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CARBON-HYDROGEN BOND ACTIVATION IN EARLY TRANSITION METAL SYSTEMS

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I. INTRODUCTION

The search for mild, homogeneous ways of activating hydrocarbon CH bonds is one of the most challenging and intellectually stimulating problems facing organo-transition metal chemists today. Many reactions in which simple CH bonds are activated by interaction with soluble transition metal complexes have been reported in the last 20 years.¹⁻³ Some systems have been developed that can carry out the relatively mild functionalization (metallation) of even the most difficult hydrocarbon CH bond, i.e. that found in methane. However, most successes have been with the intermolecular activation of aromatic CH bonds and the intramolecular activation of a range of CH bond types in coordinated ligands.⁴⁻⁶ These latter reactions, initially termed ortho-metallations but now generally referred to as cyclometallations, have allowed a great deal of controlled mechanistic studies to be carried out giving insight into how transition metals can activate such normally inert groups.

A mechanistic similarity exists for nearly all of the early systems that were developed.¹⁻⁶ In the case of cyclometallation reactions an oxidative-addition pathway involves the CH bond being added to the metal center to generate a hydride and chelated alkyl (aryl) function. In the case of metal centers such as Rh(I), Ir(I) and Pt(II) the addition occurs to a d^8 metal center to give a d^6 , oxidized configuration which is then either stable or else undergoes reductive loss of the hydride with a leaving group. In other systems either reductive loss of ligands or a dissociation step (either thermally or photochemically induced) precedes the oxidative addition of the CH bond. The most extensively studied species capable of intermolecularly activating CH bonds in simple hydrocarbons are the transition metal polyhydrides and the Pt(II)/acid systems. In the platinum systems developed by a number of workers, activation of aromatic, benzylic and even aliphatic CH bonds takes place in complex, acidic mixtures as detected by catalyzed H/D exchange reactions.⁷⁻⁹ The activation step involves oxidative-addition to a Pt(II) center; Pt metal and Pt(IV) salts being inactive under the reaction conditions. The polyhydride complexes, typified by Cp₂MH₃(M=Nb, Ta), involve initial reductive elimination of H₂ to generate the unsaturated, active species.¹⁰ Compounds of this type can cause extensive H/D exchange in aromatic rings. Special mention must be made of some recently developed systems. Tungstenocene, generated either photochemically or thermally, has been shown to be active towards both aliphatic and aromatic CH bonds,¹¹ while the unsaturated iridium cyclopentadienyl intermediates developed by Bergman¹² and Graham¹³ are very good at oxidatively adding hydrocarbons. The coupling of iridium complexes with readily hydrogenated olefins has allowed Crabtree to be able to mildly dehydrogenate saturated alkanes.¹⁴ Again in these cases the act of CH bond activation involves an oxidative-addition pathway.

It must be pointed out that although the cyclometallation reaction is believed to proceed by an oxidative-addition pathway for Pt(II), the extensive and well studied cyclopalladation reaction almost certainly is electrophilic in nature.¹⁵ Similarly the large number of oxidations and coupling reactions of aromatic compounds catalyzed by Pd²⁺ occurs via a predominantly electrophilic mechanism.¹⁶

Over the past 5 years a body of literature has developed in which a new type of hydrocarbon activation can be observed. Typically this involves early d-block, lanthanide or actinide elements in their highest formed oxidation states. For d-block elements the d° -metal configuration precludes the oxidative-addition pathway characteristic of the vast majority of CH bond activations, either by the systems mentioned or by metal surfaces. Very recent and exciting work by Watson and Marks has shown that such systems are capable of activating even methane itself. Hence, it appears that a new and potentially very important type of hydrocarbon activation is emerging. This paper reviews the present literature on this subject, dealing both with the intramolecular metallation of ligands as well as the activation of "free" hydrocarbons themselves.

II. CH BOND ACTIVATION IN ALKYL GROUPS

1. α -Hydride abstraction¹⁷

It might at first sight appear strange to find this important reaction included in a review of CH bond activation. However, from the purist's point of view it involves a cyclometallation reaction at a d° -metal center to generate a two membered ring! The reaction has a number of characteristics found in more distal CH bond activations, except that the new metal-carbon bond that is formed is a π -bond. The classical (if one can consider a reaction only nine years old as classical) example of α -hydride abstraction is the initial reaction discovered by Schrock (1).¹⁸

$$Cl_2Ta(CH_2CMe_3)_3 + 2LiCH_2CMe_3 \rightarrow Ta(=CHCMe_3)(CH_2CMe_3)_3 + 2LiCl + Me_4C$$
(1)

During the course of the reaction the α -CH bond is activated by the Ta(V) center and the hydrogen atom is lost from the complex with a leaving group, either Cl or R, to generate the alkylidene function. If one counts the alkylidene ligand as CR₂²⁻ then the tantalum maintains its highest oxidation state. It is not the purpose of this paper to review the extensive literature on α -hydride abstraction processes, a number of excellent reviews by Schrock being already available.¹⁷ However, it is important to mention that theoretical studies by Hoffman *et al.*¹⁹ have indicated that the course of the reaction proceeds through a concerted pathway in which the α -hydrogen is transferred to the leaving group with no net change in metal oxidation state throughout the course of the reaction. A four-center transition state can be postulated in which metal-carbon and carbon-hydrogen bonds are being both broken and formed (2).



This proposed pathway is of direct relevance to the mechanisms of both more distal and intermolecular CH bond activations.

Recently a number of photochemically induced α -hydride abstractions on d° -metal centers have been reported, e.g. (3),²⁰ (4)²¹

$$(OAr')_2 Ta(CH_3)_3 \rightarrow (OAr')_2 Ta(=CH_2)(CH_3) + CH_4$$
(3)
(OAr' = 2,6-di-*tert*-butylphenoxide)

$$(Bu'N)_2 Re(CH_2SiMe_3)_3 \rightarrow (Bu'N)_2 Re(=CHSiMe_3)(CH_2SiMe_3) + Me_4Si.$$
(4)

It is yet to be determined whether the thermal and photochemical activation of α -CH bonds are mechanistically related.

2. β-Hydrogen abstraction and benzyne formation

The abstraction of β -hydrogens from metal alkyl groups is a common decomposition pathway and can readily occur at d° -metal centers.²² However, the formation of an intermediate hydrido-olefin (which may or may not dissociate the olefin) must be considered a special case of CH bond activation as the alkyl group itself is acting as a unique type of leaving group (5).

$$L_{n}M \xrightarrow{H} CH_{2} \xrightarrow{H} L_{n}M \xrightarrow{H} CH_{2} \xrightarrow{H} L_{n}M \xrightarrow{H} H + CH_{2} = CH_{2} \quad (5)$$

Again a four-center transition state is the expected pathway for the reaction.

In contrast to this behavior the activation of β -(ortho) CH bonds of aryl groups has characteristics similar to more distal CH bond activations. Here the hydrogen does not remain on the metal but is lost with a suitable leaving group. A number of important examples of this reaction are known (6),²³ (7),²⁴ (8).²⁵

$$C_p^*T_aMe_3Ph \longrightarrow C_p^*T_a (C_6H_4)Me_2 + MeH$$

 $T_a \longrightarrow T_a$
(6)

In the case of the tantalum complex the resulting benzyne (o-phenylene) group is sufficiently stable to be structurally characterized. The structural data is supportive of the idea that the ligand is best considered as $C_6H_4^{2-}$, i.e. the metal maintains a d° -configuration.²³

Two other examples involve the thermal generation of intermediate benzyne complexes from the bis-phenyl compounds $Cp_2M(C_6H_5)_2$ (M=Ti, Zr)(7) and $Cp_2^*U(C_6H_5)_2$ (8)

$$Cp_2Zr(C_6H_5)_2 \rightarrow [Cp_2Zr(C_6H_4)] + C_6H_6$$
⁽⁷⁾

$$C_{p_2}^{*}U(C_6H_5)_2 \rightarrow [C_{p_2}^{*}U(C_6H_4)] + C_6H_6$$
 (8)

In both these cases the benzyne complex is too reactive to isolate, even reacting in the case of M=Ti with dinitrogen (9).²⁶

$$[Cp_2Ti(C_6H_4)] + N_2 \longrightarrow Cp_2Ti$$
(9)

The overall sequence of events can hence be considered the activation of the ortho-CH bonds and their eventual functionalization.

3. y-Hydrogen abstraction

Unlike α - and β -hydrogen abstraction, the activation of γ -CH bonds in alkyl groups is generally recognized as being an example of *distal*-CH bond activation. The rationale for this thinking is that the metal is having minimal influence through the carbon chain on the CH bond being activated. Unfortunately, the effect that metal substituents have on γ -CH bonds, for instance, in neopentyl (CH₂CMe₃) or trimethylsilyl (CH₂SiMe₃) groups is not known. It is hence not possible to say whether metals such as Ta(V), Th(IV) or Pt(II) are electronically activating (or deactivating) these CH bonds. Metallation of these types of ligands at the γ -position has been observed both at dinuclear centers²⁷ and also in mononuclear complexes.²⁸ For the case of cyclometallation at Pt(II) (10) Whitsides *et al.* have carried out a thorough kinetic and mechanistic study.²⁹

$$cis-Pt(PR_3)_2(CH_2CMe_3)_2 \rightarrow Pt(CH_2CMe_2CH_2)(PR_3)_2 + CMe_4.$$
(10)

Only one example of the cyclometallation of these groups at d° -metal centers has been reported. The complexes $C_{p_2}^*ThR_2(R=CH_2SiMe_3, CH_2CMe_3)$ undergo the smooth loss of one equivalent of Me₄X(X=C or Si) to generate a four-membered metallocycle (11.)³⁰

$$C_{p_2}^* Th(CH_2 XMe_3)_2 \rightarrow C_{p_2}^* Th(CH_2 XMe_2 CH_2) + XMe_4$$
(11)

In the case of X = Si the product was characterized by X-ray diffraction techniques. Kinetic data for the reactions showed they are unimolecular, and labelling studies showed that the γ -CH bonds are activated directly.³⁰

4. Activation of other CH bonds in alkyl groups

The γ -CH bond represents the most distal part of alkyl ligands that have been activated intramolecularly. This is not surprising due to the tight restrictions that are placed on the structure of the ligand by the presence of other more facile reactions such as α - and β -hydrogen abstraction. There are numerous reactions reported in which the sp²CH bonds of Cp co-ligands are activated to cleavage.³¹ Use of the C^{*}_p(C₃Me₅) ligand normally reduces this type of reaction. However, in the case of the thermolysis of C^{*}_p₂TiMe₂ Bercaw has shown that the product is obtained via initial α -hydrogen abstraction to generate a methylidene function which then activates and adds a CH bond of one of the C^{*}_p-methyl groups.³² Labelling studies clearly show that the generated methane does not contain hydrogen atoms from the C^{*}_p-methyl groups (12).

$$(C_5Me_5)_2Ti(CD_3)_2 \rightarrow [(C_5Me_5)_2Ti(=CD_2)] + CD_4 \rightarrow (C_5Me_5)(\eta^6 - C_5Me_4CH_2)Ti - CD_2H$$
(12)

III. CYCLOMETALLATION OF HETERO-ATOM DONOR LIGANDS

1. Activation of β -CH bonds in amido ligands

The dialkylamido ligand is an important group in early transition metal chemsitry. Its use as an ancillary ligand has made significant contributions to the isolation of metal complexes with low coordination numbers and complexes containing metal-metal bonds.^{33,34} Unlike the extensive cyclometallation chemistry associated with amine complexes of the Gp VIII metals,⁴⁻⁶ analogous reactions with early transition metals are less extensive. One of the first reactions reported in which

the β -CH bonds of dialkylamido groups is cleaved at a d° -metal center involved in the treatment of TaCl₅ with LiNEt₂ (13).³⁵

$$TaCl_{s} + 5LiNEt_{2} \rightarrow (Et_{2}N)_{3}Ta + Et_{2}NH + 5LiCl.$$
(13)
NEt

Due to the large steric pressure around the metal atom, generation of amine occurs with metallation of the β -CH bond. More recent work by Nugent *et al.* has demonstrated that this type of reaction is in fact common for a number of d°-metal dimethylamido complexes.³⁶ However, the generation of the iminomethyl group had to be inferred from its reactions. Hence, he has shown that (CH₃)₂ND in the presence of M(NMe₂)_x (M=Zr, x = 4; Nb, Ta, x = 5 and W, x = 6) undergoes catalytic scrambling of deuterium into the methyl groups This result can be explained if one proposes a reversible metallation of the dimethylamido group along with facile exchange of dimethylamine with coordinated dimethylamido groups (14).



Furthermore, it was demonstrated that once formed the azametallocyclo-propane underwent facile insertion of olefins, allowing aminomethylation of olefins to be catalyzed by complexes of this type (15).

$$Me_2NH + CH_2 = CHC_3H_7 \rightarrow MeNHCH_2C(Me)HC_3H_7.$$
 (15)

Addition of LiNMe₂ to the complex $C_p^*TaMe_3Cl$ initially generates the substitution product $C_p^*Ta(NMe_2)Me_3$.^{36b} However, at ambient temperatures this decomposes by loss of methane to generate the cyclometallated, imine complex (15a). A kinetic study showed a first order dependence with a kinetic isotope effect (k_H/k_D) of 9.7 at 34°C.^{36b} when using N(CD₃)₂.

$$C_{p_2}^*Ta(NMe_2)Me_3 \rightarrow C_p^*Ta(NMeCH_2)Me_2 + MeH.$$
 (15a)

2. γ -CH bond activation in dialkylamido and alkoxide ligands

The sterically very demanding ligand bis-(trimethylsilyl)amide, $N(SiMe_3)_2$, has received considerable attention due to its ability to impose low coordination numbers on a variety of transition metals.³³ It was demonstrated as early as 1974 by Bradley *et al.* that it was possible to activate the γ -CH bonds in this ligand leading to a cyclometallated product containing a four-membered ring (16). In this case the four-membered ring contains four different elements.³⁶

$$Cp_{2}TiCl_{2} + 2LiN(SiMe_{3})_{2} \rightarrow Cp_{2}Ti \bigvee_{CH_{2}}^{SiMe_{3}} SiMe_{2} + 2LiCl + HN(SiMe_{3})_{2}.$$
 (16)

Later work by Andersen has shown that both Zr(IV) and the actinide metal centers Th(IV) and U(IV) can similarly activate and metallate this bond. A reinvestigation of reaction (16) by this group has shown that the cyclometallation step probably occurs from a monosubstituted product Cp₂TiCl[N(SiMe₃)₂] by loss of HCl.^{36d} The zirconium analogue was prepared by addition of

LiN(SiMe₃)₂ to Cp₂Zr(H)Cl to give the metallacycle directly. Presumably the leaving group in this case is the hydride ligand.^{36d} In the case of the actinide systems,³⁷ it was shown possible to catalytically deuterate the SiMe₃ groups using D₂ (Scheme I). The catalytic cycle makes use of a hydride ligand as a leaving group for the metallation reaction coupled with the reverse hydrogenolysis of the metal–carbon bond so formed (Scheme I).

Thermal elimination of alkane from the complexes $R_2M(N(SiMe_3)_2]_2$ was shown to proceed with the loss of two hydrogens from the γ -carbon,³⁸ leading to a bridging alkylidene as shown (Scheme II). Presumably initial γ -CH bond activation is followed by α -hydride abstraction from the generated metallacycle. When equimolar mixtures of Me₂Zr[N(SiMe₃)₂]₂ and Et₂Hf[N(SiMe₃)₂]₂ were mixed and thermolyzed, a 1 : 2 : 1 mixture of dinuclear complexes containing Zr₂, ZrHf and Hf₂, respectively, was isolated.³⁹ Due to the dimeric nature of these products, confirmed by X-ray crystallography,³⁸ whether one or both of the hydrogen abstraction steps occurs intermolecularly is uncertain. On treatment with dmpe, the dimers both cleave and undergo a rearrangement to bis-cyclometallated complexes (Scheme II).³⁹ During the course of this reaction, the initially unmetallated amide ligand has transferred a γ -hydrogen to the initially bridging alkylidene group. The fact that the analogous titanium complex does not undergo the same thermal reactions is good support for the idea that the reaction does not involve a radical pathway (vide infra).

Early transition metal ethoxides have been shown to be active catalysts for H/D exchange in CH_3CH_2OD .³⁶ Deuterium is incorporated exclusively into the methyl group. The reversible formation of a four membered metallocycle was proposed (17), with a reverse alcoholysis of the metal-carbon bond formed. An intriguing observation was that multiple exchange occurred,³⁶ implying that α -hydride abstraction from the metallocycle was somehow taking place.



3. Distal CH bond activation in aryloxide ligands

The ligand 2,6-di-*tert*-butylphenoxide (OAr') has been shown to undergo cyclometallation at a number of early transition metal centers. In the case of tantalum, introduction of the ligand onto the metal by way of its lithium salt yields the tri-chloro compound shown by X-ray diffraction to be mononuclear.⁴⁰ Treatment of this compound with methyl lithium gives the expected substitution product $Ta(OAr')_2Me_3$ (Fig. 1) (18).⁴¹

$$TaCl_{5} \xrightarrow{2LiOAr'} Ta(OAr')_{2}Cl_{3} \xrightarrow{3LiMe} Ta(OAr')_{2}Me_{3}.$$
(18)

On thermolysis this complex undergoes the smooth loss of first one and then a second equivalent of methane to generate the mono-cyclometallated and bis-cyclometallated compounds (Scheme III).⁴² The cyclometallation involves the activation and cleavage of an α -CH bond to generate a six-membered metallocycle. Labelling studies using Ta(OAr')₂(CD₃)₃ show that the methane comes from direct loss of the leaving group with the activated hydrogen, giving CD₃H.⁴³ Kinetic data show that both steps of the reaction are unimolecular.⁴⁴ In contrast to these thermal reactions, the photolysis of the tri-methyl complex leads to the rapid and efficient formation of a methylidene complex with loss of one equivalent of methane (3). At 25°C over a period of a few hours this complex "isomerizes" to the mono-cyclometallated species.²⁰ This step is intriguing as it demonstrates that alkylidene groups, apart from their known importance in olefin metathesis⁴⁵ and implied involvement in olefin polymerization,⁴⁶ can be active functional groups for aliphatic CH bond activation. The CH bond is "added" to the tantalum-carbon double bond, and in some respects represents the reverse of an α -hydride abstraction.¹⁷ Labelling studies clearly differentiate the thermal and photochemical routes to the mono-metallated complex (Scheme IV).

Addition of LiCH₂SiMe₃ to Ta(OAr')₂Cl₃ leads directly to an alkylidene complex (Fig. 2).^{41,43} On thermolysis this complex again undergoes cyclometallation of the aryloxide groups, although in this case no intermediate mono-metallated complex could be isolated.⁴³ Hence, three possible pathways for the reaction exist (Scheme V). However, irrespective of which pathway is operative one of the steps must again involve addition of the aliphatic CH bond to an alkylidene group.





Fig. 1. Two ORTEP views of the molecule $Ta(OAr')_2Me_3$ showing the distorted tbp geometry and relatively close approach of ϵ -CH bonds. Some pertinent bond distances (Å) and angles (\circ) are: Ta-O = 1.94(av), Ta-C(3) = 2.136(10), Ta-C(4) = 2.138(10), Ta-C(2) = 2.248(10), O-Ta-O = 164.1(2), C(3)-Ta-C(4) = 104.7(4).

The treatment of Ta(OAr')₂Cl₃ with phenyl-lithium leads directly to a mono-metallated complex which has been structurally characterized (Fig. 3).⁴³ Presumbly this facile metallation occurs from a tri-phenyl complex, although it is possible that loss of HCl or benzene occurs from an intermediate compound Ta(OAr')₂(Ph)₂Cl. On thermolysis the mono-metallated compound undergoes loss of one equivalent of benzene and formation of a bis-metallated species. The structure of this complex can be readily deduced from its ¹H NMR spectrum (Fig. 4).⁴⁷



Scheme III. Thermal activation of the ϵ -CH bonds in Ta(OAr')₂Me₃, OAr' = 2,6-di-*tert*-butylphenoxide (from Ref. 42).



Scheme IV. Comparison of the thermal and photochemical reactivity of $Ta(OAr')_2Me_3$, OAr' = 2,6-di-tert-butylphenoxide (from Ref. 20).

If o-tolyllithium is used in the reaction then the initial product is $Ta(OCH_2)(OAr')(o-tol)_2$ $(OCH_2 = cyclometallated OAr')$. However, on thermolysis the bis-metallated product contains a mixture of meta- and para-tolyl groups, the aryl ligand having undergone isomerization.⁴⁷ The obvious explanation for this result is the intermediacy of a benzyne complex which rapidly undergoes insertion of the aliphatic CH bond. This idea breaks down when one realizes that it is impossible for an o-tolyl group to isomerize to a p-tolyl through only one intermediate, it needs two benzyne complexes to be formed successively. Furthermore, the aryl group was shown to undergo isomerization in the bis-cyclometallated product itself, a 50/50 mixture of p- and m-tolyl groups being given irrespective of the isomer initially used.⁴⁷ These results can be explained if the bis-cyclometallated complex is in equilibrium with a mono-metallated benzyne complex at high temperature (Scheme VI). Use of LiC_6D_5 conclusively shows that the benzyne complex is only formed once bis-metallation has taken place. At high temperatures the deuterium label is scrambled statistically over all aliphatic and Ta-Ph positions as a result of the equilibrium in Scheme VI.⁴⁷ Although attainable only at high temperature, the equilibrium demonstrates in the ring closure that activation of aliphatic CH bonds is possible by insertion into one of the metal-carbon bonds of a benzyne (o-phenylene) ligand.

Thermolysis of the complexes $M(OAr')_2(CH_2Ph)_2(M=Ti, Zr)$ (Fig. 5) leads to the loss of one equivalent of toluene and formation of a mononuclear, monometallated compound (Scheme VII).⁴⁸ This behavior contrasts with the case of the γ -CH activation of the $N(SiMe_3)_2$ ligands which led to dinuclear complexes with loss of two equivalents of alkane (Scheme II). If the tetraalkyl $M(CH_2SiMe_3)_4(M = Ti, Zr)$ is heated with excess Ar'OH, the mono-metallated, bis-aryloxide



Fig. 2. An ORTEP view of $Ta(OAr')_2(=CHSiMe_3)(CH_2SiMe_3)$ showing the pseudo-tetrahedral environment and almost linear Ta-O-C angles. Some pertinent bond distances (Å) and angles (•): Ta-O = 1.86(av), Ta-C(2) = 1.888(29), Ta-C(7) = 2.165(24), Ta-O-C = 170(av).

complex $M(O-CH_2)(OAr')_2$ is generated (Scheme VII). The stage at which alkane loss and cyclometallation occurs is unknown. However, the fact that the previous complex reacts with Ar'OH to give an identical product indicates the intermediacy of $M(OAr')_2(CH_2SiMe_3)_2$.⁴⁸ If only two equivalents of HOAr' is heated with Ti(CH_2SiMe_3)_4 a complex mixture is given. From this mixture a series of complexes Ti(O-CH₂)(OAr')(CH₂SiMe₃)(L) (L = neutral donor ligand) can be precipitated by addition of excess L in hexane. For L = pyridine an X-ray diffraction study clearly shows the presence of the cyclometallated chelate (Fig. 6). Although the complex $Zr(O-CH_2)(OAr')_2$ reacts with HCl to give the mono-halide $Zr(OAr')_3$ Cl all attempts to reverse this reaction, (19), i.e. cyclometallation with loss of HCl, have failed.

$$Zr(OC_6H_3Bu'CMe_2CH_2)(OAr')_2 + HCl \rightarrow Zr(OAr')_3Cl.$$
(19)

IV. MECHANISTIC ASPECTS OF INTRAMOLECULAR CH BOND ACTIVATION AT d° -METAL CENTERS

The elucidation of the mechanism of these cyclometallations is essential to our understanding of the intermolecular activation of hydrocarbons by similar metal centers. Two pathways are generally considered, one being a homolytic initiation involving free radicals while the other contains a multicenter transition state. It is difficult to see how a radical pathway could be extrapolated to intermolecular activations with ease, however, the multicenter pathway can be generalized for both inter- and intra-molecular activations. Although it is now generally accepted that the activation occurs via a four-center transition state it is important to review the data which argues against the homolytic pathway.

1. Homolytic pathway

This mechanism probably gains consideration due to the fact that the majority of cyclometallation reactions at these d° -metal centers involve alkyl leaving groups. The facile (sometimes explosive) thermal decomposition of a large number of early transition metal per-alkyl



Scheme V. Possible pathways for the observed thermal reactivity of $Ta(OAr')_2(=CHSiMe_3)$ (CH₂SiMe₃), OAr' = 2,6-di-*tert*-butylphenoxide (from Ref. 43).

complexes is thought in part to be due to initial homolysis of the metal alkyl bond leading to a radical chain process.^{49,50} Hence the impression that metal-alkyl bonds are thermally unstable on these metals. Strong support from a mixture of general chemical considerations and labelling studies is available to show that radicals are not generated during the above cyclometallations.

For example, the thermolysis of Ta(OAr')₂(CH₃)₃ in C₆D₆ or C₆D₅CD₃ does not result in the formation of any CH₃D, only CH₄ being generated (Scheme IV).⁴³ Similarly homolytic bond scission during the γ -CH bond activation of C^{*}_{p2}Th(CH₂SiMe₃)₂ is ruled out by the observations that no deuterium incorporation into the Me₄Si group occurs when the reaction is carried out in cyclohexane-d₁₂.³⁰ Strong support against homolytic initiation is also obtained by studying the thermal stability of electronically identical complexes, only some of which do undergo cyclometallation. Hence, although the complexes R₂M[N(SiMe₃)₂]₂(M=Zr, Hf) readily lose alkane at 160°C *in vacuo* to form the dimeric, γ -metallated complex (Scheme II),³⁸ the titanium analogue is thermally stable at 190°C for extended periods.³⁸ The lack of metallation in this complex will be discussed later. However, the important point is that the metal-carbon bond in these systems does not undergo homolysis under conditions where cyclometallation does not occur. In fact it is generally accepted that the Ti-R bond is significantly weaker than the alkyl bond to its 2nd and



Fig. 3. An ORTEP view of the monocyclometallated complex $Ta(OC_6H_3Bu'CMe_2CH_2)$ (OAr')(Ph)₂ emphasizing the six-membered chelate ring generated on metallation of the OAr' ligand.



Fig. 4. Expected structure and the ¹H NMR spectrum of the bis-cyclometallated complex Ta(OC₆H₃Bu'CMe₂CH₂)₂(Ph). Due to the molecular symmetry the metallated methylene protons appear as AB patterns while the CMe₂CH₂ methyl groups in the chelate ring are non-equivalent.



Scheme VI. The thermal reactivity of the complex $Ta(OC_6H_3Bu'CMe_2CH_2)(OAr')(Ph)_2$ showing high temperature equilibrium with a benzyne (o-phenylene) complex (from Ref. 47).

3rd row congeners.⁵¹ Again although the complex $Ta(OAr')_2(CH_3)_3$ undergoes thermal metallation, the complexes $Ta(OAr^*)_2Me_3(OAr^* = 2,6$ -di-isopropylphenoxide; 2,6-dimethylphenoxide) are thermally stable for large periods of time, no CH_3D being given in deuterated solvents.⁵² Hence the $Ta-CH_3$ bond in a mononuclear TaO_2C_3 environment is not inherently unstable and is only lost when groups that can be cyclometallated are present.

2. Multicenter pathway

It is now generally accepted that both α - and β -hydrogen abstraction in metal alkyl complexes occurs via a four-center transition state. This type of pathway for more distal CH bond activations



Fig. 5. An ORTEP view of the molecule $Zr(OAr')_2(CH_2Ph)_2$. Some pertinent bond distances (Å) and angles (•) are: Zr-O = 1.93(av), Zr-C = 2.25(av), Zr-O-C = 172(av).



Scheme VII. Reactivity of the complexes $R_2M(OAr')_2(M = Ti, Zr; R = CH_2Ph, CH_2SiMe_3; OAr' = 2,6-di-$ *tert*-butylphenoxide).

at d° -metal configurations is not preferred just by default, evidence being against the homolytic path. On the contrary, there is now kinetic data and other evidence in direct support of this pathway.

Marks *et al.* have reported a kinetic study of the γ -CH bond activation during the thermolysis of complexes $C_{p_2}^{\flat}Th(CH_2XMe_3)_2(X - C, Si)$ (Reaction 11).³⁰ Quantitatively monitoring the reaction by ¹H NMR showed first-order kinetics, the neopentyl group ring closing faster than the silicon analogue. Activation parameters are collected in Table 1. Similar measurements by our group at Purdue on the cylometallation of 2,6-di-*tert*-butylphenoxide have been carried out on reactions at Ta, Ti and Zr metal centers (Table 1).^{42,52} On tantalum we have compared the kinetics of the first and second ring closure reactions (Scheme III). A series of kinetic runs on the two complexes $M(OAr')_2(CH_2Ph)_2$ have also been made (Scheme VII). An example of a first-order plot for the titanium complex and also a plot of ln (k/T) vs $T^{-1}(K^{-1})$ are given in Figs. 7 and 8. Activation parameters using either Arrhenius or Activated Complex Theory are collected in Table 1.

One characteristic of all four reactions is the presence of a negative value for the entropy of activation. In the case of the four-coordinate complexes this value is both large and negative. These entropy changes suggest the presence of a highly ordered transition state and can be compared with the large, positive values found for the cyclometallation of neopentyl groups on Pt(II).²⁹ Here,



Fig. 6. A representation of the geometry found in the solid state for the complex $Ti(OC_6H_3Bu'CMe_2CH_2)(OAr')(CH_2SiMe_3)(py)$ showing only the chelate ring and donor atoms of the other ligands. Some pertinent bond distances (Å) are: Ti-O (chelate) = 1.810(4), Ti-OAr' = 1.850(4), Ti-C (chelate) = 2.095(6), Ti-CH_2SiMe_3 = 2.131(6), Ti-N(py) = 2.293(5).

Reaction	Ea	Log A	<i>∆H</i> ‡	<i>∆S</i> ‡
b	23.6 ± 0.7	10 ± 1	23.0 ± 0.7	-13 ± 2
c	22.4 ± 1.0	9±1	21.6 ± 1.0	- 19 ± 3
d	21.3 ± 0.6	9±1	20.6 ± 0.6	-17 ± 2
e	25.9 ± 0.9	11 ± 1	25.2 ± 0.9	-9 ± 1
f	27.2 ± 1.0	11 ± 1	26.4 ± 1.0	-7 ± 1
g	30.8 ± 1.0	12 ± 1	29.5 ± 1.0	-6 ± 1

Table 1. Activation parameters for a number of d° -cyclometallation reactions^a

a. Ea and $\Delta H^{\ddagger}_{\ddagger}$ in kcal mol⁻¹; $\Delta S^{\ddagger}_{\ddagger}$ in e.u.

b. Thermolysis of Ti(OAr')2(CH2Ph)2 (Scheme VII).

c. Thermolysis of Zr(OAr')₂(CH₂Ph)₂ (Scheme VII).

d. Reaction (11), X = C.

e. Reaction (11), X = Si.

f. First ring closure of Ta(OAr')₂Me₃ (Scheme III).

g. Second ring closure of Scheme III.

Whitesides has interpreted the data as indicative of a rate-determining reductive elimination of alkane from the Pt(IV) hydridoalkyl formed by oxidative-addition of the γ -CH bond.²⁹ These entropy changes (Table 1) are hence further evidence against a dissociative or homolytic pathway, the transition state clearly could not represent a process *decreasing* the coordination environment of the metal. A multicenter pathway is hence implicated. In the example shown (20)



(20)

the four-center transition state involves four-electrons, two each from the CH bond to be broken and the M-X bond of the leaving group. Evidence that the CH bond is being broken in the transition state comes from the observation of large kinetic isotope effects, e.g. a $k_{\rm H}/k_{\rm D}$ of 9.7 for reaction 15a. Consideration of this type of transition state allows one to make certain assumptions concerning the nature of complexes that will undergo such cyclometallations.

(i) Ligand geometry. Clearly this mechanistic pathway requires the CH bond that is to be activated to come into close proximity of the metal and the eventual leaving group. This requires not only the correct geometry for the ligand, but also in order to force the CH bond onto the metal one requires steric bulk. This necessity for steric bulk in the metal coordination sphere can be seen by considering the distal cyclometallation reactions outlined above. The recognition that steric pressure is essential for mild cyclometallation was recognized early by Cope *et al.* and later successfully exploited by Shaw and others in order to design, with some rationality, ligands that would more readily cyclometallate.⁵⁴

The rationale for this steric dependence has been argued to be entropic. As early as 1915 it was recognized that ring closure reactions for organic molecules were enhanced by the presence of substituents on the carbon skeleton.⁵⁵ This phenomenon is referred to as the "gem-dimethyl" or "Thorpe–Ingold" effect.^{55,56} In the case of cyclometallation reactions it can be argued that the attainment of the highly restrictive transition state in which the ligand geometry is effectively "trapped" represents a severe loss of entropy over the ground state in which the ligand is free to move. Restricting the movement of the ligand in the ground state by introducing considerable bulk both on the ligand and in the coordination sphere will hence reduce this entropic loss. The faster rate of cyclometallation of the complex Ti(OAr')₂(CH₂Ph)₂ over its zirconium analogue can be seen from Table 1 to be entropic in nature. This can be rationalized if one considers the coordination sphere about each metal. Although the four ligands are identical, Ti–X bonds are consistently



Fig. 7. First-order plot for the disappearance of $Ti(OAr')_2(CH_2Ph)_2$ at 95°C to generate the mono-cyclometallated complex (Scheme VII). Initial concentrations are 0.032M(2) and 0.005(1).

0.1-0.2A shorter than Zr-X bonds. Hence, the coordination sphere is contracted in the titanium complex. This will have the effect of not only "pulling in" the CH bond to be metallated, but also making ring closure easier.

However, the presence of too much bulk in the coordination sphere, or bulk of the wrong type, can be a hindrance and not a help in some situations. In the complexes $R_2M[N(SiMe_3)_2]_2$ (M=Ti, Zr, Hf) only the 2nd and 3rd row elements undergo thermal metallation.³⁸ It can be argued that the more compact coordination sphere of the titanium complex "cuts off" the γ -CH bond from the metal, not allowing it access to the metal center for activation. The possibility that these reactions may occur inter-molecularly due to the dimeric nature of the products is an uncertainty in considering the mechanism.

(ii) Leaving group. If one carries out a rough thermodynamic assessment of the transition state one can see that one is forming a new M-C bond along with an H-X bond. This is occurring at



Fig. 8. Plot of ln (k/T) vs T⁻¹(K⁻¹) for the cyclometallation of OAr' in Ti(OAr')₂(CH₂Ph)₂ (see Table 1).

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the expense of the C-H and M-X bonds. If one considers alkyl leaving groups, i.e. X=R, then the equation appears pretty well balanced. From the data in Table 1, it can be seen for the complexes $M(OAr')_2(CH_2Ph)_2(M=Ti, Zr)$ that there is little enthalpic difference to the reaction, despite the fact that Zr-CH₂Ph bonds are known to be at least 10 kcal mol⁻¹ stronger than the Ti-CH₂Ph bond.⁵¹ This is entirely consistent with the four-center transition state, as one is both making and breaking M-C bonds. Hence, as for a given alkyl the bond strengths run approximately parallel down a triad, it is not surprising to find little difference in ΔH^{\pm}_{+} for these two reactions.

This thermodynamic consideration may also explain why, unlike GpVIII cyclometallation reactions, halide ligands do not appear to be good leaving groups for this type of reaction. Even accounting for back reactions between the cyclometallated product and the generated HX(X=Cl, Br), early transition metal halides do not readily undergo cyclometallation reactions. For example, thermolysis of the compounds Ta(OAr')₂Cl₃, Ti(OAr')₂Cl₂ and M(OAr')₃Cl (M=Ti, Zr, Hf) under vacuum at temperatures of 170–200°C causes no reaction except sublimation.⁵² One explanation is that the halide group is sterically very small. However, the complexes M(OAr')₃Cl are extremely crowded and for M=Ti, Zr the metallated complexes M(O-CH₂) (OAr')₂ can be independently synthesized (19). This lack of metallations involving halide groups can be explained by the high strength of the M-Cl bond for early transition metals. This bond has a dissociation energy of 100–120 kcal mol⁻¹ compared to 45–60 kcal mol⁻¹ for alkyl groups bound to the same metal. The reaction appears, therefore, to be enthalpically inhibited.

A similar rationale can be applied to the use of alkoxide or dialkylamide leaving groups, but a complexity is present for these hetero-atom donor leaving groups. The four center transition state indicated (20) does not have any net charge. However, the charge distribution within the trapezoid is not indicated. Clearly this will depend on the electronegativity of the elements involved. For X=C one imagines a rather uniform distribution of charge. In the case of OR and NR₂ leaving groups, the availability of lone-pairs on the donor atom is an added complexity. This is illustrated (21).



In effect the pathway, although still multicenter, is now appearing to be highly electrophilic in character in which the metal activated CH bond is protonating the lone pair of the leaving group (base). One is then left with a coordinated alcohol or amine after the ring closure is complete. This pathway is the reverse of the alcoholysis or aminolysis of metal-carbon bonds.⁵⁷ Enthalpically the situation is now difficult to assess, because the bond to the leaving group has not been completely broken. However, structural data clearly show that on d° -metal centers bond lengths to coordinated alcohols and amines are much longer than to alkoxides and amides⁵⁸ so that the bond has been considerably weakened by its protonation.

Analysis of the postulated transition state also helps understand the high activity of alkylidene groups for intramolecular CH bond activation (Scheme IV). Although entropic factors will be similar, the new metal-carbon bond will be formed only at the expense of the π -component of the M=C bond. Hence enthalpically the situation appears more favourable than simple alkane for alkyl exchange.

(iii) The metal. Clearly the metal center must have available to it empty orbitals of the correct symmetry with which to interact with the CH bond in the transition state. This is not a problem with most early transition metal d° -compounds. There is a large body of evidence, both structural and spectroscopic, that it is possible for CH bonds to act as two-electron donating groups to electron deficient metal centers.^{59,60} This typically is found where the metal would be two electrons short of attaining a stable, 18-electron count. More recently work by Green has shown that such interactions are possible in the ground state to d° -metal centers such as Ti(IV).^{61,62} In particular, strong interaction to the α - and β -CH bonds was structurally characterized. It is hence reasonable to assume that this may be the initial type of interaction between the electron deficient metal and the CH bond to be activated (22).

$$M \xrightarrow{C} H \xrightarrow{C} H \xrightarrow{C} H \xrightarrow{C} H$$
(22)

This three-center, two-electron bond then weakens the CH bond and leads into the four-center transition state in which the hydrogen atom is transferred to the leaving group.

The solid state structure of the complex Yb[N(SiMe₃)₂]₂ (dmpe) has been found to contain an interaction between one of the methyl groups and the metal in the ground state.⁶³ The hydrogen atoms on this group were refined and shown to be pointing *away from* the metal center in contrast to situations with *d*-block metals where M... HC type interactions are prevalent. The structure was interpreted in terms of the CH₃ group bridging between the Yb metal atom and Si atom, there being considerable lengthening of the Si–CH₃ bond (Fig. 9). The implications of this observed ground state structure on the known γ -CH bond activation in this ligand is that one would expect the Yb–CH₃ interactions to increase the acidity of the γ -hydrogens. This would allow the reaction to proceed in a transfer of the acidic hydrogen to the leaving group. All evidence so far available does not point to a process in which the leaving hydrogen is lost *exo* to the complex, i.e. to an external base similar to an S_E2 process.

In the solid state structure of complexes containing the 2,6-di-*tert*-butylphenoxide (OAr') ligand, it is typically found that one of the CH bonds of the *tert*-butyl groups is pointing almost directly at the metal center. In the case of the complex $Ta(OAr')_2Me_3$ distances range from 2.8 to 3.0A while in the chloride $Ta(OAr')_2Cl_3$ (Fig. 10) one of the CH bonds seems to "occupy" the position *trans* to the axial chloride in a square based pyramidal structure. The Ta-H distance was refined to 2.67A. Although it is very doubtful that any significant ground state interaction is taking place in these complexes, the attainment of a multicenter transition state between the metal and these CH bonds is clearly very feasible.

Another factor to consider is the influence that the ancillary ligands have on both the energy and availability of metal orbitals with which the CH bond can interact. This is a difficult effect to evaluate even qualitatively. However, one would predict that ligands that reduce the electron deficiency of the metal center, e.g. strong π -donor ligands such as NR₂, will tend to inhibit interactions to CH bonds.

IV. INTERMOLECULAR CH BOND ACTIVATION

1. Mechanistic considerations

Unlike in the previous sections where mechanism was considered last, it is useful to reverse the situation for intermolecular hydrocarbon activation just so that one can see what one is up



Fig. 9. Representation of the Yb-CH₃ ground state interaction found in the solid state structure Yb[N(SiMe₃)₂]₂ (dmpe) (dmpe = Me₂PCH₂CH₂PMe₂) (from Ref. 63).



Fig. 10. An ORTEP view of the molecule $Ta(OAr')_2Cl_3$ showing the close approach of an ϵ -CH bond to the axial position of a square-pyramidal geometry.

against. Extrapolating from the results for cyclometallation reactions it is possible to envisage how a d° -metal center might activate a CH bond in a normally inert hydrocarbon. Initially, the CH bond must enter the coordination sphere of the metal, interact with one of the metal orbitals and then progress through a transition state in which the new metal-carbon bond is formed and the hydrogen atom is lost with the leaving group (23).

From the previous discussions one would clearly choose an alkyl leaving group on enthalpic grounds, and the overall reaction would hence represent an alkyl exchange. Clearly what is against the intermolecular reaction is its bi-molecular nature and the strongly negative values of ΔS^{\ddagger} one might expect in order to achieve the transition state.

An intermolecular reaction which is of direct relevance to this problem is the hydrogenolysis of d° -metal alkyl complexes.⁶⁴ This is now a common reaction and one of excellent synthetic utility.^{65,66} The mechanism of this reaction has been discussed and proposed to be via a four-center transition state.^{67,68} The more extensively documented reactivity of H₂ with d° -metal alkyls over alkyl exchange reactions may be a reflection of the steric differences between H₂ and alkane CH bonds. In terms of electron donating ability one predicts that CH bonds would be superior to H₂ due to the latter's higher ionization potential.⁶⁹

The systems that successfully activate hydrocarbons are small and can be discussed individually.

2. Activation of aromatic CH bonds by benzyne intermediates

Any reaction in which aromatic CH bonds are activated represents a somewhat special case due to the presence of the aromatic π -bonds with which the molecule can initially bond to the d° -metal allowing the CH bonds to come into close proximity with the metal for activation.





Erker has demonstrated that the thermal formation of benzyne groups from the complexes Cp_2MAr_2 (Reaction 7) (M=Ti, Zr) is reversible. Hence the thermolysis of bis-tolyl derivatives in benzene results in the formation of mixed phenyl, tolyl derivatives. Direct exchange of aromatics can be ruled out. The final products were analyzed by photolysis and characterization of the generated biphenyl molecules.⁷⁰

Marks has demonstrated similar reactivity for the uranium complex $C_{p_2}^*U(C_6H_5)_2$. Thermolysis in C_6D_6 generates the complex $C_{p_2}^*U(C_6H_4D)(C_6D_5)$, the deuterium being incorporated into the ortho-position. Under identical conditions the uranium complex undergoes benzene exchange approximately 10^2 times faster than $C_{p_2}Zr(C_6H_5)_2$.⁷¹ In both of these reactions the CH bond is inserting into the highly strained metal-carbon bond of a metallocyclopropane ring.

Although a benzyne complex has been shown to be able to reversibly activate aliphatic CH bonds intramolecularly (Scheme VI),⁴⁷ the intermolecular generation of an alkyl, aryl complex by reaction of a benzyne complex with an alkane has yet to be documented.

3. Hydrocarbon activation by $C_{p_2}^*Th(CH_2CMe_2CH_2)$

As mentioned previously, Marks *et al.* have demonstrated that complexes containing thoracyclobutane rings can be prepared by thermolysis of the complexes $C_{p_2}^*Th(CH_2XMe_3)_2$ (X=C, Si) (Reaction 11).³⁰ The neopentyl derivative $C_{p_2}^*Th(CH_2CMe_2CH_2)$ undergoes a number of intermolecular reactions with hydrocarbons (Scheme VIII).⁷² Benzene reacts to yield the di-phenyl compound with overall loss of neopentane. The first step of the reaction represents a ring opening reaction, in which the aromatic CH bond is activated. The second step may involve direct aryl for alkyl exchange, or else proceed via a benzyne intermediate. The use of toluene yields a 75/25 mixture of aromatic and benzylic products.³⁰

The thoracyclobutane ring can also activate Me₄Si and even methane itself.⁷² The products are initially the mixed alkyl, neopentyl derivatives but in the case of Me₄Si a further ring closure occurs to generate the metallo-silacyclobutane ring (Scheme VIII). This silicon analogue does not undergo any of these ring opening reactions. The rationale for this is the decrease in ring strain due to the longer C–Si bonds. Accurate thermochemical measurements⁷² indicate a difference in ring strain of 10 kcal mol⁻¹ for these metallocycles giving much more driving force for the hydrocarbon activation by $C_{p_2}^{*}Th(CH_2CMe_2CH_2)$.

4. Hydrocarbon activation by $Cp_2LuR(R=H, Me)$

In a series of papers⁷³⁻⁷⁵ Watson has reported the remarkable organometallic chemistry of complexes containing the $C_{p_2}^*Lu$ unit. Both inter- and intra-molecular activation of sp² and sp³ CH bonds can take place (Scheme IX).⁷⁴ Perhaps the most remarkable reactivity involves the observation of methane exchange on the complex $C_{p_2}^*LuMe$.⁷⁵ This reaction occurs readily at 70°C in cyclohexane- d_{12} and can be followed by ¹H and ¹³C NMR using labelled methane (¹³CH₃). A similar reactivity was noted for the yttrium analogue. Kinetic studies showed the reaction to be first-order in methane and a four-center transition state was proposed.

Both the complexes $Cp_2M(CH_3)(M=Lu, Y)$ exist as asymptric dimers in the solid state containing one bridging methyl group. The Lu-Me-Lu angle was determined to be almost linear by X-ray diffraction and can be pictured as an Lu-CH₃ group acting as a two electron donor to the other metal through one of the CH bonds. One can imagine this interaction to be a model of the initial methane-Lu interaction that eventually leads to alkane exchange.

VI. CONCLUDING REMARKS

The ability of d° -metal centers to activate, cleave and in some cases functionalize normally inert CH bonds has clearly been demonstrated. All present mechanistic data can be accommodated into a multicenter transition state in which the new metal carbon bond is formed at the direct expense of a metal-ligand (leaving group) bond. The future for hydrocarbon activation at d° -metal centers appears bright, especially in view of the recently demonstrated mild activation of even methane itself.

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