CENTENARY LECTURE*

Hydrocarbon Reactions at Metal Centres

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1 Introduction

Hydrocarbon reactions that are mediated by a metal atom or a collection of metal atoms represent an area of considerable scientific as well as technological importance. For simple hydrocarbons, there are only two fundamental classes of reactions namely carbon–carbon and carbon–hydrogen bond-breaking and -making reactions. The latter often have a lower energy of activation, thus facilitating comprehensive physicochemical studies. Carbon-hydrogen bond-breaking and -making reactions at metal centres is the better understood reaction class, at least for metal surfaces, and it is the subject of this analysis. The scope of the analysis is broad and includes the following general categories of metal species:

(i) molecular, mononuclear metal complexes, ML_x
(ii) molecular, polynuclear metal complexes, M_yL_x
(iii) metal surfaces
(iv) metal atoms.

A delineation of the thermodynamic, electronic, and stereochemical requirements for carbon–hydrogen bond reactions at metal centres will be attempted, although a definitive characterization of reaction-path profiles is not feasible yet. Since general reviews of this class of hydrocarbon reactions have been presented for the first,[1-4] second,[5] and third[6] categories, this analysis will be selective, not comprehensive.

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* The present text is based upon the lecture delivered on 13 May 1982 at a RSC Dalton Division Meeting at the Scientific Societies' Lecture Theatre, Savile Row, London W.1.

[1] G. W. Parshall, *Acc. Chem. Res.*, 1970, **3**, 139.

[2] G. W. Parshall, *Acc. Chem. Res.*, 1975, **8**, 113.

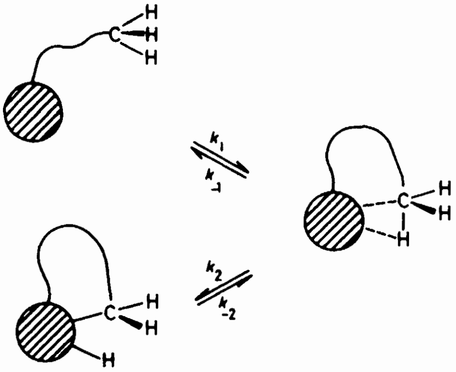
[3] G. W. Parshall in 'Catalysis', ed. C. Kemball (Specialist Periodical Reports), The Chemical Society, London, 1977, Vol. 1, p. 335.

[4] D. E. Webster, *Adv. Organomet. Chem.*, 1977, **15**, 147.

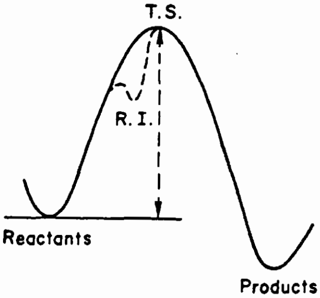
[5] E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, 1979, **79**, 91.

[6] G. A. Somorjai, 'Chemistry in Two Dimensions: Surfaces', Cornell University Press, Ithaca, N.Y., 1981, Chapt. 7 and 8. B. C. Gates, J. R. Katzer, and G. C. A. Schuit 'Chemistry of Catalytic Processes', McGraw Hill Book Co., New York, 1979.

Schematically, the basic process of carbon–hydrogen bond scission and reformation at metal centres can be set forth as below where the large hatched sphere may represent a bare metal atom, a metal atom in a mononuclear metal complex, or one or more metal atoms in a metal cluster, or a metal surface (Scheme 1). Here, for initial simplicity, it is assumed that the hydrocarbon is bound relatively firmly through some functionality, for example, an olefinic bond; later, the bonding and the subsequent reactions of saturated hydrocarbons will be explicitly considered. The scheme provides for the possibility of a reaction intermediate but there is no *a priori* basis for invoking an intermediate. A digression on intermediates *versus* transition states is appropriate here to ensure that no misunderstanding is generated in later discussions because the possible significance or necessity of intermediates in C—H oxidative addition reactions

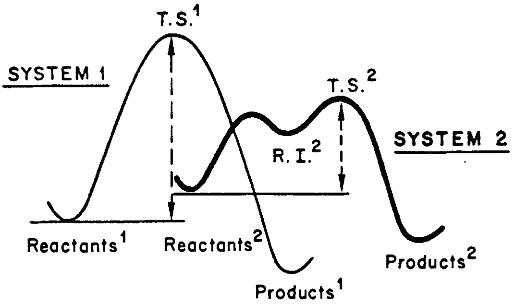


Scheme 1



Scheme 2

has been mentioned in many articles.[3] For a specific system, the existence of a reaction intermediate confers no kinetic advantage; the free-energy difference between reactants and transition state is constant, Scheme 2. An alternative scenario comprises two closely related complexes: system 1 in which there is no possibility of a reaction intermediate and system 2, related to 1, in the context of the free-energy difference between reactants and products, but differentiated in that there is a 'productive' reaction intermediate in which the hydrocarbon forms complexes with the metal species (formation of a ML_x-RH complex is not necessarily productive with respect to the C—H oxidative addition reaction). A kinetic advantage may accrue to system 2 if the ML_x-RH complex more closely resembles products than initial reactants (free-energy diagram of Scheme 3). Specifically, 'productive' here implies that the reactant metal complex has undergone a reorganization in the intermediate whereby the ML_x structure in the intermediate more closely resembles that in the product than that in the reactant, rather than an intermediate in which the C—H (or H—H) bond is significantly stretched because presently available data for oxidative addition reactions indicate that there is little stretching of the C—H bond, or H—H bond in H_2 additions, in the transition state and hence in a preceding intermediate, if there is one. Also, a productive intermediate ideally should have a triangular, not linear, M—C—H stereochemistry.



Scheme 3

The overall forward reaction in Scheme 1 is denoted as an oxidative addition reaction following an established convention[7] in organometallic chemistry: there should be some net electron-transfer, probably small in extent, from the metal centre or centres to the σ-bound hydrocarbon radical and to the hydrogen atom in the product. Accordingly, there should be some net electron transfer from the metal centre or centres to the carbon-hydrogen σ^* orbital in the transition state or intermediate—the closer the transition state resembles product, the greater the extent of electron transfer will be in the transition state as will be the degree

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[7] R. F. Heck, Organotransition Metal Chemistry, Academic Press, New York, 1974.

of C—H bond stretching. Experimental data[8] for H_2 or RH addition to a metal centre in molecular ML_x complexes show only a small k_H:k_D isotope ratio of ~1.2 to 1.3 indicating a small degree of H—H or R—H stretching in the transition state. Consistently, a theoretical analysis of hydrogen addition to the hypothetical $Pt(PH_3)_2$ molecule has indicated that there is about a 4% stretching of the H—H bond in the transition state and another analysis has made similar conclusions.[9] Analogous data for the other metal regimes do exist. For low- or moderate-temperature oxidative addition reactions at metal surfaces, the kinetic isotope ratio appears to be normal but precise ratios have not been determined. Since the activation energy is very small for H_2 dissociative chemisorption, the isotope effect for this surface mediated reaction is probably small. (Parenthetically, it is notable that carbon–hydrogen bond breaking on metal oxide surfaces, as measured for methanol oxidation to formaldehyde and propylene oxidation to acrolein on molybdenum oxide, have large kinetic isotope ratios of 3—4.[10] These C—H bond breaking processes are presumed to proceed through C—H—O rather than C—H—Mo states. It will be informative to obtain further kinetic isotope data for C—H bond breaking on metal oxide surfaces to see if relatively large k_H:k_D ratios are characteristic of processes that proceed through C—H—O interactions).

The microscopic reverse reaction of Scheme 1, reductive elimination, has many models in molecular $R(H)ML_x$ complexes. Measured[11] kinetic isotope ratios, k_H:k_D, are all normal and range in magnitude from ~1.5 to 3.3. *For these specific systems*, their microscopic reverse reactions of oxidative addition should exhibit kinetic isotope ratios that are normal and larger than their measured reverse reactions. This then implies, in apparent contradiction to the previous statements above, that the range of kinetic isotope ratios for oxidative addition reactions could be quite large and that the character of the transition states might vary substantially. However, the one reductive elimination reaction with a truly large kinetic isotope ratio of 3.3, as established by Halpern *et al.*,[11] is alkane elimination from *cis*-$R(H)Pt(PR_3)_2$ complexes — a reaction that appears to be fully irreversible. Possibly, a large normal kinetic isotope ratio may be characteristic of such irreversible alkane reductive elimination reactions and may not apply correlatively to the basic reaction, of C—H oxidative addition to metal centres, under consideration in this analysis. In any case, it is essential that a larger data set of kinetic isotope ratios be generated for the forward and reverse reactions of Scheme 1 so that a more precise outline of transition states (or range of transition states) can be realized.

Returning to Scheme 1, the overall equilibrium constant $K = K_1K_2$, will be a function of temperature, pressure (surfaces), and the electronic and

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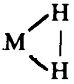
[8] P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, 1966, **88**, 3511; J. M. Brown and D. Parker, *Organometallics*, 1982,**1**, 950.

[9] K. Kitaura, S. Obara, and K. Morokuma, *J. Am. Chem. Soc.*, 1981, **103**, 2891. A. Sevin, *Nouveau J. Chim.*, 1981, **5**, 233.

[10] C. J. Machiels and A. W. Sleight, *J. Catalysis*, 1982, **76**, 238; C. J. Machiels and A. W. Sleignt, *ACS Svmp. Ser.*, 1982, **178**, 239.

[11] L. Abis, A. Sen, and J. Halpern, *J. Am. Chem. Soc.*, 1978, **100**, 2915.

stereochemical features of the metal system. In all cases, temperature increase will favour the forward reaction of dehydrogenation. On metal surfaces, the reverse reaction of hydrogenation will be favoured by a higher thermodynamic activity of the chemisorbed hydrogen atoms, an activity that is a direct function of the pressure of H_2 in the gas phase. To enhance the forward reaction, a reasonable strategy in the design of the metal system is to place a stereochemical constraint on the reactant state such that a C—H hydrogen atom is forced close to a metal centre or centres. Conceptually, this proximity effect must be a critical factor in carbon–hydrogen bond reactions. Electronic effects must also be important. If the earlier characterization of charge transfer for carbon–hydrogen bond breaking is correct, as it must certainly be at least for metal surfaces, then this forward reaction of Scheme 1 should be enhanced by selecting metal systems in which the negative charge density on the metal atom or atoms is relatively high. This would appear to be correct in a gross sense in that metal surfaces which easily effect dehydrogenation of hydrocarbons are good electron donors — the work functions, formally analogous to the ionization potentials of molecules, are relatively small. In contrast, most transition-metal complexes are not effective in hydrocarbon dehydrogenation reactions and also have high ionization potentials. An energy matching of the σ and σ^* C—H orbitals, respectively, is therefore important with unoccupied and occupied molecular orbitals of the metal species (all other factors being equal—*i.e.*, if the interaction parameters β and β^* are similar). For molecular complexes, the importance of appreciable electron density on the metal centre of the reactant complex has been presumed and has not been established by experiment. Theoretical analyses of alkane reductive elimination from $R(H)ML_2$ complexes (the reverse reaction of Scheme 1) conclude, by corollary, that the microscopic reverse reaction of oxidative addition is more favoured if electron density on the metal centre is increased.[12] However, these analyses of reductive elimination appear to be incomplete: the reverse sequence of oxidative addition must involve population of the σ^* C—H orbital, yet these theoretical analyses of reductive elimination do not explicitly correlate the σ^* C—H orbital with an appropriate filled metal orbital.

The geometric features of the oxidative addition reaction may comprise an initial linear M—H—C interaction but ultimate C—H bond cleavage requires a triangular M—H—C interaction. As documented in the following section, isolable molecular metal complexes with multicentre M—H—C interactions are more nearly triangular than linear in character. Sevin[9] in a theoretical analysis of H_2 oxidative addition concluded that H_2 initially approaches the metal centre end-on and only later tips over to give a triangular 

configuration.

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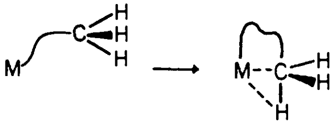
[12] K. Tatsumi, R. Hoffmann, A. Yamamoto, and J. K. Stille, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1857; A. C. Balazs, K. H. Johnson, and G. M. Whitesides, *Inorg. Chem.*, 1982, **21**, 2162; J. O. Noell and P. J. Hay, *J. Am. Chem. Soc.*, 1982, **104**, 4578.

The importance of stereochemistry and electronic structure in metal-based hydrocarbon reactions will be explored. Each regime of metal chemistry will be separately analysed in these contexts. The issue of reaction intermediates, as depicted in Scheme 1, will be examined before the actual process of bond breaking or making is considered.

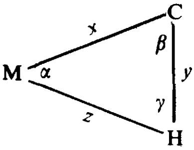
1 The Question of Reaction Intermediates in Carbon–Hydrogen Bond Breaking Reactions at Metal Sites

A. Mononuclear Metal Complexes.—There is a plethora of molecular mononuclear metal complexes which have a multicentre C—H-metal bond as judged by a crystallographically-defined short H-metal separation; a relatively comprehensive listing has been presented by Ittel *et al.*[15] The range of H-metal separations is large and the composite set of complexes could serve to delineate the geometric pathways for equation (1).



(1)

However, the accuracy of the hydrogen atom placement in this extensive set of structurally defined complexes is too low to assess accurately reaction pathways. Ideally, a selected set of complexes that outline the sequence in terms of H-metal separation should be crystallographically defined by neutron diffraction studies so that the key distance (x,y,z) and angular (α,β,γ) parameters, (1), could be



(1)

evaluated. However, this set of parameters would be a function of stereochemical constraints associated with the ligand in which the C—H-metal bond is generated. The paradigm would be a set of crystallographic data for the ML_x complexes with saturated hydrocarbons in which the only connexity between ML_x and the hydrocarbon would be the multicentre C—H-metal bond. Unfortunately, no such complex has been detected, even transitionally, much less isolated and crystallographically defined with the exception of the labile $Cr(CO)_5$ complexes with saturated hydrocarbons like cyclohexane.[13] There is increasing evidence that benzene and its derivatives can form η^2-arene–metal

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[13] J. A. Welch, K. S. Peters, and V. Valda, *J. Phys. Chem.*, 1982, **86**, 1941.

complexes as shown by the studies of Sweet and Graham.[14] These arene complexes, unlike the labile alkane complexes, are sufficiently stable that a precise structural characterization by a crystallographic study is feasible. Presumably, these η^2-arene–metal complexes will have two relatively short H—M interactions.

The only mononuclear metal complexes with C—H-metal bonding defined by neutron diffraction studies are $\{(\eta^3\text{-cyclo-octenyl})Fe[P(OCH_3)_3]_3{}^+\}(BF_4{}^-)$[15] and $\{[(CH_3)_3CCH]Ta[P(CH_3)_3]Cl_2(\mu\text{-}Cl)\}_2$.[16] Co-ordination saturation is achieved in the iron complex by the multicentre Fe—H—C interaction *via* a saturated C—H bond of a carbon atom adjacent to the allylic carbon atoms in the η^3-cyclo-octenyl ligand (Figure 1). The carbon–hydrogen distance of

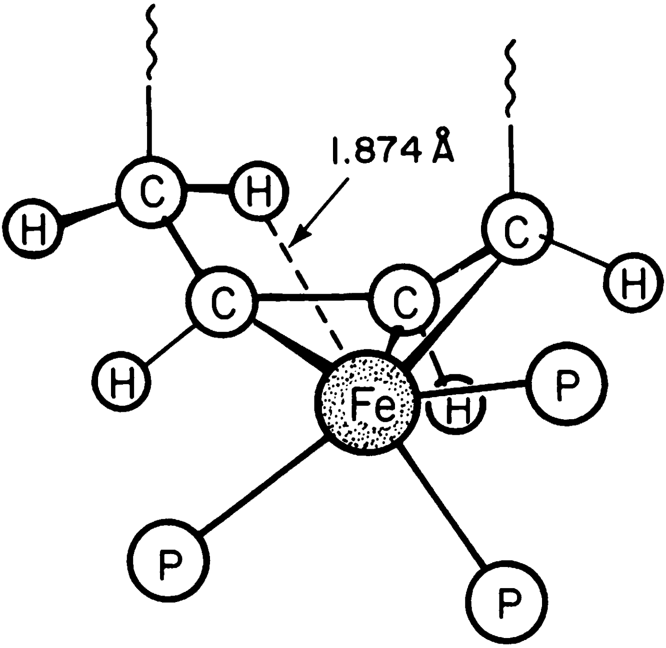


Figure 1 *In the iron complex,* $\{Fe[P(OCH_3)_3]_3(\eta^3\text{-}C_8H_{13})^+\}(BF_4{}^-)$, *the iron centre is co-ordinated to three phosphite ligands and to the allylic carbon centres of the cyclo-octenyl ligand and to a hydrogen atom attached to a carbon atom adjacent to one of the terminal allylic carbon atoms.*[15] *The hydrogen-iron distance was estimated with precision by a neutron diffraction study. The distance is* 1.874 Å. *This represents the first precisely determined three-centre* C—H—Fe *bond. The other four carbon atoms of the cyclo-octenyl ligands are not depicted in the drawing*

[14] J. R. Sweet and W. A. G. Graham, *Organometallics*, 1982, 1, in press; *J. Am. Chem. Soc.*, submitted for publication.

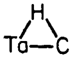
[15] R. K. Brown, J. M. Williams, A. J. Schultz, G. D. Stucky, S. D. Ittel, and R. L. Harlow, *J. Am. Chem. Soc.*, 1980, **102**, 981; R. L. Harlow, R. J. McKinney, and S. D. Ittel, *J. Am. Chem. Soc.*, 1979, **101**, 7496.

[16] A. J. Schultz, R. K. Brown, J. M. Williams, and R. R. Schrock, *J. Am. Chem. Soc.*, 1981, **103**, 169.

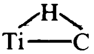
1.16 Å is significantly stretched, ~ 6 %, compared to that of normal C—H bonds. There must be some bonding interaction of the iron atom with the carbon atom, and the interaction should be characterized as a triangular three-centre bond.

Closely related to the iron complex is (η^3-6-*endo*-methylcyclohexenyl)Mn(CO)$_3$. This complex, defined by *X*-ray crystallography, has a (CH)H—Mn distance of 1.86 Å, a (C—H)C—Mn distance of 2.30 Å and a slightly elongated C—H bond of 1.07 Å.[17]

In the tantalum complex, $\{[(CH_3)_3CCH]Ta[P(CH_3)_3]Cl_2(\mu\text{-}Cl)\}_2$, the α-C—H bond of the neopentylidene ligand forms an angle of 84.8° with the Ta—C bond, and the C—H bond is significantly stretched, 1.13 Å.[16] The Ta—H separation is 2.12 Å. Thus, this system can be described as a closed or triangular three-centre bond, (2), although the Ta—H interaction is not especially strong as judged simply by the separation. However, the three-membered ring system in (2) is highly strained and this strain may be the prime cause of the relatively long Ta—H bond.



(2)

Recently, the *X*-ray diffraction study[18] of $C_2H_5TiCl_3[(CH_3)_2PCH_2CH_2P(CH_3)_2]$ established an interesting weak β-hydrogen C—H—Ti three-centre interaction with the following parameters: C—H, 1.02 Å; H—Ti, 2.29 Å; and C—Ti, 2.52(1). This structure rather nicely models an intermediate or transition state of a β-hydride elimination process for a transition-metal alkyl complex. For the complex in solution at −90 °C, there was no n.m.r. evidence of the multicentre C—H—Ti bond but this interaction should be in evidence in equilibrium isotope experiments (*vide infra*). Also, $CH_3TiCl_3[(CH_3)_2PCH_2CH_2P(CH_3)_2]$ has been shown by *X*-ray analysis to have a closed, three centre  $\mathrm{Ti}\overset{\mathrm{H}}{-\!\!-\!\!-}\mathrm{C}$ bond with a Ti—C—H angle of 70(2)° and a Ti—H distance of 2.03(4) Å.[18]

Evidence of C—H-metal bonding for the solution state of a molecular metal complex can be obtained by ^{1}H n.m.r. studies. A relatively tight C—H-metal bonding is reflected by a high field proton resonance, however, if the rate of a C—H-metal bond breaking is high the proton resonance is shifted to lower field as a function of the C—H complex to C—H—M complex concentrations. In addition, the ^{13}C—H coupling constant is substantially reduced for the C—H···M bond and raised (relative to a normal C—H bond) for the remaining, if any, C—H bonds that are not interacting with the metal atom.[15-18] Alternatively, the multicentre interaction can be detected by partial deuterium

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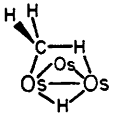
[17] M. Brookhart, W. Lamanna, and M. B. Humphrey, *J. Am. Chem. Soc.*, 1982, **104**, 2117.

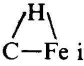
[18] Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 802; *ibid.* submitted for publication.

substitution into the CH_x site. This is a much more sensitive probe of C—H—M interactions in d.n.m.r. studies, through an equilibrium isotope effect.[19] Such evidence for C—H—M interaction in the solution state has been incisively established for the cyclo-octenyl-iron complex.[15,20]

B. Polynuclear Metal Complexes.—Four polynuclear metal complexes with multicentre C—H—M interactions have been defined by either crystallographic or n.m.r. studies or both. The first example was $CH_3(H)Os_3(CO)_{10}$.[21,22] Although this cluster has never been isolated in single crystal form and there are no precise structural parameters available to date, the ^1H d.n.m.r. studies of this complex unequivocally established the presence of Os—H—Os and Os—C(H_2)—H—Os bonding in the solution state, (3).[21,22] In the dinuclear iron complex, $\{Fe_2(\mu\text{-}CH_3)(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2[P(C_6H_5)_2]_2)\}^+(PF_6)^-$, as defined through X-ray diffraction data,[23] there is an unsymmetrically bridged CH_3 group, analogous to the osmium cluster as shown in Figure 2. Key structural parameters are respectively C—H, H—Fe, and Fe—C distances of 1.06(0.83), 1.64(1.78), and 2.108(2.118) Å with a C—H—Fe angle of ~102° (the distances given in parentheses are for the second independent complex in the unit cell).



(3)

These data incisively characterise a closed three-centre  $\overset{H}{C\text{—}Fe}$ interaction in this complex. Conventional low temperature n.m.r. experiments did not show evidence of the C—H—Fe interaction but the presence of this interaction in the solution state structure was established for this complex and a related one, $\{Fe_2(\mu\text{-}CH_3)(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2(CO)_2\}$, by ^1H d.n.m.r. studies using the μ-CH_2D derivative whereby an equilibrium isotope effect[19] favouring the C—H—Fe interaction was detected.[23,24]

A rigorously defined closed three-centre interaction for both the solid and the solution state of a cluster is found in $HFe_4(\eta^2\text{-}CH)(CO)_{12}$, the Tachikawa

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[19] M. Saunders, *Stereodyn. Mol. Syst. Proc. Symp.*, 1979, 171; F. A. L. Anet, V. J. Basus, A. P. W. Hewett, and M. Saunders, *J. Am. Chem. Soc.*, 1980, **102**, 3945.

[20] S. D. Ittel, F. A. Van-Catledge, C. A. Tolman, and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 1317; S. D. Ittel, F. A. Van-Catledge, and J. P. Jesson, *J. Am. Chem. Soc.*, 1979, **101**, 6905.

[21] R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, 1978, **100**, 7726.

[22] R. B. Calvert, J. R. Shapley, A. J. Schultz, J. M. Williams, S. L. Suib, and G. D. Stucky, *J. Am. Chem. Soc.*, 1978, **100**, 6240.

[23] G. M. Dawkins, M. Green, A. G. Orpen, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1982, 41.

[24] C. P. Casey, P. J. Fagan, and W. H. Miles, *J. Am. Chem. Soc.*, 1982, **104**, 1134.

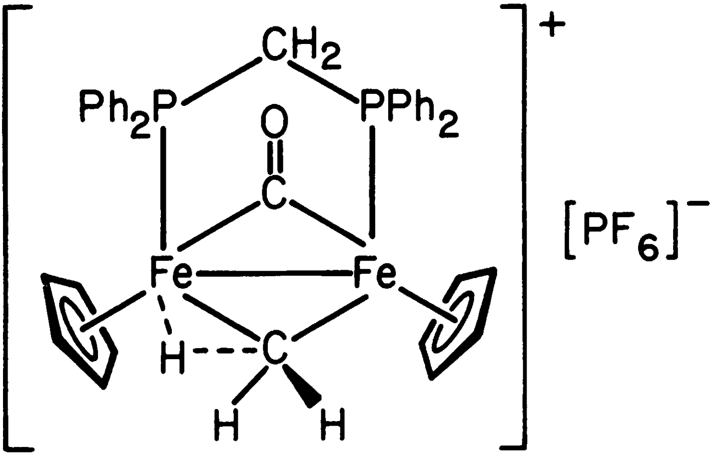
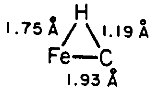


Figure 2 *In the solid state structure of* $\{Fe_2(\mu\text{-}CH_3)(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2\text{-}(\mu\text{-}CH_2[P(C_6H_5)_2]_2)\}^+(PF_6^-)$, *the methyl group is in a bridging position between two iron atoms. In addition, one of the methyl hydrogen atoms closely approaches one of the iron atoms so as to describe a closed three-centre iron-carbon-hydrogen bond.*[23] *The* C—H, H—Fe, *and* Fe—C *distances are* 1.06, 1.64, *and* 2.108 Å, *respectively*

butterfly.[25] Composite *X*-ray and neutron diffraction data[26,27] precisely define such a closed three-centre C—H—Fe interaction for the solid state (Figure 3). Here the essential distance parameters, shown in (4), are illustrated for one of



(4)

the two independent molecules.[26–28] The very long C—H bond distance of 1.19 Å is remarkable and is the longest, accurately assessed C—H bond distance of all molecular species. Consistently for the solution state, the nominal C—H hydrogen atom in the Fe—H—C bond has an n.m.r. resonance shifted substantially to high field (~ −1 p.p.m.).[25]

These complexes constitute the set of clusters in which three-centre C—H—M interactions are unambiguously defined. This number is small but should grow

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[25] M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, 1980, **102**, 4541.

[26] M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1980, **102**, 4542.

[27] M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1981, **103**, 1485.

[28] R. M. Gavin, J. Reutt, and E. L. Muetterties, *Proc. Natl. Acad. Sci., USA*, 1981, **78**, 3981; E. L. Muetterties in 'Reactivity of Metal-Metal Bonds' ed. M. H. Chisholm, A. C. S. Symposium No. 155, American Chemical Society, Washington, 1981, p. 273.

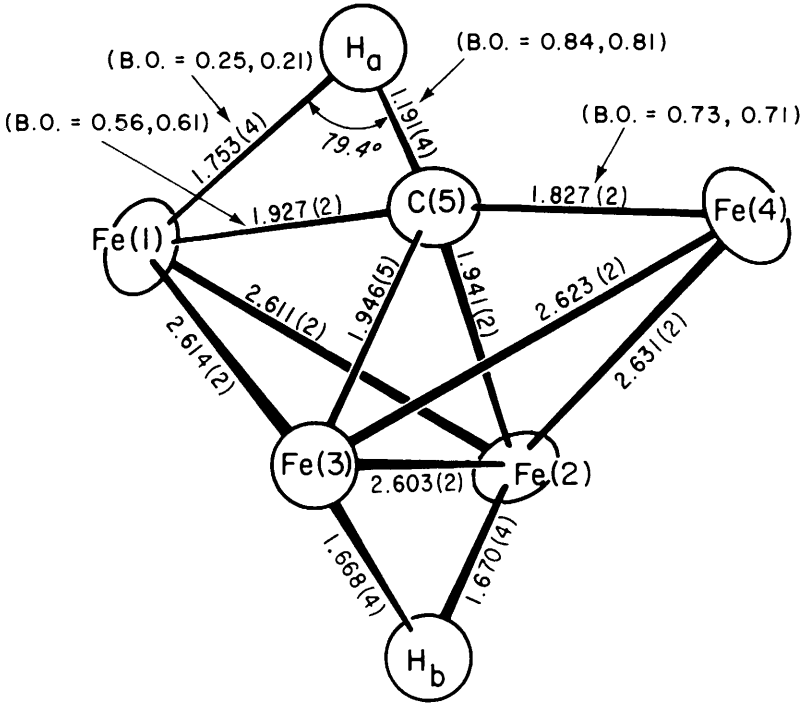

Figure 3 *The Tachikawa cluster,* $(\mu\text{-H})Fe_4(\eta^2\text{-CH})(CO)_{12}$*, has a closed three-centre* C—H—Fe *bond as established by* X-ray *and neutron diffraction data.*[25,27] *The core structure for the cluster is shown above. The twelve carbonyl ligands are not shown; each iron has three terminal* CO *ligands in this cluster. All of the core bonding distances are shown in the above drawing. Also shown are the estimated Mulliken bond orders (Hückel calculations) for some of the core atom interactions*[28]

substantially as neutron diffraction studies of clusters increase and as very low temperature n.m.r. studies of clusters and the n.m.r. technique[19] of searching for equilibrium isotope effects[19] for CH_xD—M species become more general experimental procedures (specific studies illustrating this application to C—H—M interactions are described in references 20,21,23—25).

C. Metal Surfaces.—Chemisorption states of saturated hydrocarbons on metal should be based largely on the interaction of σ C—H and σ^* C—H orbitals with appropriate surface metal atom orbitals.[28-31] Energetic considerations suggest that electron transfer from the metal surface to σ^* C—H antibonding orbitals may dominate in such bonding states.[29] Filling of the antibonding

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[29] E. Shustorovich, R. Baetzold, and E. L. Muetterties, *J. Phys. Chem.*, submitted for publication.

[30] T. E. Madey and J. T. Yates, Jr., *Surf. Sci.*, 1978, **76**, 397.

[31] J. E. Demuth, H. Ibach, and S. Lehwald, *Phys. Rev. Lett.*, 1978, **40**, 1044.

C—H orbitals should reduce substantially the C—H stretching frequency and should enhance the potential for C—H bond cleavage.

Hydrocarbons typically chemisorb reversibly on flat metal surfaces under ultra high vacuum conditions. Depending upon hydrocarbon conformation in the chemisorption state and upon the surface topography, the number of effective C—H—M multicentre interactions per carbon atom may vary from one to some fraction of one. Hence the hydrocarbon chemisorption heats should be some function of the number of carbon atoms in the hydrocarbon molecule. In fact, chemisorption bond energy appears to be a nearly linear function of the number of carbon atoms in the hydrocarbon as shown in Figure 4 from the classic study by Madey and Yates[30] for hydrocarbons chemisorbed on the

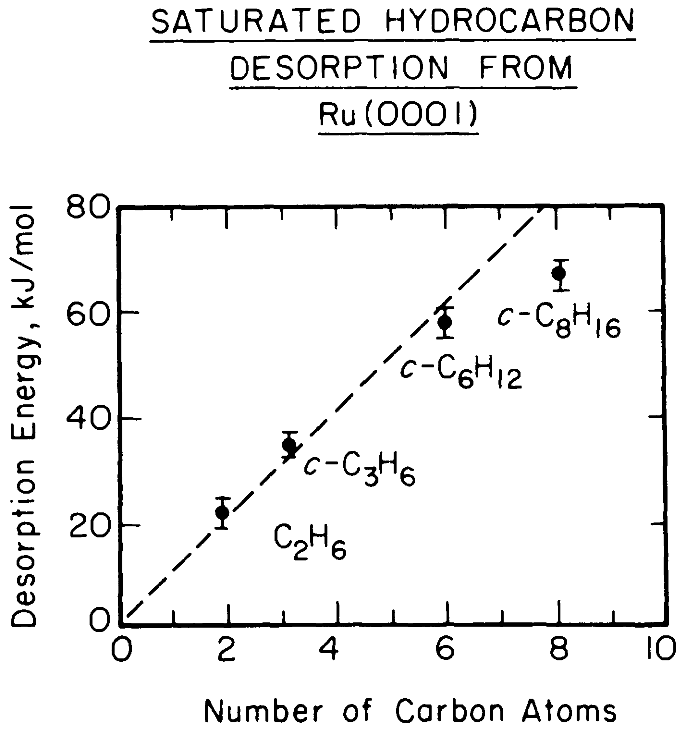


Figure 4 *In a study of hydrocarbon chemisorption on* Ru(0001), *Madey and Yates*[30] *established the desorption energies for a series of hydrocarbons on this basal plane. The magnitude of the desorption energies is a function of the number of carbon atoms in the molecule. To a first approximation, the relationship is linear, however, the value for the cyclo-octane does not follow this relationship; this apparent deviation might be due to conformational effects that limit the number of* C—H—*metal surface interactions per molecule. The hydrocarbons employed in this study were ethane, cyclopropane, cyclohexane, and cyclo-octane*

basal, close-packed plane of ruthenium, (0001). Spectroscopic data for cyclohexane chemisorbed on Ru (0001) have been interpreted[30] in terms of a model, illustrated in Figure 5, consistent with the foregoing postulate.

The proposed electronic representation for hydrocarbon chemisorption states, as described above, requires some reduction in the C—H force constant which should be evident in the vibrational spectrum. In fact, vibrational data derived

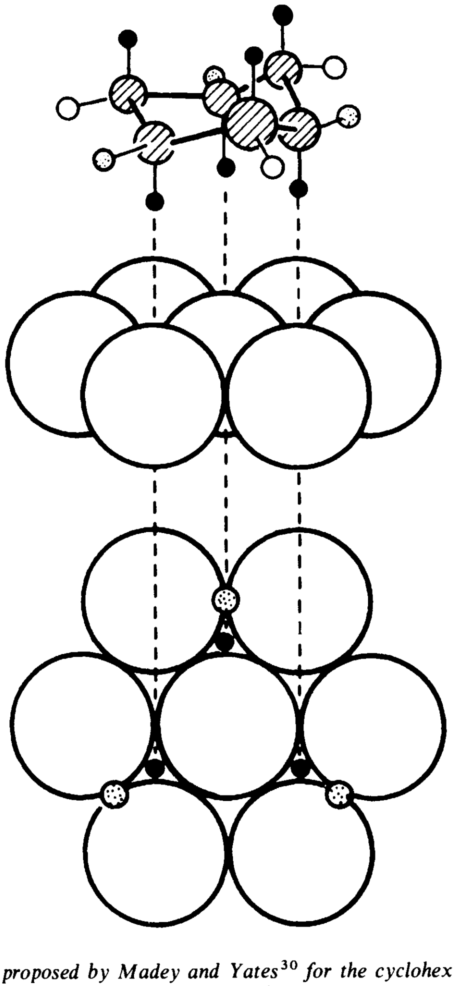
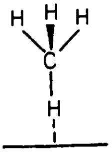


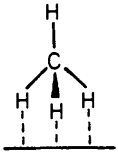
Figure 5 *A model proposed by Madey and Yates*[30] *for the cyclohexane chemisorption on ruthenium*(0001)*based on a spectroscopic study has a primary interaction of three axial* C—H *bonds in the chair form of cyclohexane with three-fold sites in this closed packed plane. At the top is a side view and at the bottom, a view looking down on the surface plane (a view that includes only the three axial* C—H *bonds that strongly interact with the surface plane)*

from high resoluton electron energy loss spectroscopic studies of the cyclohexane chemisorption states on the close-packed planes of Ni(111),[31] Pt (111),[31] and Ru(0001)[32,33] establish that there is a lower energy C—H stretching frequency. This is consistent with the postulate of C—H—M bonding but, of course, the genesis of the lower energy stretching frequency cannot be uniquely established from these data.

In a collaborative programme with E. Shustorovich and R. Baetzold, we have attempted to define on theoretical grounds the stereochemistry for methane chemisorbed on a close-packed metal surface. The preliminary results[29] suggest that (5) is favoured over (6) at high *d* level occupancy; (6) tends to be favoured at low *d* level occupancy. However, the range from high to low level *d* occupancy may be, in the theoretical calculations, comparable, larger, or smaller than the actual range for transition metals. Only the trend is significant. Energy differences are small so that rotation of methane chemisorbed on a metal surface will probably encounter a small barrier. In any case, it is interesting that configuration (5) is not a directly productive way point for dehydrogenation of methane, a process that has a large activation energy barrier on all metal surfaces.[34] The reaction of methane with a clean tungsten surface has an activation energy of 9.3 ± 1 kcal mole^{-1} at 1350—2359 K. There is a large kinetic isotopic effect, $k_{CH_4}:k_{CD_4} = 4.5$, that is ascribed to a tunnelling process.[34]



(5)



(6)

D. Metal Atoms.—Condensation of gaseous transition-metal atoms into low temperature methane matrices is suspected to yield $M(CH_4)_x$ complexes for some transition metals but there are no definitive supporting data.[35-38] Metal atoms like copper or nickel do not appear to interact strongly with methane whereas the electronic spectrum for copper atoms in an ethane matrix at 30 K shows a much larger splitting of the $^2P \rightarrow {}^2S$ band than for copper atoms in a methane or argon matrix. It has been suggested that this is an indication of a rather strong interaction between excited copper atoms and the surrounding ethane cage. A metal atom–methane complex should encounter a very small barrier to inter-

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[32] F. M. Hoffman, T. E. Felter, P. A. Thiel, and W. H. Weinberg, *J. Vac. Sci. Technol.*, 1981, **18**, 651.

[33] F. M. Hoffman, T. E. Felter, P. A. Thiel, and W. H. Weinberg, *J. Chem. Phys.*, submitted for publication.

[34] H. F. Winters, *J. Chem. Phys.*, 1976, **64**, 3495.

[35] W. E. Billups, M. M. Konarski, R. H. Hauge, and J. L. Margrave, *J. Am. Chem. Soc.*, 1980, **102**, 7393.

[36] G. A. Ozin, D. F. McIntosh, and S. A. Mitchell, *J. Am. Chem. Soc.*, 1981, **103**, 1574.

[37] G. A. Ozin, S. A. Mitchell, and J. Garcia-Prieto, *Angew. Chem. Suppl.*, 1982, 369.

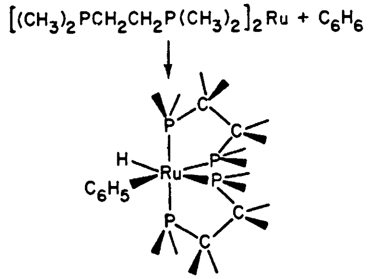
[38] P. H. Barrett, M. Pasternak, and R. G. Pearson, *J. Am. Chem. Soc.*, 1979, **101**, 222.

conversion of M—H—CH_3, M—H_2—CH_2, and M—H_3—CH configurations. Indirect evidence for such interconversions for Cu—CH_4 matrices is suggested by the selective excited state reactivities.

2 Carbon-Hydrogen Bond Breaking Process

A. Mononuclear Metal Complexes.—The first explicit description of C—H oxidative addition to a metal centre in a molecular transition-metal complex was by Chatt and Davidson in 1965.[39] Reduction of the octahedral bis(1,2-dimethylphosphino-ethane)ruthenium dichloride complex in the presence of naphthalene or benzene gave the *cis*-β-naphthyl or phenyl ruthenium hydride complex, equations (2) and (3). The significance of this finding was ignored to some degree. The reaction was remarkable because the strongest type of carbon-hydrogen bond had been cleaved and because it comprised the reaction of an initially free hydrocarbon with a molecular metal complex. Reaction *may* have been facilitated by an intermediate in which the arene molecule was co-ordinated, in some (productive) fashion, to the presumed zero-valent sixteen-electron ruthenium intermediate complex.

$$[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2RuCl_2 \xrightarrow{Na} [(CH_3)_2PCH_2CH_2P(CH_3)_2]_2Ru \qquad (2)$$



(3)

Following the original Chatt-Davidson report,[39] an enormous number of C—H addition reactions were discovered for mononuclear transition-metal complexes (an extensive set of reviews[1-4] provide a relatively comprehensive analysis of this chemistry up to 1977). The majority of reported oxidative additions were internal additions: co-ordinately unsaturated molecules, in which a C—H bond associated with one of the ligands could approach closely or was forced to approach closely the metal atom, often exhibited this facile internal oxidative addition reaction. Examples of this important proximal effect were *ortho*-palladation[40] [equations (4) and (5)] and *ortho*-metallation[41]

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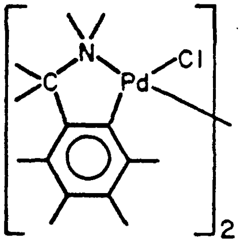
[39] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1965, 843.

[40] A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, 1965, **87**, 3272.

[41] G. W. Parshall, W. H. Knoth, and R. A. Shunn, *J. Am. Chem. Soc.*, 1969, 91, 4990.

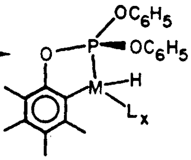
$$PdCl_4^{2-} + C_6H_5CH_2NR_2 \longrightarrow Cl^- + \{PdCl_3N(R)_2C_6H_5)^-\} \qquad (4)$$

$$2\{PdCl_3N(R)_2C_6H_5^-\} \longrightarrow 2Cl^- + 2HCl +$$



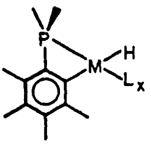
(5)

$$L_xM{-}P(OC_6H_5)_3 \longrightarrow$$

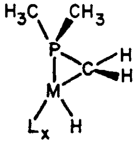


(6)

in aryl phosphite complexes [equation (6)].[1-3] In these cases, the stereochemically favoured five-membered ring is formed. Nevertheless, four- and three-membered ring systems[1-3] can be and are generated from co-ordinately unsaturated metal



(7)



(8)

arylphosphine[42] and trimethylphosphine[43] complexes, respectively, (7) and (8). There is no question but that the proximal effect in these internal oxidative addition reactions greatly enhances the facility of C—H bond breaking.

Until recently, there was no example of C—H oxidative addition reactions between a molecular metal complex and a hydrocarbon molecule that possessed no functional group or unsaturation (examples of C—H addition with aromatic molecules,[44-49] acetone,[44] and acetonitrile[44] were established as in the original

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[42] M. A. Bennett and D. L. Milner, *J. Am. Chem. Soc.*, 1969, **91**, 6983.

[43] J. W. Rathke and E. L. Muetterties, *J. Am. Chem. Soc.*, 1975, **97**, 3272.

[44] S. D. Ittel, C. A. Tolman, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, 1976, **98**, 6073.

[45] C. Giannotti and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1972, 1114.

[46] K. L. Tang Wong, J. L. Thomas, and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1974, **96**, 3694.

[47] E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Am. Chem. Soc.*, 1970, **92**, 5234.

[48] U. Klabunde and G. W. Parshall, *J. Am. Chem. Soc.*, 1972, **94**, 9081.

[49] L. P. Seiwell, *J. Am. Chem. Soc.*, 1974, **96**, 7134.

Chatt-Davidson[39] observations for benzene and naphthalene). A view developed (including the author's[50]) that there were two factors that lessened the probability of C—H oxidative addition of saturated hydrocarbon and molecular metal complex. One was the proximal effect which would be so predominant that internal oxidative additions would tend to prevail over oxidative addition of a free saturated hydrocarbon molecule (which is an extremely weak ligand) unless the co-ordinately unsaturated molecular complex were very carefully designed so as to constrain all ligand C—H hydrocarbon atoms distal to the metal centre. The other was the thermodynamic factor that stems from the relatively weak alkyl-metal bond strength whereby the equilibrium constant for addition would be rendered very small. The ubiquitous facile reductive elimination of alkane from *cis*-$ML_x(H)(R)$ complexes was a supportive observation.

Competition between internal C—H oxidative addition involving the metal centre and a ligand and external C—H oxidative addition involving the metal centre and a hydrocarbon molecule must be evaluated on kinetic and thermodynamic grounds. Entropic considerations generally favour the internal oxidative addition reaction; however, enthalpic factors may favour the external addition. *Assuming* a reversible process for internal C—H addition it follows that, for some molecular species, molecular design to inhibit internal C—H addition may not be a critical factor *vis-a-vis* external C—H addition from a hydrocarbon molecule if the enthalpy contribution from the carbon-metal bond for the 'external' adduct is substantially greater than that for the 'internal' adduct.

Listed in Table 1 are values for C—H bond strengths for a variety of saturated and unsaturated hydrocarbons. The decreasing order of bond strength probably also mirrors the probable trend in bond strengths for carbon-metal bonds, *e.g.* $C_6H_5—M > CH_3—M > \sigma$-allyl—M > σ-benzyl—M. Since a reasonable estimate

Table 1 *Carbon-hydrogen bond dissociation energies*[a]

Bond	*Energy*/kcal mol^{-1}
Ph—H	110
vinyl—H	108
Me—H	104
Et—H	98
Pr^i—H	95
Bu^t—H	91
allyl—H	87
$PhCH_2$—H	87

[a] Data taken from A. Streitweiser, Jr. and C. H. Heathcock, 'Introduction to Organic Chemistry', MacMillan Publ. Co., Inc. New York, 1981 2nd. Ed., p. 1194

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[50] E. L. Muetterties in 'Fundamental Research in Homogeneous Catalysis', Vol. 2, ed. Y. Ishii and M. Tsutsui, Plenum Publishing Corp., 1978, p. 1.

for the range in M—H bond enthalpic contributions is 50—65 kcal $mole^{-1}$, an observable addition of a saturated hydrocarbon like pentane or cyclohexane to a metal complex would require a C—M bond energy of 40—55 kcal $mole^{-1}$. One factor that would favour such an addition would be a 5*d* metal centre. Stability for an alkyl-metal bond should increase, through a larger ionic contribution, in going from 3*d* to 4*d* to 5*d* metal [the high stability of compounds like *cis*-$CH_3(H)Os(CO)_4$ probably resides *partly* in the relatively large CH_3—Os (and H—Os) bond energy; for the 3*d*-metal cobalt, it has been estimated[51] that metal-alkyl bond energies do not exceed the range of 20—30 kcal $mole^{-1}$ at least alkyl-cobalamin complexes. A more extensive discussion of the metal-atom carbon bond enthalpies is presented by Connor[52]].

The first observation of C—H oxidative addition for a saturated hydrocarbon to a metal centre in a molecular complex was by Crabtree and co-workers in 1979.[53,54] Cyclopentane reacted with the cationic $\{IrH_2[P(C_6H_5)_3]_2[\text{solvent}]_2{}^+\}$ complex in the presence of 3,3-dimethylbut-1-ene to form $\{(\eta^5\text{-}C_5H_5)IrH[P(C_6H_5)_3]_2{}^+\}$; the solvate molecules were either water or acetone. Also, cyclo-octane reacted under these conditions with the iridium complex to form $\{Ir(\text{cyclo-octa-1,5-diene})[P(C_6H_5)_3]_2{}^+\}$. However, cyclohexane did not yield an $\{Ir(C_6H_6)L_x{}^+\}$ complex ostensibly for stereochemical reasons. The function of the olefin was as a hydrogen acceptor for the hydrogen atoms excised from the cycloalkane; a less sterically demanding olefin like ethylene was not effective, presumably because it formed too stable a complex with the iridium centre. The metal centre in this complex was described as an electrophile — not a nucleophile. Unfortunately, it is difficult to characterise the reactant complex as either electrophilic or nucleophilic; the reactant complex is cationic and cannot be electronically defined by a gas-phase photoelectron-spectroscopic study. An extension of the iridium reaction to rhenium [equation (7)] has been reported.[55]

$H_7Re[P(C_6H_5)_3]_2$ +  $\xrightarrow{\text{3,3-dimethylbut-1-ene}} (\eta^5\text{-}C_5H_5)ReH_2[P(C_6H_5)_3]_2$ (7)

In 1982, three groups[56-58] independently discovered reversible saturated-hydrocarbon addition to molecular iridium and rhodium complexes. Bergman and Janowicz[56] found that irradiation of $\eta^5\text{-}C_5(CH_3)_5IrH_2P(CH_3)_3$ in hydrocarbon media, *e.g.*, cyclohexane and neopentane, led to hydrogen elimination and formation of the corresponding alkyliridium hydride complex, $\eta^5\text{-}C_5(CH_3)_5IrH(R)P(CH_3)_3$. Elimination of alkane from these complexes occurs thermally at +110 °C allowing conversions such as that shown in equation (8).

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[51] J. Halpern, F. T. T. Ing, and G. L. Rempel, *J. Am. Chem. Soc.*, 1979, **101**, 7124.

[52] J. A. Connor, *Topics Curr. Chem.*, 1977, **71**, 71.

[53] R. H. Crabtree, J. M. Mihelcic, and J. M. Quirk, *J. Am. Chem. Soc.*, 1979, **101**, 7738.

[54] R. H. Crabtree, M. F. Mellea, J. M. Mihelcic, and J. M. Quirk, *J. Am. Chem. Soc.*, 1982, **104**, 107.

[55] D. Baudry, M. Ephiritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, 1980, 1243; 1982, 606.

[56] A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1982, **104**, 352; *ibid.*, submitted for publication.

[57] W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1982, **104**, 4240; personal communication.

[58] J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 3722.

Thus, the addition reaction does not simply result from some unique photoexcited state.

$$\eta^5\text{-}C_5(CH_3)_5IrH(\text{cyclohexyl})P(CH_3)_3 + \text{neopentane} \longrightarrow \text{cyclohexane} + \eta^5\text{-}C_5(CH_3)_5IrH(\text{neopentyl})P(CH_3)_3 \qquad (8)$$

Interestingly, the presumed intermediate η^5-$C_5(CH_3)_5IrP(C_6H_5)_3$, generated also by photolysis of the hydride, reacts with benzene but there is a competition with internal oxidative addition of an *ortho* C—H in the phenyl substituent on the phosphorus atom to give η^5-$C_5(CH_3)_5\overline{IrP(C_6}H_4)(C_6H_5)_2(H)$. This competitive internal oxidative addition is not *seen* for the trimethylphosphine analogue.

The Bergman–Janowicz reaction system apparently has many desirable features. The attendant ligands in the presumed intermediate $C_5(CH_3)_5IrP(CH_3)_3$ are good donors and the ionization potential of this intermediate should be relatively low. In addition, the metal is a 5*d* metal and the Ir–alkyl bond should be and obviously is relatively robust. Nevertheless, the same chemistry can be effected with the rhodium analogue of the iridium complex as shown by Jones and Feher,[57] although the resultant alkylrhodium hydride complexes, explicably, are less thermally stable than the iridium analogues. Also, the electron density at the metal atom in such intermediates can be substantially reduced without losing the reactivity toward saturated hydrocarbons: Hoyano and Graham have shown[58] that the photolysis of η^5-$C_5(CH_3)_5Ir(CO)_2$ in cyclohexane yields η^5-$C_5(CH_3)_5IrH(\text{cyclohexyl})(CO)$, ostensibly through the analogous CO intermediate, η^5-$C_5(CH_3)_5IrCO$. Interestingly, Jones and Feher[57] report that η^5-$C_5H_5RhP(CH_3)_3(H)(C_6H_4R)$ complexes are converted, on warming, into η^5-$C_5H_5RhP(CH_3)_3(\eta^2\text{-}C_6H_5R)$, which is another indication of an intermediate complex in the oxidative addition of arenes to ML_x species.

To summarise, factors that apparently enhance the probability of oxidative addition of C—H bonds in saturated or unsaturated hydrocarbons to molecular ML_x complexes are as follows:

(i) The ML_x complex should be a high energy species; this is probably the most important single factor. All other factors being equal, the addition reaction should be more favourable with a 5*d* than a 4*d* metal centre and least with a 3*d* metal because in going down a transition-metal group, the M—H and M—C (alkyl) bond strengths increase. The other thermodynamic factor of importance is the proximal or entropic effect.

(ii) The capability of a reactant metal species to complex the hydrocarbon prior to the oxidative addition step may convey an entropic advantage to the metal species in oxidative addition reactions.

(iii) If the metal complex has ligands with C—H bonds that can, or are forced to, approach closely the metal centre, then internal C—H addition may be favoured for entropic reasons. Thus, a metal complex designed so as to keep all ligand C—H bonds distal to the centre is sterically ideal for the *external* addition of a saturated hydrocarbon molecule. But this ideal is not necessarily required for external addition of a saturated hydrocarbon. An interesting example of competitive internal and external C—H addition was discussed above for the Bergman-Janowicz system.

(iv) Co-ordination unsaturation in the reactant ML_x complex is essential, of course. The complex should have a low lying unfilled orbital for interaction with the σ C—H bonding orbital. Important also is an appropriate high lying filled ML_x orbital for interaction with the σ^* C—H antibonding orbital. In the initial phase of the oxidative reaction, either of these two interactions could be dominant. Hence, either an electron rich or electron deficient ML_x species could be effective in the oxidative addition of a saturated hydrocarbon. Accordingly, there could be a range of transition states in such oxidative addition reactions. As noted earlier, a sensitive probe of the transition state is the measurement of the kinetic isotope ratio, $k_H:k_D$. Clearly, many more experimental data are required to assess objectively the key features of saturated hydrocarbon addition reactions to ML_x species. The importance of the σ^* C—H interaction with a metal orbital should increase in progressing from metal atoms and mononuclear ML_x complexes to clusters and finally to metal surfaces because this is the increasing energy level trend for the metal *d*-band of these species. However, 'energy matching' is not necessarily critical here because the interaction parameters β and β^* may in fact be quite disparate in magnitude.

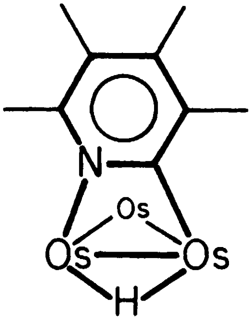
(v) Because of the aforementioned energy considerations in the matching of σ C—H bonding and σ^* C—H antibonding levels with appropriate unfilled and filled metal orbitals, it may well be that photochemically or thermally excited states of ML_x species are better suited to the oxidative addition of saturated hydrocarbons (provided that ΔG for the reaction is not adversely affected by temperature increase in the case of the *thermally* excited ML_x species).

The ongoing studies by the Bergman, Crabtree, Graham, and Jones research groups may soon provide the necessary background to a more incisive and quantitative characterization of this type of hydrocarbon reaction for molecular, mononuclear metal complexes.

B. Molecular Metal Clusters.—External oxidative addition of a C—H bond in a saturated-hydrocarbon molecule to metal centres in molecular clusters has not been demonstrated to date but internal oxidative addition reactions have. Electronically, stereochemically, and thermodynamically, the issues are fundamentally no different than for mononuclear metal complexes except that the *d* 'band' is higher in energy for clusters than for mononuclear metal complexes.

The proximal effect also operates in clusters.[5] One example is the thermal conversion of a simple $Os{-}NC_5H_5$ bond into a bridged α-pyridyl system, (9), in the triosmium carbonyl cluster, [equation (9)].[59] Many such examples

$$Os_3(CO)_{12} \xrightarrow{C_5H_5N} Os_3(CO)_{11}NC_5H_5 \xrightarrow{\Delta} HOs_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}NC_5H_4) \quad (9)$$



(9)

of internal oxidative additions of C—H bonds in molecular clusters have been reported. The development of metal cluster hydrocarbon chemistry thus appears to be following that of mononuclear metal complexes. One may anticipate that photolysis of a second- or third-row metal cluster of the form $H_2M_xL_y$ or M_xL_{y+1} will generate a M_xL_y intermediate which will react directly with a hydrocarbon. One very interesting cluster is $(\mu\text{-}CH_3)(\mu\text{-}H)Os_3(CO)_{10}$ in that it provides information about the transition state (or reaction intermediate) for C—H bond breaking in polynuclear metal arrays and shows reversible C—H bond breaking in the solution state.[21,22] As noted earlier, ^1H d.n.m.r. studies have shown that this cluster has the methyl group bridging a cluster edge as $Os—CH_2—H—Os$ and the hydrogen atom also bridging the same edge, (3). The bridging C—H bond is reversibly cleaved on a time scale such that in solution, over a wide temperature range, there is an equilibrium of the methyl complex with $(\mu\text{-}CH_2)(H)(\mu\text{-}H)Os_3(CO)_{10}$, Figure 6 (the rate of C—H bond breaking is, however, not fast with respect to the n.m.r. timescale). Notably, the methyl complex does not reductively eliminate methane, rather dehydrogenation is the favoured process [suggesting that $Os_3(CO)_{10}$, the fragment that would be generated in methane elimination is a relatively high energy species]. In fact, at elevated temperatures, further dehydrogenation occurs converting the methylene complex into a very stable, triply bridging methylidyne cluster, $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CH)(CO)_9$. The reversibility of this last step has been demonstrated: either CO or a phosphine converts the methylidyne complex, apparently through a series of methylene and methyl complexes, ultimately into methane and, respectively, $Os_3(CO)_{12}$ or phosphine derivatives thereof.[60]

The beauty of this osmium cluster chemistry is that it is an excellent formal analogy to metal surface chemistry whereby dehydrogenation processes are facile. The dehydrogenation process can be followed stepwise by n.m.r. spectroscopy, and the bridging $Os—CH_2—H—Os$ interaction of the methyl complex is an explicit model of a transition state or intermediate in a C—H bond breaking process. Of substantial merit would be a crystallographic study, ideally

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[59] C. C. Yin and A. Deeming, *J. Chem. Soc., Dalton Trans.*, 1975, 2091.

[60] R. B. Calvert, Ph.D. Thesis, University of Illinois, 1978.

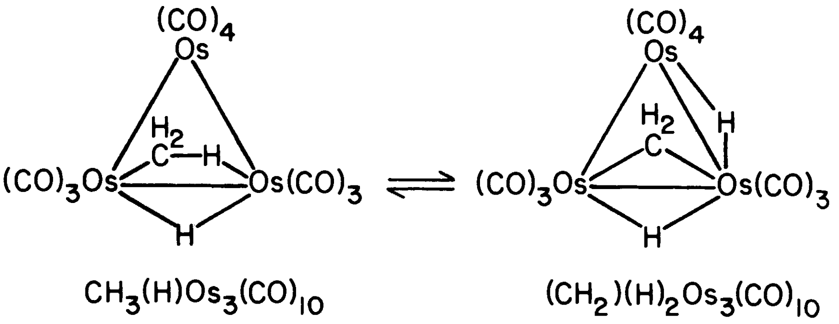

Figure 6 *The two triosmium carbonyl clusters shown above, one with an unsymmetrically bridging methyl ligand and the other with a bridging methylene ligand, are in equilibrium with each other in the solution state.*[21,22] *This is a classic example of facile* C—H *bond breaking centred on metal atoms in a cluster molecule and represents a simple, formal model of* C—H *bond breaking for metal surfaces*

based on neutron diffraction, of $(\mu\text{-}CH_3)(H)Os_3(CO)_{10}$ or a derivative thereof; attempts to obtain single crystals of this complex have been unsuccessful to date.

A related and informative system is based on methylrhodium and methyliridium complexes. Reaction of methyl-lithium with the corresponding $\{(\mu\text{-}Cl)M(\text{cyclo-octa-1,5-diene})\}_2$ complexes yields methyl bridged dimers, $\{(\mu\text{-}CH_3)M(\text{cyclo-octa-1,5-diene})\}_2$.[61] The rhodium methyl dimer displayed no n.m.r. evidence at low temperatures of an unsymmetric methyl bridging interaction, M—CH_2—H—M; however, the more sensitive n.m.r. experiments with CH_2D methyl groups has not been completed. An *X*-ray crystallographic study of the more stable rhodium dimer established a near symmetric methyl bridging unit but hydrogen atom positions were not accurately established, Figure 7.[61] Nevertheless, both the rhodium and the iridium complexes undergo facile C—H bond breaking reactions. For the rhodium complex, this reaction is moderately fast at 0— +20 °C. The major overall process is reductive elimination of methane and the formation of rhodium metal. This process probably proceeds first through an α-hydrogen abstraction from a methyl group to yield some $\{(CH_3)(H)(\mu\text{-}CH_2)Rh_2(\text{cyclo-octa-1,5-diene})\}_2$ species (monitoring of the overall process by ^1H n.m.r. did give evidence for an intermediate complex with a bridging methylene group, Rh—CH_2—Rh). In contrast, the major process with the 5*d* iridium complex was α-hydrogen abstraction, hydrogen elimination, and formation of the stable bridging methylene complex, $\{(\mu\text{-}CH_2)Ir(\text{cyclo-octa-1,5-diene})\}_2$. Thus, in the polynuclear metal complexes as in the mononuclear complexes, the tendency to eliminate methane when there are *cis* or *vicinal* H and CH_3 groups appears to decrease sharply in going from 3*d* to 4*d* to 5*d* metal centres.

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[61] G. F. Schmidt, E. L. Muetterties, M. A. Beno, J. M. Williams, *Proc. Natl. Acad. Sci., USA*, 1981, **78**, 1318.

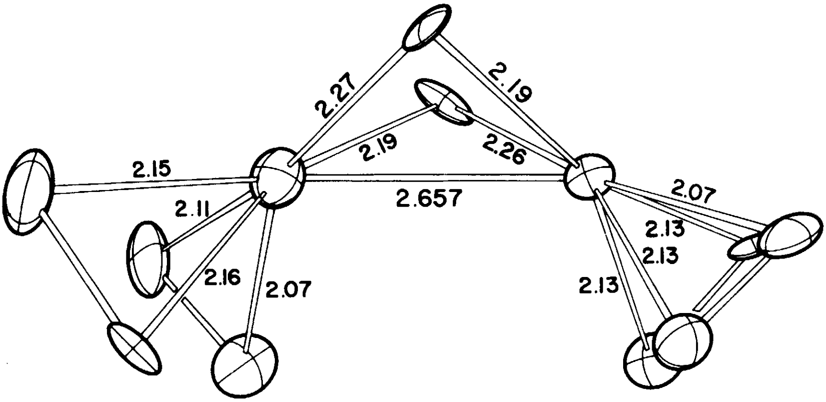

Figure 7 *The structure of* $\{(\mu\text{-CH}_3)\text{Rh}(\textit{cyclo-octa-1,5-diene})\}_2$, *as established by an X-ray crystallographic study,*[61] *has bridging methyl groups. The core structure is shown above with the exclusion of all hydrogen atoms and also the saturated carbon centres of the cyclo-octadiene ligand. Ignoring the rhodium–rhodium interaction, each rhodium centre has effectively four-coordinate planar geometry involving the two carbon atoms of the bridging methyl groups and the midpoints of the two olefinic bonds of the bound cyclo-octadiene ligand*

In the Tachikawa butterfly, Figure 3, which has the closed three centre Fe—H—C bond, (4), there are a number of dynamic processes that for the solution state are fast on the n.m.r. time scale as shown in Figure 8. One of these is hydrogen atom site exchange between the Fe—H—C and the Fe—H—Fe multicentre sites.[25] Such an exchange is an expected process in that the methylidyne C—H bond is significantly stretched in the ground-state form. The barrier to H atom site exchange in $\{(\mu\text{-H})\text{Fe}_4(\mu\text{-}\eta^2\text{-CH})(\text{CO})_{12}\}$ is $\sim 21\ \text{kcal mole}^{-1}$. Substitution of carbonyl groups by more electron donating ligands such as phosphines or phosphites lowers the exchange barrier to values of 12—16 kcal mole^{-1}

Thus, like the methyl triosmium cluster, this methylidyne iron cluster *formally* models the facile process of C—H bond breaking that is a general property of metal surfaces. Also, the closed three-centre Fe—H—C interaction of the methylidyne group is an energy minimum for this iron cluster system.

C. Metal Atoms.—Transition-metal atoms isolated in methane matrices show no tendency to react with the methane up to temperatures of ~80 K although there is some spectroscopic evidence of a complex between the methane molecule and the metal atoms.[35,36] However, photolysis that leads to excitation of the metal atoms elicits metal-atom insertion into a methane C—H bond to give initially CH_3MH[35,36] which in a secondary photolysis gives $\text{CH}_3\text{M} + \text{H}\cdot$ and $\text{HM} + \text{CH}_3\cdot$. Curiously, the first row transition metals of titanium through vanadium failed to show this C—H oxidative addition reaction, however, the manganese through to zinc series of metal atoms, with the notable exception

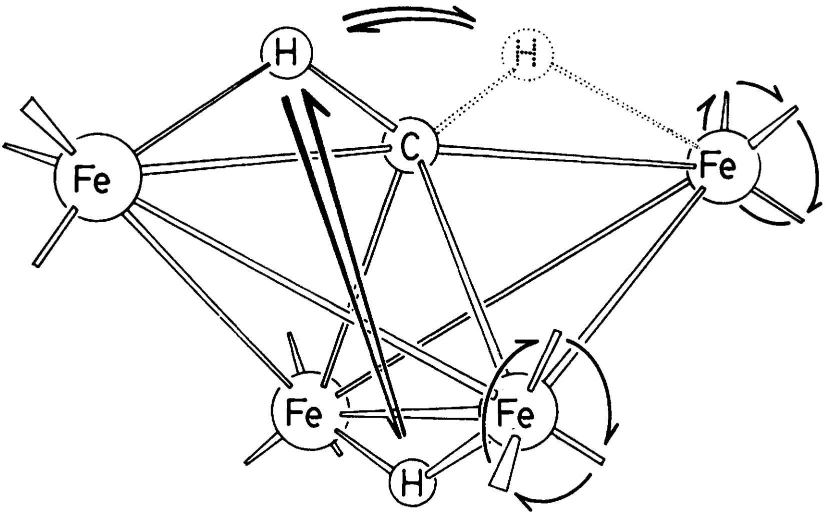

Figure 8 *A number of dynamic processes involving substituent ligands occur in the Tachikawa cluster,* (μ-H)Fe_4(η^2-CH)$(CO)_{12}$ *(see earlier description of the cluster structure, Figure 3). Two of the processes involve the hydrogen atom in the multicentre carbon-hydrogen-iron bond. One process is a flip of this hydrogen atom from one side of the cluster to the other,* i.e., *to the other apical iron atom in the cluster. The other process comprises a site exchange of the* C—H *hydrogen atom with the hydrogen atom that bridges the two basal iron atoms. The activation energy for this site exchange is about* 21 *kcal mole*$^{-1}$

of nickel, underwent the C—H addition reaction.[35] Ethane also adds oxidatively to photo-excited copper atoms to form, apparently, C_2H_5CuH intermediate species; there was no spectroscopic evidence of CH_3, CH_3Cu, or $(CH_3)_2Cu$ species formed in this photolytic reaction.[37] It has been suggested that the failure of a metal like nickel to react with methane may be due to the non-formation of a metal-atom-methane complex.[35] However, it is not at all evident why cobalt and copper atoms would complex methane and a nickel atom would not. Perhaps, the lack of CH_4 addition for some of the metal atoms has more to do with the nature of the electronic state of the photoexcited metal atoms than any other factor or set of factors (photoexcited non-metal atoms such as sulphur also insert in the C—H bonds of hydrocarbons.

The preferred reaction to explore is the *thermal* reaction of a metal atom with a saturated hydrocarbon. For this type of study, the matrix isolation experiment has serious temperature constraints because the metal atoms condense to form dimers, trimers... and larger aggregates or clusters at relatively low temperatures. Actually, the iron dimer is reported to react with methane at −196 °C presumably to form CH_3FeFeH.[38] Also, Klabunde[62] has found that nickel aggregates formed from metal atoms react with saturated hydrocarbons

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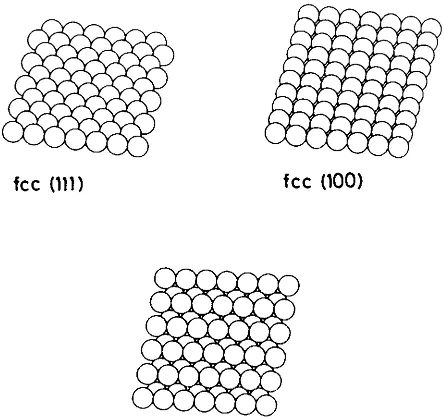
[62] S. C. Davis, S. J. Severson, and K. J. Klabunde, *J. Am. Chem Soc.*, 1981, **103**, 3024.

at the very low temperature of ~ −140 °C. Alternatively, the hydrocarbon reactions of metal atoms, metal dimers, *etc*., of established electronic states could be studied in the gas phase. Gas-phase studies of this character have been made but not based on hydrocarbon reactants.

D. Metal Surfaces.—(i) *Introduction*. A major objective in our study of metal surfaces has been the identification of the key factors that facilitate carbon–hydrogen bond breaking. To control separately the variables of surface crystallography (topography), surface composition (carbon, oxygen or sulphur impurity), and surface coverage by the adsorbate, ultra high vacuum conditions and techniques were employed. Some of the crystal planes examined are illustrated in Figures 9—11.

To anticipate the results from all studies to date, the proximal effect appeared to be the most important one in eliciting facile carbon–hydrogen bond breaking reactions.

(ii) *Saturated Hydrocarbons*. Atomically flat metal planes such as the (111) and (100) planes of face-centred cubic metals like nickel[63] and platinum[63] and the close-packed (0001) plane of hexagonal close-packed ruthenium metal[30] are remarkably non-reactive towards cyclohexane under ultra high vacuum conditions (cyclohexane desorption from the metal surfaces at these low pressures is fast at temperatures in the range of −60 to ~0 °C for these flat metal planes). Stepped nickel surfaces such as Ni(110) and Ni9(111) × (111) were similarly nonreactive.



fcc (111)

fcc (100)

fcc (110)

Figure 9 *Shown above are the three low Miller index planes for a face-centred cubic lattice. For the* (111) *close-packed plane, the co-ordination number of surface metal atoms is* 9, *for the flat* (100) *plane, the co-ordination number is* 8 *and for the super-stepped* (110) *plane, the co-ordination number of metal atoms in step 'sites' is* 7 (*those just below in the next plane have a co-ordination number of* 11)

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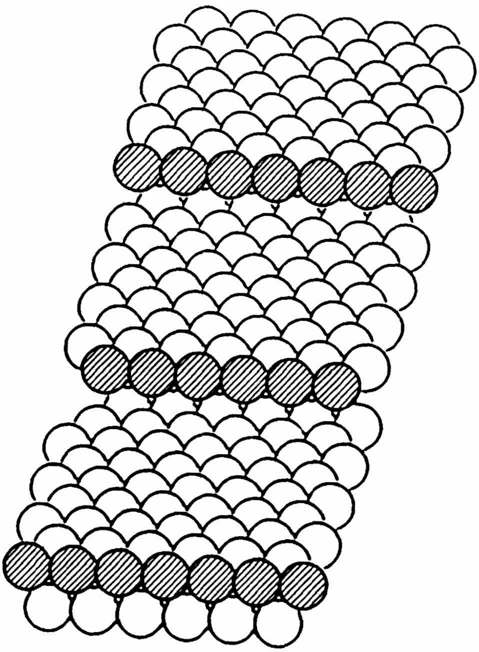
[63] M.-C. Tsai, C. M. Friend, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1982, **104**, 2539.



fcc 9(111)x(111)

Figure 10 *This is a depiction of a stepped surface in which terrace atoms (clear circles) are close packed and have a co-ordination number of 9. The steps are 1 atom high and the step atoms (hatched circles) have a co-ordination number of 7. In this particular surface, the width of the steps is nine atoms*

More reactive was the stepped platinum surface, 6(111) × (111) which effected modest conversions of cyclohexane into chemisorbed benzene at $\sim 20\,°C$.[63] A general discussion of stepped surface reactivity has been presented by Somorjai.[64]

In sharp contrast, the reconstructed Ir(110) surface, Ir(110)—(1 × 2), is very reactive toward saturated hydrocarbons as shown by Weinberg and co-workers.[65,66] Saturated hydrocarbons like ethane and n-pentane irreversibly chemisorb — only hydrogen, H_2, desorbs as the temperature is raised. Spectroscopic studies indicated that dehydrogenation of the adsorbed saturated hydrocarbons begins at temperatures of $\sim -140\,°C$. This extraordinary reactivity cannot be traced solely to unique electronic properties of this surface: the reconstructed surface is of lower surface free energy than the (110) plane. The

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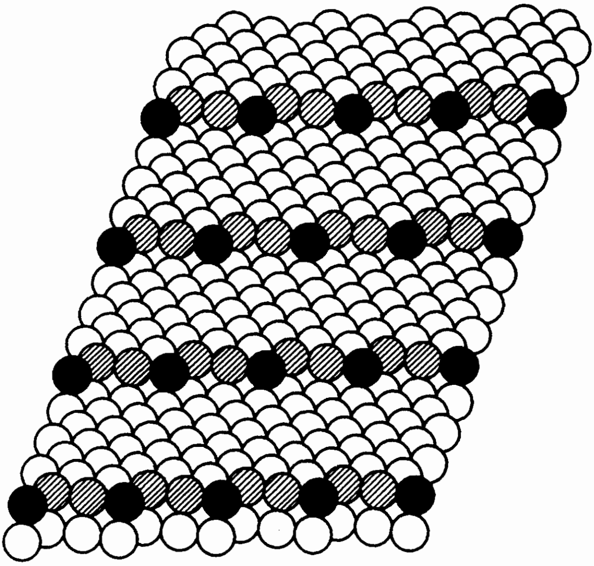
[64] G. A. Somorjai, 'Chemistry in Two Dimensions: Surfaces', Cornell University Press, Ithaca, N.Y. 1981, Chapt. 8.

[65] T. S. Wittrig, P. D. Szuromi, and W. H. Weinberg, *J. Chem. Phys.*, 1982, **76**, 716.

[66] T. S. Wittrig, P. D. Szuromi, and W. H. Weinberg, *J. Chem. Phys.*, 1982, **76**, 3305.



fcc (10,8,7)

Figure 11 *In this surface there are terrace atoms (clear circles), step atoms (hatched circles) and kink atoms (dark circles). The co-ordination number of the atoms at the kink sites is* 6

reconstructed surface is believed to have a saw-toothed form; one possible representation is depicted in Figure 12. Coincidentally, or possibly not, hydrocarbon dehydrogenation on this iridium surface begins at the same temperature observed for saturated hydrocarbon reactions with small nickel particles.[62]

The low reactivity of atomically flat metal planes (under ultra-high vacuum conditions) may have a largely stereochemical genesis. The primary chemisorption bond(s) for the molecular chemisorption state of saturated hydrocarbons on metal surfaces probably is the multicentre C—H—M interaction. On flat metal surfaces, most of these multicentre interactions may be of the open and nearly colinear three-centre form and would not be directly productive with respect to C—H bond breaking (see earlier discussion of alkane chemisorption states). On the more deeply grooved or grossly irregular surfaces, some C—H—M interactions may be forced to take closed form, $\overset{\diagup\mathrm{C}\diagdown}{\mathrm{M}_x\text{—}\mathrm{H}}$, which would be directly productive with respect to C—H bond breaking reactions. Stereochemistry is emphasized here but the actual differences among these classes of surfaces derive from interrelated geometric and electronic factors.

A reasonable projection based on the limited data for saturated hydrocarbon reactions on clean metal surfaces is that stereochemistry is important and the

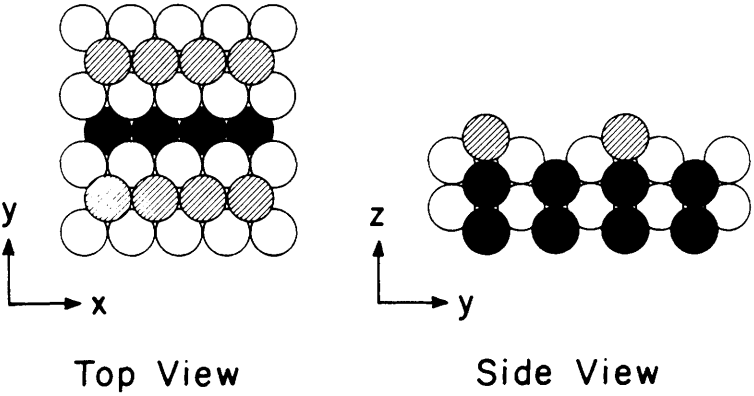
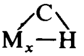


Figure 12 *Shown above is a top and side view of a* possible *model*[65,66] *for reconstructed* Ir(110) *surface,* Ir(110)-(1 × 2). *For an alternative, see the model proposed by H. P. Bonzel and S. Ferrer* (Surf. Sci., 1982 **118**, L263)

key variable is surface topography whereby the extent of closed multicentre  $\overset{\diagup C \diagdown}{M_x{-}H}$ interactions is determined. The proximal effect so evident in C—H oxidative addition reactions in molecular metal complexes may be important also in metal surface reactions of saturated hydrocarbons.

(iii) *Benzene.* Benzene chemisorbs on atomically flat, clean metal surfaces like Ni(111), Ni(100), Pt(111), and Pt(100) by interaction of the ring π and π^* orbitals with appropriate metal surface orbitals; the C_6 ring is largely parallel to the surface plane.[67-71] Whether the benzene C—H hydrogen atoms are nearly in the C_6 plane or displaced either toward or away from the surface cannot be established from available spectroscopic data (nor is this point likely to be established in the near future). In any case, all the chemical studies suggest that the benzene C—H hydrogen atoms are relatively distal to the surface plane.[72-74] There is no detectable evidence of C—H bond breaking, reversible or irreversible, for benzene chemisorbed on Ni(111) or Ni(100) up to temperatures of ~115 °C and ~220 °C respectively.[72] These are the respective temperatures at which benzene thermally desorbs from these surfaces; *i.e.*, there is no benzene C—H bond breaking on these flat planes until a temperature is attained where benzene desorption from the surface begins. Similar chemistry was observed for benzene chemisorbed on Pt(111). At temperatures close to molecular desorption, there

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[67] S. Lehwald, H. Ibach, and J. E. Demuth, *Surf. Sci.*, 1978, **78**, 577.
[68] J. C. Bertolini and J. Rousseau, *Surf. Sci.*, 1979, **89**, 467.
[69] J. E. Demuth and D. E. Eastman, *Phys. Rev. B.*, 1976, **13**, 1523.
[70] F. P. Netzer and J. A. Matthew, *Solid State Commun.*, 1979, **29**, 209.
[71] E. L. Muetterties and M.-C. Tsai, *Bull. Soc. Chim. Belg.*, 1980, **89**, 813.
[72] C. M. Friend and E. L. Muetterties, *J. Am. Chem. Soc.*, 1981, **103**, 773.
[73] M.-C. Tsai and E. L. Muetterties, *J. Am. Chem. Soc.*, 1982, **104**, 2534.
[74] M.-C. Tsai and E. L. Muetterties, *J. Phys. Chem.*, 1982, **86**, in press.

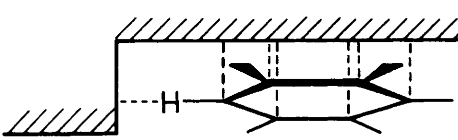

Figure 13 *On stepped surfaces, the benzene molecule is π-bonded much as it is on atomically flat surfaces. However, because of the steps, some of the benzene molecules have substituent atoms that will closely approach step metal atoms. Because of this proximal effect, some of the benzene molecules should undergo* C—H *bond breaking at relatively low temperatures. On a stepped nickel surface, these bond breaking reactions are irreversible under ultra high vacuum conditions and do occur at temperatures below* 100 °C

should be some thermally excited states in which benzene C—H hydrogen atoms approach close to surface metal atoms. This stereochemical feature probably accounts for C—H bond breaking processes competitive with molecular desorption on these flat nickel surfaces.

Some irreversible C—H bond breaking for chemisorbed benzene on the stepped nickel surface, 9(111) × (111), occurs at low temperatures.[72] The extent is about 10%. This is attributed to the features of a stepped surface whereby benzene π bound on the flat terraces necessarily has some benzene C—H hydrogen atoms close to stepped metal sites (Figure 13).

The proximal effect appears to be a dominant factor for benzene C—H bond breaking processes on metal surfaces.

(iv) *Toluene.* Toluene initially should chemisorb on flat metal surfaces in an electronic and stereochemical fashion analogous to benzene,[72] but low temperature angle-resolved photoemission studies will be required to support this presumption. At moderate temperatures, toluene appears to be converted into benzyl and H surface-bound species. Labelling studies with $C_6H_5CD_3$ and $C_6D_5CH_3$ species support this proposal of benzyl formation for Ni(111), Ni(100), and Pt(100) surfaces.[72,74] Conversion of a π-toluene molecule into a π-benzyl species is fully anticipated in terms of the proximal effect: if toluene initially π-bonds to a flat surface with the C_6 aromatic ring nearly parallel with the surface plane, then an aliphatic CH_3 hydrogen atom will be forced into close proximity to surface metal atoms and the associated C—H bond should cleave to give M(*xxx*)—$CH_2C_6H_5$ and M(*xxx*)—H. All seven of the p_z orbitals associated with the benzyl radical could then interact with appropriate, symmetry-adapted surface-metal orbitals. Spectroscopic (vibrational and photoemission) tests of the putative π-benzyl surface state are in progress.

Toluene chemisorption (submonolayer coverage) is fully irreversible on the low Miller index planes of nickel. Rapid heating of such crystal planes with chemisorbed toluene under ultra-high vacuum conditions yields only H_2(g) and a surface nickel plane with chemisorbed carbon atoms. Rate of H_2 desorption

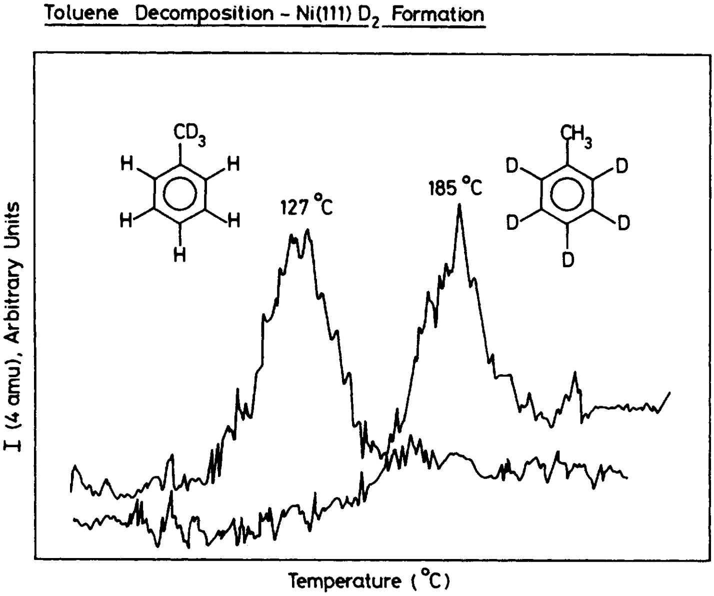

Figure 14 *Toluene irreversibly chemisorbs on the* Ni(111) *surface. As the temperature is raised,* C—H *bonds are broken and ultimately hydrogen is desorbed from the surface. In the thermal decomposition of perdeuterotoluene, there are two* D_2 *thermal desorption maxima of relative intensities* 3 *and* 5 *at* ~130 *and* 185 °C. *Separate experiments with the specifically labelled toluene molecules,* $CD_3C_6H_5$ *and* $CH_3C_6D_5$, *established a regioselective bond breaking sequence. The thermal desorption spectra of deuterium,* D_2, *from the thermal decomposition of the two labelled toluene molecules on the* Ni(111) *surface are shown here. Deuterium from the* $CD_3C_6H_5$ *molecule appears only in the low temperature region whereas, as shown in the second experiment with* $CH_3C_6D_5$, *there is no deuterium desorption in the low temperature range; deuterium appeared only in the high temperature region characteristic of aromatic* C—D *bond breaking*

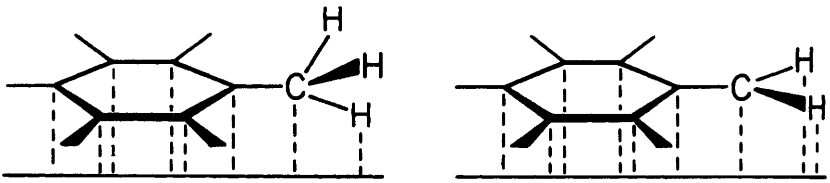

Figure 15 *Toluene irreversibly chemisorbs on flat nickel surfaces. The initial chemisorption state probably comprises π-bonding analogous to that proposed for benzene on such surfaces but this necessarily places methyl* C—H *atoms close to the surface. This should lead to irreversible* C—H *bond breaking at relatively low temperatures. It has been proposed that one of the first states generated in the dehydrogenation of toluene on flat surfaces involves the benzyl species which could be very strongly bonded to the metal atoms in such flat surface planes as shown in the figure above*

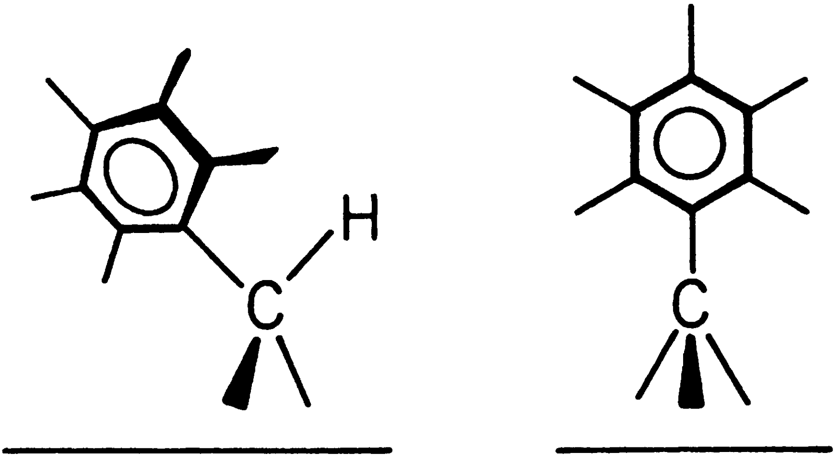

Figure 16 *On the two flat* Ni(111) *and* Ni(100) *planes, toluene undergoes regioselective* C—H *bond breaking whereby all aliphatic bonds are cleaved before any aromatic* C—H *bond are broken* (*Figure* 14). *The composite sequences shown in Figures* 15 *and* 16 *depict* possible *models for intermediate states up to the state where all aliphatic* C—H *bonds have been broken. Spectroscopic studies are required to resolve precisely stereochemical issues*

under these conditions has two maxima, with a lower temperature maximum of intensity three and a higher one of intensity five for the two flat planes, (111) and (100), but only a single maximum for the 'super stepped' nickel (110) surface. A study of the thermal decomposition of $C_6H_5CD_3$ and $C_6D_5CH_3$, monitoring the desorption profiles of H_2, D_2, and HD, rigorously established a fully regioselective C—H bond-breaking sequence in which all aliphatic C—H bonds were broken before any aromatic C—H bonds were broken for the two flat Ni(111) and Ni(100) planes (Figure 14).[72] One possible stereochemical pathway is shown in Figures 15 and 16 for the overall dehydrogenation process.

(v) *Pyridine.* Pyridine chemisorbed on Ni(100) undergoes two thermal processes: desorption and decomposition of the pyridine molecule to give H_2(g), N_2(g), and Ni(100)—C.[75] In the decomposition of chemisorbed pyridine, there are three H_2 desorption maxima of relative intensities, one, two, and two. A study of the thermal decomposition of [2,6-$^2H_2$]pyridine, [3,5-$^2H_2$]pyridine, and [4-$^2H_1$]pyridine established that the low temperature hydrogen maximum of intensity one was basically only composed of D_2, H_2, and H_2, respectively, for the three labelled pyridines. These results incisively indicated facile formation of a 2-pyridyl surface species from an initially molecularly bound pyridine. If some or all of the initially bound pyridine molecules are bonded to the surface through the nitrogen atom, with the ring plane normal to or at least nominally tipped away from the surface plane, then the proximal effect, if operative, should lead to formation of a 2-pyridyl surface species (Figure 17), a feature fully

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[75] R. M. Wexler, M.-C. Tsai, C. M. Friend, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1982, **104**, 2034.

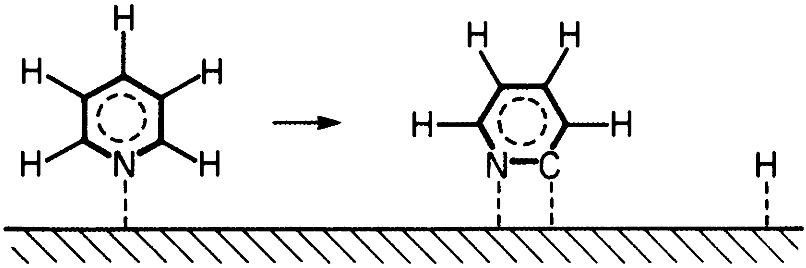

Figure 17 *On the* Ni(100) *surface, pyridine chemisorbs initially as a molecule and is then readily converted into a 2-pyridyl species as shown in the drawing. This process is reversible and is relatively fast at temperatures* at least as low as 70 °C

consistent with the experimental results.[75] Note that some pyridine molecules, especially at low surface coverages, could be largely π bound in a plane parallel to the surface plane, provided that such a state were in rapid equilibrium with molecular states in which the pyridine bonding were largely, or solely, through the nitrogen atom. Again, careful spectroscopic studies are required to establish the partitioning among η^6-NC_5H_5, η^1-NC_5H_5, and η^2-2-pyridyl chemisorption states.

The reversible (thermal) desorption of pyridine is preceded by the pre-equilibrium of molecularly bound pyridine with a 2-pyridyl state.[75] If pyridine is co-chemisorbed with D_2 on Ni(100), the fraction of pyridine molecules that desorb as pyridine in the thermal desorption experiment consist of C_5H_5N, C_5H_4DN, and $C_5H_3D_2N$ (but no $C_5H_2D_3N$) molecules. The stereochemistry in this H—D exchange was incisively established in the H_2 and D_2 co-chemisorption experiments with the three labelled pyridines as shown in Table 2. Only the α-C—H hydrogen atoms are exchanged in the pre-equilibrium step.

All the observable chemistry[75] for pyridine on Ni(100) can be summarized as shown in Figure 18; chemistry that is fully explicable in terms of the proximal effect.

Table 2 *Reaction of Ni(100)—pyridine with* D_2 *and* H_2

Starting pyridine	*Hydrogen added*	*Pyridines formed in the thermal desorption experiment*
[2,6-$^2H_2$]pyridine	H_2	[$^2H_0$], [$^2H_1$], and [$^2H_2$]pyridine
	D_2	[$^2H_2$]pyridine only
[3,5-$^2H_2$]pyridine	H_2	[$^2H_2$]pyridine only
	D_2	[$^2H_2$], [$^2H_3$], and [$^2H_4$]pyridine
[4-$^2H_1$]pyridine	H_2	[$^2H_1$]pyridine only
	D_2	[$^2H_1$], [$^2H_2$], and [$^2H_3$]pyridine

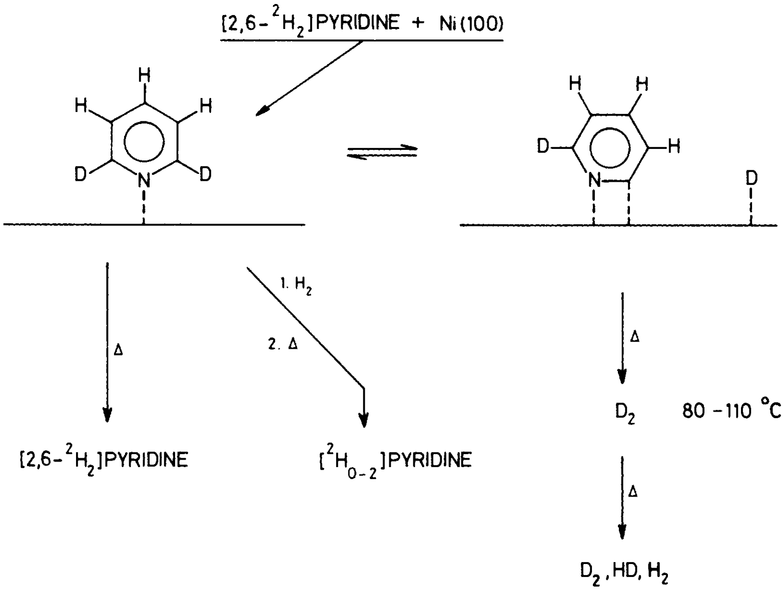

Figure 18 *The dynamic surface behaviour of pyridine on* Ni(100) *is summarized in the above drawing with the specifically labelled molecule,* $[2,6\text{-}^2H_2]$*pyridine*

(vi) *Cyclic Olefins and Cyclic Polyenes.* Initial chemisorption of a cyclic olefin such as cyclohexene should be based on a π bound state as shown in (10). Irrespective of the C_6 ring conformation in the π bound state, there should be close approach of methylene C—H hydrogen atoms to the surface metal atoms. Ultimately, the sequential dehydrogenation process should generate chemisorbed benzene, a process well established in heterogeneous catalysis. In fact, the chemisorption of cyclohexene on a variety of nickel and platinum surface planes resulted in benzene formation at temperatures ranging from 20 to 100 °C, as established by benzene displacement from the crystal into the gas phase by the strong field ligand, trimethylphosphine.[63]

Conceptually, a cycloalkene or cyclic polyene should chemisorb on a flat or nearly flat metal surface and then undergo a series of dehydrogenations to generate a delocalized C_nH_n chemisorbed species [equation (10)]

$$M{-}C_nH_m \longrightarrow H_{m-n}{-}M{-}C_nH_n \qquad (10)$$

In support of this generalization is the observation that cyclo-octene and cyclo-octa-1,5-diene are converted into cyclo-octatetraene as demonstrated by trimethylphosphine displacement of cyclo-octatetraene from the metal surface states from cyclo-octene and from cyclo-octa-1,5-diene.[76] Cyclobutene chemisorption did not lead to a cyclobutadiene species that could be either thermally

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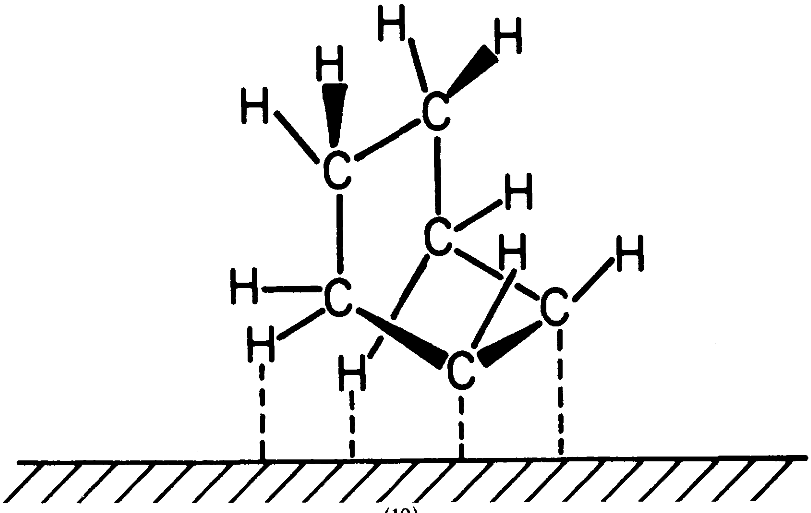
[76] M.-C. Tsai, J. Stein, C. M. Friend, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1982, **104**, 3533.



(10)

desorbed or displaced by strong field ligands. These last experiments were indeterminate; spectroscopic studies are required (angle resolved vibrational and photoemission experiments).

Cycloheptatriene appears to chemisorb onto metal surfaces with facile conversion into H—M—C_7H_7.[76] Cyclopentane probably chemisorbs and reacts to form H—M—(C_5H_5) but again spectroscopic studies (in progress) are required for verification of this hypothesis.[76]

(vii) *Acetylene.* Acetylene chemisorbs initially onto metal surfaces in a π bonded fashion. Subsequent to chemisorption a series of processes may occur. These processes may include dehydrogenation, [1,2] hydrogen atom shifts and hydrogenation. The rates of such processes are a sensitive function of temperature, metal *d* level occupancy and metal surface topography.[77-93] Chemisorbed

[77] J. E. Demuth, *Surf. Sci.*, 1979, **84**, 315.

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species like $C{=}CH_2$, $CH{=}CH_2$, and $C{-}CH_3$ have been proposed for specific stages of the Pt(111) reaction with acetylene (and ethylene).[77-93] The 'final' state, stable at moderate temperatures, appears to be best characterized as μ_3-ethylidyne with the C—C vector normal to the surface plane and directed towards three-fold sites.[85,86,93]

Reaction of $Pt(100){-}C_2H_2$ with D_2 at 20—50 °C resulted in rapid H—D exchange at the C—H sites with *no net reaction of either hydrogenation or dehydrogenation.*[94] In contrast, $Pt(111){-}C_2H_2$ reacted with D_2, but with no H—D exchange between C—H and Pt—H sites, to give a new state that compositionally appeared to be $Pt(111){-}C_2H_2D$,[94] presumably the aforementioned[85,86,93] $Pt(111){-}CCH_3$ state. These results of the isotopic labelling studies can be interpreted in terms of a proximal effect. Apparently on Pt(111), the C—H hydrogen atoms, for all states beginning with π-bound acetylene and ending with the ethylidyne complex, are relatively far removed from the surface metal atoms and undergo no H—D exchange reactions. However, on Pt(100), at least one of the C—H hydrogen atoms in the π-bound acetylene state must closely approach the surface plane. One possible geometric rationalization is as follows. The initial π-bound acetylene can tip with respect to the surface plane if one carbon atom drops into a three-fold site on Pt(111) or a four-fold site on Pt(100). Because of the size difference of these three sites, the C—C tipping with respect to the surface plane can be ~45° for Pt(100) but only ~13° for Pt(111) (Figure 19).[94] Thus, in such a tipped configuration, one C—H hydrogen atom will be quite close to the surface metal atoms on $Pt(100){-}C_2H_2$ but both C—H hydrogen atoms will be relatively far removed for $Pt(111){-}C_2H_2$. In fact, a low-energy electron diffraction study of $Pt(100){-}C_2H_2$ was interpreted in terms of such a tipped configuration with an angle of ~50° between the C—C vector and the surface plane.[95]

For species like $C{=}CH_2$ and $C{-}CH_3$ on the Pt(111) surface, none of the C—H hydrogen atoms will be close to the surface if the C—C bond vector is normal or nearly normal to the surface plane, a plausible geometric feature for such chemisorbed species.

(viii) *Acetonitrile.* On the atomically flat Ni(111), acetonitrile chemisorbs in a nearly fully reversible fashion; under ultra high vacuum conditions acetonitrile, initially chemisorbed at 20 °C, desorbs at ~90 C.[96] Spectroscopic[96] and diffraction[97] data for $Ni(111){-}NCCH_3$ and $Ni(100){-}NCCH_3$ indicate that the nitrile is bridge bonded through the nitrogen atom to two, three, or four surface atoms. In this configuration, the acetonitrile has the C—N bond more or less normal to the surface plane. Accordingly, the methyl hydrogen atoms are relatively far removed from the metal surface atoms.

In contrast to $Ni(111){-}NCCH_3$, $Ni9(111)\times(111){-}NCCH_3$ displays only about 80—90% reversible thermal desorption of acetonitrile.[96] The competing

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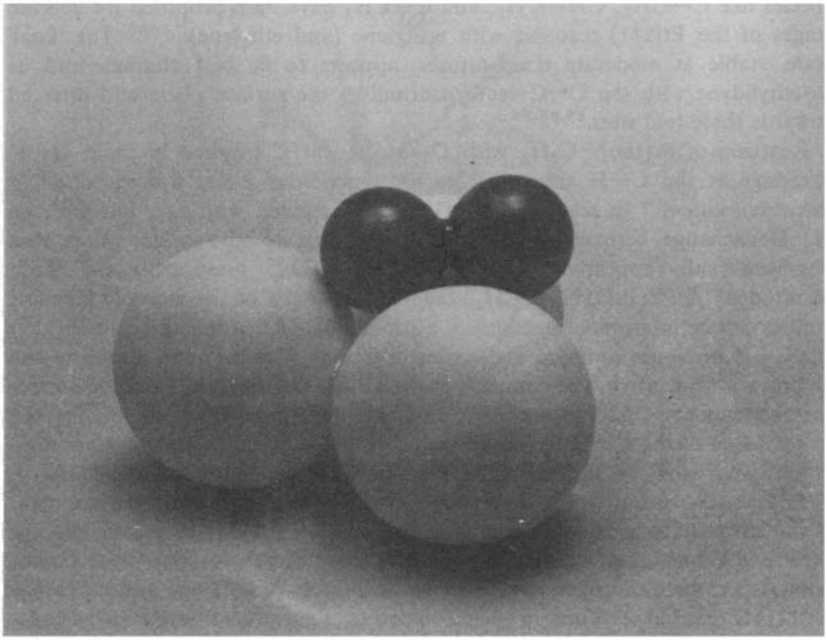
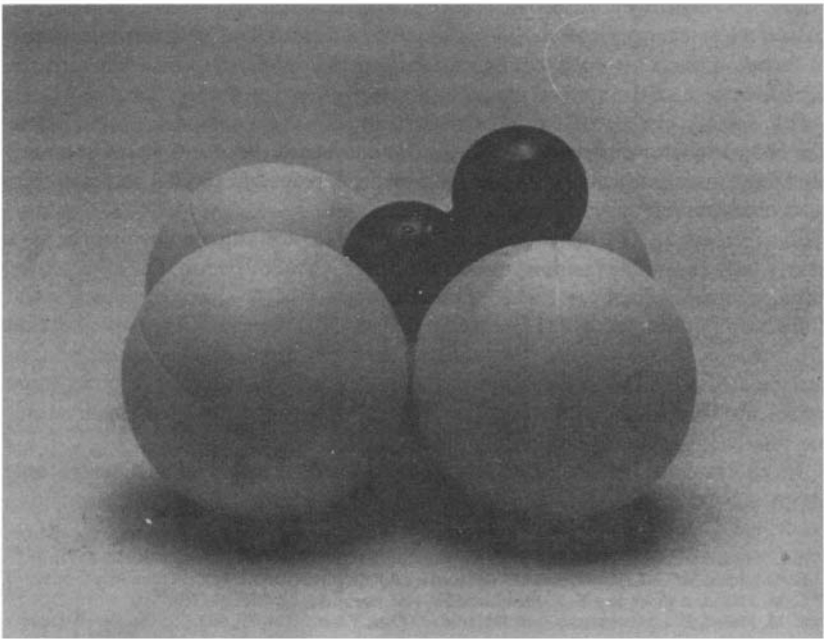
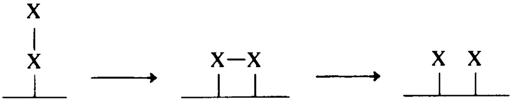




process is acetonitrile thermal decomposition *via* C—H bond scission. This difference between these two surfaces is attributed to close approach of methyl hydrogen atoms, of chemisorbed acetonitrile, to the surface metal atoms specifically at step sites on the stepped surface (Figure 20). On the super stepped Ni(110) surface, acetonitrile chemisorption is nearly irreversible.[96]

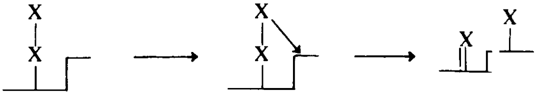
(ix) *Diatomic Molecules.* Diatomic molecules like H_2, N_2, NO, and CO may initially chemisorb on a flat metal surface with the bond vector normal or parallel. Data and theory[29] suggest that the dominant state for these diatomic molecules on flat surfaces is with the bond vector normal to the surface. Hence to proceed from a molecular chemisorption state to a dissociated chemisorption state [equation (11)] requires some



(11)

activation energy — small for H_2 and larger for a molecule like CO.

Interestingly, there are data that indicate that dissociative chemisorption of diatomic molecules proceeds more readily on stepped metal surfaces than on atomically flat metal surfaces.[6,98–102] This again may reflect the operation of the proximal effect [equation (12)].



(12)

(x) *Conclusions.* Essentially all our observations on C—H bond breaking processes on nickel and platinum surfaces can be explained simply by a proximal effect: if hydrogen atoms of a chemisorbed hydrocarbon or hydrocarbon derivative are forced close to the surface metal atoms or readily approach the surface in thermally excited states, then C—H bond breaking will tend to occur. Thermodynamically, these are favourable processes for these transition metals under high vacuum conditions (the reverse reaction requires a relatively high

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Figure 19 *Shown opposite are photographs of scale models of three-atom and four-atom sections of* Pt(111) *and* Pt(100) *with the two carbon atoms (smaller dark spheres) of an acetylene adsorbate that illustrates topographical features for potential tipping of the* C—C *bond vector with respect to the surface plane. A constraint that both carbon atoms maintain a bonding interaction with surface platinum atoms is imposed here. The maximal tipping angles are approximately* 13 *and* 45° *for the* (111) *and* (100) *surfaces respectively. These topological differences between* Pt(111)—C_2H_2 *and* Pt(100)—C_2H_2 *may account for their qualitatively different chemical behaviour*

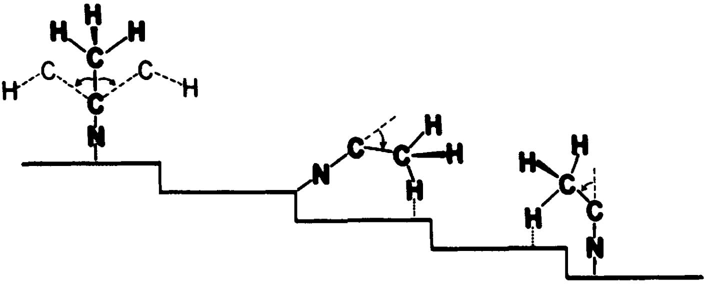

Figure 20 *On flat nickel surfaces, acetonitrile chemisorbs associatively,* i.e., *the chemisorption state is molecular in character. On these flat metal surfaces, very little* C—H *bond breaking occurs even at temperatures where acetonitrile desorbs molecularly from the surface. In contrast, on stepped nickel surface, there is evidence of* C—H *bond breaking at low temperatures. This difference can be explained in a stereochemical context in that* C—H *hydrogen atoms can more readily approach step metal atoms than terrace atoms as schematically outlined above*

thermodynamic activity of the chemisorbed hydrogen atoms, a feature that is enhanced by higher hydrogen pressure).

The observed variation in behaviour of chemisorbed benzene, toluene, and pyridine on flat metal surfaces can be traced to the proximal effect. Similarly, the variation in behaviour of molecules like benzene, toluene, acetylene, and acetonitrile as a function of surface crystallography can also be explained in terms of a proximal effect, *e.g.*, the much greater extent of C—H bond breaking for molecules like benzene and acetonitrile on stepped surfaces can be explained most readily in terms of stereochemical factors.

There has been a general assumption, often stated in the literature, that surface metal atoms at stepped or kinked sites possess a unique reactivity because of electronic effects and of lower co-ordination numbers. This assumption may well be correct but it has not been established unambiguously by either experiment or theory. Possibly, the proposed proximal effect is a very important factor that embraces both an electronic and a geometric effect in these stepped-surface reactions.

Acknowledgement. The research on metal–hydrocarbon chemistry has been supported generously by the National Science Foundation and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48. I am also indebted to Professors R. G. Bergman, W. A. G. Graham, W. D. Jones, M. L. H. Green, and W. H. Weinberg for information about unpublished work, Professor R. Hoffmann for a discussion of the oxidative addition reaction, the Miller Institute for Research in Basic Science for a grant in the form of a Miller Professorship, and the students in my research group. Constructive comments concerning isotope effects by Dr. A. Shusterman are especially acknowledged.