by way of initial π-coordination of the olefin. Evidence with $Re(PPh_3)_2H_7$,[35] $CpRe(PMe_3)_3$,[25c,d] and $Fe(dmpe)_2H_2$[36] all indicates that a direct oxidative addition pathway exists in addition to π-coordination. Furthermore, reductive elimination of the vinyl hydride can also lead directly to the π-olefin complex. Consequently, there must be two independent pathways for forming an olefin complex from free olefin and a coordinatively unsaturated metal: (1) direct π-complexation and (2) vinylic oxidative addition followed by intramolecular reductive elimination. It is also interesting to note that the microscopic reverse of this sequence implies that olefin dissociation from the metal also can occur by two pathways, one of which involves intramolecular vinylic activation followed by reductive elimination of free olefin!

Finally, the factors controlling intramolecular activation of the C–H bond of a ligand remains poorly understood in a general sense. It is still not clear why species such as $[Fe(PMe_3)_4]$[37] and $[(C_5Me_5)Re(PMe_3)_2]$[23c] undergo cyclometalation whereas $[(C_5Me_5)Rh(PMe_3)]$ and $[(C_5Me_5)Ir(PMe_3)]$ do not. It is also not clear why $[(C_5Me_5)_2W]$ metalates the C_5Me_5 methyl group[38] whereas $[(C_5Me_5)Rh(PMe_3)]$ and $[(C_5Me_5)Ir(PMe_3)]$ do not. It may be that relief of steric compression is the driving force for metalation of the PMe_3 ligand, a force that is not so important in the $[(C_5Me_5)M(PMe_3)]$ intermediates. The more crowded $[(C_5Me_5)Re(PMe_3)_2]$ intermediate appears to sit in the middle, with both phosphine metalation and intermolecular hydrocarbon activation in balance. Further elucidation of this important side reaction is warranted.

Acknowledgement is made to the U. S. Department of Energy (DE-FG02-86ER13569) for their partial support of this work. W.D.J. also thanks the Alfred P. Sloan and Camille and Henry Dreyfus Foundations for awards.

Registry No. $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$, 81971-46-2; $(C_5Me_5)Rh(PMe_3)(C_6D_5)D$, 84624-02-2; $(C_5Me_5)Rh(PMe_3)(CH_3)H$, 84624-01-1; $(C_5Me_5)Rh(PMe_3)H_2$, 84624-03-3; C_6H_6, 71-43-2; $CH_3CH_2CH_3$, 74-98-6; $(C_5Me_5)Rh(PMe_3)(CH_2CH_2CH_3)H$, 84624-04-4; $(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4Me)H$, 81971-48-4; $(C_5Me_5)Rh(PMe_3)(m\text{-}C_6H_4Me)H$, 81971-47-3; $(C_5Me_5)Rh(PMe_3)(C_6H_3\text{-}2\text{-}CH_3\text{-}5\text{-}CD_3)H$, 88704-02-3; $(C_5Me_5)Rh(PMe_3)(C_6H_3\text{-}2\text{-}CD_3\text{-}5\text{-}CD_3)H$, 88704-03-4; $(C_5Me_5)Rh(PMe_3)(C_6H_3\text{-}2\text{-}CH_3\text{-}5\text{-}CD_3)Br$, 88704-30-7; $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$, 88704-00-1; $t\text{-}Bu\text{-}p\text{-}C_6H_4\text{-}Bu\text{-}t$, 1012-72-2; $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_6H_3\text{-}2,5\text{-}(Bu\text{-}t)_2)$, 118831-49-5; D_2, 7782-39-0; $(C_5Me_5)Rh(PMe_3)(CH_3)D$, 118831-50-8; $(C_5Me_5)Rh(PMe_3)(C_6H_3\text{-}3,5\text{-}Me_2)H$, 88704-08-9.

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Possible Surface Intermediates in Alkane Reactions on Metallic Catalysts

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The knowledge of the mechanism of action of most heterogeneous catalysts remains limited. At the most primitive level, the overall product distribution is often known, but the nature of the catalyst–reactant interactions remains unknown. In a few cases, a more detailed proposition of mechanism can be advanced, but these propositions remain modest and ineffective in comparison with mechanistic details that have been developed in molecular organic and organometallic chemistry. It must be recognized, however, that, by comparison with strictly molecular systems, heterogeneous catalysts are intrinsically much more complicated.

Concerning metal catalysis, the making and breaking of C–H and C–C bonds by metal catalysts is a domain where our knowledge appears to be rather good (e.g., hydrogenation of olefins, skeletal rearrangement of hydrocarbons). Although the skeletal rearrangement of hydrocarbons on metals has been known for a long time,[1,2] the main questions arising are the nature of the intermediate species responsible for the observed kinetics (various mechanisms) and the nature of the sites, correlated, for instance, to particle-size effects.[3]

A detailed description of the two main classes of reaction mechanisms, cyclic and bond shift, can be made by the use of carbon-13. Metallacyclobutanes, metallacarbenes, and metallacarbynes were proposed as

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precursors in bond shift and "cyclic isomerizations" of hydrocarbons on metals.[4] These proposed mechanisms account for a number of experimental facts: selectivity, structural effects, and kinetic data which could not be explained previously.

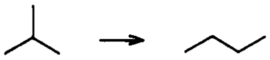
The proposed species require one or several surface metal atoms with high coordination number, such as those located on the edges or corners of the crystallites. This statement results from extensive work on the reaction mechanisms of skeletal isomerization of hydrocarbons on metals which led to the conclusions that, on large particles of platinum[5,6] and on iridium[7] catalysts, metallacarbynes are involved in the skeletal rearrangement. On the other hand, a straightforward interpretation was given for the catalytic behavior of small metallic particles of platinum where metallacarbenes are involved.

These species have their equivalent in coordination chemistry. As early as 1967,[8] carbyne intermediates were suggested. In 1970, Herisson and Chauvin[9] put forward a mechanism of olefin metathesis involving the disproportionation of metallacyclobutanes into metallacarbenes and π-bonded olefins. Kirmse[10] in 1971 and Fischer[11] in 1976 have studied and reviewed these species.

As carbenes and carbynes were proposed on platinum and synthesized on cobalt,[12,13] Zyade et al.[14] postulated recently the presence of an alkyne adsorbed species as an intermediate in these reactions (hydrocracking, hydrogenolysis, and isomerization). The cleavage of the alkyne produces surface carbynes, the driving force being a negative charge transfer to the hydrocarbon or an activated adsorption of hydrogen on these catalysts, which modifies the availability of the surface hydrogen.

Gault and Rooney have studied catalytic reactions with deuterium[15] on cobalt films. Metallacyclobutanes and metallacarbenes were invoked to explain the selective deuterolysis of *gem*-dimethyl groups in polymethylcyclopentanes with the incorporation of four deuterium atoms; surface carbyne species have also been implicated. Such cobalt species have analogues in homogeneous chemistry. Sutton and Dahl[16] determined the molecular structure of the organocobalt complex ($Co_3(CO)_9CCH_3$) synthesized by Markby et al.,[12] containing an aliphatic carbon atom triply bridged to three cobalt atoms. The molecular configuration ideally possesses C_{3v} symmetry and consists of an apical ethylidyne group CH_3C symmetrically coordinated by three Co–C σ bonds to a basal $Co_3(CO)_9$ fragment.

Scheme I



In 1980, Fritch and Vollhardt, with a trinuclear cobalt cluster,[13] described a general synthesis of biscarbyne clusters prepared by the direct cleavage of alkynes. On the other hand, in heterogeneous catalysis, carbyne recombination was postulated for the selective isomerization of methylpentanes on iridium catalysts[7] before such species had been isolated. Finally, Schrock et al.[17] and Chisholm et al.[18,19] have seen evidence for this dicarbyne recombination reaction represented as

$$2M{\equiv}CR \rightleftarrows (RC{\equiv}CR) + M{\equiv}M$$

Many bimetallic complexes contain an acetylene bonded with the two metal atoms.[20] The most commonly observed mode of acetylene bonding is the tetrahedral M_2C_2 core.[17] This type of reaction was also postulated on large platinum particles and on iridium catalysts for the selective dehydrocyclization of alkanes.[5,7] At this stage it is not intended to propose new mechanisms, rather, it seems more appropriate to try to combine the various past proposals with the intention of improving our understanding of hydrocarbon reactions over metallic catalysts. It is also not the intent of this paper to present a review. The reader is referred to ref 21–28 for further information on skeletal isomerization of alkanes.

As a general remark, all the different proposals for adsorbate intermediates in the reactions of hydrocarbons on metals are very similar.[29] Recent work of Frennet[30,31] on one side and Green[32,33] on another side pointed out two interesting problems relevant to the skeletal rearrangement of hydrocarbons. Frennet et al.[31] demonstrated that the coadsorption before rupture of the C–C bond surrounded by adsorbed hydrogen atoms and hydrocarbon entities is related to the number

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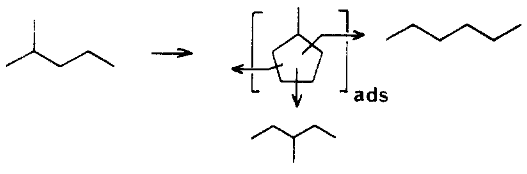
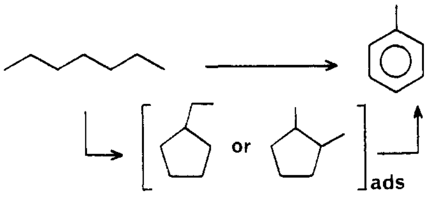
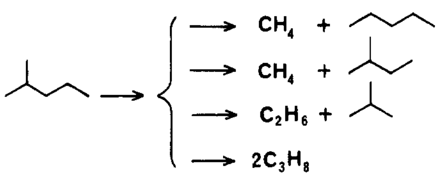
Scheme II



Scheme III



Scheme IV



of free adsorption sites (or landing sites) in a stationary regime, which is a function of the experimental parameters (pH_2, pHC, *T*). Furthermore, during the reaction, recombinations (or nonrecombinations) of adsorbed entities will occur specifically before the desorption step. All these factors affect the kinetics and are related to the active site, which is a major problem in heterogeneous catalysis.

Why not consider an active site as constituted by metal atoms plus hydrogen atoms and adsorbed hydrocarbon entities? For C–H activation, Brookhart and Green introduced an original formalism,[33] proposing the term "agostic" to refer specifically to situations in which a hydrogen atom is covalently bonded simultaneously to both a carbon atom and a transition-metal atom, such representation $M \leftharpoondown H — C$ differing from those proposed in the literature.[21,34,35] This agrees very well with the kinetic model proposed by Frennet et al.[31] where a reactive adsorption step occurs, followed by reactive surface dehydrogenation steps without any release of the sites occupied by adsorbed hydrogen.[36] These new concepts and data led us to reexamine the various mechanisms of skeletal rearrangement of hydrocarbons (cyclic mechanisms, bond-shift mechanisms, hydrogenolysis mechanisms) on the basis of adsorbed species deduced from organometallic concepts and data and to think of possible implications of agostic interactions in transition metal catalyzed reactions of hydrocarbons.

Approach to the Different Skeletal Rearrangement of Hydrocarbons Reaction Mechanisms on Metals

Two basic mechanisms were proposed for the skeletal isomerization of hydrocarbons on metals: (a) the bond-shift mechanism,[34] Scheme I, which corresponds to a simple carbon–carbon bond displacement, as in the Wagner–Meerwein rearrangement; and (b) the cyclic mechanism,[37] Scheme II, which involves dehydrocyclization to an adsorbed cyclopentane intermediate, followed by ring cleavage and desorption of the products. In addition to these two isomerization processes, when the main carbon chain has six or more carbon atoms, aromatization reactions[21] (Scheme III) can occur under more severe experimental conditions than those needed for the two previous reactions. Finally, hydrogenolysis reactions leading to smaller hydrocarbons occur as parallel or consecutive reactions (Scheme IV).

Table I
Kinetic Data for Isomerization and Hydrogenolysis Reactions on Low-Dispersed Platinum–Alumina Catalysts[a]

reaction	activation energy, kJ mol^{-1}	kinetic order with respect to hydrogen
cyclic mechanism		
n-pentane → *n*-pentane	299 ± 6	−3.4 ± 0.1
bond shift without hydrogenolysis		
n-pentane → isopentane	232 ± 6	−1.8 ± 0.1
isopentane → *n*-pentane	228 ± 6	−2.3 ± 0.1
bond shift with hydrogenolysis		
isopentane → isopentane	190 ± 6	−1.9 ± 0.2
isopentane → neopentane	189 ± 12	−1.65 ± 0.15
isopentane → propane + ethane	189 ± 12	−1.65 ± 0.2
n-pentane → propane + ethane	188 ± 12	−1.3 ± 0.2
demethylation		
isopentane → methane + isobutane	147 ± 12	−0.7 ± 0.1
isopentane → methane + *n*-butane	147 ± 12	−0.7 ± 0.1
n-pentane → methane + *n*-butane	161 ± 12	−0.6 ± 0.2

[a] References 21, 25, 38.

With the use of ^{13}C-labeled molecules, we have shown that the isomerization of hexanes and pentanes on platinum catalysts takes place according to two basic reaction mechanisms: the cyclic mechanism is favored on highly dispersed catalysts, and the bond-shift mechanism is favored on catalysts with large metal particles.[21,25] A classification of the various contact reactions of labeled *n*-pentane and isopentane was made according to their apparent activation energies as mentioned in Table I. A distinction was made between two groups of bond-shift isomerizations.[38] The first, including methyl shift and isopentane → neopentane isomerization, requires the same activation energy as hydrogenolysis of an internal C–C bond. The second group, including *n*-pentane → isopentane isomerization and the reverse reaction, requires higher activation energies.

For a hydrocarbon reaction to occur, it is necessary that both hydrocarbon molecule and hydrogen are adsorbed on the catalyst. The adsorbed hydrogen is itself a reactant, but the most important factor that needs to be specified in a detailed reaction mechanism is the way in which the hydrocarbon is adsorbed. Large negative orders versus hydrogen pressure have been found for the isomerization of pentanes (Table I)[38-40] and hexanes.[21] One explanation is that the rate-determining step is the rearrangement of highly dehydrogenated species. But with the kinetic model proposed by Frennet,[31] one does not need to invoke the presence of highly dehydrogenated species to explain

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the large variations in orders from highly negative to positive values obtained for heptane hydrocarbons.[36] In this model, Frennet et al. assumed that hydrocarbon and hydrogen both compete for chemisorption on the same "potential" sites of the surface; while hydrogen chemisorption requires only one of these sites, an ensemble of Z contiguous free potential sites is required for hydrocarbon adsorption.

In this case, the adsorption–desorption step is written

$$C_nH_{2n+2} + H_{ads} + ZS \rightleftarrows (C_nH_{2n+2},H)_{ads} \rightleftarrows (C_nH_{2n-1})_{ads} + WS + H_2$$

where H_{ads} is a chemisorbed hydrogen atom in equilibrium of adsorption–desorption with the gaseous hydrogen, that is associated with an "ensemble" of Z free potential sites that were assimilated to the hydrogen chemisorption sites.[31] W is the difference between the number of sites S occupied by the chemisorbed radicals and the number of sites needed to form the complex $(C_nH_{2n+2},H)_{ads}$. If the adsorption is rate determining, the adsorption rate equation is written $R_{ads} = k_{ads}\theta_H\theta_S{}^ZP_{HC}$. The model of Frennet et al. is in perfect agreement with the kinetic results obtained by ^{13}C labeling.

Proposed Precursor Species for Bond-Shift and Cyclic Mechanisms on Platinum Catalysts. Bond-Shift Mechanisms. At the beginning of the 1970s, intermediate species were proposed using as a basis gas-phase hydrocarbon structure and deuterium-exchange reactions. Anderson,[41] Gault,[42] and Rooney[43] could explain the bond-shift mechanism by assuming respectively the following species: (a) a precursor $\alpha\alpha\gamma$ triadsorbed species evolving to a bridged intermediate[41] as the π complex of Dewar; (b) an $\alpha\alpha\gamma$ triadsorbed precursor evolving to an adsorbed cyclopentane intermediate;[42] and (c) a σ-alkyl precursor evolving to a transient chemisorbed species having partial double-bond character;[43] the complex can first be considered as a three-center free radical. However, these species, which can explain the chain-lengthening or chain-shortening reactions without hydrogenolysis, were not able to explain a decrease or an increase of the initial carbon chain; perhaps the existence of a second mechanism which is less activated must be invoked.

With the use of labeled C_5 hydrocarbons, it has been possible to isolate the various elementary reactions and to determine their apparent activation energies. As mentioned in Table I, the results in the isopentane isomerization[38] pointed out that methyl migration and neopentane formation have the same apparent activation energy as hydrogenolysis of the internal carbon–carbon bonds for *n*-pentane and methylbutane. Another bond-shift mechanism was proposed involving metallacyclobutanes and metallacarbene species such as those proposed by Herisson et al.[9] for the mechanism of olefin metathesis. These species exist on large particles. The bond-shift mechanism occurring via metallacyclobutanes is less important on highly dispersed catalysts[39,40] such as 0.2% $Pt-Al_2O_3$ catalysts. On the other hand, the adsorbed metallacyclobutane complex was similar to the trimethylene di-σ-complex of platinum, as proposed by Chatt, which was readily formed from hexachloroplatinic acid and cyclopropane.[44]

Cyclic Mechanisms. With the use of C_6 labeled hydrocarbons and of methylcyclopentane, two types of cyclic mechanisms were found to occur on metallic catalysts. Considering adsorbed methylcyclopentanes as intermediates for ring opening, the selective mechanism results in ring opening where the carbon–carbon bonds with the tertiary carbon atom are not broken, and the nonselective cyclic mechanism leads to an equal chance of carbon–carbon bond rupture of all the bonds of the C_5 cyclic species intermediate. These mechanisms involving the hydrogenolysis of cycloalkanes are very sensitive to metallic particle size.[21] As the mean metallic diameter of the particles decreases, the relative contribution of the nonselective cyclic mechanism increases. The selective cyclic mechanism operates on large platinum particles and predominates on iridium catalysts.[4,7,25] The following species were proposed to take into account these results:[4] (a) the nonselective cyclic mechanism is due to a 1–5 dicarbene species; (b) a 1–5 dicarbyne species is responsible for the selective cyclic mechanism; the site involved for this mechanism is larger than the site for the dicarbene species.

As these two species have lost four and six hydrogen atoms, respectively, Finlayson et al.[35] and Pàal et al.[45] have raised some criticisms mainly based on the degree of dehydrogenation of these precursor species. The former group studied mechanisms of 1,5-dehydrocyclization and isomerization of tetramethylpentane and 3,3-dimethylpentane on iridium, rhodium, palladium, and platinum films. Thus Rooney proposed that these precursor species are simply bonded to one individual metal atom on the basis of results of deuterium-exchange reactions.[46]

Hydrogenolysis Reactions on Platinum and Platinum-Based Bimetallic Catalysts

Hydrogenolysis Reactions on Platinum Catalysts. Two bond-shift mechanisms and two cyclic mechanisms have been attributed to isomerization reactions, one mechanism in each group being favored on large metallic particles. Concerning the hydrogenolysis reaction, an important question arises: Are the hydrogenolysis reactions also structure sensitive on platinum catalysts?

To study these reactions we will consider the two groups of carbon–carbon bond ruptures introduced previously by Anderson:[26] (a) the *C_2-unit mode*, involving C–C bond rupture between only primary and secondary carbon atoms, noted respectively C_I and C_{II}; the rupture occurs for the carbon–carbon bonds C_I–C_I, C_I–C_{II}, and C_{II}–C_{II}; and (b) the *iso-unit mode*, involving rupture between two carbon atoms in which a tertiary and/or a quaternary carbon atom is present; C–C bond ruptures for the bonds C_I–C_{III}, C_I–C_{IV}, C_{II}–C_{III}, and C_{II}–C_{IV} are possible. The difference in the operation of these two modes is the number of hydrogen atoms present on the carbon atoms involved in the mechanism. It may also be that different adsorbed precursor species are involved for each mode. For the C_2-unit mode, at least two hydrogen atoms can be removed per

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Table II

catalyst	iso/C_2	ref	catalyst	iso/C_2	ref
Pt (755)	0.9	6	2% Pt-Al_2O_3	0.9	6, 47
Pt (311)	0.9	47	5% Pt-Al_2O_3	1.1	–
Pt (911)	0.85	6	0.2% Pt-Al_2O_3	1.2	–
Pt polycr	1.0	47	10% Pt-Al_2O_3	1.2	–

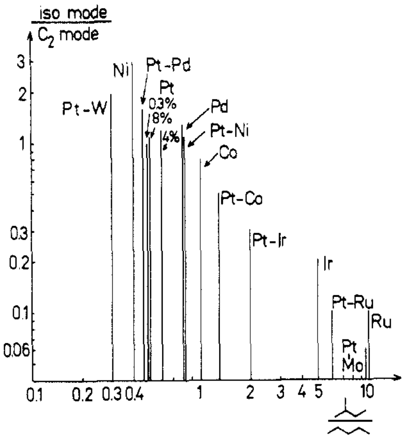

Figure 1. 2-Methylpentane hydrogenolysis reactions.

carbon atom, leaving behind adsorbed carbene species. This is not the case for the iso-unit mode where only one H atom is available on the C_{III}. For this hydrogenolysis mode, a σ-alkyl species could be involved.

For the reaction of 2-methylpentane on platinum,[6,47] the ratios iso/C_2 presented in Table II are obtained from the stoichiometric mole distribution of the cracked products. The "iso mode" is equal to the amount of propane plus pentane formed, and the "C_2 mode" is equal to isopentane plus isobutane formed.

We can see that the ratios iso/C_2 are nearly constant as a function of the crystallographic orientation of the platinum or as a function of the metallic dispersion varying between $D = 0.04$ for the 10% Pt by weight catalyst to $D = 1$ for the 0.2% Pt catalyst.[21] These results show that, on platinum catalysts, the selectivity in the hydrogenolysis reactions is not structure sensitive; the two proposed precursors, σ-alkyl and carbene species, need the same size for the active sites.

Hydrogenolysis Reactions on Platinum-Based Bimetallic Catalysts. An important question is, Can bimetallic platinum catalysts be compared to monometallic platinum catalysts? Results obtained with 2-methylpentane are summarized in Figure 1 and Table III. The data show that the C_2-unit mode is favored on Pt-Ir, Pt-Mo, Pt-Co, and Pt-Ru catalysts, and the iso-unit mode is favored on Pt-Ni, Pt-W, and Pt-Pd catalysts.

General Discussion and Conclusions

All the proposed species discussed until now were mainly related to isomerization reactions occurring on pure platinum catalysts. For the determination of the mechanisms of hydrocarbon reactions occurring on metals, two effects are generally assumed: electronic (or ligand) and geometric (or ensemble size) effects. It is a relatively easy task to identify the ensemble effect, but the electronic or ligand effect is more elusive.

The work of the Berkeley[28] and Strasbourg[25] laboratories has demonstrated that particular crystallographic orientation initiates specific selectivities, as for example the B_5 sites with the (311) orientation of platinum.[47] Moreover, the selectivity in isomerization reactions is a function of the metallic dispersion for platinum catalysts. This does not seem to be the case for palladium or iridium catalysts, however.

Table III
Hydrogenolysis Reactions from 2-Methylpentane

catalyst: % of metal on Al_2O_3	atomic ratio	reaction temp, °C	p = iso-unit mode/C_2-unit mode
10% Ru		160	0.05 ± 0.01
0.2% Ru		200–280	0.18 ± 0.04
10 wt % Pt-Ru	0.34 ≤ Pt/Ru ≤ 4.6	220	0.15 ± 0.02
10 wt % Pt-Co	Pt/Co = 1.5	300	0.8
	Pt/Co = 1	300	0.35 ± 0.15
	Pt/Co = 0.5	300	0.2
10% Ir, 0.5% Ir, 0.25% Ir		220	0.25 ± 0.05
1% Ir-SiO_2		220	0.35
10 wt % Pt-Ir	Pt/Ir = 32	220	0.27 ± 0.02
3 wt % Pt-Mo	Pt/Mo = 0.33	250	0.22
	Pt/Mo = 1		0.06
	Pt/Mo = 6		1
25% Ni-SiO_2 (Euro Ni)		180	0.5
10% Ni		280	3.1
0.2% Pt		254	1
0.2% Pt		390	2
0.2% Pt-TiO_2		390	1
2%, 5%, 10% Pt-TiO_2		390	1.5 ± 0.1
10 wt % Pt-Ni	0.25 ≤ Pt/Ni ≤ 4	300	1.3 ± 0.3
bulk alloys Pt-Ni	(Pt/Ni)(s) = 100[a]	350	1.1
	(Pt/Ni)(s) = 4	350	1.1
	(Pt/Ni)(s) = 1	350	1.1
	(Pt/Ni)(s) = 0.33	350	1.4
	(Pt/Ni)(s) = 0	350	2.6
10% Pd		300	1.4 ± 0.2
10 wt % Pt-Pd	Pt/Pd = 19	300	1.5 ± 0.4
7 wt % Pt-W	Pt/W = 50	300	1.9 ± 0.1
Pt-Au	Pt/Au = 0.03	330	1.6 ± 0.01
	Pt/Au = 0.18	350	0.8
Pd-Au	Pd/Au = 0.28	350	0.95 ± 0.05
Cu-Ni	Ni/Cu = 3	330–380	1.1 ± 0.01

[a] The s means surface.

Electronic effects are very important in determining the nature of the reaction pathway. When supported catalysts of platinum, palladium, and iridium with nearly the same particle size (80 Å) are compared, the nature of the predominant isomerization reaction mechanism for C_6 hydrocarbons depends upon the metal; a bond-shift mechanism occurs on platinum, a nonselective cyclic mechanism occurs on palladium, and a selective cyclic mechanism occurs on iridium.[48] These results show that reactive intermediate species in the various reactions have very different electronic requirements.

When these "model reactions" are performed under hydrogen on well-defined structures, some experimental results are obtained that illustrate how the electronic configuration influences the chemistry: (a) From studies on single-crystal surfaces, stepped surface reconstructions by hydrogen, oxygen, sulfur, or carbon occur.[49,50] This suggests that new sites with their own local density of states may be formed during the catalytic reactions.[49] (b) On metals such as Ni, Co, and Ru, Bartholomew et al.[51-53] have shown that hydrogen

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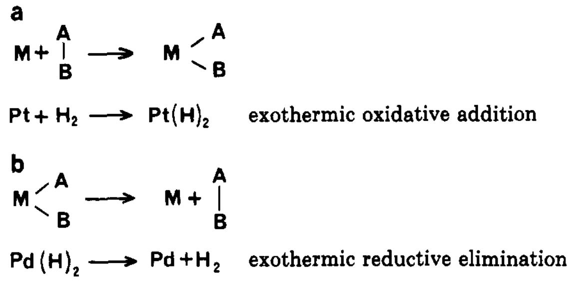
Scheme V[a]

Example of Oxidative Addition and Reductive Elimination



[a] (a) Oxidative addition. Example: catalytic hydrogenation–exchange reaction. (b) Reductive elimination. Example: cross-coupling reaction.

chemisorption is activated and strong metal support interactions on these catalysts lead to a more strongly activated adsorption of hydrogen. (c) To understand the differences observed between palladium and platinum, Goddard et al.[54] have undertaken theoretical studies on oxidative addition and reductive elimination from palladium and platinum complexes. Scheme V illustrates these mechanisms. The difference in the driving force for reductive elimination from Pd(II) and Pt(II) complexes with the same R groups is very close to the difference in the s^1d^9–d^{10} state splittings of these elements as mentioned by Low and Goddard.[54] Thus reductive elimination is exothermic from palladium complexes, since Pd prefers d^{10}, and endothermic from Pt complexes, since Pt prefers s^1d^9, where the metal product is in its d^{10} state. (d) Platinum, palladium, and iridium show also differences in hydrogenolysis behavior. On platinum catalysts, the carbon–carbon bonds are statistically broken; on palladium, the main hydrogenolysis reaction is demethylation; and on iridium, deethylation is favored.

On monometallic catalysts like Pt and Pd, the relative rates for isomerization are much higher than those for hydrogenolysis, and the bond-shift and cyclic mechanisms were interpreted according to the above-mentioned factors: geometric and electronic. However, on other monometallic catalysts like Ir and Ru, or on bimetallic catalysts (see ref 7, 21, 25, 48), the relative rates for isomerization are much lower compared to those for hydrogenolysis. Furthermore, the changes in the selectivity of hydrogenolysis (iso mode versus C_2 mode) are important from one catalyst to another. For Ir or Ru monometallic catalysts, as for bimetallic catalysts compared to Pt or Pd monometallic catalysts, we think that other species can be the activated complexes of the adsorbed species proposed previously. Then the question to be addressed is, How is the C_2-unit mode or iso-unit mode formed and how are interconverted species involved in these two modes?

Using Frennet's model to interpret the kinetic results, the multiple adsorption–dehydrogenation steps can be represented as follows: the hydrocarbon and the hydrogen on the surface below it form a van der Waals complex or, as shown recently by Brookhart and Green,[33] an agostic entity.

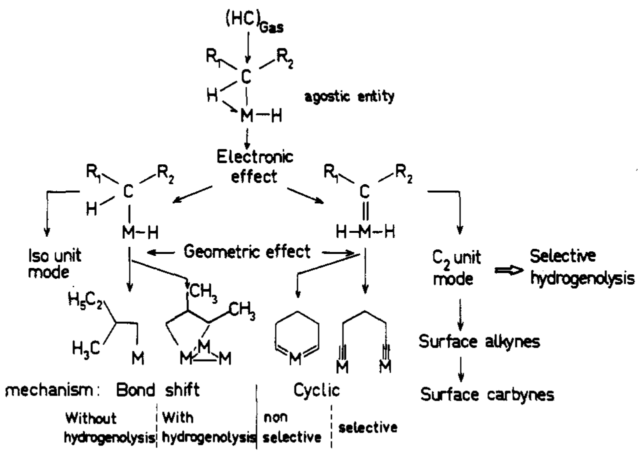


Figure 2. For C_5 hydrocarbons: (1) R_1 = H, R_2 = *sec*-butyl for metallacyclobutane species and σ-alkyl species; (2) R_1 = H, R_2 = *n*-butyl for cyclic mechanisms.

Taking these two concepts into account, we propose a general mechanism (Figure 2) which can explain the following: (a) the differences observed in the hydrogenolysis patterns for obtaining branched or linear smaller hydrocarbons; (b) the selectivities in the isomerization products. In Figure 2, the agostic species is shown as the first species adsorbed on the surface. This species leads to the precursors σ-alkyl for the iso mode or the carbene for the C_2 mode. The relative contribution of these two precursors is governed by an electronic effect. Then a geometric effect leads to the bond shift or to the cyclic mechanisms. It can be seen how electronic and geometric effects can influence the various selectivities obtained on pure platinum catalysts or on platinum-based bimetallic catalysts. These mechanisms fill the gap between adsorption processes, hydrogenolysis reactions, and isomerization reactions.

These hydrogenolysis precursors have different apparent activation energies; when the temperature is increased, the iso-unit mode is favored, as can be seen in Table II. Anderson observed the same behavior.[26] On the other hand, the two hydrogenolysis modes are not influenced by the particle size; the same observation was made for iridium catalysts by Anderson.[26] The interconversion between σ-alkyl and metallacarbene species via an agostic species was proposed first by Green[33] and used by Rooney[55] to explain stereospecific reactions mediated by coenzyme B_{12}. It can also explain the superficial migration of dicarbyne species responsible for the selective cyclic mechanism.[29]

Finally, to try to understand the high selectivity for the hydrogenolysis reactions where bonds with tertiary carbon atoms are not affected, we proposed the formation on the surface of surface alkynes which are cleaved and lead to biscarbyne species.[14] Several laboratories have studied this type of oxidative addition and reductive elimination, either from an experimental point of view[13,56,57] or from theoretical approaches.[58,59] Fritch and Vollhardt[13] described a general synthesis of biscarbyne clusters prepared by the direct cleavage of

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alkynes, and Clauss et al.[59] pointed out the conversion of an alkyne complex into a dialkylidyne complex either from theoretical analysis on cobalt or from experimental evidence on rhodium and iridium. If Ru, Co, Ir, and Mo behave differently than Ni, Pd, (W), it may be, as pointed out by Saillard et al.[58] from the plot of relative electron distribution as a function of electron count, that, at the right side of the transition series, surfaces should be negative relative to the bulk, and at the left side of the transition series, surfaces should be positive.

Our general conclusions will then be that possible surface intermediates in alkane reactions on metallic catalysts have only indirect proof in their support; however, they account for many experimental facts. We proposed an agostic precursor species which initiates the formation of σ-alkyl or carbene species to explain (a) the bond-shift, the cyclic, and the hydrogenolysis reactions; (b) less dehydrogenated species on the surface,[35,45] in agreement with the kinetic model proposed by Frennet et al.;[31] (c) dicarbyne mobility on the surface as proposed in ref 29. The $\alpha\alpha\gamma$ triadsorbed species proposed by Leclercq et al.[60] and Anderson et al.[26,27,34] can be rationalized with such an agostic precursor. Furthermore, the surface reconstructions of platinum single crystals by hydrogen correlated to change in the selectivity in isomerization and hydrogenolysis reactions reinforce the proposed agostic precursor.

More generally, our proposal for an agostic precursor species has the advantage of simplifying the interpretation of the different reaction mechanisms for isomerization and hydrogenolysis via a limited number of precursor species. It also allows us to account for the first steps of adsorption as well on platinum, palladium, and iridium catalysts as on bimetallic or alloy catalysts and agrees very well with the kinetic model proposed by Frennet,[30] where a reactive adsorption step occurs, followed by reactive surface dehydrogenation steps without any release of the sites occupied by adsorbed hydrogen.

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Structural Aspects of High-Temperature Cuprate Superconductors†

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Introduction

High-temperature superconductivity constitutes the most sensational discovery of recent times. Since these new superconductors are complex metal oxides, chemistry has had a big role to play in the investigations. For the first time, stoichiometry, structure, bonding, and such chemical factors have formed central themes in superconductivity, an area traditionally dominated by physicists. These oxide superconductors have given a big boost to solid-state chemistry.

The first group of high-temperature superconductors discovered[1] were oxides of the type $La_{2-x}(Ca,Sr,Ba)_xCuO_4$ with T_c values in the 25–40-K range, soon followed by the so-called 123 oxides of the general formula $LnBa_2Cu_3O_7$ (Ln = Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, or Yb) with T_c values in the 90-K region. The chemistry of these two classes of oxide superconductors has been reviewed recently.[2-7] The discovery of ma-

C. N. R. Rao (born 1934) obtained his M.Sc. degree from Banaras, D.Sc. degree from Mysore, and Ph.D. and D.Sc. (honoris causa) degrees from Purdue. He is the founder–Chairman of the Solid State and Structural Chemistry Unit at the Indian Institute of Science, where he continues as a Professor and Director. He is a Fellow of the Royal Society, London, and a foreign honorary member of the American Academy of Sciences and Arts as well as of the Polish and U.S.S.R. science academies. He is a centennial foreign fellow of the American Chemical Society. His main research interests are solid-state chemistry of metal oxides, surface science, and chemical spectroscopy.

B. Raveau (born 1940) studied engineering as an undergraduate and obtained his doctorate degree in chemistry at Caen in 1966. He soon became professor at Caen, where he heads a flourishing school in solid-state chemistry. He now has an active team working on superconductivity and is collaborating with industry in developing devices. His main areas of interest are phosphate–bronze alloys, mixed-valent copper oxides, and applied solid-state chemistry.

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