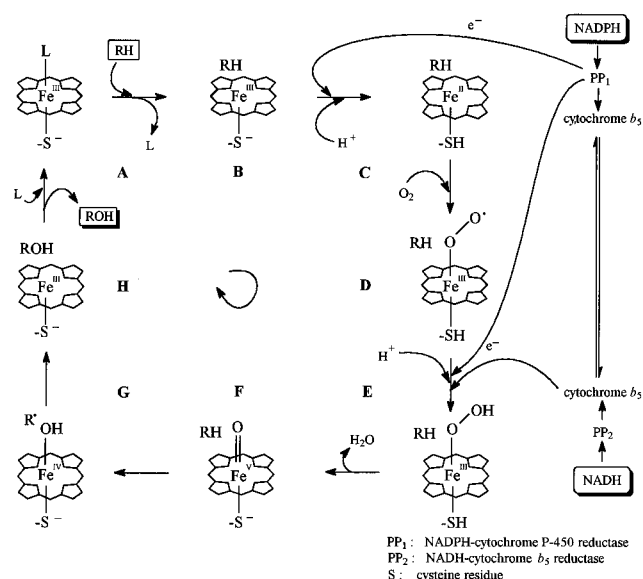
oxygen atom donor	catalyst	substrate	ref
PhIO	$P_2W_{17}O_{61}(M^{n+}\cdot Br)^{(n-11)}$ ($M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$)	cyclohexane, heptane, adamantane	112a
PhIO	metalloporphyrins (on imidazole propyl gel)	cyclohexane	112b
PhIO	Ru(III) diphosphino complexes	adamantane, hexane	112c
PhIO	$[Mn_2L_2(\mu-OAc)_2]^{2+ a}$	cyclohexane, adamantane	112d
PhIO	$CrO_3, VOCl_2$	2,3-dimethylbutane	
PhIO	$CrO_3, VOCl_2$	cyclohexane, ethylbenzene	112e
PhIO	Mn-Salen complex	benzylic C-H bond	112f
PhIO	iron porphyrin	cyclohexane	112g
PhIO	manganese porphyrin	cyclohexane	112h
$LiClO_4$	Ru(II) complexes	adamantane, decane, cyclohexane	113a
$KHSO_5$	$SiRu(H_2O)W_{11}O_{39}^{5-}$	adamantane, cyclohexane	113b
$KHSO_5$	Ru complexes	ethylbenzene	113c
$KHSO_5$	Mn, Fe porphyrins	2-methylnaphthalene	113d
$NaIO_4$	$SiRu(H_2O)W_{11}O_{39}^{5-}$	adamantane, cyclohexane	113b
Me_3NO	L_2Cu^b	aromatics	113e
$pyCl_2NO$	Ru pentafluorophenylporphyrin	alkanes	113f
$(Ad=Ad + ^1O_2)^c$	metalloporphyrins	adamantane, cyclohexane	114a
XeO_3	CrO_3 ; Mn, Fe porphyrins	benzene, alkylbenzenes	114b

^a L: *N,N*-dimethyl-*N,N*-bis(2-pyridylmethyl)ethane-1,2-diamine. ^b L: 2-(*N*-amido)-4-nitrophenolate. ^c Ad=Ad: adamantyl-deneadamantane; ¹O₂: singlet oxygen.

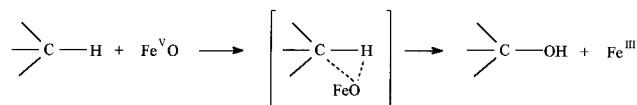
capable of oxidizing alkanes, arenes, and their derivatives (for example, prostaglandins and aliphatic acids). A number of books¹¹⁷ and reviews¹¹⁸ describe cytochrome P450, and recent papers have been devoted to its crystal structure,¹¹⁹ mechanism of action,¹²⁰ theoretical studies,¹²¹ and some reactions.¹²²

1. Mechanism of Oxidation Catalyzed by Cytochrome P450

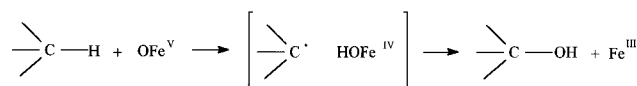
The oxidation of hydrocarbons and their derivatives has been investigated in great detail using the liver cell microsomes of warm-blooded animals and also bacterial monooxygenases, both of which involve iron porphyrin-based cytochrome P450. In the presence of liver microsomes, alkanes, and aliphatic acids are hydroxylated predominantly at the terminal (ω) carbon atom. The mechanism proposed for alkane oxidation by dioxygen catalyzed by cytochrome P450 is shown in Scheme 38. The oxidation of an alkane, RH, includes at least eight steps. The first step converts low-spin cytochrome P450 into high-spin B. Reduction takes place in the second step of the process, after which a dioxygen molecule is coordinated to the iron(II) atom. Cytochrome P450's X-ray structure is known for camphor hydroxylating P450_{cam} with and without the substrate. The structure confirms that the iron atom inside the porphyrin ring is open to O₂ addition and activation and that the substrate molecule is in close enough proximity to the iron core to be directly involved in C-H hydroxylation. An X-ray diffraction analysis of the related complex of myoglobin with dioxygen showed that the oxygen is coordinated such that the O₂ molecular axis forms a 120° angle with the plane of the porphyrin ring (Pauling's structure D). The fourth and fifth steps terminate with the reduction of the complex to form oxenoid F and the elimination of a water molecule. A C-H bond in the substrate molecule is cleaved in the step 6, and two alternative mechanisms have been proposed for this crucial step. The first is a direct oxygen atom insertion by an oxenoid mechanism, while the second is a radical C-H bond cleavage with subsequent recombination in the cage (the "oxygen rebound" radical mechanism) (Scheme 38). The latter mechanism is widely accepted in the

Scheme 38

The oxenoid mechanism:



The "rebound" radical mechanism:



literature, and its main evidence includes the following observations: (1) high kinetic H-D isotope effects, (KIEs reaching 8–12) are obtained, which presume a linear transition state as would be expected for the radical cleavage of a C-H bond; and (2) isomerization is often observed during the process of O-atom insertion which indicates the presence of a supposedly free-radical intermediate.

However, high KIE values can be due to proton tunneling and do not necessarily correspond to a linear transition state. Moreover, isomerizations may indicate the presence of an intermediate, but also may be explained^{120l} by a five-coordinate carbon mechanism in which a metal-bound O atom ini-

tially coordinates to a C–H group. This coordination is similar to the coordination between a hydrogen atom and a superacid or an electron-rich metal complex, such as is seen with Pt(II) complexes in water solutions. Lippard *et al.*^{120m} studied reactions of methylcubane with P450 and concluded that the results were consistent with a concerted enzyme-catalyzed hydroxylation involving “side-on” approach to the C–H bond of the hydrocarbon substrate.

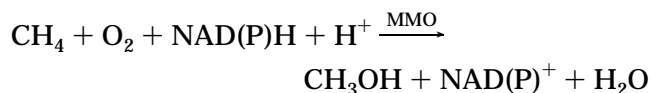
2. Modeling Oxidation Catalyzed by Cytochrome P450

When modeling cytochrome P450 (see ref 123), porphyrin complexes of iron(III) as well as manganese(III), chromium(III), and ruthenium(III) are usually employed as the catalysts. If molecular oxygen is the oxidant, a reducing agent is required. An electric current,¹²⁴ metallic zinc,^{125a} or ferrocene^{125b} can serve as the reductant. Instead of the dioxygen–reductant pair, an oxo compound containing an oxygen atom which is already partly reduced, such as H₂O₂,¹²⁶ ROOH,¹²⁷ PhIO¹²⁸ (however, see ref 128e), NaOCl,¹²⁹ KHSO₅,¹³⁰ *N*-oxides,¹³¹ or magnesium monoperoxyphthalate, can be employed.¹³² Free radicals are definitely intermediates in some reactions, particularly for hydrocarbons with weak C–H bonds; however, as with their biological analogs, some mechanisms certainly proceed by direct O-atom insertion, possibly following precoordination of the alkane to form a five-coordinate carbon intermediate.

B. Methane Monooxygenase and Other Non-Heme Iron-Containing Oxygenases

1. Methane Monooxygenase

The enzymes isolated from methane oxidizing bacteria are known under the general name of methane monooxygenases (MMO).¹³³ These enzymes oxidize methane in accordance with the equation:

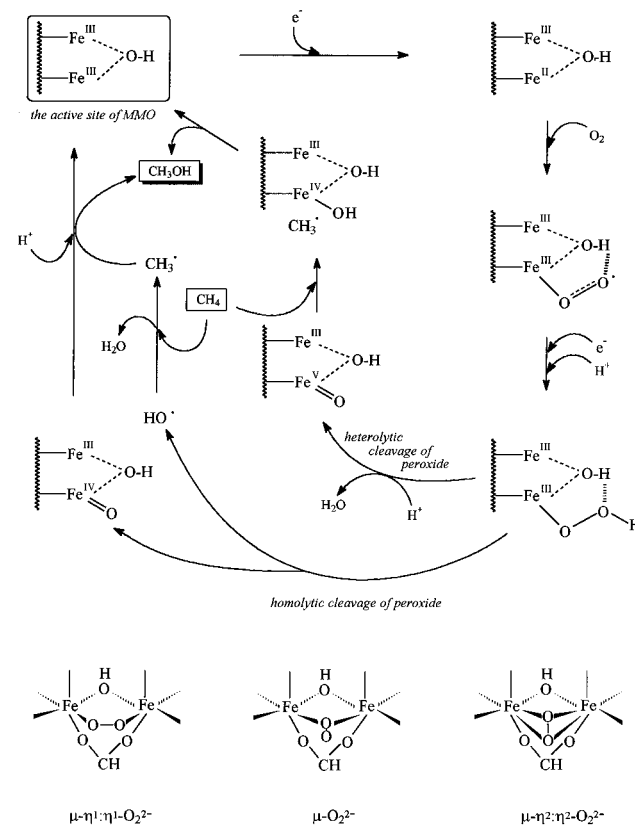


Methane monooxygenases catalyze the oxidation of alkanes in general, although methane shows the highest activity.¹³⁴ The rate of oxidation falls on going from methane to butane, and higher alkanes have following specific activities (milliunits/mg):¹³⁵ pentane (22), hexane (16), heptane (12), neopentane (8), 2-methylpropane (33), 2,3-dimethylpentane (20), adamantane (3).

Aromatic hydrocarbons are not oxidized by MMO. It has been shown¹³⁶ that MMO isolated from *Methylococcus capsulatus* contains four atoms of non-heme iron and one atom of copper per molecule with a molecular weight of 240 000. The *Methylococcus capsulatus* enzymes also include cytochrome *c*, but its presence does not influence the activity of the MMO. The active center of the MMO contains a binuclear iron complex.¹³⁷ X-ray structural analysis has confirmed this binuclear structure at the MMO active center.

One of the methane oxygenation mechanisms^{135,138} proposed for this binuclear MMO center, is similar to cytochrome P450 hydroxylation and involves a hydrogen abstraction preceding an hydroxylation, as

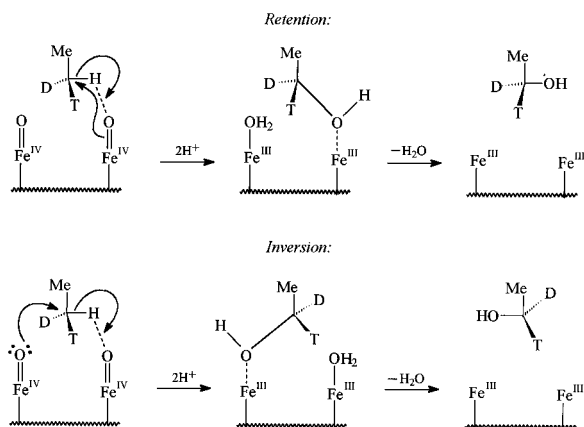
Scheme 39



illustrated in Scheme 39. A theoretical study of the three possible oxygen coordination modes, $\mu\text{-}\eta^1\text{:}\eta^1\text{-O}_2^{2-}$, $\mu\text{-O}_2^{2-}$, and $\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2^{2-}$, of $\text{Fe}_2(\mu\text{-OH})(\mu\text{-OOCH})(\text{OH})_6$ (Scheme 39) has been carried out.^{138j} The calculations suggested that the $\mu\text{-}\eta^1\text{:}\eta^1\text{-O}_2^{2-}$ mode is the most favorable.

Recent investigations into the intermediates found in MMO reactions with dioxygen and hydrocarbons may bring important corrections to the current mechanistic scheme which is based mainly on analogy to cytochrome P450. The transient kinetics of the reduced $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ hydroxylase reaction with dioxygen was studied by Lipscomb *et al.* and also by Lippard *et al.* (for example, see refs 138c–h). Three consecutive intermediates, termed compounds P, Q, and T were identified during one catalytic cycle of the MMO from *Methylosinus trichosporium* OB3B. P is a colorless intermediate which formed immediately after mixing the reduced hydroxylase with O₂. P then slowly transformed into the colored intermediate Q. Substrates were found to have little effect on the rate of formation of compound Q, but they greatly accelerated its decay. The decay rate depend on both the concentration and the type of substrate present. Therefore, compound Q may be the activated form of the enzyme which leads directly to substrate hydroxylation, or its immediate precursor. Compound Q was trapped using a rapid freeze–quench technique and was characterized by Mössbauer spectroscopy. The results indicated that the iron atoms in compound Q are in Fe^{IV} oxidation states. The spectra recorded at 4.2 and 50 K show that the Fe^{IV} sites of compound Q are diamagnetic, and the Fe^{IV} spectrum originated from clusters containing two indistinguishable, coupled iron atoms. A huge kinetic isotope effect (50–100) was reported for the reaction of Q with CH₄ and CD₄, and proton

Scheme 40



From ref 138k. Copyright 1997 American Chemical Society.

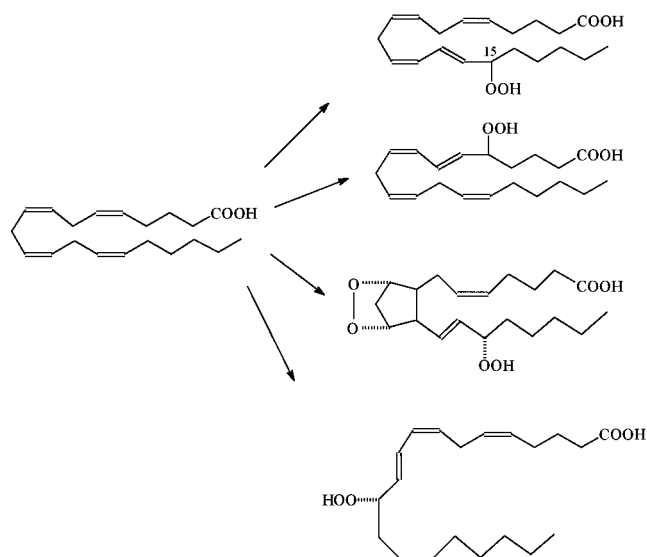
tunneling was proposed as the explanation. It is interesting that the k_H/k_D was only ~ 4 for ethane (C_2H_6 vs C_2D_6). Studies with another kind of MMO, the so-called particular one pMMO, confirmed that the rate-controlling step of methane hydroxylation has a very high KIE, while ethane produces only a moderate KIE. MMO is similar to P450 with respect to its mechanism for O atom insertion into a C–H bond, but apparently MMO is less electrophilic than P450. Thus, even though MMO hydroxylates methane, which is the most inert alkane, it does not hydroxylate aromatic rings. Therefore, another another kind of active center containing an $Fe^{IV}Fe^{IV}$ core was proposed for MMO.

In very recent work, Floss and Lippard *et al.*^{138k} studied the oxidation of tritiated chiral alkanes by soluble MMO from *Methylococcus capsulatus* (Bath). The product alcohol displayed only a 72% retention of stereochemistry at the labeled carbon for (*S*)-[1-²H₁,1-³H]ethane and (*R*)-[1-²H₁,1-³H]ethane. These results are best accounted for by a nonsynchronous concerted process, which is shown conventionally in Scheme 40 which intermediate Q depicted as a diiron(IV) dioxo species. The alkane molecule can be doubly activated by one iron and its bound oxygen atom, thus leading to retention. However, inversion can occur either by backside attack from the other oxygen atom (as presented in Scheme 40) or by the pseudorotation of a pentavalent carbon species (see ref 120l).

2. Iron-Containing Oxygenases

Certain mono- and dioxygenases which are capable of activating a C–H bond contain non-heme iron sites. Phenylalanine hydroxylase^{139a} is one example of such a non-heme oxygenase. It catalyzes the first step of phenylalanine degradation in mammals, by which phenylalanine is converted into tyrosine. This enzyme has one tightly bound, non-heme iron atom per subunit. Tyrosine hydroxylase is another non-heme oxygenase which catalyzes the hydroxylation of tyrosine to produce dihydroxyphenylalanine (DOPA), as the first step in the biosynthesis of catecholamine neurotransmitters.^{139b} This enzyme also contains one ferrous iron atom per subunit. These two enzymes, together with tryptophan hydroxylase, constitute a family of tetrahydropterin-dependent aromatic acid hydroxylases (monooxy-

Scheme 41



genases).^{139c} Other non-heme dioxygenases catalyze dioxygenation of arenes.¹⁴⁰ The iron-containing enzymes catechol-2,3-dioxygenase,^{140e} gentisate 1,2-dioxygenase,^{140f} and phthalate dioxygenase^{140g} from *Pseudomonas* catalyze the oxidative cleavage of catechol, gentisic acid and phthalate, respectively. *Comamonas testosteroni* T-2 oxidizes toluene-*p*-sulfonate by monooxygenating the methyl group to its corresponding alcohol, following which 4-sulfobenzoate 3,4-dioxygenase induces the degradation of the *p*-sulfobenzoate.^{140h}

Lipoxygenase is a dioxygenase which incorporates one molecule of oxygen at a specific position on an unsaturated fatty acid¹⁴¹ for example, arachidonate 15-lipoxygenase peroxidizes the 15-carbon of arachidonic acid as depicted in Scheme 41. Scheme 41 shows a variety of products which are formed under the action of different lipoxygenases.^{141a} Lipoxygenases contain non-heme iron. Thus the purified 12-lipoxygenase of porcine leukocytes contains 0.45 atoms of iron per mole of enzyme, while the rabbit reticulocyte 15-lipoxygenase contains about one atom of iron per mole of enzyme. α -Ketoglutarate-dependent dioxygenases^{142a–c} catalyze various oxidation reactions of nonactivated C–H bonds, while consuming α -ketoglutarate simultaneously with substrate and molecular oxygen. The substrate is transformed into a hydroxylated derivative, and α -ketoglutarate produces succinate and carbon dioxide. In this manner, γ -butyrobetaine hydroxylase catalyzes the hydroxylation of 4-(trimethylamino)butyrate, which is the terminal step in the biosynthesis of carnitine.^{142a} α -Ketoglutarate-dependent dioxygenases act as oxygenation catalysts only in the presence of iron ions. Their formation of thermodynamically stable CO_2 helps them to produce a high-valent $Fe^{IV}O$ center. Recently the importance of high-valent $Fe=O$ in the mechanism of antimalarial trioxane analogs of artemisinin has been demonstrated.^{142d} Finally, chloroperoxidase is able to catalyze not only the chlorination of organic compounds but it is an oxygenase which can also oxidize indoles.^{142e}

3. Chemical Models

Various hydrocarbon oxidation systems which contain iron ions and can be considered as models of non-

heme mono- and dioxygenases have been described. Mononuclear iron derivatives have been used as models for of methane monooxygenase and other proteins;¹⁴³ however, binuclear iron complexes are more commonly employed as MMO active-site models.¹⁴⁴ Various iron¹⁴⁵ and ruthenium(III) complexes¹⁴⁶ were investigated as catalysts in oxidation reactions which mimic iron-containing dioxygenase oxidations. A manganese porphyrin bound to bovine serum albumin modified with poly(ethylene glycol) was also reported to exhibit enzymatic tryptophan 2,3-dioxygenase-like activity.¹⁴⁷ Finally, iron(III) perchlorate or a bis(salicylidene ethylenediamine) iron(III) complex in the presence of dioxygen, a reductant (zinc amalgam), a mediator (methylviologen) and an effector (pyruvic acid) was found to model α -ketoglutarate-dependent dioxygenases.¹⁴⁸

C. Enzymes Containing Other Metals and Their Models

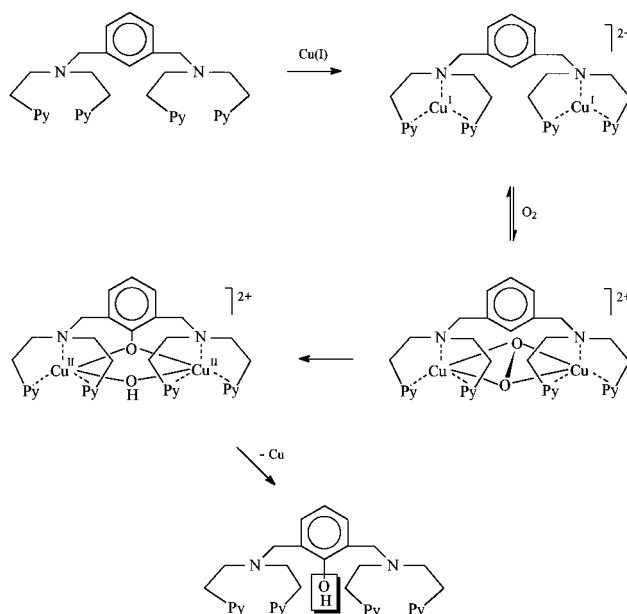
1. Copper-Containing Enzymes

Certain enzymes which are capable of oxidizing C–H bonds contain copper ions.¹⁴⁹ For example, tyrosinase contains a coupled, binuclear copper active site which reversibly binds dioxygen as a peroxide that bridges between the two copper ions. This enzyme catalyzes the orthohydroxylation of phenols, with further oxidation of catechol to an *o*-quinone.¹⁵⁰ In bacterial (*Chromobacterium violaceum*) pterin-dependent phenylalanine hydroxylase, a cupric ion resides in a tetragonal coordination environment with several nitrogen donors.¹⁵¹ Dopamine β -monooxygenase, another copper-containing enzyme, is part of the biosynthetic pathway for the production of epinephrine from tyrosine.¹⁵² Numerous papers have been published in recent years which are devoted to the synthesis,¹⁵³ spectroscopy,¹⁵⁴ and structural analysis¹⁵⁵ of copper complexes, especially multinuclear complexes which are related to aromatic and aliphatic hydroxylation enzymes. The reactions between molecular oxygen and these complexes usually give rise to the formation of hydroxylated compounds.¹⁵⁶ An example of this intramolecular hydroxylation is shown in Scheme 42.¹⁵⁶ⁿ Copper ions and their complexes also are known to catalyze the oxygenation and even the oxidative rupture of the aromatic ring in phenols.¹⁵⁷

2. Enzymes Containing Vanadium, Molybdenum, and Manganese

Vanadium plays an important role in biological systems.¹⁵⁸ One vanadium-containing enzyme, vanadium bromoperoxidase, has been isolated from several species of marine brown algae. This enzyme catalyzes the oxidation of bromide anions by hydrogen peroxide, resulting in the bromination of organic compounds. Certain vanadium complexes have been reported to mimic the binding site reactions of vanadium haloperoxidases.¹⁵⁹ Oxidation with H_2O_2 catalyzed by MoO_4^{2-} also has been shown to mimic the action of vanadium-containing enzymes.^{159f} Actual molybdenum-containing enzymes are known, and these enzymes mostly catalyze the oxidation of C–H compounds.¹⁶⁰ Manganese also is a constituent of some enzymes which oxygenate C–H compounds.

Scheme 42



From ref 156n. Copyright 1994 American Chemical Society.

For example, chlorocatechol 1,2-dioxygenase from *Rhodococcus erythropolis* 1CP is a protein which contains one atom each of iron and manganese per homodimer.¹⁶¹ This enzyme oxidizes different catecholes. The biodegradation of lignine,¹⁶² a major plant polymer, also occurs with the participation of a manganese-containing enzyme, manganese peroxidase.

VII. Conclusions

The field of chemistry devoted to the activation of hydrocarbons, especially alkanes, by metal complexes has developed vigorously during recent decades. In the future, new, especially catalytic, activation processes will be discovered for methane and its homologues, which will find practical applications. This will intensify the interest in alkanes as starting materials for selective chemical processes. Thus, this new chemistry of alkanes will allow us to more economically consume our existing alkane raw materials. This need is becoming ever more urgent as we deplete the hydrocarbon resources which have taken billions of years to accumulate on our planet.

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IX. References

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