Coordination Chemistry Reviews, 15 (1975) 109—205

TRANSITION METAL CATALYSIS OF PERICYCLIC REACTIONS

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(Received June 10th, 1974)

CONTENTS

A. Introduction 109
B. Theoretical treatments 111
C. Cycloadditions 117
  (i) Norbornadiene systems 117
  (ii) Metallocyclic intermediates 121
  (iii) Acetylenes 123
  (iv) Other systems 141
D. Olefin metathesis 152
  (i) The reaction 152
  (ii) The mechanism 154
E. Valence isomerization 164
  (i) General 164
  (ii) Cubane 174
  (iii) Bicyclobutane 178
F. Electrocyclic reactions 188
G. Sigmatropic rearrangements 191
H. Conclusions 196
References 199

A. INTRODUCTION

Transition metals have, for some time, catalyzed what are now known to be "forbidden pericyclic" reactions. The Reppe, nickel-catalyzed synthesis of cyclooctatetraene, reported in 1948, is perhaps the outstanding example [1]. The early literature was mainly directed to the synthetic aspects of metal catalysis and thus tended to be fragmented with respect to the theme of this review. We will not attempt to cover much of this work, particularly that material published prior to Woodward and Hoffmann's initial paper [2] of 1965. Reference to selected pre-1965 papers will only be made where their impact on this field is particularly relevant to the subject at hand. Fortunately, a large body of this literature has already been reviewed. Schrauzer covered a number of cycloadditions in a treatise dealing with his proposed "π multicentered reactions" exemplified in some reactions of norbornadiene [3]; Heimbach et al., have published papers covering metal-catalyzed polyene oligomerizations [4].

Special attention was first brought to this subject in 1967. Concurrent theoretical and experimental publications appeared dealing specifically with the catalysis of symmetry-forbidden pericyclic transformations. The theoretical proposal suggested a novel role for the metal in which it totally removes the forbidden restrictions to the concerted pericyclic process [5]. Hogeveen and Volger offered experimental support to the new theoretical framework in their disclosure of a facile, rhodium-catalyzed transformation [6] of quadricyclene (I) to norbornadiene (II).

Other reports of metal-assisted forbidden pericyclic reactions quickly followed. Volger and Hogeveen [7] disclosed a rhodium-catalyzed disrotatory cyclobutene electrocyclic isomeriation; Merk and Pettit published the facile disrotatory ring opening of a variety of cyclobutene compounds catalyzed by cuprous and silver salts [8]. Experimental activity in this area then increased almost exponentially, covering the spectrum of pericyclic processes. The fresh interest in this one special area of metal catalysis was, to a large extent, due to the enormous impact of the Woodward—Hoffmann theory itself. Organic chemistry had seen no single event of that past decade causing so great a surge of activity and interest as did the theory of orbital symmetry conservation. It was not surprising, therefore, that organic experimentalists would turn their attention to the catalysis of pericyclic reactions. Indeed, activity in this field has been dominated by organic chemists with fewer contributions coming from those disciplines generally associated with metal catalysis.

A single theme tends to dominate much of the experimental work devoted to this subject. A number of papers in this review keynote a persistent attempt to define some unifying principle or mechanism embracing the role of all transition metals in catalyzing all pericyclic reactions. This affinity to some unitarity in mode of catalytic action should perhaps be anticipated in view of the subject's genesis, its direct line of development from pure organic chemistry. Uncatalyzed pericyclic processes in fact possess just this kind of singularity. Predictability in mode of action is striking, simply definable in the Woodward—Hoffmann rule, one single, intellectually satisfying sentence [2].

However, no such theoretical framework embracing the transition metals evolved, and nor should one have in view of the wide diversity found in transition metal chemistry. Striking differences in simple chemical properties exist between members of the transition metal series. Significant differences persist within chemical groups, isoelectronic elements, and even for individual metals in their various oxidation states and ligand environments. It is, therefore, not surprising that their catalytic properties would be at least as diverse as their chemical properties. We may expect different transition metal systems to catalyze a given pericyclic reaction, but we should not assume a common mode of catalytic action. Indeed, a wide variety of mechanisms are to be anticipated. In some pericyclic transformations, and particularly those characterized by high exothermicity, variations in mode of catalysis should be a dominant feature, if not the rule. In others, a certain degree of mechanistic uniformity may exist. We shall focus on these aspects of the published work and, wherever possible, highlight apparent generalities in modes of catalysis.

B. THEORY

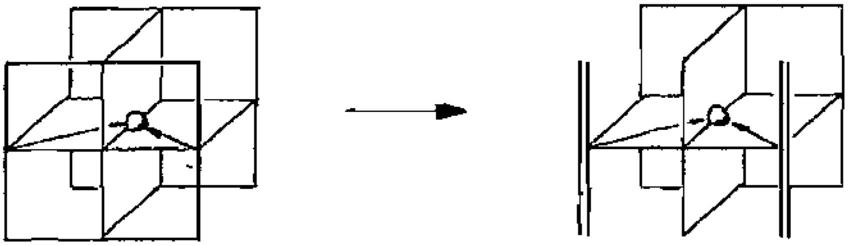
Mango and Schachtschneider proposed the first mechanism describing the catalysis of symmetry-forbidden reactions by transition metals [5]. Stated briefly, a given forbidden transformation, A → B, is rendered allowed when the reactant, A, is coordinated to a transition metal capable of injecting an electron pair into the transforming ligand and accepting one in return. The exchange proceeds through orbitals of specific symmetries and results in a reordering of the metal's valence electrons. It was subsequently shown that this special type of catalytic operation would be limited to metal systems possessing "nonrestrictive" ligand fields [9]. This subject is complex, however, and a full description would be inappropriate here. It has been reduced to simpler, qualitative valence bond representations which will be illustrated later. For the present, most nonrestrictive metal systems possess a principle symmetry axis, namely the coordinate bonding axis of the reacting ligand A, which is C_∞, C_3 or higher with respect to the nonreacting ligands.

Shortly after the initial theoretical disclosure, Merk and Pettit published their work describing extremely facile silver and copper ion catalyzed disrotatory isomerizations of a variety of highly strained cyclobutenes [8]. They rationalized their results in terms of a metal-assisted, symmetry-allowed transformation, proposing a mechanism similar to that given above [5]. Later, a full paper was published including theoretical arguments to support their proposals [10].

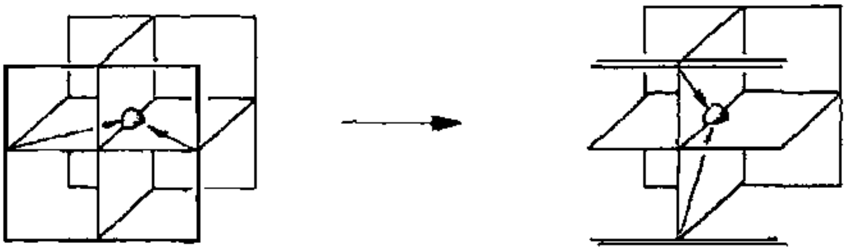
Pettit's theoretical description of silver's role in catalyzing forbidden reactions has received critical attention. Van der Lugt, doubting this interpretation, noted that correlation diagrams displaying ground state processes could not be drawn for the silver (I), d^{10} system [11]. He offered configuration interaction to explain the metal's function. Mango expressed similar doubts regarding silver's role [12]. A concerted mechanism, particularly one involving the exchange of electron pairs between metal and ligand, was seriously questioned. This argument was based on the large energy gaps separating ground and appropriate excited states in the silver ion system. The case for silver and similar ions thus remains in a state of some uncertainty. Unfortunately, the experimental sections to follow which deal with the variety of silver-catalyzed pericyclic processes, do little to clarify this situation.

It should be pointed out that concerted catalytic roles for silver should not be hastily ruled out. Mechanisms are conceivable involving concerted ligand rearrangements along allowed pathways of unusual character. Thus, silver could, through its special kind of coordination and charge density, inject sufficient molecular distortions into highly strained ligands to open allowed pathways not otherwise accessible. This subject will be discussed further in the appropriate sections to follow (page 187). It should be further noted that silver ion may very well act in a unique way in the catalysis of certain forbidden reactions, possibly effecting concerted transformations through a yet undescribed mode of action.

Van der Lugt [11] rejected the forbidden-to-allowed role generally, essentially arguing that ground state-excited state correlations inevitably attend the concerted ligand rearrangement. However, he specifically addressed [2 + 2] transformations in which the metal's focus of biscoordination remained spatially fixed, e.g., III → IV. It was later shown that these processes, involving a static display of metal coordination focus, would invariably remain forbidden [9]. The allowed mode, involving the exchange of electron pairs, necessarily rotates the bonding focus 90°. Thus, the metal-assisted allowed change was not III → IV, but III → V. This description is necessarily simplified, specifically addressing the III → IV reaction rather than the general situation. A general description of the forbidden-to-allowed process would be VI → VII, where the nonreacting ligand system L would dictate the positions of coordination focus on the cyclobutane ring. Where L defines a ligand field (nonrestrictive) focusing biscoordination as defined by the arrows in VI, VI → VII is totally ground state and symmetry allowed, while



III IV



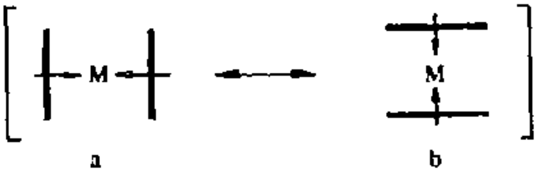
III V

VI VII

ring opening in the opposite direction (i.e., as in III → IV) remains forbidden [9].

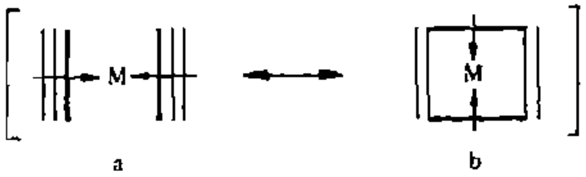
A note was later published relating the forbidden-to-allowed process to the conservation of coordinate bonding [13]. It was proposed that two fully coordinated bonds capable of a $[2_s + 2_s]$ pericyclic change would necessarily correlate with their symmetry-forbidden partners along the otherwise forbidden path. Moreover, this correlation would exist between fully coordinated bisligand systems. Thus, full biscoordination is conserved all along the ligand's $[2_s + 2_s]$ transformation. The theoretical proposal indicated an intimate tie between the forbidden-to-allowed process and coordinate bonding, one that should find relevance to all pericyclic processes.

The conservation of coordinate bonding was expressed concisely in a simplified, valence bond description [14]. Molecular orbital correlation diagrams and the more complex orbital symmetry arguments were replaced by valence bond, resonance structures. A general rule was proposed for the $[2_s + 2_s]$ pericyclic process: "Transition metal coordination of two bonds capable of a $[2_s + 2_s]$ pericyclic process means the formation of a new molecular species. It is represented by a resonance hybrid (VIII) composed of contributing structures that reflect the bonding configurations of the symmetry-forbidden partners along the $[2_s + 2_s]$ path. The two bonds are thus rotated 90° from one structure to the other with the metal's centers of coordination remaining fixed to these bonds."



VIII

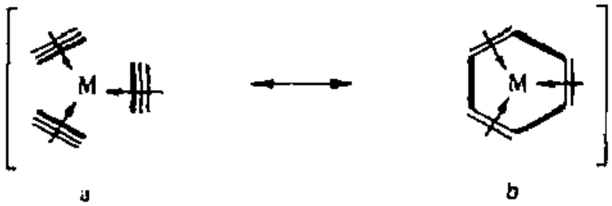
The valence bond picture proved useful in describing inherent limits set on all transition elements. For example, symmetry restrictions should counteract the $[2_s + 2_s]$ fusion of bonds bridging nuclei possessing additional centers of strong metal coordination. $[2_s + 2_s]$ acetylene cycloadditions are outstanding examples. Restrictions to metal-assisted acetylene fusion, which had been described earlier in a more complex molecular orbital treatise [15], are greatly simplified [12,14] in resonance structure IX. Because the metal's centers of coordinate bonding are rotated 90° off the preferred centers in



IX

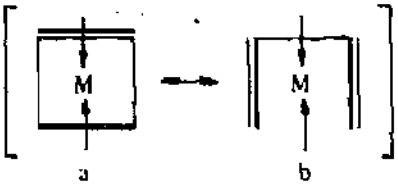
contributing structure IXb, the transformation represented by [IXa ≫ IXb] → [IXa ≪ IXb] would proceed with an almost complete loss of coordinate bonding.

It was further proposed that the opposite would be true when the multicoordinate ligand transformation, A → B, is itself allowed [12]. Thus, three acetylenes are free to undergo an allowed $[2_s + 2_s + 2_s]$ pericyclic process with full retention of coordinate bonding since the metal's centers of coordination do not, necessarily, undergo a spatial rotation in these cases, e.g., [Xa ≫ Xb] → [Xa ≪ Xb].

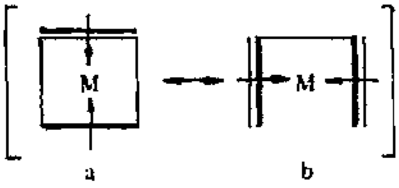


X

The fixed focus of coordination which generally attends allowed ligand reactions has apparent predictive value [12]. For the fully coordinated cyclobutene ligand, the conrotatory and disrotatory modes of change are represented by XI and XII, respectively. This suggests that full biscoordination is



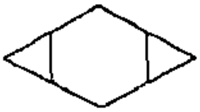
XI



XII

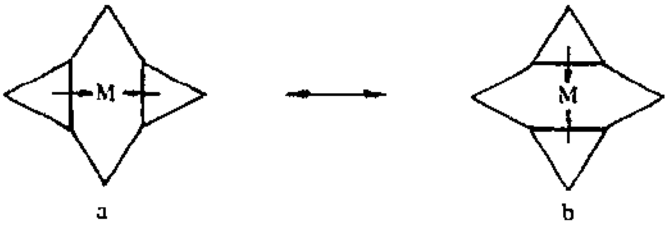
preserved only along the otherwise forbidden path [XIIa ≫ XIIb] → [XIIa ≪ XIIb]. It was stressed that catalysis could only be anticipated among metals with nonrestrictive ligand fields. The preferred systems would possess a *d* band with sufficient valence electrons to give a coordinatively saturated complex in which the bonding axis of the π, σ-coordinated cyclobutene would be C_3 or higher with respect to the nonreacting ligands [12,16].

Other predictions based on the resonance-valence bond description have been offered [14]. Syntricyclooctane XIII was suggested as an attractive



XIII

experimental tool for seeking facile $[2_s + 2_s]$ valence isomerizations on the metal systems suggested. Full coordinate bonding to these metal complexes transform XIII to XIV. Dynamic behavior of the kind [XIVa ≫ XIVb] ⇌



XIV

[XIVa ≪ XIVb] was proposed for appropriate metal systems. A more interesting possibility would be the totally symmetrical "crown" ligand [XIVa ≡ XIVb]. It was noted, however, that the ultimate fate of XIII as a ligand would rest on the energetics of the system, the ligand field restrictions, coordinate bonding properties of the metal and other related factors.

Others have contributed to the theoretical framework of this field. Dewar, building from earlier work of Evans [17], recently injected the importance of ligand "aromaticity" to explain the metal's function [18]. He concludes that, "transition metals may catalyze pericyclic reactions if, and only if, they involve antiaromatic transition states." In other words, metals may catalyze forbidden transformations, but not those that are allowed. This treatment makes no distinctions between the metals or their particular ligand field properties. Indeed, Dewar exemplifies his "amended Evans' rule" by citing a variety of silver-catalyzed rearrangements of cyclobutene systems.

The generality and utility of Dewar's amended Evans' rule has been questioned [12]. It was suggested that certain allowed pericyclic processes, for example [Xa ≫ Xb] → [Xa ≪ Xb], could, in theory, proceed with as much ease (or "aromaticity") as their forbidden counterparts. It was further argued that clear forbidden—versus allowed catalytic specificity would be quite rare, limited to only a few processes and then tightly constrained to well defined metal systems. Dewar's proposed "aromaticity" at the transition states of silver-catalyzed pericyclic processes was essentially rejected. The importance of coordinate bond preservation in the catalysis of allowed and forbidden reactions was offered in place of "aromaticity" as the central feature to the metal's catalytic function. In the catalysis of the variety of conceivable allowed processes, metal assistance might be anticipated when coordinated bonding would be preserved. This analysis generally cautioned against the implications inherent to Dewar's rule, noting some reversals and apparent ambiguities in the concept of "aromaticity" applied to the transition states of certain metal complex, allowed processes.

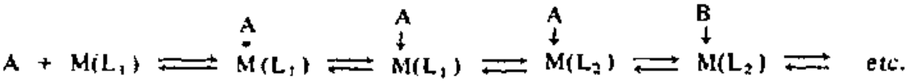
Orbital symmetry principles have also been applied to butadiene cycloadditions [19]. This same system was viewed theoretically from a purely stepwise point of view [20]. Other notable theoretical contributions to subjects similar to that of this review can be cited [21]. There are also certain theoretical contributions which more specifically address individual subjects to be treated subsequently. We shall defer discussing these to the appropriate sections to follow.

Before leaving this section, we shall briefly review one critical aspect of the metal's role in catalyzing pericyclic reactions, namely the question of "concertedness". It is, of course, the focal point of most investigations for it bears on the intimate orbital and electronic details of the metal's function. It has, however, been the subject of considerable confusion.

A specific reaction of interest, for example $A \rightarrow B$, may be catalyzed by a metal in a variety of ways, some involving a concerted ligand transformation $A \rightarrow B$ and others clearly stepwise in that A transforms first to some speices X or a series of species before final generation of product B. However, these two catalytic processes (concerted and nonconcerted) can and very likely will proceed along kinetic pathways which are stepwise in nature.

Consider the concerted case. At the one extreme, the substrate A could transform to B along the forbidden path upon mere "interaction" with the catalytic center. It is implied here that the active species is always prepared to act catalytically with substrate A. That is, (i) the metal is properly ordered electronically to immediately trigger reaction, (ii) exhibits the appropriate degree of coordinative unsaturation and (iii) maintains its nonreacting ligands in a nonrestrictive geometry. Rates here could approach collisional frequency. Although such a system is conceivable (perhaps more so for heterogeneous catalysts and highly reactive and suitably structured substrates like quadricyclene (I)), it would seem the rare exception and should in no way represent the general case.

A substrate A is more likely to pass through a series of reactions with the catalytic system, all along, however, retaining its bonding configuration intact. The reaction steps to full coordination, for example, can be complex, particularly for substrates where more than one bond must fully coordinate to the metal center for catalysis to proceed. Consider further the importance of having the nonreacting ligands in nonrestrictive geometries. The fully coordinated substrate A might have to await a chemical change within the bonding framework of the nonreacting ligands before $A \rightarrow B$ can occur (e.g., $L_1 \rightleftarrows L_2$ in eqn. 1). Each of these processes constitutes a step in the overall catalytic reaction and each metal complex in the series constitutes an intermediate in the overall reaction. Yet the ligand transformation $A \rightarrow B$ can be clearly concerted along an otherwise forbidden path. A highly simplified example is illustrated in eqn. 1, where $M \cdot A$ and $M \leftarrow B$ denote partial and full coordination, respectively; L_1 and L_2 denote restrictive and nonrestrictive ligand systems, respectively. The example in eqn. 1 does not consider



$$A + M(L_1) \rightleftharpoons \overset{\overset{A}{\bullet}}{M}(L_1) \rightleftharpoons \overset{\overset{A}{\downarrow}}{M}(L_1) \rightleftharpoons \overset{\overset{A}{\downarrow}}{M}(L_2) \rightleftharpoons \overset{\overset{B}{\downarrow}}{M}(L_2) \rightleftharpoons \text{etc.} \qquad 1.$$

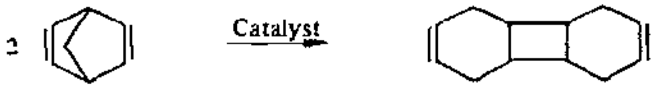
other obvious factors in a catalytic scheme of events such as ligand displacement steps leading to full coordination.

The nonconcerted counterpart would involve the intermediacy of a distinctly different ligand species X resting somewhere between M(A) and M(B). It should be structurally different from A and B and, unlike them, would generally not have counterparts in the thermal chemistry of the pure organic systems. Intermediate ligand systems may be metallocycles, hydride addition or elimination products, carbenoid, or cationics. A more detailed discussion of this subject and its implications in catalysis has recently appeared [2]. We should just note here that arguments aimed at excluding the concerted ligand transformation are tenuous at best if based solely on kinetic data implicating "stepwise" processes (see page 167).

C. CYCLOADDITIONS

(i) Norbornadiene systems

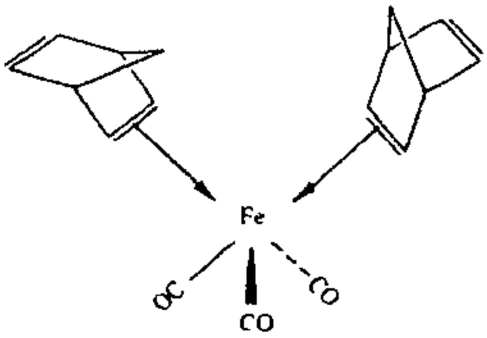
Norbornadiene (NBD) has proven to be one of the more reactive and certainly more extensively studied olefins to undergo metal catalyzed [2 + 2] cycloadditions (eqn. 2). Stereospecificity at the cyclobutane ring varies with



2.

the particular metal system employed; however, it remains rigorously selective with respect to the suprafacial nature of ring fusion. Facile dimerizations have been catalyzed by low-valent complexes of Fe [23], Ni [24] and Co [25]. Very little mechanistic attention has been directed to these systems. They remained, for the most part, intriguing synthetic curiosities. Much of this chemistry was reviewed by Schrauzer [3], who first postulated a concerted "π-complex multicenter reaction" mechanism. It is noteworthy that at least some of these systems ($Fe_2(CO)_9$ [25], for example) should be capable of generating bis(NBD)metal complexes with nonrestrictive ligand fields. For the iron carbonyl system, XV is such a species. This metal system is potentially catalytic for $[2_s + 2_s]$ pericyclic ligand transformations, since the nonreacting CO ligands describe a nonrestrictive C_3 axis.

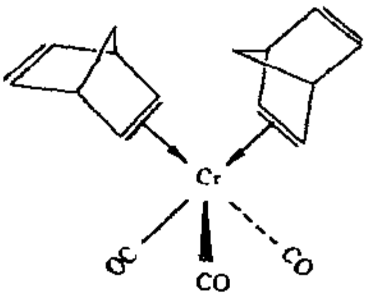
Schrock and Osborn [26] have recently reported a [2 + 2] cycloaddition of NBD catalyzed by the novel ionic species $[Rh(NBD)_2]^+$. The complex is stable in acetone while ca. 10^3 mol dimer is produced per mole of Rh in the



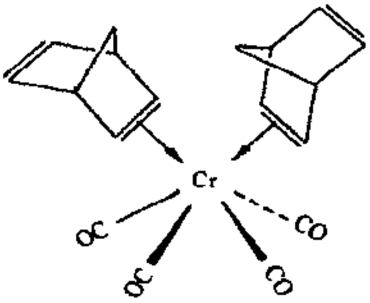
XV

presence of NBD in 8 to 12 hours at 25°. They suggest NBD attack at the fifth, open coordination site of the complex. Stable adducts of the catalyst were obtained ($[Rh(NBD)_2L]^+$, L = CO, $As(C_6H_5)_3$, $As(CH_3)_2C_6H_5$ or $Sb(C_6H_5)_3$) which showed negligible catalytic activity toward NBD dimerization. Interestingly, the temperature dependent ^1H NMR spectra of the stable complex showed rapid intramolecular rearrangement at ambient temperatures. This might suggest similar NBD lability in the active $[Rh(NBD)_2]^+$ at catalytic temperatures.

Iron-catalyzed NBD dimerization can be assisted photochemically [27]. Jennings and Hill have recently reported some interesting studies [28a] using $Cr(CO)_6$. In this system, three dimers are formed: (*exo—trans—exo*), (*endo—trans—exo*), and (*endo—trans—endo*). Irradiation of neat NBD with no metal present under reaction conditions produces no dimer products. (NBD) chromium tetracarbonyl is one of the intermediates in the Cr-assisted dimerizations [28a]. Irradiation of this complex under reaction conditions produced the observed products in the proper ratios. Significantly, neither (NBD)chromium tetracarbonyl nor $Cr(CO)_6$ produce dimeric products thermally (under their photolytic conditions) with NBD. Thus some complex appears to be photolytically activated. An interesting speculation can be offered. Consider a photolytically-induced rearrangement from a restrictive-field complex (e.g., octahedral) to a bis(NBD)chromium carbonyl complex which is nonrestrictive; for example, complexes XVI or XVII. However, the



XVI



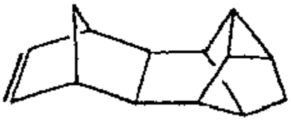
XVII

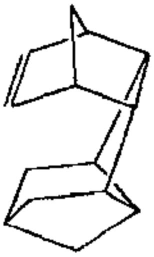
experimental results do not allow a distinction between concerted and nonconcerted [2 + 2] cayalysis in any of the photo-catalytic systems.

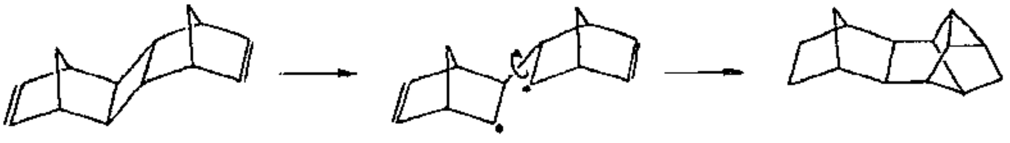
In sharp contrast to $Cr(CO)_6$, photolytic activation of $Fe(CO)_5$ transforms strained polycyclic olefins into cyclopentanones [28b]. The reaction is stoichiometric and very likely proceeds through metallocycles. Cyclobutane products are occasionally obtained. However, the cyclopentanone and cyclobutane products appear to form from two different metallic species and not a common intermediate.

Katz and Acton have investigated the stereochemical course of metal-catalyzed NBD dimerizations on carbon-supported rhodium [29]. Three dimers were suggested: XVIII, XIX and XX. Based on the stereochemistry of these structures and from similar dimers obtained from other group VIII metals, they proposed a formal relationship, or mechanism, linking the multitude of products obtained from metal-catalyzed cycloadditions. The radical-like processes illustrated in eqns 3 and 4 were offered to exemplify the catalytic course.


XVIII


XIX


XX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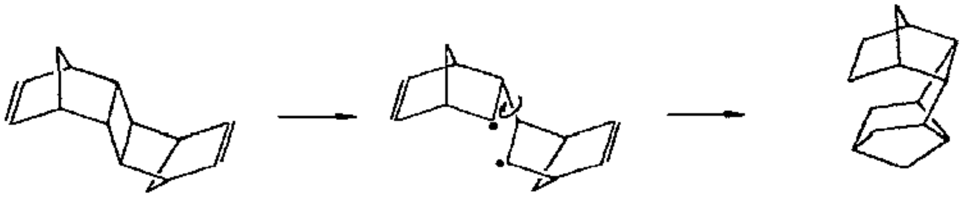
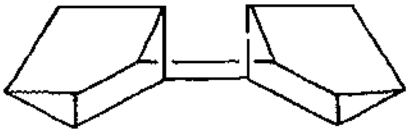
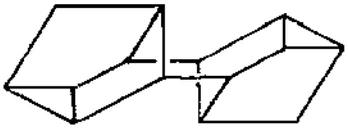

4.

However, only one dimer of NBD, termed "Binor-S" by Schrauzer et al. [30] who proposed structure XXI, appeared to Katz to be inconsistent with his generalized proposal. He suggested that Schrauzer's structural assignment could be in error and that structure XXII might be Schrauzer's Binor-S [29]. X-ray studies have now confirmed that Binor-S is, in fact, the structure first offered, [31] XXI. It thus stands out as a significant exception to the gener-



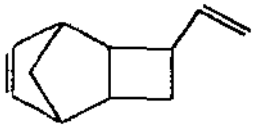
XXI



XXII

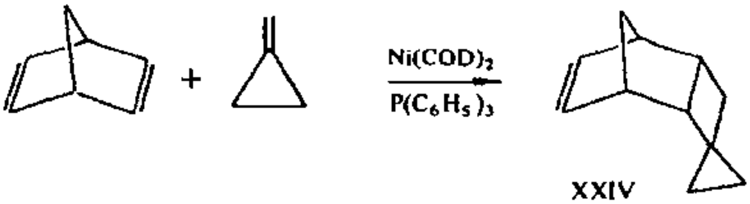
alized free radical proposal of Katz. The radical rearrangements suggested might very well contribute to the chemistry of supported rhodium. However, they may be somewhat unique to this system and not necessarily general to the catalytic properties of other group VIII complexes.

Norbornadiene undergoes cycloaddition with a variety of activated olefins [3]. Cannell [32] and Dall'asta et al., [33] have reported the [2 + 2] product XXIII from NBD and butadiene. Cannell's C_5H_5 $Ti(CH_2Ph)_2$ homogeneous system proved quite active and selective giving XXIII in 90% yield. The low-valent iron complexes employed by Dall'Asta yielded a spectrum of cycloaddition products including the usual [2 + 2] NBD dimers. The titanium system moreover proved sufficiently active to couple norbornene to butadiene through a [2 + 2] cycloaddition.



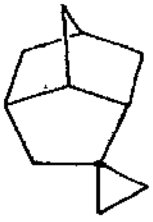
XXIII

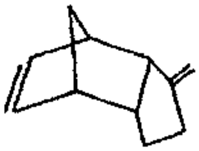
Noyori et al. reported a highly stereospecific cross-coupling reaction between NBD and methylenecyclopropane catalyzed by a phosphine-modified nickel (0) catalyst [34]. The product, obtained in 85% yield after 24 h at 20°, proved to be exclusively the *endo* isomer XXIV. Cyclobutane dimers of NBD or methylenecyclopropane were minor products. Formation of XXIV was supressed when the chelating ligand bis(diphenylphosphine)ethane was used. In the absence of any phosphine ligand, a significant decrease in both stereoselectivity (*endo/exo* XXIV) and "perispecificity" resulted. Most notably, dimers XXV and XXVI were formed in 24% and 6% yields, respectively.

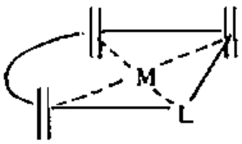


XXIV

When the catalytic reaction was assisted with optically active phosphine ((−)benzylmethylphenylphosphine), optically active XXIV was formed. These authors rationalized their results in terms of the Ni(0) complex of general structure XXVII in the rate-determining step. The clean cross-cou-


XXV


XXVI



XXVII

pling was reasonably attributed to the coordination preference of the substrates: L ≫ bidentate diene > olefin > monodiene ligand. They also noted the especially good coordination properties of strained olefins, suggesting that the strain energy in methylenecyclopropane, released in part upon coordination [16], should place it in coordination power between the bidentate and monodentate NBD ligands. Noyori's overall results clearly implicate XXVII as a critical intermediate in this most novel catalytic system.

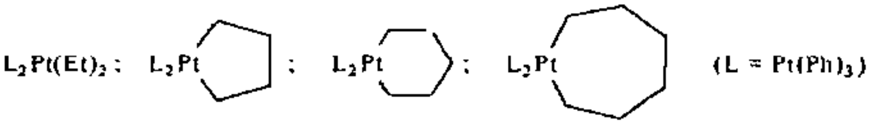
(ii) Metallocyclic intermediates

Considerable controversy exists regarding the mechanistic nature of metal-catalyzed [2 + 2] cycloadditions. The division lies primarily between the concerted, forbidden-to-allowed process discussed earlier and nonconcerted pathways. Of the latter, those incorporating metallocyclic intermediates have received the greatest support [35—37]. Although this subject is relevant to sections to follow and shall be treated in them, we have chosen to introduce it here, following norbornadiene cycloadditions, where it appears particularly pertinent. This section, therefore, will serve both as a "mechanism" extension of the previous section and an introduction to the general subject of metallocycles as intermediates in the variety of pericyclic processes to be reviewed.

It should be noted at the outset that little, if any, direct evidence exists supporting any particular mechanism. Arguments suggesting metallocyclic species have been based mainly on kinetic data indicating stepwise processes [35], the isolation of stable metallocyclic intermediates [36] or the chemical fate of certain synthetic metallocycles [37]. These examples represent a very narrow band of metal systems: specifically, tris(triphenylphosphine)-rhodium(I) chloride [35], $[Rh(CO)_2Cl]_2$ [36] and tungsten chloride [37]. It is significant that the catalytic chemistry addressed in these studies can change dramatically from even subtle changes in the electronic character of a metal's ligands [39]. Even greater changes in catalytic behaviour should thus be anticipated as one moves to entirely different metals and ligand systems, the Co, Fe, Ni, Cr or Ti systems, for example. To our knowledge, metal-$(NBD)_2$ metallocycles involving these metals, in catalytic systems, have not been isolated or otherwise detected.

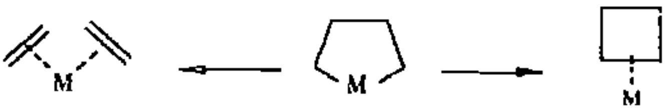
Osborn et al. [40] reported the formation of the iridium(III) metallocyclic complex Ir(NBD)$_3$ Cl from the reaction of [Ir(1,5-cyclooctadiene)Cl]$_2$ with excess NBD in acetone at room temperature. The metallocycle is composed of two NBD molecules, each contributing one of its double bonds to the five-membered iridiocycle. It inserts CO yielding the corresponding six-membered ketonic derivative in a similar fashion to the rhodium system (see page 177) noted above [36], and discussed in greater detail elsewhere [22]. In further similarity to [Rh(CO)$_2$ Cl]$_2$, Osborn's iridium complex is not catalytic; the [2 + 2] fusion of NBD noted in eqn. 2 was not reported as a catalytic feature of the iridium reaction. The iridium metallocycle does, however, give the *exo—trans—exo* dimer, but only in 35% yield when refluxed in CHCl$_3$ with a five-fold excess of P(C$_6$H$_5$)$_3$. The apparent catalytic inertness of this system coupled with the poor yield of dimer in the stoichiometric reaction tend to detract from its mechanistic relevance to the catalytic chemistry of other metal complexes. Rather than modeling key catalytic intermediates, thermally stable and catalytically inactive metallocyclic complexes may instead reflect an energy minimum in these d^8 systems, one representing catalytic truncation.

A recent publication by Whitesides et al. [41] may bear significantly on the catalytic role of d^8 metallocycles in metal-catalyzed [2 + 2] cycloadditions. The following series of Pt(II) complexes were prepared and thermally decomposed:



Several points are noteworthy in the results. Most important, not a single product resulting from carbon—carbon bond formation was reported. Neither cyclobutane, cyclopentane nor cyclohexane were indicated as products from the decomposition of the related metallocycles. The products were exclusively associated with initial hydride elimination, followed by reductive elimination of alkene. Moreover, all platinocycles proved to be markedly more stable thermally than were the acyclic platinum(II) alkyls. In addition, no carbon—carbon bond cleavage was observed in the thermal decomposition. At 120°, the five-membered platinocycle yielded butenes exclusively; ethylene and cyclopropane were not formed, and, as mentioned earlier, cyclobutane was not reported to be a product. The stability of the five-membered platinocycle proved substantial, its relative rate of decomposition being approximately 1.7×10^4 times slower than L$_2$ Pt(n-Bu)$_2$.

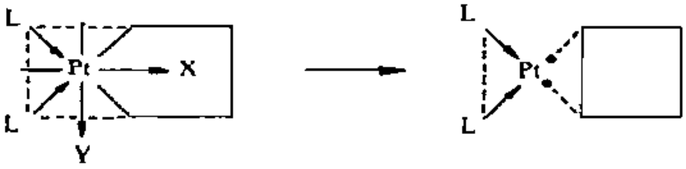
The limited ability of Whitesides' d^8 platinum metallocycles to undergo either of the two critical transformations of reductive elimination (see eqn. 5) at 120° would seem to cast some doubt on the role of such species as



high energy, kinetically labile intermediates in [2 + 2] catalysis, at least for some of the d^8 metal systems examined. Platinum's relative inertness in this regard should be contrasted to the high lability of a d^0 tungsten halide metallocycle which undergoes smooth transformation to ethylene (eqn. 6)

presumably at ambient temperatures [37]. Neither cyclobutane nor butene were reported, the ethylene being essentially quantitatively produced. This system relates quite significantly to olefin metathesis, and will be discussed in greater detail in that section (see page 162).

The reversible transformations in eqn. 5 can be viewed as simple cycloaddition processes in which the metal participates. Orbital symmetry principles therefore apply and could very well account for the high lability of the d^0 system and the inertness of the d^8 platinum system. The role of the transition metal as a participant in pericyclic processes was recently introduced [22]. These processes would appear subject to symmetry restraints from restrictive ligand fields, and they should become more pronounced in the d-electron rich metal complexes. In the reductive extrusion of a cyclobutane ring from a square planar, d^8 platinocycle (eqn. 7), the metal participates in a [d_a^2] configuration, thus withdrawing an electron pair through an antisymmetric (with respect to the ZX plane) atomic orbital [22]. Negative anti-

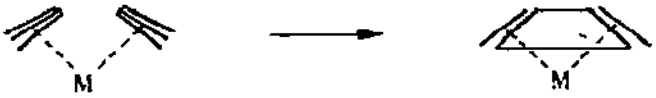


bonding character should grow in the XY plane as electron density accumulates in the d_{xy} orbital with carbon—carbon bond fusion. A symmetry-forbidden assignment need not be attached to this process. Nevertheless, ligand field restrictions should inject higher activation energies into these kinds of molecular transformations relative to their nonrestrictive counterparts.

(iii) Acetylenes

The chemistry of metal-catalyzed acetylene oligomerization has and continues to be one of the more complex areas in metal catalysis. Acetylenes undergo intriguing reactions when transition metals intervene. This chemistry has, therefore, received close attention both for its mechanistic implications and synthetic utility. Much of the earlier work was extensively reviewed [42] and discussed mechanistically [43].

We are treating this general subject here, under [2 + 2] cycloadditions, because this specific mechanistic pathway has been a major focus in much of the literature. The orbital symmetry aspects of metal-catalyzed [2 + 2] acetylene cycloadditions were briefly noted earlier (see page 113). In the theory proposed, two acetylenes may not undergo the $[2_s + 2_s]$ π bond fusion in eqn. 8 on any transition metal without a loss of essentially all coordinate bonding [14,15,22]. The transformation may proceed with preservation of coordinate bonding, however, when two transition metals, sharing opposite faces of the incipient cyclobutadiene, catalyze the process (see eqn. 9). This hypothetical process would only be anticipated with nonrestrictive-field metal complexes.



8.

9.

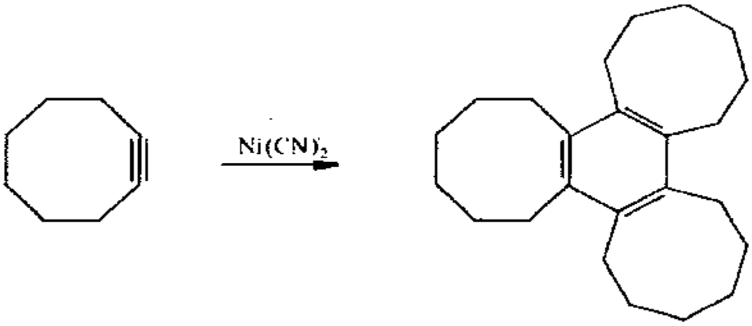
Serious attention was first directed to metal-catalyzed [2 + 2] cycloadditions of acetylenes in 1956 when Longuet-Higgins and Orgel proposed that cyclobutadiene should be stabilized by suitable transition metal ions [44]. They further offered that the bisacetylene ligand system should be less stable than the corresponding cyclobutadiene ligand, and thus might be expected to undergo the transformation in eqn. 8. Their predictions regarding the stability of the cyclobutadiene ligand have nicely materialized [45]. But such has not been the case for the seemingly reasonable transformation of eqn. 8. Although acetylenes do many things with transition metals (both catalytic and stoichiometric), the [2 + 2] bisacetylene → cyclobutadiene transformation is apparently not one of them. The symmetry restriction associated with this transformation may provide the blocking force, and be an explanation for the experimental results.

Acetylenes undergo facile metal-catalyzed oligomerization to a variety of linear and cyclic compounds. Of the cyclics, benzene and, from the Reppe reaction (1), cyclooctatetraene have received the broadest attention, mechanistically. A metal—cyclobutadiene intermediate has been a most popular species in the mechanistic schemes of the earlier proposals [46]. Schrauzer et al. offered the first compelling experimental results casting serious doubt on the intermediacy of metal-cyclobutadiene in the Reppe reaction [47]. They also noted an important point, namely that cyclobutadiene should be a strongly π-bonding ligand and kinetically more stable than its parent catalytic species. The rate of cyclooctatetraene formation would thus be controlled by the consecutive reactions of the cyclobutadiene complex, a fact not compatible with their experimental results. An important point begins to emerge here: because the cyclobutadiene—metal complex should possess unusual stability, it will therefore be an unlikely intermediate in catalytic schemes involving its transformation to ligands (e.g., cyclooctatetraene) whose coordination properties are predictably inferior. Thus for theoretical [14,15,22] and thermodynamic [47] reasons, cyclobutadiene—metal complexes are unlikely intermediates in the oligomerization of acetylenes to cyclooctatetraenes.

Schrauzer proposed a concerted, "π-complex multicenter reaction" mechanism for the nickel-catalyzed tetramerization of acetylene to Reppe's cycloactatetraene [47]. By blocking one of the required four coordination sites on nickel with appropriate ligands, Reppe's system yields benzene. Schrauzer proposed the concerted [2 + 2 + 2] process here. As discussed earlier (see page 000), three acetylenes may, in theory, undergo the concerted cycloaddition to benzene with retention of coordinate bonding [12]. Such a mechanistic scheme would thus not suffer from the symmetry restraints and thermodynamic defficiencies in eqn. 8.

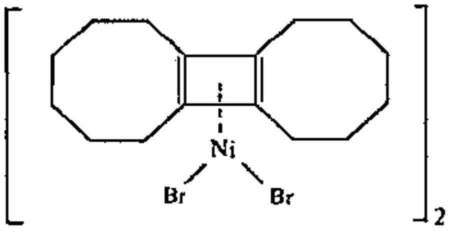
Zeiss et al. had first reported the [2 + 2 + 2] cyclotrimerization of acetylenes in a chromium-promoted synthesis of benzenes [48]. Disubstituted acetylenes were cyclically condensed by triaryl- and trialkyl-chromium compounds to benzene derivatives, polynuclear aromatic hydrocarbons and aromatic π-complexes. Zeiss suggested that the chromium reagent, $(Ph)_3Cr(tetrahydrofuran)_3$, suffered stepwise replacement of the THF ligands by the reacting acetylenes. The formation of 1,2,3,4-tetramethylnaphthalene from 2-butyne and $(Ph)_3Cr(THF)_3$ was rationalized in terms of a tetramethylcyclobutadiene (THF)Cr $(Ph)_3$ complex. The subsequent mechanistic route to product was not specified. Bisaromatic π-complexes, also products in this reaction, were ruled out as intermediates in the synthesis of aromatic products. A simple [2 + 2 + 2] cycloaddition of chromium-coordinated acetylenes was proposed instead.

Wittig and Fritze [49] have catalytically trimerized cyclooctyne to XXVIII using Reppe's cyclooctatetraene nickel catalyst (eqn. 10). Anhydrous nickel bromide catalyst yields XXVIII essentially quantitatively. In the presence of small amounts of water, a bis(cyclooctyne) nickel bromide dimer



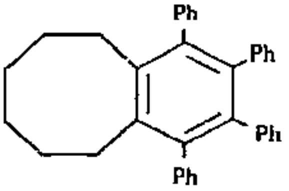
10.

XXVIII



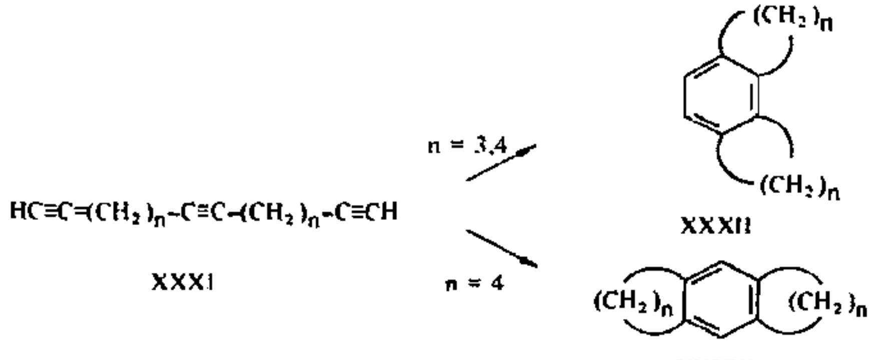
XXIX

is formed (9.4%) along with the benzene trimer. This complex is believed to be the cyclobutadiene complex XXIX. Complex XXIX proved to be quite stable in the presence of cyclooctyne, and not the catalytic species. Nickel carbonyl was also examined for catalytic activity. A cyclooctyne-nickel carbonyl solution was treated in turn with an oxidizing agent $[(NH_4)_2Ce(NO_3)_6]$ and tetracyclone, yielding XXVIII (70%) and the Diels—Alder adduct XXX (15%). Wittig and Fritze suggested that cyclooctyne—nickel complexes were intermediates in this system, offering a bis(cyclooctyne)nickel dicarbonyl complex as a possible structure.



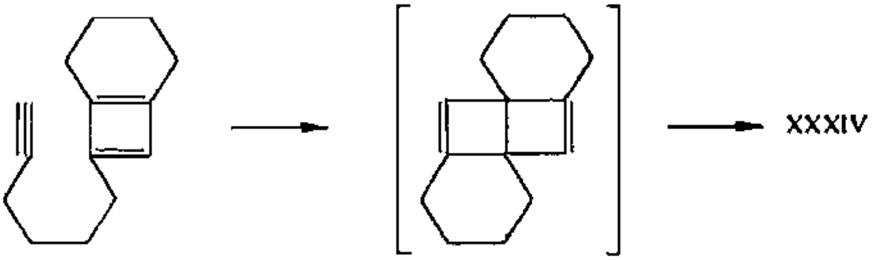
XXX

Triynes XXXI undergo titanium-catalyzed internal trimerizations [50] to the aromatic derivatives XXXII and XXXIII. A Ziegler system ($TiCl_4$ + R_3Al) was used to catalyze this novel cycloaddition. The expected product, XXXII, could reasonably result from a direct metal assisted [2 + 2 + 2] process or involve a titanocycle intermediate with subsequent Diels—Alder like



ring closure such as that in eqn. 11. The formation of product XXXIII, however, is not as easily rationalized. This fused ring system suggests the intermediacy of cyclobutadiene species. Complex XXXIV, a possible Diels—Alder adduct of a cyclobutadiene derivative with its pendant acetylene, was suggested as the intermediate in this system (eqn. 12). A mechanism involving the assistance of a reduced titanium catalyst in a forbidden-to-allowed mode, however, must be considered with caution. Simple Lewis acids ($AlCl_3$) are known to smoothly transform 2-butyne to hexamethyl-Dewarbenzene [51]. Ionic mechanisms have been proposed for this process [52], and a quite reasonable proton-initiated carbonium ion stepwise path to XXXIV can be drawn.

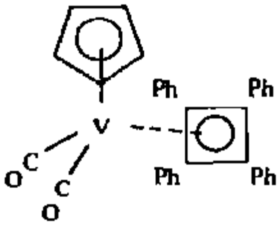
11.



12.

XXXIV

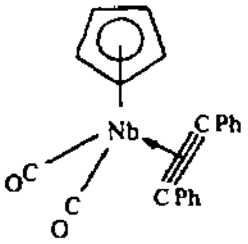
Nesmeyanov et al have examined the Group V transition metal series [53]. By UV irradiation of $C_5H_5V(CO)_4$ in diphenylacetylene (DPA), they obtained $C_5H_5V(CO)_2(Ph_2C_2)$, $C_5H_5V(CO)(Ph_2C_2)_2$ and tetracyclone. When $C_5H_5V(CO)_2(Ph_2C_2)$ was heated at 100° in diphenylacetylene (without UV irridiation), the cyclobutadiene complex XXXV was obtained. The authors note that the precursor to XXXV in the thermal reaction contains two CO ligands in contrast to the photolytic process where a second CO is



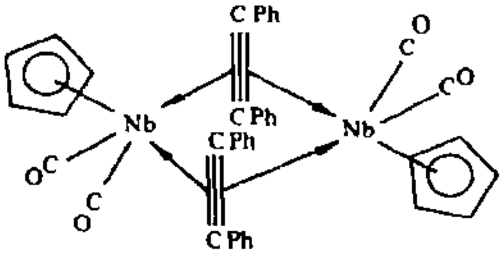
XXXV

lost in the formation of the bisacetylene complex, $C_5H_5V(CO)(Ph_2C_2)_2$. Thus the cycloaddition of acetylenes leading to XXXV is attributed, at least in part, to the steric factors associated with the seven-coordinate species preceding XXXV vs. a probable six-coordinate species preceding $C_5H_5V(CO)(Ph_2C_2)_2$.

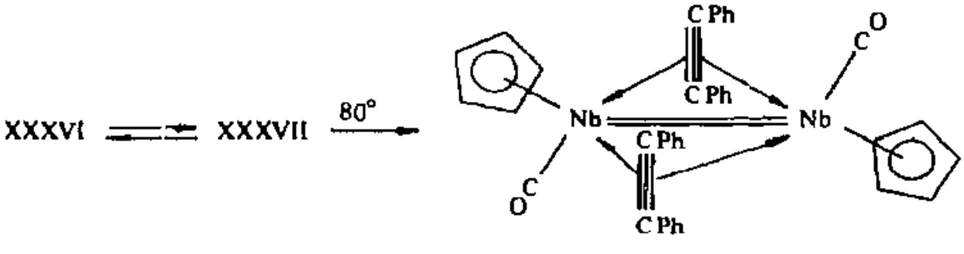
Earlier work by this group [54] focused on the niobium system $C_5H_5Nb(CO)_4$. The niobium complex $C_5H_5Nb(CO)_2(Ph_2C_2)$ (XXXVI) appears to dimerize reversibly in benzene solution and in the solid state to complex XXXVII. The dimer structure XXXVII was based on the disappearance of the $\nu_{c \equiv c}$ band in the IR spectrum of XXXVI in KBr. The vanadium counterpart to XXXVI, believed to be monomeric in solution and the solid state, differs in this respect. It was further observed [55] that dimeric XXXVII undergoes facile loss of CO in good coordinating solvents at 80° to dimer XXXVIII in accordance with Scheme 1. The structure of XXXVIII was confirmed by crystal analysis. A Nb—Nb bond of 2.74 Å was reported, indicating double bond character, consistent also with the 18-electron rule. The tight Nb—Nb bond noted in XXXVIII would tend to maintain the bridging acetylenes sufficiently far from each other to minimize any carbon—carbon bonding interaction between the two coordinated acetylenes. Such should not be the case for XXXVII, however. This dimeric complex enjoys complete coordinative saturation (i.e., seven-coordinate) at each d^4 metal nucleus. Metal—metal interaction, contributing to hypercoordination and to some extent antibonding, would not be anticipated. Greater vibronic flexibility would thus be open to the rectangular bridging system defined by the $Nb_2(Ph_2C_2)_2$ system of XXXVII.



XXXVI



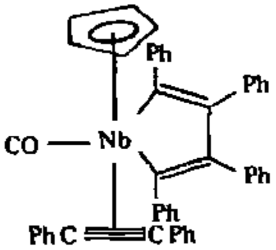
XXXVII



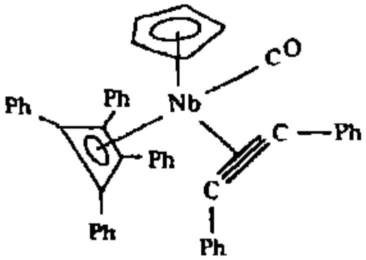
XXXVIII

SCHEME 1

Nesmeyanov et al. have also reported the formation of $C_5H_5Nb(CO)(Ph_2C_2)_2$ (XXXIX) by UV irradiation of XXXVI in diphenylacetylene [56]. XXXIX proved to have a simple bisacetylene structure. When XXXIX was heated with DPA in boiling benzene or in the melt at 120°, DPA adds to XXXIX yielding $C_5H_5Nb(CO)(Ph_2C_2)_3$ (XL). Significantly, the formation of XL at 80° was accompanied by the appearance of considerable amounts of hexamethylbenzene. It was also noted that hexamethylbenzene was a decomposition product of XL, and not a catalyzed product. The actual structure of XL was thus of some importance since it offered clues to at least one route to a [2 + 2 + 2] cycloaddition product, and perhaps, even a [2 + 2]. The authors speculated on its structure, basing their proposed structure on its spectral and chemical properties. A trisacetylene complex was ruled out primarily for steric reasons. The metallocycle structure A was settled on, because an analogous cobalt metallocycle yielded hexaphenylbenzene when treated with diphenylacetylene while certain cyclobutadiene metal complexes did not.



A



XL

A later crystal analysis [57] of XL, however, indicated the cyclobutadiene structure, and not A.

XL is thus structurally similar to its iso-electronic vanadium complex XXXV. The facility with which the niobium system undergoes the dimerization XXXVI ⇌ XXXVII suggests a reasonable path to XL. The bisacetylene niobium complex XXXIX might easily undergo a dimerization similar to its iso-electronic and structurally similar counterpart XXXVI. The bimetallic dimer could undergo the [2 + 2] process noted in eqn. 9 (page 124), and with the addition of one incoming DPA ligand, yield XL and XXXIX.

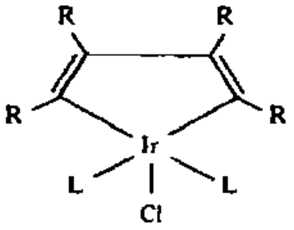
One point of significance here is the inherent danger in making assumptions in one metal systems based on similar chemistry from other, distinctly different metal systems. Because some tetraphenylcyclobutadiene complexes fail to undergo the [4 + 2] cycloaddition with DPA in certain metal systems [58] does not mean that the niobium systems cannot. As noted above, XL undergoes smooth decomposition to hexamethylbenzene, and the [4 + 2] pericyclic process is most likely. Moreover, because a cobalt metallocycle does yield hexamethylbenzene when treated with DPA [59], it should not suggest a generality embracing most of the transition elements. Indeed, the various transition metals, and particularly those of different groups, are likely to exhibit their own, sometimes distinctly different modes of catalysis just as they exhibit chemical properties unique to themselves.

The facility with which the niobium complex XXXVI dimerizes to XXXVII may suggest a possible route for the iso-electronic vanadium cyclobutadiene complex XXXV. The chemical similarities in these two metal systems would lend some reliability to chemical comparisons. Assuming a vanadium counterpart to XXXVII can exist in equilibrium with its monomer, a symmetry-allowed [2 + 2] cycloaddition may occur with two metal centers assisting [see page 124; eqn. 9], assuming ligand-field effects are relatively nonrestrictive [14,15,22]. If such were the case, coordinate bonding may be preserved in the thermal reaction of $C_5H_5V(CO)(DPA)$/DPA, with a DPA displacement on the vanadium face-sharing cyclobutadiene dimeric complex, yielding the starting complex $C_5H_5V(CO)_2(DPA)$ and the observed product XXXV.

It was noted that the niobium dimeric complex XXXVII and a vanadium counterpart are coordinatively saturated while the monomeric species XXXVI formally possesses one degree of unsaturation. A [2 + 2] ring fusion of the bridging acetylenes would constitute a loss of one coordination center at each metal nucleus. It would be similar, in this regard, to undergoing cleavage to the monomeric structures. A [2 + 2] ring fusion, however, assisted by an incoming DPA ligand would tend to preserve full coordination and nicely provide a route to the fully coordinated cyclobutadiene product XXXV and the six-coordinate starting monomer $C_5H_5V(CO)_2(DPA)$.

Such a course of events would indeed be novel, yet theoretically possible and mechanistically reasonable. However, as this review will show, other routes to cycloaddition exist. Unfortunately, experimental evidence differentiating between reasonable possibilities is lacking, and difficult to obtain.

Collman et al. has reported the reactions of metallocyclopentadiene complexes of iridium and rhodium with disubstituted acetylenes [60]. Iridocycle XLI (L = $P(C_6H_5)_3$; R = CO_2CH_3) was synthesized and found to catalyze



XLI

the trimerization of dimethyl acetylenedicarboxylate to the hexasubstituted benzene. The reaction takes place at reasonable rates in boiling toluene and slowly in boiling benzene. The analogous rhodocycle is an effective catalyst in boiling benzene. Collman et al. suggested the mechanism outlined in Fig. 1. Catalysis could be inhibited under 60 psi of CO, presumably from CO competition for open coordination sites on XLI. A Diels—Alder mechanism was discarded because maleic anhydride fails to react with XLI. It was further noted that trimerization was quite sensitive to steric effects. Diphenylacetylene, for example, does not react. Even diethyl acetylenedicarboxylate does not form appreciable amounts of trimer.

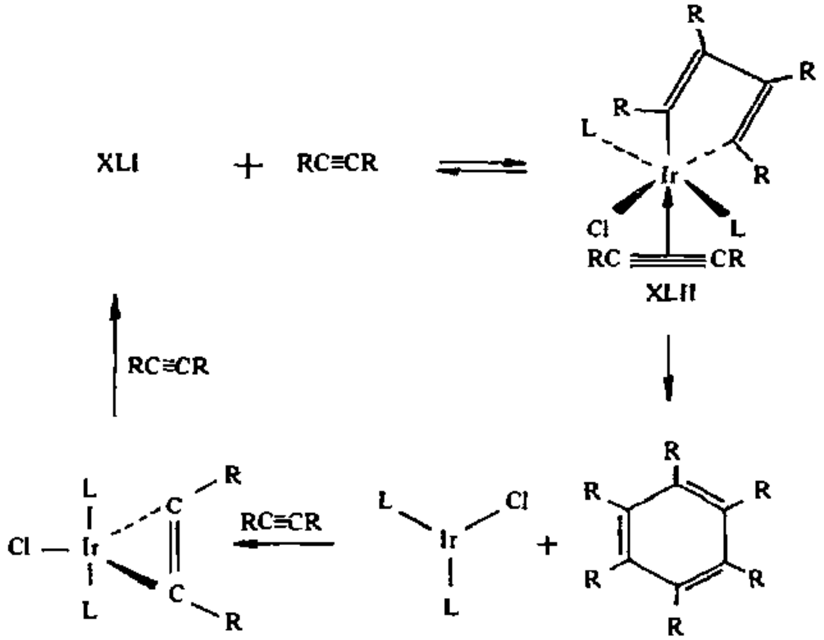
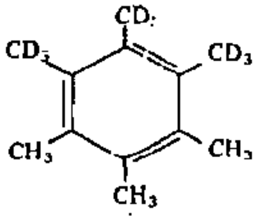


Fig. 1. Mechanism suggested by Collman et al. [60] for iridium-catalyzed trimerization of acetylenes.

Collman et al. entertain two mechanistic possibilities in the crucial transformation of XLII to the benzene derivative and IrL_2Cl. Since the stereochemistry suggested in XLII would not allow a concerted ring closure, the possibility of a molecular rearrangement to an iridium complex that could undergo the concerted [4 + 2] cycloaddition was suggested. Alternatively, ring closure may proceed stepwise, through a metallocycloheptatriene form. Aside from the fine points of ring formation, deuterium labeling experiments were offered supporting the general stepwise nature of the catalytic process outlined in Fig. 1.



XLIII

Whitesides and Ehmann have investigated the cyclotrimerization of 2-butyne-1,1,1-d_3 by a variety of transition metal complexes [61]. Among the benzene products that may conceivably form, only XLIII could be formed exclusively from some intermediate species having cyclobutadiene symmetry. The absence of such a product therefore ruled out the intervention of a cyclobutadiene metal complex or the free cyclobutadiene itself. Triphenyltris(tetrahydrofuran) chromium(III), dimesitylcobalt(II), dicobalt octacarbonyl, bis(acetonitrile)nickel(0) and the Ziegler system titanium tetrachloride—triisobutylalumnium all gave hexamethyl benzene products free of XLIII. Dichlorobis(benzonitrile)palladium, however, gave 9.5% XLIII which is approximately intermediate between the theoretical yields of the two extremes; viz. the intermediacy of some species having cyclobutadiene symmetry (12.5% XLIII) and mechanisms having only intermediate metallocycles, metal acetylene complexes (see page 114) or π-allylic organometallic compounds (0% XLIII). The route to XLIII is thus not clear. More than one active catalyst may be intervening or some entirely unrelated symmetrizing process could be taking part. Whatever the case, palladium in this system clearly stands apart yielding the mechanistic probe XLIII in more than 75% of what would be expected from the purely cyclobutadiene reaction path.

Whitesides and Ehmann have also investigated the formation of 1,2,3,4-tetramethylnapthalene from 2-butyne and triphenyltris(tetrahydrofuran) chromium [62]. Using the general labeling technique cited above, the free or metal-complexed cyclobutadiene was excluded as an intermediate by the observation that 1,2-dimethyl-3,4-di(methyl-d_3)naphthalene was not a

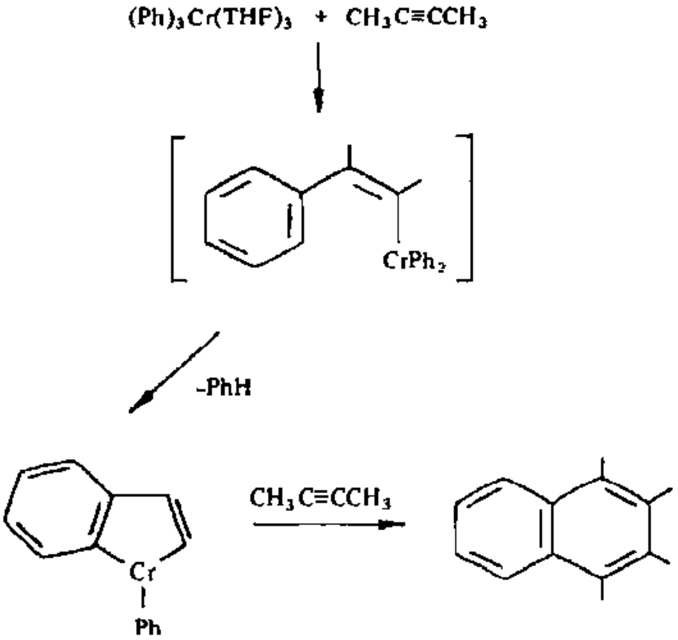


Fig. 2. Mechanism suggested by Whitesides and Ehmann [62] for triphenyltris-(tetrahydrofuran)chromium oligomerization of 2-butyne.

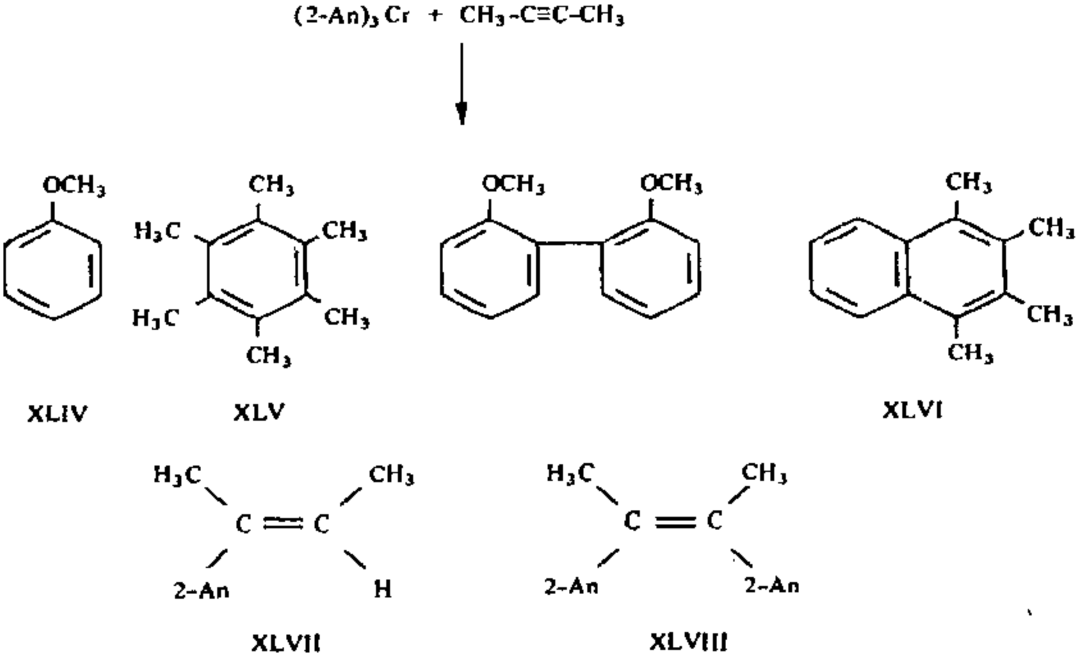
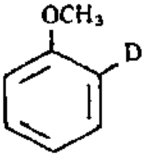


Fig. 3. Products obtained by Sneeden and Zeiss [63] in the triarylchromium promoted oligomerization of 2-butyne.

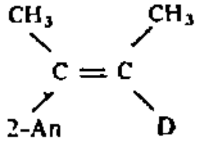
product from reaction with 2-butyne-1,1,1-d_3. Based on this and other data, the general reaction scheme outlined in Fig. 2 was proposed.

Sneeden and Zeiss have published results from the reaction of tris(2,3, and 4-methoxyphenyl) chromium with 2-butyne [63]. This paper also summarizes their earlier work and those of others working in similar systems. Experiments were carried out under mild conditions (0 to 20°) for long periods of time (1 to 2 weeks). Tris(2-methoxylphenyl)Cr gave the products listed in Fig. 3 (where An represents anisyl).

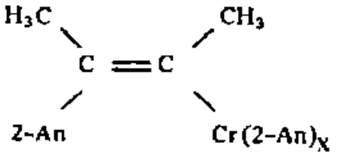
The major products were XLIV, XLV, the methoxy-free naphthalene XLVI and the two *cis*-butenes XLVII and XLVIII. Significantly, the methoxy-substituted naphthalene was observed only in trace amounts. Deuterolysis of the total reaction mixture (after one week) gave XLIX and L as the only major deuterium-containing products. The production of L implicates the insertion product LI as a major reaction intermediate.



XLIX



L

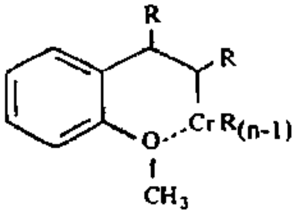


LI

The products from (3- and 4-An)$_3$Cr were similar to those in Fig. 3 except that the methoxynaphthalenes were produced in place of XLVI. Moreover, these reactions produced both *cis* and *trans* isomers of the mono and dianisylbutenes. The methoxyl extrusion process was therefore unique to the *ortho*-anisyl chromium reagent.

Sneeden and Zeiss focused on three groups of products of mechanistic significance: Group 1, those derived from one or two of the organic groups bonded to chromium (or a fragmentation product thereof) and one acetylenic unit, e.g., the mono and disubstituted butenes XLVII and XLVIII; Group 2, those derived from one or two of the organic groups bonded to chromium and two acetylenic units; Group 3, those derived from three acetylenic units with and without the organic groups bonded to chromium.

Group 1 products were rationalized in terms of intermediates like LI. The high specificity to *cis*-butenes noted from (2-An)$_3$Cr was attributed to stabilization by the *ortho*-CH$_3$O group as in LII. The *trans*-butenes were sug-



LIII

gested to form from isomerized intermediates of LI.

Products in Groups 2 and 3 remain subject to speculation. Metallocycle LIII, forming from some intermediate such as LI, was considered in the schemes discussed. This intermediate, proposed earlier by Whitesides and Ehmann [62], was thought unlikely by Sneeden and Zeiss. Their argument was based on the fact that the formation of 1,2,3,4-tetramethylnaphthalene [from $(2\text{-An})_3Cr$ + 2-butyne] clearly involved loss of OCH_3. They noted:

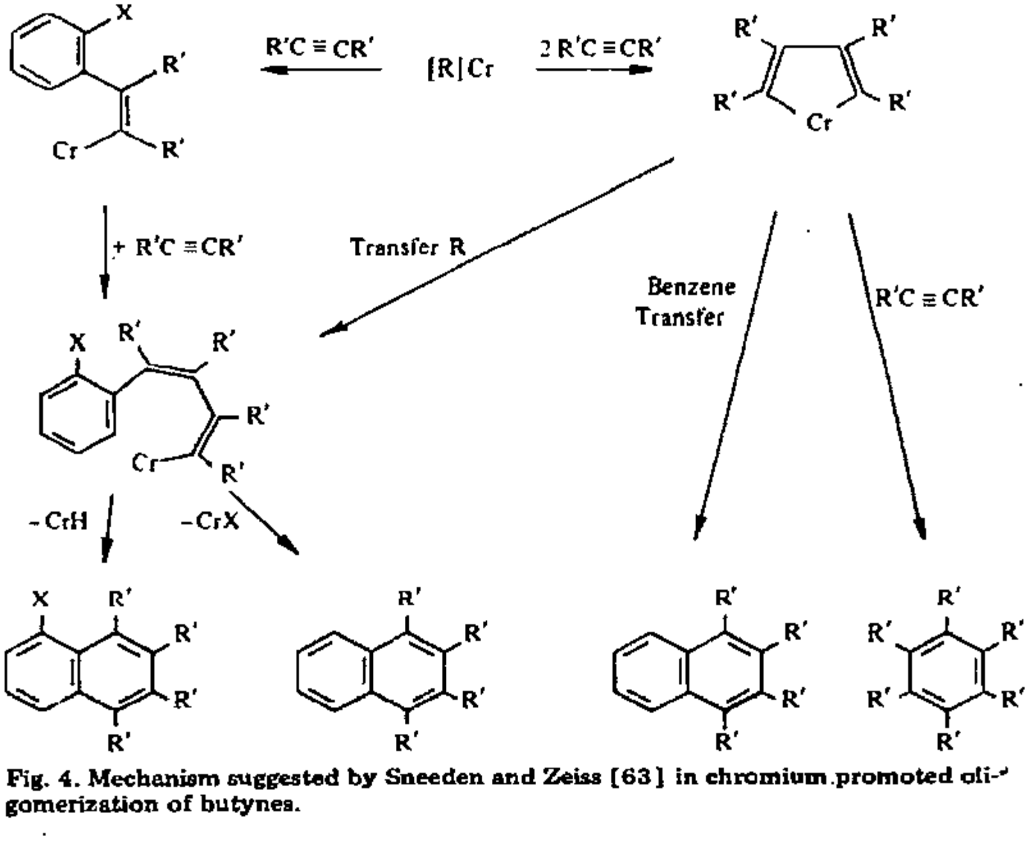
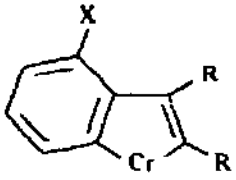


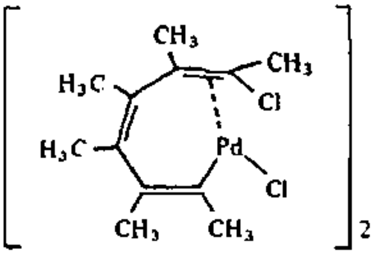
Fig. 4. Mechanism suggested by Sneeden and Zeiss [63] in chromium promoted oligomerization of butynes.



LIII

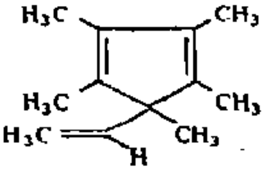
"Were this to occur in the formation of the chromocycle [i.e., to give LIII ($X = H$)] then the corresponding phenylbutenes should be found amongst the products. The presence of neither *cis-* nor *trans*-phenyl-2-butene could be detected amongst the trace products." These authors indicated the scheme outlined in Fig. 4, or combinations of the various paths in it, as possible explanations for products derived from the interesting reactions between the organochromium reagent and acetylenes.

Maitlis et al. have done considerable work on the reactions of acetylenes with palladium, platimum and rhodium systems. 2-Butyne combines with dichlorobis (benzonitride) palladium at —50° yielding a π-complex wich reacts at -25° with more 2-butyne yielding an intermediate (LIV), proposed to be some palladium derivative of 2-chloro-3,4,5,6-tetramethyl-2-*trans*, 4-*cis*, 6-*trans*-octatriene σ bonded to a PdCl at the 7 position and π bonded at the other end [64]. At higher temperatures LIV decomposes to $PdCl_2$ and

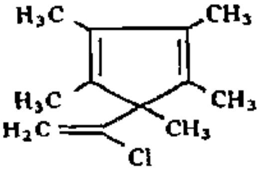


LIV

hexamethylbenzene. The structure of LIV was based on: (a) the PMR spectrum showing high asymmetry of the organic ligands; (b) the IR spectrum indicating an asymmetric $PdCl_2Pd$ bridge and no terminal PdCl bonds, a coordinated $C = C$, and a bond assigned to vinylic Cl; and (c) reaction of LIV yielding hexamethylbenzene, LV and LVI.

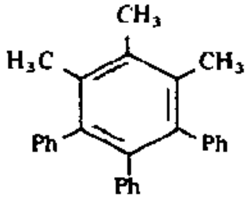


LV



LVI

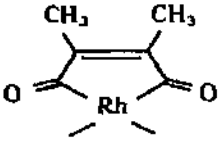
Blomquist and Maitlis had much earlier suggested that cyclobutadiene palladium complexes were unlikely intermediates in this chemistry [65]. Diphenylacetylenes were catalytically trimerized to hexaphenylbenzene by dichlorobis(benzonitrile) palladium. However, catalyst deactivation was invariably associated with the formation of a tetraphenylcyclobutadiene-palladium chloride complex, which was shown not to be an intermediate in the trimerization reaction. Methylphenylacetylene also trimerizes catalytically yielding the expected substituted benzenes [66]. One product, LVII, formed in only 3% yield, was not consistent with an intermediate like LIV. Its formation may suggest an alternate course of reaction intervening, one containing an organic species with cyclobutadiene symmetry. We have already noted a similar departure from the norm involving palladium from the work of Whitesides and Ehmann (see page 132).



LVII

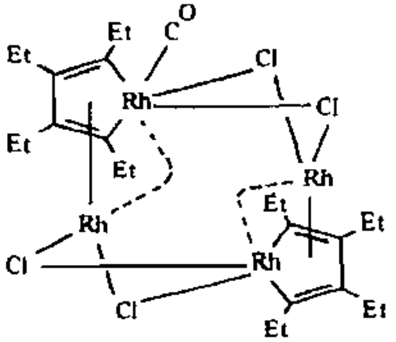
Zero-valent palladium and platinum appear to exhibit quite different catalytic behavior [67]. Dibenzylideneacetone-palladium(0) and -platinum(0) complexes react with dimethylacetylenedicarboxylate giving the corresponding metallocycles, which are intermediates in the formation of hexamethyl mellitate. These results underscore the importance of the formal oxidation state of the catalyst in the mechanistic paths adopted. Both metal complexes in this case react only with acetylenes bearing at least one strongly electron-withdrawing substituent, strongly suggesting nucleophilicity in the palladium and platinum low-valent systems.

Chlorodicarbonylrhodium dimer ($[Rh(CO)_2Cl]_2$) reacts with 2-butyne at 80° in benzene giving a mixture of compounds including hexamethylbenzene, duroquinone, chloro(π-duroquinone)rhodium dimer and chloro-(π-tetramethylcyclopentadiene)rhodium [68]. The distribution of products and mechanistic studies suggested the intermediacy of rhodocycle species such as LVIII.

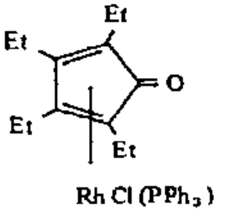


LVIII

This catalyst system was further reacted with 3-hexyne and diphenylacetylene [69]. At 80° diethylacetylene gave chloro(tetraethylcyclopentadienone)rhodium(III), duroquinone and a blue complex believed to be the polynuclear complex LIX. Maitlis discusses the possible role of LIX as an intermediate in the formation of the cyclopentadienones, particularly since LIX gives LX upon treatment with triphenylphosphine. Such a transformation would involve a phosphine-induced CO insertion into the Rh—C bond, a process with considerable precedence. However, no other reactions tried on LIX led to a cyclopentadienone complex. LIX, in fact, proved to be exceptionally stable, thermally. It thus appears possible that LIX is a stable, isolable artifact in the reaction and not a true catalytic intermediate. An alternative possibility discussed was that LIX is not an intermediate in the formation of the cyclopentadienone but rather of the benzenoid trimer.

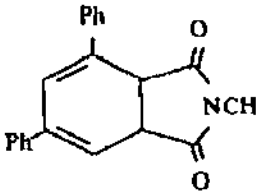


LIX

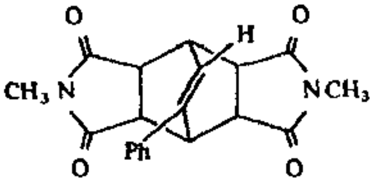


LX

Chalk has reported the nickel(0)-catalyzed cyclotrimerization of acetylenes with *N*-substituted maleimides [70]. Phenyl acetylenes reacted with the maleimide catalyzed by $Ni(CO)_2(PPh_3)_2$ yielding the Diels—Alder adducts LXI and LXII. The similar reaction with hexyne-1 yielded the analog to LXII but of different stereochemistry. This chemistry was suggested to proceed through metallocyclopentadiene intermediates which apparently suffer Diels—Alder attack by *N*-methyl maleimide. Interestingly, the reaction is catalyzed by the nickel complex, but not $PdCl_2$. Since both metal systems



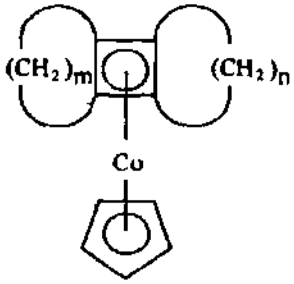
LXI



LXII

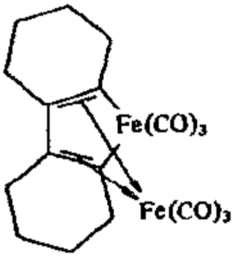
catalyze the cyclotrimerization of acetylenes, the case for different mechanisms is strengthened.

King and Efraty have explored some interesting synthetic routes to novel cyclobutadiene complexes. Treating macrocyclic diacetylenes with transition metal complexes, intramolecular cyclization was effected [71]. Complexes of general structure LXIII were obtained by reacting equimolar quantities of cyclopentadienyldicarbonylcobalt with 1,7-cyclotridecadiyne or 1,8-cyclo-



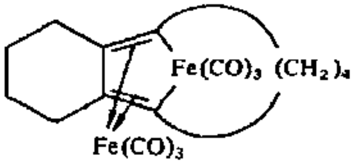
LXIII

tetradecadiyne in boiling octane for 17 h. Similar reactions with the macrocyclic alkadiynes and $Fe(CO)_5$ and $Fe_3(CO)_{12}$ proved more complex. Thus intramolecular transannular cyclization reactions were observed yielding tricyclic cyclobutadiene-iron tricarbonyl derivatives $(alkadiyne)Fe(CO)_3$, a tricarbonylferrole-iron tricarbonyl derivative of structure LXIV ($m = 4$, $n = 4$) [72], or tricyclic cyclopentadienyliron carbonyl derivatives of stoichiometry $[(alkadiyne\text{-}H)Fe(CO)_2]_2$ depending upon the macrocyclic alkadiyne used. The interesting metallocycle LXIV was first assigned structure



LXIV

LXV based on various spectral data and a reasonable guess as to a probable course of formation. X-ray analysis [72], however, established structure LXIV, and not LXV. Structure LXIV is most intriguing, for it introduces

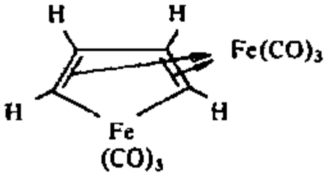


LXV

some unusual mechanistic possibilities. Clearly, a straightforward cycloaddition between two acetylene bonds and a metal nucleus would give LXV, not LXIV. A LXV-to-LXIV rearrangement was suggested, and the intermediacy of the cyclobutadiene-iron derivative, isolated in the reaction in trace amounts, was speculated [72]. These authors have further suggested that metallocyclic intermediates may play prominent roles in the mechanism of tungsten-catalyzed alkyne metathesis reported earlier [73].

That these two reactions might bear serious mechanistic similarities, however, is doubtful. The reported disproportionation of alkynes over tungsten is heterogeneous, and proceeds in moderate yields only at high temperatures (200° to 400°). Moreover, it also yields benzene derivatives and the absence of 1,2,3-substituted benzenes from the reactions of propyne, 1-butyne and 1-pentyne at temperatures below 300° rigorously rules out intermediates of cyclobutadiene symmetry in the formation of trimer products [74]. At the higher temperatures, some of this isomer is formed, but side reactions reasonably account for its formation.

$Fe(CO)_5$ reacts with acetylene at very high pressure (9,000 atm, 110°) yielding cyclobutadieneirontricarbonyl and complex LXVI among other products [75]. Significantly, LXVI was shown not to be an intermediate in the formation of the cyclobutadiene complex under the reaction conditions. Thus, the

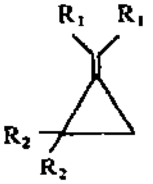


LXVI

most reasonable alternative mechanism to a bis(iron)-catalyzed [2 + 2] cycloaddition (see page 124) appears to be ruled out in this system. A bis(irontricarbonyl)-catalyzed [2 + 2] cycloaddition might reasonably proceed in this system yielding the observed cyclobutadieneiron carbonyl product. Moreover, a reversible, metathesis-like transformation would also provide a path to the bis-alkyne system prerequisite to products like LXIV.

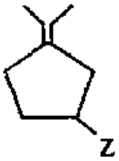
(iv) Other systems

Vinylcyclopropenes (LXVII) undergo a number of [2 + 2] cycloaddition



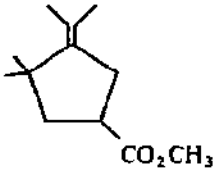
LXVII

catalyzed by zero-valent nickel. Noyori et al. [76] reported the formation of 3-methylenecyclopentanes (LXVIII) from the catalytic (bis(acrylonitrile)-

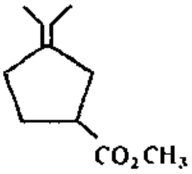


LXVIII

nickel(0)) fusion of LXVII and various substituted olefins (Z = $COOCH_3$, $COCH_3$ and CN). The intermediacy of the highly symmetric (C_{3v}), trimethylenemethane was considered but rejected since LXVII (R_1 = H; R_2 = CH_3) and methyl acrylate gave LXIX while LXVII (R_1 = CH_3; R_2 = H) yielded LXX. A



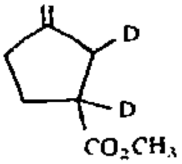
LXIX



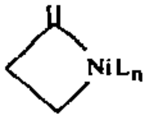
LXX

symmetric intermediate would have given similar product distributions.

This system was subsequently given closer mechanistic scrutiny [77]. Methylenecyclopropane, treated with methyl acrylate-α,β-d_2 in the presence of bis(acrylonitrile)nickel(0), yielded methylenecyclopentane LXXI in 70% yield. Noyori et al. proposed the intervention of metallocycle LXXII. The efficiency

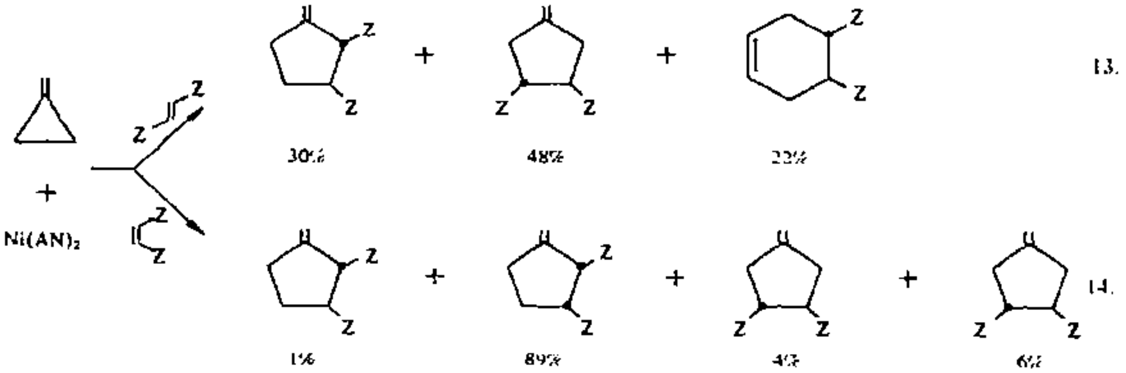


LXXI

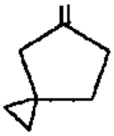


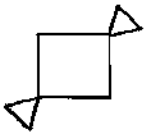
LXXII

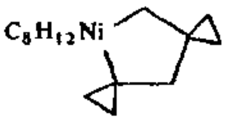
and the course of reactions were found to be influenced by the olefinic substrates which act as metal ligands. In the absence of substrate, treatment of methylenecyclopropane with $Ni(AN)_2$ in benzene resulted in recovery of starting material. More significantly, 1,2-disubstituted olefins react sluggishly, giving rise to the products in eqns. 13 and 14. It was noted that the major catalytic reactions of disubstituted olefins proceeds in a highly, if not completely, stereospecific manner, with retention of configuration at the olefinic carbon—carbon double bonds. Clearly, dual mechanisms appear to be operative in this system.



Binger [78] reports the direct [2 + 2] cycloaddition of methylenecyclopropane to LXXIII (62%) and LXXIV (20%) catalyzed by bis(1,5-cyclooctadiene)-nickel(0) at —15° C. A common, metallocycle intermediate was proposed (LXXV). The transformation LXXV → LXXIII is suggested to proceed

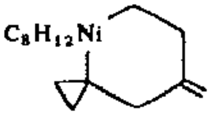

LXXIII


LXXIV



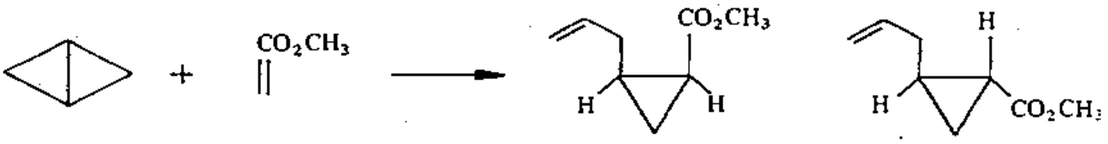
LXXV

through the six-membered metallocycle LXXVI. The proposed mechanism was based in part on reported chemistry of Li, Mg and B.



LXXVI

Noyori et al. [79] have examined the cycloaddition chemistry of bicyclo(1.1.0)butanes with olefins catalyzed by $Ni(AN)_2$. Bicyclobutane LXXVII and methyl acrylate yield LXXVIII and LXXIX in a 65 : 35 ratio. The cyclo-



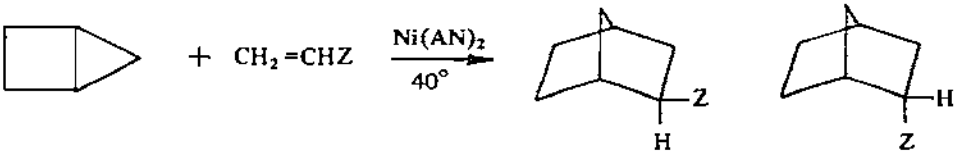
LXXVII LXXVIII LXXIX

propane rings in the products, constructed of two carbon atoms from methyl acrylate and one from LXXVII, implicate a skeletal rearrangement of LXXVII occurring in the catalytic fusion of substrates. Reactions with dimethylfumarate and maleate yielded similar products whose structures indicated highly stereospecific condensations with retention of configuration. The intermediacy of carbene complex LXXX was postulated. Alternative nickellocycles were also presented in sequential, unspecified mechanisms.

$$\left[\begin{array}{c} CH_2{=}CH{-}CH_2{-}CH{=}NiL_n \\ \updownarrow \\ CH_2{=}CH{-}CH_2{-}\overset{\ominus}{C}H{-}\overset{\oplus}{N}iL_n \\ \updownarrow \\ CH_2{=}CH{-}CH_2{-}\overset{\oplus}{C}H{-}\overset{\ominus}{N}iL_n \end{array}\right]$$

LXXX

Where bicyclobutane, a [1.1.0] fused ring system, fails to undergo the nickel-catalyzed [2 + 2] cycloaddition, bicyclo[2.1.0]pentane (LXXXI) suffers [2 + 2] bond fusion smoothly [80]. Methyl acrylate reacts with LXXXI at 40°

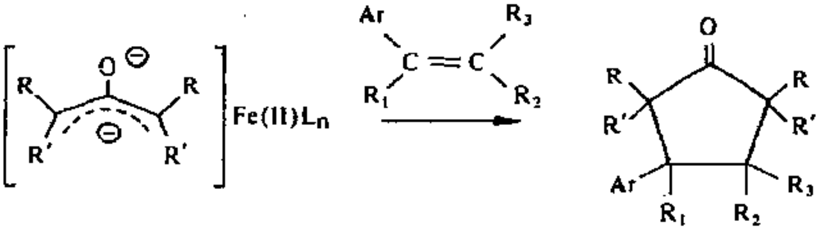


15.

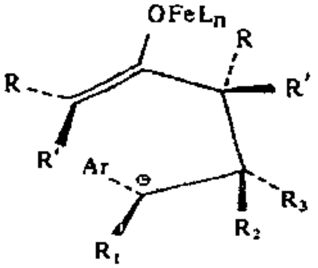
LXXXI

after 36 h yielding the *exo* and *endo* products indicated in eqn. 15 in a 50 : 50 ratio and 66% combined yield. The other product identified was 3-(cyclopent-2-enyl) propionate. Similar catalytic reactions of LXXXI with dimethylfumarate and dimethylmaleate yielded [2 + 2] cycloaddition adducts with near absolute sterospecificity.

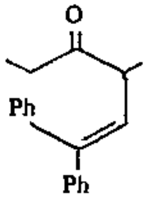
Noyori et al. have also studied the stereochemistry of a cationic "3 + 2 → 5 cycloaddition" [81]. Ionic complexes LXXXII condense with a variety of arylolefins yielding the corresponding cyclopentanones LXXXIII. The cycloaddition was explained by assuming a stepwise mechanism with an ionic intermediate of type LXXXIV. Direct cyclization yields LXXXIII, while prototropy from LXXXIV (i.e., R_2 or R_3 = H) would give rise to products of type LXXXV, obtained in 7% yield from the reaction of LXXXII with 1,1-diphenylethylene.



LXXXII LXXXIII



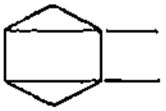
LXXXIV



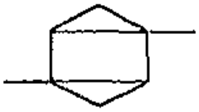
LXXXV

Particularly noteworthy, arylolefins undergo [2 + 2] cycloaddition stereospecifically, with retention of configuration. Addition of *cis*-β-deuteriostyrene to LXXXII (R, R′ = CH_3) gave *cis*-cyclopentanone adduct LXXXIII in 10% yield. It was noted that the observed stereospecificity in cycloaddition need not reflect concertedness but could instead be attributed to rapid ring closure of the hypothetical intermediate LXXXIV or to some charge-transfer interaction.

1-Methylcyclopropene undergoes facile cycloaddition catalyzed by a variety of palladium complexes [82]. Catalytic amounts of palladium chloride cyclodimerizes the cyclopropene vigorously at 0° to cyclobutanes LXXXVII and LXXXVIII. *Syn* or *anti* stereochemistry was not established, although



LXXXVII



LXXXVIII

dimerization of 1,3,3-trimethylcyclopropene catalyzed by π-allylpalladium chloride yielded the two *anti*-tricyclohexane structures LXXXIX and XC.

LXXXIX

XC

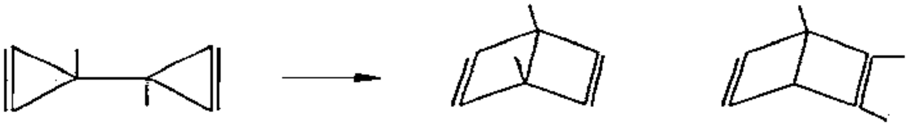
Attempts to dimerize 1,2-dimethylcyclopropene under similar conditions yielded only polymer. Neither bicyclobutane nor cyclobutane oligomerized in these catalytic systems. Significantly, dichlorobis(triphenylphosphine)palladium(II) did not catalyze the cycloaddition of cyclopropenes, and could be recovered unchanged from thermal oligomerization products of cyclopropenes. This sharp change in the catalytic behavior of a particular metal with changes in the electronic properties of its ligands has been seen before [39].

Chlorides of Pt(II), Os(III), Ru(III) and Re(V) produced no significant amount of [2 + 2] product from the cyclopropenes. However, methylcyclopropene when heated rapidly to room temperature in the presence of molybdenum hexacarbonyl yielded some of LXXXVII and LXXXVIII. The similarities in modes of catalytic action of both $Mo(CO)_6$ and $Cl_2Pd(PPh_3)$ were stressed by Baird et al [82]. It was noted that the catalytic scheme followed by methylcyclopropene mirrored that of 2-butyne in its trimerization to benzenes in the similar Pd system (see page 136). The cyclobutadiene intermediate suggested in the acetylene case [61] was likened to the tricyclohexanes LXXXVII and LXXXVIII, which were considered in this regard "bishomocyclobutadienes". Because of the theoretical arguments directed against a direct, concerted [2 + 2] metal-catalyzed fusion of acetylenes [15], a similar mechanism (i.e., [2 + 2] concerted) was considered unlikely for the cyclopropenes. Valence bond-resonance arguments [12,14,16], indicated in XCI, would tend to support this interpretation. A fully coordinated

XCI

biscyclopropene system is exactly represented by resonance hybrid XCI. Any [2 + 2] cycloaddition of the bisligand π bonds (i.e., [XCIa ≫ XCIb] → [XCIa ≪ XCIb]) would mean continuous enrichment of contributing structure XCIb into XCI as this system approached its transition state. The coordination bonds in XCIb are rotated 90° off the centers of maximum bonding in this ligand. It is thus an antibonding state, the direct counterpart to IXb (see page 114) for a bisacetylene system.

Silver ion catalyzes [83] the valence isomerization of 1,1′-dimethylbicyclopropenyl (XCII) to Dewar benzenes XCIII and XCIV. A simple [2 + 2]



XCII XCIII XCIV

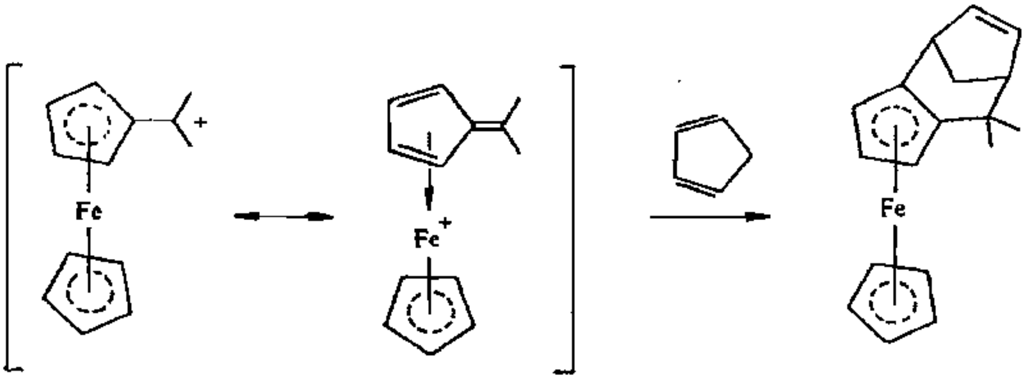
cycloaddition was considered as a possible reaction path. However, a prismane intermediate would reasonably have led to Dewar benzene XCV, which was not among the products.

XCV

Sneeden and Zeiss [84] have reported some cycloaddition products from allylchromium complexes with 2-butyne. Various methyl-substituted benzenes formed from combination of allylic moieties and 2-butyne. The product of interest here is 1,2,3,4-tetramethylbenzene, formed from the fusion of two allyl groups and one 2-butyne. This product was considered inconsistent with the generally proposed stepwise processes. A synchronous cyclization of one acetylene and two allyl groups was offered (eqn. 16).

16.

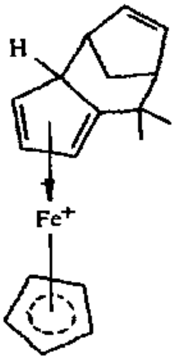
Metal-coordinated fulvene undergoes stereospecific cycloaddition with dienes [85]. The cationic fulvene complex XCVI reacts with cyclopentadiene yielding the single 1 : 1 adduct XCVII. The process was considered a [6 + 4] cycloaddition of the diene to the complexed fulvene followed by



XCVI

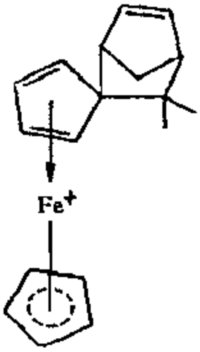
XCVII

rapid proton elimination from the proposed intermediate XCVIII. The alternative mechanism considered involved the production of XCVIII by a [1,5]



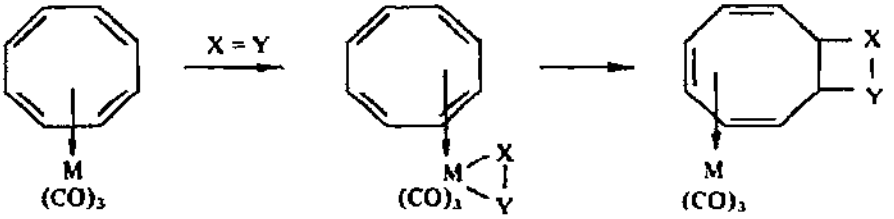
XCVIII

sigmatropic rearrangement of the spiro-intermediate XCIX, the product of a [4 + 2] cycloaddition of the diene to the exocyclic fulvene double bond.



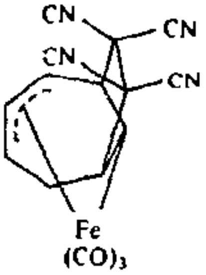
XCIX

Green and Wood have reported [2 + 2] cycloaddition products of various electrophilic dienophiles to cyclooctatetraene coordinated to ruthenium and iron tricarbonyls [86]. The dienophiles [X═Y: X = O, Y = $C(CF_3)_2$; X = $C(CN)_2$, Y = $C(CF_3)_2$; X = Y = $C(CN)CF_3$; X = Y = $C(CN)_2$; X = $C(CN)_2$, Y = $C(CF_3)_2$] apparently select the 1,2-addition path to the usual 1,4-route preferred in the thermal addition to a 1,3-diene moiety. This mode of reaction suggested the metal-assisted role indicated in eqn. 17. Dieneophiles (e.g.,



17.

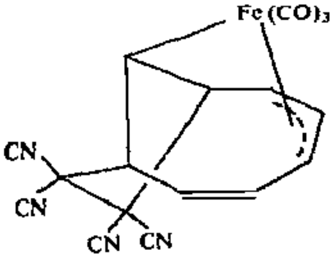
$C_2(CN)_4$) add in an *exo*-1,3-fashion to the triene ligand of tricarbonylcycloheptatrieneiron yielding the π-allyl complex C. Green et al. [88] have also reported the addition of tetrafluoroethylene and hexafluoropropene to

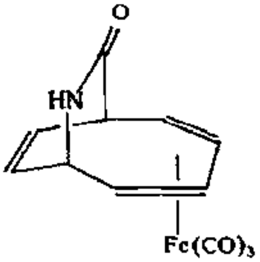


C

$Fe(CO)_3$ (diene) (diene = buta-1,3-diene, isoprene or cinnamaldehyde). Tricarbonyltrimethylenemethaneiron also fused with the electrophilic agent to form π-allylic complexes in which the iron atom and allylic groups were linked through a fluorocarbon chain. Green proposed a general mechanism for these systems involving the transformation of a 3-membered metallocycl to a 5-membered metal species.

Paquette et al. have recently reexamined the cycloaddition chemistry of tetracyanoethylene (TCNE) and chlorosulfonyl isocyanate (CSI) with cyclooctatetraeneiron tricarbonyl [89]. X-ray analysis of the products indicated that TCNE and CSI attack the cyclooctatetraene ligand stereospecifically, from its less hindered side giving, respectively, the 1,3 and 1,4-adducts CI and CII. The 1,3-addition yielding CI is thus the counterpart to that reporte

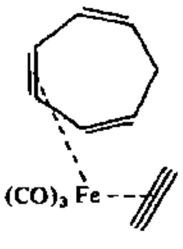




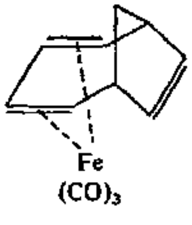
CI CII

by Green et al. [87] for the cycloheptatriene ligand which gave C. These processes, involving the direct participation of the metal in the cycloadditio process [22], fall outside of that class of catalytic processes where the transi tion element removes the symmetry restrictions to otherwise forbidden ligand transformations.

Pettit has reported preliminary results of what appear to be the first clear example of a metal-catalyzed, forbidden [6 + 2] cycloaddition [90]. Cycloheptatrieneiron tricarbonyl adds an acetylene ligand under UV irradiation yielding CIII. This complex then undergoes a thermal [6 + 2] *endo*-cycloaddition to complex CIV, confirmed by X-ray analysis. The cycloaddition (CIII → CIV) is very likely intramolecular and is indeed thermal, having been reproduced in the dark. Stepwise mechanisms involving certain metallocycles perhaps can be invoked here, but such proposals would be without experimental justification. Ligand field factors (see page 111), the *endo*-specificity of addition, and the intramolecular nature of ligand fusion make a metal-assisted, forbidden-to-allowed mechanism most attractive and difficult to avoid.



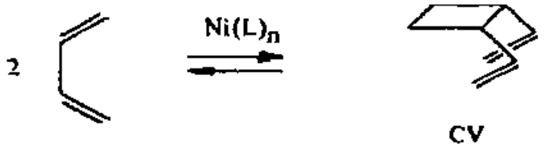
CIII



CIV

1,3-Dienes undergo a variety of metal-catalyzed cycloadditions. We noted earlier the work of Cannell in which norbornenyl systems undergo smooth [2 + 2] fusion to 1,3-butadiene (see page 120). These same titanium systems also catalyze the [2 + 2] cycloaddition of 1,3-butadiene and ethylene yielding, in high selectivity (75%), vinylcyclobutane [32]. This novel process constitutes the first example of the catalytic fusion of these two simple substrates. Piperylene and ethylene codimerized to 64% cyclics: *cis*- and *trans*-1-methyl-2-vinylcyclobutane (52%) and *n*-propenylcyclobutane (12%). 3-Methyl-*cis*-1,4-hexadiene was the other principal product. Isoprene and ethylene, however, gave only 2-methyl-*n*-hexadienes (96%) and 3-methyl-*n*-hexadienes (4%) as codimers. The formation of linear products was suggestive of Ti—H intervention. The stepwise mechanism, with hydride addition and elimination denoting initiation and termination of the catalytic cycle, was thus favored over an alternative, concerted [2 + 2] fusion to cyclobutane products.

By far the major work in the catalytic cyclooligomerization of 1,3-dienes has been centered at the Max-Planck-Institute at Mülheim. Wilke, Heimbach et al. have developed a beautiful body of synthetic chemistry associated with nickel-catalyzed 1,3-diene cyclooligomerizations. The reactions of interest here are those associated with the highly stereospecific dienyl fusions to *cis*-1,2-divinylcyclobutane (CV, eqn. 18). Other products in this catalysis are



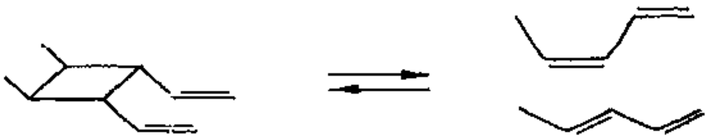
18.

CV

1,5-cyclooctadiene and 4-vinylcyclohexene. In the earlier reports of this chemistry [91], CV was not cited as a product. Later studies, however, revealed that CV is in equilibrium — an intermediate — with this system [92]. At low diene conversion (30%), CV, cyclooctadiene and vinylcyclohexene are formed in 36, 2 and 61% selectivities, respectively. The *cis*-divinylcyclobutane reacts smoothly with the catalyst yielding 1,3-diene and the cyclooligomers. A forbidden-to-allowed role for zero-valent nickel has been suggested [19] for the reversible process described in eqn. 18. A correlation diagram for the interconversion: [bis-1,3-butadienenickel ⇌ *cis*-1,2-divinylcyclobutanenickel] was shown to be ground-state, and particularly favorable for d^{10} metal systems. Molecular orbital arguments indicate only that a ground-state reaction path exists for a particular interconversion; they imply no mechanistic constraints in the system regarding any particular parth of reaction. The concerted path was thus introduced as a possible contributor to the complex catalysis of the d^{10} nickel system.

Subsequent experimental results, however. were not consistent with the concerted path of reaction, at least as a major contributor in the overall process. The strongest evidence against the concerted pathway was presented by Heimbach and Hey [93]. Operating at low pressure (30 torr), where primary products could be drawn off, the various cyclobutane products from *cis-* and *trans*-piperylene consistently gave the skeletally rearranged 1,3-dienes. The reported results were remarkably stereospecific as well as mechanistically puzzling. Eqns. 19 and 20 are representative.

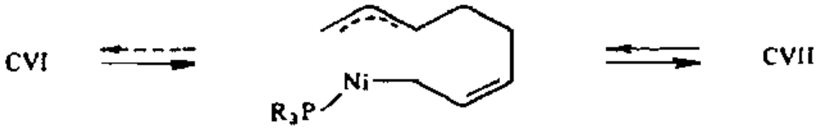
19.



20.

The Mülheim group has consistently viewed nickel-catalyzed diene oligomerization as stepwise, proceeding through intermediate π-allyl species. Evidence in support of the π-allyl intermediate in diene-cyclobutane interconversion has been offered [94]. Bis(butadiene)tricyclohexylphosphinenickel(0) [$(BD)_2NiPR_3$, (CVI)] is reported to react at 80° giving 65% BD dimer product; at −78°, CVI reacts with CO giving exclusively vinylcyclohexene (VCH). The corresponding divinylcyclobutane complex [(DVCB) $NiPR_3$, (CVII)], prepared in an analogous way, reacts with CO at −78° giving DVCB. If it is first warmed to room temperature, however. the CO treatment at −78° gives exclusively VCH. CVI is recovered unchanged from toluene solution at room temperature; under the same conditions, CVII partially rearranges to CVI.

From these observations, it was concluded that CVI and CVII rearrange in solution to a common intermediate, namely CVIII. Evidence supporting the common intermediate included an identical NMR spectrum for cyclohexane solutions of CVI and CVII.



CVIII

The surprisingly low yield of BD noted by Wilke in the thermal (80°) triphenylphosphine treatment of CVI has been at least partially explained by Brown et al. [95]. A careful analysis of Wilke's "bisdiene" complex CVI indicated that in both solution and the solid state it possesses the π-allyl structure described by CVIII. Thus the equilibrium CVIII $\rightleftharpoons$ CVI suggested in Wilke's reaction scheme is in a state of doubt. Clearly, a bisdienenickel complex might reasonably precede CVIII, but it does not appear to be the isolated complex described nor an intermediate in the equilibrium implied. How the observations of Brown alter the mechanism proposed by Wilke is at this time unclear.

Traunmüller et al. have published arguments extending the Woodward—Hoffmann rules to the stepwise processes that they propose in these reactions [20]. A recent review [96] of this chemistry attempts to explain the novel transformations of piperylene through the intermediates in eqn. 20. The equilibrium CVI $\rightleftharpoons$ CVIII is suggested to proceed suprafacially while CVIII $\rightleftharpoons$ CVII operates antarafacially. The suprafacial-antarafacial assignments stem from the number of electrons in the respective metal-ligand systems engaged in the pericyclic process (i.e. $10e^-$: suprafacial; $8e^-$: antarafacial). The stereochemical paths taken by the piperylene ligands along the reactions of eqn. 20, however, appear unclear with respect to their indicated symmetry assignments. That CVI and CVIII are identical [95] further obscures this interpretation.

In any case, treating the transition metal participant as a typical participant in a Woodward—Hoffmann pericyclic process is in variance with other descriptions of the metal's role [9,22]. In these treatments, the metal is viewed as a very versatile "pseudo-organic" participant capable of participating in any given pericyclic process in either stereochemical configuration (i.e., $[{}_d2_s]$ or $[{}_d2_a]$) depending on the positioning of its valence electrons in the d orbitals. When d orbitals of both symmetries may participate, the metal is free to act in either a suprafacial $[{}_d2_s]$ or antarafacial $[{}_d2_a]$ way. When such is the case, organic participants are no longer locked into a particular stereochemical course dictated by orbital symmetry factors; steric effects would thus override orbital symmetry factors.

The mechanistic details associated with this novel chemistry appear to remain somewhat clouded, hopefully the subject of future experimental attention. It is doubtful that simple concerted schemes might play significant roles.

A stepwise mechanism coupling steric effects and proximity factors might explain the peculiar stereospecificity observed in the formal [2 + 2] cycloadditions of piperylene [93] (see eqns. 19 and 20). Such a scheme is outlined below (eqns. 21 and 22), where two assumptions are made: (1) the initial oxidative cycloaddition proceeds preferentially to the *anti*-π-allyl complex (CIX, eqn. 21); (2) the final reductive cycloaddition proceeds only from the rearranged *syn*-π-allyl complex (eqn. 22). Simple steric factors associated with the methyl groups on the piperylenes would dictate methyl stereochemistry in eqn. 21 (i.e., *trans* where possible: *cis* + *cis* and *trans* + *trans*-piperylene; otherwise *cis*: *cis* + *trans*-piperylene).

CIX

21.

CX

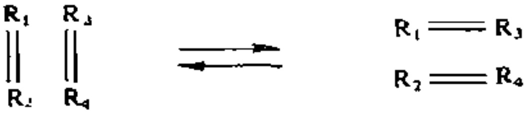
22.

This review has barely touched this broad area of descriptive chemistry. Others have appeared discussing both the synthetic and mechanistic aspects of the subject [97].

D. OLEFIN METATHESIS

(i) The reaction

Olefin metathesis, described in eqn. 23, must be considered the most remarkable, metal-catalyzed organic reaction discovered this past decade. It proceeds with great facility and striking specificity. Metathesis is an equilibrium catalytic system and the number of π and σ bonds in the starting and product systems remains unchanged. When simple open-chain olefins transform, the reaction is essentially isothermal, underscoring the novelty of this reaction. Thus, in the absence of thermodynamic driving force, double bond scrambling occurs effortlessly, at room temperature, with activation energies [98] as low as 6—8 kcal mole^{-1}.



23.

Olefin metathesis was first disclosed in the open literature in 1963 by Banks and Bailey [99]. It was then described as an olefin "disproportionation" process, a somewhat narrow definition focusing on just one aspect of a broader body of reactions. Cyclic olefins, for example, do not "disproportionate" as the term implies, but instead follow the molecular events intrinsic to the reactions of eqn. 23, yielding high molecular weight polymers. The term "metathesis", assigned to this chemistry at a later date [100], more realistically reflects the organic chemistry of this catalytic system. It was not until 1967 that the true nature and potential breadth of application was first disclosed [101].

The actual genesis of olefin metathesis, however, extends beyond 1963, to 1957 in a patent disclosure, filed by Peters et al. [102] describing the disproportionation of propylene to ethylene and butene over a heterogeneous MoO_3 catalyst, partially reduced with a trialkyl aluminium reagent. In this system, completely oxidized Mo is inactive, the highly reduced metal polymerizes olefins and the metal at some intermediate stage of oxidation disproportionates and isomerized olefins (i.e., *cis*-2-butene $\rightleftharpoons$ *trans*-2-butene, another manifestation of metathesis). It is now generally accepted that Mo and W metathesis catalysts are at some intermediate oxidation state, somewhere between 0 and +6. In a homogeneous tungsten system, a careful study [103] implicates an oxidation state of $+4(d^2)$.

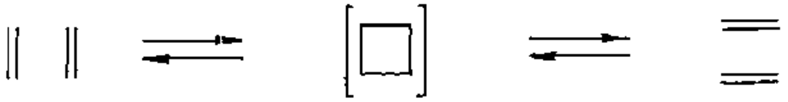
Heterogeneous Mo and W metathesis catalysts are generally prepared as oxides, supported on oxides of silica or alumina. They are activated at high temperatures (540 to 590°), usually in air [104]. It has been known for some time that these conditions of activation transform the group VI metal oxides into suboxides of varying composition, containing metal centers in reduced states of oxidation [105]. It thus appears that both groups of early workers, Peters et al. at Standard of Ind., and Banks and Bailey at Phillips arrived at identical catalyic species, by using different reductive procedures. However, there can be little doubt now that the novel organic transformation termed "metathesis" was first discovered and disclosed at least as long ago as 1957.

In historical perspective, it is indeed surprising that such an intriguing catalytic reaction could have enjoyed so long a period of gestation, that its utter novelty and scope of application were not recognized and appreciated sooner than they ultimately were. It can safely be said that the olefinic transformations intrinsic to metathesis are without counterparts in pure organic chemistry and catalysis. Perhaps it is this, the stark novelty of this chemistry which shrouded if from earlier recognition and an appropriate debut into the scientific community. Whatever the reasons, as an organic reaction, metathesis is clearly a late bloomer and perhaps even now not broadly recognized nor appreciated in its appropriate perspective.

This review will not attempt to cover the descriptive chemistry of this area, which has recently received exhaustive review [106]. Instead we shall focus on the mechanistic aspects, for it is here that the relevance to the subject of this review rests.

(ii) The mechanism

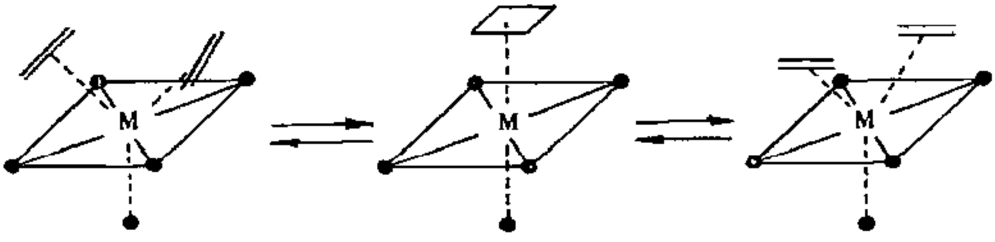
In metathesis, carbon—carbon double bonds are cleaved and reformed. The vinylic σ bonds attaching the two substituents to each of the olefinic carbons are not cleaved; thus the alkylidene moieties remain intact throughout the catalytic transformation. These observations in themselves provide the first approximation of a model for the critical transformation (eqn. 24). This mechanism in fact has enjoyed the major attention.

 24.

CXI

Intermediate species CXI, initially proposed [101] as a "quasicyclobutane", was subsequently termed [107] "pseudocyclobutane", "absorbed cyclobutane" [108], "metal-coordinated cyclobutane" [9,14,22] and simply "cyclobutane" [10,100]. Equation 24, of course, reflects only the reaction path of the organic reactants; it does not imply any assumed role for the catalytic species.

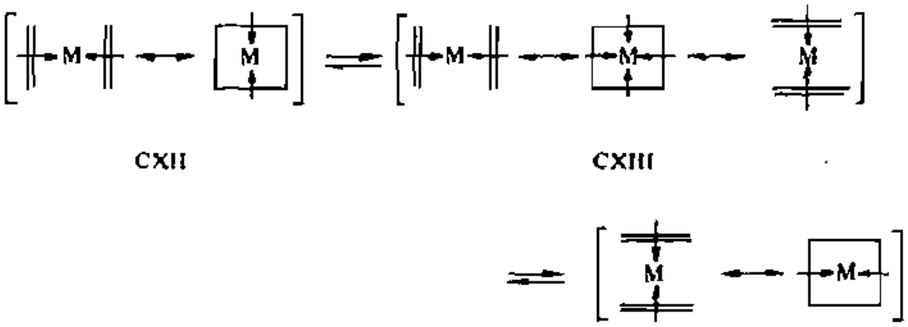
The forbidden-to-allowed mechanism [5] was proposed for this reaction [100]. In this mechanism, a bisolefin tungsten complex transforms through CXI to the product bisolefin complex. The role of orbital symmetry conservation has received additional theoretical development, primarily directed to the orbitral symmetry restrictions associated with the nonreacting ligands [9]. In this scheme, the transition metal is considered in its experimentally-indicated oxidation state [103] (i.e., IV, d^2). Seven-coordination was suggested. The reactions in eqn. 25 proceed totally free of symmetry restrictions. In a later development of this theoretical view (see page 113), the various intermediates in eqn. 25 were described [14] as



25.

CXII CXIII CXIV

the resonance structures in eqn. 26. A complete molecular orbital account (Fig. 5) of this process has recently appeared [109]. The correlation diagram in Fig. 5 is for a d^2 metal system possessing a nonrestrictive ligand field. Both σ and π bonds of the bisolefin system are represented in the



CXII CXIII

CXIV

26.

correlation. Intermediate species CXIII is generated in its ground state with the metal's two valence electrons equally distributed between orbitals of AS and SA symmetries. It is this electron pair assignment which directs the metal's coordination focus equally to each of the four bonds in cyclobutane and accounts for the three contributing structures in CXIII of eqn. 26. The ground state interconnections indicated in Fig. 5 reflect a highly facile course of transformation open to bisolefin ligand systems in metal complexes of appropriate energies. Where CXIII is of slightly higher free energy than CXII and CXIV, CXIII may exist as a transition state or a short-lived intermediate. Like metathesis itself, this aspect of the proposed mechanism has no counterpart in pure organic chemistry; that is, there are no examples of three interconverting organic valence bond systems in which a central intervening species corresponds to a stable molecular system, yet exists only as a transition state in the interconverting system. This interesting dichotomy, however, would in fact be anticipated if the transition metal were to remove the symmetry restriction to a forbidden organic reaction as this mechanism assumes.

There are other attractive features to the mechanism implied in eqns. 25 and 26. In metal complexes CXII and CXIV, the two carbon—carbon double bonds would necessarily be closer to each other in this seven-coordinate system than in other lower coordination-number complexes. Close proximity results in stronger carbon—carbon interaction, tending to lower the energy barriers to CXII → CXIII and CXIV → CXIII by relief of steric compression. Since only metals lean in valence electrons can assume seven-coordination, just a few metal complexes would be candidates for this special type of catalysis. In fact, this is found to be the case. Metathesis is essentially limited to catalysts of Mo, W and Re. Seven-coordination is known to play an important role in their coordination chemistry [110].

Pearson has offered an interesting interpretation of metathesis based also on the conservation of orbital symmetry [111]. He assumes a zero-valent molybdenum (d^6) biscarbonyl catalytic species in a square planar diolefin complex. Metathesis through a cyclobutane ring results in a tetrahedral

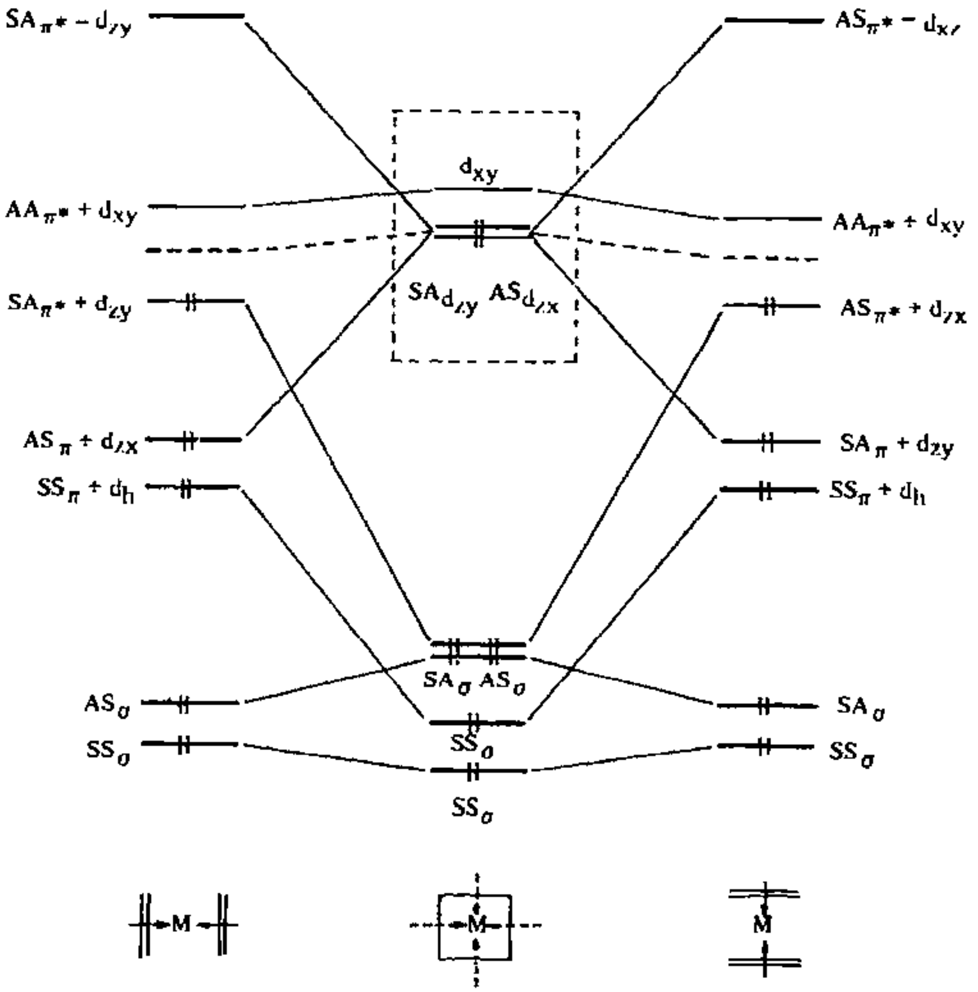
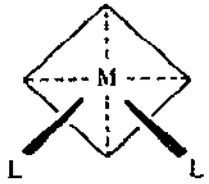


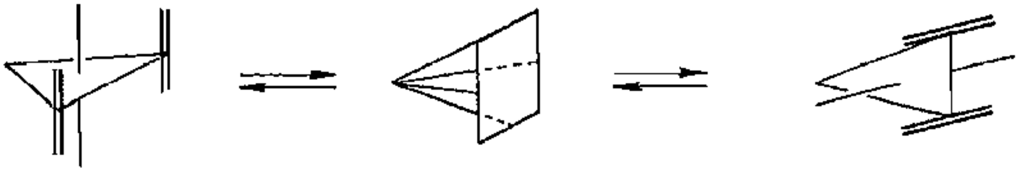
Fig. 5. A molecular orbital correlation diagram for the CXII ⇌ CXIII ⇌ CXIV interconversion [109].

complex and, necessarily, an orbital crossing. This is precisely the case noted earlier, namely that this particular (i.e., d^6) square planar-to-tetrahedral transformation encounters ligand field restrictions [9]. Pearson avoids ligand field restrictions (or an "intended orbital crossing") by rotating his olefin ligands 45° at the transition state (CXV). The A_2 motion reduces the symmetry from C_{2v} to C_2. In the lower group, the two critical d orbitals of b_1 and b_2 symmetries are rendered equivalent, allowing the required exchange of electron pairs to proceed smoothly between them. Although this particular model of the active catalyst (i.e., square planar, d^6) is an unlikely one, Pearson's proposal can be generally invoked where ligand field restrictions confront a [2 + 2] ligand pericyclic process.



CXV

Caldow and MacGregor have also applied molecular orbital arguments to an understanding of metal-catalyzed [2 + 2] cycloadditions [112]. They note the square planar-tetrahedral dilemna discussed above. The symmetry restrictions are avoided through an axial-equatorial-bipyramid (D_{3h}) exchange involving a square-pyramidal (C_{4v}) intermediate (eqn. 27). C_{2v}

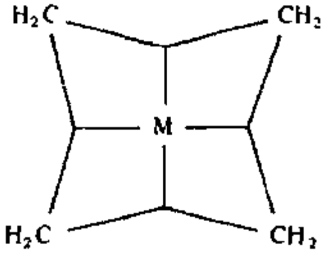


27.

symmetry is thus preserved throughout and ligand field restrictions circumvented. In this model, however, ligands must be lost and gained as the system traverses the transformations in eqn. 27. Thus, the three metal complexes in eqn. 27 are regarded as intermediates. This model favors a d^6 low-spin metal atom (i.e., zero-valent W and Mo) over less attractive d^1 and d^2 metal centers. Experimental evidence for the zero-valent assignment is cited by Hughes [113] — where molecular orbital symmetry principles are also applied to a metathesis mechanism — and the initial paper by Bank and Bailey where tungsten and molybdenum hexacarbonyl/alumina systems were discussed [99]. However, it now appears that zero-valent metal species are not obtained in the alumina-supported $W(CO)_6$ and $Mo(CO)_6$ catalystic systems described [114]. X-ray photoelectron spectra of these catalysts indicate that the metals do not exist as hexacarbonyls, but are displaced to higher binding energies. The active metals are reported to be in oxidation states greater than zero and less than six. Question might also be directed to the zero-valent assignment by Hughes, since convincing evidence on the nature of the actual catalytic species was not presented.

One source of considerable confusion regarding the actual mechanism of olefin metathesis is the absence of free cyclobutanes in product mixtures. Cyclobutanes are clearly not free intermediates since they do not react nor are they observed as distinct products [115]. However, does this mean then that starting olefins cannot transform to product olefins through a cyclobutane ring as, for example, is indicated in eqns. 25 and 26? It has been argued yes [116, 117] and no [9, 109]. If it is assumed that the metal-cyclobutane complex (CXIII) is either a transition state or a short-lived intermediate (see page 155), then the rate of cyclobutane escape from the metal into the product mixture would be zero in the first instance and approaching that in the latter. Because of microscopic reversibility, the rate of cyclobutane ring-opening would be likewise zero or approaching it. In some catalytic systems [116], a very slow rate of cyclobutane formation and consumption are in fact observed. In others, as noted earlier, these rates are zero [115].

Those citing the absence of cyclobutane intervention in the metathesis system as evidence against its involvement in any form, offer somewhat bizarre alternatives. Lewandos and Pettit propose the tetracarbene species CXVI, the four carbons apparently coexisting on the same metal center but



CXVI

not exhibiting carbon—carbon bonding [116]. The tetracarbene complex is distinguished from the simpler metal-coordinated cyclobutane intermediate and molecular orbital arguments are given to support its possible intervention. To make a realistic distinction from the metal-coordinated cyclobutane, it must be assumed that the tetracarbene ligand is, in fact, just that and not simply an alternative orbital description of CXIII. Structural distortions from a normal cyclobutane ring would not seem to suffice [109].

Pettit constructs CXVI from two sets of orbital couples. Assuming minimum carbon—carbon bonding, this yields eight molecular orbitals (MO's) in two sets, set 1 of slightly lower energy than set 2. These are then mixed with metal atomic orbitals of appropriate symmetries and seven electron pairs injected into the seven lowest-energy MO's yielding the coordinate bond: three electron pairs from the metal (d^6) as back-bonds and four pairs from the tetracarbene as donor bonds. This necessarily requires the population of both sets of SA and AS MO's. Pettit's basic description should not be altered significantly even if carbon—carbon bonding is allowed to grow.

However, the tetracarbene complex, in which both the SA and AS MO's of set 2 are occupied, may not correlate in symmetry to either ground-state bisolefin complex responsible for its genesis [109]. The correlation diagram in Fig. 6 was offered in support of serious symmetry restrictions restraining these reactions. The highest occupied MO's in the bisolefin complexes which match SA_2 and AS_2 are antibonding combinations. Although empty orbitals would exist beneath them, they would apperently not symmetry-match. It

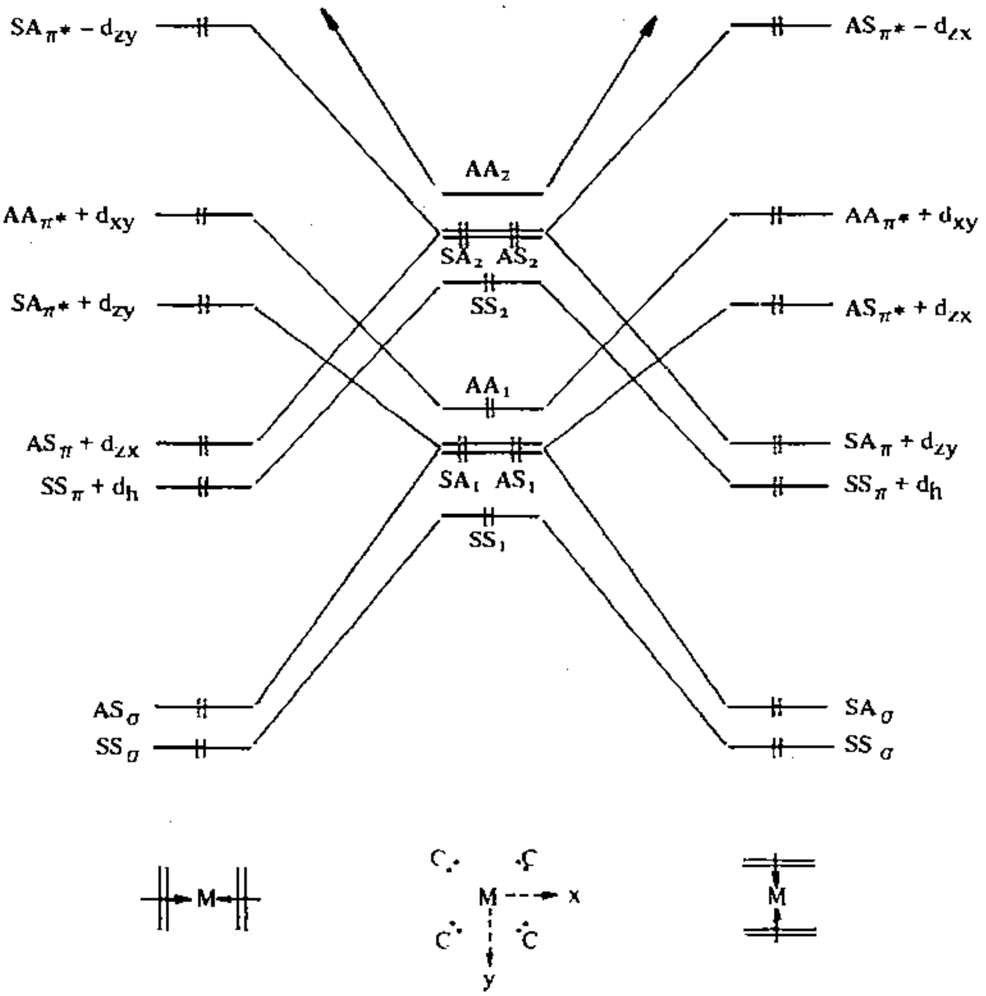


Fig. 6. A molecular orbital correlation diagram for a bisolefin ⇌ XCVI interconversion [109].

was stressed that the proposed population of SA_2 and AS_2 essentially precludes the required exchange of electron pairs between metal and ligands and thus would result in the indicated orbital crossing in any four-carbon species of cyclobutane symmetry irrespective of the degree of carbon—carbon interaction.

Lewandos and Pettit have presented experimental results presumably supporting the tetracarbene theory [118]. Reactions of toluene—$W(CO)_3$ with 4-nonene were carried out in heptane at 98° in open and closed systems. In closed systems, the extent of olefin metathesis was negligible. In open systems, CO was evolved and metathesis proceeded: 28% conversion out of a theoretical conversion of 50% in 24 h at 98°. In the presence of excess olefin, isomerization, a competing reaction in this particular system, dominated the product (i.e., 5% isomerization and 2% metathesis). These results were interpreted in terms of an active bis(olefin)tungsten dicarbonyl complex in equilibrium with CXVI, bis(olefin)tricarbonyl, tris(olefin)dicarbonyl, and tris(olefin)tricarbonyl tungsten complexes.

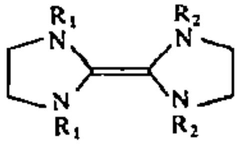
It should be noted that this metathesis system exhibits only marginal catalytic activity at best (i.e., 28% conversion at 98° in 24 h) and, further, that the various metal complexes proposed were not isolated or otherwise identified. Loss of CO and toluene appear to precede activation and an excess of olefin does curtail metathesis. However, a critical step to some active species not included in Pettit's scheme is also compatible with these observations. A coordinatively unsaturated tungsten complex, for example, may be the precursor to the active metathesis catalyst. Coordination saturation, either from CO or olefin ligands, would tend to diminish the rate of catalyst formation.

O'Neill and Rooney have offered experimental results seemingly in support of the tetracarbene proposal [119]. Using an activated (i.e., heating at 773°K in O_2 and in vacuo for 18 h at 823°K) cobalt molybdate heterogeneous catalyst, diazomethane was shown to decompose smoothly to ethylene and nitrogen at a level of activity that paralleled that for propylene metathesis under the same conditions. A catalyst not activated by a similar pretreatment (heated at 773°K in O_2, and in vacuo for only 1 h) gave negligible metathesis of propylene and had little activity for diazomethane decomposition. These results were reasonably ascribed to the existence of sites on the active catalyst which both metathesize propylene and decompose diazomethane to ethylene and nitrogen.

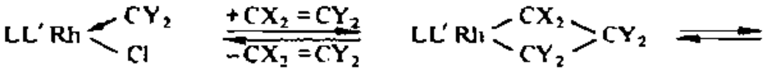
However, the connection between the diazomethane experiments and the existence of intermediate species such as CXVI is unclear. First, Pettit does not propose distinct metal-carbene intermediates nor does he propose their interconversion with CXVI. Second, the fact that diazomethane undergoes decomposition over the "activated" catalyst and not the base metal oxide is not in itself surprising. Activation of the metal oxide undoubtedly involves a reduction to some lower valent suboxide [105]. The active metal centers must shed some of their ligands in the course of activation (or subsequent to it) so as to ultimately accommodate olefin ligands, irrespective of the actual metathesis mechanism. Thus, the active site is very likely coordinatively unsaturated or at least approaching that state (through the attachment of some loosely held ligands). The active metal centers, with either existing or easily available coordination positions, may thus be looked upon as a highly electrophilic, Lewis acid-like species. Systems such as these are known to decompose diazomethane smoothly and catalytically to either ethylene + nitrogen or polymethylene, depending on the electrophilicity of the metal center [120]. The popular iridium complex $IrCl(CO)(Ph_3P)_2$, for example, with an open coordination site decomposes diazomethane cleanly and catalytically at −30° to ethylene and nitrogen [121]. A methylene–metal bond is suggested; however, this complex is not noted for its catalytic activity in metathesis.

Lappert et al. also discard any mechanism containing an intervening cyclobutane species for essentially the same reason as Pettit, namely the absence of free cyclobutane intervention in metathesis reactions [117,122]. A variety of metal-carbene intermediates were suggested in alternative paths of reaction [122]. Since much of this mechanistic speculation was presented in review form with the appropriate supporting references cited, this material will not be repeated here.

Lappert has, however, presented some interesting experimental results presumably linking certain carbene complexes of rhodium to metathesis [117]. Using rather special electron-rich olefins (CXVII, where the R substituents are varied between Ph and p-MeC_6H_4), metathesis was shown to proceed in the presence of a variety of rhodium (I) complexes in boiling xylene (2 h). A dicarbene complex ($L(Cl)Rh(CX_2)(CY_2)$) was implicated in the process and one complex (L=CO) was isolated from the system. The carbenes that are proposed are likely species in this system. The actual metathesis step was suggested to proceed through an oxidative addition to the metallocycle CXVIII in eqn. 28. This same mechanism had been proposed earlier to explain the metathesis of cyclic olefins [123].



CXVII



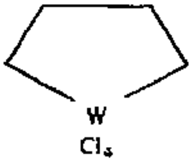
CXVIII

28.

There are certain features to this work which render the proposed mechanistic relevance to actual metathesis questionable. First, and perhaps most striking, rhodium is not generally considered a metathesis catalyst, particularly for simple olefins [106]. Second, carbene complexes of the alkylidene moieties in CXVII are well known in coordination chemistry [122] and it is not surprising that the rhodium(I) complex, known for facile oxidative addition, would yield the species proposed. Third, olefin metathesis is sterospecific (*cis*-to-*cis* and *trans*-to-*trans*) [106], and this is difficult to rationalize in terms of the species proposed. Finally, are extrapolations from certain catalytic systems to distinctly different catalytic systems meaningful? To put this another way, should mechanistic similarities be assumed when two different catalytic systems effect the same overall chemical reaction, such as that in eqn. 23? If we assume that rhodium, which does not metathesize propylene, "disproportionates" the very special olefin CXVII by the mechanism proposed by Lappert, does this realistically suggest the same mechanism for tungsten and molybdenum in their metathesis of propylene? This reviewer thinks not. Past extrapolations of this kind have proven deceptive. Acetylenes, for example, indeed undergo the "disproportionation" reaction implied in eqn. 23. The reaction, in fact, proceeds over a metathesis catalyst (tungsten oxide on silica); further, 2-pentyne yields the anticipated products 2-butyne and 3-hexyne in the theoretical ratio. However, the cyclobutadiene intermediate implied has been ruled out, at least in the by-product benzene derivatives [74]. Considering the severe conditions of this reaction (i.e., 200° to 400°), alternative mechanisms involving ionic species are reasonably implicated [124].

Of the mechanisms not invoking cyclobutane intervention, none have enjoyed more attention than that proposing a five-membered metallocycle intermediate (see page 123). This mechanism was first proposed by Cassar et al. [36] based on their results from the reaction of $[Rh(CO)_2Cl]_2$ with the highly strained hydrocarbon cubane. Since this chemistry will be treated in a subsequent section, details of their work will not be discussed here. One point, however, will be made. The reaction implicating the intervention of a metallocycle in the cubane system was stoichiometric, not catalytic. Other rhodium complexes affected a catalytic valence isomerization of cubane to its diene valence isomer. Because the stoichiometric reaction yielded a six-membered (from CO insertion) rhodocycle, intermediate rhodocycles were proposed generally for rhodium-catalyzed valence isomerizations; moreover, intermediate metallocycles were suggested to intervene broadly, playing a role in all metal-catalyzed, symmetry-forbidden [2 + 2] reactions, including metathesis. It should again be noted that $[Rh(CO)_2Cl]_2$ is not reported to be a metathesis catalyst. In fact, for the metathesis of simple, unstrained olefin such as ethylene, propylene and their higher homologues, all group VIII transition elements are conspicuously devoid of catalytic vigour.

Experimental evidence genuinely implicating the intervention of a five-membered metallocycle in metathesis was reported by Grubbs and Brunck [37]. The metallocycle CXIX was synthesized and decomposed under metathesis conditions. Significantly, CXIX generated large quantities of ethylene.



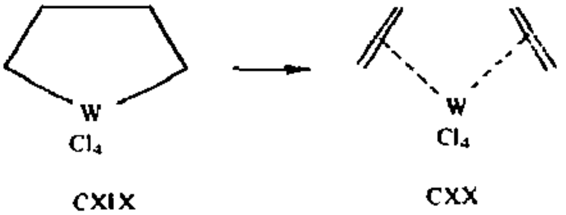
CXIX

This should be contrasted to the relative inertness and distinctly different modes of reaction of a similar platinocycle discussed earlier (see page 122).

Most important, labeling experiments established clearly that the ethylene produced had undergone metathesis to the extent of 12%. Moreover, the critical metathesis step had not occurred in a subsequent reaction of the generated ethylenes. The rearrangement of a single four-carbon unit had thus occurred on the metal center to which it was initially attached. This evidence would seem to firmly lock the metallocycle into the catalytic chain of events describing metathesis.

However, some important questions remain unanswered. (1) Is the metallocycle a critical intermediate in the chain of events and not simply a side-path by which a bisolefin system might transform? (2) If the intermediate is in fact critical, how does it rearrange and scramble the alkylidine moieties with activation energies as low as 6 to 8 kcal mole^{-1}? (3) Finally, are the experimental observations inconsistent with a catalytic system which operates along the path indicated in eqn. 26?

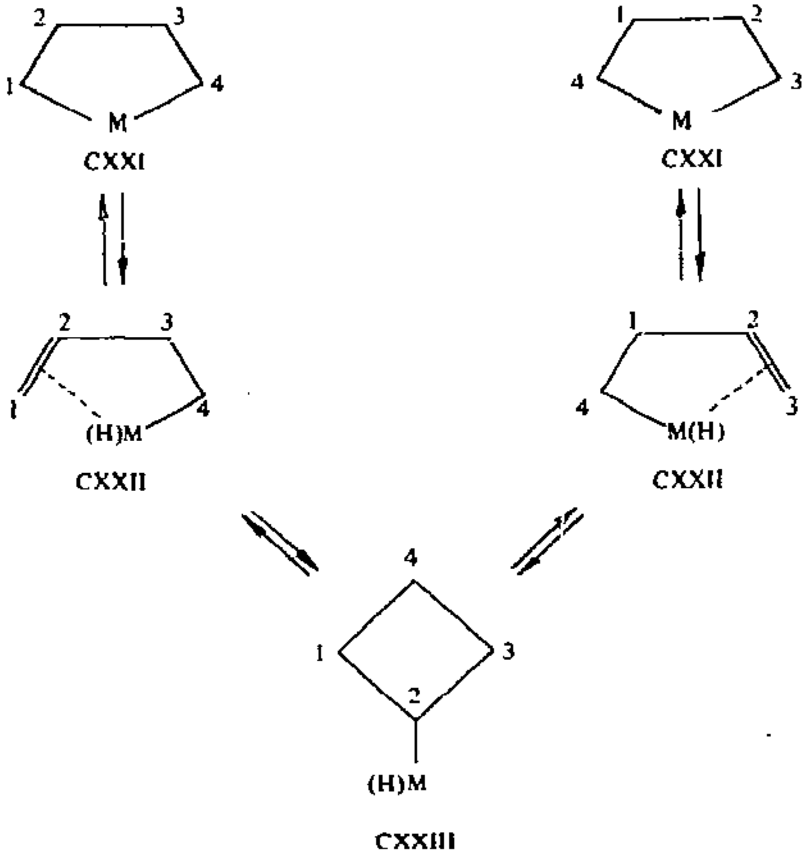
Regarding this final question, the most important result would seem to be the smooth generation of ethylene from the synthetic metallocycle. Most of the work reported to date [103] indicates that organotungsten compounds generated under these conditions undergo facile reduction, giving the active metal catalyst which, in the WCl_6 system, appears to be WCl_4. It might be anticipated, therefore, that the proposed metallocycle would be no exception in this regard but would undergo a similar (but not identical) reductive transformation. The most reasonable reductive path open to CXIX would seem to be the one proposed by the proponents of this mechanism, namely a simple reductive elimination to the bisethylene complex CXX, eqn. 29. This should be a smooth reductive step, directly yielding W(IV), a likely candidate for the metathesis catalyst. The CXIX-to-CXX transformation is additionally attractive because it proceeds with full retention of six-coordination. Metathesis, now, might easily proceed on CXX with CXIX serving only as a means of generating the active species (WCl_4) with the two reactants fully coordinated to it.



29.

The crucial question regarding the mechanistic mode of catalysis is whether or not carbon scrambling occurs prior to the transformation of CXIX to CXX or after. The experimental results clearly establish that metathesis does not occur after the olefins leave the metallic center responsible for their formation (i.e., WCl_4 in CXIX or CXX). Molecules of ether presumably replace departing olefins, precluding subsequent metathesis. However, the experimental results do not bear on the rearrangement of CXX itself, undergoing the series of transformations in eqn. 26. Thus, the critical question in this system seems unresolved at this time and the actual mode of metathesis appears to remain an open question.

If metallocycle CXIX is a critical intermediate in metathesis, its rearrangement leading to the observed scrambling of alkylidene moieties becomes the focal point of interest. Totally satisfying mechanisms are not easily drawn. Osborn and Whitesides have independently suggested an interesting course of reactions not without precedence [125]. A metallocycle species (CXXI) suffers β-elimination to the ω-alkenyl intermediate CXXII which, in turn, undergoes intramolecular alkyl addition yielding the critical intermediate CXXIII which possesses the appropriate symmetry element to render the alkylidene moieties equivalent.



E. VALENCE ISOMERIZATIONS

(i) General

Symmetry-forbidden valence isomerizations catalyzed by transition metals have been almost exclusively [$2_s + 2_s$]. Other reviews of this chemistry have appeared [10,22,38,126]. Our focus here will continue to be on the mechanistic significance of reported work. This section will attempt to cover most of the relevant literature not covered by earlier reviews and selectively treat the more significant portions of the older literature.

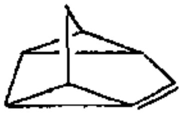
Hogeveen and Volger reported the first instance of a transition metal-promoted valence isomerization, namely the smooth, rhodium-catalyzed isomerization of quadricyclene (I) to norbornadiene (II) (6). The reaction is unusually facile; at −26°, *t*½ for I was found to be 45 min in a 0.7 *M* chloroform solution of $[Rh(II)Cl]_2$. Bis(ethylene)rhodium(I), palladium(II) and platinum(II) complexes behaved similarly. Because of the high exothermicity of this transformation (I contains approximately 65 kcal $mole^{-1}$ more strain energy [127] than II), it proceeds almost explosively at room temperature when small crystals of the catalyst are added to pure quadricyclene.

Volger et al. [128] have also reported the valence isomerization of *exo*-tricyclooctene CXXIV to tetracyclooctane CXXV (eqn. 30). This reaction,


CXXIV CXXV

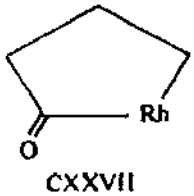
30.

which is far less exothermic than that of quadricyclene, is catalyzed at room temperature using 10 mole % $[Rh(CO)_2Cl]_2$. Unlike the thermal (200°) and photochemical reactions which yield a mixture of isomers (CXXVI and CXXV (20%)), the rhodium-catalyzed process is clean, yielding the [$2_s + 2_s$] product quantitatively. It is significant that the *endo*-isomer of CXXIV re-


CXXVI

mains unchanged in the presence of the catalyst, even at 100°. Photolysis of *endo*CXXIV takes a course of reaction similar to CXXIV giving CXXV in about the same yield (19%).

During the reaction of CXXIV, the red catalyst $[Rh(CO)_2Cl]_2$ was converted to a yellow, less active complex. Elemental analysis, and IR data indicated the presence of CXXVII in the yellow complex. $[Rh(CO)_2Cl]_2$ was known to insert into cyclopropane yielding the CXXVII moiety indicated in the yellow complex [129].


CXXVII

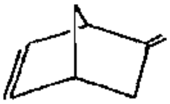
Several attempts were made to catalyze the isomerization of *exo,exo*-tetracyclononane CXXVIII to triasterane CXXIX. Starting material

CXXVIII CXXIX

CXXVIII, however, was recovered unchanged. Only the complex $[Rh(CO)_2Cl]_2$ was converted into a yellow complex, presumably containing the metallocycle moiety CXXVII.

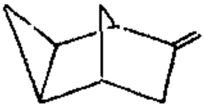
The Amsterdam group has also examined the reactions of CXXIV and CXXVIII with a variety of different transition metal complexes [130]. This work underscores the fact that the transition metals are capable of a variety of molecular rearrangements in addition to those of interest here. Metal complexes, quite similar in structure and electronic make-up, may effect totally different and distinct transformations on identical substrates with striking selectivities. The chemistry of $IrCl(CO)(Ph_3P)_2$, isoelectronic with $[Rh(CO)_2Cl]_2$, is an outstanding example.

In the presence of catalytic amounts of the iridium complex, CXXIV rearranges quantitatively to CXXX; no trace of the $[2_s + 2_s]$ rearrangement



CXXX

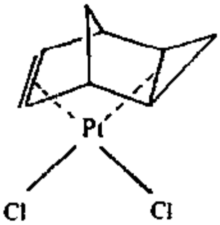
product CXXV was detected. Under similar conditions, CXXVIII yields CXXXI; the second cyclopropane ring in CXXVIII did not undergo a similar



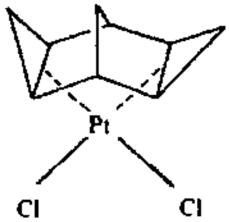
CXXXI

fate. It should be noted that the highly selective rearrangements promoted by $IrCl(CO)(Ph_3P)_2$ involve a skeletal rearrangement of the hydrocarbon framework, a reaction common to the transition elements and unrelated to the valence isomerization in eqn. 30.

Other transition metal complexes were examined for activity. $Mo(CO)_6$, $W(CO)_6$, Cu_2Cl_2, $RhCl(CO)(Ph_3P)_2$, $(PhCN)_2PdCl_2$, $IrHCl_3(Ph_3P)_3$ and $Rh_2(nor\text{-}C_7H_8)_2Cl_2$ were found to be inactive. Surprisingly, $RhCl(CO)(Ph_3P)_2$ is both isoelectronic and isostructural with $IrCl(CO)(Ph_3P)_2$, yet is without activity of any kind. With $[(C_2H_4)PtCl_3]_2$ or $K[(C_2H_4)PtCl_3]$, CXXIV and CXXVIII gave CXXXII and CXXXIII, respectively. If it is assumed that these complexes are square planar, ligand field restrictions



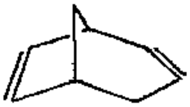
CXXXII



CXXXIII

would seem to preclude any rearrangement along the $[2_s + 2_s]$ reaction path [9,13,14,22].

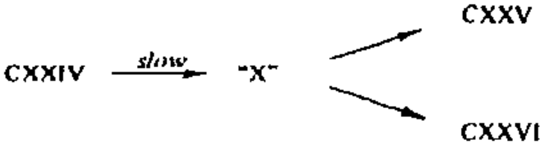
Katz and Cerefice [35] have also examined the valence isomerization of CXXIV. Using catalytic amounts of $(Ph_3P)_3RhCl$ at 90° for 2 h, CXXIV is converted into CXXV. CXXVI and CXXXIV in the ratio 32 : 62 : 6. The products appear primary, not changing in composition under the reaction



CXXXIV

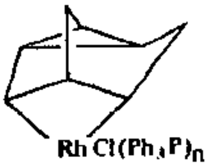
conditions. Thus, unlike the catalytic systems studied by the Amsterdam workers, which were highly selective in their modes of rearrangement, this rhodium system promoted both skeletal rearrangement and valence isomerization.

Katz and Cerefice present kinetic results establishing the reaction scheme outlined in eqn. 31. The existence of intermediate "X" was implied to pre-



31.

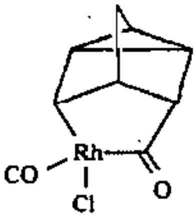
clude a "concerted" reaction path to CXXV. However, species "X" was not characterized, although the authors suggested the metallocycle CXXXV as a possibility. A variety of other structures might also be offered, including



CXXXV

interconverting species. Included among these would be one in which CXXIV is a bidentate ligand in some rhodium complex. It would seem that some metal complex "X", formed slowly from CXXIV + $(Ph_3P)_3RhCl$, could reasonably yield CXXV by a concerted $[2_s + 2_s]$ process or give CXXVI through a hydrogen shift. The mechanism excluded, namely an independent concerted transformation of CXXIV to CXXV, would be almost inconceivable if an intermediate complex of some kind were not invoked (see page 116). The alternative kinetic results would have required virtually independent intermediates ("X" and "Y") which would not interconvert at rates competing with their rates of formation. It is important to keep in mind that the mechanism presumably ruled out, namely a concerted CXXIV → CXXV, ideally requires full bidentate coordination and a nonrestrictive ligand field. The slow step of "X" → CXXV could be either of these processes; they may as well have been involved in the slow step CXXIV → "X".

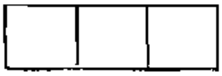
Cassar and Halpern [131] have reported to results of a stoichiometric reaction between quadricyclene (I) and $[Rh(CO)_2Cl]_2$, a rhodium complex known for its facile insertion into cyclopropane rings [128,129]. An excess of I was added to a hexane solution of rhodium complex (ca. 1.5×10^{-3} M) at room temperature. After 20 min, the yellow color of the initial complex disappeared, yielding the white product CXXXV in 80% yield. An excess of quadricyclene was required since the reaction with $[Rh(CO)_2Cl]_2$ is accompanied by some loss of quadricyclene through isomerization no norbornadiene, particularly if the quadricyclene is initially contaminated by norbornadiene. The presence of the latter was reported to promote the formation of $[Rh(norbornadiene)Cl]_2$, a powerful catalyst for the isomerization of quadricyclene to norbornadiene.



CXXXV

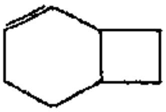
The mechanistic implications of the stoichiometric reaction yielding CXXXV were extrapolated to the catalytic isomerization of I → II by the highly reactive $[Rh(norbornadiene)Cl]_2$. The rate of this reaction was determined at 40° ($k = 2.2 \pm 0.2$ M^{-1} in $CHCl_3$), and shown to remain unchanged by the addition of excess norbornadiene. Reversible displacement of the norbornadiene ligand from the catalyst by quadricyclene was thus shown not to be a feature of the mechanism. However, it has been argued that highly strained valence isomers such as quadricyclene, where the very act of achieving full coordination transforms it to its less-strained isomer norbornadiene, may not be capable of surviving even partial coordination to some metal complexes [13,14,16,22]. In this case, displacement of quadricyclene from the catalytic center by norbornadiene would not be a feature of the reaction.

Pettit et al. [132] have also contrasted the stoichiometric behavior of $[Rh(CO)_2Cl]_2$ to catalytic systems in the valence isomerization of *syn*- and *anti*-tricyclooctane CXXXVI. It should be noted that only *syn*-CXXXVI should be capable of bidentate coordination to suitable metal centers. Steric factors and the "shape" of the two bridging σ bonds should both contribute to this coordination preference.



CXXXVI

Anti-CXXXVI remains unchanged after 5 days of heating with equimolar amounts of $AgBF_4$ in acetone. Under identical conditions, *syn*-CXXXVI is completely converted in ca. 1 min to a mixture of CXXXVII, CXXXVIII and CXXXIX in a ratio of 18:80:2, respectively.



CXXXVII

CXXXVIII

CXXXIX

Syn-CXXXVI reacts with [Rh(norbornadiene)Cl]$_2$ completely within 3 h in benzene at 63° yielding the same mixture of valence isomers in the ratio 70:2:28; *anti*-CXXXVI under these conditions remained unchanged after 20 h.

Interestingly, $[Rh(CO)_2Cl]_2$ continued its contrary ways, reacting with both the *syn*- and *anti*-tricyclooctanes under similar conditions giving acylrhodium complexes presumably of type CXXXV, essentially the same reaction noted earlier for its stoichiometric addition to cubane, *exo*-tricyclooctene (CXXIV), *exo, exo*-tetracyclononane (CXXVIII), cyclopropane and quadricyclene (I). The indiscriminate reaction with both *syn*- and *anti*-isomers suggests a separate course of reaction for $[Rh(CO)_2Cl]_2$, very likely insertion into one of the bridging σ bonds. The fact that the catalytic species [Rh(norbornadiene)Cl]$_2$ reacted exclusively with *syn*-CXXXVI would seem to suggest that monocoordination through one bridging σ bond is not sufficient for valence isomerization. Thus, one reaction mode clearly open to $[Rh(CO)_2Cl]_2$ would appear to be closed to [Rh(norbornadiene)Cl]$_2$ and $AgBF_4$.

However, the directional character of bridging σ bonds in the *syn*- and *anti*-CXXXVI may be an intervening factor. To begin with, simple valence isomerization to 1,5-cyclooctadiene requires full coordination to one or ideally both σ bonds [12,14,16] as indicated in resonance hybrid CXLa (see page 113). Metal ccodination at the other two σ bonds of the central cyclobutane ring would correlate CXXXVI with a biscyclobutene ligand system, not 1,5-cyclooctadiene. The energetics of this system would undoubtedly weigh aganst this kind of coordination over that indicated in CXL. Similarly, either mono- or biscoordination correlates *syn*-CXXXVI to *cis, cis*-1,5-cyclooctadiene and *anti*-CXXXVI to *trans, trans*-1,5-cyclooctadiene. The former resonance hybrid would clearly be of lower energy meaning a lower energy barrier to the *cis, cis*-1,5-cyclooctadiene valence isomer. Another possible reason for the facile isomerization of *syn*-CXXXVI over *anti*-CXXXVI could be the degree of relative overlap between the respective bridging σ bonds. In the *syn*-isomer, the two σ bonds are "bowed" upward, out of the cyclobutane plane. They would, however, be directionally parallel and bond overlap would be maximized. In the *anti*-isomer, these bonds are "bowed" in opposite directions, one above the cyclobutane plane, the other below. Bond overlap, and thus interaction, should be significantly less in this case than in the former. Valence isomerization, through a concerted mechanism involving the transformation of both bonds, (even through monodentate coordination), is greatly assisted by maximum interaction of the participating bonds. These factors would seem consistent with the catalytic selectivites reported.

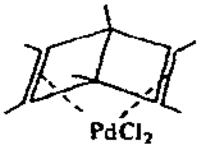
CXL

Hexamethylprismane (CXLI) has been shown [133] to undergo smooth

CXLI CXLII

and highly selective valence isomerization to Dewar hexamethylbenzene (CXLII). This reaction is catalyzed by [Rh(CXLII)Cl]$_2$; at temperatures below 0°, CXLII and hexamethylbenzene are produced in the ratio 20:1. At −30°, the half life of CXLI was 40 min. Acid catalysis (HF—BF$_3$) at low temperatures (−80°) yielded CXLII and the benzene derivative in equal amounts.

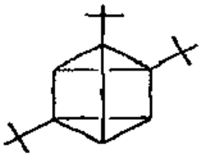
Dietl and Maitlis [134] have prepared the palladium(II) chloride complex of CXLII, (CXLIII). A freshly prepared solution of CXLIII in CDCL$_3$ was stable for 20 minutes at 33°; After this induction period, rapid decomposition gave hexamethylbenezene and PdCl$_2$. In the presence of small amounts



CXLIII

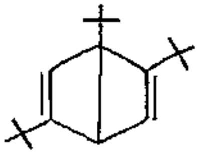
of free CXLII, however, CXLIII was stable for long periods of time. Maitlis was able to show that the catalytic species responsible for the decomposition was $PdCl_2$. The addition of catalytic amounts of $PdCl_2$ to solutions of CXLIII gave immediate valence isomerization, without an induction period.

Maitlis et al. [135] also reported the valence isomerization of the tri-*tert*-butyl (Dewar benzene) CXLIV. A variety of metal complexes were tested,

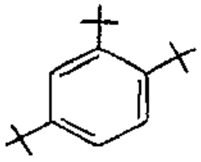


CXLIV

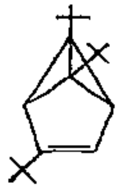
including the metals: Hg(II), Sn(II), Zn(II), Pd(II), Rh(I), Cu(II), Ru(0), Ph(II), Rh(III), Ag(I) and Co(III). 1,3,5-Trinitrobenzene was also examined. Reactions were carried out in methanol or pyridine solutions at 30°. The following products were observed in varying compositions. The genesis of some of the products appears straightforward. However, others clearly suggest multiple rearrangements. Maitlis suggests that CXLVII slowly transforms to CXLVI (as does CXLV), and that an intermediate isomer of CXLVII (not isolated) yields CXLVIII and, by solvolysis, CXLIX in fast reactions. An ion radical mechanism involving the metal center functioning as a Lewis acid was then proposed for this and most other valence isomerizations (eqn. 32).



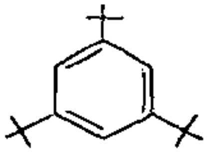
CXLV



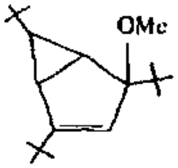
CXLVI



CXLVII

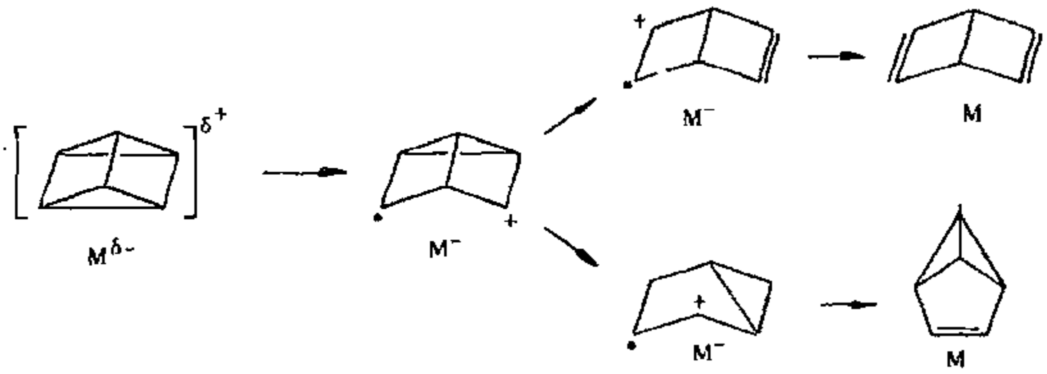


CXLVIII



CXLIX

An ion radical mechanism in this particular system is most reasonable. To begin with, the hydrocarbon substrate is one of extraordinary strain and unusual steric inhibitory properties. Molecules of very high strain possess high-energy molecular orbitals containing the orbital hybrids defining the strained bonds. These molecular orbitals will, of course, possess loosely held

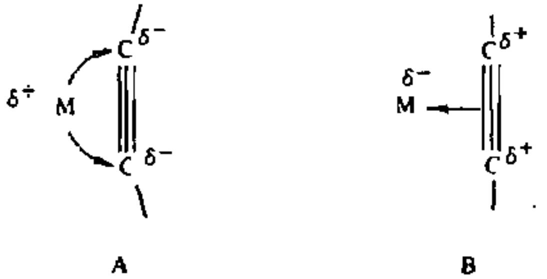


32.

electrons and they may very well be looked upon as Lewis bases, certainly with respect to Lewis acids possessing empty orbitals of lower energy. Electron transfer of the sort implied in eqn. 32 might reasonably proceed, particularly in solvents such as methanol and pyridene.

The ion radical mechanism has been proposed by others for some of the valence isomerizations of silver and similar ions [13,22] as well as one possible mechanism for metathesis (cf. ref. 126, p. 311). Deposition of metallic silver, which strongly suggests electron transfer at some point, has been noted to attend the valence isomerization of quadricyclene [136]. Failure of the rearranged ion radical to recapture its electron from Ag(0) may be the route to metallic silver, and some as yet unidentified oxidation products.

Ion radicals would thus seem to play a role in the valence isomerization of certain substrates by certain metals used under certain conditions. But whether it should be considered as broadly as implied [135], is subject to serious question. It is interesting to note that Maitlis had earlier described the relationship between a metal and its ligand as a "continuum of bond types, the extremes of which may be pictorially depicted as shown", i.e., A and B of CL [137]. The point is clearly made that coordinate bonding of the type



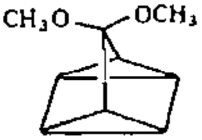
CL

reflected in A (CL) imparts to the acetylene the electronic properties of its excited state, and also the geometrical shape of that excited state. If this is true and we then replace the acetylene in CL A with another ligand X, one whose excited state corresponds to a ground state valence isomer Y, will not

X assume the shape of Y? It would seem that any direct extension of the arguments proposed by Maitlis et al. [137] to these ligands, which have associated with them the symmetry-forbidden paths to their valence isomers, would inexorably lead to the forbidden-to-allowed mechanism, the ligand transformation M + X → M · Y.

Perhaps the continuum in bonding types resting between A and B of CL reflects also a continuum of reaction mechanism available to the transition elements. The ion radical path may lie to the right (B), and the forbidden-to-allowed near the left (A), where metal *d* orbitals rest in energy approximately between a ligand's bonding and antibonding orbitals. Experimental evidence seems to support this possibility [39]. Depending on the nature of the substrate, the reaction conditions, and other related factors, a variety of other mechanisms might reasonably be anticipated.

Perhaps the most interesting metal-catalyzed valence isomerization reported to date is one stemming from an experimental anomaly [138]. 7,7-Dimethoxyquadricyclene CLI has been considered [139] inherently unstable relative to thermal isomerization to its valence isomer 7,7-dimethoxynorbornadiene (CLII). The 2,3-dimethyl derivative of CLI, for example, reverts slowly to diene at 0° and rapidly isomerizes at higher temperature [138]. This compound proved stable only at Dry Ice temperature.



CLI

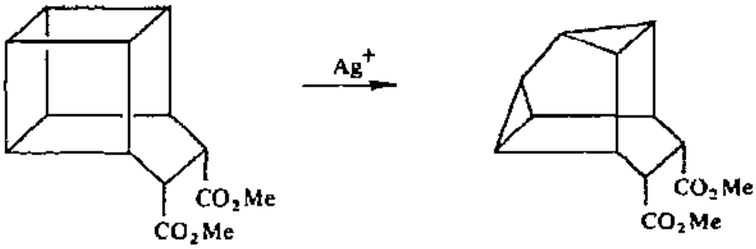
However, the instability of CLI proved to be strongly dependent on the purity and history of CLII, its precursor. The norbornadiene was generally purified by fractional distallation through a spinning-band column. When a stainless steel spinning-band column was used, the quadricyclene derivative CLI was unstable and rapidly reverted to CLII. When diene CLII was purified through a Teflon spinning-band and photolytically converted to CLI, the resulting quadricyclene was so stable that numerous attempts to convert it thermally into CLII were unsuccessful.

It thus appears likely that norbornadiene entrains a metal species in distillation, retaining it in subsequent photolysis, and that it is this captured metal that then catalyzes the isomerization of quadricyclene to its diene valence isomer. These events would clearly be remarkable. One could only speculate on the nature or concentrations of the active metal. Unfortunately, a closer examination of this system was not undertaken. The entrained catalyst may have appeared more of an experimental nuisance, perhaps of no further interest once removed from the system. But which metal in stainless steel could be captured by CLII at distillation temperatures? Do the methoxy functions on CLII play a role in metal capture; will norbornadiene itself do likewise? Finally, how long does this catalyst species live, what is its composition, concentration, and what are the activation energies of this catalysis? Each of these questions would seem deeply interesting. Hopefully, future experimentalists will return to this intriguing system giving it the sharp attention it clearly deserves.

(ii) Cubane

The first metal-catalyzed valence isomerizations of cubane systems were reported essentially simultaneously by Dauben et al. [140] and Paquette, and Stowell [141]. The diester of bishomocubane CLIII was converted [140] to the pentacyclic derivative CLIV in an aqueous methanol solution of $AgNO_3$. The reaction, carried out at room temperature for three days, was quantitative. Interestingly, Dauben was prompted to carry out this reaction by a structural misassignment reported by Furstoss and Lehn [142]. These workers had reported the synthesis of several 1,1′-bishomocubane derivatives. However, comparisons of physical and spectral properties of Dauben's CLIV showed that they had unknowingly prepared the new isomer presumably through purification of CLIII by silver nitrate—silica gel chromatography.

The isomerization of eqn. 33 was almost exclusive to silver ion:



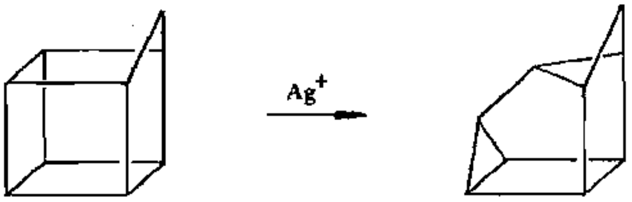
33.

CLIII CLIV

mineral acid, mercuric, cuprous, zinc, iron or rhodium compounds failed to function catalytically [140]. However, it was subsequently shown that other homocubane derivatives suffered this isomerization when refluxed in quinoline with copper-bronze for 2 hours [143].

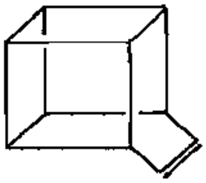
Paquette and Stowell [141] reported the isomerization of homocubane CLV to the pentacyclo hydrocarbon CLVI (eqn. 34). The catalytic reaction proceeds with small amounts of silver fluoroborate in dilute $CDCl_3$ or acetone-d_6 at 25° within one day. This isomerization was assigned the symmetry-forbidden $[\sigma^2{}_s + \sigma^2{}_s]$ course of rearrangement.

Dauben et al. extended their silver-catalyzed bishomocubane (CLIII) studies to bishomocubene, the homocubane system, and the secocubane structure [144]. Bishomocubene CLVII rearranges to its pentacyclo deriva-



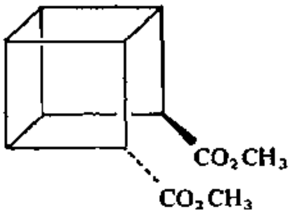
CLV CLVI

34.



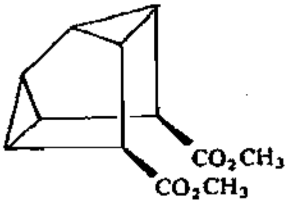
CLVII

tive approximately 100 times slower than does CLV under similar condition. The *endo,endo*-diester CLVIII also undergoes silver ion catalyzed rearrange-



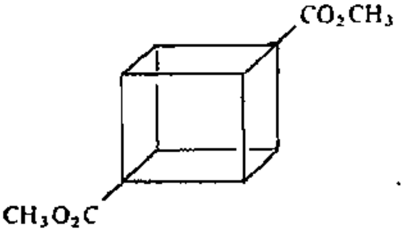
CLVIII

ment of the usual kind, but the reaction was found to be the most sluggish of all. Refluxing for two days in aqueous methanolic silver nitrate solution was required for complete reaction. Significantly, *endo,endo*-configuration was retained throughout the rearrangement. Paquette et al. [145] reported similar results. Rearrangement of the diester was carried out in dry benzene ($AgClO_4$). In a like manner, *endo,exo*-diester was transformed stereospecifically to diester CLIX. The *exo,exo*-diester similarly rearranged with retention of carbomethoxy configuration. The rates of these rearrangements,



CLIX

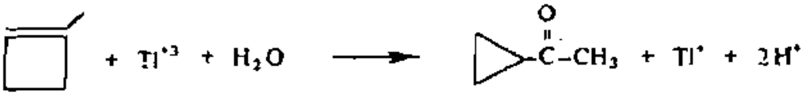
termed "secocubane-to-secocuneane" rearrangements, were compared to rearrangement rates for carbomethoxycubane itself (CLXI) and the dicarbomethyoxy cubane (CLXI). The relative rates of reaction at 40° ($AgClO_4$, benzene) were: CLX(310) > *endo,endo*-secocubane diester (4.5) > *endo,exo*-secocubane diester (2.5) > *exo,exo*-secocubane diester (2.4) > CLXI (1).



CLXI

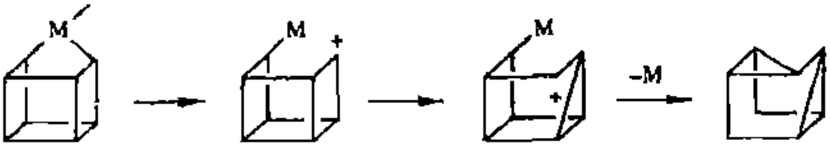
Molecular models were used to approximate the relative steric decompressions that might attend the various secocubane-to-secocuneane rearrangements. Significant steric decompression was noted for *endo,endo*-secocubane relative to its two isomers. Since this contrast was not reflected in the three relative rates (they were about the same), it was concluded that a concerted path was not operative.

Halpern et al. [146] examined the rearrangement of cubane to cuneane catalyzed by silver(I) and palladium(II) systems. They also noted a rapid and quantitative oxidation of 1-methylcyclobutene (CLXII) to cyclopropyl methyl ketone (CLXIII) by thallium (III) in aqueous $HClO_4$ (eqn. 35). A carbonium ion mechanism with suitable rearrangements was reasonably suggested. Ready oxidation of the type CLXII → CLXIII was also affected by palladium(II) chloride and mercury(II) perchlorate with accompanying formation of metallic palladium or mercury, respectively. The results of these stoichiometric, redox systems prompted a mechanistic extrapolation to the cubane-to-cumeane catalytic systems. The mechanism in eqn. 36 was proposed. Cubane oxidation products were apparently not side reactions to the catalytic reactions of Pd(II) and Ag(I).



35.

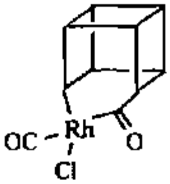
CLXII CLXIII



Cuneane

36.

Cassar et al. [36] have reported results on rhodium-catalyzed cubane isomerizations which many feel are definitive regarding the general intervention of metallocycles. Stoichiometric amounts of $[Rh(CO)_2Cl]_2$ added to cubane led to the stoichiometric reaction, now characteristic of this reagent, namely insertion of the Rh—CO moiety yielding CLXIV.



CLXIV

A variety of rhodium diene complexes ($[Rh(diene)Cl]_2$) affected the [2 + 2] transformation described in eqn. 37. Three cubanes were examined

37.

(cubane, dicarbomethoxy and carbomethoxy cubane). The ratio of the rate constants of the $[Rh(NOR)Cl]_2$-catalyzed isomerizations to the rate constants of the corresponding reactions with $[Rh(CO)_2Cl]_2$ was nearly constant for the three cubanes, despite the fact that the two sets of constants varied by a factor of 100. Moreover, the distribution of isomeric products from the reaction of the monosubstituted cubane with $[Rh(NOR)Cl]_2$ and $[Rh(CO)_2Cl]_2$ remained essentially unchanged. The product distribution in both cases was governed by an approximately statistical attack at the two alternative sterically favored modes of attack.

These observations led these authors to postulate a common mechanism for both the catalytic, $[Rh(diene)Cl]_2$-catalyzed valence isomerization of cubane and the stoichiometric reaction of $[Rh(CO)_2Cl]_2$. A second view of this chemistry, however, has been expressed [22]. $[2_s + 2_s]$ valence isomerization of the type addressed here (eqn. 37), can in theory be catalyzed through monodentate coordination of one of the bonds involved in the subsequent isomerization. Since simple bond coordination, as implied in CLA, for example (see page 172), and complete metal insertion into the same σ bond as suggested by Halpern et al., are extensions of each other [22,137] quite similar attack selectivities should be anticipated for $[Rh(diene)Cl]_2$ and $[Rh(CO)_2Cl]_2$. The self-consistency noted would therefore be compatible with the intervention of two different mechanisms.

Dauben and Kielbania [39] reported the catalytic reactions of bishomocubane diester CLIII with a variety of rhodium and palladium complexes. Recall that with cubane, the rhodium complexes led cleanly to dienes (eqn. 37) while Ag(I) and Pd(II) gave cuneane product [146]. The distinguishing feature of Dauben's work is a striking change in product mix with changes in ligand σ-donor and π-acceptor character. In general, the rhodium complexes gave exclusively diene while silver(I) gave the cuneane derivative, as Halpern had earlier observed. Palladium(II), however, switched its catalytic selectivity as its ligands were changed. For example, diene predominated with Pd(II) complexes containing ligands which were both good σ donors and π acceptors, i.e., triphenylphosphine, triphenylarsine and triphenylstilbene. With complexes of very strong π acceptor but weak σ donor ligands (e.g., phosphites), mixtures of diene and cuneane were obtained. It was also noted that by increasing the polarizability of the halogens from chlorine to iodine, increased amounts of diene obtained (i.e., 13% diene, 86% cuneane for PdI_2 (NOR); 100% cuneane for $PdCl_2$(NOR)). Transition metal complexes containing ligands which are weak σ donors and π acceptors and which are not polarizable (e.g., $PdCl_2$(NOR), $PdCl_2$ $(pyr)_2$, $PdCl_2$ $(PhC{\equiv}N)_2$ and PdI_2 $(PhC{\equiv}N)_2$) act in the same manner as the uncomplexed metal ion, giving exclusively the cuneane derivative. A mechanism similar to that proposed by Halpern (eqn. 36) was suggested for complexes such as these.

Dauben suggested a different mechanism for the diene formation, one involving metal coordination to the strained bonds of the cubane system. A forbidden-to-allowed role for the metal was implicated. The blending of pure oxidative addition (as indicated by Halpern et al.) and a release of symmetry restrictions through strong donor-acceptor coordinate bonding as metal systems approached from extrema was also suggested. Most important, these results demonstrate for the first time that transition metal-catalyzed rearrangements of strained compounds are not simple processes, but are sensitive to subtle electronic effects imparted to the active metal centers by variations in their nonreacting ligands.

(iii) Bicyclobutane

Bicyclo[1.1.0]butane (CLXV) remains isolated from low-energy paths of

CLXV

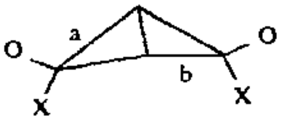
rearrangement to its energetically preferred valence isomers, the 1,3-dienes. It is highly strained (ca. 64 kcal mol^{-1} [127]), yet does not rearrange under 150°, even by symmetry-allowed pericyclic processes [147]. The bridging σ bond is most reactive, exhibiting the greatest p character of the five carbon—carbon bonds describing its structure [148]. Like other highly strained, multicyclic structures, CLXV should be a strong ligand, coordinating to most metal nuclei through its center of maximum strain, the bridging σ bond [16].

Given its unusual thermal stability, its degree of strain energy and its inherent affinity to coordinate to transition metals or centers of high electrophilicity generally, it is not surprising that bicyclobutane would exhibit the breadth of catalytic chemistry that it does. CLXV carries within its strained structure more than enough driving energy to propel it along a number of catalytic routes to 1,3-dienes. Transition metal complexes would thus be expected to rearrange CLXV under mild conditions through a variety of catalytic mechanisms.

The chemistry of metal-catalyzed bicyclobutane valence isomerization has perhaps received more attention than that of any other hydrocarbon. This literature is quite broad, unusually complex and spotted with heated controversy. Much of the work has been directed to mechanistic questions associated with distinctly nonconcerted modes of valence isomerization. Mechanistic proposals involving ionic and carbenoid intermediates are prime examples. Because these subjects fall outside the scope of this review, we will give them only cursory treatment here. Recent reviews have appeared which hopefully compliment that to follow [122,149].

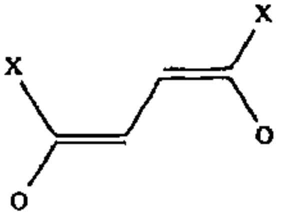
Bicyclobutane may safely be called the Lorelei of hydrocarbons. Its intriguing modes of catalyzed rearrangement have lured a number of organic chemists into metal-catalyzed organic chemistry and its maze of mysteries. Seeking some ultimate, all-embracing answer to the riddle of metal-catalyzed pericyclic rearrangements, most have instead found diversion and deeper enigmas. A brief examination of bicyclobutane's more obvious modes of concerted transformation will, perhaps, underscore the uniqueness of this hydrocarbon and suggest reasons why it should not mirror the catalyzed behavior of other substrates.

Bicyclobutane CLXVI can undergo either an allowed $[2_s + 2_a]$ pericyclic

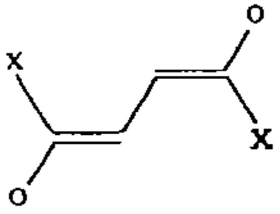


CLXVI

process yielding CLXVII or a forbidden $[2_s + 2_s]$ process giving diene



CLXVII

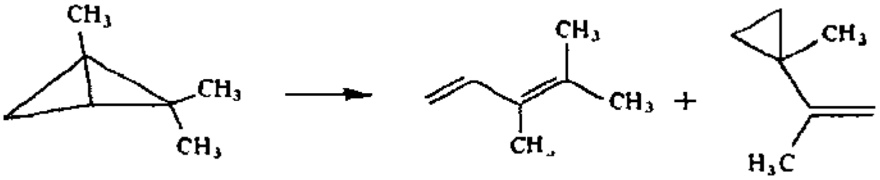


CLXVIII

CLXVIII. Other modes of rearrangement need not concern us here. In either of the above modes, bonds a and b cleave with a respective conrotatory or disrotatory rotation about the remaining nonbridging σ bonds. Significantly, the bonds undergoing the pericyclic process, a and b, are (1) spatially quite removed from each other and thus bond overlap should be negligible, and (2) these bonds are not the σ bonds of maximum strain, where metal coordination would be preferred. This type of rearrangment bears a strong resemblance to the cubane-to-cuneane rearrangement discussed earlier (see page 174). In both systems, coordination of both bonds (a and b) to a single metal center would be most difficult. With cubane itself, biscoordination of this type would, in fact, be impossible.

To catalyze any forbidden pericyclic process along the forbidden-to-allowed reactions path requires an exchange of electron pairs between the metal and ligand substrate (see page 111). This proceeds ideally when the bonds undergoing transformation are fully coordinated to the metal and retain full coordination throughout the pericyclic process. This kind of coordination to bonds a and b in CLXVI would be most difficult to achieve at any transition metal center and virtually impossible to maintain as CLXVI transformed to CLXVIII. Thus, a forbidden-to-allowed role for the metal, as it has been described previously [9,12—14,16,22], would not be anticipated in the catalytic chemistry of bicyclobutane, nor should it be in the cubane-to-cuneane rearrangement. According to this view, CLXV stands somewhat isolated from other hydrocarbon systems with respect to its possible involvement in forbidden-to-allowed catalytic processes.

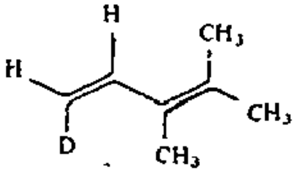
1,2,2-Trimethylbicyclo[1.1.0]butane (CLXIX) undergoes [150] facile isomerizations to diene CLXX and CLXXI (eqn. 38) at room temperature in



CLXIX CLXX CLXXI

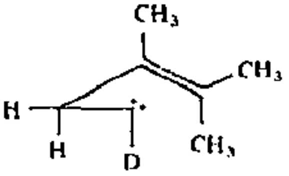
38.

the presence of catalytic amounts of $[Rh(CO)_2Cl]_2$. Deuterium labeling at the bridgehead carbon of CLXIX produced CLXXII with high stereospecificity. Thus, this reaction clearly does not proceed with cleavage of



CLXXII

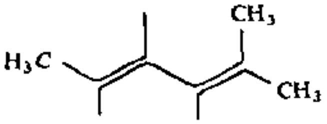
bonds a and b in CLXVI; it proceeds instead with cleavage of the bridging σ bond, a flanking σ bond and a 1,2-hydrogen shift. This process was interpreted in terms of a formal "retrocarbene addition". The formal intervention of the carbene species CLXXIII was introduced. The retrocarbene proposal was also suggested for the metal-catalyzed [Rh(I), Pd(0) and Pt(0)] isomerization [151] of CLXXIV to CLXXV. Gassman and Armour [152] have also extended this type of rearrangement to strained propellanes (tricyclo-[3.2.1.0^{1,5}]octane).



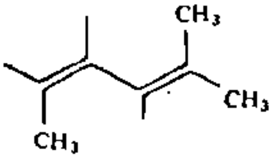
CLXXIII

CLXXIV CLXXV

Subsequent catalytic studies on bicyclobutane CLXIX using pentafluorophenylcopper tetramer as catalyst yielded results in striking contrast to that of earlier work [153]. An immediate exothermic reaction occurs in chloroform solution at 0° yielding diene products CLXXVI and CLXXVII and a vinylcyclopropane derivative. Bond cleavage of the bridging σ bond thus again occurs, but this time the flanking σ bond that also cleaves is the one opposite to that which cleaves in eqn. 38. These perplexing results prompted Gassman to express a need for a much larger body of empirical data before "a general theory of predictive value can be established for these metal-induced rearrangements", anticipating the "advent of a cohesive theory concerning these facile metal promoted rearrangements".



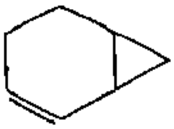
CLXXVI



CLXXVII

However, more surprises were to come. It was soon discovered that a single metal, Pd(II), would switch its mode of catalytic behavior from that in eqn. 38 to that of the copper tetramer noted above as its ligands changed [154] from dichlorobis(benzonitrile) to chloro-π-allyl. How a change in ligand could cause such a dramatic switch in catalytic chemistry was not explained.

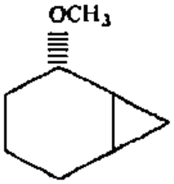
Gassman extended his studies on variations in catalyst using polycyclic CLXXIV and a methyl derivative [155]. Catalysts ranged from $AgBF_4$ through Rh,Ir,Pd,Ru down to PtO_2, Sn and $AlCl_3$. Products varied between CLXXV, CLXXVII and cycloheptadiene (CLXXVIII). Gassman proposed a general theory involving stepwise bond cleavage with the various transition metal catalysts acting as "extremely specific" Lewis acids. He extended his view of the carbene species, blending carbonium ion character into it (CLXXIX). Support for the intervention of carbonium ion species was offered by the isolation of ethers CLXXX from CLXXIV + $[Rh(CO)_2Cl]_2$ in methanol.



CLXXVII

CLXXVIII

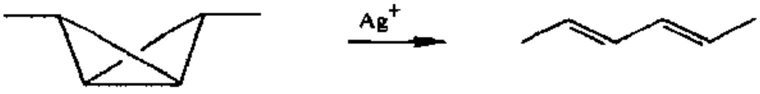
CLXXIX



CLXXX

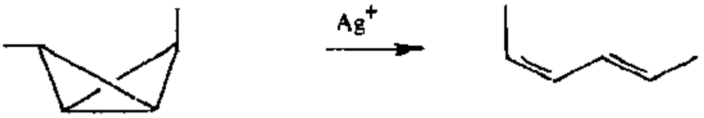
We shall see later that the $[Rh(CO)_2Cl]_2/CH_3OH$ system is far from simple. Protonic acids can be generated raising serious questions regarding the value of certain mechanistic generalizations in this complex chemistry. Subsequent work by Gassman and Williams [156] appeared to rule out the intervention of protonic acids. However, later work [157] revealed that "under special conditions, a very acidic media can be generated from methanol, $[Rh(CO)_2Cl]_2$ and CLXIX, even in the presence of base". The results obtained indicated an overall picture more complex than had been anticipated. However, Gassman maintained a strong allegiance to his proposed intermediate, CLXXIX. Regarding the isomerization of strained hydrocarbons like CLXIX by various metal systems, the current picture seems clouded, subject to changes in "the metal, oxidation state of the metal, ligands attached to the metal, nature of the substitution on the bicyclo[1.1.0]butane and, perhaps, on the nature of the solvent used in the reaction" [157].

Paquette et al. [156] first published the facile silver ion catalyzed rearrangement of tricycloheptane CLXXIV to cycloheptadiene CLXXVIII, interpreted as a $[2_a + 2_a]$ pericyclic process. Subsequent kinetic studies implicated a bicyclobutane—silver complex as an intermediate in the isomerization [159]. It was also established, almost simultaneously by two groups of workers [159,160], that silver ion catalyzes ring opening of nonbridgehead-substituted bicyclobutanes with striking specificity along the symmetry forbidden pericyclic path. Bicyclobutanes CLXXXI and CLXXII transform to their respective dienes (cf. eqns. 39 and 40) with stereospecificities as high as 78% and 99%, respectively. These results are perhaps the most remarkable and significant in this area of catalysis. Ninety-nine percent stereospecificity along an otherwise forbidden reaction path when an apparently equal-energy allowed path option exists is difficult to explain without invoking orbital symmetry factors at some stage of the process [160].



39.

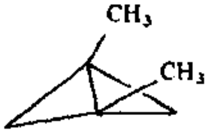
CLXXXI



40.

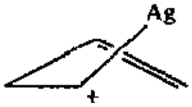
CLXXXII

Paquette later reported silver ion-catalyzed rearrangements of bridgehead-substituted bicyclobutanes (e.g., CLXIX and CLXXXIII) [149]. In these studies skeletal isomerization, very much like those noted by Gassman and Williams [153], dominated the chemistry. Quite clearly, orbital symmetry factors could not be intervening here since these rearrangments were not simple pericyclic valence isomerizations. Paquette, thus abandoned his view of the earlier bicyclobutane isomerizations being examples of a $[2_a + 2_a]$ pericyclic process, and proposed the general intervention of "argento carbo-



CLXXXIII

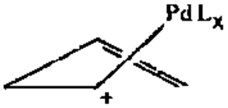
nium ions", such as CLXXXIV. The stereospecificity noted in eqns. 39 and 40 was suggested to reflect "not orbital symmetry control in the bond reorganization but rather a combination of steric, kinetic and thermodynamic factors" [149]. The possibility that silver might be doing one thing with the bridgehead-unsubstituted bicyclobutanes and other things to their substituted counterparts was not addressed in the early interpretation.



CLXXXIV

Deuterium isotope effects in the silver-catalyzed rearrangements of tricycloheptanes (CLXXIV) later revealed that the bridgehead σ bond cannot be the initial bond cleaved in this system [161]. Silver ion attack at a flanking σ bond generating an argento carbonium ion was suggested to intervene. However, subsequent studies on the silver-catalyzed rearrangements of a broader variety of substituted bicyclobutanes suggested the distinct possibility of a changeover in mechanism with methyl substitution [162]. When the bridging carbons, C_1 and C_3, were unsubstituted, the cleavage of diametrically opposed edge bonds occurred, a reaction which was accelerated with 2,2,4,4-tetramethyl substitution. This pathway was also operative in the 1,2,2,4,4-pentamethyl derivative. Paquette's kinetic data, although limited, prompted the proposal of a possible bond reorganization process that is concerted in these cases where "this level and type of substitution prevail". In other cases where C_1 and/or C_3 carry substituents, intermediate argento carbonium ions were offered as intermediates.

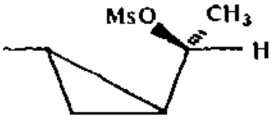
Sakai and Masamune have also contributed to an ultimate elucidation of the mechanistic aspects of metal-catalyzed bicyclobutane isomerization. Following Masamune's initial disclosure of the highly stereospecific isomerization of CLXXXI and CLXXII (see eqns. 39 and 40), distinct differences between Ag(I) and Pd(II) in this chemistry were reported [163]. Palladium was found to give products resulting from cleavage of the bridging σ bond (i.e., $C_1—C_3$) and the flanking $C_1—C_2$ bond. The intermediate CLXXXV was proposed. Carbene character of the type discussed earlier (CLXXIX) was indicated. Diazo compounds corresponding to the various intermediates CLXXXV were prepared and their metal-catalyzed decomposition products compared to those from Pd(II) and Ag(I) catalyzed bicyclobutane products. Product distributions from the bicyclobutanes and diazo



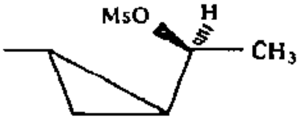
CLXXXV

compounds with Pd(II) were similar in all cases. Those from Ag(I) differed significantly.

Masamune proposed a reaction path for silver catalysis "not involving a carbenoid but rather the heterolytic cleavage of the C_1-C_2 bond followed by a cyclopropylcarbinyl—allycarbinyl-type rearrangement". In support of this proposal, mesylates CLXXXVI and CLXXXVII (among others) were



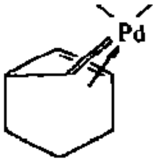
CLXXXVI



CLXXXVII

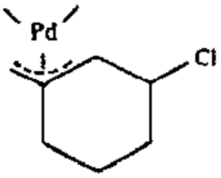
shown to undergo elimination reactions in benzene/pyridine yielding the dienes in eqns. 39 and 40 in respective selectivities of 70% and 86%. These should be compared to the selectivities of the assumed parent bicyclobutanes CLXXXI and CLXXXII of 78% and 99%, respectively. Thus, the two quite different systems exhibit strikingly similar product distributions suggesting similarity in mode of reaction.

Dauben and Kielbania [164] have reported NMR studies of metal-catalyzed bicyclobutane arrangements. By using high concentrations of catalyst, organometallic complexes were observed to intervene in the isomerization of tricycloheptane (CLXXIV) to diene CLXXV. Stoichiometric amounts of $PdCl_2-(PhCN)_2$ and CLXXIV gave an intermediate reflecting structure CLXXXVIII. Within minutes, the original complex transformed to



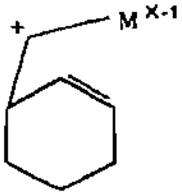
CLXXXVIII

one consistent with the π-allyl complex CLXXXIX. Both complexes when reacted with excess triphenylphosphine gave diene CLXXV. Additional experiments indicated that tricycloheptane reacts with the Pd(II) catalyst giving complex CLXXXVIII which decomposes to π-allyl CLXXXIX. Diene product CLXXV in the presence of the Pd(II) catalyst gives CLXXXIX. Intermediate CLXXXVIII was compared to those suggested by Gassman and



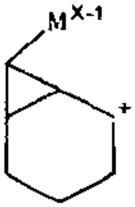
CLXXXIX

Masamune (CXC), the distinguishing feature being metal-coordination to the double bond. This intermediate was considered to result from the metal



CXC

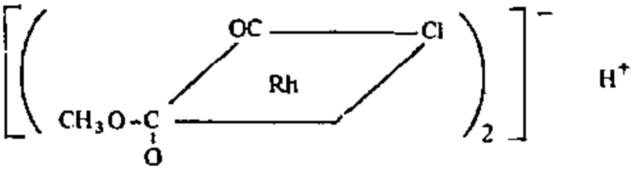
cyclopropylcarbinyl cation CXCI. Since earlier reports suggesting the possi-



CXCI

bility of this intermediate had involved $[Rh(CO)_2Cl]_2$ in methanol [155,163], and NMR evidence of CXCI was not obtained, this system was reexamined by Dauben. His results suggested that $[Rh(CO)_2Cl]_2$ in methanol directly catalyzed the rearrangement of bicyclobutane CLXXIV to diene CLXXV and that the formation of ether products reported earlier was apparently due to side reactions resulting from acidic impurities.

More recent results from Dauben et al. support the intervention of an unusual acidic species in the $[Rh(CO)_2Cl]_2$/methanol system [165]. Tricycloheptane apparently reacts with $[Rh(CO)_2Cl]_2$ in methanol yielding a short-lived intermediate. Infrared and p*H* studies suggested the intervention of an anionic carbene complex like CXCII which is unstable and disproportionates to a diene (CLXXV) and starting Rh(I) catalyst. $PdCl_2(PhCN)_2$



CXCII

behaved similarly. The acidic species here was suggested to result from the reaction of a palladium π-allyl complex with methanol. The π-allyl complex apparently forms from the reaction of Pd(II) with diene product in CH_3OH, methoxide having been incorporated yielding HCl.

In these systems, the bicyclobutane moiety may be considered a strong π-acceptor, attacking the metal at an open coordination site, withdrawing electron density with a relaxation of its strain; thus rendering the metal complex electron difficient, and subject to further reaction with the solvent. The protonic acids generated then catalyze the formation of ether products in methanol and may be significant participants in the valence isomerization of bicyclobutane to its diene valence isomers.

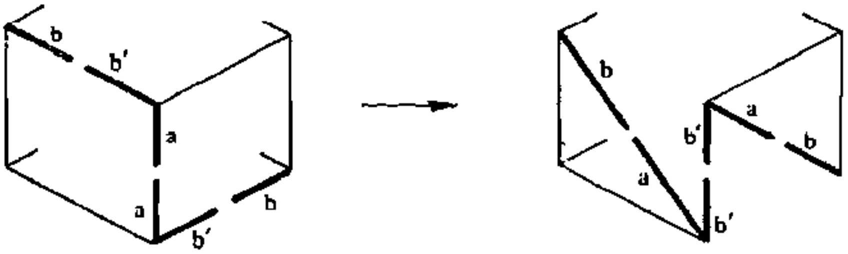
One significant point of Dauben's work should be emphasized: systems obtained from a combination of certain transition metal complexes and highly strained hydrocarbons are hardly simple. Even when an initial complex can be recovered unchanged after a catalytic reaction has occurred — as was the case with $[Rh(CO)_2Cl]_2$ in methanol — the actual catalytic complex may differ sharply from that of the initial system. Thus, catalytic mechanisms inferred from the composition of starting and product systems alone can be misleading.

We have already discussed some of the work of Noyori et al. [79] involving nickel(0)-catalyzed reactions between bicyclobutanes and olefins (see page 142). Highly stereospecific [2 + 2] cycloadditions were observed with bond cleavage occurring at the bridging σ bond and an adjacent carbon—carbon bond. This catalysis was suggested to proceed through an open-chain carbene—nickel complex or, alternatively, through sequential steps with intervening metallocycles. In a later paper, Noyori discussed the bonding nature of the carbene—metal species generated from the reaction of various transition metals and bicyclobutane [166]. The variety of valence isomerizations as well as other reactions were rationalized in terms of a metal—carbene resonance hybrid. An increase in a metal's π donor capacity, for example, would weight one canonical form (i.e., the ylide structure) and thus alter the reaction characteristics of the carbenoid species.

Highly strained molecules such as bicyclobutane and cubane should be capable of metal-catalyzed rearrangements to energetically preferred valence isomers through essentially any conceivable mechanism that maintains a reasonable preservation of bonding throughout that rearrangement. The variety of mechanisms suggested in these past two sections would seem to illustrate this. Thus, a blend of nonconcerted, stepwise processes and concerted, pericyclic processes can be anticipated. In our review of metal-assisted concerted pericyclic rearrangements, perhaps the forbidden types were overemphasized. This would certainly seem to be the case for the proposed $[2_a + 2_a]$ rearrangements of cubane and bicyclobutane. An allowed pericyclic path exists which would yield the observed products in both cases. This rearrangement, a $[2_s + 2_s + 2_s]$ pericyclic process, is outlined for bicyclobutane in eqn. 41. Cubane transforms along the $[2_s + 2_s + 2_s]$ reac-

41.

tion path yielding cuneane, as the simplified version of this process in eqn. 42 illustrates.



42.

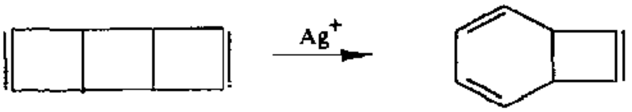
It should be stressed that we do not propose that the $[2_s + 2_s + 2_s]$ process indeed attends the respective metal-catalyzed rearrangements to these products. Certainly the high stereospecificity noted for the silver-catalyzed rearrangement of bicyclobutane (cf. eqns. 39 and 40) can be explained by the stepwise mechanisms proposed. We only note that the $[2_s + 2_s + 2_s]$ process, being symmetry-allowed and reflecting a reasonable preservation of bonding, should be carefully considered as one of the possible contributors to this chemistry.

The role of the catalyst in such processes would be clearly distinct from that indicated in the forbidden-to-allowed process. It is most unlikely that an exchange of electron pairs would attend the $[2_s + 2_s + 2_s]$ rearrangement. Because it is allowed, electron injection into an antibonding MO and withdrawal from a bonding MO would only seem to impede reaction, and not contribute to a restoration of bonding to the transforming ligand. Thus, a different role for the metal would be indicated if this catalytic process in fact occurs. The metal may, for example, simply induce a spatial perturbation into the a—b bonding framework. An appropriate a—b, b′—b′-overlap might thus result, thereby launching the strained system along the indicated pericyclic pathway.

F. ELECTROCYCLIC REACTIONS

The first reports of a metal-catalyzed electrocyclic process appeared almost simultaneously. Volger and Hogeveen [7] described a [(Dewar-benzene)RhCl]$_2$ catalyzed valence isomerization of hexamethyl-Dewar-benzene to hexamethylbenzene. While the corresponding thermal isomerization proceeds between 100 and 140°, the catalyzed reaction was examined in the range of 60—75°. This isomerization, if concerted, constitutes a symmetry-forbidden disrotatory ring opening of a cyclobutene system. Later work by Volger and Gaasbeek [167] showed the rate of this reaction to be less than first order. This suggested that a monomeric rather than dimeric rhodium complex was involved. The species $Rh(C_{12}H_{18})_2Cl$, containing two molecules of hexamethyl-Dewar-benzene as bidentates, was suggested.

Merk and Pettit [8] reported a similar cyclobutene isomerization involving a variety of multicyclic systems catalyzed by the metal ions Cu^+ and Ag^+. This and later work along similar lines has been reviewed [10]. Pettit rationalized this catalysis in terms of a reversal of the symmetry restrictions by these metal ions. This explanation, however, has been subjected to critical points of view [11—13]. Questions regarding Pettit's forbidden-to-allowed proposal were focused primarily at the d^{10} electronic configuration for silver ion and the required promotional energies to lift the ground state ion to appropriate product states. As noted in previous sections, silver ion tends to act in a novel way relative to most other transition elements. Its mode of catalysis, although remarkable, remains the subject of diverse points of view. It should be noted that silver ion has only been reported to catalyze the disrotatory ring-opening of highly strained systems in which an alternative allowed conrotatory twist is not a realistic option (e.g., eqn. 43). Simple cyclobutenes capable of isomerization along either electrocyclic mode of transformation have been treated with silver ion, but have failed to exhibit isomerization to dienes [159,160]. However, stereospecific ring-opening along the forbidden disrotatory path has been predicted for other transition metals, namely those possessing a d band occupied with sufficient metal valence electrons to give a coordinatively saturated complex in which the bonding axis of the fully coordinated cyclobutene (CXCIII) is C_3 or higher with respect to the nonreacting ligands [12,16]. Reports on the catalytic behavior of the metal systems suggested have not yet appeared.



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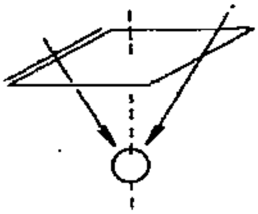
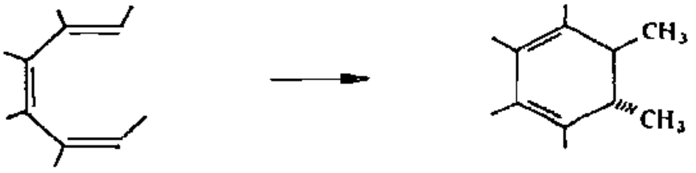


CXCIII

The catalysis of hexamethyl-Dewar-benzene to hexamethylbenzene was examined for a broad variety of d^8 and d^{10} metal complexes [168]. No apparent correlation between activity and a metal's d orbital configuration for the various d^{10} and d^8 complexes was noted. The inactivity of some complexes was ascribed to possible steric factors from bulky phosphine ligands hindering an appropriate substrate approach to the metal center.

Tetramethyl-2,4,6-octatriene CXCIV would be expected to undergo an allowed disrotatory electrocylic process to cyclohexadiene CXCV (eqn. 44). Unlike Dewar-benzene and the polycyclic systems studied by Pettit, triene

CXCIV is geometrically free to transform along either the conrotatory or

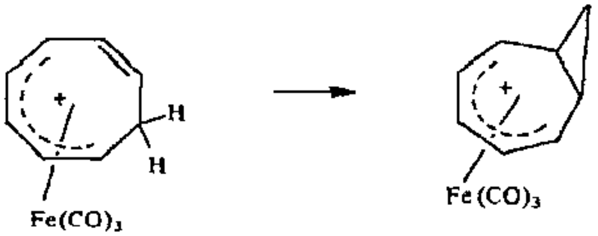


44.

CXCIV CXCV

disrotatory reaction paths, symmetry restrictions not withstanding. This system has thus been examined under the influence of various metal catalysts to see if stereospecificity switched from disrotatory to conrotatory [169]. Of the metals examined, only $AgBF_4$ in equimolar amounts gave a facile conversion to product, hexamethylbenzene. The desired cyclohexadiene was apparently bypassed by rapid dehydrogenation to benzene. The actual mode of electrocyclic ring-closure thus remained unknown.

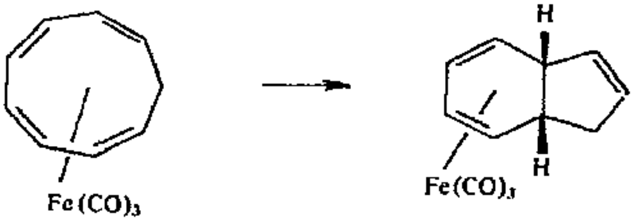
Brookhart et al. [170] were the first to report an allowed electrocyclic ring-closure of a metal-coordinated cyclopolyene. Cation CXCVI undergoes smooth disrotatory ring-closure to CXCVII (eqn. 45) at —60° ($\Delta F \pm = 15.7$ kcal $mole^{-1}$).



45.

CXCVI CXCVII

Reardon and Brookhard [171] later reported a similar disrotatory ring-closure of an $Fe(CO)_3$-coordinated cyclononatetraene (eqn. 46). The rearrangement appeared best consistent with a unimolecular electrocyclic ring-closure of the bound cyclononatetraene ligand. This disrotatory closure of



46.

the triene moiety proved only slightly higher in energy ($\Delta F \pm = 28.4$ kcal $mole^{-1}$) than the metal-free, symmetry-allowed disrotatory process ($\Delta F \pm =$ 23 kcal $mole^{-1}$). The differential of 5.4 kcal $mole^{-1}$ was suggested to arise from the 1,2-iron shift which must attend the ligand transformation in eqn. 46.

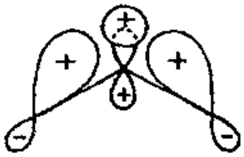
Pettit et al. have recently reported an iron carbonyl-catalyzed forbidden electrocyclic process [172]. Iron tetracarbonyl complexes of both *syn*- and *anti*-tricyclooctadiene (CXCVIII) underwent smooth thermal reaction (60°) in hexane yielding the iron tricarbonyl complexes CXCIX (eqn. 47). Complex CXCIX is stable in contrast to the free ligand which readily rearranges to cyclooctatetraene.

CXCVIII CXCIX

The disrotatory pericyclic process in eqn. 47 was found to be impeded by CO pressure and no evidence for ionic intermediates was reported. A forbidden-to-allowed mechanism was proposed. This interpretation appears most reasonable in this system, particularly since the $Fe(CO)_3$ moiety displays a nonrestrictive ligand field.

G. SIGMATROPIC REARRANGEMENTS

A transition metal can, in theory, restore bonding to symmetry-forbidden [*i,j*] sigmatropic reaction paths [5,38,126]. The suprafacial corridor of a [1,3] sigmatropic transformation, for example, has been shown to exhibit an increase in bonding of approximately 44% when a naked iron atom is coordinated to the π bond [126]. The molecular orbital calculations used in that study were carried out on model systems. The absolute degree of restored bonding indicated in the calculations is, of course, not particularly meaningful. The calculations were semiempirical, using approximations of real wave functions. Further, the models used were purely fictitious, chosen to reflect the general changes in ligand molecular orbitals that occur upon introducing a transition metal. Nevertheless, the calculations support the general contention that bonding along the suprafacial corridor of the [1,3] sigmatropic path does indeed increase upon metal coordination to the π bond. Moreover, the increased bonding resulted from an injection of metal valence electrons into the π^* molecular orbital of the olefin which correlates smoothly with $\Psi_3(CC)$, the third π molecular orbital of the π-allyl transition state.

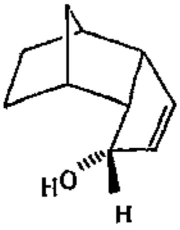


CC

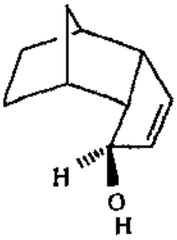
A theoretical proposal regarding a possible forbidden-to-allowed sigmatropic catalytic role for the transition elements is just that and nothing more. It does not reflect any likelihood that a transition metal will in fact catalyze a suprafacial [*i,j*] sigmatropic process. This is in contrast to [2 + 2] valence isomerizations where, in some cases, metal coordination should virtually transforms the ligand along its symmetry-forbidden path. The ultimate scope of metal-assisted sigmatropic processes therefore remains an open question, the rightful subject of experimental chemistry.

Ross and Orchin [173] have reported an allylbenzene isomerization catalyzed by deuteriocobalt tetracarbonyl. Only small amounts of D were found in the product propenylbenzene and the reaction rates for both the $HCo(CO)_4$ and $DCo(CO)_4$-catalyzed reactions were approximately the same. These observations seemed to suggest that the D—Co bond remained intact throughout the reaction. A metal-assisted [1,3] sigmatropic process was thus implicated. However, subsequent work by Taylor and Orchin in the $HCo(CO)_4$ isomerization of $CD_3{-}CD{=}CD_2$ was not consistent with this interpretation. A 1,2-addition-elimination mechanism was implicated, at least in part [174].

Cowherd and von Rosenberg [175] have explored a possible iron-assisted [1,3] sigmatropic isomerization of *endo*- and *exo*-alcohols CCI and CCII. Because of steric factors, only the *exo*-alcohol CCII would be expected to



CCI

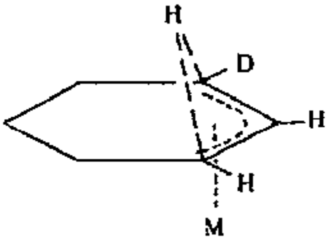


CCII

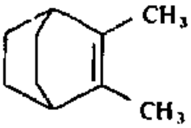
undergo an $Fe(CO)_3$-catalyzed [1,3] sigmatropic isomerization. However, at 130°, only CCI underwent iron-catalyzed isomerization. Even under prolonged heating at 160°, CCII remained unchanged. The mechanism of allyl alcohol isomerization to propionaldehyde was then reasonably ascribed to the intervention of a π-allyliron hydride complex.

Smith and Swoap [176] have proposed a [1,3] sigmatropic isomerization to explain the dueterogenation of cyclohexene over heterogeneous platinum and palladium catalysts. Desorbed cyclohexene was found to contain deuterium in either its allylic or olefinic position. The intermediate species CCIII was suggested.

Pecque and Maurel reported the direct *trans* hydrogenation of bicyclooctene CCIV over heterogeneous platinum catalysts [177]. These results were felt to be inconsistent with the classical Horiuti and Polanyi 1,2-addition-elimination mechanism or the π-absorbed allylic species often proposed.



CCIII



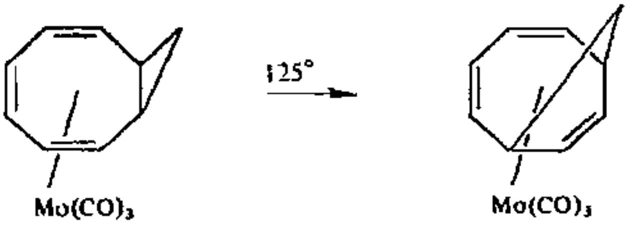
CCIV

A metal-assisted [1,3] sigmatropic shift of the π double bond to the exocyclic position followed by underside hydrogenation might have intervened.

Heterogeneous catalytic systems, however, are unusually complex and other mechanisms may certainly intervene. We might just cite certain deuterium exchange studies on various polycyclic hydrocarbons over heterogeneous palladium [178]. Compounds were chosen because their structural features presumably would allow a distinction in mechanisms for the peculiar "*trans*-effects" noted above. The results suggested a "roll-over" of intermediate olefin and not direct *trans*-additions to π-allyl intermediates or a suprafacial [1,3] shift of hydrogen.

Further complicating the picture, Hilaire and Gault have published a rather extensive study of the deuteration, isomerization and exchange of cycloolefins over palladium catalysts [179]. Evidence was presented implicating two apparently unrelated or separate catalytic processes proceeding simultaneously. The authors concluded that the interconversion between disadsorbed species and π-allylic species determine the nature of the saturated products; however, double-bond migration and olefin exchange apparently involve entirely different intermediates. The general [1,3] sigmatropic hydrogen shift first proposed by Smith and Swoap was suggested to intervene.

Certain homogeneous systems involving stroichiometric transformations of one metal complex to another perhaps provide the cleanest evidence in support of metal-assisted [1,3] sigmatropic changes. Grimme has reported one of the earliest and possibly most interesting examples [180]. Tricyclononatriene complex CCV undergoes the [1,3] sigmatropic rearrangement to complex CCVI (eqn. 48). Retention or inversion of configuration at the bridging methylene was not determined. Although a forbidden-to-allowed

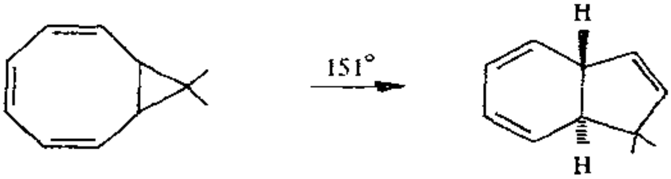


48.

CCV CCVI

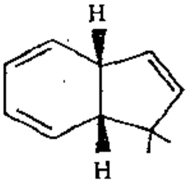
process was thus not definitively established, it appears most likely in this system.

Grigg et al. [181] have reported a closely related rearrangement catalyzed by rhodium(I). Whereas heating 9,9-dimethylbicyclononatriene CCVII at 151° gave primarily *trans*-dihydroindene (eqn. 49), heating at 140° for 30 min in the presence of a catalytic amount of $[Rh(CO)_2Cl]_2$ gave *cis*-dihydroindene CCVIII. Their preliminary results indicated that $[(CCVII){-}RhCl]_2$ was not the catalyst for the rearrangement of CCVII. The transformation CCVII → CCVIII is formally a [1,3] sigmatropic shift of the bridging cyclopropane σ bond. However, proposals regarding a catalytic role for the metal must await additional mechanistic information.



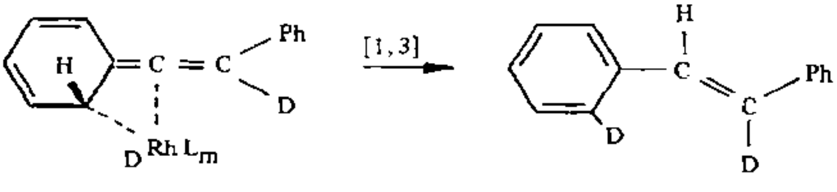
CCVII

49.



CCVIII

Abley and McQuillen [182] have reported some interesting results regarding a homogeneous rhodium-catalyzed hydrogenation of diphenylacetylene to *trans*-stilbene. Deuterium addition gave *trans*-stilbene with one deuterium atom at the *ortho*-position of one of the phenyl groups and the other deuterium on a vinyl carbon. The authors proposed the intermediacy of CCIX which then undergoes the metal-catalyzed [1,3] sigmatropic shift outlined in eqn. 50. These results are consistent with the suggested [1,3] sigmatropic process accompanied by *ortho*-deuteration. *ortho*-Hydrogen exchange independent of deuterium addition to the triple bond would give a

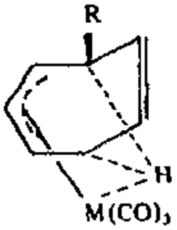


CCIX

50.

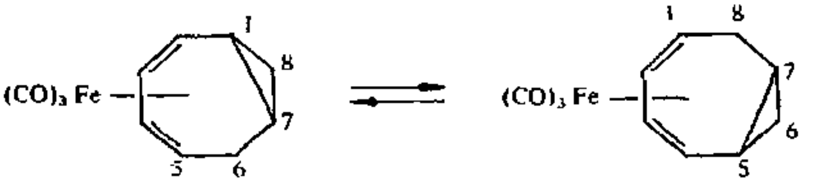
different pattern of deuterium incorporation and would also leave the unusual stereochemistry observed unexplained.

Pauson et al. [183] have reported some interesting [1,5] sigmatropic transformations apparently catalyzed by the group VI metal carbonyls. Significantly, the migrating hydrogen atom travels from the *endo*, or underside of a metal-coordinated cycloheptatriene ligand. The rearrangement was shown to be stepwise in nature and stereospecific. A distinct metal hydride intermediate, which had been postulated earlier [184], was rejected because the ring carbon atoms had not equilibrated in the isomerization. The transition state CCX was suggested. This apparent concerted *endo*-assisted process is similar to an *endo* [1,3] sigmatropic transformation postulated by Pettit et al. [10] to explain the results of Cowherd and von Rosenberg [175] (see page 192).



CCX

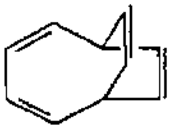
Aumann has reported a ligand valence isomerization which may constitute a rather novel [1,5] sigmatropic rearrangement [185]. The degenerate rearrangement indicated in eqn. 51 was observed in benzene at 90°. With deuterium in the 6-*pseudoaxial* position, redistribution of the deuterium between ring position 6-*pseudoaxial* and 8-*endo* is observed. In contrast, the thermal rearrangement of uncomplexes bicyclo[5.1.0]-2,4-octadiene presumably does not proceed [186] with retention at C-6 and C-8.



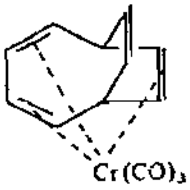
51.

Perhaps the most remarkable example of a possible metal-catalyzed forbidden sigmatropic transformation [187] involves a Cr(CO)$_3$-catalyzed valence isomerization of bullvalene (CCXI) to bicyclo[4.2.2]deca-2,4,7,9-tetraene (CCXII). While both Mo and W carbonyls simply suppressed the degenerate Cope rearrangement, [bullvalene · Cr(CO)$_4$] rearranged quantitatively to a new complex (CCXIII) at 80°.

CCXI

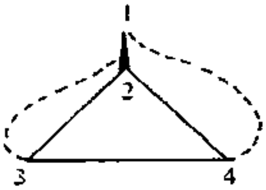


CCXII



CCXIII

Model studies of bullvalene by this reviewer suggest that the symmetry-forbidden $[{}_{\sigma}2_s + {}_{\sigma}2_s]$ pericyclic process described in CCXIV may be the path of the metal-catalyzed rearrangement. This process would proceed with



CCXIV

retention at carbons 1 and 2 and inversions at carbons 3 and 4. Although Aumann does not specify any particular forbidden ligand transformation, he does note that CCXI does not yield CCXII on thermolysis, but that this transformation does proceed photolytically. Thus, under the influence of the metal, a rearrangement occurs that is otherwise only permitted photochemically. A forbidden pericyclic mode is clearly indicated.

H. CONCLUSIONS

This review of metal-catalyzed pericyclic reactions displays a broad diversity of catalytic chemistry. Reactants seem to fall into two distinct classes: (1) the high-energy molecules, exhibiting unusual strain and generally in polycyclic ring systems, and (2) the low-energy systems such as simple olefins, acetylenes, dienes and low-energy valence isomers. High-energy molecules then define two subgroups. In the first, the forbidden paths to their respective low-energy valence isomers are generally simple and transition metal coordination virtually launches these systems along these reaction paths. Quadricyclene and cubane are good examples. In the second subgroup, geometrically simple forbidden paths to energetically preferred valence isomers are not easily available. Moreover, metal-coordination does little to open these paths of reaction to the ligand. Thus metal-catalyzed concerted reactions along otherwise forbidden reactions would be anticipated in the first subgroup but they should not play significant roles in the second. Bicyclobutanes are clear examples of the latter subgroup.

Regarding the catalytic chemistry of all high-energy valence isomers, one important point should be made. Their propensity to transform to their respective low-energy isomers is unusually strong. Thus they should take any reasonable reaction path available to reach their energy minima. A variety of catalysts should therefore exhibit different reaction profiles since these substrates carry within their strained molecular frameworks more than enough excess energy to propel them over the various activation barriers to low-energy products. We have seen this diversity, I believe, quite dominant in the second subgroup and perhaps, to some extent, in the first.

Low-energy systems should reasonably exhibit a narrowing spectrum of distinct catalytic routes to rearranged pericyclic products as the energy of isomerization approaches isothermal. This certainly appears to be so in olefin metathesis, irrespective of what the actual mechanism is. A narrow scope of distinct mechanisms might further be expected for the isomerization of *exo*-tricyclooctane CXXIV to tetracyclooctane CXXV (see page 165), and energetically similar processes.

Unique chemistry associated with the various metal catalysts is another striking feature that emerges from this review. Dauben and Kielbania's paper [39] showing the changes in mode of cubane isomerization which attend ligand changes on palladium(II) is a good illustration (see page 177). We have also seen that silver and certain palladium complexes were catalytically distinct (i.e., yielding cuneane) from what might be considered softer metals, such as $[Rh(diene)Cl]_2$, which transform cubane into its diene isomer. Sharp distinctions between groups of metals have been noted by others. Regarding the thermodynamic properties of various metal-olefin complexes, Hartley [188] has divided the transition elements into two groups. The first group, comprising silver(I) and copper(I), shows a decrease in the stability and enthalpy of formation of the metal—olefin complex as the electrophilicity of the olefin increases. Metals of the second group, nickel(0), platinum(0), platinum(II), rhodium(I) and iridium(I), all show increases in the stability and enthalpy of formation of their olefin complexes as the electrophilicity of the olefin increases. These thermodynamic properties clearly stem from electronic and orbital properties of the metals, as noted earlier [137] (see page 172). That there should be a continuum of bonding properties within and between groups should now be clear. And, similarly, since the coordinate bond to an olefin does not differ in kind from that to the variety of substrates that we have adressed here, the existence of a similar continuum in catalytic behavior should come as no surprise.

We have seen considerable interest directed to the concertedness or nonconcertedness of metal-catalyzed pericyclic reactions. One nonconcerted mechanism of unusual popularity involved metallocycle intermediates [35,36,40,41] (see page 121). Halpern [131] has established unequivocally that $[Rh(CO)_2Cl]_2$ inserts into cubane [36] and quadricyclene [131] yielding the corresponding six-membered ketonic metallocycles (see page 168). Volger et al. [128] had earlier shown that this same complex very likely inserts, in an identical fashion, into tetracyclooctane (CXXV) (see page 165); this insertion appeared as a side reaction to the valence isomerization CXXIV

→ CXXV. Wilkinson et al. [129] were the first to demonstrate the facility with which $[Rh(CO)_2Cl]_2$ inserts into cyclopropane rings yielding the ketonic products noted. Thus, the ability of this particular rhodium complex to insert into strained rings had been clearly established.

Halpern has reasonably generalized this mechanism, suggesting the possible intervention of metallocycles in [2 + 2] valence isomerizations catalyzed by the transition elements. However $[Rh(CO)_2Cl]_2$ in its reaction with cubane and quadricyclene is a reagent, acting essentially stoichiometrically. It is not catalytic, at least in the way other rhodium(I) complexes are. Halpern, in fact, notes that in the reaction of $[Rh(CO)_2Cl]_2$ with quadricyclene, an excess of quadricyclene is needed (particularly if norbornadiene impurities exist) to prevent the formation of [Rh(norbornadiene)Cl]$_2$, "a powerful catalyst for the isomerization reaction" (see page 168). The crucial question thus remains: is $[Rh(CO)_2Cl]_2$ a legitimate model for all the catalytic metals reported to facilitate forbidden pericyclic reactions, or does it instead reflect a finite number of metal systems at one segment along the continuum describing the catalytic properties of the transition elements?

Osborn et al. [40] were next to offer experimental evidence presumably in support of Halpern's metallocycle proposal (see page 121). His iridiocycle, containing two norbornadiene segments, was again formed stoichiometrically. Although it was to model high-energy intermediates in metal-catalyzed norbornadiene dimerizations, the starting complex and the iridiocycle itself were not catalytic for this reaction. Moreover, the cyclobutane dimer (i.e., the actual product of catalysis) could only be extracted from the iridiocycle in 35% yield from refluxing $CHCl_3$ in a five-fold excess of triphenylphosphine.

Whitesides et al. [41] have also suggested the intervention of metallocycles in pericyclic catalysis. However, their reported work on a variety of platinocycles, including the critical five-membered species, indicate that these compounds are (1) unusually stable and (2) undergo the two required transformations involved in [2 + 2] pericyclic reactions "sluggishly" (see page 122, eqn. 5).

The strongest evidence implicating the possible intervention of a metallocycle in a catalytic system would appear to be that of Grubbs et al. [37] (see page 162). Their synthetic tungstenocycle, legitimately reflecting a real catalytic system, undergoes smooth and quantitative transformation to metathesized ethylene at the appropriate temperature. These results clearly place this metallocycle firmly in the forefront of possible intermediates in metathesis. However, one question remains. Does the tungstenocycle itself metathesize or does metathesis occur subsequently, through the bisethylene tungsten complex?

A number of reported reactions are best viewed as concerted processes, examples of metal-catalyzed symmetry-forbidden ligand transformations. The dimer of norbornadiene, "Binor-S", reported by Schrauzer et al. [30], should be placed in this category (see page 119). The radical process proposed by Katz and Acton [29] is not consistent with the reaction's stereospecificity. Other mechanisms may perhaps be drawn, but they would seem to be either without precedence, or merely alternative valence bond representations of the concerted process.

Pettit's $Fe(CO)_x$-catalyzed disrotatory isomerization of tricyclooctadiene CXCVIII may be concerted [172] (see page 191). The implication of $Fe(CO)_3$ as the active catalytic species is suggestive of a forbidden-to-allowed process. $Fe(CO)_3$ contains a nonrestrictive ligand field and is thus capable of affecting the disrotatory electrocyclic process with full retention of coordinate bonding [12].

Grimme's reported [180] $Mo(CO)_3$-catalyzed rearrangement of the cyclic triene (see page 193) is best described as a metal-catalyzed [1,3] sigmatropic rearrangement. Other strong examples of [1,3] pericyclic processes were reported by Abley and McQuillen [182] (see page 194). The remarkable $Cr(CO)_3$-catalyzed rearrangement of bullvalene along a possible $[2_s + 2_s]$ pericyclic path must also be noted in this regard [187] (see page 195).

Perhaps the strongest case reported to date is that of Pettit's, the first example of a metal-catalyzed [6 + 2] cycloaddition [90] (see page 148). The catalytic step is clearly thermal, intramolecular, and proceeds directly to the metal-coordinated product. Like many of those noted above, the catalytic species ($Fe(CO)_3$) possesses a nonrestrictive ligand field and is thus clearly in that category of metal systems expected to catalyze forbidden pericyclic processes. One particularly impressive feature of this work is the synthetic approach employed in generating the catalytically active iron complex. An olefin π bond from the cycloheptatriene ligand on the precursor to the active catalyst was first dislodged photolytically, allowing the acetylene reactant to coordinate to the iron. A distinct, five-coordinate iron complex was thus generated, with the two substrates neatly positioned around the iron, ideally spaced for the subsequent [6 + 2] cycloaddition. Thermal fusion of the two ligands gave a new, five-coordinate complex (CIV). The overall [6 + 2] ligand transformation proceeded with retention of coordination. Speculation regarding the actual nature of the catalytic species was thus circumvented, CIII clearly transformed to CIV. Intermediate species might be wedged between CIII and CIV, but they would be proposed without experimental justification.

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