Coordination Chemistry Reviews, 109 (1991) 207–222
Elsevier Science Publishers B.V., Amsterdam

Coordination equilibria and coupling reactions of unsaturated hydrocarbons at a metal centre

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(Received 20 July 1990)

CONTENTS

A. INTRODUCTION

The field of hydrocarbon catalysis has been an area of intensive research and major progress in recent years attributed to the remarkable catalytic effect of various types of transition metal coordination compounds. Although the interaction of saturated hydrocarbons with some metal complexes has recently attracted interest, unsaturated hydrocarbons have much more important scientific as well as industrial aspects. This review therefore summarizes recent views of some of the fundamental chemical processes resulting from the interactions of unsaturated hydrocarbons with metal species.

The formation of olefin complexes is the first step in these processes and the equilibria involved have been analyzed to find the many factors regulating them, i.e. the electronic state of the metal species, the donor/acceptor character of the ligands, steric and electronic effects of the olefins, etc. Recent progress in the chemistry of olefin complexes of the early transition metals has made it possible to compare the factors originating from the difference in the number of *d* electrons and from their effective oxidation states throughout the Periodic Table. I think that more general views on olefin coordination should be established at the present time.

When olefin coordination is complete, the next important steps are (a) insertion into one of the metal—ligand σ bonds, and (b) coupling with other unsaturated ligands, typically olefin, acetylene or other hetero-unsaturated ligands. The former process is designated as the sp^2—sp^3 and the latter as the sp^2—sp^2 bond formation.

0010-8545/91/$5.60

The sp^2—sp^2 process also exists in metallacyclization involving metal-carbene and olefin to give metallacyclobutane species. Since the insertion reaction has been well documented [1], I confine myself in this review to discussion on the coupling process.

B. COORDINATION EQUILIBRIA OF OLEFINS

The nature of metal–olefin bonding is of fundamental importance for understanding mutual olefin coupling. Since the advent of the well-known Dewar–Chatt–Duncanson theory of bonding, the mode of bonding has been repeatedly discussed from various points of view. For Pd(II)— or Pt(II)—olefin bonding, recent systematic studies from the research groups of Powell and Kurosawa [2] indicate the importance of σ-type donation from olefin to the metal in cationic complexes, such as $[PdCp(PPh_3)(styrene)]^+$ and $[Pt(\eta\text{-methallyl})(PPh_3)(styrene)]^+$, or in neutral complexes, e.g. $[PtCl_2(py)(styrene)]$. Electron-donating *p* substituents on styrene increase the formation constants and negative Hammett ρ values of -1.4, -1.32, and -0.82 are obtained, respectively. When η^1-carbon ligands such as phenyl are introduced, the metal–olefin bonding becomes somewhat different and π-type back donation gains importance for $[Pd(\eta\text{-methallyl})(tetrachlorophenyl)(styrene)]$ and $[Pt(\eta\text{-allyl})(pentafluorophenyl)(styrene)]$. The ρ values for these neutral complexes are -0.24 and -0.38, respectively. A delicate interplay of energy levels of filled and vacant metal orbitals for interaction with the olefin is thus apparent.

On the other hand, when more electron-rich low-valent metal complexes of $d^8 \sim d^{10}$ configuration are involved, electron-withdrawing substituents on the olefin remarkably increase the stability. Thus, the $Pt(PPh_3)_2$ species is found to bind tetracyanoethylene extremely strongly. Some relevant data for Ni(0) and Rh(I) species are shown in Tables 1–3 [3].

A remarkable steric effect in olefin coordination (see Table 4) was recently reported for $IrH_2(CF_3CO_2)(PAr_3)_2$ [4]. This property of the complex was success-

TABLE 1

Selected examples of equilibrium constants in NiL_3—olefin sytems [3a]

$NiL_3 + \text{olefin} \xrightleftharpoons{K} NiL_2(\text{olefin}) + L$

$(L = P(O\text{-}o\text{-tolyl})_3)$

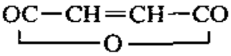
Olefin	K^a
Trans-NCCH=CHCN	1.6×10^8
CH_2=CHCN	4.0×10^4
CH_2=CHPh	1.0×10^1
Trans-EtCH=CHEt	2.7×10^{-3}
Cis-EtCH=CHEt	2.3×10^{-3}

[a] In benzene at 25°C.

TABLE 2

Equilibrium constants and thermodynamic parameters for the reaction [3b]

$$\mathrm{Ni(bipy)\,(solvent) + olefin \xrightleftharpoons{K} Ni(bipy)\,(olefin) + solvent}$$

Olefin	log K^a
 $\mathrm{OC{-}CH{=}CH{-}CO}$ (bridged by O)	4.52
$CH_2{=}CHCONH_2$	3.31
$CH_2{=}CHCN$	2.82
$CH_2{=}C(CH_3)CN$	2.37
$CH_2{=}CHCHO$	3.62
$CH_2{=}CHCOCH_3$	2.58
$CH_2{=}CHCOOCH_3$	2.49
$CH_2{=}C(CH_3)CO_2CH_3$	1.07
$CH_2{=}CHOCOCH_3$	−0.68

[a] In THF at 27°C.

TABLE 3

Equilibrium constants for the reaction [3c]

$$\mathrm{Rh(acac)\,(C_2H_4)_2 + olefin \xrightleftharpoons{K} Rh(acac)\,(C_2H_4)\,(olefin) + C_2H_4}$$

Olefin	K^a
i-C_4H_8	3.5×10^{-4}
Trans-C_4H_8	2.0×10^{-3}
Cis-C_4H_8	4.1×10^{-3}
$CH_2{=}CHOCH_3$	1.8×10^{-2}
$CH_2{=}CHCH_3$	7.8×10^{-2}
$CH_2{=}CHCl$	1.7×10^{-1}
$CH_2{=}CHF$	3.2×10^{-1}
Trans-$CHF{=}CHF$	1.2
Cis-$CHF{=}CHF$	1.6
$CH_2{=}CHCN$	>50
$CH_2{=}CF_2$	59
$CHF{=}CF_2$	88

[a] In toluene at 25°C.

fully utilized for dehydrogenation catalysis where bulky olefins, e.g. t-BuCH$=$CH$_2$, are employed as the hydrogen acceptor from an alkane.

The olefin complexes of early transition metals such as Ti, Zr, etc. are less well known at present. This paucity is caused by the instability of most of these olefin complexes toward air and water. The electropositive character of the metal coupled with the high reactivity caused by the open-shell structure, e.g. 14e to 16e, of the metal has hampered development of the chemistry in this area. This situation is now

TABLE 4

Equilibrium constants, K, for the reaction [4]

$[IrH_2(CF_3CO_2)(PPh_3)] + \text{Olefin}$

Alkene	K^a
$PhCMe{=}CH_2^b$	~0
$t\text{-}BuCH{=}CH_2^b$	0.58
Cyclopentene^b	1.9
Cyclodecene^b	2.3
$EtOCH{=}CH_2$	6.3
$n\text{-}BuCH{=}CH_2$	17
$PhCH{=}CH_2$	32
$Me_3SiCH{=}CH_2$	1250
Cyclooctene	5500
$CH_2{=}CH_2$	Large
Norbornene^c	Large

[a] In CH_2Cl_2 at −80°C ($L\ mol^{-1}$).

[b] These compounds are sterically congested in comparison with others.

[c] The bicyclo [2.2.1] ring provides particular ease in coordination at the double bond.

being considerably improved and many examples of olefin or diolefin complexes are reported [5].

Substituted arylethylene complexes of Nb, $Cp_2NbH(CH_2{=}CHAr)$, have been examined for intramolecular insertion to give $[Cp_2Nb(CH_2{-}CH_2Ar)L]$ where the geometry of the olefin complex, *endo* or *exo*, is important. The Hammett plots gave $\rho = 2.2$ for the complex formation, and $\rho = -1.1$ for the *endo* and $\rho = +0.7$ for *exo* isomers for the insertion [6]. Partial ionic character in determining the rates of these reactions is apparent.

Coordination equilibria for organolanthanoid/ethylene have been reported, and the value K_{eq} as measured by ^1H NMR was very small [6].

Ethylene complexes of Ti and Zr, $Cp^*_2Ti(C_2H_4)$ [7] and $Cp_2Zr(C_2H_4)(PMe_3)$ [8] are prepared, taking advantage of the stabilization effect of the bulky C_5Me_5 (abbreviated as Cp*) ligand or a ligand combination, 2Cp and PMe_3. The severe steric effect of the bis-Cp* ligands, however, precludes preparation of substituted olefin complexes of this type for Ti. Recently, butadiene complexes, $Cp^*_2M(C_4H_6)$, were prepared [5].

An MO study on these early transition metal complexes indicates the importance of back-bonding and therefore the bonding may be expressed by the limiting metallacyclopropane structure (B) as in Fig. 1 [9]. J_{C-H} data for coordinated olefins also provide evidence for structure (B) [5]. Comparison of bond strengths, coordination geometry (bond lengths and angles), and the nature of bonding among a wide variety of transition metals is now possible [5,10]. Throughout the series of transition metals arranged according to the Periodic Table, there is a definite trend of the *d*-orbital

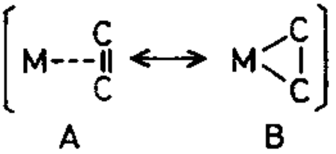


Fig. 1. Two limiting structures for metal–olefin bonding.

energy levels falling with successive filling of electrons. The late metals are thus more electronegative. This trend is clearly reflected in the nature of bonding with olefins. Apart from this general trend, the bonding is also influenced by a combined effect of co-ligands; e.g. carbon-, nitrogen-, oxygen-, or halo-ligands. Due to its electronegative character, the halo-ligand gives a positive metal centre and enhances σ donation from the olefin, e.g. in Zeise's salt. The carbon co-ligands, e.g. Cp, allyl, generally give a neutral metal atom. Back donation from the metal is thus promoted and metallacylopropane character is conferred. This means partial oxidation at the metal and the metal site is thus more electrophilic. The coordinated olefin part is anionic and enters into reaction with electrophilic unsaturated bonds such as C=O, or C≡N as shown by many kinds of reaction, e.g. observed for $Cp^*_2Ti(C_2H_4)$ and Cp_2Zr(diene) [5,7].

The equilibrium constants for the reaction of carbene complexes of the type, $M(=CHSiMe_3)(OR)_2(NAr)$, with vinyl-trimethylsilane were recently measured; $5.1 \times 10^{-1}\ M^{-1}$ (−40°C) for M = Mo, $3.3 \times 10^2\ M^{-1}$ (−38°C) for M = W, where R = $OCMe_2CF_3$ and Ar = 2,6-diisopropylphenyl. The enhanced stability of the tungstenacyclobutane ring system is thus apparent [11(a)]. Although a combination of steric and electronic effects seems to be determining these values, the tungsten analog definitely has a larger value, reflecting a higher affinity for the olefin. Since this type of reaction is important as an elementary reaction in olefin metathesis, further research in this area is needed.

In connection with asymmetric hydrogenation, the coordination equilibria of $[Rh(p—p)(solv)_2]^+$ (p—p = chelating diphosphine ligand) with various olefins have been reported [11(b)]. The K_{eq} values indicate a remarkable chelating effect of the tri-substituted functionalized olefin (MAC) for this Rh(I) complex. The observed high affinity for this type of chelating olefin forms a basis of effective asymmetric catalysis. The size of the chelate ring of the diphosphine influences the coordination equilibrium with 1-hexene or methyl acetoamidocinnamate (MAC) to a different extent, as shown in Table 5. The remarkably high K_{eq} value for a combination, dppe and MAC, indicates the stabilizing effect of a 5-membered chelate ligand for the functionalized olefin (MAC).

Trans-bis(olefin) complexes were recently isolated in the d^6-octahedral geometry, $M(C_2H_4)_2(CO)_4$ (M = Cr, Mo, W) from irradiation of $M(CO)_6$ with ethylene at −178°C. These are relatively stable (m.p. 67—68°C for Cr, m.p. 70—73°C for Mo, m.p. 130—135°C for W) [11(d)].

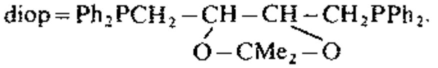
TABLE 5

Equilibrium data, $[Rh(p—p)(solv)_2]^+$/olefin, for 1-Hexene and MAC [11]

(MAC = $PhCH{=}C(NHCOCH_3)CO_2CH_3$)

Ligand[a]	Chelate ring size	1-Hexene	MAC
		K_{eq}[b] (M^{-1})	K_{eq}[c] (M^{-1})
dppe	5	1.7	2.2×10^4
dppp	6	2.7	2.2×10^2
dppb	7	1.3	2.2×10^2
diop	7	1.8	2.2×10^2
$(PPh_3)_2$			2.9×10^2

[a] Chelating ligand (p—p): dppe = $Ph_2P(CH_2)_2PPh_2$; dppp = $Ph_2P(CH_2)_3PPh_2$; dppb = $Ph_2P(CH_2)_4PPh_2$; diop =



$Ph_2PCH_2-CH(-O-CMe_2-O-)CH-CH_2PPh_2$.

[b] At 40°C.

[c] At 25°C.

Bis(olefin) complexes of heavy late transition metals, in a *trans* configuration such as *trans*-$PdX_2(olef)_2$, or *trans*-$RhX(L)$-$(olef)_2$, are not stable because coordination equilibria favour olefin dissociated species, especially in coordinating solvents [12]. When the two olefinic ligands are connected to give a chelating diolefin, e.g. 1,5-hexadiene or cod, the bis(olefin)-type complexes are more stable [12]. Thus, the perpendicular geometry of olefin coordination in square planar complexes is important for the stability. However, η^4-1,3-diene coordination is not stable for these d^8 metals. Conversion to η-allyl species has generally been observed by an intra- or intermolecular attack of nucleophiles [12]. Partially positive carbons are implied for these olefin or diolefin complexes in which the metal–olefin interaction is considered to be mainly σ donation from the olefin [12].

Although equilibrium constants for sequential coordination of two or more olefin molecules are important for the olefin coupling reaction, no such data are available so far. In the case of propadiene, the enhanced ability for coordination with one double bond has been clearly shown by the formation of a pentakis(propadiene)iridium(I) complex and also by selective formation of a cyclic propadiene pentamer complex of Rh, $RhCl(C_3H_4)_5$ [13,14].

Recently, many examples have been found for s-*trans*-η^4-coordination of 1,3-dienes [5]. In particular, butadiene or terminally substituted dienes definitely favour this novel type of coordination when the metal species contains second-row early transition metals such as Zr and Nb [15]. Pertinent examples are Cp_2Zr(s-*trans*-C_4H_6) and Cp(s-*cis*-C_4H_6)Nb(s-*trans*-C_4H_6). The MO and NMR analysis of the bonding indicated the presence of essentially bis(monoene) coordination on the metal.

This type of diene coordination is thus quite different from that in Cp_2Zr(s-*cis*-diene) where a considerable degree of metallacyclopentene limiting structure is proposed based on analysis of bonding, NMR and structural parameters [15].

An equilbrium for partially dissociated species, Cp_2Zr-(η^2-C_4H_6), is suggested to account for the reactivity in many of its reactions with a variety of unsaturated compounds, e.g. olefins, dienes, etc. [5].

C. NMR STUDIES

NMR parameters, e.g. chemical shifts, $^1J_{C-H}$, and $^3J_{H-H}$ values, provide important information on the lability of metal–olefin coordination and the nature of the bonding involved. In particular, the recent accumulation of $^1J_{C-H}$ values in a series of non-labile metal–ethylene as well as metal–butadiene complexes enables us to evaluate quantitatively the extent of sp^n hybridization at the coordinating carbons [9]. Selected values of these parameters are shown in Table 6. A clear trend has been observed for the coupling constants, favouring low values for low-valent early transition metals. However, the chemical shift values are influenced by many factors and no clear trend has been observed. In Table 7, the relevant C–C bond lengths and the extent of bending of the hydrogens as measured by the angle α (see Fig. 2) are listed.

TABLE 6

NMR C—H coupling constants of coordinated ethylene and butadiene [10]

d electrons	Formal oxidation state	Compound	$^1J_{C-H}$(Hz)	
			Terminal	Internal
		C_2H_4	165	
2	2	$Cp^*_2Ti(C_2H_4)$	145	
2	2	$Cp_2Zr(C_4H_6)$	145	154
2	2	$Cp^*TiCl(C_4H_6)$	154	165
2	2	$Cp^*TiBr(C_4H_6)$	158	157
2	3	$CpTaCl_2(C_4H_6)$	146	169
4	1	$CpTa(C_4H_6)_2$	150 148	156 155
6	0	$W(C_4H_6)_3$[a]	151	165
10	0	$Ni(C_2H_4)_3$[b]	161	

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[a] Ref. 31.

[b] Ref. 32. These authors concluded that there is no change in the coupling constants upon metal complexation. Subsequent studies, however, showed the trend above (decreasing coupling constants of terminal C—H bonds), indicating an approach to a metallacyclopropane limiting structure with early transition metal coordination.

TABLE 7

Structural parameters of coordinated ethylene

d-electrons[a]	Formal oxidation state[a]	Compound	C—C (Å)	α[b] (deg)
		C_2H_4	1.337(2)	0
10	0	$(Ph_3P)_2Ni(C_2H_4)$	1.431(15)	
8	2	$K[PtCl_3(C_2H_4)]$	1.375(4)	32.5
8	1	$CpRh(C_2F_4)(C_2H_4)$	1.358(9)	42.4
6	2	$(PMe_2Ph)_2RuCl_2(CO)(C_2H_4)$	1.376(10)	24
6	0	$Mo(PMe_3)_3(CO)(C_2H_4)$	1.403	59
2	3	$Cp^*Ta(=CHBu)(PMe_3)(C_2H_4)$	1.477(4)	68.5
2	3	$Cp_2Nb(C_2H_5)(C_2H_4)$	1.406(13)	52.5
2	2	$Cp^*_2Ti(C_2H_4)$	1.438(5)	70

[a] These values are obtained by assuming complete ionic structure for Cp—M and C—M (sigma) bondings.

[b] Data taken from ref. 33.

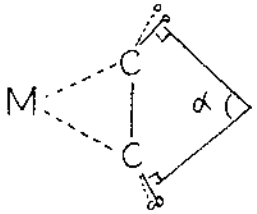


Fig. 2. Angle (α) between normals of C–H–H planes in ethylene complexes.

The combined results, as apparent in Tables 6 and 7, clearly indicate stronger coordination of olefin to low-valent early transition metals, especially for heavier metals. The remarkable strength of metal–olefin or metal–diene bonding in some Ta complexes, as revealed by structural and spectroscopic data, is explicitly shown by their inertness in catalytic hydrocarbon conversion, e.g. oligomerization and polymerization. For example, an extensive series of bis(diene) complexes of Ta, $Ta(C_5R_5)(diene)_2$, were examined for catalysis with olefins or dienes but none has so far been found [10]. Analogous Nb complexes are active as catalysts for diene polymerization and/or oligomerization [10].

The $^3J_{H-H}$ values can be utilized in determining the geometry of coordinated butadiene ligands in some butadiene complexes. For example, one of the two butadiene ligands was found, by detailed analysis of the ^1H NMR data, to coordinate in s-*trans* geometry in $CpNb(butadiene)_2$. Since the separation of pure isomers was difficult due to similar overall molecular shape, high-resolution NMR spectra of the isomer mixtures allowed successful analysis by complete decoupling of all nonequivalent butadiene protons. The ${}^3J_{H-H}$ value for the internal CH–CH part was found to be 13.7 Hz, which is similar to the corresponding coupling constants (15.5 Hz) found for Cp_2Zr(s-*trans*-butadiene) [10(c)]. The values for s-*cis*-butadiene ligands in many other known examples are ca. 7 Hz. The utility of the coupling constants is thus demonstrated for assignment of the novel s-*trans* geometry of butadiene coordination.

D. COORDINATION EQUILIBRIA FOR ACETYLENES

Generally, interaction of acetylenes with metal atoms or low-valent metal ions is stronger than that of olefins. Pertinent examples are $Cp_2Mo(C_2H_2)$ and $Pt(PR_3)_2(C_2H_2)$ [16]. However, when the metal prefers σ donation from the π_b orbitals of acetylene, coordination of acetylene may be weaker than olefin. Thus, the Ag(I) ion is found to interact less with disubstituted acetylenes. Formation of acetylides is preferred with mono-substituted acetylenes in many cases since the acetylides are stabilized by formation of polynuclear species in solution by formation of bridged species and tend to precipitate from the solution.

To eliminate such intermolecular interaction, *o*-phenanthroline was utilized as a co-ligand in a system, Cu(I)/acetylene. The coordination equilibrium was investigated in acetone containing 0.3 M acetonitrile by spectrophotometry. For acetylene, a log K value of 1.2 was obtained. This is similar to that of CO ($\log K = 1.3$) and smaller than that of ethylene ($\log K = 2.2$) under similar conditions [17]. The electronic effect on the equilibrium was studied but no clear trend was obtained for substituted olefins or acetylenes. Therefore, the bonding is not only simple σ donation-type but considerable back donation from Cu(I) is indicated.

The coordination of acetylenes to low-valent early transition metal species such as $Cp_2Nb(R)$ ($R = H$, C_2H_5) or $Cp_2Ti(PMe_3)$ is considerably stronger than to the later transition metals [18]. Effective back donation in these examples is indicated by the enhanced di-σ-bonded (or metallacyclopropene cf. Fig. 1 (B)) character of the acetylene–metal bonding. The substituent electronic effects in these complexes have not been investigated systematically.

E. REACTIVITY OF COORDINATED OLEFINS

The reactivity of a complexed olefin reflects the nature of metal–olefin bonding and thereby olefin reactions should be quite different, depending on the identity of the metal. However, almost the same ethylene oligomerization or polymerization has been found to occur by catalysis with late transition metal complexes such as Ni(I ∼ II) and with early transition metal complexes such as Ti(III) or Cp_2Zr^{2+} species activated with alkylaluminium [1]. The difference in structure and bonding of these metal–ethylene complexes has already been described. The reactivity strongly depends on the coordination geometry and the electron count of the metal. Thus, stable complex formation with an olefin occurs with metal species, leading to a stable electronic structure (18e configuration) coupled with the unique stereochemistry of the complex.

Ethylene complexes of middle transition metals, e.g. $W(CO)_5(C_2H_4)$ or $Cp_2Mo(C_2H_4)$, are generally not very reactive. A bis(ethylene) complex, *trans*-$Cr(C_2H_4)_2(CO)_4$, is also stable. Most of these complexes have an 18e configuration with stabilized geometry. In contrast, the nickel triad metal complexes with 16e configuration and in three-coordination, e.g. $M(C_2H_4)(PPh_3)_2(M = Ni, Pd, Pt)$ are highly labile and rapid C_2H_4 exchange has been observed [3,12]. Metallocenes of the Ti triad elements also coordinate ethylene to give a complex with 16e configuration, e.g. an elusive $Cp_2Ti(C_2H_4)$, which is reactive to 2e donors. A further attack of ethylene gives a bis(ethylene) complex in a reversible manner. Here, the Ti species favour both 16e and 18e configurations and this trend renders this type of complex highly reactive. The presence of bulky C_5Me_5 ligands allows isolation of a monoethylene complex, $Cp^*_2Ti(C_2H_4)$ for Ti, and a combination of Cp and PMe_3 for Zr (e.g. $Cp_2Zr(C_2H_4)(PMe_3)$) [19]. Analogous higher olefin complexes remain unisolated, presumably due to steric congestion. Recently, a Hf complex of isobutene, $Cp_2Hf(PMe_3)(i\text{-}C_4H_8)$, was prepared by alkane elimination from $Cp_2Hf(R)(i\text{-}C_4H_9)$ but not by coordination of the olefin [20].

Cis-bis(olefin) complexes have been postulated as crucial intermediates for oxidative coupling of two olefin molecules. This coupling forms a basis of catalytic olefin dimerization (see Fig. 3). The bis(olefin) complexes are accessible by sequential coordination of two olefin molecules on highly reactive metal species such as Cp_2Ti or $(R_3P)Ni$. Although the Ti complex, $Cp_2Ti(olefin)_2$, is an 18e species, it is kinetically labile and still remains unisolable. With three cyclohexyl groups on the P ligand, $(Cy_3P)_2Ni(C_2H_4)$, a 16e complex was isolated [21].

The bis(ethylene) titanocene complex has two ethylene molecules in just the right geometry for oxidative coupling (as shown in Fig. 4 (a)) to give a titanacyclopentane, Cp_2Ti which is thermally unstable even at −30°C [22]. One of the thermal reactions is β-hydrogen elimination to give a still more unstable hydridoalkyl com-

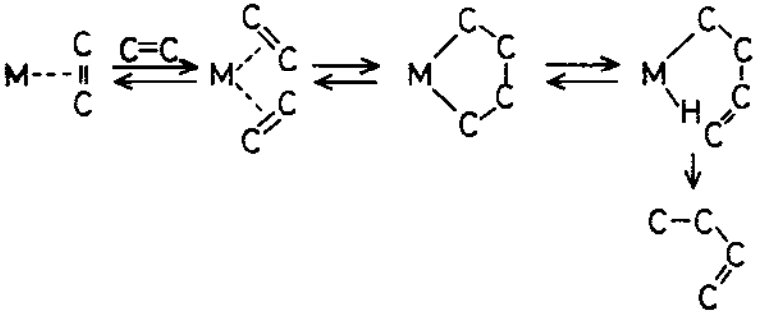


Fig. 3. Pathways for olefin coupling on a metal.

plex, $Cp_2TiH($$)$. Reductive elimination of 1-butene would give free titanocene, which is also highly reactive and enters into various reactions. Since the regeneration of bis(ethylene) titanocene is practically precluded by these side reactions, titanocene species are not good catalysts for the linear dimerization of ethylene. The same reason also holds for zirconocene and hafnocene.

When butadiene is used as a ligand for these metallocenes, the catalytic linear dimerization of butadiene or isoprene is realized [23]. Here, the precursor diene complex is more stable, especially for Zr and Hf analogs, and the oxidative coupling stage between the two dienes is thus easier to attain. Regeneration of the diene complex occurs readily in the presence of excess diene and the catalytic cycle shown in Fig. 4(d) is maintained.

Free Cp_2Zr (14e species) is never liberated in the case of the above reactions with dienes. The olefin coupling followed by reductive elimination on the metal produces dienes which remain coordinated to the same metal. This is clearly different from the similar reductive elimination from a late transition metal with a 16–18 electron configuration. The stability of low-valent metal species with two- or three-coordination accounts for the above difference in the elimination step. Actually, two-coordinate Pt(0) complexes have been isolated with highly bulky phosphine ligands [24].

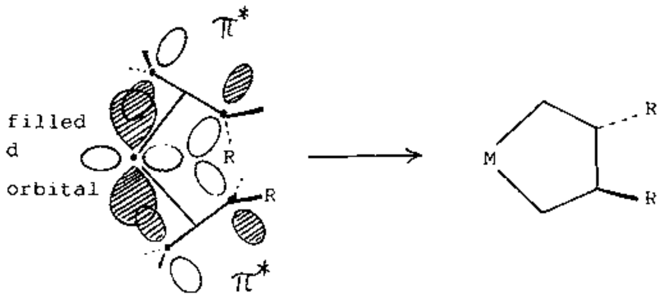
In contrast to the lability of the titanium–bis(olefin) complexes, the corresponding 1,3-diene complexes of Zr, e.g. Cp_2Zr(butadiene), are kinetically more stable, especially in the s-*cis*-diene isomer (C) (Fig. 5). The s-*trans* isomer (A) is more reactive due to its propensity to generate the η^2-butadiene species (B) which is a 16e species ready to receive coordination of another unsaturated molecule. In the s-*cis*-diene form, the diene complexes are in equilibrium with the metallacyclic form (D) which is also a 16e species and has reactive metal–carbon bonds.

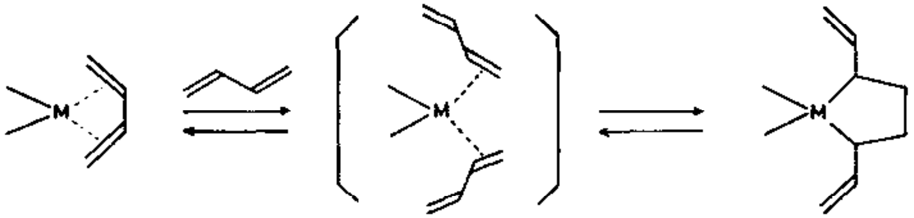
The elementary steps involved in the olefin coupling have been analyzed by MO methods. In particular, an EHMO analysis of the oxidative olefin coupling on a metal atom was performed by Stockis and Hoffmann [25]. In the case of *cis*-$Fe(CO)_3(C_2H_4)_2$, the geometry of the ligands was found to be crucial for a smooth C–C bond-forming reaction to give a metallacycle. A typical steric course of this pathway was thus proposed in Fig. 6. In the case of metallocenes of the Ti triad, the orbital requirement around the metal is just right to promote the olefin coupling.

In the C–C bond-forming stage, the energy gained by the C–C and two M–C bonds must be balanced by the loss of two 'olefin–metal bond energies' coupled with rehybridization at the metal. In the case of titanocene or zirconocene, the energy balance favours metallacycle formation but in other cases, e.g. $Os(CO)_3(C_2H_4)_2$, the metallacycle $(OC)_3Os$ is rather unstable because of its 16e configuration. Here, the activation energy seems to be so large as to prevent formation of any metallacycles for the Os analog [25].

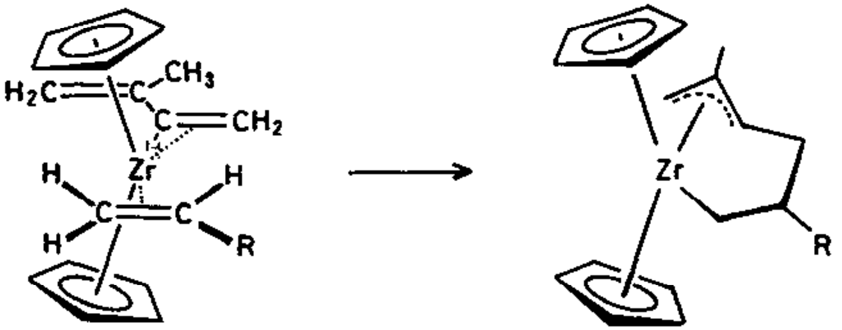
An interesting coupling of two ethylene molecules to 1,3-butadiene has been observed in the presence of 'titanocene' (a binuclear dihydride with a fulvalene ligand)

[26]. Formation of a metallacycle is implicated followed by double hydride elimination. Similarly, $WH(CH_2PMe_2)(PMe_3)_4$ gives a bis(butadiene) complex, $W(C_4H_6)_2(PMe_3)_2$ in 4% yield, presumably by oxidative addition of ethylene followed by reductive coupling of two vinyl ligands [27]. This mode of ethylene coupling

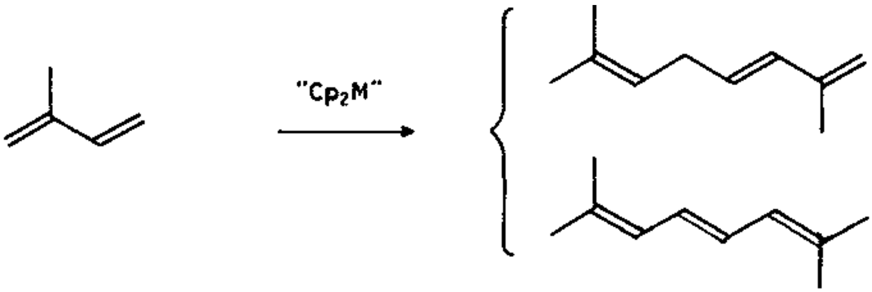




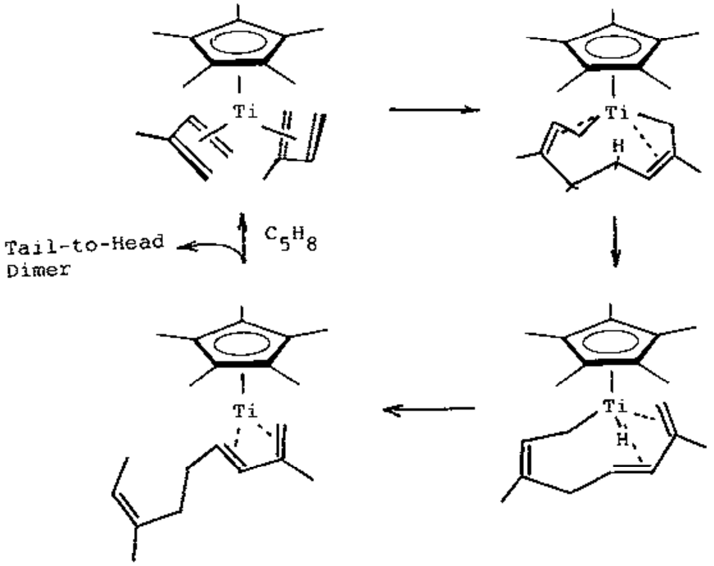
(a)



(b)



(c)



(d)

Fig. 4. (a) Orbital interaction and regio-selective bis(olefin) and bis(diene) coupling. (b) Stoichiometric coupling between isoprene and 1-olefins on Cp_2Zr species. (c) Catalytic coupling of isoprene by Cp_2Zr species. (d) Selective tail-to-head coupling of isoprene on $(C_5Me_5)Ti$ species.

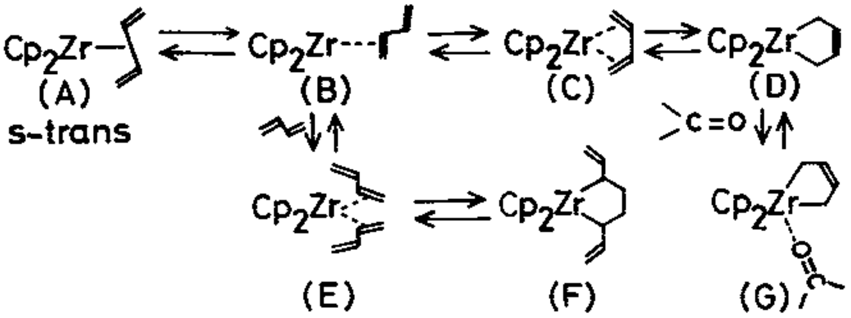


Fig. 5. Variety of bonding modes in Cp_2Zr (butadiene) and reactions therefrom.

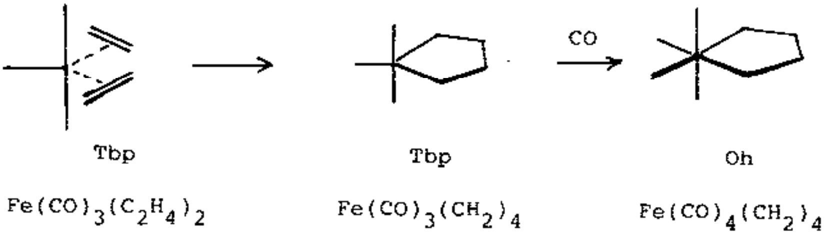


Fig. 6. Preferred steric course for olefin coupling in the case of $Fe(CO)_3(C_2H_4)_2/CO$.

results from high electron density at the metal species that favours oxidative addition of the C–H bond of ethylene.

F. REGIO-SELECTIVITY IN THE OLEFIN COUPLING

When substituted olefins are employed, regio-selection at the metallacyclization gives a clue to the mechanism of the olefin coupling. The MO analysis of Stockis and Hoffmann [25] (see Fig. 4(a)) predicts regio-control through preferred C–C bonding at the carbon bearing the larger lobe of the π^* orbital. Actually, such a case is observed for coupling of methyl acrylate on iron(0) or other metals [28]. The coupling of propylene on Ta(III) occurs through formation of an intermediate with quasi-parallel orientation of two propylene ligands to give a 2,3-dimethylmetallacycle with a Cp^*TaCl_2 fragment [29]. The observed selectivity may also be explained by the same reasoning with the EHMO theory.

The regio-selectivity in these reactions is important in organic synthesis, e.g. olefin dimerization, cyclization to cyclopentanones (from olefin and CO) and related organic transformations involving such transition metal species as $Ni(PR_3)_x$ and Cp_2M, ($M = Ti$, Zr) which promote bis(olefin) coupling.

In the catalytic linear dimerization of dienes, the regio-selectivity observed has been discussed in the case of zero-valent nickel catalysts. Recent progress in this area in the early transition metal complex catalysts has focussed on the regio-chemistry of diene coordination and C–C bond formation between the dienes, as typically illustrated in Fig. 4. In particular, the supine–prone mode of bis(diene) coordination to species, CpNb and CpTa, seems to add a unique feature to the emerging organometallic chemistry of these and other metals [10].

G. COUPLING OF ACETYLENES

Just as in the coupling described for olefins, acetylenes are coupled on a metal to form metallacyclopentadiene complexes. Since acetylenes give generally more stable complexes with many kinds of metal species, metallacyclopentadiene complexes have been accessible even in the early days of organometallic chemistry. In particular, a detailed ab initio MO analysis of the process involved in the formation of cobaltacyclopentadienes was carried out by Wakatsuki et al. [30]. The most important conclusion is the preferred geometry of two acetylene molecules that results in the observed high regio-selectivity with mono-substituted acetylenes. Bulky substituents (e.g. *t*-Bu) selectively occupy the position nearer to the metal in forming the metallacycle. Steric congestion at the C–C bond-forming site is thus important and the electronic effect of the substituent group is a minor factor. This trend is in contrast to the regio-selection observed in olefin coupling at tri(carbonyl)iron species, where the regiochemistry is controlled by the overlap of π^* orbitals of the olefin molecules as indicated by an MO study [25]. Thus, electron-withdrawing CO_2R groups occupy the α positions of the ferracyclopentane ring [28].

Since the recent activity of research in this area is high, a comprehensive coverage was not attempted in this review. Nevertheless, a general trend in the strength of coordination of olefins and acetylenes is already apparent: the nature of metal–olefin bonding changes gradually with change of the positions of the metal in the Periodic Table from left to right and from top to bottom. This point may be clearly manifested in the ^1H NMR parameters; some examples are shown in Table 6.

A future view of this area will certainly include the coordinating tendency and reactions on two or more metal atoms. Much new important research is now appearing on these aspects and will be reviewed at a later date.

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