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CHAPTER **11**

Organometallic complexes of dienes and polyenes

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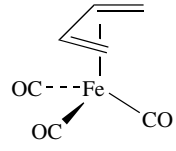
I. INTRODUCTION

The first complex of a conjugated diene was reported in 1930 by Reihlen and coworkers[1]. Reaction of butadiene with $Fe(CO)_5$ gave a yellow-brown oil with the molecular formula $(C_4H_6)Fe(CO)_3$. The elucidation of the structure of ferrocene eventually lead Hallam and Pauson[2] to propose a π-complex **(1)** for $(C_4H_6)Fe(CO)_3$ and this was eventually confirmed by crystal structure analysis at low temperature[3]. Since that time interest in

diene–metal complexes as starting materials for organic synthesis or as intermediates in stoichiometric or catalytic processes has led to the preparation and/or characterization of (conjugated diene)metal complexes of nearly all of the transition metals. This chapter will focus on monometallic transition metal complexes of cyclic and acyclic conjugated dienes and cyclobutadienes, particularly on structure, bonding, spectral characterization, fluxional behavior and reactivity.



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II. STRUCTURE AND BONDING

The bonding in conjugated diene- and cyclobutadiene–metal complexes differs from that for 'isolated' diolefin complexes due to differences in the π-type molecular orbitals for each system. For 'isolated' diolefins, there are two degenerate bonding symmetry combinations and two degenerate antibonding combinations (Figure 1). For a conjugated diene, these pairs of degenerate orbitals are each split into higher and lower energy cases due to interaction across the C2–C3 bond[4]. Both the s-*cis* and s-*trans* conformers may be considered for acyclic or non-constrained dienes (Figure 2). For square cyclobutadiene (D_{4h}), the four molecular orbitals consist of one bonding orbital, two degenerate non-bonding orbitals and one antibonding orbital (Figure 3)[5].

Overlap of the π-type orbitals with the corresponding appropriate metal fragment orbitals lead to new bonding and antibonding combinations. The frontier orbitals of two isolobal[6] cases are frequently encountered. For both the ML_3 and the CpM fragments the frontier orbitals consist of a doubly degenerate *e* set and a higher energy a_1 orbital (Figure 4)[7]. It should be noted that for the ML_3 fragment, these orbitals are tipped with respect to the orientation of the orbitals for the CpM fragment. Due to the double degeneracy of the *e* set of orbitals, diene complexes of these two fragments prefer coordination of the ligand in the s-*cis* η^4-1,3-diene fashion since the nodal plane of the $\pi 2$ orbital and the nodal plane of the $\pi 3$ orbital are perpendicular to each other. In comparison, the frontier

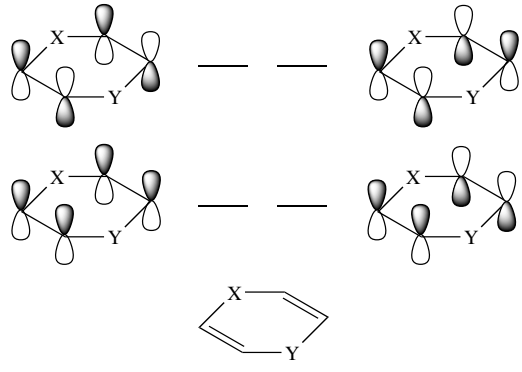


FIGURE 1. π-Molecular orbitals for unconjugated dienes

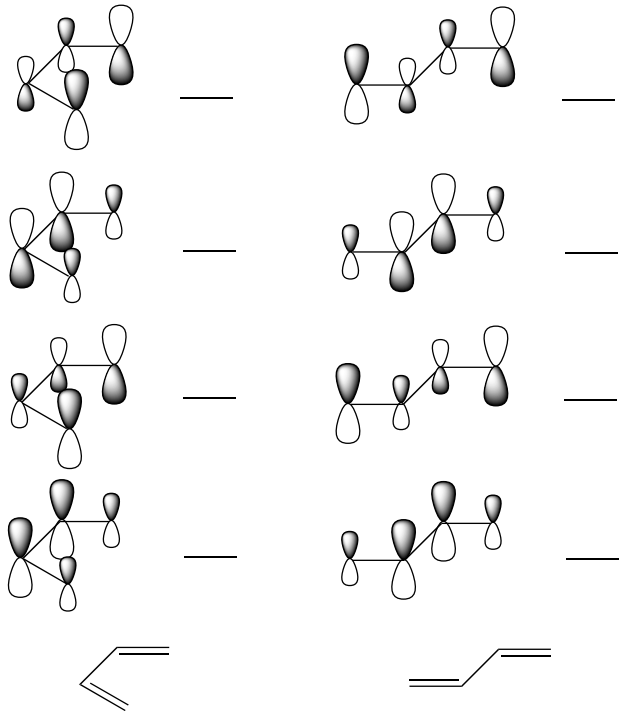


FIGURE 2. π-Molecular orbitals for conjugated dienes

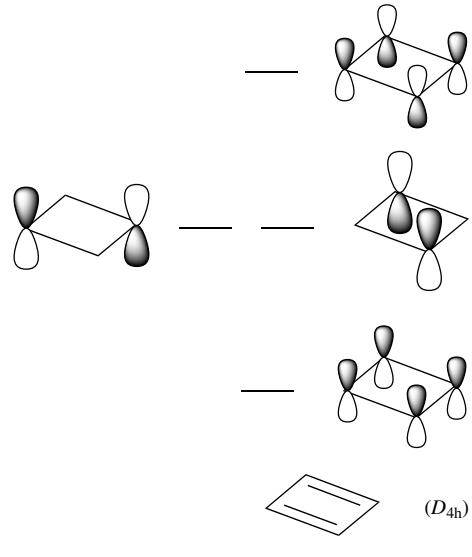


FIGURE 3. π-Molecular orbitals for cyclobutadiene

orbitals for the ML_4, ML_2Cp and the bent MCp_2 fragments (Figure 5) are characterized by sets of orbitals which primarily lie in a single plane[7,8]. This absense of a degenerate pair of orbitals for these fragments allows for a considerably wider range of complexation modes such as exemplified by non-conjugated dienes and s-*trans* η^4-1,3-dienes.

Complexation of the s-*cis* 1,3-diene conformer has been described as a hybrid of two extreme coordination modes: an η^4-diene **(2a)** and a σ^2,π metallacyclopent-3-ene **(2b)**.

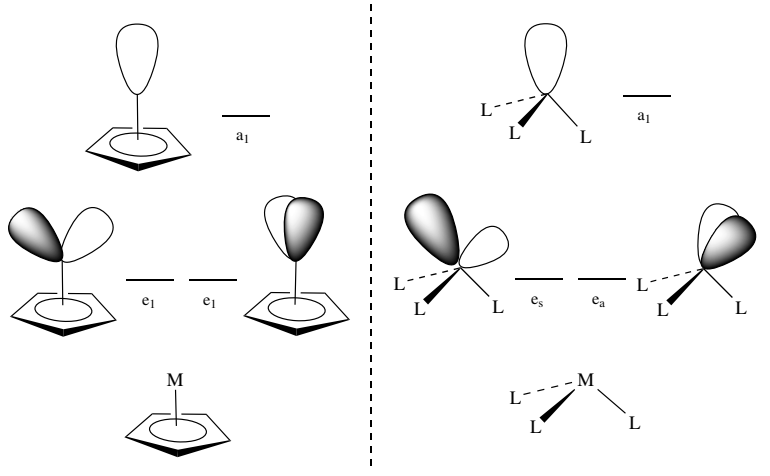


FIGURE 4. Molecular orbitals for MCp and ML_3 fragments

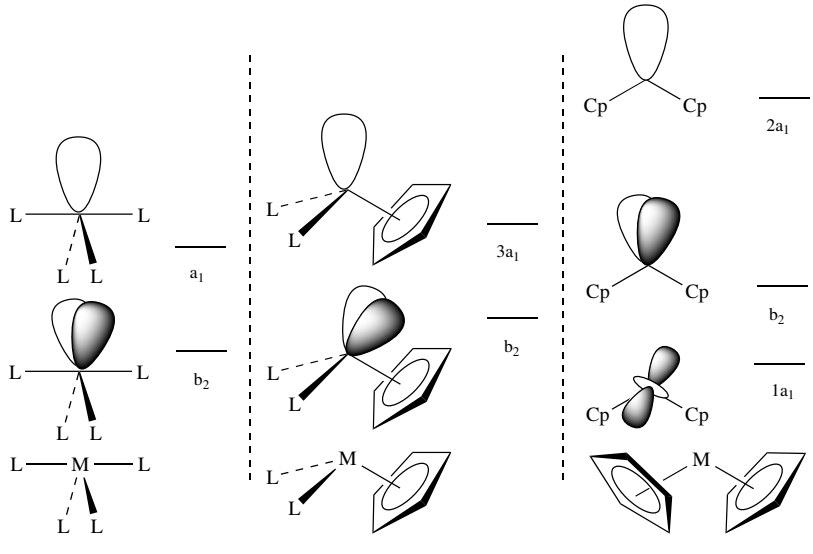
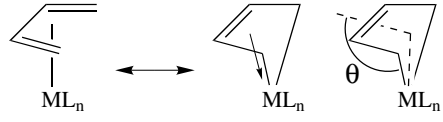


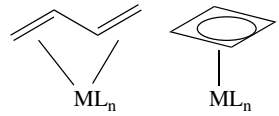
FIGURE 5. Molecular orbitals for ML_4, ML_2Cp and MCp_2 fragments

Complexes which may be best described by structure **2a** are distinguished by (1) nearly sp^2 hybridization at the terminal carbon atoms, (2) relatively similar lengths of the central (C2−C3) and the lateral bonds (C1−C2 and C3−C4) and (3) slightly longer distances for the metal to terminal carbon atoms (M−C1 and M−C4) vs the metal to internal carbon atoms (M−C2 and M−C3). In contrast, complexes which may be described as closer to **2b** are distinguished by (1) near sp^3 hybridization at the terminal carbon atoms, (2) distinctly shorter central bonds (C2−C3) and longer lateral bonds (C1−C2 and C3−C4) and (3) longer distances for the metal to internal carbon atoms (M−C2 and M−C3) vs the metal to terminal carbon atoms (M−C1 and M−C4). Nakamura and coworkers[9] have conducted a statistical analysis of the crystal structures of a series of s-*cis* (diene) complexes of various transition metals. They defined three parameters: the angle Θ between the C1−M−C4 plane and the diene plane (cf **2c**), the difference Δd between the average M−terminal carbon and average M−internal carbon distances, and the difference Δl between the average of C1−C2 and C3−C4 distances and the C2−C3 distance. The early transition metal complexes (Zr, Hf, Ta, Nb) are best described by the structure **2b** ($95^\circ < \Theta < 120^\circ$, -0.4 Å$< \Delta d < 0.0$ Å, 0.0 Å $< \Delta l < 0.2$ Å) while the later transition metal complexes (Mn, Fe, Os, Co, Rh, Ir) are best described by the structure **2a** ($80^\circ < \Theta < 85^\circ$, 0.0 Å $< \Delta d < 0.1$ Å, -0.1 Å $< \Delta l < 0.0$ Å).



(2a) **(2b)** **(2c)**

The crystal structures of a number of s-*trans* (diene)metal complexes **(3)** have been determined[10−14]. The diene ligand in all s-*trans* complexes is distinctly non-planar; the torsional angle between the two olefin groups is between 114° and 127°. In general, the terminal carbon to metal distance is greater than for the internal carbon to metal distance, and the C1−C2/C3−C4 bonds are shorter than the C2−C3 bond.



(3) **(4)**

Crystal structure data[15] indicate that in the vast majority of (cyclobutadiene)metal complexes **(4)** the cyclobutadiene ligand is approximately square-planar with nearly equal C−C bond distances (*ca* 1.46 Å) and bond angles of *ca* 90°. Within a given complex the cyclobutadiene carbon-to-metal distances are roughly equal.

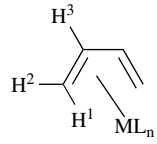
III. NMR SPECTROSCOPIC CHARACTERIZATION AND FLUXIONAL BEHAVIOR

A. Conjugated 1,3-Diene Complexes

1. ^1H NMR spectral data

In the following discussion, chemical shifts and coupling constants will be presented for the static structure of a complex. In general, the signals for protons attached to an s-*cis*

TABLE 1. ^{1}H NMR spectral data (chemical shift δ in ppm; coupling constants J in Hz) for (s-*cis*-butadiene)metal complexes



Entry	ML_n	Solvent/temp[a]	H^1	H^2	H^3	$^2J_{1-2}$	$^3J_{2-3}$	$^3J_{1-3}$	Reference
1	$Ti(\eta^8-C_8H_8)$	C_7D_8/30 °C	−0.19	4.12	3.72	−1.31	8.37	10.70	16
2	$Zr(\eta^8-C_8H_8)$	C_7D_8/30 °C	0.37	2.60	4.31	−4.14	9.41	11.09	16
3	$Hf(\eta^8-C_8H_8)$	C_7D_8/30 °C	0.45	1.79	4.85	−6.70	9.63	9.55	16
4	$ZrCp_2$	C_7D_8/−70 °C	−0.69	3.45	4.78	−10.0	9.5	10.5	17
5	$HfCp_2$	$CHFCl_2$/−120 °C	−0.73	2.74	5.0	*b*	*b*	*b*	18
6	$NbCp^*Cl_2$	C_6D_6/30 °C	0.46	1.35	7.07	6.0	6.5	7.5	19
7	$TaCpCl_2$	C_6D_6/30 °C	0.19	0.96	7.03	−6.5	7.5	6.5	9a
8	$Cr(CO)_4$	C_6D_6/RT	0.55	1.68	4.37	1.25	7.93	12.08	20
9	$MoCp(CO)_2^+$	C_3D_6O/−70 °C	2.28	3.07	6.45	*b*	7.4	9.6	21
10	$MoCp[P(OMe)_3]_2^+$	C_6D_6/[c]	0.86	2.26	5.60	*b*	*b*	*b*	22
11	$[Mn(CO)_3]^-$[d]	THF-d_8/25 °C	−1.3	0.6	4.4	*b*	4.0	7.0	23
12	$Fe(CO)_3$	C_6D_6/25 °C	−0.03	1.46	4.89	−2.42	6.93	9.33	24
13	$Fe(CO)_2PPh_3$	C_6D_6/[c]	−0.11	1.35	4.83	2.1	5.3	7.9	25
14	$Ru(CO)_3$	C_6D_6/[c]	0.12	1.44	4.88	−2.77	6.94	8.65	26
15	$Os(CO)_3$	C_6D_6/[c]	0.14	1.70	4.93	−3.48	6.86	7.78	26
16	$RuCp^*(OTf)$	$CDCl_3$/20 °C	2.32	3.86	4.70	*b*	6.2	10.3	27
17	$RuCp^*Br_2^+$	CD_3NO_2/−20 °C	2.41	3.97	7.27	1.2	7.5	7.8	27
18	$Co(CO)_3^+$	CD_3NO_2/[c]	2.5	3.6	6.7	3	3.5	10	28
19	CoCp	C_7D_8/30 °C	−0.37	1.69	4.91	−1.46	6.79	9.36	16
20	RhCp	$CDCl_3$/[c]	0.9	2.94	5.00	*b*	*b*	*b*	29

[a] $C_7D_8 = C_6D_5CD_3$; $C_3D_6O = (CD_3)_2CO$.
[b] Not reported.
[c] Temperature not reported, presumably ambient temperature.
[d] Data are for the (isoprene)ML_n complex.

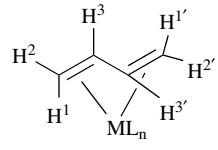
complexed diene appear upfield of those of the free ligand, and protons attached to the terminal carbons appear upfield of those attached to the internal diene carbons (Table 1). The proton NMR chemical shifts for a particular complex depend upon the metal, the charge of the complex, the orientation of the diene ligand with respect to the anisotropy of the peripheral ligands, the substituents present on the diene ligand, and the solvent. For isoelectronic complexes, the proton signals for anionic complexes appear upfield of neutral complexes, which appear upfield of cationic complexes (Table 1, entry 11, 12, 18). The nature of the diene bonding (i.e. η^4-π **2a** vs σ^2, π **2b**) is manifested in the $^2J_{gem}$ coupling constants. For complexes which are best described by **2b** (e.g. entries 4–7), the increased sp^3 character of the terminal carbons is reflected in larger magnitude J_{gem} (6–10 Hz) than for those complexes best described by the η^4-π **2a** bonding mode (e.g. entries 8, 12–14, 17–19; J_{gem} *ca*1–3 Hz). In general, for s-*cis* complexes **2**, the ^3J coupling constants are smaller than those of the corresponding free ligand.

There are considerably fewer examples of s-*trans* diene complexation (Table 2). For s-*trans* diene complexes, the signals for protons on the terminal carbons (C1/C4) of the diene generally appear downfield of those for the corresponding s-*cis* complex, while the signals for protons on the internal (C2/C3) carbons appear upfield of those for the corresponding s-*cis* complex (cf Table 1, entry 4 vs Table 2, entry 1; also Table 1, entry 9 vs Table 2, entry 2). This may reflect shorter metal–carbon distance of the internal carbons compared to the terminal carbons. In general, the $^3J_{a-c}$ coupling constants for s-*trans* diene complexes are larger than those observed for s-*cis* diene complexes.

2. ^{13}C NMR spectral data

The ^{13}C NMR signals of a diene are shifted far upfield upon complexation to a transition metal[33]. The terminal carbons (C1/C4) for a complexed diene are *ca* 50 to 80 ppm more shielded than the free ligand, while the internal carbons (C2/C3) are *ca* 20 to 60 ppm more shielded (Tables 3 and 4). The σ^2,π bonding mode **(2b)** which is found for Zr, Hf and Nb s-*cis* diene complexes is revealed in the diminished $^1J_{C-H}$ coupling to the terminal carbons (Table 3, entries 1–3) as compared to the later transition metal complexes. This decrease in the $^1J_{C-H}$ coupling constant is consistent with an increase in the p-character[35] for the hybridization of the terminal carbons in structures of type **2b**. Benn and Rufinska have measured and compared the $^1J_{C1-C2}$ and $^1J_{C2-C3}$ values for four complexes of isoprene[35]. For those complexes which exhibit the σ^2,π bonding mode **2b** [$ML_n = ZrCp_2$ and Hf(*t*-BuCp)$_2$] the $^1J_{C1-C2}$ values are considerably smaller than the $^1J_{C2-C3}$ values (by *ca* 20 Hz), while for those complexes which exhibit the $\eta^4 - \pi$ bonding mode **2a** [$ML_n = Fe(CO)_3$ and CoCp] there is only a small difference in magnitude (*ca* 2 Hz). These data are consistent with the concept that for complexes **2b**, the terminal carbons are closer to sp^3 hybridized and the internal carbons are close to sp^2 hybridized, while for complexes **2a** both the terminal and internal carbons have similar hybridization.

TABLE 2. ^1H NMR spectral data (chemical shift δ in ppm; coupling constants J in Hz) for (s-*trans*-diene)metal complexes



Entry	ML_n	Solvent/temp[a]	H^1	H^2	H^3	$^2J_{1-2}$	$^3J_{1-3}$	$^3J_{2-3}$	$^3J_{3-3}$	Reference
1	$ZrCp_2$	C_7D_8/38 °C	1.22	3.22	2.90	−4.0	7.1	16.4	*b*	17
2	$[MoCp^*(CO)_2]^{+c}$	CD_2Cl_2/−60 °C	3.24	4.24	3.65	*b*	6.8	12.9	7.0	30
3	$MoCp^*NO^c$	C_6D_6/amb[d]	2.85	2.43	1.51	2.5	6.8	14.0	11.4	31
4	$[RuCpCO]^{+c}$	CD_2Cl_2/−40 °C	4.31	4.21	4.15	*b*	6.8	12.7	7.7	32

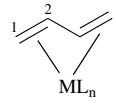
[a] $C_7D_8 = C_6D_5CD_3$.
[b] Not reported.
[c] Data are for the (1,3-pentadiene)ML_n complex.
[d] Ambient temperature.

TABLE 3. ^{13}C NMR spectral data (chemical shift δ in ppm; coupling constants J in Hz) for (s-*cis*-butadiene)metal complexes

Entry	ML_n	Solvent/temp	C^1	C^2	$^1J_{C_1-H}$	Reference
1	$ZrCp_2$	C_6D_6/30 °C	49	112	144	34
2	$HfCp_2$	C_6D_6/amb[b]	45	114.5	140	18
3	$NbCpCl_2$	C_6D_6/30 °C	60.1	123.0	145	19
4	$Cr(CO)_4$	C_6D_6/amb[b]	56.5	86.4	*a*	20
5	$MoCp[P(OMe)_3]_2^+$	C_6D_6/[b]	45.9	86.0	*a*	22
6	$[Mn(CO)_3]^-$[c]	THF-d_8/25 °C	38.5	78.6	152	23
7	$Fe(CO)_3$	C_6D_6/25 °C	40.53	85.49	161.5, 160	24
8	$Ru(CO)_3$	C_6D_6/[b]	32.7	86.3	159.6, 156.2	26
9	$Os(CO)_3$	C_6D_6/[b]	24.19	82.32	*a*	26
10	$RuCp^*Br_2^+$	CD_3NO_2/−20 °C	72.1	125.4	*a*	27
11	CoCp	C_7D_8/37 °C[d]	31.30	78.54	157	35

[a]Not reported.
[b]Temperature not reported, presumably an ambient temperature(amb).
[c]Data are for the (isoprene)ML_n complex.
[d]$C_7D_8 = C_6D_5CD_3$.

TABLE 4. ^{13}C NMR spectral data (chemical shift δ in ppm; coupling constants J in Hz) for (s-*trans*-diene)metal complexes

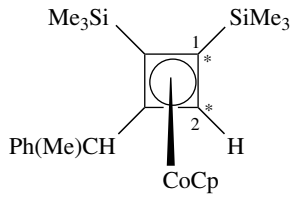


Entry	ML_n	Solvent/temp	C^1	C^2	$^1J_{C_1-H}$	Reference
1	$ZrCp_2$	C_7D_8/−10 °C[a]	59	96	149, 159	18
2	$[MoCp^*(CO)_2]^+$[b]	CD_2Cl_2/−45 °C	68.8	87.7 (94.6)	165.3	30
3	$MoCp^*NO$[b]	C_6D_6/amb[c]	58.50	88.42	158	31

[a]$C_7D_8 = C_6D_5CD_3$.
[b]Data are for the (1,3-pentadiene)ML_n complex.
[c]Ambient temperature.

B. Cyclobutadiene Complexes

The ring protons of neutral cyclobutadiene–metal complexes generally appear in the range δ_H 3.5–5 ppm[15,36] while those of cationic cyclobutadiene–metal complexes appear further downfield in the range δ 6–7 ppm[37,38]. Notably, there is no detectable $^3J_{H-H}$ or, $^4J_{H-H}$ 'W' couplings observed for unsymmetrically substituted cyclobutadiene complexes. The unsubstituted ring carbons of cyclobutadiene complexes appear in the range δ_C 60–70 ppm, and $^1J_{C-H}$ couplings are in the range 185–200 Hz[33]. The $^1J_{C-C}$ coupling for two ^{13}C enriched cobalt cyclobutadiene complexes **5** (24.1 Hz)[39a] and **6** (40.8 Hz)[39b] have been reported, and these represent some of the lowest values for one-bond coupling between two formally trigonal carbon atoms.



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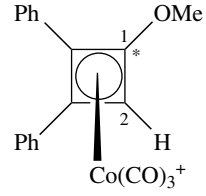

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* = Position of ^{13}C enrichment

C. Fluxional Behavior

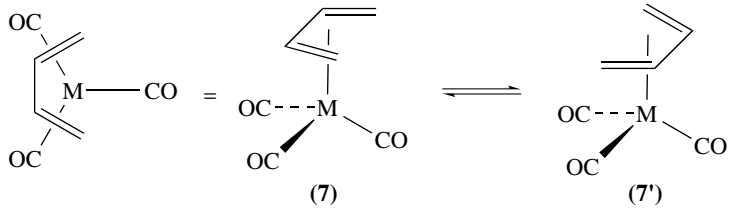
Dynamic intramolecular rearrangements are observed for a variety of diene–metal complexes at, or near, ambient temperature. This stereochemical non-rigidity may be detected by variable temperature NMR experiments[40] in which the signals observed for a static structure coalesce into time averaged signals for the fluxional process. For purposes of this section, processes with activation energies $> ca\ 25$ kcal mol^{-1} or which are irreversible will be considered to be isomerization phenomena and will be discussed in Section IV.

1. Ligand rotation[41]

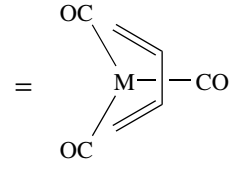
Except for MCp complexes, most (diene)metal complexes consistently exhibit particular molecular orientations in the solid state. While this is the case, rotation about the metal–ligand axis may be rapid in the solution phase. For example, the crystal structures of a variety of cyclic and acyclic (diene)$Fe(CO)_3$ complexes indicate a staggered geometry (**7**)[2,42]; one of the carbonyl ligands is oriented such that it bisects the 'open' end of the diene while the other two carbonyl ligands lie underneath the C1–C2 and C3–C4 diene bonds (equation 1). Molecular orbital theory[43a] rationalizes the preferred static structure on the basis that the tilt of the degenerate *e* pair of orbitals (Figure 4) provides the necessary asymmetry such that the mirror plane of the diene ligand is aligned with the *yz* mirror plane. A significant barrier to rotation about the metal–ligand axis is expected. This is due to the higher energy of the structure generated by 60° rotation, in which one of the carbonyl ligands is eclipsed with the central C–C bond (**7′**). Earlier calculations at the EHT level[43a] indicate this barrier to be 14.2 kcal mol^{-1}, while more recent DFT calculations[43b] indicate the barrier to be 9.6 kcal mol^{-1}. The ^{13}C NMR spectra of these complexes, at ambient temperature, exhibit only a single resonance for the carbonyl ligands, while at lower temperatures signals due to the static structure **7** are observed. The experimentally derived barriers[44] for this process are in the range of $\Delta G^{\ddagger}\ ca\ 9–13$ kcal mol^{-1}. For acyclic diene complexes, electron-withdrawing substituents on the terminal carbons tend to increase the barrier-to-ligand rotation, while electron donating substituents tend to decrease the barrier[44f]. Phospine substituted complexes [i.e. (diene)$Fe(CO)_2PR_3$] show a decreased barrier to rotation[25], while $Ru(CO)_3$ and $Ru(CO)_2PR_3$ complexes exhibit slightly higher barriers to rotation than their Fe counterparts[45].

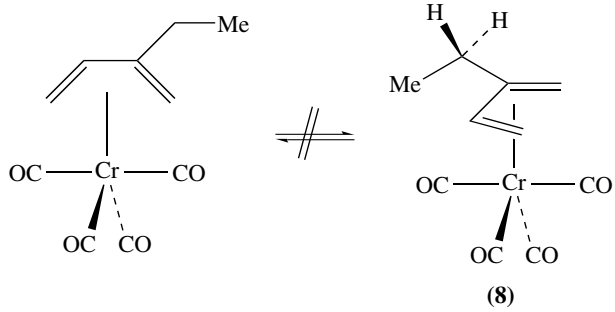
From their crystal structures, (1,3-diene)CrL_4 complexes[46] are found to be approximately octahedral coordinate. The low temperature (−90 °C) ^{13}C NMR spectrum of (butadiene)$Cr(CO)_4$, which consists of 3 M–CO signals (1 : 2 : 1 ratio), is consistent with this static structure. At higher temperature, these coalesce into a single signal[20]. The chiral complex (2-ethyl-1,3-butadiene)$Cr(CO)_4$ **(8)** shows similar behavior, however

the diastereotopic methylene proton signals of **8** remain distinct in its ^{1}H NMR spectrum at a temperature where scrambling of the carbonyl ligand signals is observed. These results[20,47] rule out a flip of the diene ligand from one face to the other (Section III.C.2), and strongly implicate a ligand rotation mechanism (equation 2). The experimentally derived barriers are *ca* 10–11 kcal mol^{-1}. Since all four carbonyl ligands scramble with each other simultaneously, ligand rotation by 90° must involve a synchronous change in C–Cr–C angles which is related to a Berry pseudorotation in trigonal bipyramidal structures.

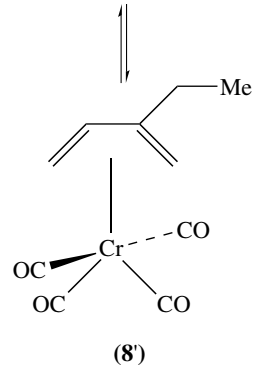


(1)

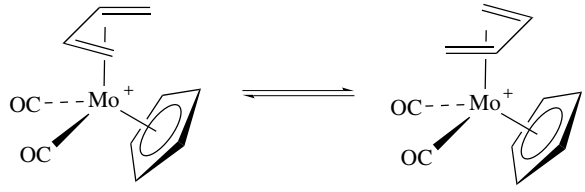




(2)



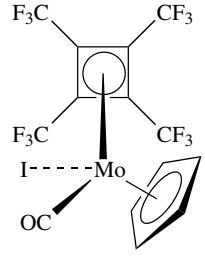
Fluxional behavior is observed for $(C_4H_6)MoCp(CO)_2^+$ (**9**). At low temperature (−60 °C) both *endo* and *exo* conformers (*ca* 5 : 1 ratio) are observed (equation 3), the signals of which coalesce at higher temperature ($\Delta G^{\ddagger} = 14.1$ kcal mol^{-1})[21]. Since the H_{syn} and H_{anti} signals (where *syn* and *anti* refer, respectively, to the substituent (or H) which is *syn* and *anti* with respect to the C2-substituent of the polyenyl ligand) remain distinct during this scrambling, a ligand rotation mechanism is proposed. For (1,3-pentadiene)$MoCp(CO)_2^+$, ligand rotation is observed along with a flip of the ligand ('envelope-flip', Section III.C.2). The ligand rotation occurs with a lower barrier than the envelope-flip process. The corresponding neutral (diene)WCp(CO)(acyl) complexes exhibit similar barriers to ligand rotation (13.8–14.6 kcal mol^{-1})[48].



(3)

(**9-*endo***) (**9-*exo***)

For conjugated (diene)metal complexes, the π-molecular orbitals of cyclobutadiene consist of a degenerate e_g pair (Figure 3). Because of this orthogonality, there is not a single electronically preferred conformer[43] and barriers for rotation of the cyclobutadiene ligand are generally low[15]. For (cyclobutadiene)$Fe(CO)_3$, in the solid state, NMR spin relaxation data indicate that there are two inequivalent lattice sites. For each of these inequivalent lattice sites, barriers for rotation of the cyclobutadiene have been measured to be 3.63 and 5.28 kcal mol^{-1}, respectively[49]. Davidson[50] has observed temperature-dependent NMR spectra for certain cyclobutadiene complexes. For cyclobutadiene complex **10**, four separate signals were observed in its ^{19}F NMR spectrum at −60 °C; these signals coalesce to a single signal at > 25 °C. Unfortunately, complexity due to $^{19}F-^{19}F$ coupling prevented a determination of the exact barrier for this fluxional process.

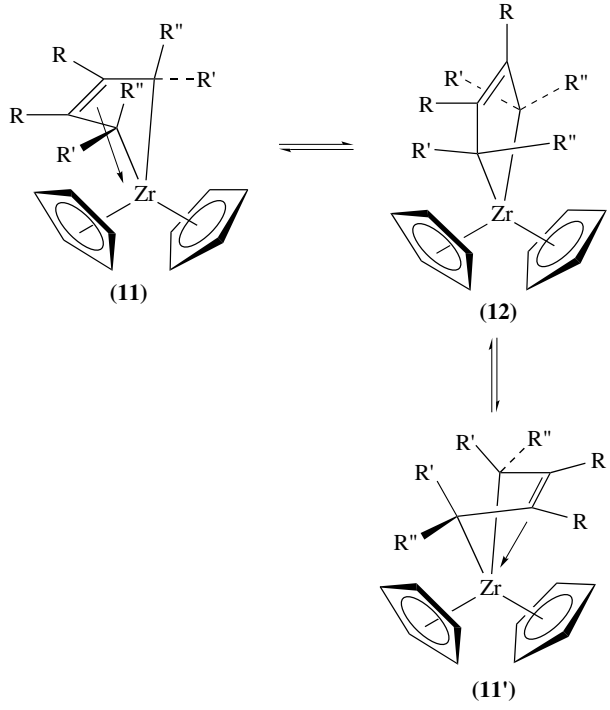


(**10**)

2. Metal migration from one face to the other ('envelope flip')

In solution, certain complexes are observed to undergo an 'envelope-flip' from one face of the diene ligand to the other. The ^1H NMR spectra of Cp_2Zr(s-*cis* diene) complexes (**11** $R' = R'' = H$) at ambient temperatures indicate a fluxional process which equilibrates the Cp signals as well as the terminal protons (equation 4). At lower temperature, signals for a

static structure are observed (i.e. two signals for the non-equivalent Cp groups and separate signals for the H_{syn} and H_{anti} terminal protons)[10,17,51–53]. An envelope-flip mechanism, involving a planar symmetric σ^2-metallacyclopent-3-ene intermediate **12**, is consistent with the fact that these sets of signals coalesce at the same rate. For Cp_2Zr(s-*cis* butadiene), the barrier for this process is 12.6 kcal mol^{-1}. The presence of substituents on the internal carbons (C2/C3) or on the cyclopentadienyl ligands (i.e. C_5Me_5) lowers the barrier for the envelope flip[10,53]. For Cp_2Zr(s-*cis* diene) complexes with substituents at the terminal carbons (C1/C4), the envelope-flip process is non-degenerate and generally the conformer which has the substituents in the less hindered *exo*-positions is greatly thermodynamically preferred[52,54]. Thus envelope-flip fluxionality is not observed in these cases. The corresponding Cp_2Hf(s-*cis* diene) complexes are also fluxional, however barriers for the envelope flip are considerably lower ($\Delta G^{\ddagger} = ca\,8$ kcal mol^{-1})[55].



(4)

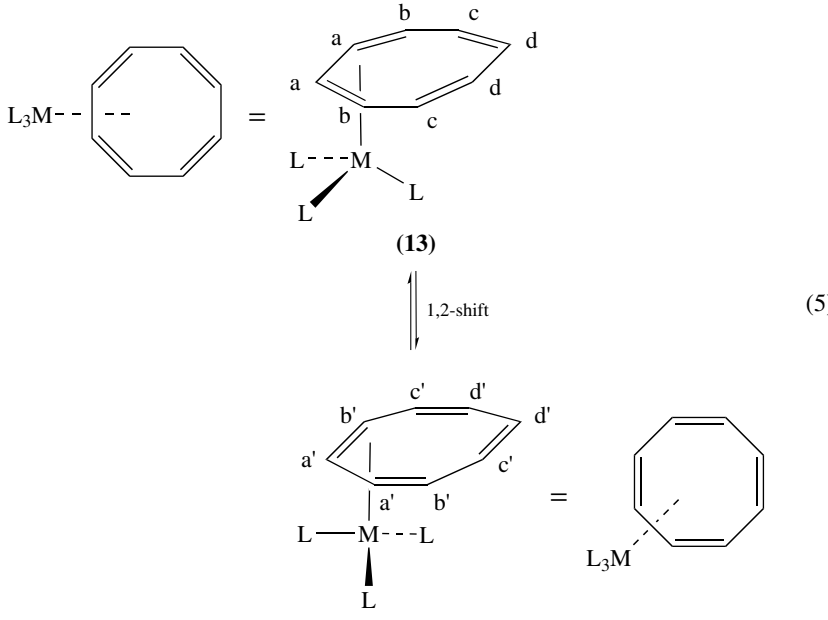
In the isoelectronic series (butadiene)M($\eta^8 - C_8H_8$) (M = Ti, Zr, Hf), the Hf complex exhibits an NMR spectrum at $> 30\,^{\circ}$C consistent with an envelope flip ($\Delta G^{\ddagger} =$ 17.6 kcal mol^{-1}). The same process can be detected for the Zr complex at $> 40\,^{\circ}$C only via magnetization transfer experiments ($\Delta G^{\ddagger} > 20$ kcal mol^{-1}). The Ti complex exhibits a static structure by NMR spectroscopy[16].

3. Metal migration about a π-complexed polyene ligand ('ring-whizzing')

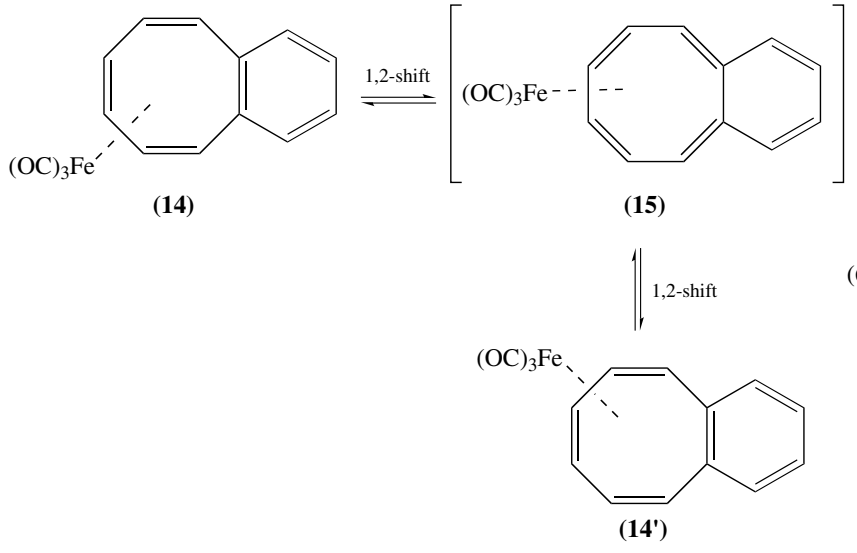
(η^4-Cyclooctatetraene)metal complexes **(13)** were some of the first recognized fluxional organometallic complexes. The (η^4-cyclooctatetraene)Mn(CO)$_3^-$ anion [**13**, ML_3 =

$Mn(CO)_3^-$] exhibits only one signal in its ^1H NMR spectrum. Unfortunately, a limiting spectrum could not be reached at $-110\,^\circ C$, at which temperature the salt precipitates from solution[56]. With this temperature as an upper limit, the barrier for migration about the ligand is < 8 kcal mol^{-1}.

While the crystal structure of **13** [$ML_3 = Fe(CO)_3$] indicates complexation as an η^4-diene ligand, the ^1H NMR spectrum of this complex exhibits a single signal (δ 5.24 ppm) at ambient temperature. At lower temperature ($-155\,^\circ C$) this signal eventually becomes two broad asymmetric signals, however, a definitive explanation of the fluxional process from these data is hampered by lack of a limiting spectrum[57]. In contrast, while (cyclooctatetraene)$Ru(CO)_3$ [**13**, $ML_3 = Ru(CO)_3$] likewise gives a single ^1H NMR signal at ambient temperature, a limiting ^1H NMR spectrum, consisting of four separate signals, is obtained at low temperature ($-147\,^\circ C$, $E_a = 9.4 \pm 1.5$ kcal mol^{-1})[58a]. Specific assignments for the upfield signals may be made by comparison to other (diene)$Ru(CO)_3$ complexes. A 1,2-shift mechanism (equation 5) was deduced on the basis that the signal assigned to the terminal η^4-protons (b or b′) initially broadens/exchanges more rapidly than that for the internal η^4-protons (a or a′). Analysis of the variable-temperature ^{13}C NMR spectrum of the ruthenium complex supports this proposal and gave the same activation barrier within error limits (8.6 kcal mol^{-1})[58b]. The variable-temperature ^{13}C NMR spectrum of the iron complex [**13**, $ML_n = Fe(CO)_3$] likewise indicated a 1,2-shift mechanism with a lower activation barrier (8.1 kcal mol^{-1})[58b]. Scrambling of the carbonyl ligands in **13** (M = Fe, Ru) occurs with essentially the same activation energy. Iron migration in the benzocyclooctatetraene complex **14** to **14′** (equation 6) has a considerably higher activation energy (18.6 kcal mol^{-1}). The higher barrier for this sequential set of 1,2-shifts is due to the higher energy intermediate **15**, in which aromaticity of the benzene ring is disrupted[59].

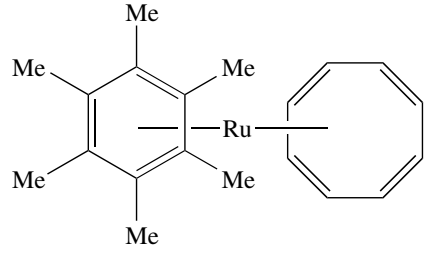


(5)



(14) **(15)** **(14')** (6)

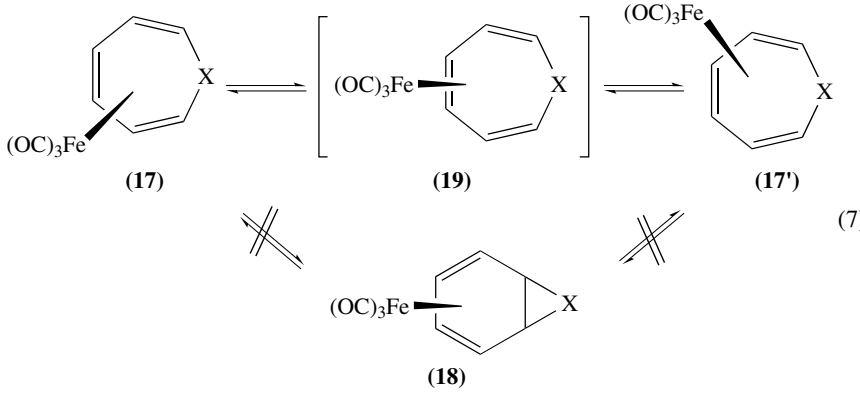
The crystal structure of (η^4-cyclooctatetraene)(hexamethylbenzene)ruthenium **(16)** indicates bonding as a tetrahapto ligand[60]. For this complex and similar iron–, ruthenium- and osmium–(η^4-cyclooctatetraene)(arene) complexes, their ^{1}H and ^{13}C NMR spectra exhibit only a single signal for the cyclooctatetraene ligand at temperatures as low as $-145\,^\circ$C. Using this temperature, the barrier-to-metal migration is estimated to be $\leqslant$6.6 kcal mol^{-1}.



(16)

Migration about the π-system is also observed in certain η^4-cyclic triene complexes **17** (equation 7). For the parent (η^4-cycloheptatriene)Fe(CO)$_3$ (**17**, X = CH$_2$), the barrier for this fluxional process is high enough that it is detectable only by Forsén–Hoffman spin-saturation techniques ($\Delta G^{\ddagger} = ca\,22.3$ kcal mol^{-1})[61a]. For (η^4-azepine)- and (η^4-oxepine)Fe(CO)$_3$ complexes (**17**, X = NCO$_2$Et or O), the barrier-to-iron migration is low enough to be measured by line-shape analysis of variable-temperature ^{1}H NMR spectra ($\Delta G^{\ddagger} ca 15.5–15.8$ kcal mol^{-1})[61b,c]. While metal migration occurs in (η^4-tropone)Fe(CO)$_3$ complexes (see Section IV.E.1.d), this process is too slow to result in coalescing signals in their NMR spectra. Early investigators had proposed that the metal migration

in complexes **17** to give **17′** occurred via sequential 1,2-shifts involving the norcaradiene complex **18** as an intermediate[61d]. However, EHT calculations[60] indicate that an electrocyclic ring closure of **17** to **18** is symmetry-forbidden. Furthermore, (heptafulvene) $Fe(CO)_3$ complexes (e.g. **17**, X = C=CHPh) , for which the norcaradiene ring intermediate would be expected to be more strained, show a lower barrier than for the parent cycloheptatriene system. The proposed intermediate is a symmetrical (η^2-cycloheptatriene) $Fe(CO)_3$ complex (**19**, X = CH_2) and EHT calculations indicate that the optimum geometry has the metal distorted toward the center of the cycloheptatriene ring[61a].

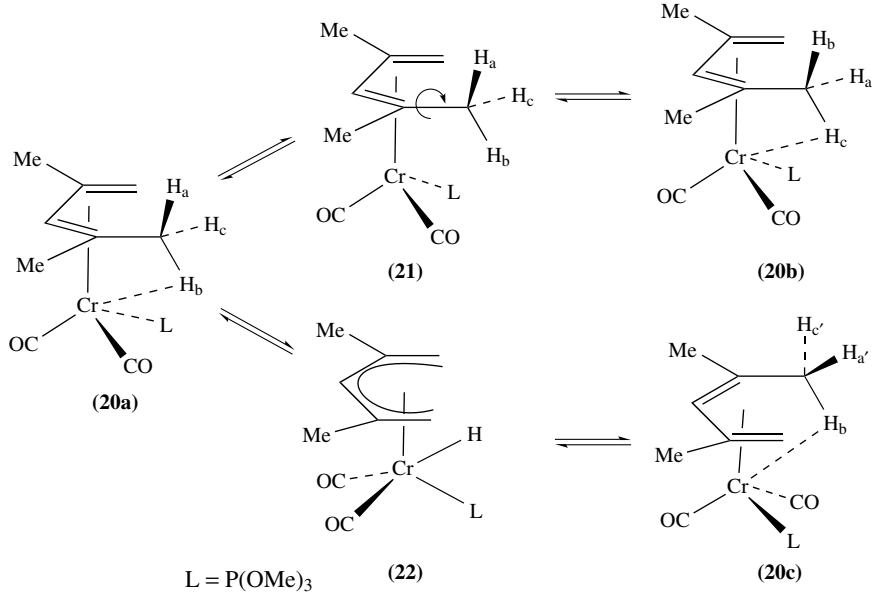


(7)

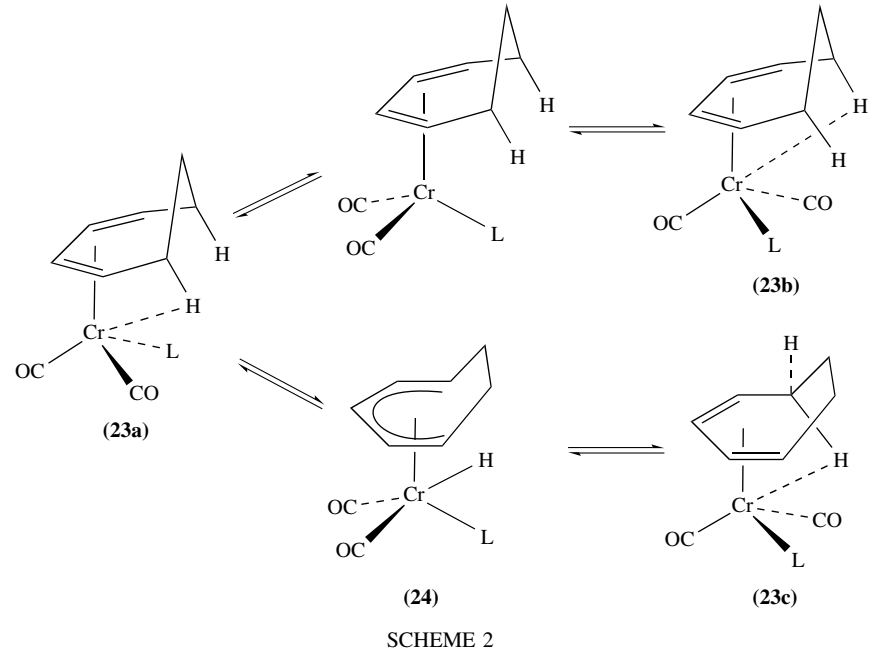
4. Bridging hydrogen exchange

The photochemically induced substitution of three CO ligands from $Cr(CO)_5P(OMe)_3$ by 2,4-dimethyl-1,3-pentadiene gives complex **20** (Scheme 1)[62a]. The crystal structure of **20** indicates that the ligand is bound as an (η^4-diene-μ-H) species (Cr−H distance = 1.94 Å). The three center-two electron donation inherent in the μ-H allows for coordinative saturation at Cr. At low temperature, the ^{1}H NMR spectrum of **20** consists of three separate signals for the three different protons of the *anti*-C5−methyl group, while at higher temperatures these three signals collapse to give rise to a single signal. This fluxionality is rationalized on the basis of hindered rotation about the C4−C5 bond due to a bridging hydrogen (agostic hydrogen). The barrier to this rotation ($\Delta G^{\ddagger} = 6.83$ kcal mol^{-1}) is due to formation of the coordinatively unsaturated 16-electron (η^4-diene) complex **21**. At still higher temperatures a second dynamic process occurs ($\Delta G^{\ddagger} =$ 16.3 kcal mol^{-1}) which is characterized by coalescence of the C2−Me and C4−Me signals as well as coalescence of the *anti*-C5 methyl signal with the signals for the C1 methylene protons. This process involves insertion of Cr into the H−C5 bond to generate a (η^5-pentadienyl)chromium hydride intermediate **22**. Since **22** possesses a plane of symmetry, the reverse of this insertion leads either to **20a** or to **20c**, thus accounting for the fluxionality.

Two related dynamic bridging hydrogen processes are observed for (η^4-cycloheptadiene-μ-H)$Cr(CO)_2L$ [**23**, L = CO, PMe_3, $P(OMe)_3$] (Scheme 2)[62b]. The lower energy process involves equilibration of the *endo* protons α to the complexed diene (i.e. **23a** to **23b**), while the higher energy process involves migration of the metal about the cyclic ligand (i.e **23a** to **23c**) via the (η^5-pentadienyl)chromium hydride intermediate **24**. The barriers for these two processes are similar to the analogous processes in the acyclic complex **22**.

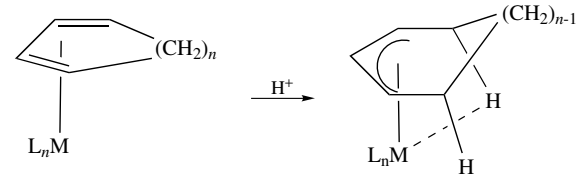


SCHEME 1



SCHEME 2

Similar bridging hydrogen exchange processes have been observed for neutral and cationic (η^3-allyl-μ-H)ML_n complexes **25** (Scheme 3)[23,58,63]. Many of these complexes are prepared by the protonation of the corresponding anionic or neutral (η^4-diene)ML_n complexes **26** (see Section V.C.1). Migration of the metal about a cyclic η^3-allyl ligand (i.e. **25a** to **25b**) is proposed to involve an (η^4-diene)ML_n hydride intermediate/transition state **27**.

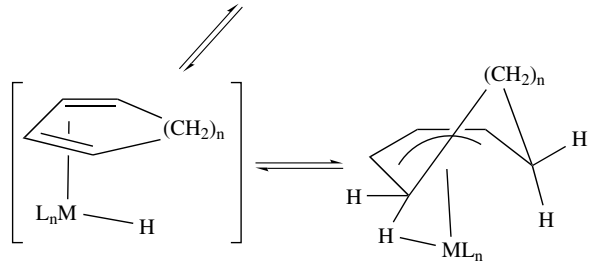


(26)

$ML_n = Mn(CO)_3^-$, $Fe(CO)_3$, $Fe(PR_3)_3$, Ru(arene), Os(arene) CoCp, RhCp, IrCp

(25a)

ground state for $ML_n = Mn(CO)_3$, $Fe(CO)_3^+$ $Fe(PR_3)_3^+$, $Ru(arene)^+$ $CoCp^+$, $RhCp^+$



(27)

ground state for $ML_n = Os(arene)^+$, $IrCp^+$

(25b)

SCHEME 3

IV. PREPARATION AND ISOMERIZATIONS OF CONJUGATED DIENE COMPLEXES

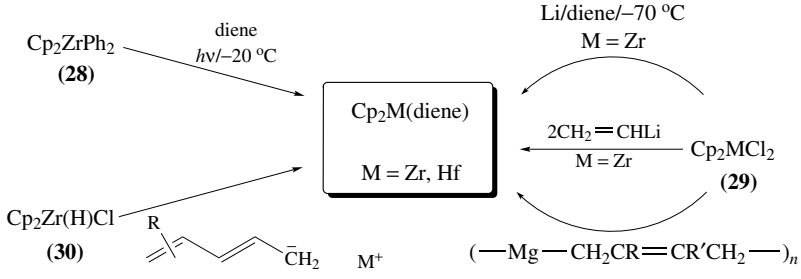
The preparation of conjugated diene complexes will be presented by groups. In addition, isomerization reactions, or degenerate rearrangements with activation energies >25 kcal mol^{-1}, will be considered in this section.

A. Complexes of Ti, Zr and Hf

1. (1,3-Diene)MCp_2 complexes (M = Zr, Hf)

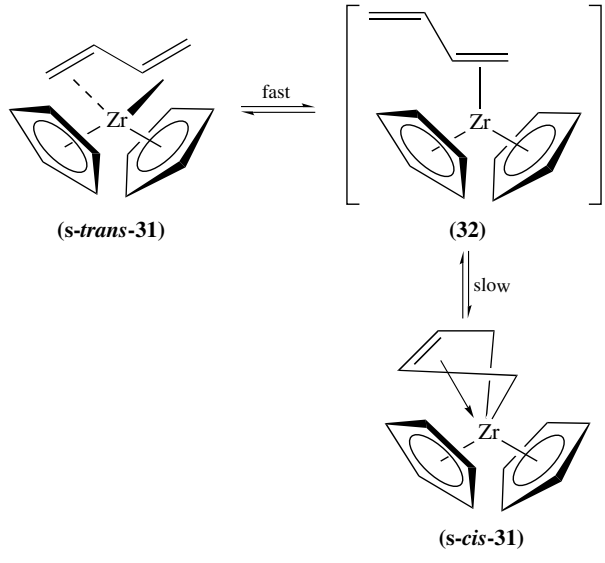
The preparations of acyclic and exocyclic diene complexes of $ZrCp_2$ and $HfCp_2$ were reported almost simultaneously by Erker and coworkers[10] and by Nakamura and coworkers[52a]. These complexes may be prepared (Scheme 4) (1) by direct complexation

of dienes to coordinatively unsaturated 'ZrCp$_2$' [generated either by photolysis of diphenylzirconocene **28** or by reduction of zirconocene dichloride **29** (M = Zr with Li metal][10,34,54,64], (2) by reaction of Cp_2MCl_2 (M = Zr, Hf) and substituted variants with (2-dien-1,4-diyl)magnesium reagents[17,18,50,53,65], (3) by reaction of substituted dienyl anions with zirconocene chloride hydride **(30)**[52], and (4) by reaction of zirconocene dichloride **29** with two equivalents of vinyl lithium[66]. There are no examples of endocyclic diene complexes of this type.



SCHEME 4

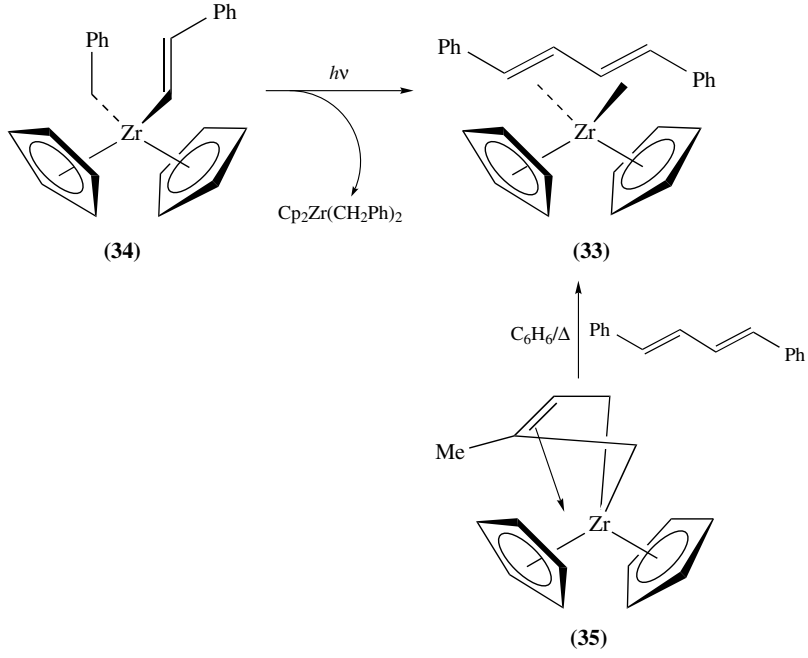
Preparation of the parent (butadiene)ZrCp$_2$ by either of the first two methods, *at low temperature* ($< -20\,^{\circ}C$), results in exclusive formation of the isomer s-*trans*-**31** (Scheme 5). Above $> -10\,^{\circ}C$ this begins to isomerize to an equilibrium mixture of s-*trans*-**31** and s-*cis*-**31** (55 : 45 ratio, $\Delta G^{\ddagger} = 22.7 \pm 0.3$ kcal mol^{-1})[18]. The isomerization of s-*trans*-**31** to s-*cis*-**31** is proposed to occur via the coordinatively unsaturated η^2-butadiene intermediate **32**. Since the s-*trans*-**31** isomer is the exclusive product at low



SCHEME 5

temperature, collapse of **32** to s-*trans*-**31** was deemed to be faster than collapse of **32** to s-*cis*-**32**. The parent butadiene complex **(31)** and (diene)$ZrCp_2$ complexes in which the diene bears substitution only at the terminal carbons (e.g. 1,3-pentadiene, 2,4-hexadiene) exist as both the s-*cis* and s-*trans* isomers at equilibrium. In comparison, for complexes in which the diene bears substitution at the internal carbons (e.g. isoprene, 2,3-dimethyl-1,3-butadiene, 2,3-diphenyl-1,3-butadiene etc.) the equilibrium is shifted exclusively toward the s-*cis* isomer[10,52].

Preparation of (1,4-diphenyl-1,3-butadiene)$ZrCp_2$ **(33)** may be accomplished by photolysis of (β-styryl)(benzyl)zirconocene **(34)**[67] or by displacement of isoprene from (isoprene)$ZrCp_2$ **(35)** at elevated temperature (Scheme 6)[17]. For complex **33**, the s-*trans*/s-*cis* equilibrium lies far toward the s-*trans* isomer (95 : 5).

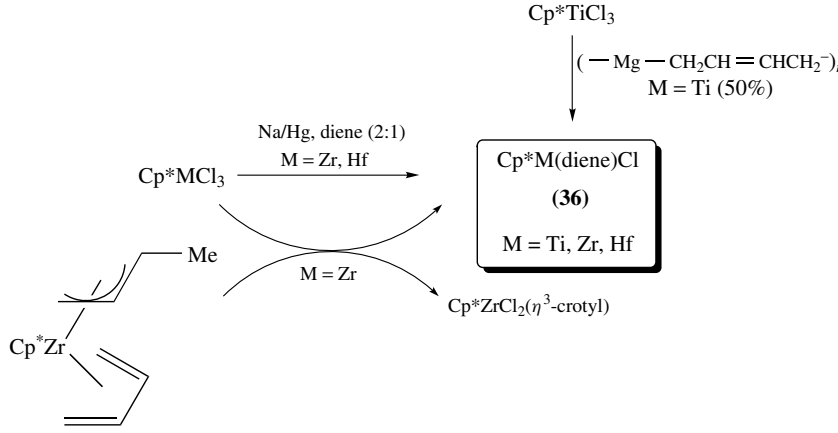


SCHEME 6

*2. (1,3-Diene)MCp*X complexes (M = Ti, Zr, Hf)*

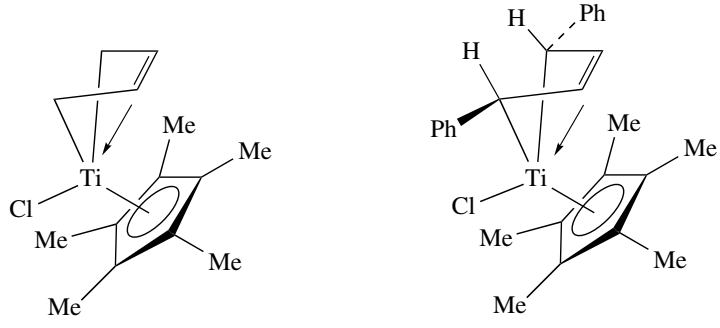
Coordinatively unsaturated 14-electron complexes of Ti, Zr and Hf, which contain an s-*cis* diene ligand **(36)**, have been prepared by Hessen and Teuben[68] and by Nakamura and coworkers[69]. The titanium complexes may be prepared by reaction of Cp^*TiX_3 with (2-dien-1,4-diyl)magnesium reagents (Scheme 7)[70]. In addition, these complexes may be prepared by direct complexation of a diene to 'Cp*TiX' [generated by reaction of Cp^*TiX_3 with two equivalents of a Grignard reagent][69b]. The analogous zirconium and hafnium complexes are primarily prepared by direct complexation of a diene to 'Cp*MCl' (generated by reduction of Cp^*MCl_3 with sodium amalgam)[70a,71]. When THF is used as solvent, these complexes are generally produced as solvated adducts which lose solvent

upon purification. The reaction of Cp^*MCl_3 with $Cp^*(\eta^3\text{-crotyl})M(butadiene)$[72] produces the above complexes **36** along with $Cp^*(\eta^3\text{-crotyl})MCl_2$; however, difficulties in separation render this method useful only for zirconium (Scheme 7)[71]. All of these complexes are described as being very air sensitive. There are no examples of endocyclic diene complexes of this type.

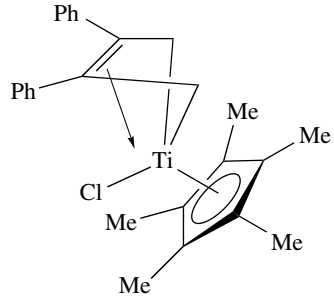


SCHEME 7

Crystal structures[69b,71] of titanium complexes **36a**, **36b** and **36c** and of hafnium complex **36d** indicate that the diene–metal interaction is best characterized by the σ^2, π bonding mode. In general, the diene ligand adopts an s-*cis* 'supine' conformation with respect to the Cp^* ligand (e.g. **36c** and **36d**). However, Nakamura and coworkers have noted that the Cp^*TiCl complexes of butadiene **(36a)**, 1,3-pentadiene and 1,4-diphenyl-1,3-butadiene **(36b)** adopt the s-*cis* 'prone' geometry in the solid state and in solution. Extended Hückel calculations of complex **36a** indicate that the 'prone' and 'supine' conformers are relatively close in energy[69b] and thus the preference for one of the two possible conformations may be determined by steric interactions between the Cp^* ligand and substituents present on the diene ligand. Isomerization between the two conformers is not observed.

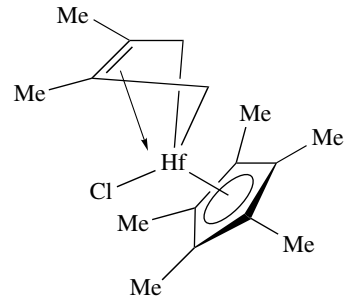


(**36a**) 'prone' (**36b**)



(36c)

'supine'



(36d)

B. Complexes of Nb and Ta

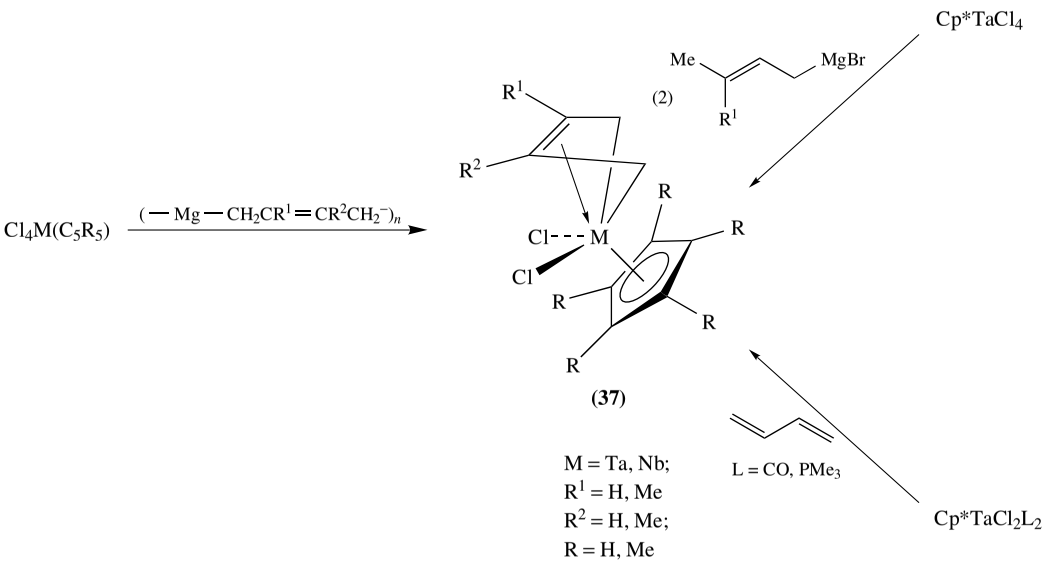
Mono- and bis-diene complexes of niobium and tantalum have been reported[73]. The mono-diene, 16 electron complexes **37** may be prepared (1) by the reaction of $CpMCl_4$ or Cp^*MCl_4 (M = Nb, Ta) with one equivalent of (2-dien-1,4-diyl)magnesium reagents[9a,19] or (2) by reaction of Cp^*TaCl_4 with two equivalents of a crotyl Grignard reagent (Scheme 8)[74]. The parent (butadiene)$TaCp^*Cl_2$ may also be prepared by ligand displacement of $Cp^*TaCl_2L_2$ (L = CO, PMe_3) with butadiene in solution (Scheme 8)[75]. For the mono–diene complexes, crystal structures indicate that these complexes adopt the 'supine' conformation in which the open end of the diene is directed toward the Cp ligand. No evidence has been found for either ligand rotation or envelope flip fluxionality/isomerization in these complexes.

The complex $(C_4H_6)Cp_2Ta^+MeB(C_6F_5)_3$ **(38)**, whose cationic part is isoelectronic with the neutral Zr and Hf complexes (Section IV.A.1), has been prepared by the reaction of complex **37** ($R = R^1 = R^2 = H$) with two equivalents of NaCp, followed by abstraction of the σ-bound cyclopentadienyl ligand (Scheme 9)[76]. Bonding of the butadiene ligand in **38** in the s-*trans* conformation was determined by X-ray diffraction analysis.

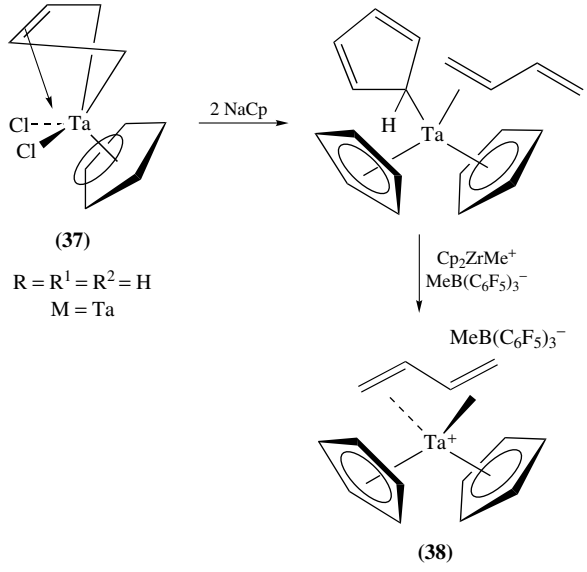
C. Complexes of Cr, Mo and W

1. Neutral metal–carbonyl complexes[47]

A wide variety of diene complexes of group 6 metal carbonyls have been prepared. Either attempted coordination of 1,3-cyclooctadiene (cod) via thermally induced ligand substitution of $Mo(CO)_6$ or $W(CO)_6$ or cocondensation of Cr vapor with 1,3-cod and CO gives the (1,5-cod)$M(CO)_4$ complexes in abysmally low yield (Scheme 10)[77]. These results indicate that isolated bisolefin $M(CO)_4$ complexes are more stable than the corresponding conjugated diene complexes. Significantly higher yields of the conjugated diene complexes are afforded under photochemical induced ligand displacement. Thus, photolysis of $M(CO)_6$ or $M(CO)_5L$ [M = Cr, Mo, W; L = $P(OMe)_3$, PMe_3, PBu_3] in the presence of a conjugated diene generates the corresponding (diene)$M(CO)_4$ **(39)**[20,78] or (diene)$M(CO)_3L$ **(40)**[79] complexes respectively in good yields (Scheme 10). In general, for acyclic diene complexes **40**, the phosphine/phosphite ligand is aligned along the 'mouth' of the conjugated diene, while for cyclohexadiene complexes the metal-to-phosphine/phosphite bond eclipses the C2–C3 bond. Similar photolyses of $M(CO)_4L_2$ [M = Cr, Mo, W; L_2 = $(P(OMe)_3)_2$, $(PMe_3)_2$, $(PBu_3)_2$, $Me_2PCH_2CH_2PMe_2$] produce the (diene)$M(CO)_2L_2$ complexes **(41)**[80]. The bisphosphine complexes **41** adopt structures


Cp*TaCl4
Me
MgBr
(2)
R1
R1
R2
R
R
Cl
M
Cl
R
R
R
(37)
M = Ta, Nb;
R1 = H, Me
R2 = H, Me;
R = H, Me
L = CO, PMe3
Cp*TaCl2L2

SCHEME 8



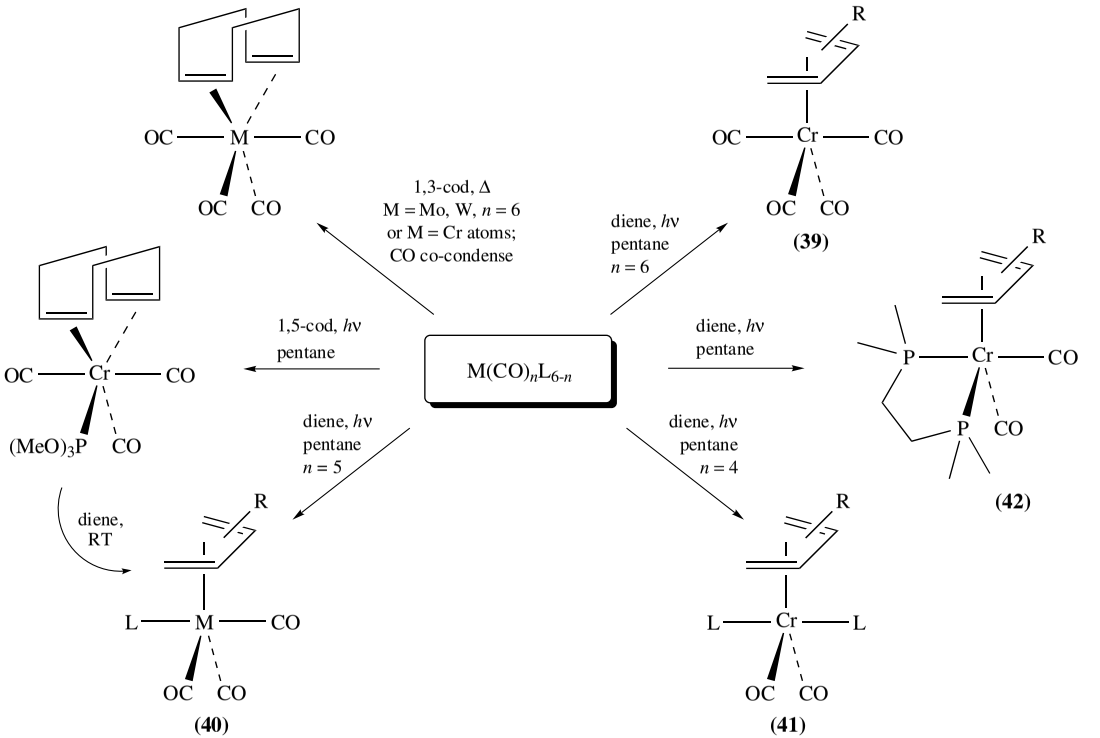
SCHEME 9

in which the phosphines occupy the two axial coordination sites, while the chelating bis(dimethylphosphino)ethane complexes **42** adopt structures in which one of the phosphorous atoms occupies the axial site aligned with the 'mouth' of the diene and the other phosphorous atom occupies an equatorial coordination site. The photochemical formation of ($\eta^4 - \mu$-H-diene)$Cr(CO)_2P(OMe)_3$ complexes (e.g. **20** or **23**) has previously been mentioned (Section III.C.4)[62].

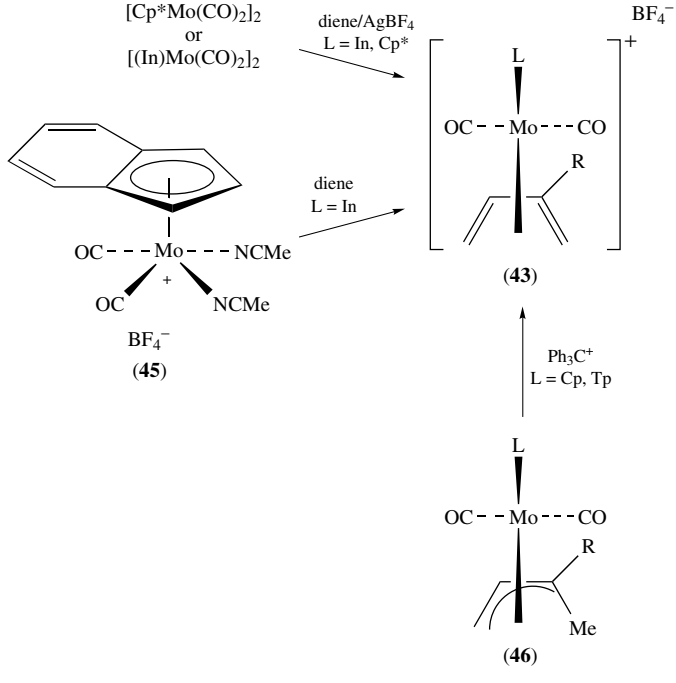
2. Cationic (diene)MCp(CO)$_2^+$ complexes (M = Mo, W)

A wide variety of s-*cis* acyclic **(43)** and cyclic **(44)** and (diene)$Mo(CO)_2L^+$ cations [L = Cp, Cp*, indenyl (In), trispyrazolylborohydride (Tp)] have been prepared. Direct complexation may be achieved by reaction of the stable cation [(η^5-indenyl)$Mo(CO)_2(NCMe)_2]^+$ BF_4^- **(45)** (prepared by the reaction of [(η^5-indenyl)$Mo(CO)_2]_2$ with $AgBF_4$ in MeCN) with a solution of the diene ligand (Scheme 11)[81]. It is not necessary to isolate **45**, since treatment of [(η^5-indenyl)$Mo(CO)_2]_2$ or [Cp*$Mo(CO)_2]_2$ with $AgBF_4$ in the presence of the diene ligand gives the corresponding cation **43** (L = indenyl)[82].

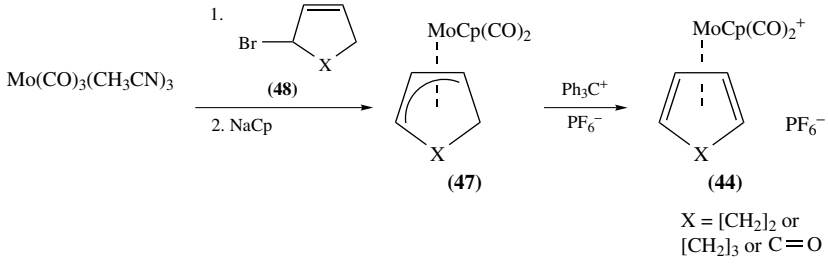
(Diene)$Mo(CO)_2L^+$ cations [L = Cp, Tp] may also be prepared by hydride abstraction from the corresponding neutral (η^3-allyl)$Mo(CO)_2L$ complexes, e.g. **(46)** or **(47)**, with triphenylmethyl cation[21,83] (Schemes 11 and 12). Hydride abstraction occurs only from a carbon in the *anti*-position of the η^3-allyl ligand. For this reason, hydride abstraction from cyclic (η^3-allyl)$(CO)_2$MoCp complexes **(47)**, in general, gives high yields of the corresponding cationic 1,3-cyclodiene complexes **44** (Scheme 12)[84]. The (η^3-allyl)$(CO)_2$MoCp precursors **47** are prepared by reaction of the appropriate allylic bromide **(48)** with $Mo(CO)_3(CH_3CN)_3$ [generated *in situ* from $Mo(CO)_6$ and CH_3CN] followed by treatment with cyclopentadienyl anion. Hydride abstraction occurs on the


M(CO)nL6-n
1,3-cod, Δ
M = Mo, W, n = 6
or M = Cr atoms;
CO co-condense
diene, hν
pentane
n = 6
(39)
1,5-cod, hν
pentane
diene, hν
pentane
(42)
diene, hν
pentane
n = 5
diene, hν
pentane
n = 4
diene,
RT
(40)
(41)

SCHEME 10



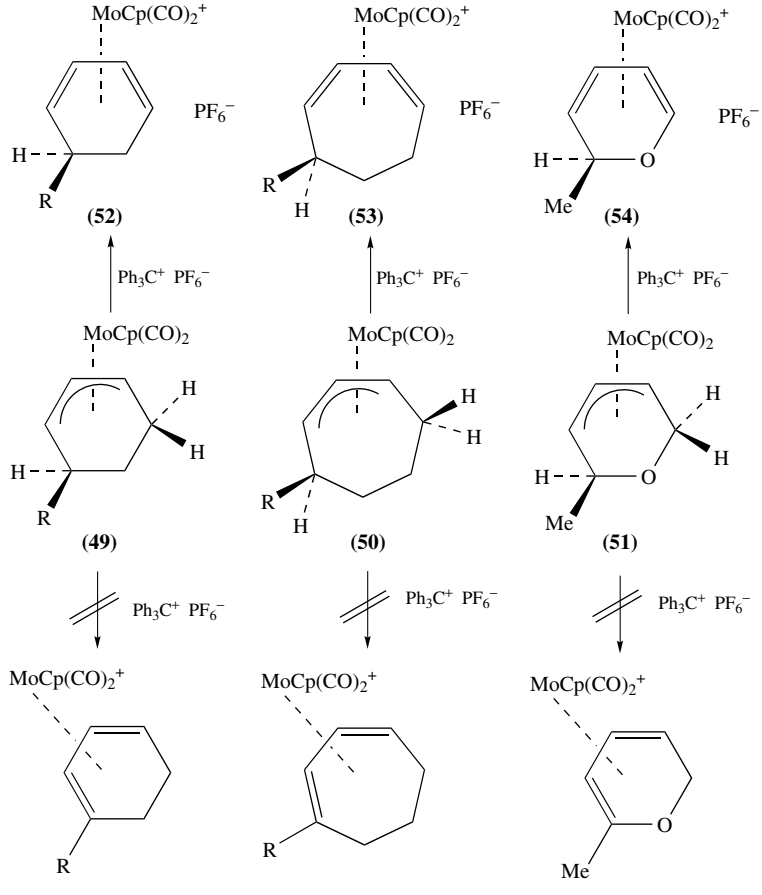
SCHEME 11



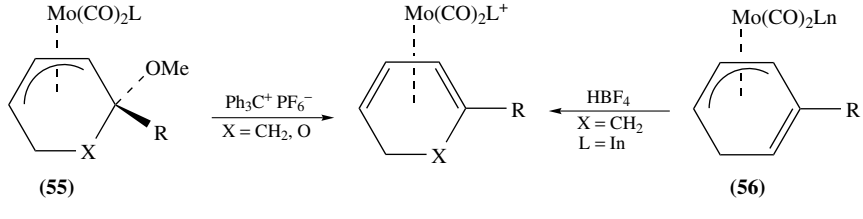
SCHEME 12

face opposite to molybdenum. This restriction has regiochemical implications for substituted cyclic η^3-allyl complexes. For example, complexes **49**, **50**, and **51** all undergo regioselective hydride abstraction with Ph_3C^+ to give the (diene)$(CO)_2MoCp^+$ cations **52**, R = Me, CH_2CO_2Me[84a,c], **53**, R = Me, allyl, $p-C_6H_4OMe$[84b] and **54**[85], respectively (Scheme 13).

Cyclic (diene)$Mo(CO)_2Cp$ (or In) cations have been prepared by trityl cation mediated alkoxide abstraction from cyclic (η^3-allyl)$Mo(CO)_2Cp$ (or In) complexes bearing a *syn* alkoxy in the α position (e.g. **55**, Scheme 14)[81b,86]. Additionally, protonation of (η^3-allyl)$Mo(CO)_2In$ (or Cp*) complexes bearing a vinyl group (e.g. **56**, Scheme 14) affords the corresponding (diene)Mo^+ cations[81b,87].

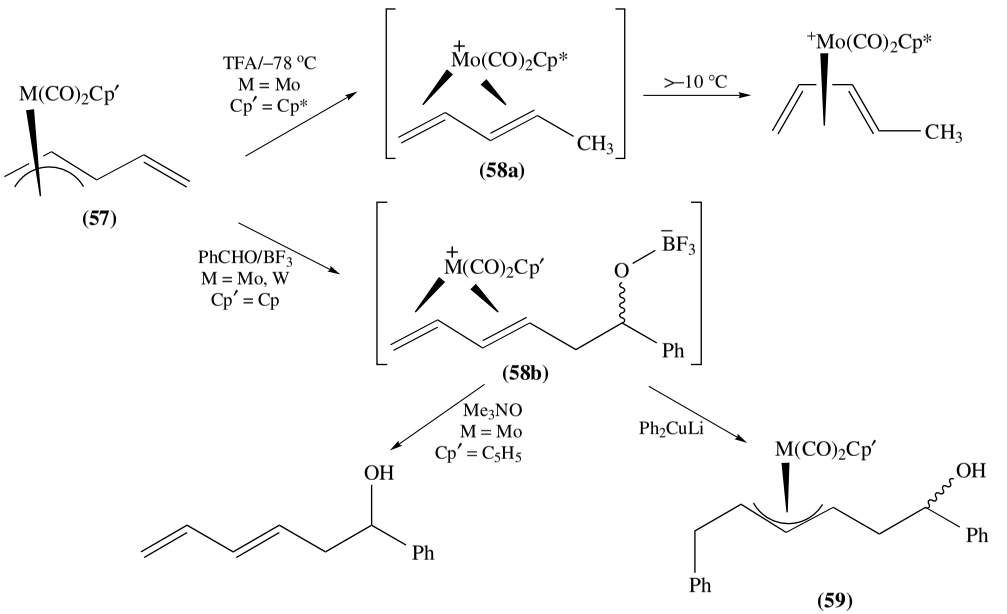


SCHEME 13



SCHEME 14

The reaction $< -40\,^{\circ}C$ of *syn*-vinyl substituted acyclic (η^3-allyl)$M(CO)_2Cp'$ complexes **57** (M = Mo, W; Cp′ = Cp, Cp*) with CF_3CO_2H or a mixture of BF_3 and an aldehyde generates the s-*trans* (diene)$M(CO)_2Cp'$ cations **58a** or **58b** respectively, which may be isolated by precipitation from ether (Scheme 15)[30,88]. At higher temperature

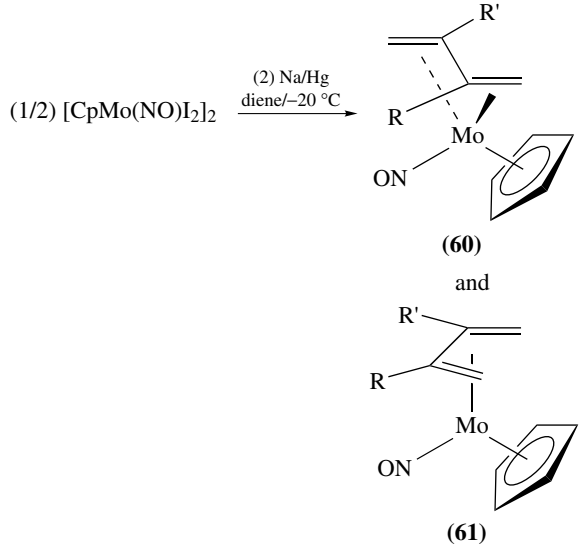

M(CO)2Cp′
(57)
TFA/–78 °C
M = Mo
Cp′ = Cp*
+Mo(CO)2Cp*
CH3
(58a)
>–10 °C
+Mo(CO)2Cp*
CH3
PhCHO/BF3
M = Mo, W
Cp′ = Cp
+M(CO)2Cp′
O
BF3
Ph
(58b)
Me3NO
M = Mo
Cp′ = C5H5
OH
Ph
Ph2CuLi
M(CO)2Cp′
OH
Ph
Ph
(59)

SCHEME 15

(>−10 °C), the s-*trans* pentadiene cation **58a** irreversibly rearranges to the s-*cis* diene cation **59**[30,88a]. The s-*trans* geometry of cations **58** has been ascertained by NMR spectroscopy at low temperature[30,88a] and by decomplexation of **58b** to give the *trans*-diene ligand[88b]. Reaction of nucleophiles, such as diphenylcuprate, with *in situ* generated **58b** gives the corresponding *syn*,*syn*-1,3-disubstituted allyl complex (**59**)[88].

3. (s-trans Diene)MoCp(NO) complexes

Reduction of the metal dimer $[CpMo(NO)I_2]_2$ with Na/Hg in the presence of a variety of acyclic dienes generates the (diene)MoCp(NO) complexes in moderate to low isolated yield (equation 8)[12,31,89]. For the majority of diene ligands, complexes **60** are formed exclusively as the s-*trans* isomers as evidenced by NMR spectroscopy and single-crystal X-ray diffraction analysis. In comparison, complexation of the 2,3-dimethyl-1,3-butadiene initially gives a separable mixture of the s-*trans* **(60)** and s-*cis*-complex **(61)**. The s-*cis* isomer isomerizes to the more thermodynamically stable s-*trans* isomer in solution (THF, $t_{1/2} = 5$ min; C_6H_6, $t_{1/2} = 24$ h).



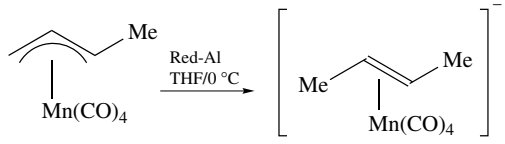
(8)

D. Complexes of Mn and Re

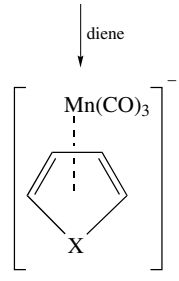
1. Anionic Mn–carbonyl complexes

(η^4-Diene)$Mn(CO)_3^-$ anions are stable in solution, and have been characterized by infrared and NMR spectroscopy. However, exposure of the anion solution to oxygen results in decomposition to give the free ligand. Reduction of (crotyl)$Mn(CO)_4$ **(62)** gives the manganese-carbonyl transfer reagent (*E*-2-butene)$Mn(CO)_4^-$. Reaction of 1,3-cycloheptadiene, 1,3-cyclooctadiene, 1,3,5-cycloheptatriene or 1,3,5,7-cyclooctatetraene

with (*E*-2-butene)$Mn(CO)_4^-$ affords complexes **63a–d** (equation 9)[58].



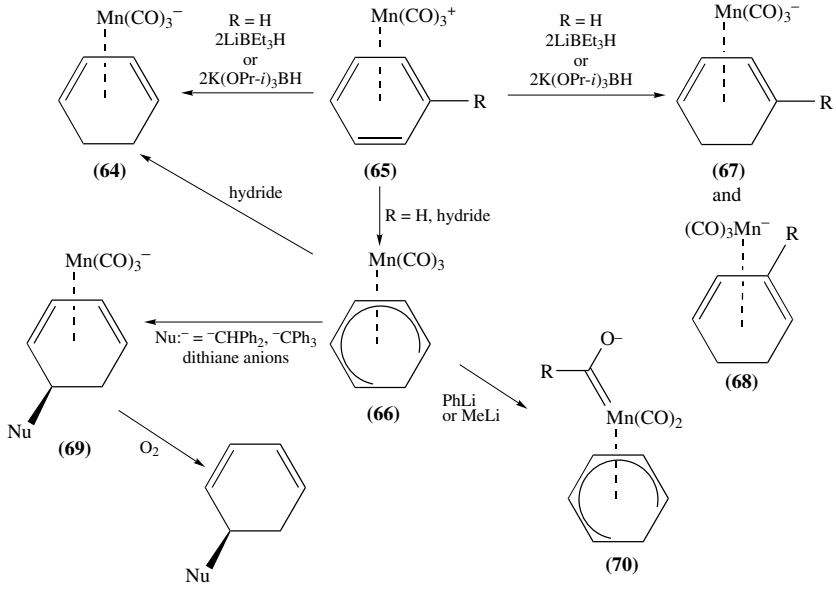
(62)



(9)

(63a) X = $[CH_2]_3$
(63b) X = $[CH_2]_4$
(63c) X = $CH_2CH{=}CH$
(63d) X = $[CH{=}CH]_2$

The 1,3-cyclohexadiene complex **64** may be prepared by addition of two equivalents of hydride to the $(C_6H_6)Mn(CO)_3^+$ cation **65** (R = H, Scheme 16)[90]. The first equivalent of hydride generates the neutral (η^5-cyclohexadienyl)$Mn(CO)_3$ complex



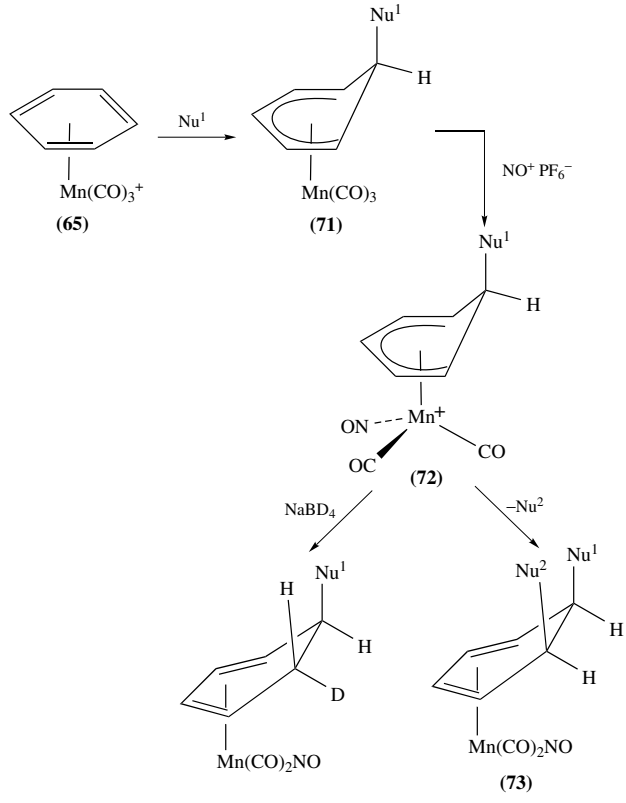
SCHEME 16

(66), which undergoes a second nucleophilic addition to give **64**. Reduction of substituted (arene)$Mn(CO)_3^+$ cations **65** (R = alkyl, aryl, alkoxy) with two equivalents of hydride leads to mixtures of isomeric (cyclohexadiene)$Mn(CO)_3^-$ anions **(67)** and **(68)**[90c,d]. Addition of certain stabilized nucleophiles (e.g. $LiCHPh_2$, $LiCPh_3$, $LiCMe_2CN$, $LiCMe_2CO_2Et$) to **66** gives the substituted cyclohexadiene anions **69**; air oxidation affords the free ligand[91]. In contrast, reaction of phenyl lithium or methyl lithium with **66** yields the acylate anion **70** via nucleophilic attack at one of the carbonyl ligands[92].

(Diene)$Mn(CO)_3^-$ anions are also prepared by deprotonation of the (η^3-allyl-μ-hydride) $Mn(CO)_3$ complexes (**25** $ML_n = Mn(CO)_3$) with potassium hydride[23,90a,c]. However, since complexes **25** $ML_n = Mn(CO)_3$ are generally prepared by protonation of the corresponding anions, this method is mostly of regenerative value.

2. Neutral Mn and Re carbonyl–nitrosyl complexes

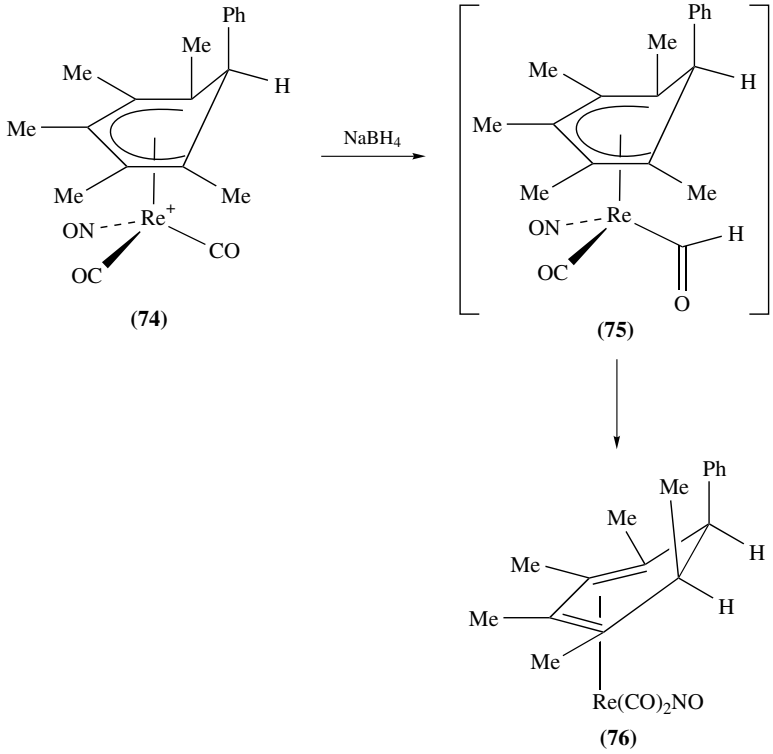
Neutral (cyclohexadienyl)manganese complexes **71**, generated by nucleophilic addition to (arene)$Mn(CO)_3^+$ cations **65**, undergo ligand substitution with nitrosyl hexafluorophosphate to give the corresponding (cyclohexadienyl)$Mn(CO)_2NO^+$ cations **72** (Scheme 17)[93]. Attack by a wide variety of nucleophiles on cations **72**



SCHEME 17

gives the neutral (cyclohexadiene)$Mn(CO)_2NO$ complexes **73**. Beginning with the (cycloheptadiene)$Mn(CO)_3^+$ cation, a similar sequence of reactions generates 5,7-disubstituted (1,3-cyclohexadiene)Mn complexes[94]. In a number of cases, nucleophilic attack on the face of the dienyl ligand opposite to the metal has been established by crystal structure analysis. Nucleophilic addition to (cyclohexadienyl)$Mn(CO)(PR_3)NO^+$ cations which are chiral at the metal occurs with modest diastereoselectivity (*ca* 33% de)[93e,g].

In contrast, spectroscopic and crystal structure analysis indicates that nucleophilic attack of hydride on **72** occurs on the face of the ligand which is coordinated to the metal (Scheme 17). No intermediate species could be detected for this latter reaction. Monitoring of the reduction of the rhenium analog **74** with sodium borohydride indicated the intermediacy of a rhenium formyl complex **75**, presumably formed by attack on a coordinated carbon monoxide. Signals for **75** eventually disappear and are replaced by those of the (diene)rhenium product **76** (Scheme 18)[95].

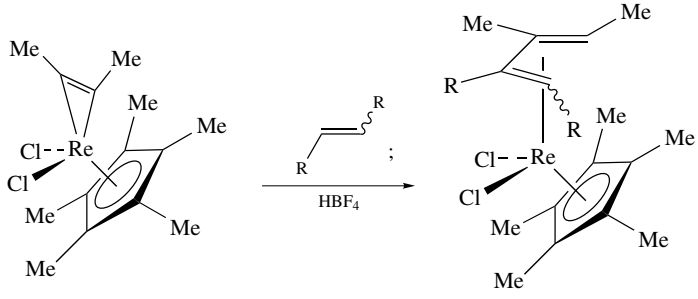


(74) **(75)** **(76)**

SCHEME 18

3. Miscellaneous

Herrmann and coworkers reported that the metallocyclopentene complex **77** reacts with ethylene or 2-butene to produce the (diene)rhenium complexes **78** (equation 10)[96].



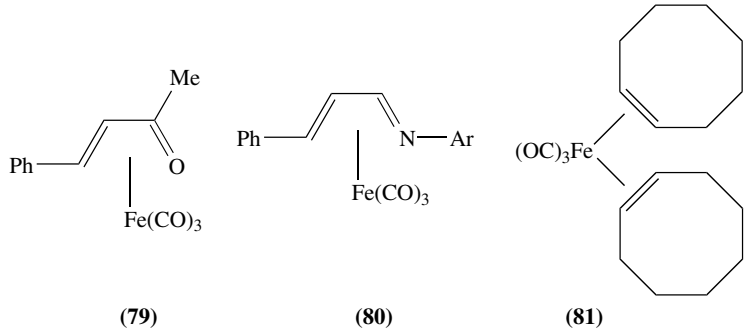
(77) (78) (10)

E. Complexes of Fe, Ru and Os

1. Neutral Fe–carbonyl and phosphine complexes

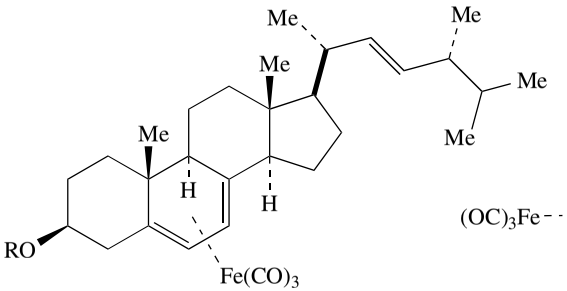
By far the greatest number of diene–metal complexes are of the type (diene)$Fe(CO)_3$. All of these complexes exhibit the s-*cis* η^4-diene coordination mode.

a. Preparation by direct complexation. In general, the most common method of preparation is by direct complexation of the free ligand using either $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$, either thermally, photochemically, under the influence of ultrasonic stirring or by dry state-adsorption techniques[97,98]. Room temperature complexation using $Fe(CO)_5$ may be accomplished by decarbonylation with trimethylamine N-oxide[99]. Complexation of non-conjugated dienes under thermal conditions usually leads to isomerization to afford the conjugated (1,4-η^4-diene) complex[97b,100], except in cases where the non-conjugated diene is constrained in a bicyclic or polycyclic ring system. Complexation under mild reaction conditions can be achieved by using (α,β-enone)$Fe(CO)_3$ complexes **(79)**, (1-aza-1,3-diene)$Fe(CO)_3$ complexes **(80)** or bis(η^2-cyclooctene)$Fe(CO)_3$ **(81)** as metal transfer species[101].

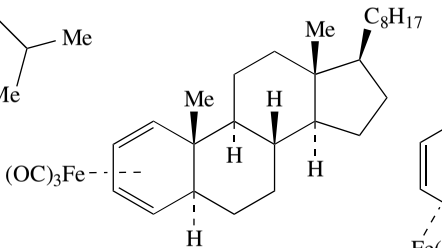


(79) **(80)** **(81)**

For diene ligands which are prochiral, complexation results in the formation of a racemic mixture. Resolution of this racemic mixture has been accomplished via either classical methods[102], chromatographic separation on chiral stationary phases[103] or kinetic resolution[104]. For certain acyclic or cyclic dienes possessing a pendent chiral center(s)



(82)



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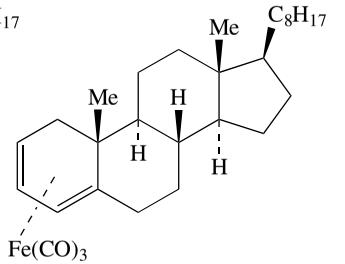

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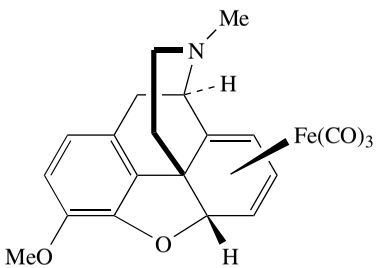

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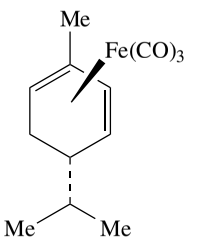

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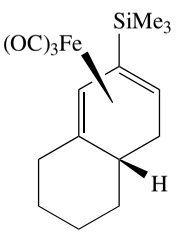

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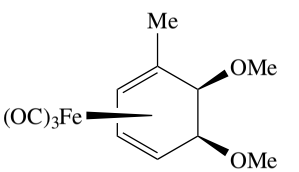

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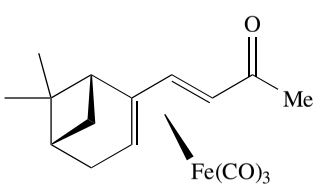

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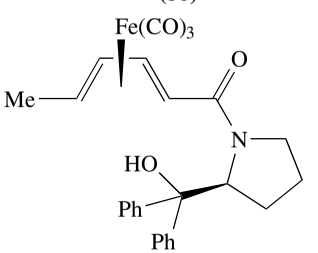

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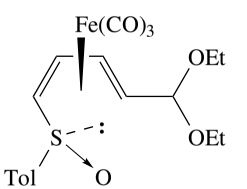

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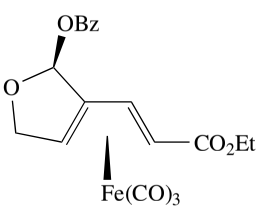
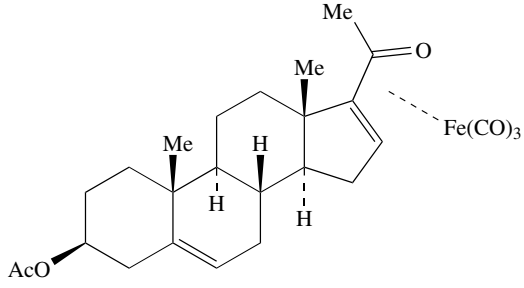
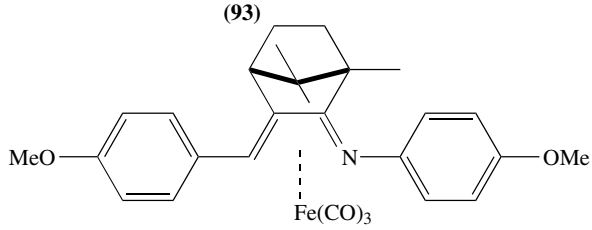


(92)



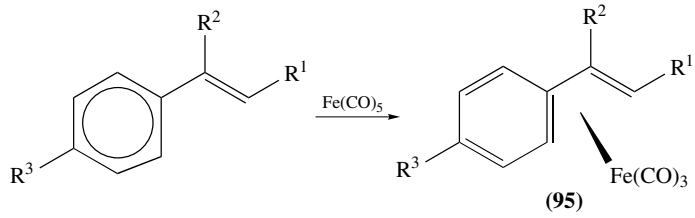
(93)



(94)

complexation may occur in a diastereoselective fashion (e.g. **82**–**92**)[105]. Enantioselective complexation (max. 64% ee) of prochiral dienes via optically active metal transfer reagents (e.g. **93**, **94**) has been reported[106].

Coordination of vinylarenes to an $Fe(CO)_3$ group gives rise to a complex **(95)** in which the metal is bound to the vinyl carbons and two of the carbons within the six-membered ring (equation 11)[107]. Crystal structure analysis indicates substantial bond localization in the uncomplexed portion of the ring. This has been interpreted as a loss of aromatic character due to participation of some of the π-electrons in coordination to iron.



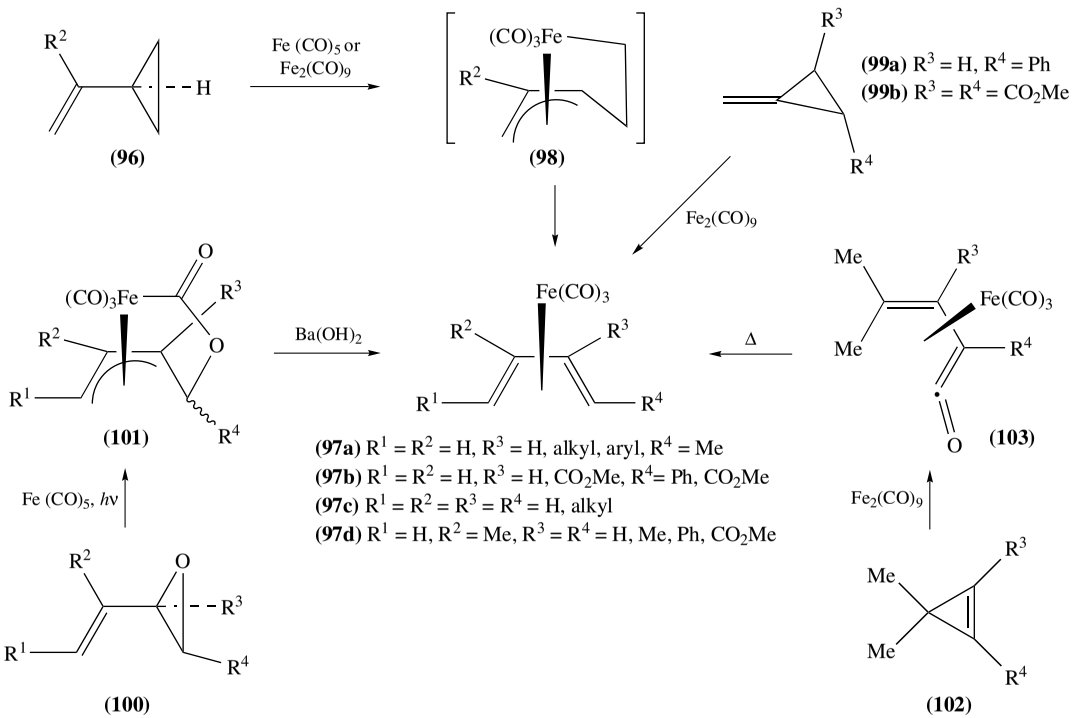
(11)

(95)

The reaction of *o*-halomethylene benzyl halides, 1,4-dihalobut-2-enes, cyclo-2-hexenols or 2,5-dihydrothiophene-1,1-dioxides with $Na_2Fe(CO)_4$ or $Fe_2(CO)_9$ results in the formation of (diene)$Fe(CO)_3$ complexes[108]. In each case, the precursor is transformed *in situ* into the free diene ligand, followed by complexation.

Metal vapor deposition of Fe atoms with a variety of acyclic and cyclic dienes, followed by treatment of the condensate with excess trimethylphosphite, give the corresponding (diene)$Fe[P(OMe)_3]_3$ complexes in low yield[109].

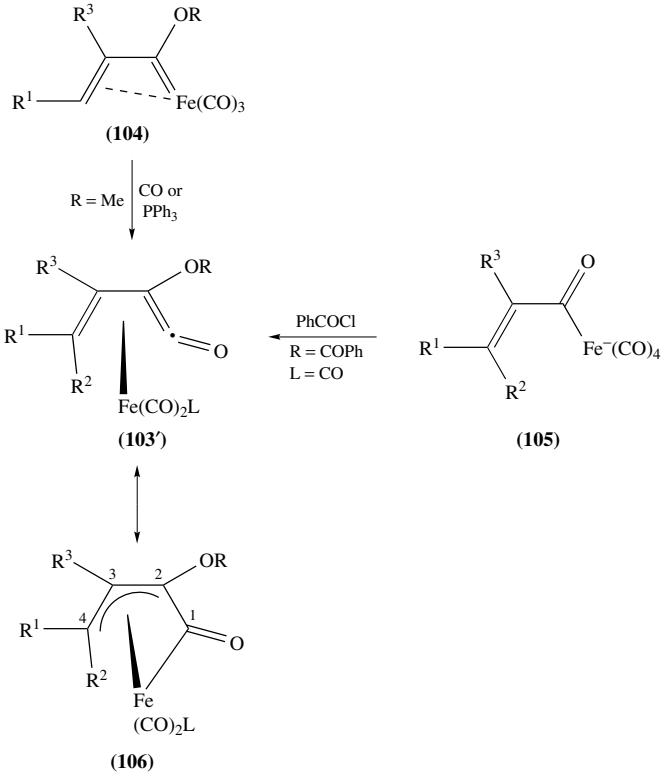
b. Diene formation within the coordination sphere of Fe. In certain cases, ring opening of strained cyclic compounds results in the formation of (η^4-diene)$Fe(CO)_3$ complexes (Scheme 19). The thermal reaction of vinylcyclopropanes **96** with $Fe(CO)_5$ or $Fe_2(CO)_9$


Fe (CO)5 or
Fe2(CO)9
(96)
(98)
(99a) R3 = H, R4 = Ph
(99b) R3 = R4 = CO2Me
Fe2(CO)9
Ba(OH)2
Δ
(97a) R1 = R2 = H, R3 = H, alkyl, aryl, R4 = Me
(97b) R1 = R2 = H, R3 = H, CO2Me, R4= Ph, CO2Me
(97c) R1 = R2 = R3 = R4 = H, alkyl
(97d) R1 = H, R2 = Me, R3 = R4 = H, Me, Ph, CO2Me
(101)
(103)
Fe (CO)5, hν
Fe2(CO)9
(100)
(102)

SCHEME 19

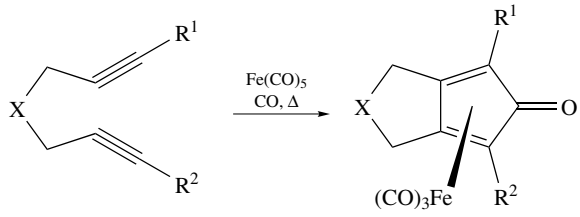
affords pentadiene complexes **97a**[110]. The intermediacy of a (pentenediyl)iron species **98** has been proposed. Reaction of methylenecyclopropanes **99a** and **99b** with $Fe_2(CO)_9$ yields diene complexes **97b**[111]. Ring opening of vinyloxiranes **100** with $Fe(CO)_5$ produces the corresponding π-allyl iron lactone complexes **101**. Treatment of **101** with barium hydroxide leads to diene complexes **97c** via decarboxylation[112]. Ring opening of 1,1-dimethylcyclopropenes **102** with $Fe_2(CO)_9$ proceeds with incorporation of a carbonyl ligand to afford the vinylketene complexes **103**[113]. Heating complexes **103** at reflux results in the loss of CO and hydride migration to give diene complexes **97d**[113c]. Direct thermolysis of **102** with $Fe_2(CO)_9$ produces the same products.

In addition to the ring opening of cyclopropenes noted above, vinylketene complexes **103′** have been prepared by (1) ligand initiated carbonyl insertion of vinyl carbene complexes **104** and (2) benzoylation of α,β-unsaturated acyl ferrates **105** (Scheme 20)[114]. X-ray diffraction analysis of these vinylketene complexes indicates that the structure may be best represented as a hybrid between an η^4-diene type complex **(103′)** and an η^3-allyl-η^1-acyl complex **(106)**. The Fe–C1 distance (*ca* 1.92 Å) is shorter than the Fe–C2, Fe–C3, or Fe–C4 distances (*ca* 2.1–2.2 Å)[113a–c]. In addition, the C–C–O ketene array is not linear (bend angle *ca* 135°).



SCHEME 20

Thermal cyclization of alkynes with $Fe(CO)_5$ proceeds predominantly with CO incorporation to afford (cyclopentadienone)$Fe(CO)_3$ complexes, however small amounts of cyclobutadiene complexes can be isolated (see Section VI.B.)[15]. 1,6-Heptadiyne and 1,7-octadiyne substrates **107** have been utilized to prepare bicyclo[3.3.0] and bicyclo[4.3.0] complexes **108** in excellent yield (equation 12)[115], while 1,8-nonadiynes gave bicyclo [5.3.0] complexes in low yield.

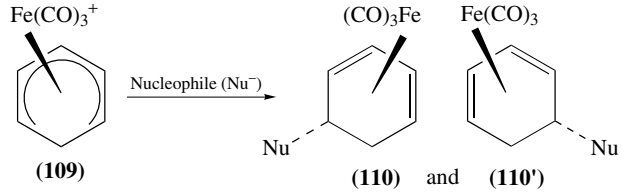


(107)

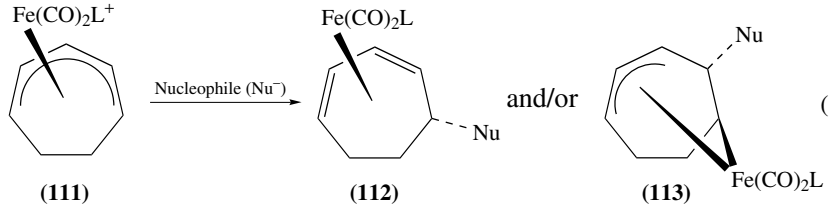
X = CH_2, $(CH_2)_2$, O, NR

(108) (12)

c. Preparation by nucleophilic addition to η^5-dienyl cations. The tricarbonyl(cyclohexadienyl)iron(1+) cation **(109)** is an excellent electrophile toward a wide variety of nucleophiles. Thus the reaction of **109**, and substituted variants, with halides, alkoxides, amines, phosphines and phosphites, organometallic anions, main group alkyl metals, enolates and electron-rich aromatics, proceeds via attack at the dienyl terminus to afford substituted (cyclohexadiene)$Fe(CO)_3$ complex **110** and its enantiomer **110′** (equation 13)[116]. Nucleophilic attack is generally observed to occur on the face of the dienyl ligand opposite to the coordinated metal. Compared to the reaction of cyclohexadienyl cation **109** the reaction of the (cycloheptadienyl)iron(1+) cations **(111)** with nucleophiles proceeds with differences in regioselectivity. While nucleophilic attack on the (dicarbonyl)phosphine- and (dicarbonyl)phosphite iron cations (**111**, L = PR_3) proceeds with excellent regioselectivity, nucleophilic attack on the tricarbonyl iron cation (**111**, L = CO) frequently affords mixtures of diene complexes **(112)** and pentenediyl complexes **(113)** (equation 14)[117].



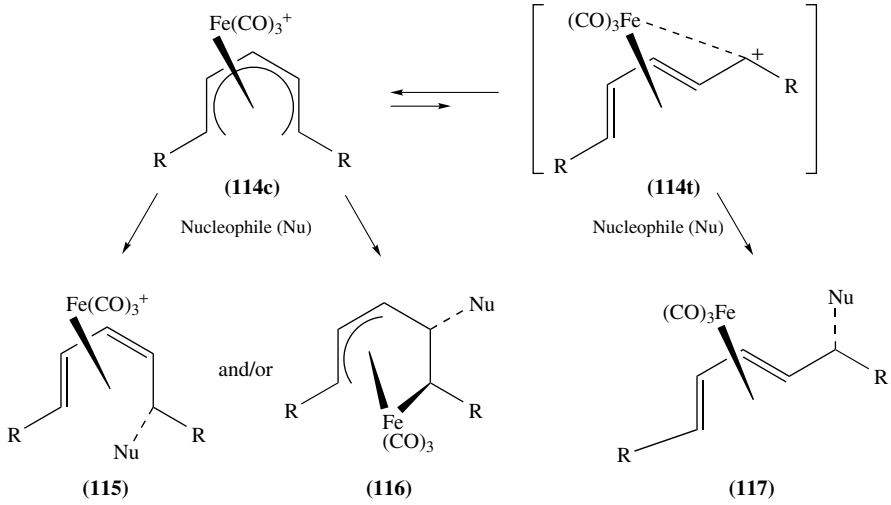
(109) **(110)** and **(110')** (13)



(111) **(112)** **(113)** (14)

Acyclic (pentadienyl)iron(1+) cations present additional possibilities for nucleophilic attack. The transoid form **114t** is known to exist in equilibrium with the more thermodynamically stable cisoid form **114c** (Scheme 21)[118]. Depending upon the nucleophile,

attack can take place on the cisoid form of the pentadienyl cation at either the termini or the internal atoms of the ligand to afford *E*,*Z*-diene complexes **115** or pentenediyl complexes **116**. Alternatively, nucleophilic attack on the transoid pentadienyl cation generates *E*,*E*-diene complexes **117**[119]. For symmetrically substituted dienyl cations **109**, **111**, and **114** nucleophilic attack on one of the terminal carbons of the ligand or the other results in the formation of mirror image products. Preferential (diastereoselective) attack on these symmetrical cations has been achieved using chiral nucleophiles[120]. For unsymmetrically substituted dienyl cations, the regioselectivity for nucleophilic attack is dependent upon the substituents present on the dienyl ligand, the nature of the nucleophile as well as on spectator ligands.

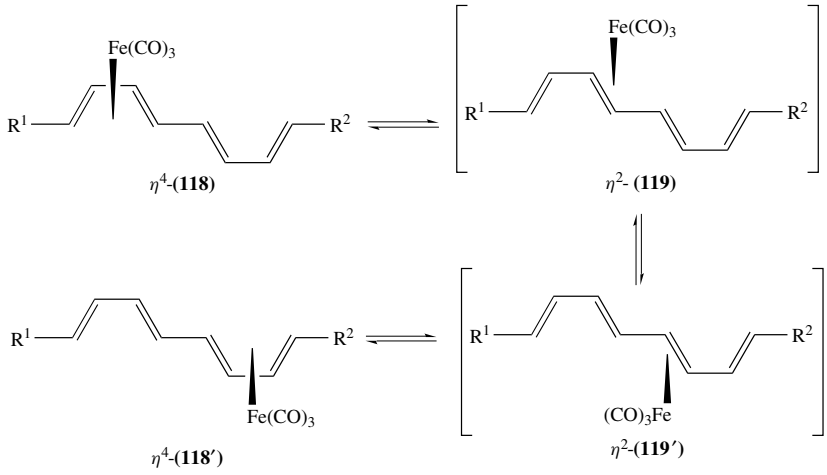


SCHEME 21

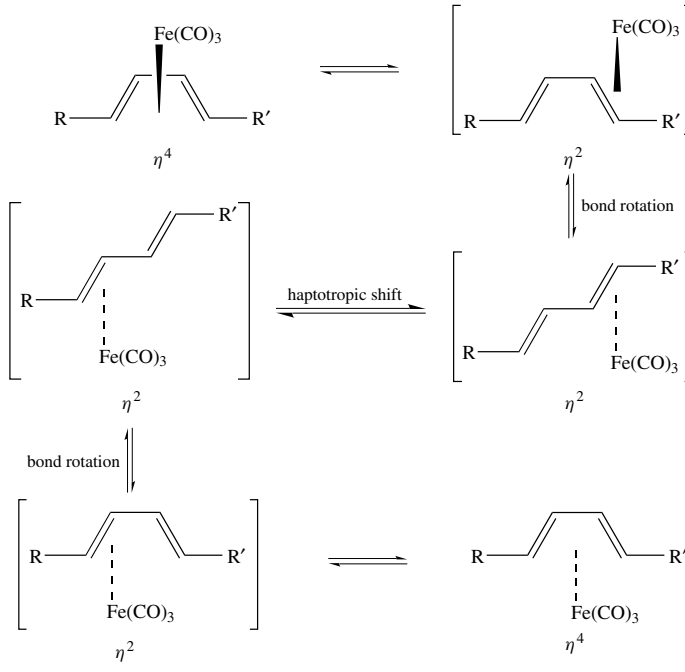
d. Isomerization reactions. Migration of iron about certain η^4-cyclic triene ligands occurs with relatively low energy barriers ($\Delta G^{\ddagger}$*ca* 15–23 kcal mol^{-1}, Section III.C.3). However, for (tropone)Fe(CO)$_3$ complexes iron migration occurs sufficiently slowly so that isomeric structures may be separated. The enantiomers of (tropone)Fe(CO)$_3$ may be separated by chiral chromatography[121]; the racemization of the resolved complex is observed to occur with an activation energy of 25.8 kcal mol^{-1}. Similar activation barriers have been reported for unsymmetrically substituted tropone complexes.

A significantly higher barrier (*ca* 32 kcal mol^{-1}) is observed for iron migration in linear polyene complexes, e.g. **118** → **118′** (Scheme 22). This isomerization is believed to proceed via $\eta^4 \rightarrow \eta^2$ coordination **(118 → 119)** followed by migration of the iron in the η^2 coordination mode **(119 → 119′)** (Scheme 22)[122]. While racemization of acyclic (diene)Fe(CO)$_3$ does not occur at ambient temperatures, it is observed at elevated temperatures. This process is also proposed to occur via η^2 coordination (Scheme 23); however the rate for racemization (*ca* 2.3–2.7 × 10^4 at 119 °C) is approximately half the rate of polyene migration[122].

(*E*,*Z*-Diene)Fe(CO)$_3$ complexes are configurationally stable under ambient conditions, however irreversible *Z* → *E* isomerization is observed at elevated temperatures. Since

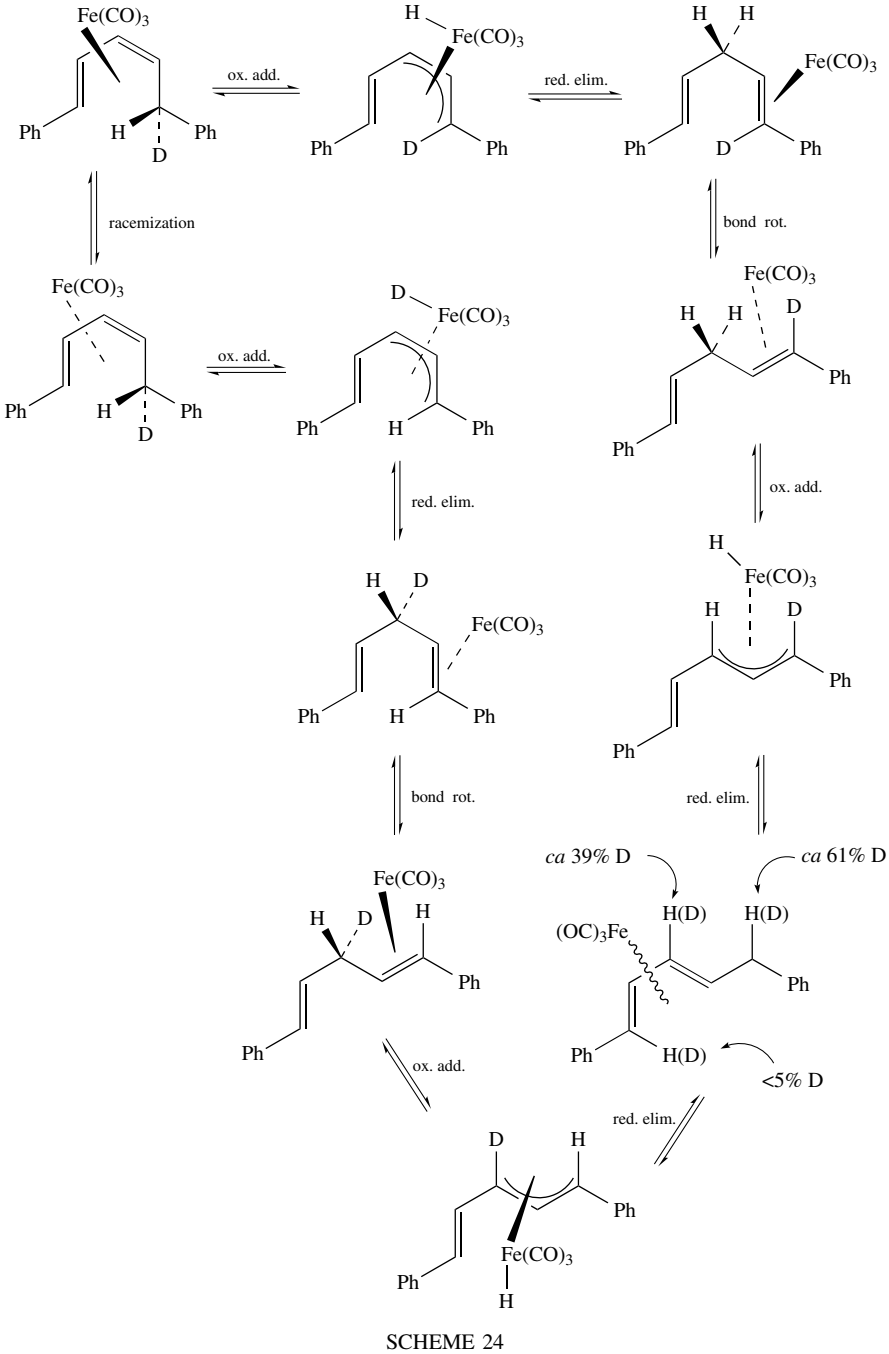


SCHEME 22



SCHEME 23

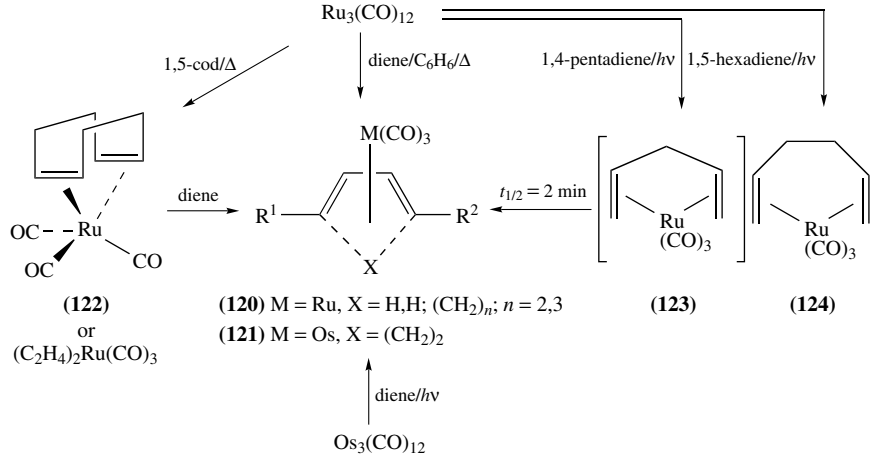
this isomerization occurs at one diene terminus and not at the other, an 'envelope flip' mechanism is excluded (Section III.C.2). In one study racemization was observed to occur at a rate slightly faster than $Z \rightarrow E$ isomerization. These results, along with deuterium labelling experiments, suggest a mechanism involving sequential oxidative insertion, reductive eliminations and bond rotations (Scheme 24)[123].


Fe(CO)3
ox. add.
red. elim.
racemization
bond rot.
Ph
H
D
ca 39% D
ca 61% D
H(D)
(OC)3Fe
<5% D

SCHEME 24

2. Neutral Ru and Os carbonyl complexes

The reaction of cyclic and acyclic 1,3-dienes with $Ru_3(CO)_{12}$ in refluxing benzene[124] or with $Os_3(CO)_{12}$ under photolytic conditions[26b,125] affords the corresponding (diene)Ru$(CO)_3$ complexes **(120)** or (diene)Os$(CO)_3$ complexes **(121)** respectively (Scheme 25). The thermal complexation of 1,5-cyclooctadiene with $Ru_3(CO)_{12}$ gives the non-conjugated (1,5-cod)Ru$(CO)_3$ complex **(122)** without rearrangement[126]. Heating **122** at reflux in benzene[26a,127], or reaction of $(C_2H_4)_2Ru(CO)_3$ at ambient temperature[128], in the presence of a 1,3-diene gives complexes **120**. Photolysis of $Ru_3(CO)_{12}$ with 1,4-pentadiene or 1,5-hexadiene affords the non-conjugated diene complexes **123** or **124**. Complex **123** is stable only at low temperatures, isomerizing rapidly ($t_{1/2} = 2$ min) at 25 °C to the 1,3-pentadiene complex[129], while complex **124** is stable for hours at 25 °C. These isomerizations are believed to occur via intermediates similar to those in Scheme 24. In contrast to the innumerable examples found in organoiron chemistry, there are only a limited number of examples for the preparation of substituted (cyclohexadiene)M$(CO)_3$ complexes from nucleophilic attack on (cyclohexadienyl)M$(CO)_3^+$ cations (M = Ru, Os)[125,130].

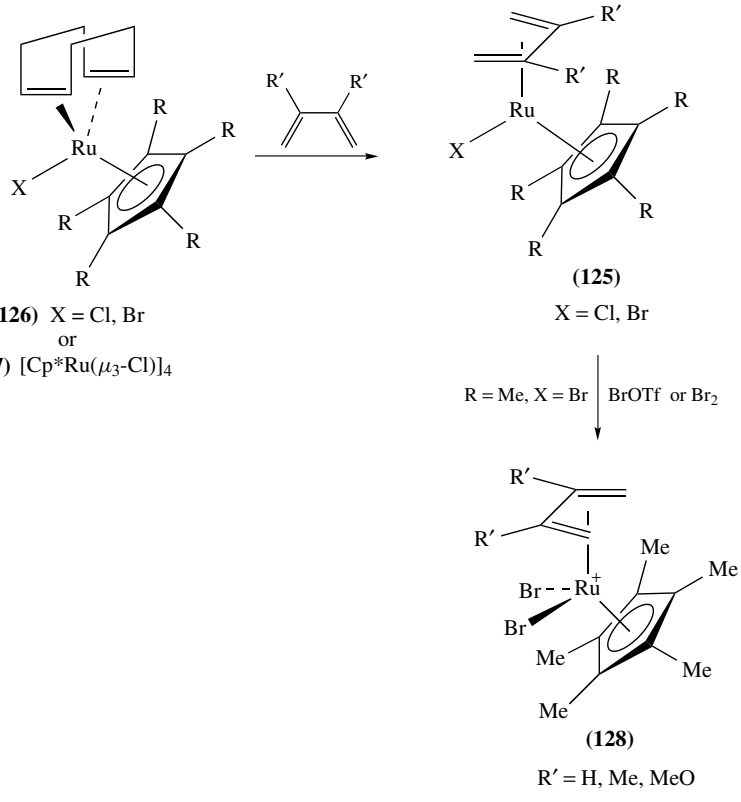


SCHEME 25

3. (Diene)RuCpX and related complexes

The preparation of cyclic or acyclic (diene)RuCp′X complexes **125** (Cp′ = C_5H_5 or C_5Me_5) via direct complexation has been reported (Scheme 26)[131]. This may be accomplished using either (1,5-cod)RuCpX **(126)** or the tetrameric species $[Cp^*Ru(\mu_3 - X)]_4$ **(127)**. Complexes **125** exhibit the s-*cis* η^4-diene coordination mode as evidenced by X-ray diffraction analysis. The ligands are oriented such that the open end of the diene is eclipsed with the Ru−X bond. Treatment of complexes **125** with $AgOSO_2CF_3$ or AgO_2CCF_3 effects replacement of the halide ligand X with either a triflate or trifluoroacetate ligand[27]. Oxidation of diene complexes **125** (R = Me), which lack alkyl substituents

at the terminal carbons, with Br_2 or bromonium triflate affords (diene)RuCp*Br_2^+ cations **128** (Scheme 26)[9b,27,132]. In contrast to complexes **125**, X-ray diffraction analyses of cations **128** provide evidence for coordination via the σ^2, π bonding mode. In addition, crystal structure data and NOE evidence indicate that the ligands in cations **128** are oriented such that the open end of the diene is eclipsed with the Cp* ligand.



(126) X = Cl, Br
or
(127) $[Cp^*Ru(\mu_3\text{-}Cl)]_4$

(125)
X = Cl, Br

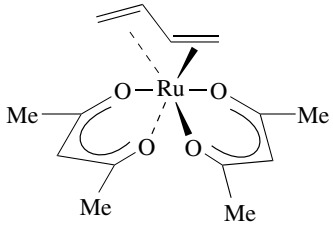
R = Me, X = Br | BrOTf or Br_2

(128)
R′ = H, Me, MeO

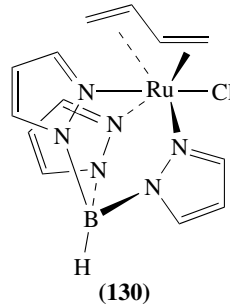
SCHEME 26

4. (s-trans Diene)Ru(II) complexes

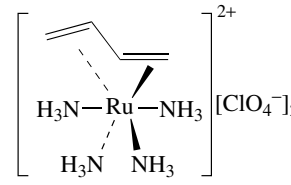
The preparation and characterization of several octahedral Ru(II) complexes containing s-*trans* coordinated dienes have been reported. The Zn mediated reduction of $Ru(acac)_3$ in the presence of a 1,3-diene affords (diene)$Ru(acac)_2$ complexes as a mixture of diastereomers (eg. **129**)[13a,b]. Reaction of $[(trispyrazolylborate)RuCl]_x$ or $[(NH_3)_4Ru(acetone)_2]_2^+$ $[ClO_4^-]_2$ with acyclic dienes yields complex **130** or cation **131** respectively[13c,14]. Coordination of the ligand as an s-*trans* diene was indicated either by crystal structure or by determining C_{2v} symmetry on the basis of NMR spectroscopy.



(129)



(130)

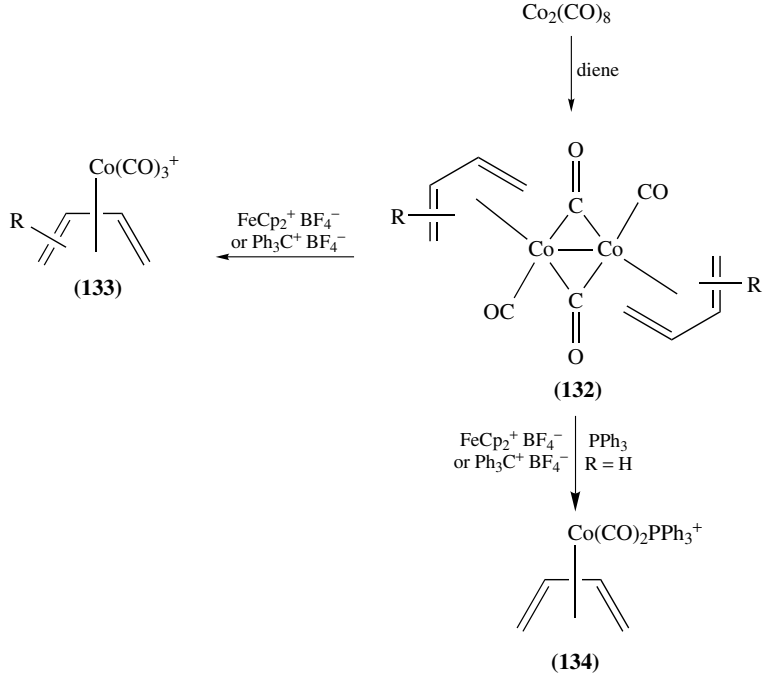


(131)

F. Complexes of Co, Rh and Ir

1. Cationic Co-carbonyl and phosphine complexes

The thermal reaction of 1,3-dienes with $Co_2(CO)_8$ gives the corresponding bimetallic dimers $[(diene)Co(CO)_2]_2$ **132** as orange red solids in good yields (Scheme 27)[28,133]. Oxidation of the dimeric complexes **132** with ferricinium tetrafluoroborate or triphenylcarbenium tetrafluoroborate gives the monomeric $(diene)Co(CO)_3^+$ cations **133** in modest



(133)

(132)

(134)

SCHEME 27

yields (20–45%)[28,134]. While this oxidation is limited by the amount of carbon monoxide present in **132**, performing the oxidation under CO atmosphere does not improve the yield. Oxidation of **132** in the presence of PPh_3 give the corresponding (diene)$Co(CO)_2PPh_3^+$ cations **134**. Reaction of cyclohexadiene with $HCo(CO)_4$ followed by hydride abstraction by trityl cation affords the (cyclohexadiene)$Co(CO)_3^+$ cation[134a]. The reduction of $Co[ClO_4]_2$ in the presence of excess phosphine and butadiene followed by anion metathesis gave (butadiene)$Co(PR_3)_3^+ Ph_4B^-$ salts as crystalline solids[135].

2. Neutral (diene)MCp complexes (M = Co, Rh, Ir)

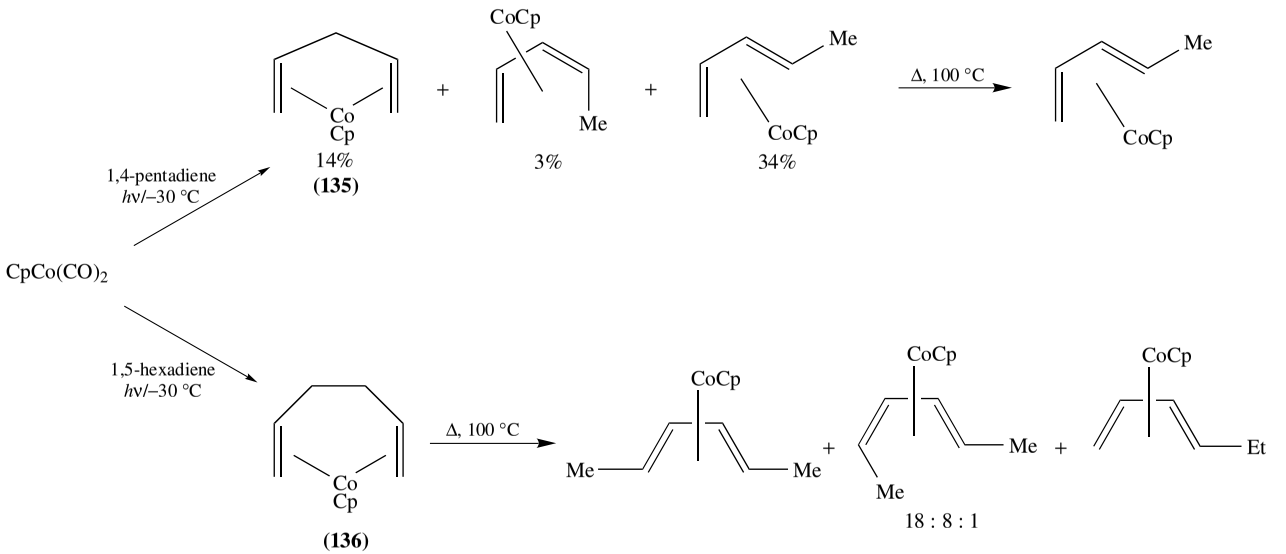
Cyclopentadiene(diene)cobalt complexes, the largest catagory of diene complexes of Co, may be prepared by direct complexation, by preparation of the dienes within the coordination sphere of Co and by nucleophilic addition to (η^5-dienyl)CoCp cations. In comparison to (diene)CoCp complexes, there are considerably fewer examples of (diene)RhCp and (diene)IrCp complexes known.

a. Preparation by direct complexation to Co. Direct complexation may be accomplished (1) by thermal or photochemical reaction of $CpCo(CO)_2$, $CpCo(PPh_3)_2$, $CpCo(C_2H_4)_2$ in the presence of the diene ligand[136], (2) by reduction of $[CpCoI_2]_2$ in the presence of a diene ligand[137], or (3) by reduction of $Co(acac)_3$ in the presence of a diene and monomeric cyclopentadiene[138]. Complexation of 1,4-pentadiene with $CpCo(CO)_2$ gave a mixture of 1,4-diene **(135)** and 1,3-diene complexes while use of 1,5-hexadiene gave only the non-conjugated complex **(136)** (Scheme 28)[136c]. The non-conjugated diene complexes may be isomerized into conjugated diene complexes under thermal conditions.

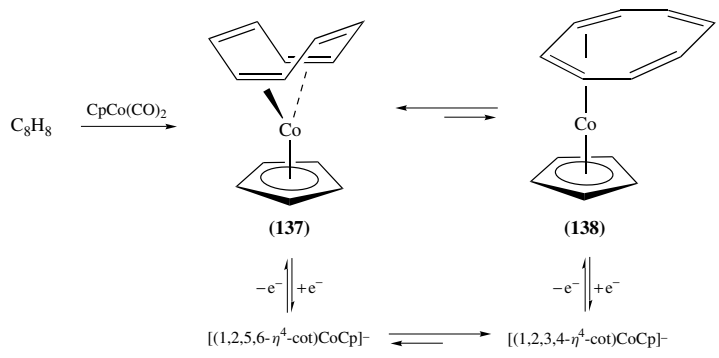
The complex (C_8H_8)CoCp, prepared from $CpCo(CO)_2$ and C_8H_8, was originally assigned the (1,2,5,6-η^4) structure **137** (Scheme 29)[139]. Further examination by Moraczewski and Geiger revealed that a minor amount of the (1,2,3,4-η^4) complex **138** existed in equilibrium with thermodynamically more stable **137**[139b]. The NMR spectrum of **138** consists of only two signals, consistent with a 'ring-whizzing' fluxionality. Electrochemical reduction of **137** gives the (1,2,5,6-η^4) anion, which isomerizes to the more stable (1,2,3,4-η^4) anion.

Migration of the metal along the polyene chain in (1,1-d_2-1,3,5-hexatriene)CoCp occurs with an activation energy of 25.6 kcal mol^{-1} (equation 15)[136b]. This barrier is *ca* 5–8 kcal mol^{-1} lower than that for metal migration in (triene)- or (tetraene)$Fe(CO)_3$ complexes (see Section IV.E.1.d).

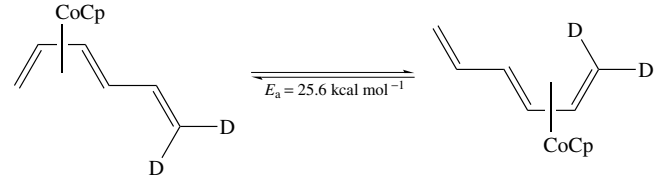
b. Preparation of dienes within the coordination sphere of Co. The $CpCo(CO)_2$ mediated [2 + 2 + 2] cyclization of an alkene with two alkynes leading to the formation of (hexadiene)CoCp complexes has been reviewed[140]. The reaction is considerably more efficient if two of the components are linked via an alkyl, aryl or heteroatom containing chain. The stereochemistry of substituents on the sp^3 hybridized carbons in the cyclohexadiene ring mirrors that originally present in the alkene component. As the product (cyclohexadiene)CoCp complexes may be decomposed under oxidation conditions to render the 'free' ligand, this cyclization has been utilized in the synthesis, or formal synthesis, of a variety of natural products (equations 16–18)[141].


CpCo(CO)2
1,4-pentadiene
hν/–30 °C
1,5-hexadiene
hν/–30 °C
Co
Cp
14%
(135)
CoCp
Me
3%
Me
CoCp
34%
Δ, 100 °C
Me
CoCp
Co
Cp
(136)
Δ, 100 °C
CoCp
Me
Me
CoCp
Me
Me
18 : 8 : 1
CoCp
Et

SCHEME 28



SCHEME 29



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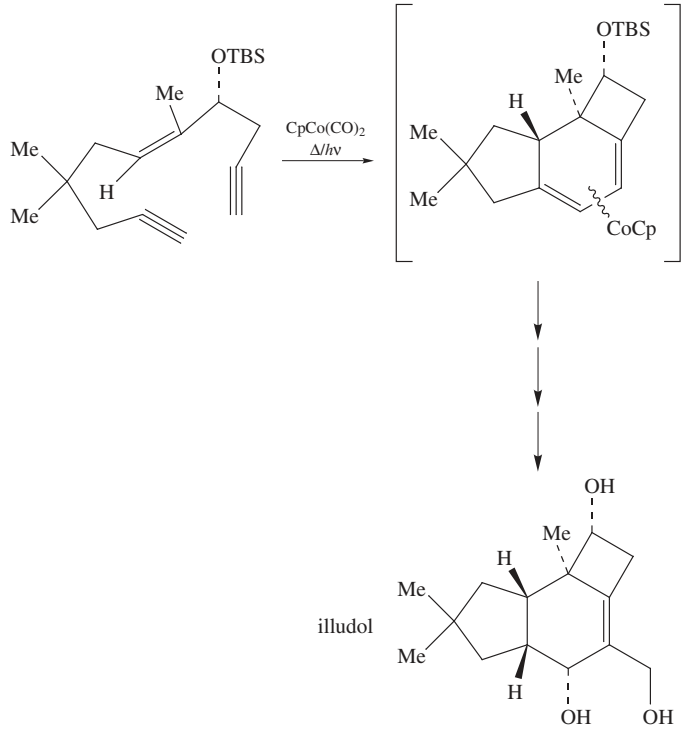
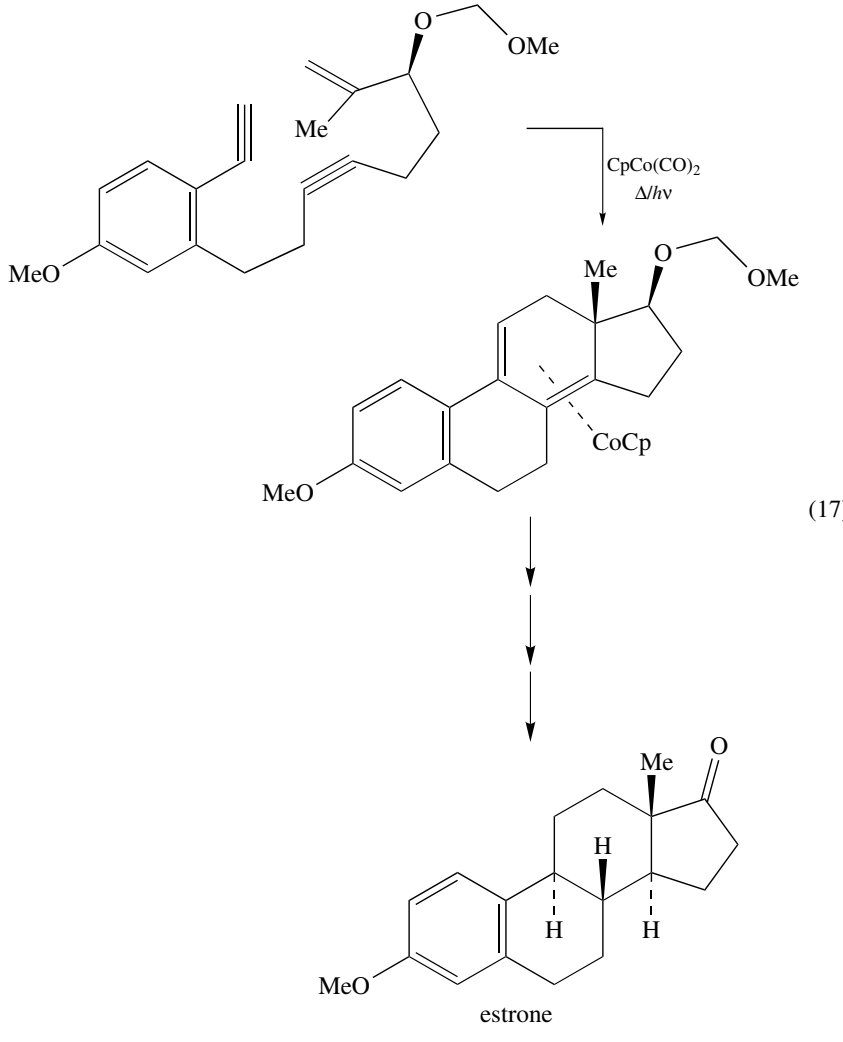


(16)



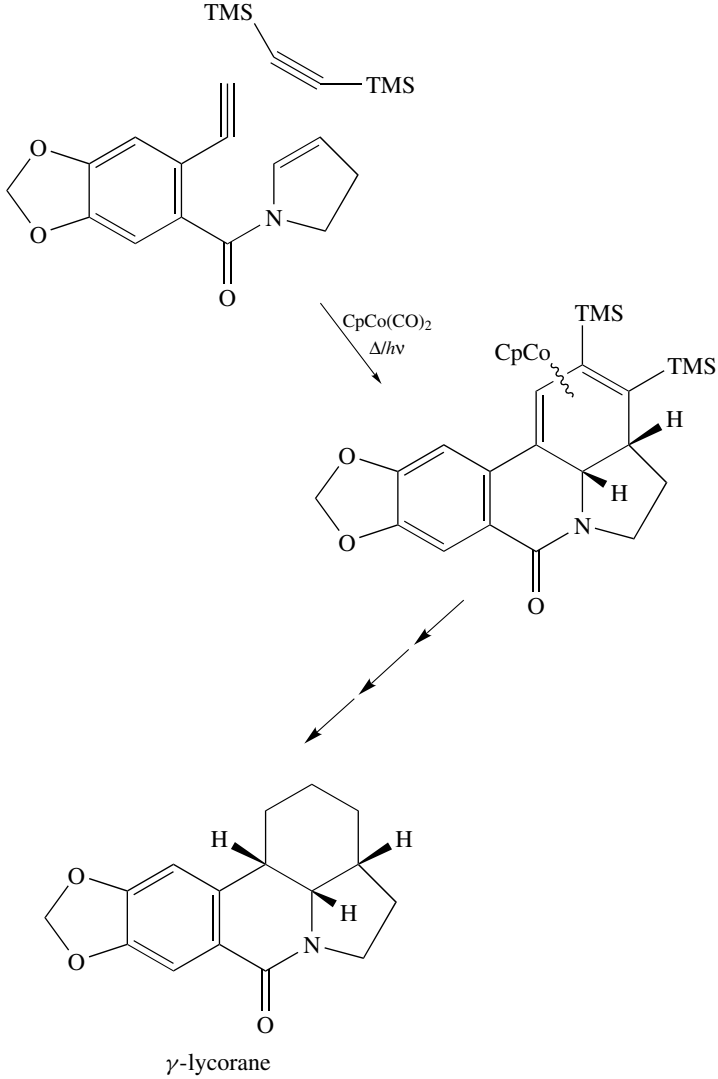
(17)

estrone

Low-temperature photochemical cyclization of alkynes bearing a bulky substituent, mediated by $CpCo(CO)_2$, proceeds with CO insertion to give cyclopentadienone complexes. Higher reaction temperatures lead to cyclotrimerization. The intramolecular variant of this reaction gives the bicyclic cyclopentadienones **139** and **139′** (equation 19)[142]. Cyclization of unsymmetrically substituted diynes with the chiral $R^*CpCo(CO)_2$ (R^* = 8-phenylmenthyl) leads to the formation of a mixture of diastereomers; modest diastereoselectivity was found.

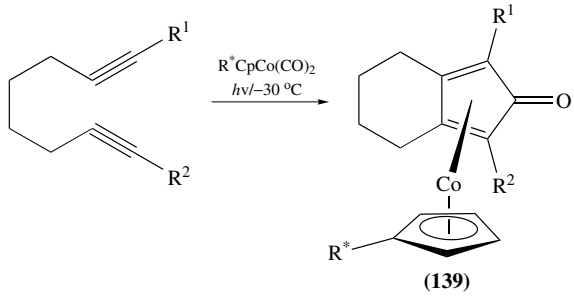
The reaction of $Cp(alkyne)CoPPh_3$ complexes **140** with 1 equivalent of ethyl diazoacetate in the presence of PPh_3 yields the cobaltacyclobutene **141**, which upon further reaction with the diazoacetate affords (diene)CoCp complexes **142** as a mixture of *E*,*E*-

and *E*,*Z*- isomers (Scheme 30)[143]. Treatment of **140** with excess of ethyl diazoacetate or diazoketones gives directly the diene complexes. At elevated temperatures, the complexes *E*,*Z*-**142a** and *E*,*Z*-**142b** interconvert with each other but not with *E*,*Z*-**142c**. This interconversion is proposed to occur via an 'envelope flip' mechanism (Section III.C.2). The photochemically induced isomerization of dideuteriated (diene)CoCp complex **143a** to **143b** provided further evidence for an 'envelope flip' mechanism (equation 20)[144]. The investigators noted that *syn–anti* isomerization occurs synchronously with diastereoisomerization.



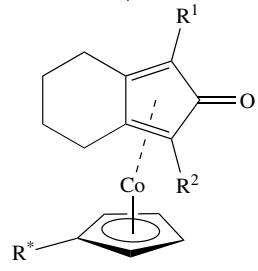
(18)

γ-lycorane



(139)

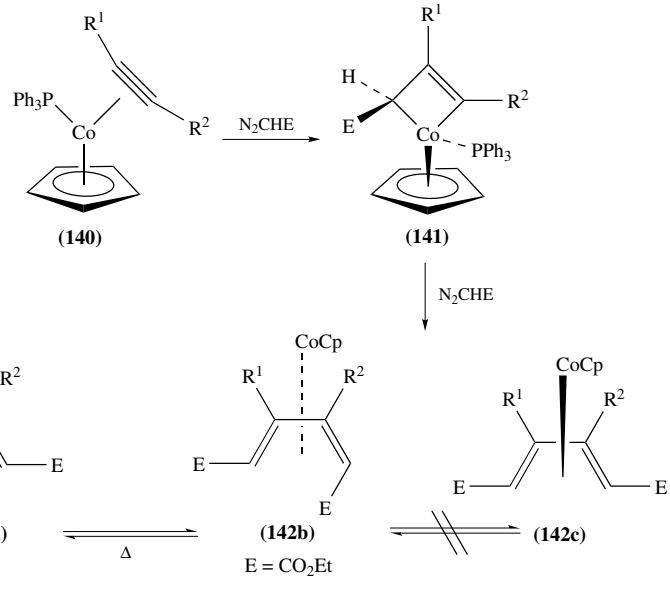
+



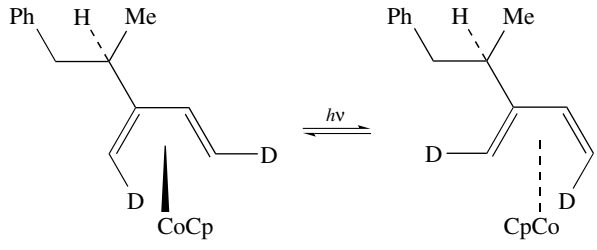
(139')

(19)

R* = 8-phenylmenthyl

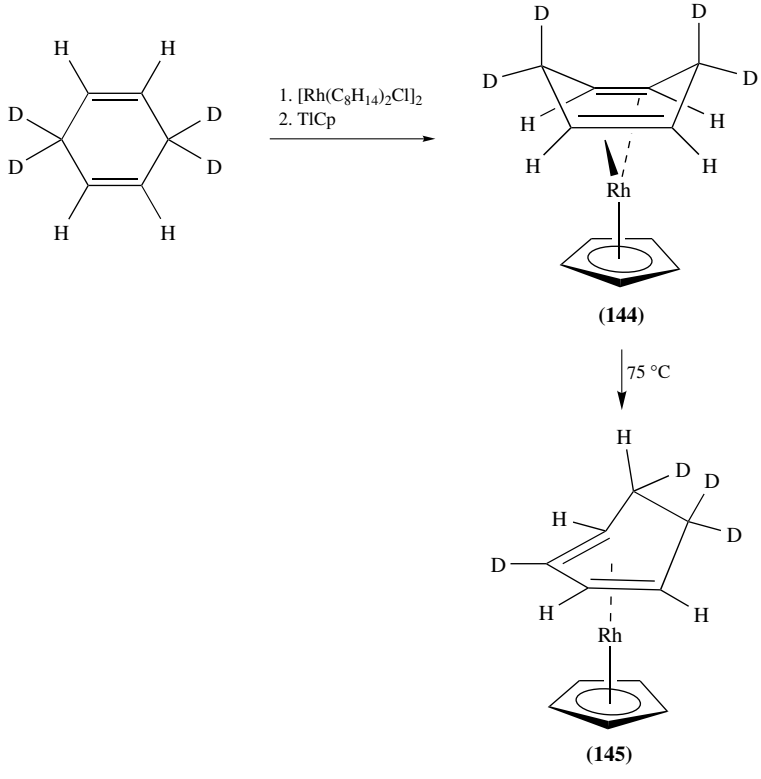


SCHEME 30



(143a) (143b) (20)

c. Preparation by direct complexation to Rh or Ir. Ligand substitution of ethylene in $[(C_2H_4)_2RhCl]_2$ or cyclooctene in $[(C_8H_{14})_2RhCl]_2$ with a diene or polyene gives the corresponding $[(diene)RhCl]_2$ dimer. Treatment of the dimer with cyclopentadienyl thallium gives the monomeric (diene)RhCp complexes[29]. Coordination of non-conjugated dienes (e.g. 1,4-cyclohexadiene) gives the non-conjugated diene complex (**144**, Scheme 31)[145]. Isomerization of **144** to the thermodynamically more stable conjugated diene complex **145** occurs at elevated temperatures ($\Delta G^{\ddagger} = 26$ kcal mol^{-1}). Deuterium labelling indicates a 1,3-hydride shift. Isomerization from a non-conjugated diene to a conjugated diene

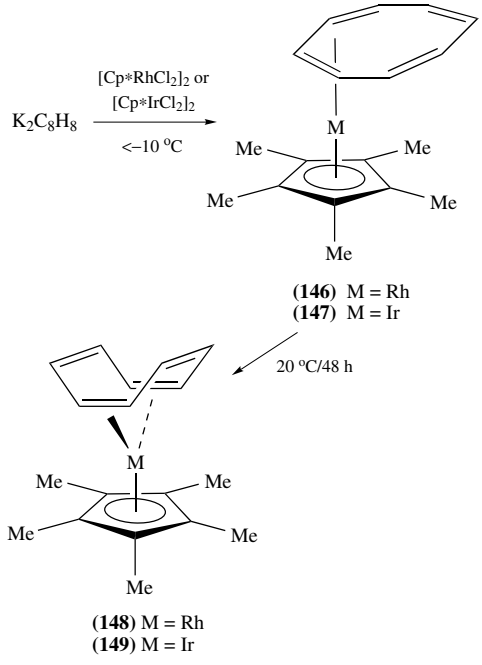


(144) (145)

SCHEME 31

in acyclic (diene)RhCp complexes occurs with a greater barrier ($\Delta G^{\ddagger} = 30$ kcal mol^{-1}) than for cyclic (diene)RhCp complexes. The energy for *anti* → *syn* isomerization is greater still ($\Delta G^{\ddagger} = 33$ kcal mol^{-1}). A mechanism similar to that for the isomerization of (diene)Fe(CO)$_3$ complexes (Scheme 24, Section IV.E.1.d) which involves the intermediacy of a π-allyl–metal–hydride intermediate is proposed.

Reaction of the cyclooctatetraene dianion with [Cp*RhCl$_2$]$_2$ or [Cp*IrCl$_2$]$_2$ at low temperature (< −10 °C) gave the (1,2,3,4-η^4) complexes **146** or **147**, respectively (Scheme 32)[146]. The NMR spectra of both **146** and **147** consists of only two signals even at −50 °C, indicative of fluxional 'ring-whizzing' with a low barrier. The initially obtained (1,2,3,4-η^4) complexes isomerize to (1,2,5,6-η^4) complexes **148** and **149**, respectively, after 48 h at 20 °C.



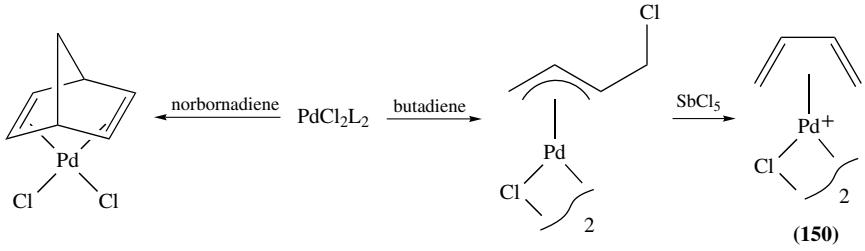
SCHEME 32

d. Preparation by nucleophilic addition to η^5-dienyl cations. There are limited examples of the addition of hydride, carbon or heteroatom nucleophiles to Cp$_2$M$^+$ cations or (cyclohexadienyl)MCp$^+$ cations to produce (cyclopentadiene)MCp or (cyclohexadiene) MCp products (M = Co, Rh)[136a,147]. While *endo* attack was originally proposed, crystal structure analysis eventually validated attack from the face of the ligand opposite to the metal.

G. Complexes of Ni, Pd and Pt

Non-conjugated dienes constrained within a rigid polycyclic system (e.g. norbornadiene) react with Na$_2$PdCl$_4$ or PdCl$_2$(PhCN)$_2$ to give the corresponding (diene)PdCl$_2$

complexes[148], while acyclic conjugated dienes undergo chloropalladation to form (π-allyl)PdCl dimers (Scheme 33)[149]. Ionization of (1-chloromethylallyl)PdCl with $SbCl_5$ generates the cationic (diene)Pd complex **150**. The reaction of 1,3-cyclooctadiene with $PdCl_2(PhCN)_2$ produces the non-conjugated (1,5-cyclooctadiene)$PdCl_2$ complex, demonstrating the greater stability of this coordination mode[150].



SCHEME 33

V. REACTIONS OF CONJUGATED DIENE COMPLEXES

(Diene)- and (polyene)metal complexes undergo a variety of reactions, including decomplexation and insertion reactions, and reactions with electrophiles or nucleophiles. In addition, the transition metal may serve as a protecting and/or stereodirecting group for a complexed diene. In order to compare similarities and differences in reactivity as a function of the coordinated metal, this section will be organized by reaction type rather than by metal group.

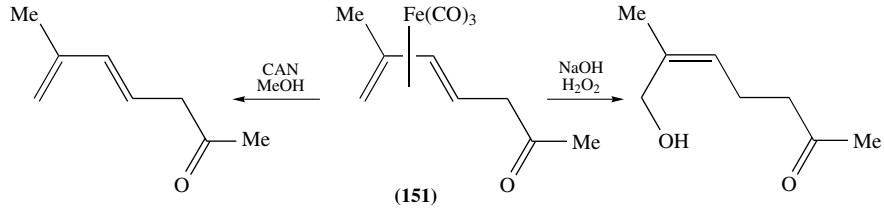
A. Decomplexation

1. Oxidative decomplexation

Liberation of a complexed diene ligand may be accomplished under oxidizing conditions. (Diene)$ZrCp_2$ complexes[151], (diene)TiCp*X complexes[69b], and (diene)$Mn(CO)_3^-$ anions[23,91] are all relatively sensitive and undergo oxidative decomplexation upon exposure to air to afford the free ligand. The majority of other diene–metal complexes are somewhat stable in air. In the case of the neutral complexes (diene)$Mn(CO)_2NO$[93f,g], (diene)$Fe(CO)_2L$ (L = CO, PR_3)[116–118], and (diene)CoCp[141b,142a], or cationic (diene)Mo $(CO)_2Cp^+$ complexes[81b,88b], stronger oxidizing agents such as $FeCl_3$, $CuCl_2$, $(NH_4)_2$ $Ce(NO_2)_6$ [CAN], or Me_3NO are necessary for the liberation of the diene ligand. While oxidation of (6-oxo-1,3-diene)$Fe(CO)_3$ complexes **(151)** with CAN gives the free ligand, oxidation with hydrogen peroxide gives allylic alcohols (Scheme 34)[152]. Oxidation of (cyclohexadiene)$Fe(CO)_3$ complexes **152**, prepared from the addition of aryl amines to (cyclohexadienyl)$Fe(CO)_3^+$ cations, with very active MnO_2 or I_2 proceeds with cyclization, decomplexation and oxidative aromatization to generate carbazole products (Scheme 35)[116d,153]. An extensive series of natural products has been prepared by this general method[116d].

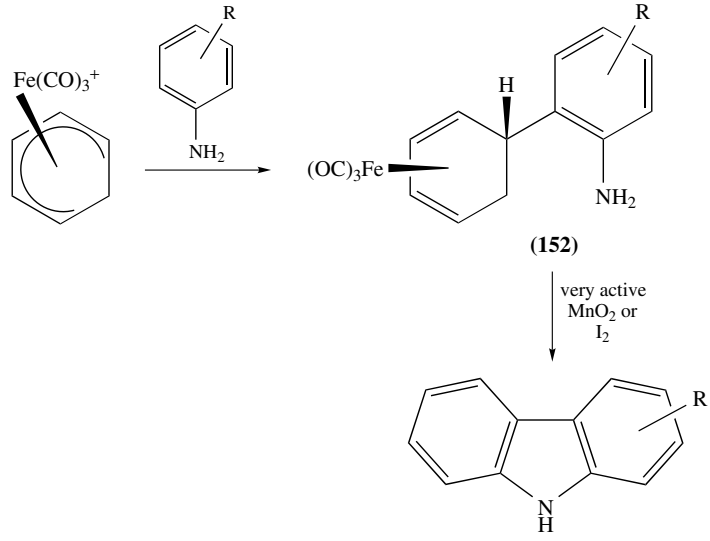
2. Reductive decomplexation

Exposure of (2,3-dimethyl-1,3-butadiene)HfCp*Cl **(36d)** to hydrogen (10 atm/$PhCH_3$/ 70 °C) gave a mixture of 2,3-dimethyl-2-butene and 2,3-dimethylbutane along with the



(151)

SCHEME 34



(152)

SCHEME 35

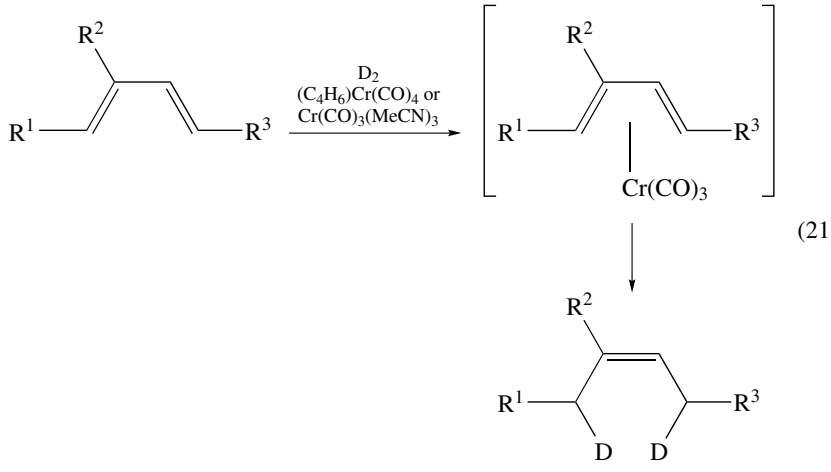
$[Cp^*Hf(H_2)Cl]_4$ tetramer[154]. Photochemical reduction of (diene)iron complexes in acetic acid gives the corresponding alkene[155]; this methodology has been used in the synthesis of the novel terpene lasiol[155b]. The regioselectivity for this reduction is good only if the diene is substituted by an electron withdrawing group.

(Diene)$Cr(CO)_4$ complexes serve as catalysts for the addition of hydrogen to 1,3-dienes to give 2*Z*-alkenes (equation 21)[78a]. Alternatively, $Cr(CO)_3(MeCN)_3$ may also be used as a catalyst for this reduction[156]. Use of deuterium instead of hydrogen affords the 1,4-dideuterio-2*Z*-alkene. The rate of reduction for uncomplexed acyclic dienes decreases in the order $E,E->E,Z->Z,Z$-dienes. This order parallels the ease of formation of the corresponding (diene)$Cr(CO)_4$ complexes. These results implicate the formation of a 16 valence electron [VE] (diene)$Cr(CO)_3$ intermediate as part of the catalytic cycle.

3. Carbonylative decomposition

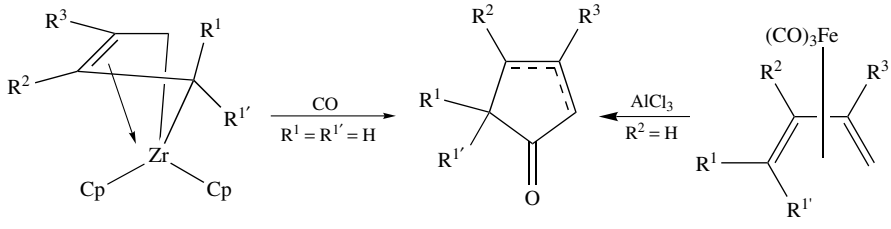
Direct displacement of a diene ligand by CO is rare and the only report of this involves treatment of (η^5-indenyl)(diene)$Mo(CO)_2^+$ cations with carbon monoxide (10 atm/50 °C) to generate the 'free' diene ligand[81b]. In this case, ligand substitution may be due to

a decrease in the metal-to-ligand backbonding due to the cationic charge. In addition, it is known that 18-VE (η^5-indenyl)metal complexes undergo ligand substitution via an associative mechanism due to $\eta^5 \rightarrow \eta^5$ ligand 'slippage'.



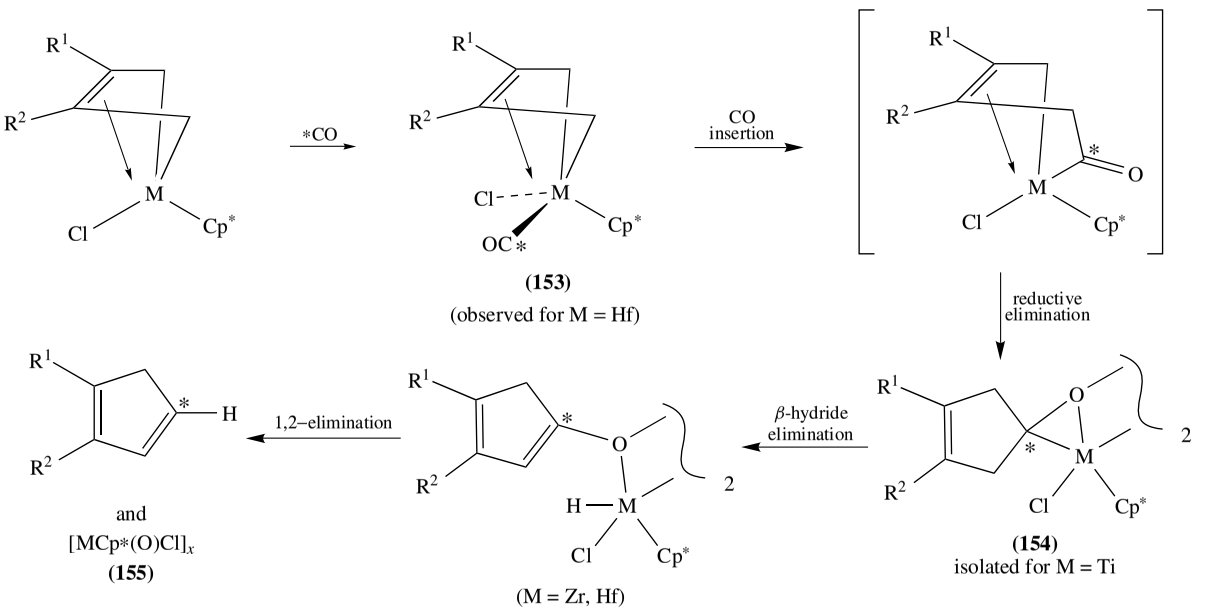
(21)

Carbonylation of (diene)$ZrCp_2$ complexes gives cyclopentenones (Scheme 36)[51]. Since the relative rates of this carbonylation parallel the relative rates for 'envelope flip' of these σ^2, π complexes, it might be speculated that initial coordination of CO to the σ^2-metallacyclopent-3-ene intermediate **12** is involved. (Diene)$Fe(CO)_3$ complexes undergo $AlCl_3$ mediated cyclocarbonylation to afford 2-cyclopentenones, however, the yields are acceptable only for 1,1,3-trisubstituted diene complexes (Scheme 36)[157].



SCHEME 36

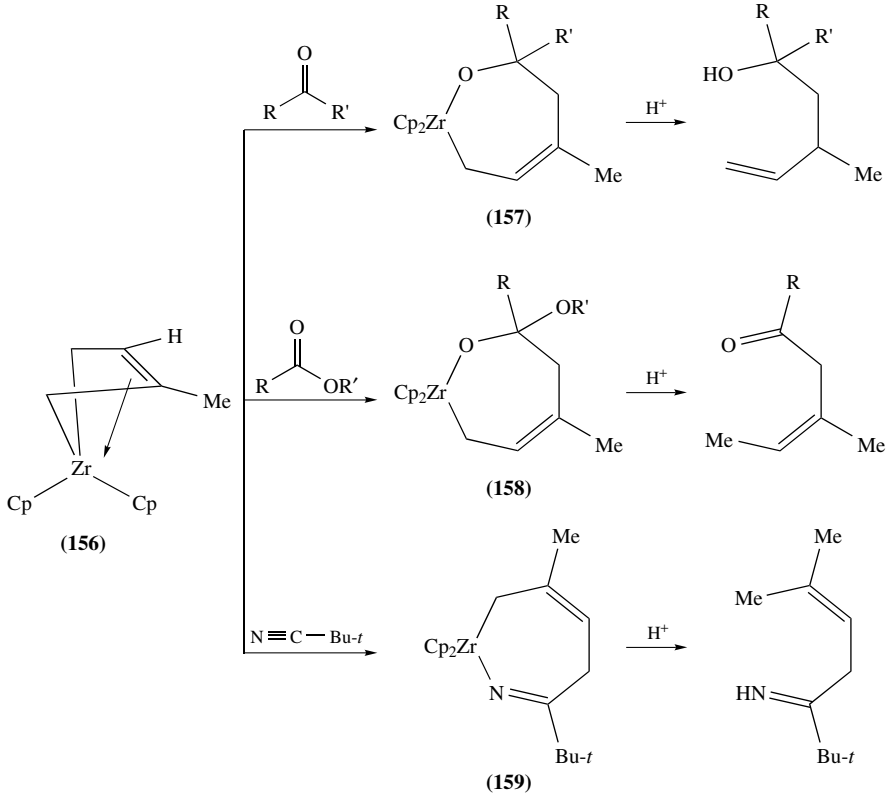
In contrast, exposure of 14-VE (diene)MCp^*Cl complexes (M = Zr, Hf) to CO (1 atm) results in the formation of cyclopentadienes[70]. The mechanism proposed for this transformation was elucidated with a carbon labeled CO (*CO) as requiring an initial coordination of CO to generate a (diene)$MCp^*(CO)Cl$ complex **153** (Scheme 37). For the hafnium complex, the intermediate **153** (M = Hf) was observed by infrared spectroscopy. Insertion of CO into the σ^2, π diene generates a metallacyclohexenone, which undergoes reductive elimination to generate the dimeric metallaoxirane species **154**. β-Hydride elimination from **154** (M = Zr, Hf) followed by 1,2-elimination produces substituted cyclopentadienes and the polymeric metal-oxide **155**. Treatment of (diene)$TiCp^*Cl$ with CO leads to isolation of the metallaoxirane complex **154** (M = Ti).


R1
R2
M
Cl
Cp*
*CO
Cl
M
Cp*
OC*
(153)
(observed for M = Hf)
CO
insertion
R1
R2
*
O
M
Cl
Cp*
reductive
elimination
R1
R2
O
*
M
Cl
Cp*
2
(154)
isolated for M = Ti
β-hydride
elimination
R1
R2
*
O
H
M
Cl
Cp*
2
(M = Zr, Hf)
1,2–elimination
R1
R2
*
H
and
[MCp*(O)Cl]x
(155)

SCHEME 37

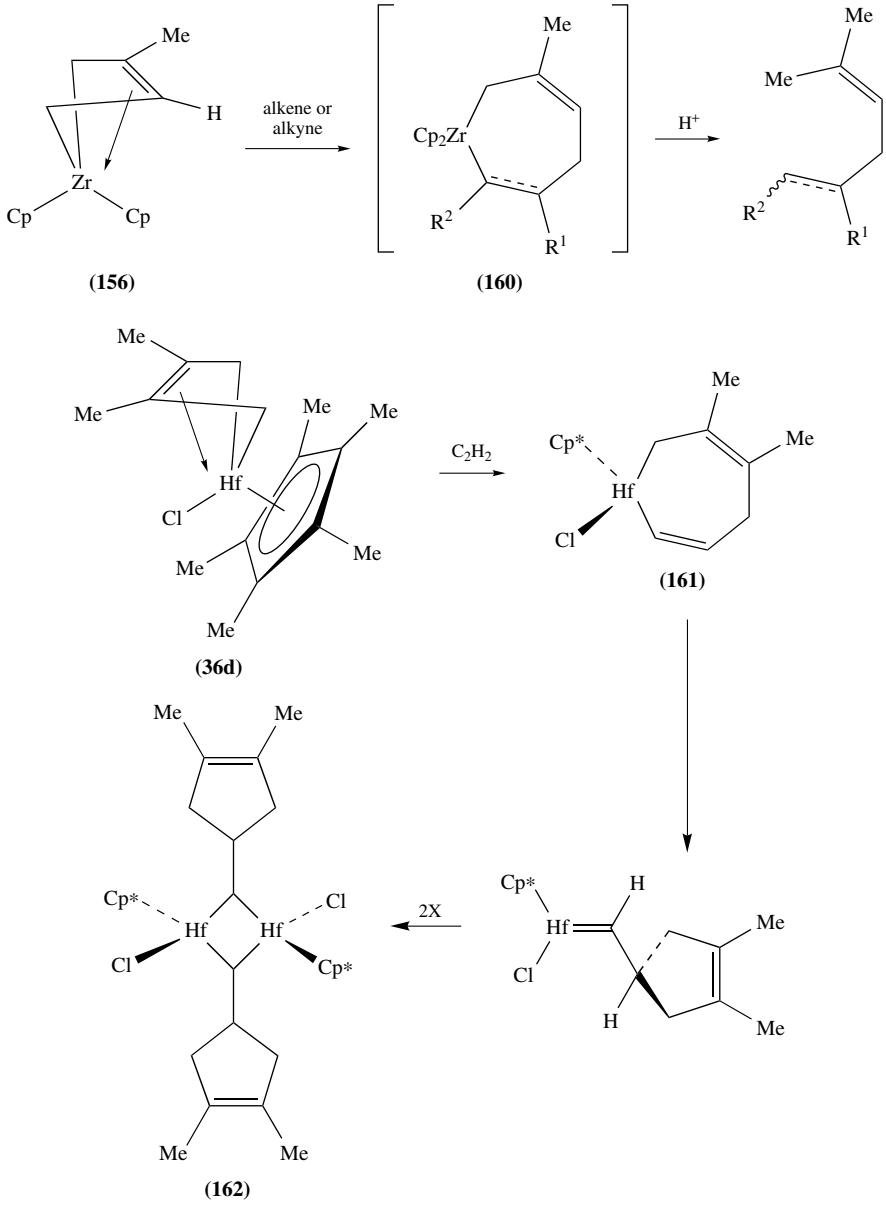
B. Insertion Reactions

Reaction of (isoprene)$ZrCp_2$ **(156)** with ketones[53,158,159], esters[160] and nitriles[159] gives addition products **157**, **158** and **159** respectively (Scheme 38). Protonolysis of **157**, **158** and **159** affords alcohols, ketones, and imines. The addition of ketones to (s-*trans*-C_4H_6)$ZrCp_2$ (s-*trans*-**31**) occurs more rapidly than to (s-*cis*-C_4H_6)$ZrCp_2$ (s-*cis*-**31**), and this evidence implicates a mechanism in which addition of the unsaturated functionality occurs via intermediacy of the η^2-bonded diene complex **32**. Similar insertion reactions have been reported for the (s-*trans*-C_4H_6)$TaCp_2^+$ cation (**38**)[76].



SCHEME 38

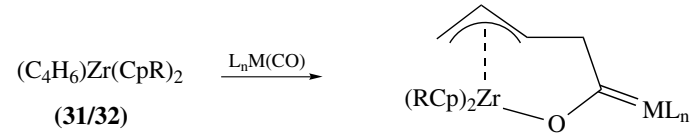
Insertion of alkenes or alkynes to complex **156** generates the metallacycloheptene or metallacycloheptadiene species **160** (Scheme 39)[161]. Protonolysis gives the corresponding hydrocarbons in good yields. In contrast, insertion of acetylene to (2,3-dimethylbutadiene) HfCp*Cl **(36d)** generates the metallacycloheptadiene intermediate **161** which rearranges to the bridging complex **(162)**[162]. The structure of **162** was assigned on the basis of X-ray diffraction analysis.



SCHEME 39

Reaction of (butadiene)$ZrCp_2$ **(31/32)**, and substituted Cp variants, with a wide range of metal–carbonyl complexes, generates the chelated metal–carbene complexes **163** (equation 22)[163]. The crystal structure of a number of these complexes has been determined

by X-ray diffraction analysis.



(31/32) (22)

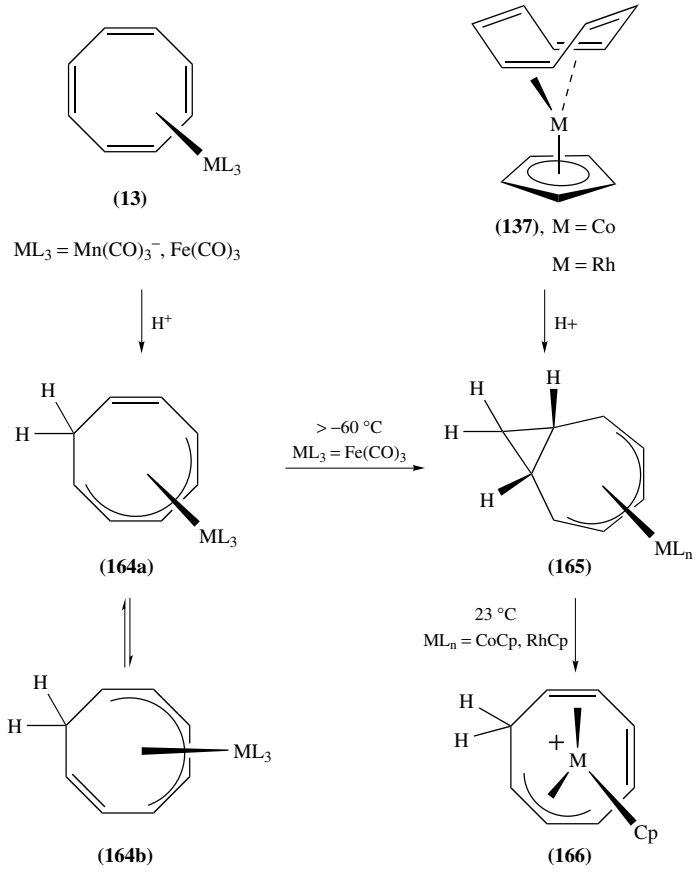
(163) ML_n = $V(CO)_3Cp$, $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $Fe(CO)_4$, $Fe(CO)_3PPh_3$, Co(CO)Cp, Rh(CO)Cp, $Pt(CO)(C_6F_5)_2$

C. Reactions with Electrophiles

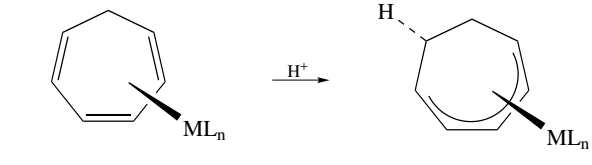
1. Protonation

Brookhart and others have studied the protonation of a variety of (polyene)- and (diene)metal complexes. Protonation of the $(\eta^4 - C_8H_8)Mn(CO)_3^-$ anion [**13**, ML_3 = $Mn(CO)_3^-$], leads to the (η^5-cyclooctatrienyl)$Mn(CO)_3$ complex [**164**, $ML_3 = Mn(CO)_3$, Scheme 40)[56]. This complex exhibits metal migration fluxionality with the uncomplexed olefin within the cyclooctatrienyl ring (eg. **164a** → **164b**). Low-temperature line-shape analysis indicated a free energy of activation for this process of 12.6 kcal mol^{-1}. Upon heating to 65 °C, partial isomerization of **164** to **165** [$ML_n = Mn(CO)_3$) is observed, however, the cyclooctatrienyl complex is still the major species present. Reaction of $(C_8H_8)Fe(CO)_3$ with acid at low temperature (−120 °C, FSO_3H/SO_2F_2) initially generates the (η^5-cyclooctatrienyl)$Fe(CO)_3$ cation [**164**, $ML_3 = Fe(CO)_3^+$] which may be spectroscopically observed[164]. Above −60 °C, cation **164** [$ML_3 = Fe(CO)_3^+$] *irreversibly* rearranges to the bicyclo[5.1.0]octadienyl cation **165** [$ML_n = Fe(CO)_3^+$] which was isolated as a salt. In comparison, protonation of (C_8H_8)CoCp **(137)** leads to the initial formation of a 1 : 1 mixture of the bicyclo[5.1.0]octadienyl cation **165** (ML_n = $CoCp^+$) and the (π-allyl-η^2-olefin) cation (**166**, M = Co)[165]. Upon standing at 23 °C for 48 h, the bicyclo[5.1.0]octadienyl cation completely converts into **166**. Protonation of (C_8H_8)RhCp initially gives only the cation **165** ($ML_n = RhCp^+$). However, as is the case for the Co complex, this eventually isomerizes completely to **166** (M = Rh) (Scheme 40). In contrast, protonation of anionic or neutral (polyene)ML_n complexes, other than those of C_8H_8, gives the corresponding (η^5-dienyl)ML_n complexes or cations (equation 23–25)[50,166,167].

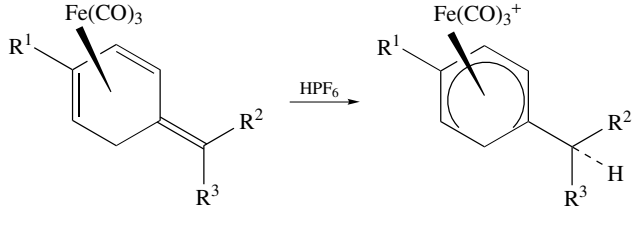
Acid mediated elimination of cyclic (dienyl ether)- and (dienol)$Fe(CO)_2L$ complexes leads to the formation of (cyclodienyl)$Fe(CO)_2L$ cations (equation 26 and 27)[105f,168]. Protonation of (pentadienol)- or (pentadienyl ether)$Fe(CO)_3$ complexes generates the corresponding (pentadienyl)$Fe(CO)_3^+$ cations **167** (Scheme 41)[118]. Lillya and coworkers have demonstrated that ionization of the hydroxyl substituent occurs with anchimeric assistance from iron, and that isomerization of the initially generated transoid pentadienyl cation **168** to the more stable cisoid cation occurs with retention of configuration about the C1−C2 bond[169]. The *in situ* generated transoid pentadienyl cations may also undergo reaction with heteroatom, hydride or carbon nucleophiles to afford substituted (*E*,*E*-diene)$Fe(CO)_3$ products **(169)**[170]. Acyclic (pentadienyl)MCp^+ cations (M = Rh, Ir) may be prepared by acidic dehydration of (dienol)MCp complexes[171].



SCHEME 40



(23)



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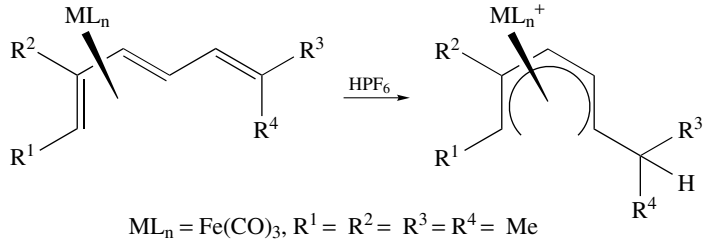
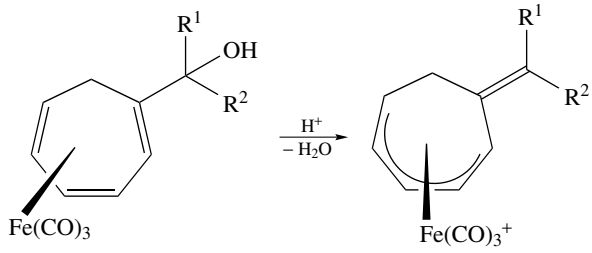


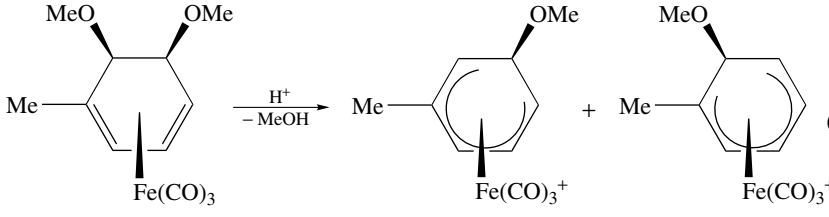
(25)

$ML_n = Fe(CO)_3$, $R^1 = R^2 = R^3 = R^4 = Me$

$ML_n = RhCp$, $R^1 = Ph$, $R^2 = R^4 = H$, $R^3 = COPh$



(26)



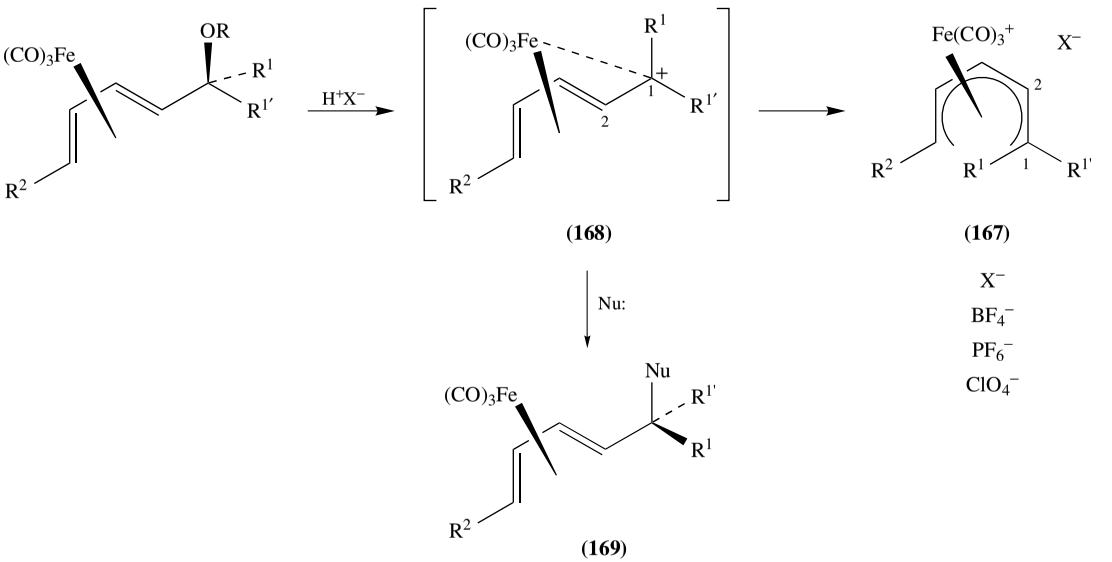
(27)

(1 : 1)

In contrast to the above reactions, protonation of (diene)ML_n complexes **(26)** occurs initially at the metal to give an (η^4-diene)ML_n(H) complex (**27**, Scheme 3)[23,58,63,90,136a]. For third-row transition metal complexes [**26**, ML_n = Os(arene), IrCp*] the M−H bond is stronger than a C−H bond, thus the ground state is this (diene)hydride complex. For the first- and second-row transition metals, [**26**, $ML_n = Mn(CO)_3^-$, $Fe(CO)_3$, $Fe(PR_3)_3$, CoCp, RhCp] the proton is transferred from the metal to the ligand to generate the corresponding (η^3-allyl-μ-hydride)ML_n complexes (**25a**, Scheme 3). As mentioned previously (Section III.C.4) the metal may migrate about a cyclic diene ligand via the intermediacy of (η^4-diene)ML_n(H) **27**. Use of deuteriated acid (instead of proton) leads to deuterium incorporation only at the methylene carbons on the same side as the metal. Protonation of acyclic (diene)$Fe(CO)_3$ complexes with HBF_4/CF_3CO_2H in the presence of CO results in the isolation of (π-allyl)$Fe(CO)_4^+$ cations, while protonation with HX leads to formation of the neutral (π-allyl)$Fe(CO)_3X$ complexes[172].

2. Reaction with carbon electrophiles

a. Triphenylmethylcarbenium ion. The reaction of cyclic (diene)ML_n complexes [ML_n = $Fe(CO)_2L$, $Ru(CO)_3$, $Os(CO)_3$, CoCp, RhCp] with triphenylmethyl carbenium ion (Ph_3C^+) results in abstraction of hydride from the *exo* face of the diene ligand to generate



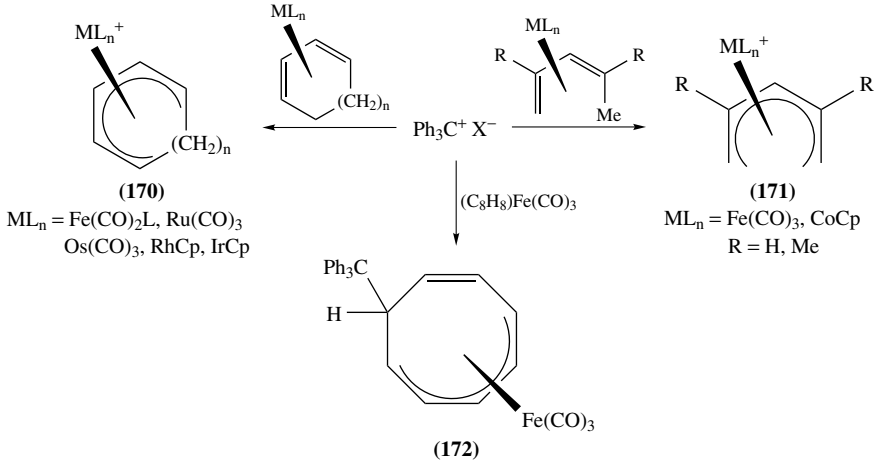
(168) **(167)**

X^-
BF_4^-
PF_6^-
ClO_4^-

(169)

SCHEME 41

(cyclodienyl)ML_n^+ cations (**170**, Scheme 42)[116,117,124a,125,136a,163b,173]. The regioselectivity of hydride abstraction from a variety of substituted (cyclohexadiene)$Fe(CO)_3$ complexes has been examined[116a–c]. There are only a few examples of hydride abstraction for the preparation of *acyclic* (pentadienyl)ML_n^+ cations **(171)**, since the success of this reaction requires the presence of a *cis*-alkyl substituent on the diene[138,174]. In comparison, reaction of Ph_3C^+ with $(C_8H_8)Fe(CO)_3$ generates the (η^5-cyclooctatrienyl)$Fe(CO)_3^+$ cation **172** via C–C bond formation rather than via hydride abstraction[175].

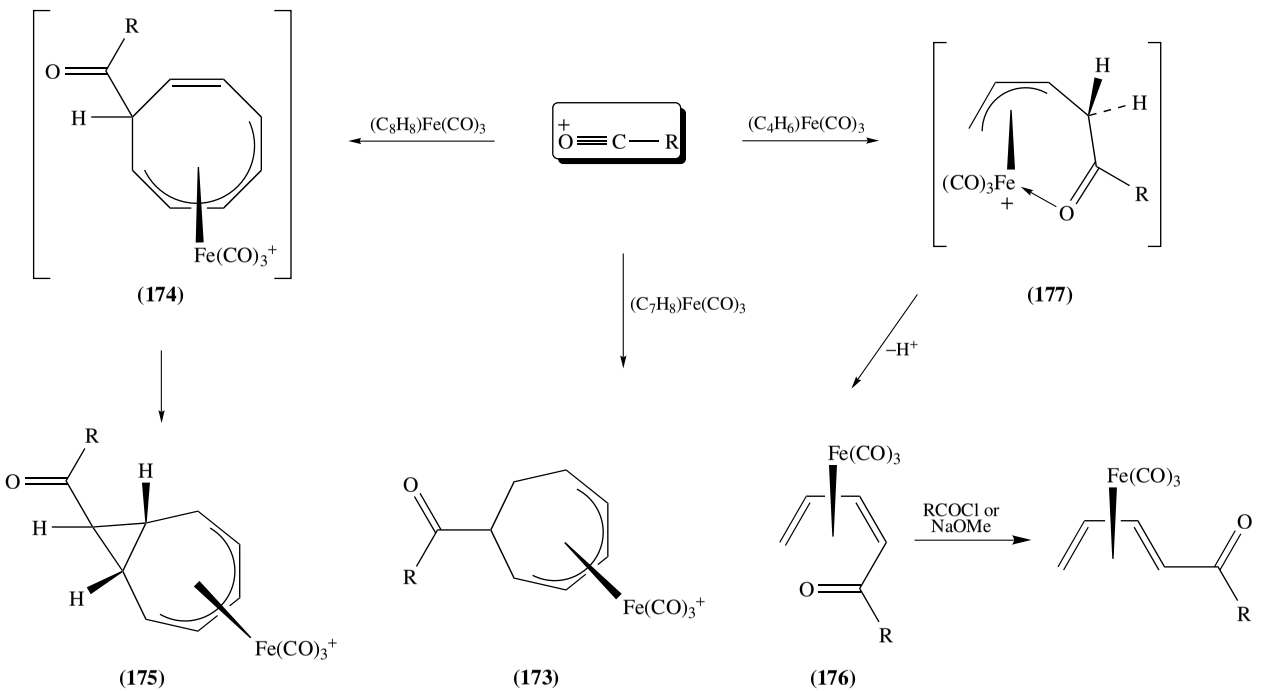


SCHEME 42

b. Acylium ions. Reaction of acylium ions with (cycloheptadiene)- or (cyclooctatetraene)$Fe(CO)_3$ occurs at an uncomplexed double bond to afford the acyl substituted (dienyl) $Fe(CO)_3^+$ cations **173** and **174** respectively (Scheme 43)[176]. While cation **174** is observable by NMR spectroscopy at low temperature, warming the solution results in cyclization to generate the final product **175**. In general, attempted acylation of uncomplexed 1,3-dienes results in polymerization. Coordination of the $Fe(CO)_3$ group moderates the electrophilic acylation of diene complexes to generate the corresponding *cis*-dienone complexes **176** (Scheme 43)[177]. Electrophilic attack occurs on the same face of the ligand as that bound to the metal to initially generate the cationic (η^3-allyl) complex **177**. Deprotonation gives **176**. The initially formed **176** may be subsequently isomerized to the more stable *trans*-dienone complex under the influence of additional acyl halide or base. Substitution is always observed to occur at the diene termini. In contrast to former assertions in the literature, Franck-Neumann and coworkers have reported that complexes bearing electron-withdrawing substituents slowly undergo acylation in the presence of two or more equivalents of $AlCl_3$[177a]. Electrophilic substitution of (diene)$Fe(CO)_3$ complexes with alkoxychloromethane or with orthochloroformates has been reported[178]. Acylation of the (cyclohexadiene)RhCp complex occurs at the cyclopentadienyl ligand[136a].

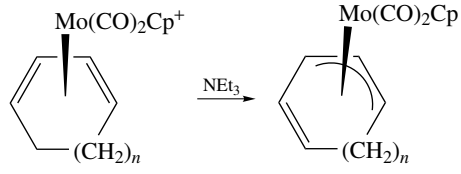
D. Deprotonation

A number of cationic (diene)metal complexes undergo α-deprotonation. Treatment of (cyclodiene)$Mo(CO)_2Cp^+$ cations (e.g. **44**) with NEt_3 or other non-nucleophilic bases

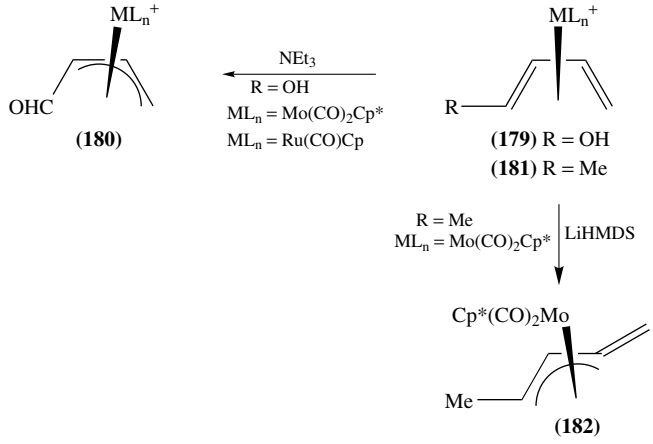

R
O
H
Fe(CO)3+
(174)
(C8H8)Fe(CO)3
+
O C R
(C4H6)Fe(CO)3
H
H
(CO)3Fe
+
O
R
(177)
(C7H8)Fe(CO)3
–H+
R
O
H
H
H
Fe(CO)3+
(175)
O
R
Fe(CO)3+
(173)
Fe(CO)3
O
R
(176)
RCOCl or
NaOMe
Fe(CO)3
O
R

SCHEME 43

yields the neutral (η^3-cyclodienyl)Mo(CO)$_2$Cp complexes (**178**, equation 28)[81b,179]. Deprotonation of (1-hydroxy-1,3-butadiene) cations **179** [ML_n = Mo(CO)$_2$Cp*, Ru(CO)Cp] with NEt_3 affords the *anti*-1-formyl-π-allyl products **180**[30,32] while the (1,3-pentadiene)Mo(CO)$_2$Cp^{*+} cation **(181)** requires a stronger base for deprotonation to give **182** (Scheme 44)[87].



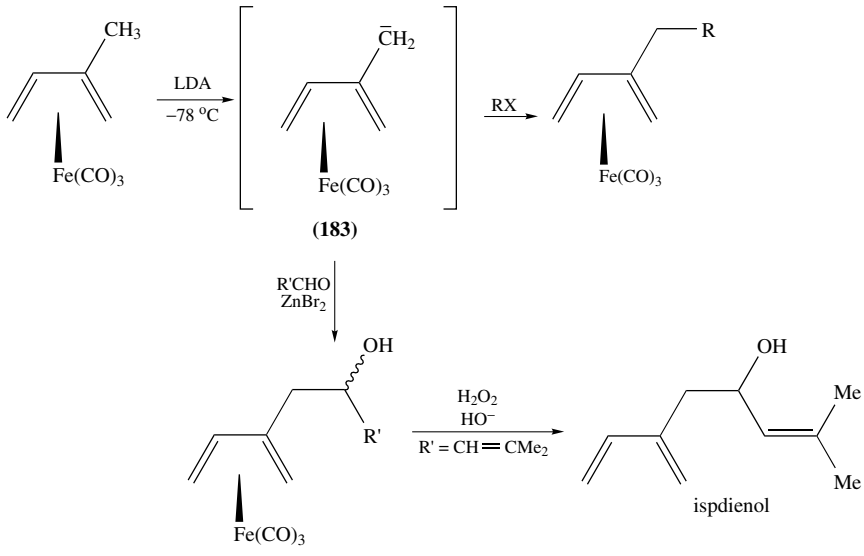
(44) $n = 1, 2$ **(178)** $n = 1, 2$ (28)



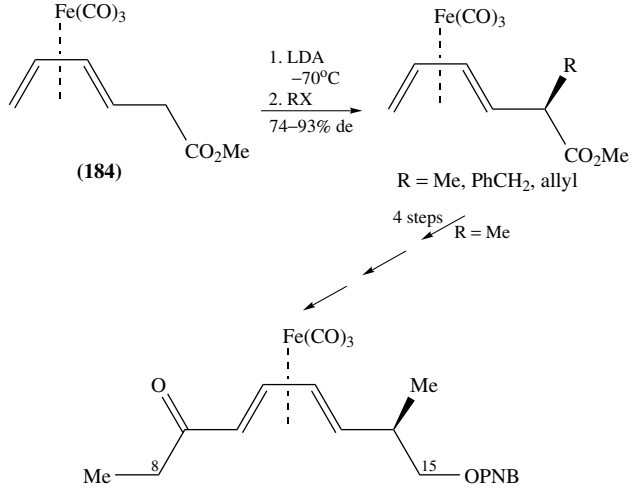
(180) **(179)** R = OH **(181)** R = Me **(182)**

SCHEME 44

In contrast, deprotonation of neutral (diene) metal complexes results in the formation of carbanions. Deprotonation of (isoprene)Fe(CO)$_3$ with LDA (−78 °C) generates the anion **183** (Scheme 45)[180]. The anion reacts directly with alkyl, benzyl or allyl halides or, in the presence of $ZnBr_2$, with aldehydes. The insect pheromone, ipsdienol, has been prepared by this method. In a similar fashion, deprotonation of cyclic and acyclic (diene)Fe(CO)$_3$ complexes bearing an electron-withdrawing group occurs α to this group and on the *exo* face of the complex. Alkylation of the resultant cyclic anions occurs in a diastereospecific fashion, also on the *exo* face of the ligand due to the steric bulk of the metal–ligand array[181]. This has been extended to acyclic dienes; alkylation of (methyl 3,5-hexadienoate)Fe(CO)$_3$ **(184)** occurs in a highly diastereoselective fashion (Scheme 46)[182]. This is proposed to occur via approach of the electrophile to the s-*trans* rotamer of the ester enolate anion on the face opposite to Fe(CO)$_3$. This methodology, along with electrophilic acylation (Section V.C.2.b), was utilized in the preparation of the C8–C15 segment of protomycinolide IV. Attempts to generate and alkylate a dithianyl anion adjacent to (butadiene)Fe(CO)$_3$ were unsuccessful[183].



SCHEME 45

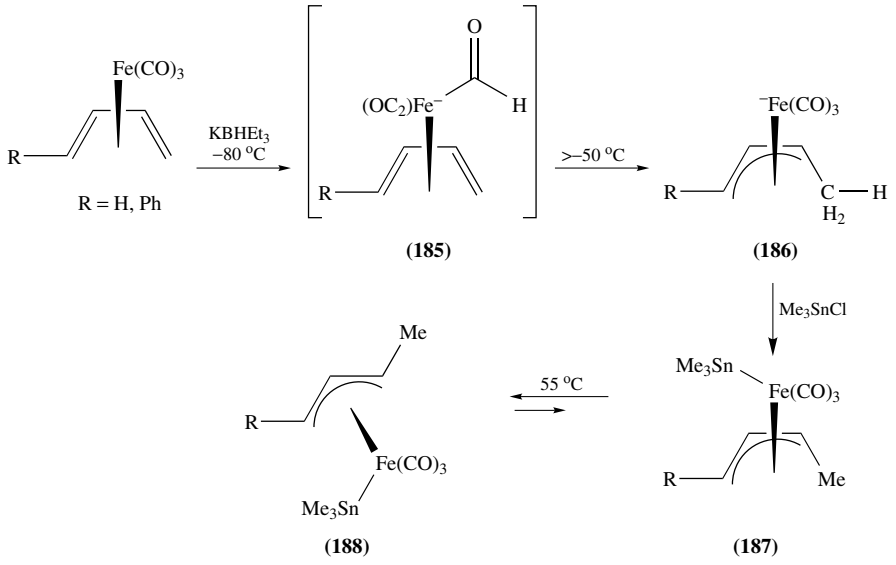


SCHEME 46

E. Nucleophilic Addition

1. Neutral (diene)iron complexes

Zerovalent transition metal carbonyl moieties may act as electron acceptors, and thus activate coordinated polyene ligands toward nucleophilic attack. Reaction of (C_4H_6)-$Fe(CO)_3$ with $KBHEt_3$ ($-80\,^{\circ}C$) proceeds via attack at a coordinated carbon monoxide to generate the anionic iron-formyl species **185** (Scheme 47)[184]. Upon warming to

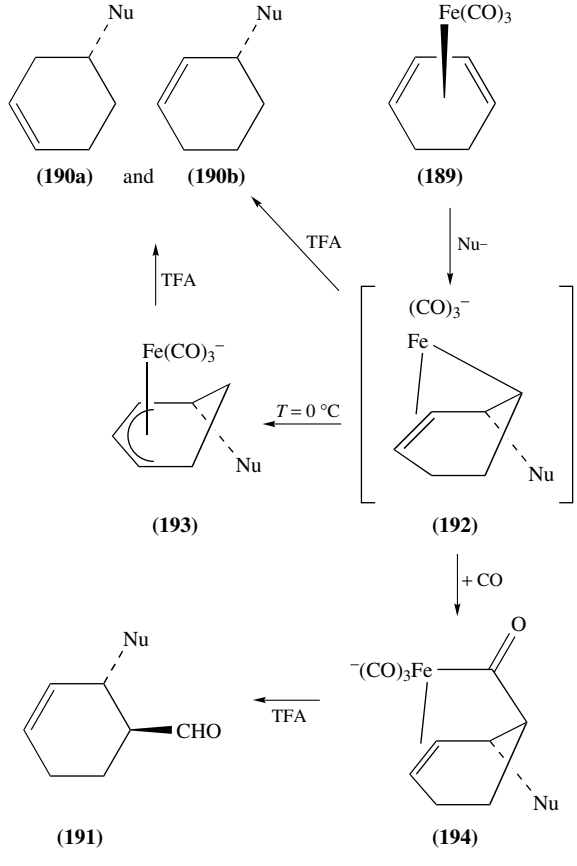


SCHEME 47

−50 °C, complex **185** isomerizes to the (*anti*-allyl)$Fe(CO)_3^-$ anion **(186)**, which may be trapped by reaction with Me_3SnCl to give the corresponding (*anti*-crotyl)$Fe(CO)_3SnMe_3$ complex **(187)**. Isomerization of **187** to the thermodynamically more stable (*syn*-crotyl) isomer **(188)** occurs only at a higher temperature (55 °C).

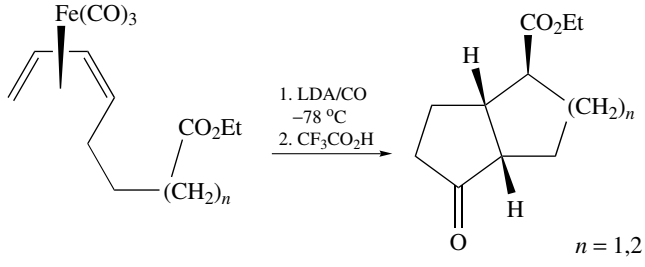
In contrast, reaction of (cyclohexadiene)$Fe(CO)_3$ **(189)** with strong carbon nucleophiles (conjugate acid $pK_a > ca\,28$) in THF/HMPA/−78 °C, followed by protic workup, gives cyclohexene products **190a** and **190b** (Scheme 48)[185]. If the reaction is run under an atmosphere of carbon monoxide, products incorporating CO (e.g. **191**) may be obtained. This reaction is proposed to occur via nucleophilic attack at an internal diene carbon on the face opposite to iron, to afford a (1,3,4-η^3-butenyl)$Fe(CO)_3^-$ anion **192** which has been partially characterized by ^1H NMR spectroscopy at low temperature (−60 °C)[186]. Upon warming the solution to 0 °C, the signals attributed to **192** disappear and are replaced by signals corresponding to the (allyl)$Fe(CO)_3^-$ species **193**. Protonation of either **192** or **193** gives the olefinic products **190a** and **190b**. Under a positive pressure of carbon monoxide, CO insertion into **192** gives the anionic acyl species **194** which has been characterized by IR and ^1H NMR spectroscopy[186]. Protonation of **194** yields **191**.

Examination of the reactivity of acyclic (diene)$Fe(CO)_3$ complexes indicates that this nucleophilic addition is reversible. The reaction of $(C_4H_6)Fe(CO)_3$ with strong carbon nucleophiles, followed by protonation, gives olefinic products **195** and **196** (Scheme 49)[187]. The ratio of **195** and **196** depends upon the reaction temperature and time. Thus, for short reaction time and low temperature (0.5 h, −78 °C) the product from attack at C2 (i.e. **195**) predominates while at higher temperature and longer reaction time (2 h, 0 °C) the product from attack at C1 (i.e. **196**) predominates . This selectivity is rationalized by kinetically controlled attack at the more electron-poor carbon (C2) at low temperature. Nucleophilic attack is reversible and, under conditions where an equilibrium is established, the thermodynamically more stable (allyl)$Fe(CO)_3^-$ is favored. The regioselectivity for nucleophilic attack on substituted (diene)$Fe(CO)_3$ complexes has been reported[187]. The

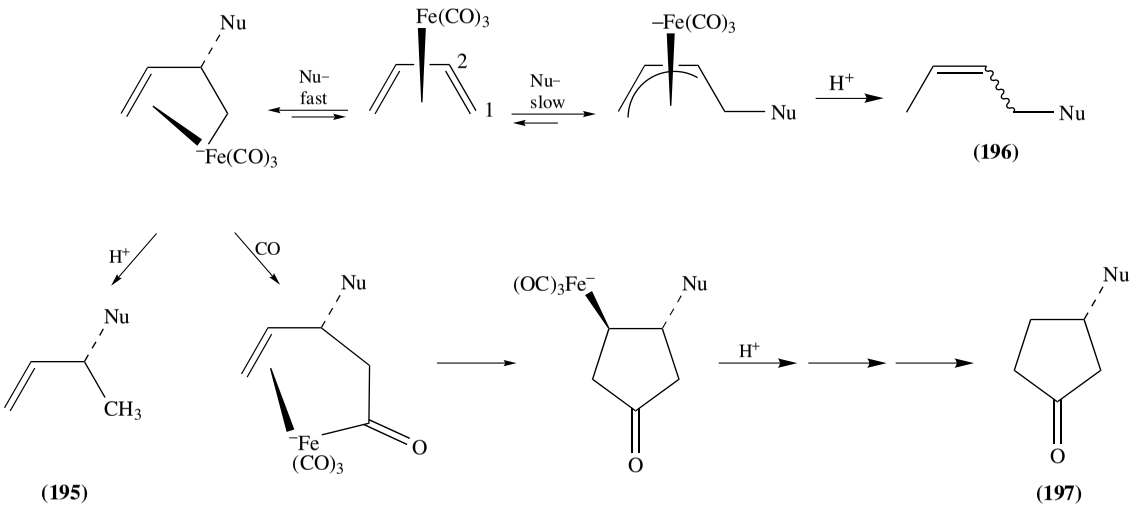


SCHEME 48

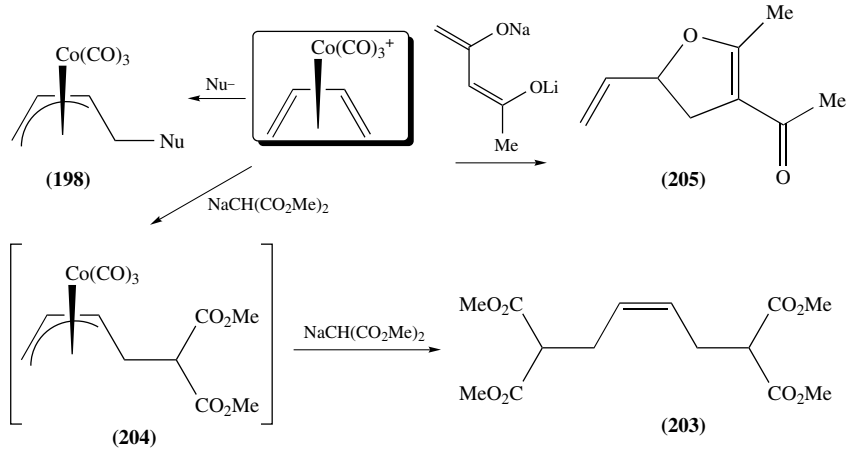
reaction of $(C_4H_6)Fe(CO)_3$ with carbon nucleophiles under CO pressure (*ca* 2 atm, $-78 \rightarrow 0\,^{\circ}C$) gives cyclopentanone products (**197**, Scheme 49)[188]. Intramolecular variants of this reaction have been reported for the preparation of bicyclo[*n*.3.0]alkanones (equation 29)[189].



(29)


Nu
Fe(CO)3
Nu–
fast
2
1
Nu–
slow
–Fe(CO)3
Nu
H+
Nu
(196)
H+
CO
Nu
CH3
(195)
Nu
–Fe
(CO)3
O
(OC)3Fe–
Nu
O
H+
Nu
O
(197)

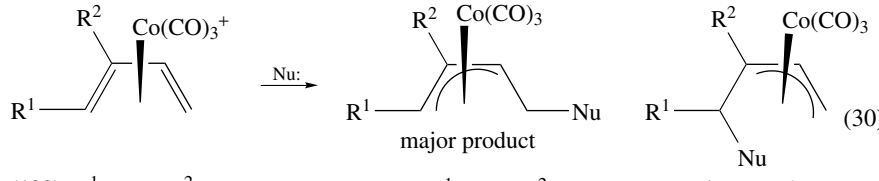
SCHEME 49



SCHEME 50

2. Cationic (diene)cobalt complexes

The reaction of (diene)$Co(CO)_3^+$ cations with a range of carbon and heteroatom nucleophiles has been examined. As might be expected, since these are positively charged species the range of nucleophiles which are reactive is more extensive than for neutral (diene)$Fe(CO)_3$ complexes (see Section V.E.1) and includes such nucleophiles as pyridine and phosphines. In contrast to the (diene)$Fe(CO)_3$ complexes, nucleophilic attack on the (diene)$Co(CO)_3^+$ cations occurs exclusively at the diene terminus to give neutral (*anti*-1-substituted-allyl)$Co(CO)_3$ complexes **198** in 'moderate to good yield' (Scheme 50)[28]. The regioselectivity for nucleophilic attack on substituted (diene)$Co(CO)_3^+$ cations has been examined[134b]. In general, for hydride, phenyl magnesium bromide or pyridine as nucleophile, attack at the less hindered diene terminus is preferred; 1-substituted (diene)$Co(CO)_3^+$ cations **199** give predominantly **200**, while 2-substituted (diene)$Co(CO)_3^+$ cations **201** give predominantly **202** (equation 30).



(199) $R^1 = Me$, $R^2 = H$ **(200)** $R^1 = Me$, $R^2 = H$

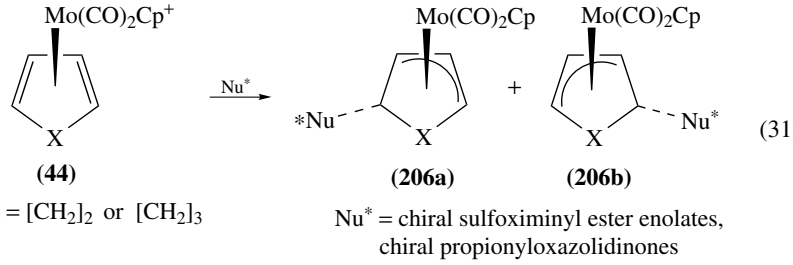
(201) $R^1 = H$, $R^2 = Et$ **(202)** $R^1 = H$, $R^2 = Et$

The neutral (allyl)$Co(CO)_3$ products are themselves susceptible to nucleophilic attack. Thus reaction of $(C_4H_6)Co(CO)_3^+$ with *two* equivalents of sodium dimethyl malonate anion gives the tetraester **203**, presumably via initial attack at C1 to generate the intermediate π-allyl complex **204** followed by regiospecific attack by the second equivalent at C4 (Scheme 50)[28]. The intramolecular variant of this reaction using a single equivalent of a dinucleophile, such as a β-dicarbonyl dianion or the corresponding 1,3-bis(silyloxy)diene, leads to the formation of vinyldihydrofuran products **205**[190]. For these reactions, it would

appear that initial electrophilic attack occurs at what is the less reactive nucleophilic site of the dianion/bis(silyloxy)diene. The mechanistic details of this annulation are not yet complete.

3. Cationic (diene)molybdenum complexes

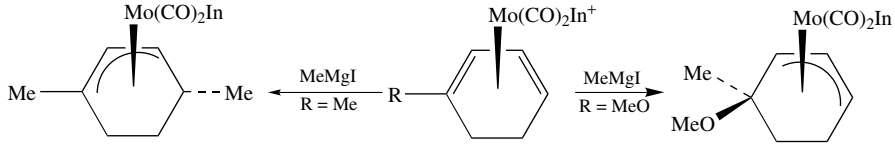
Cyclic (diene)$Mo(CO)_2L^+$ (L = Cp, Cp* or indenyl) cations react with a variety of carbon and heteroatom nucleophiles to generate (π-allyl)Mo complexes[84]. In a fashion similar to the (diene)Co^+ cations (Section V.E.2), nucleophilic atttack on the (diene)Mo^+ cations occurs exclusively at the terminal carbons of the diene. While the products from reaction of amine or alkoxide nucleophiles are difficult to handle, those resulting from reaction with carbon nucleophiles are relatively stable. In these cases, nucleophilic attack occurs on the face of the diene ligand opposite to the metal. For C_s symmetric cations **44** (X = $[CH_2]_2$ or $[CH_2]_3$), reaction with chiral nucleophiles(Nu*) gives mixtures of diastereomers **206a** and **206b** with moderate to good diastereoselectivity (10–86% de) (equation 31)[191]. The regioselectivity of nucleophilic attack on unsymmetrically substituted (cyclodiene)Mo^+ cations has been extensively studied. For 1-alkyl substituted complexes **(207)**, nucleophilic attack occurs at the unsubstitued terminus presumably due to steric hindrance, while for 1-alkoxy substituted complexes **(208)** attack occurs at the substitued terminus (Scheme 51)[81b]. A substituent on one of the sp^3 carbons of a (cyclohexadiene)Mo^+ cation (e.g. **52**) directs nucleophilic attack exclusively at the opposite terminus to give **209** (Scheme 52)[84a,c,179b,192]. Since complexes **52** may be readily prepared from the parent (cyclohexadiene)Mo^+ cations via nucleophilic addition, followed by hydride abstraction (see Scheme 13), these steps constitute a method for the preparation of a *cis*-1,3-disubstituted cyclohexene. This methodology has been utilized for the stereocontrolled synthesis of the C4–C9 segment of tylosin[192]. For similarly substituted (cycloheptadienyl)Mo^+ cations (e.g. **53**) nucleophilic attack occurs predominantly at the less hindered diene terminus. However, a minor amount of the other regioisomeric product is obtained depending upon the steric bulk of the nucleophile[84b].



(44) (206a) (206b) (31)

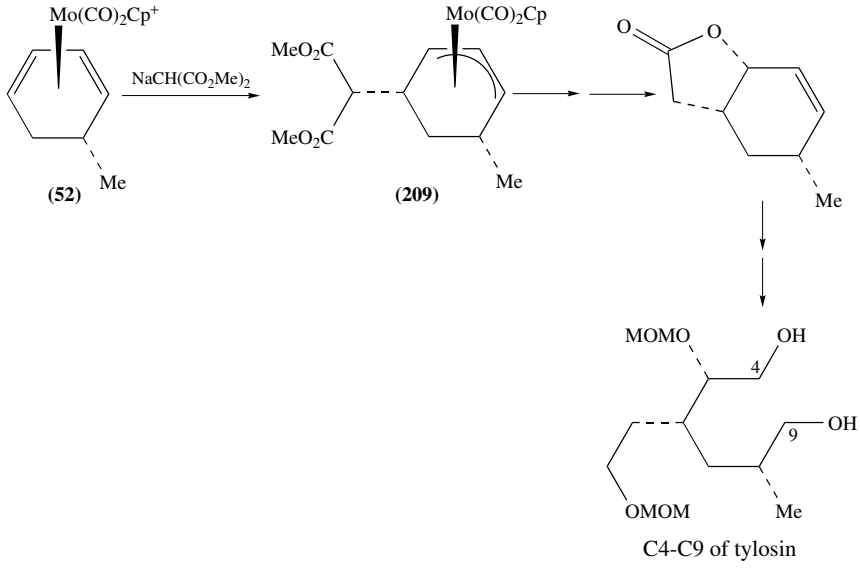
X = $[CH_2]_2$ or $[CH_2]_3$

Nu* = chiral sulfoximinyl ester enolates, chiral propionyloxazolidinones

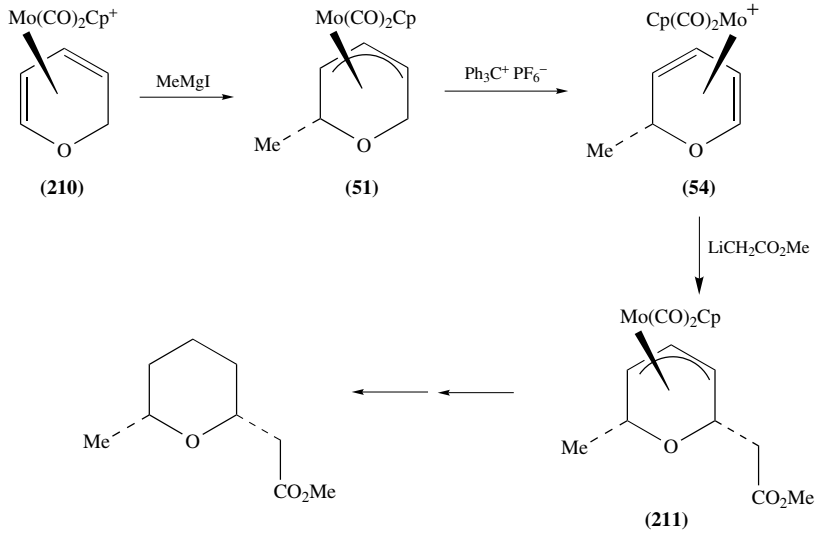


(207) R = Me
(208) R = OMe

SCHEME 51



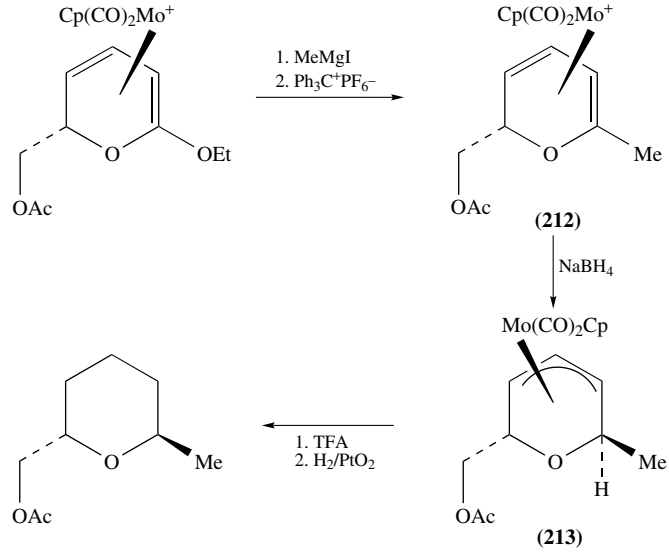
SCHEME 52



SCHEME 53

Liebeskind and coworkers have examined the reactivity of (2*H*-pyran)$Mo(CO)_2Cp^+$ cations **210**, which may be prepared in optically active form from carbohydrate precursors. Nucleophilic attack on cation **210** occurs at the diene terminus bonded to the ring oxygen to give π-allyl complexes **51** (Scheme 53)[85]. Hydride abstraction from **51** gives the cation **54**; addition of a second nucleophilie occurs regioselectively to give

a *cis*-2,6-disubstituted (pyranyl)Mo complex **211**. This methodology has been utilized for the preparation of a scent secretion of *Viverra civetta*. Preparation of a *trans*-2,6-disubstituted (pyranyl)Mo complex **(213)** is also possible via hydride addition to the substituted (2*H*-pyran)$Mo(CO)_2Cp^+$ cation **212** (Scheme 54)[86].



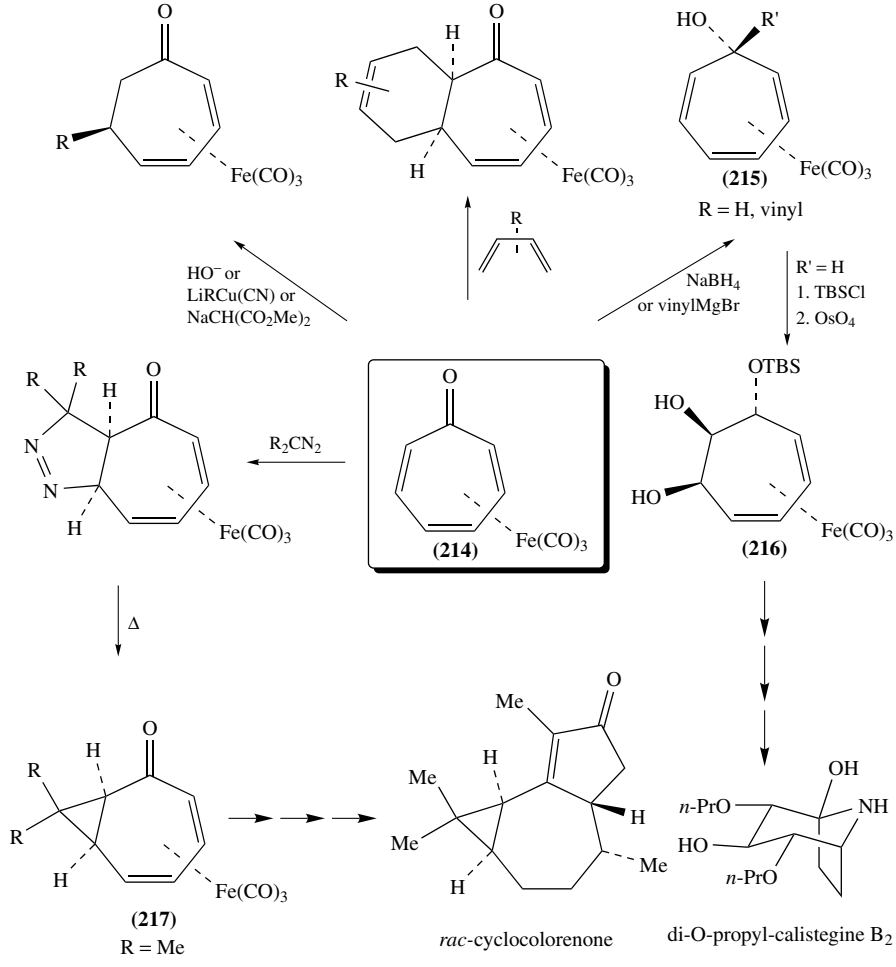
SCHEME 54

Nucleophilic addition to acyclic (diene)Mo^+ cations has been examined. For (isoprene) $Mo(CO)_2L$ (L = Cp, Cp*, In), the regioselectivity for nucleophilic attack has been found to depend on the nature of the nucleophile, the ligand L, the reaction solvent and the temperature[21,81a,83a,193]. The generation and *in situ* reactivity of transoid acyclic (diene)molybdenum and tungsten cations with nucleophiles has been previously mentioned (Section IV.C.2).

F. Use of the Metal as a Stereodirecting Functionality

In general, reagents approach a (diene)metal complex on the face opposite to the metal due to the steric bulk of the attached metal-ligand array. Due to the relatively low cost of iron, the vast majority of examples of these type of reactions utilize the $Fe(CO)_3$ fragment.

Tropone reacts with nucleophiles at C2 via an extended Michael addition and undergoes [6 + 2] cycloaddition reactions. In contrast, (tropone)$Fe(CO)_3$ **(214)** undergoes conjugate addition at C-3 and reacts with dienes via [4 + 2] cycloaddition (Scheme 55)[194]. Addition of borohydride or vinyl magnesium bromide to **214** gives cycloheptatrienols **(215)**[194a,195]. Osmylation and hydroboration/oxidation of cyclic trienes proceeds stereospecifically on the face opposite to the metal[195]. The partially protected (cycloheptadienetriol)iron complex **216** has been utilized in a synthesis of di-*O*-propyl-calistegine B_2. Complex **214** undergoes [3 + 2] cycloaddition with diazoalkanes to give the corresponding pyrazoline, which upon heating extrudes N_2 to give the bicyclo[5.1.0]octa-3,5-dien-2-one complex **(217)**[196]. Complex **217** (R = Me) has been used in a synthesis of cyclocolorenone[196b].

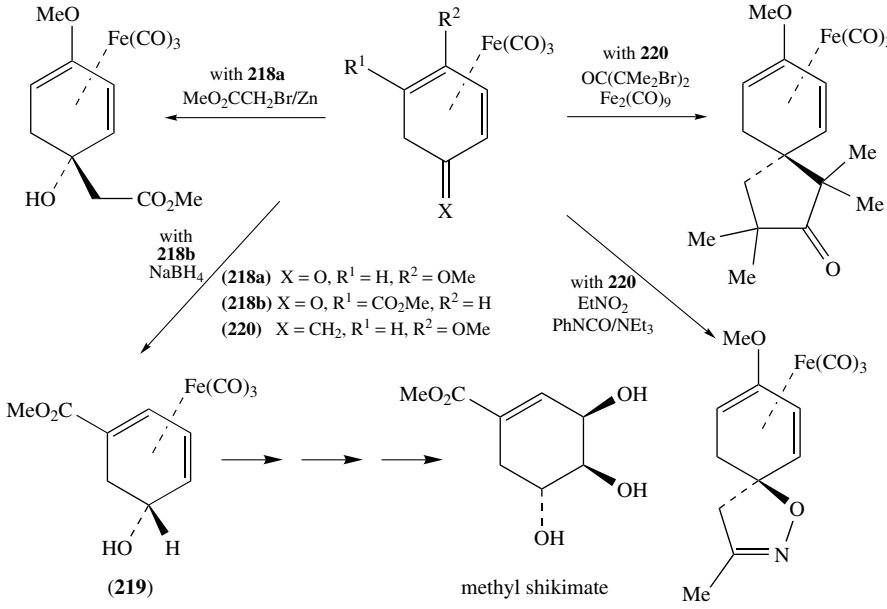


SCHEME 55

All of these reactions occur on the face of the ligand opposite to the sterically bulky $Fe(CO)_3$ moiety.

Nucleophilic additions to (cyclohexadienone)$Fe(CO)_3$ complexes **(218)** occur in a diastereospecific fashion (Scheme 56)[197]. For example, the Reformatsky reaction of ketone **(218a)** affords a simple diasteromeric alcohol product[197b]. The reduction of (1-carbomethoxycyclohexa-1,3-dien-5-one)$Fe(CO)_3$ **(218b)** to give **219** has been utilized in the enantioselective synthesis of methyl shikimate. In a similar fashion, cycloadditions of (2-methoxy-5-methylenecyclohexa-1,3-diene)$Fe(CO)_3$ **(220)** occur in a diastereospecific fashion[198].

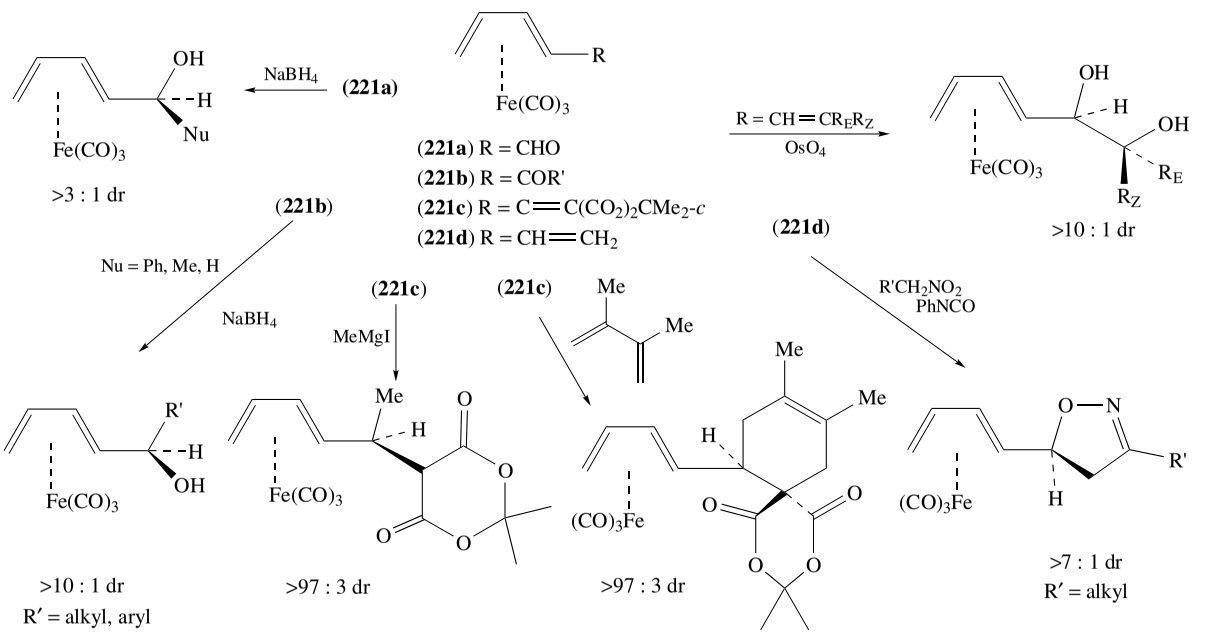
In comparison to the above *diastereospecific* reactions of cyclic polyene complexes, the reaction of acyclic (diene)$Fe(CO)_3$ complexes **(221)** with pendant unsaturated functionality has been found to occur in a *diastereoselective* fashion. The diastereoselectivity in



SCHEME 56

these reactions depends, in part, on the unsaturated functionality occupying a preferred, or more reactive, conformer about the diene-to-unsaturated functionality bond. Nucleophilic addition to (2*E*,4-dienal)$Fe(CO)_3$ complexes (**221a**) proceeds with variable diastereoselectivity, depending on both the complex and the nucleophile (Scheme 57)[199]. In general, the diastereomeric secondary alcohol products are easily separable by chromatography, with the Ψ-*exo* isomer being less mobile than the Ψ-*endo* isomer[200]. In comparison, reduction of the corresponding (*E*,*E*-dienone)$Fe(CO)_3$ complex (**221b**) proceeds with high diastereoselectivity (>90% de) to afford predominantly the Ψ-*endo* alcohol (Scheme 57)[201]. This high diastereoselectivity has been rationalized on the basis of the approach of borohydride to the dienone in the s-*trans* conformer on the face opposite to the bulky $Fe(CO)_3$ adjunct[201b,c]. Nucleophilic addition to complexed dienals has been utilized in the enantioselective syntheses of 5-HETE methyl ester[199b], AF toxin IIc[199c], LTB_4[199d], the LTB_4 antagonist SM 9064[199e] and lipoic acid methyl ester[199f], while reduction of a complexed dienone was utilized in an enantiospecific synthesis of LTA_4[201a]. Michael addition to activated (triene)$Fe(CO)_3$ complexes [**221c**] proceeds in a stereospecific fashion; only the *exo*-methyl adduct is obtained (Scheme 57)[202]. This reactivity has been utilized in the synthesis of (−)-verbenalol and (−)-epiverbenalol[202a] and the *as*-indacene unit of ikarugamycin[202b].

The cycloaddition of (triene)$Fe(CO)_3$ complexes occurs in a highly diastereoselective fashion via approach of the organic component to the complex in the s-*trans* conformation on the face opposite to the metal. Thus the Diels–Alder cycloaddition of the activated (triene)$Fe(CO)_3$ complex [**221c**] is reported to afford a single cycloadduct[203]. Intermolecular addition of nitrile oxides to triene complexes (**221d**) results in the formation of the corresponding isoxazolines in good yield, with good diastereoselectivity (*ca*


NaBH4
(221a)
R
Fe(CO)3
(221a) R = CHO
(221b) R = COR'
(221c) R = C═C(CO2)2CMe2-c
(221d) R = CH═CH2
R = CH═CREZRZ
OsO4
OH
H
OH
RE
RZ
>10 : 1 dr
(221b)
Nu = Ph, Me, H
NaBH4
R'
H
OH
>10 : 1 dr
R′ = alkyl, aryl
(221c)
MeMgI
Me
H
O
O
O
O
>97 : 3 dr
(221c)
Me
Me
(CO)3Fe
>97 : 3 dr
(221d)
R'CH2NO2
PhNCO
O—N
R'
H
(CO)3Fe
>7 : 1 dr
R′ = alkyl

SCHEME 57

80% de) (Scheme 57)[204]. This methodology has been used in an enantioselective synthesis of (+)-gingerol[204b], the carbon skeleton of (+)-streptenol D[204c] and the C11−C24 fragment of macrolactin A[170b].

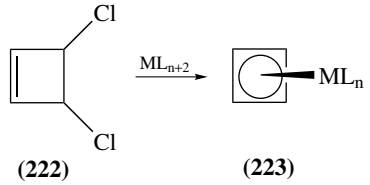
Osmylation of C−C double bonds adjacent to the (diene)$Fe(CO)_3$ functionality has been reported (Scheme 57)[205]. This methodology has been used in the enantiospecific synthesis of 5,6- and 11,12-diHETEs.

VI. PREPARATION OF CYCLOBUTADIENE–METAL COMPLEXES

The synthesis and reactivity of cyclobutadiene–metal complexes was extensively reviewed in 1977 by Efraty[15]. While the following two sections will mostly deal with newer developments, pertinent information from this review may be briefly presented in the following sections. Since most cyclobutadienes are highly reactive species, direct complexation of the ligand is generally not possible. Only one example has been reported; the reaction of $Fe_2(CO)_9$ with 1,2,3-tri-*t*-butyl-4-trimethylsilyl-1,3-cyclobutadiene gives the corresponding $Fe(CO)_3$ complex[206].

A. Preparation from Four-membered Ring Precursors

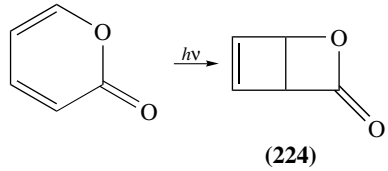
The reduction of 3,4-dichlorocyclobutene **(222)** in the presence of metal carbonyls has been utilized to prepare the parent complex [**223**, $ML_n = Cr(CO)_4$, $Mo(CO)_3$, $W(CO)_3$, $Fe(CO)_3$, $Ru(CO)_3$ or $Co_2(CO)_6$] (equation 32)[15]. More recently, reaction of $Ni(CO)_4$ with 3,4-dihalocyclobutenes (X = Br or I) or with **222** in the presence of $AlCl_3$ produced the corresponding (cyclobutadiene)nickel dihalides[207]. Methodology for the preparation of 1,2- or 1,3-disubstituted (cyclobutadiene)$Fe(CO)_3$ complexes from 1,2- or 1,3-disubstituted-3,4-dibromocyclobutenes has been presented[15,208]. In turn, the substituted dibromocyclobutenes are prepared from squaric esters. The reaction of *cis*-3,4-carbonyldioxycyclobutene and substituted variants with $Fe_2(CO)_9$ or $Na_2Fe(CO)_4$ also produces (cyclobutadiene)$Fe(CO)_3$ complexes[15,209]. Photolysis of α-pyrone generates 3-oxo-2-oxabicyclo [2.2.0]hex-5-ene **(224)** which undergoes photolysis with a variety of metal carbonyls to afford the parent cyclobutadiene complex **223** [$ML_n = CpV(CO)_2$, $Fe(CO)_3$, CoCp, or RhCp] (equation 33)[15,210].



(222) **(223)**

ML_n	
$Cr(CO)_4$	$Fe(CO)_3$
$Mo(CO)_4$	$Ru(CO)_3$
$W(CO)_4$	$Co_2(CO)_6$
	NiX_2

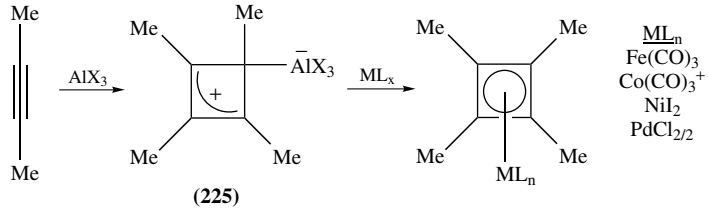
(32)



(224) **(223)**

ML_n
$CpV(CO)_2$
$Fe(CO)_3$
CoCp
RhCp

(33)



(225)

SCHEME 58

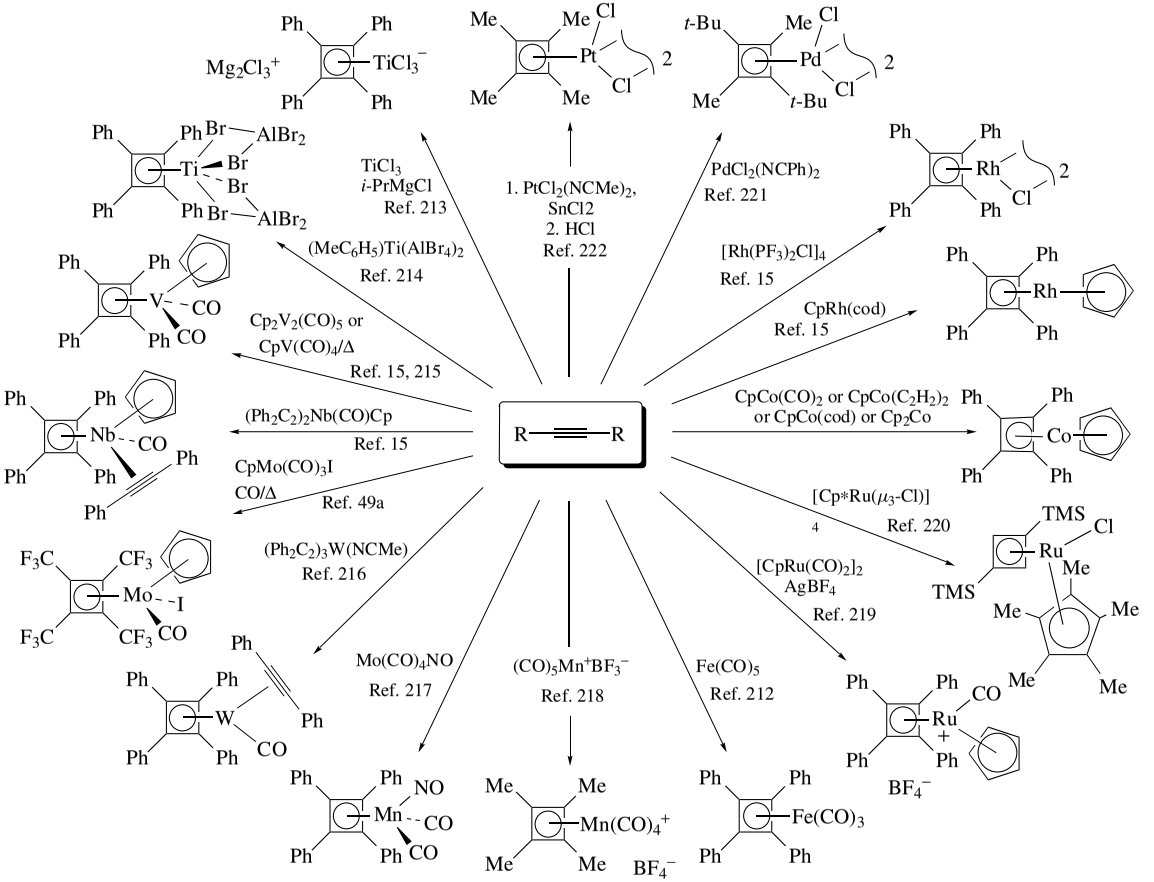
The reaction of alkynes with AlX_3 at $-78\,^{\circ}C$ has been shown, by NMR spectroscopy, to generate a zwitterionic σ-cyclobutadiene aluminum species **225** (Scheme 58)[211a]. Transfer of the cyclobutadiene ligand from **225** to a variety of transition metals has been reported[211].

B. Preparation by Alkyne Cyclodimerization

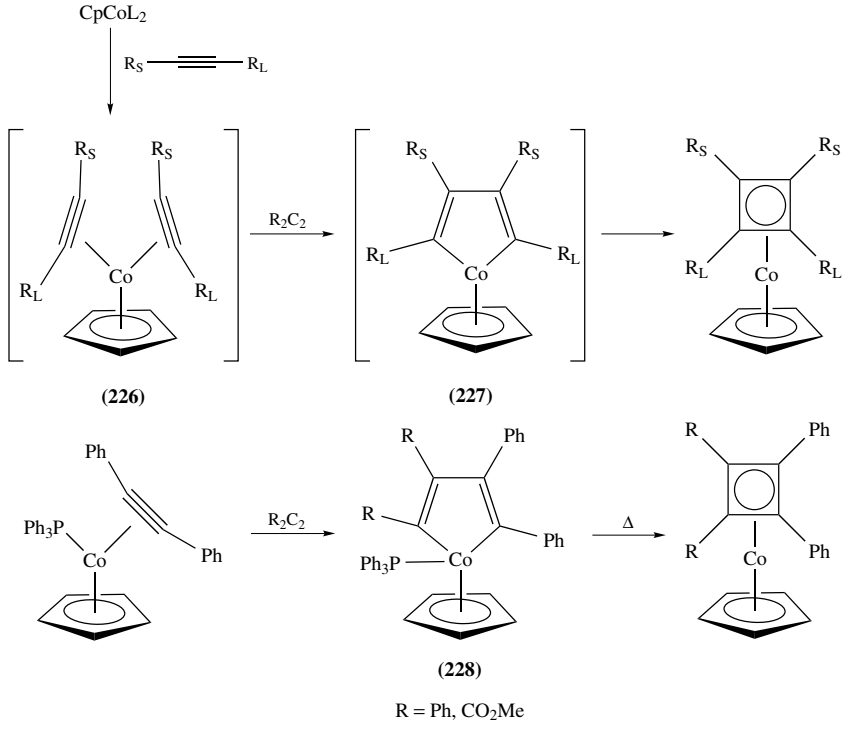
While one of the first preparations of a cyclobutadiene–metal complex involved the cyclodimerization of diphenylacetylene in the presence of $Fe(CO)_5$ at high temperature[212], the thermal reaction of alkynes with $Fe(CO)_5$ gives predominantly cyclopentadienone complexes (Section IV.E.1.b). The cyclization of alkynes by a wide variety of metal complexes has been reported (Scheme 59)[15,213–222].

Alkyne dimerizaton using CpCo(cod), $CpCo(C_2H_4)_2$ or $CpCo(CO)_2$ remains the method of choice for the preparation of (cyclobutadiene)CoCp complexes[223]. The overall mechanism for formation is believed to involve generation of a bis-alkyne complex **226** which undergoes reductive coupling to form a coordinatively unsaturated cobaltacyclopentadiene complex **227** (Scheme 60). A coordinatively saturated cobaltacyclopentadiene complex **228** has been isolated as the product from the reaction of $CpCo(PPh_3)(Ph_2C_2)$ with diphenylacetylene or with dimethyl acetylenedicarboxylate[224]. Heating of **228** at highly elevated temperatures results in the formation of differentially substituted (cyclobutadiene)CoCp complexes. For unsymmetrically substituted alkynes, coupling generally proceeds such that the more bulky substituents or electron-withdrawing substituents are located next to the cobalt. For cyclization with $CpCo(CO)_2$, one competing pathway to cyclobutadiene formation is the formation of cyclopentadienone complexes (cf Section IV.F.2.b, equation 19). Formation of these complexes may be avoided by use of the non-carbonyl reagents [e.g. CpCo(cod) or $CpCo(C_2H_4)_2$).

The cobalt mediated cyclodimerization of cyclic alkadiynes to afford tricyclic (cyclobutadiene)Co complexes **229** was previously examined by King and Efraty (Scheme 61)[225]. More recently, Gleiter and coworkers discovered that cyclization of 1,6-decadiyne, 1,8-tetradecadiyne or 1,10-octadecadiyne affords the tetra-bridged cyclobutadiene cyclophane complexes **230**, **231** and **232** in 12, 7 and 1% yields, respectively, in addition to complexes of type **229**[226]. The yield of the [3.3.3.3]-cyclophane could be increased to *ca* 30% if (η^5-indenyl)Co(cod) was used instead of $CpCoL_2$. X-ray diffraction analysis indicated that the distances between cyclobutadiene rings for **230**, **231** and **232** are 3.00 Å, 5.34 Å and 7.83 Å, respectively, and the Co–Co distances are 6.30 Å, 8.70 Å and 11.17 Å, respectively. In general, superphane formation occurs only for hydrocarbon cyclic diynes if the two alkyl chains contain an odd number of carbons and are of the same length. An exception to this generalization is the cyclodimerization of 1,5-cyclononadiyne with the sterically bulky $Cp^*Co(C_2H_4)_2$ to form **233** ($X = CH_2$) (Scheme 61)[227]. The cyclodimerization of certain large ring disilacyclodiynes **234** ($n = 5, 6$) with $Cp'Co(C_2H_4)_2$ was shown to


TiCl3 i-PrMgCl Ref. 213
1. PtCl2(NCMe)2, SnCl2 2. HCl Ref. 222
PdCl2(NCPh)2 Ref. 221
(MeC6H5)Ti(AlBr4)2 Ref. 214
[Rh(PF3)2Cl]4 Ref. 15
Cp2V2(CO)5 or CpV(CO)4/Δ Ref. 15, 215
CpRh(cod) Ref. 15
CpCo(CO)2 or CpCo(C2H2)2 or CpCo(cod) or Cp2Co
(Ph2C2)2Nb(CO)Cp Ref. 15
CpMo(CO)3I CO/Δ Ref. 49a
[Cp*Ru(μ3-Cl)]4 Ref. 220
(Ph2C2)3W(NCMe) Ref. 216
[CpRu(CO)2]2 AgBF4 Ref. 219
Mo(CO)4NO Ref. 217
(CO)5Mn+BF3− Ref. 218
Fe(CO)5 Ref. 212
R R

SCHEME 59



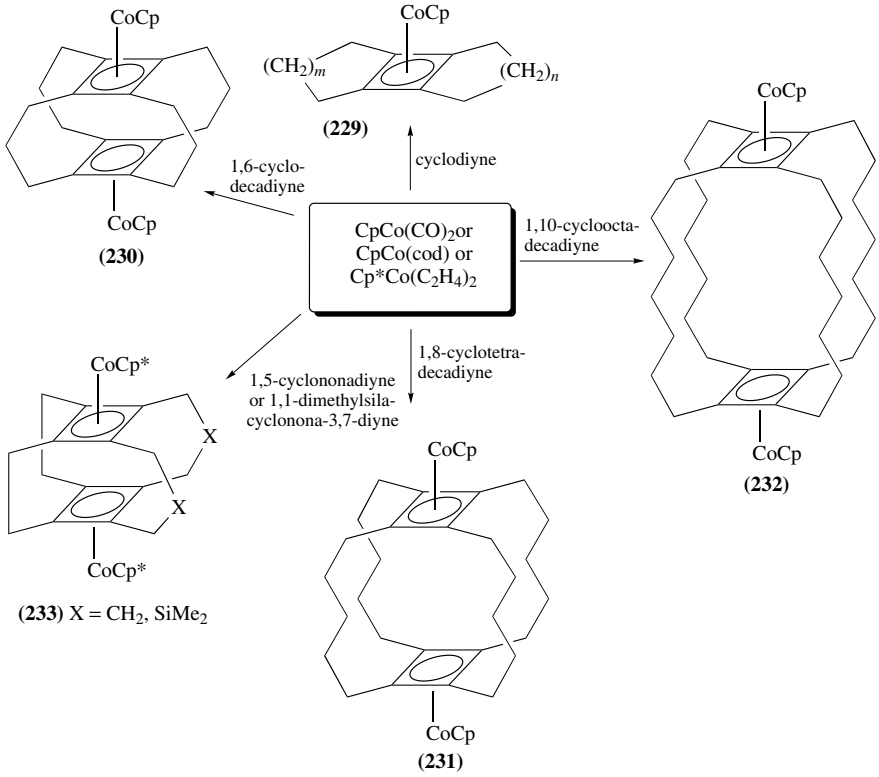
SCHEME 60

afford the corresponding silicon containing superphanes **235** (Scheme 62)[227b,c]. In contrast, reaction of the smaller 1,1,2,2-tetramethyl-1,2-disilacycloocta-3,7-diyne (**234**, $n = 2$) with $CpCo(cod)_2$ proceeded via intermolecular trimerization to generate the trimetallic complex **236**. Notably, the hydrocarbon bridges are all on one side of the macrocyclic structure. This is expected on the basis of the mechanism of cyclobutadiene formation which couples carbons carrying the sterically less bulky substituents together (cf Scheme 60). The crystal structure of **236** indicates that this compound possesses a conical shape; the diameters of the silyl bridged and the hydrocarbon bridged macrocyclic rings are 6.9 Å and 4.5 Å, respectively[227b].

Heteroatom-containing (cyclobutadiene)Co complexes (e.g. **237**, **238** and **239**) have been prepared by the reaction of heteroatom containing cobalt precursors with diphenylacetylene or by the reaction of cobalt precursors with phospha-alkynes[228].

C. Miscellaneous Methods of Preparation

Flash vapor pyrolysis of the (η^4-thiophene 1,1-dioxide)cobalt complexes results in extrusion of SO_2 to generate (cyclobutadiene)cobalt complexes (Scheme 63)[229]. The absence of ligand crossover products indicates that this reaction occurs in a unimolecular fashion. Pyrolysis of the diastereomerically pure complex **240** gave the cyclobutadiene complex as an equimolar mixture of diastereomers **241a** and **241b**. In addition, the recovered starting material (37%) was shown to have *ca* 40% scramble of the diastereomeric

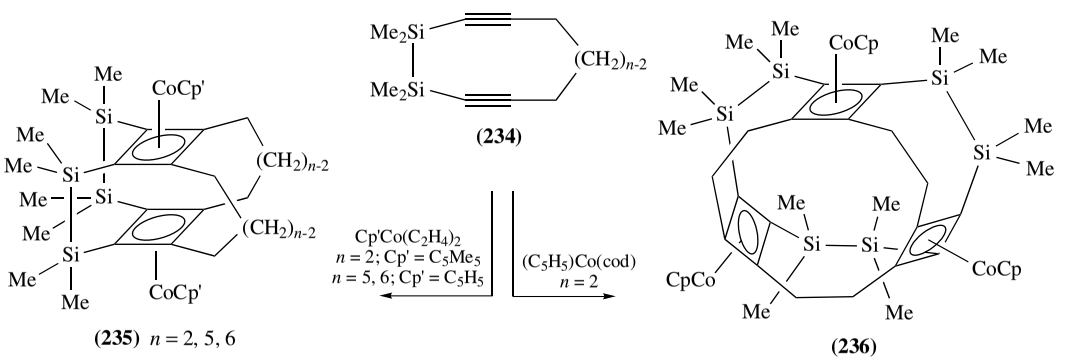


SCHEME 61

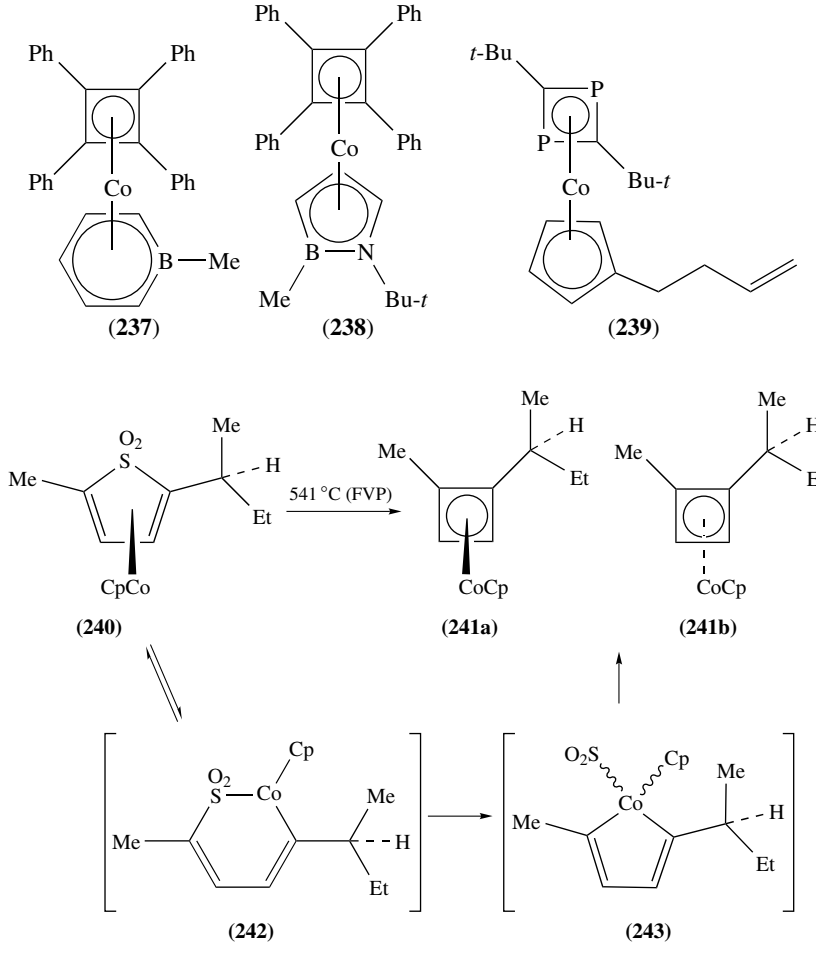
label. These results are consistent with a mechanism which involves reversible insertion of CoCp into the carbon–sulfur bond to generate a planar species **242**. Deinsertion of SO_2 from **242** generates the cobaltacyclopentadiene **243** which closes to the cyclobutadiene product.

The carbonyl oxygen in (3-oxocyclobutenyl)metal complexes is relatively polarized. Thus alkylation of the iron complex **244** or the cobalt complexes **245** with trialkyloxonium salts affords the corresponding (alkoxycyclobutadiene)metal cations **248** or **249**, respectively (Scheme 64)[38,230]. In a similar fashion, reaction of complexes **245** with BF_3 generates the zwitterionic complexes **250**. Olefination of the (3-oxocyclobutenyl)molybdenum complex **246** or tungsten complexes **247** gives the (3-methylenecyclobutenyl) complexes **251** (Scheme 64)[231]. Protonation of complexes **251** with HBF_4 give cationic (cyclobutadiene) species **252**.

Cyclopropene rings are stable, yet highly strained, ring systems. Under the influence of transition metals, facile ring-opening reactions may occur. The reaction of vinylcyclopropene **253** with $[RhCl(C_2H_4)_2]_2$ followed by treatment with $LiCp^*$ affords the metallacyclobutene complex **255** (Scheme 65)[232]. Heating **255** in chloroform generates the Cp^*Rh(cyclobutadiene) product **256**. In a somewhat similar fashion, reaction of vinylcyclopropene **254** with $Fe_2(CO)_9$ gave the η^2-complex **257**, which upon photolysis (but not thermolysis) gave a cyclobutadiene product **(258)**[233].


Me2Si
Me2Si
(CH2)n-2
(234)
Cp'Co(C2H4)2
n = 2; Cp' = C5Me5
n = 5, 6; Cp' = C5H5
(C5H5)Co(cod)
n = 2
CoCp'
(CH2)n-2
(CH2)n-2
CoCp'
(235) n = 2, 5, 6
CoCp
CpCo
CoCp
(236)

SCHEME 62



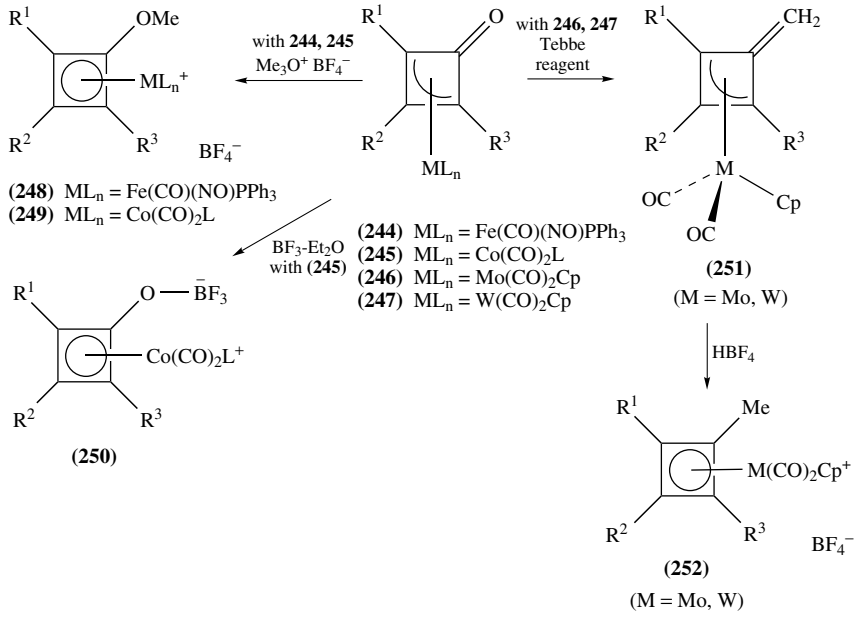
SCHEME 63

The (tetraphenylcyclobutadiene)PdX_2 dimer reacts with a variety of metal complexes via transfer of the cyclobutadiene ligand to another metal. These reactions and other ligand transfer reactions have been reviewed by Efraty[15].

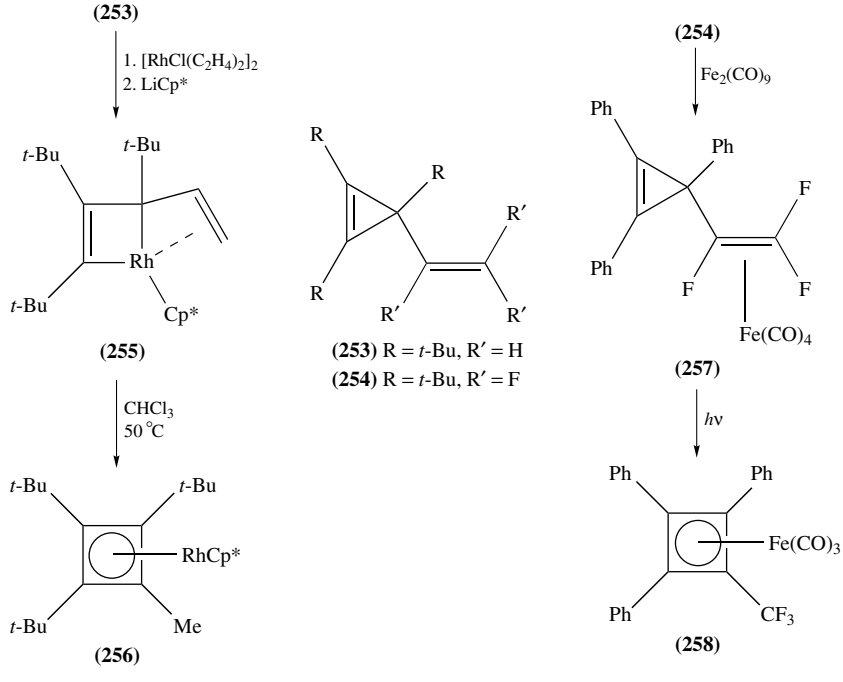
VII. REACTIONS OF CYCLOBUTADIENE–METAL COMPLEXES

A. Isomerizations

1,2-Disubstituted (cyclobutadiene)$Fe(CO)_3$ complexes in which the two substituents are different may exist as enantiomers. Racemic cyclobutadiene carboxylic acids or cyclobutadiene amine complexes of this type have been separated by classical resolution methodology[234]. These optically active (cyclobutadiene)$Fe(CO)_3$ complexes are stable with respect to racemization at 120 °C for 24 h. This stability contrasts with acyclic



SCHEME 64



SCHEME 65

(diene)$Fe(CO)_3$ complexes which have been shown to undergo racemization at this temperature (see Section IV.E.1.d).

In a similar fashion, 1-substituted-2,3-bis(trimethylsilyl) (cyclobutadiene)CoCp complexes in which the substituent contains a chiral center (e.g. **259**) exist as a mixture of diastereomers[235]. These diastereomers may be separated either by column chromatography or HPLC. Diastereoisomerization of either **259a** or **259b** requires extremely vigorous reaction conditions; either flash vacuum pyrolysis (>520 °C) or solution thermolysis (301 °C). The absence of ligand crossover products indicates that the diastereoisomerization occurs in a unimolecular fashion. Two possible pathways may be considered (Scheme 66). Pathway a involves insertion of cobalt into one side of the cyclobutadiene ligand to generate a cobaltacyclopentadiene intermediate. Notably, this type of intermediate is implicated in the cyclodimerization of alkynes to form (cyclobutadiene)CoCp complexes (see Scheme 60). Alternatively, in pathway b, a retro [2 + 2] cyclization would generate a bis-alkyne cobalt complex, which can undergo 'propeller' rotation about the alkyne-to-cobalt bond axis followed by [2 + 2] cyclization. Examination of the hexalabeled complex **260a** (two stereocenters, two different silyl groups, two ^{13}C labels) sheds light on these possibilities (Scheme 67). Thus, isomerization of **260a** leads only to isomer **261b** (but *not* to diastereomer **261a**) while isomerization of the **260b** leads only to **261a** (but not diastereomer **260a**). Since **260a** and **260b** should interconvert via the cobaltacyclopentadiene intermediate, the above results cannot be adequately explained by the 'pathway a' mechanistic possibility. The results are most consistent with a retro [2 + 2] alkyne cyclization ('pathway b') in such a fashion that the cyclobutadiene ring bond between the two silyl substituents is not broken.

Flash vacuum pyrolysis of deuterium-labeled [1,2-bis(ethynyl)cyclobutadiene]CoCp **262a** affords the rearranged product **262b** and recovered starting material (Scheme 68)[236]. None of the dideuteriated product **262c** or any of the potential [1,3-bis(ethynyl)cyclobutadiene] CoCp isomers were observed. These results are difficult to reconcile with a mechanism involving a bis(diyne)CoCp intermediate **(263)** and are most consistent with the intermediacy of either cyclooctadiendiyne complex **264** or cyclooctahexaene complex **265**.

B. Ligand Substitution

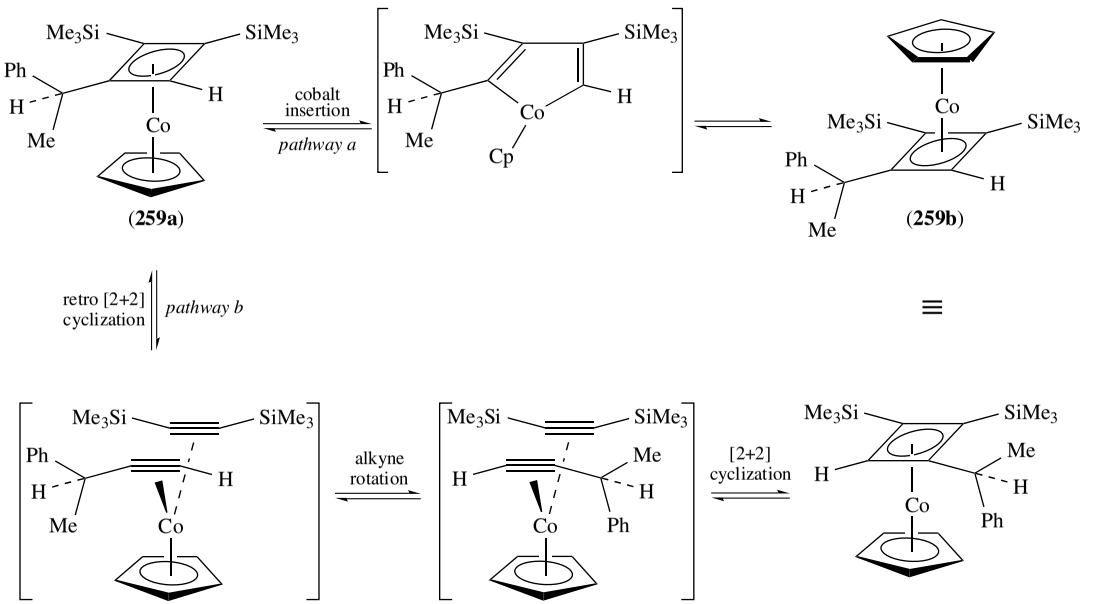
Tetramethyl- or tetraphenyl- (cyclobutadiene)nickel dihalides undergo reductive ligand substitution with nitrogen donor ligands such as 2,2′-bipyridine or 1,4-diaza-1,3-dienes with the addition of sodium metal[237]. The 2,2′-bipyridyl ligand is readily displaced and reaction of this complex with a variety of olefins and alkynes leads to cycloaddition reactions with the cyclobutadiene ligand.

Neutral (cyclobutadiene)$Co(CO)_2X$ complexes and (cyclobutadiene)$Co(CO)_3^+$ cations undergo displacement in the presence of arenes to generate (η^4-cyclobutadiene)(η^6-arene) Co^+ cations (Scheme 69)[38,211e,228a]. Neutral (cyclobutadiene)MoCp(CO)I complexes[50c] and (cyclobutadiene)$RuCp(CO)^+$ cations[219] also undergo ligand displacement of a coordinated carbon monoxide.

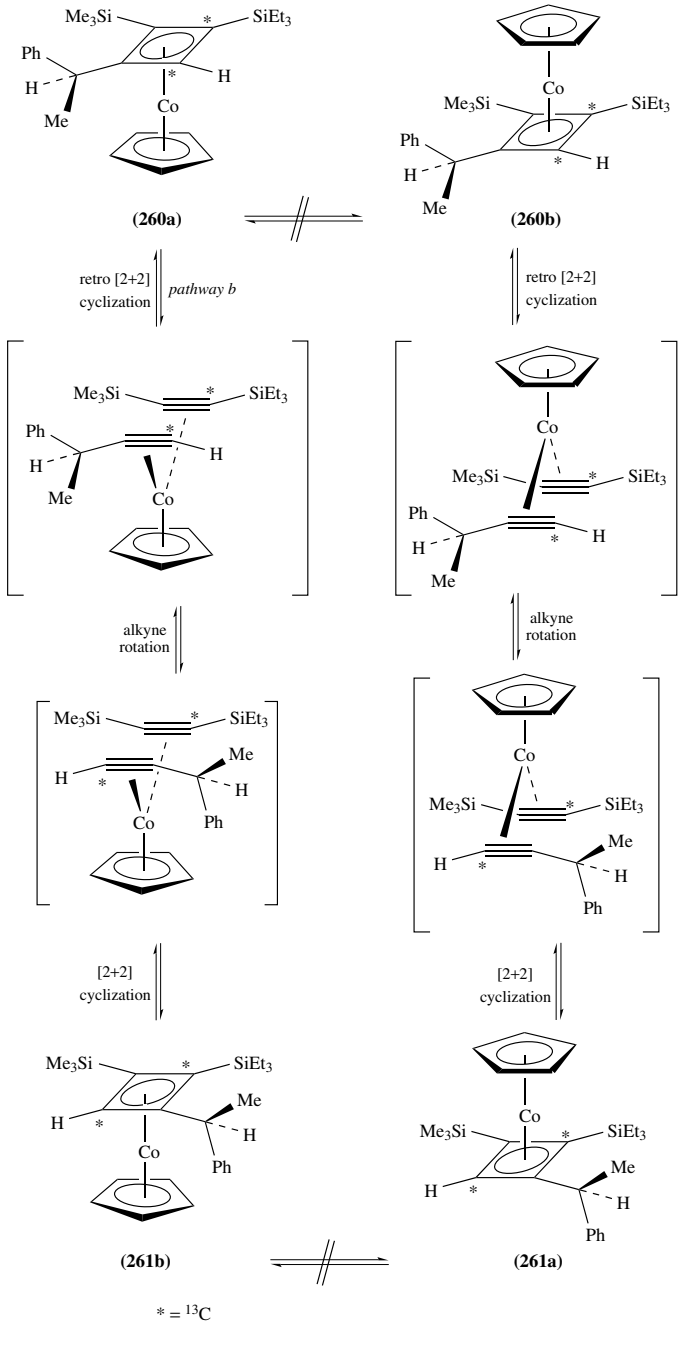
Neutral (cyclobutadiene)$Fe(CO)_3$ complexes undergo thermal and photochemical ligand substitution with phosphines, with alkenes such as dimethyl fumarate and dimethyl maleate and with the nitrosonium cation to generate the corresponding (cyclobutadiene)$Fe(CO)_2L$ complexes[15]. These types of complexes are presumably intermediates in the reaction of (cyclobutadiene)$Fe(CO)_3$ complexes with perfluorinated alkenes and alkynes to generate the insertion products **266** or **267** respectively (Scheme 70)[15,238].

C. Decomplexation

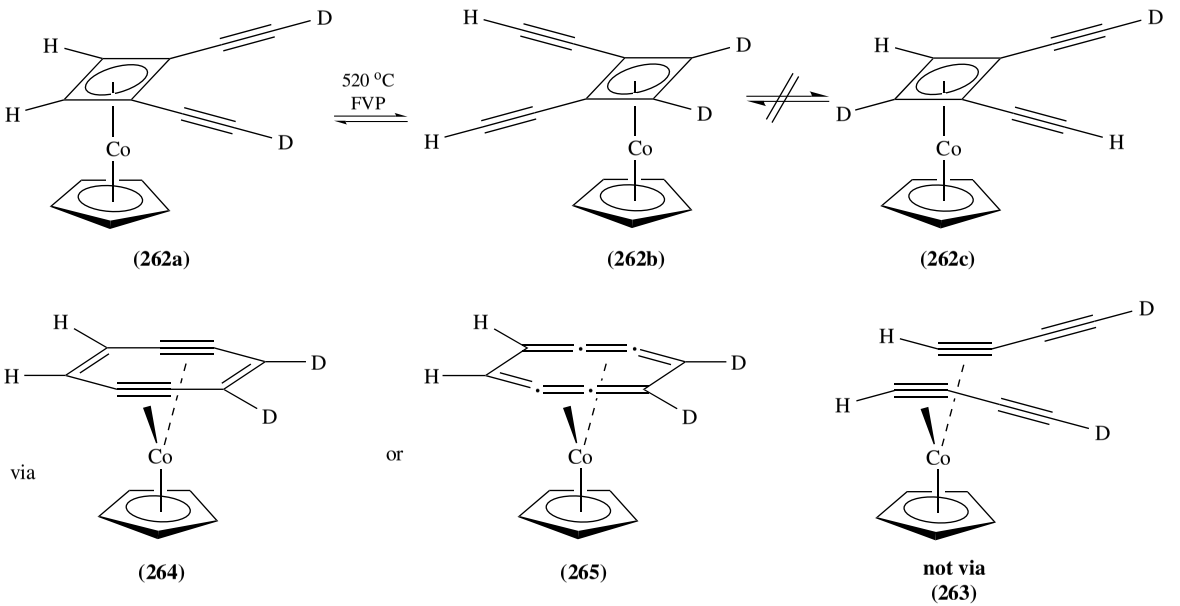
The majority of studies concerning decomplexation have been carried out on (cyclobutadiene)$Fe(CO)_3$ [**223**, $ML_n = Fe(CO)_3$] and substituted derivatives. As is the case


Me3Si
SiMe3
Ph
H
Me
Co
H
(259a)
cobalt
insertion
pathway a
Cp
(259b)
retro [2+2]
cyclization
pathway b
≡
alkyne
rotation
[2+2]
cyclization

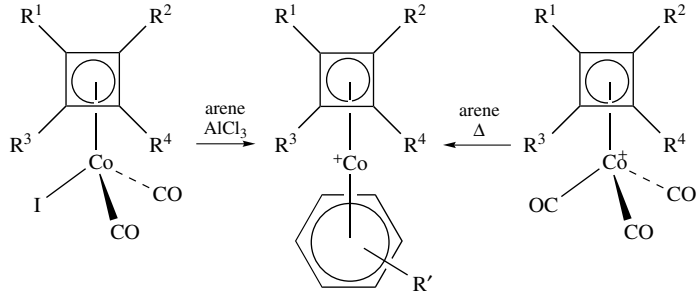
SCHEME 66


Me3Si
SiEt3
Ph
H
Me
Co
(260a)
(260b)
retro [2+2] cyclization
pathway b
alkyne rotation
[2+2] cyclization
(261b)
(261a)
* = 13C

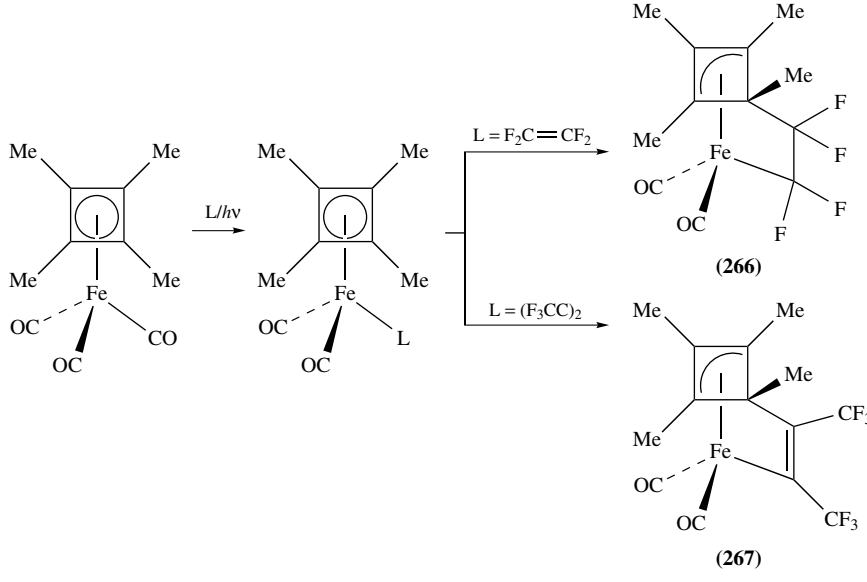
SCHEME 67



SCHEME 68



SCHEME 69



SCHEME 70

for acyclic butadiene and cyclohexadiene iron complexes (Section V.A.1), oxidation of (cyclobutadiene)$Fe(CO)_3$ liberates the organic ligand[239]. In the absence of other reactants the cyclobutadiene ligand undergoes dimerization to afford a mixture of *syn*- and *anti*-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (Scheme 71)[240]. In the presence of alkenes, alkynes or conjugated dienes, the liberated cyclobutadiene can act as either a diene or dienophile in Diels–Alder cycloadditions. Cycloaddition occurs in a stereospecific fashion with respect to the geometry of the alkene component and with *endo* selectivity. Oxidation of optically active (1,2-disubstituted cyclobutadiene)$Fe(CO)_3$ complexes leads to racemic products[234]. Thus the chemical oxidation appears to generate the ligand as a singlet diene. Additional evidence for the presence of the 'free' ligand was provided by the 'three phase test'. Transfer of the ligand from a polymer-bound (cyclobutadiene)iron complex by oxidation in the presence of a separately polymer-bound dienophile can only be accounted for by the

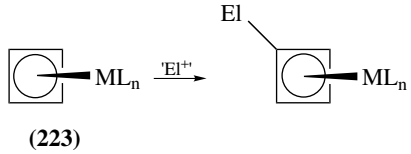
generation of the free ligand, since there is negligible contact between the functionalized sites of the two different polymeric supports[241]. The 'free' cyclobutadiene generated via the oxidation of (cyclobutadiene)$Fe(CO)_3$ has been utilized to prepare a variety of strained and theoretically interesting molecules (e.g. 'cubane', 'homocubanone', Dewar benzenes, and Dewar furan)[242].

Photolysis of substituted (cyclobutadiene)$Fe(CO)_3$ complexes (**268**, R = Me, CO_2Me, OEt) in the presence of alkynes affords substituted benzenes as a mixture of regioisomers[243]. The mechanism which is proposed involves initial loss of a carbon monoxide ligand and coordination of the alkyne (Scheme 72). Insertion of the alkyne into the cyclobutadiene–iron bond (cf Scheme 70) followed by reductive elimination affords a Dewar benzene intermediate. Secondary photolysis of the Dewar benzene gives the observed aromatic product. In a similar fashion, CAN oxidation of (cyclobutadiene) $Fe(CO)_3$ complexes **268** bearing a tethered alkyne or alkene (R = $CH_2OCH_2C{\equiv}CMe$, $CH_2OCH_2CH{=}CHPr$-*n*) generates tricyclic products **269** and **270** respectively (Scheme 72)[244]. The Dewar benzene product **(269)** opens to the substituted phthalan **271** under these oxidizing conditions.

D. Reactions with Electrophiles

The organic chemistry of (cyclobutadiene)metal complexes is much like that of ferrocene. Thus protonation of (cyclobutadiene)$Fe(CO)_3$ in HSO_3F/SO_2 generates a cationic species which exhibits a signal at $\delta -11.16$ ppm, consistent with a metal hydride species. However, spin–spin coupling of this signal to one of the ring protons is indicative that a bridging hydride species is more likely[245].

The reaction of (cyclobutadiene)metal complexes with X_2 results in the oxidative decomplexation to generate either dihalocyclobutenes or tetrahalocyclobutanes. In comparison, substitution of (cyclobutadiene)ML_n complexes **223** [ML_n = $Fe(CO)_3$, CoCp, and RhCp] with a variety of carbon electrophiles has been observed (equation 34)[15]. Electrophilic acylation of 1-substituted (cyclobutadiene)$Fe(CO)_3$ complexes gives a mixture of regioisomers predominating in the 1,3-disubstituted product and this has been utilized for the preparation of a cyclobutadiene cyclophane complex **272** (equation 35)[246]. For (cyclobutadiene)CoCp complexes, in which all of the ring carbons are substituted, electrophilic acylation occurs at the cyclopentadienyl ligand.



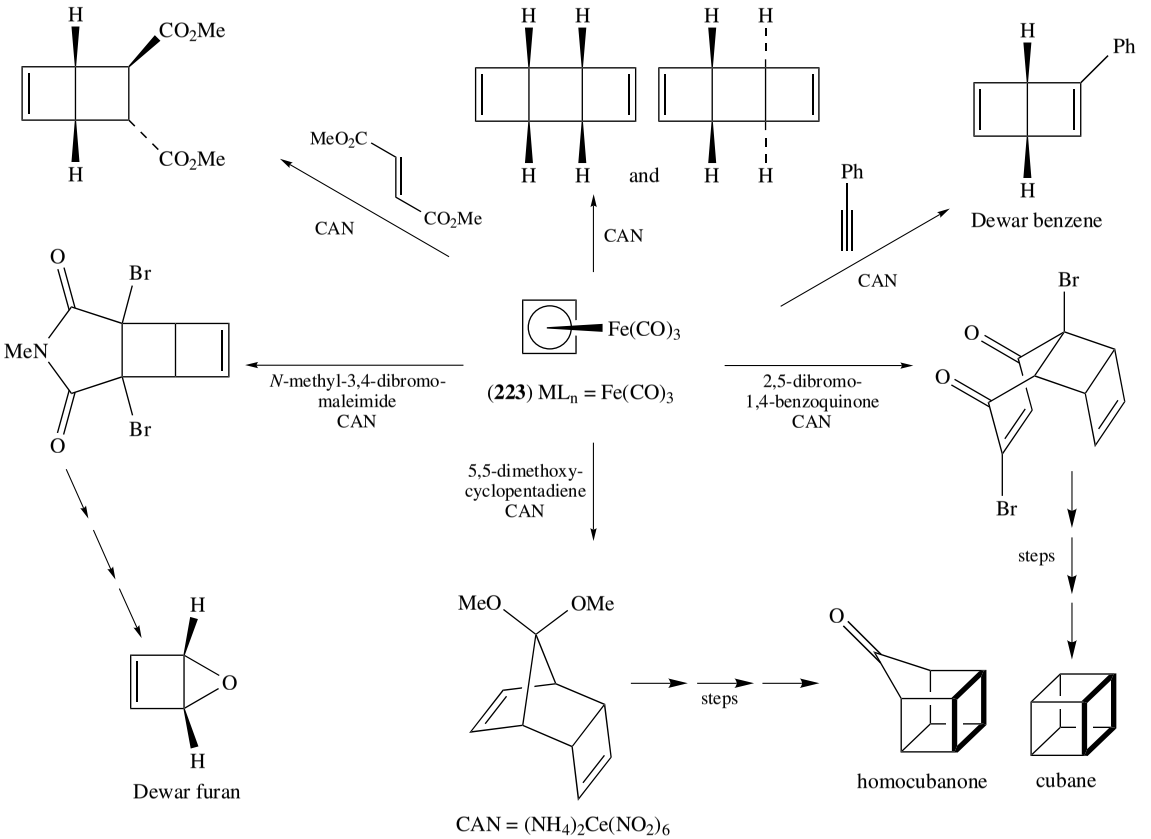
(223)

ML_n	'El^+'
$Fe(CO)_3$	COMe
CoCp	CHO
RhCp	CH_2Cl
	CH_2NMe_2
	HgCl
	SO_3H

(34)

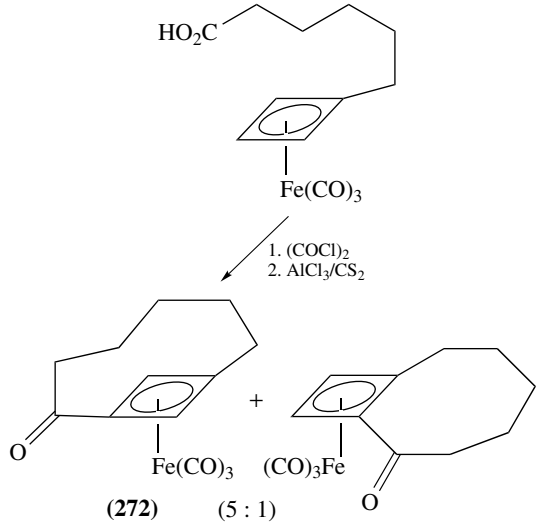
E. Reactions with Base or Nucleophiles

Deprotonation of (cyclobutadiene)$Fe(CO)_3$ with methyl lithium or *n*-butyl lithium is not possible[15], however lithiation is achieved by use of *s*-butyl lithium[247], or by transmetalation of (chloromercurycyclobutadiene)$Fe(CO)_3$. The metalated cyclobutadiene

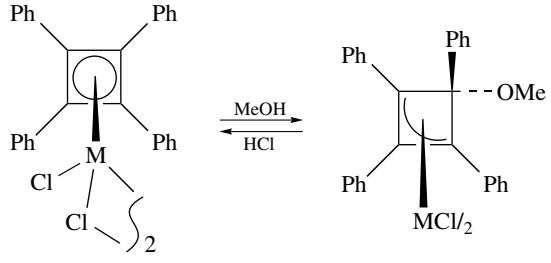

CO2Me
CO2Me
MeO2C
CO2Me
CAN
and
CAN
Ph
CAN
Ph
Dewar benzene
O
Br
MeN
O
Br
N-methyl-3,4-dibromo-
maleimide
CAN
Fe(CO)3
(223) MLn = Fe(CO)3
2,5-dibromo-
1,4-benzoquinone
CAN
Br
O
O
Br
5,5-dimethoxy-
cyclopentadiene
CAN
steps
H
O
H
Dewar furan
MeO
OMe
steps
O
homocubanone
cubane
CAN = (NH4)2Ce(NO2)6

SCHEME 71

can undergo reaction with Me_3SiCl, $(MeS)_2$, MeI, $(CH_2I)_2$ and ketones. Lithiation of (cyclobutadiene)CoCp with *n*-butyl lithium occurs predominantly at the cyclobutadiene ligand, as evidenced by carboxylation and esterification. However, a minor amount of product from lithiation at both the cyclobutadiene and cyclopentadienyl ligand is also isolated.

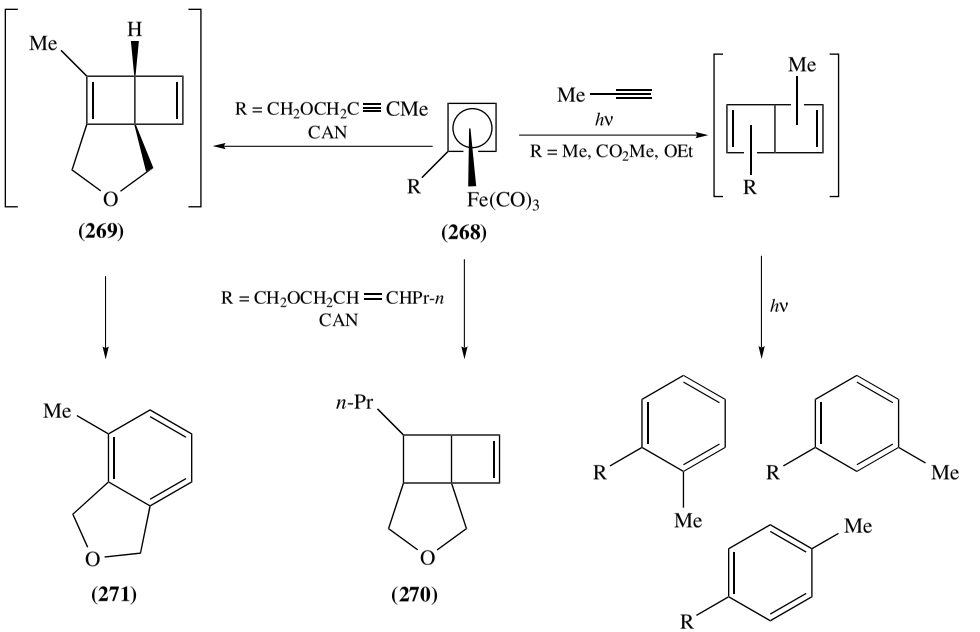


(272) (5 : 1) (35)

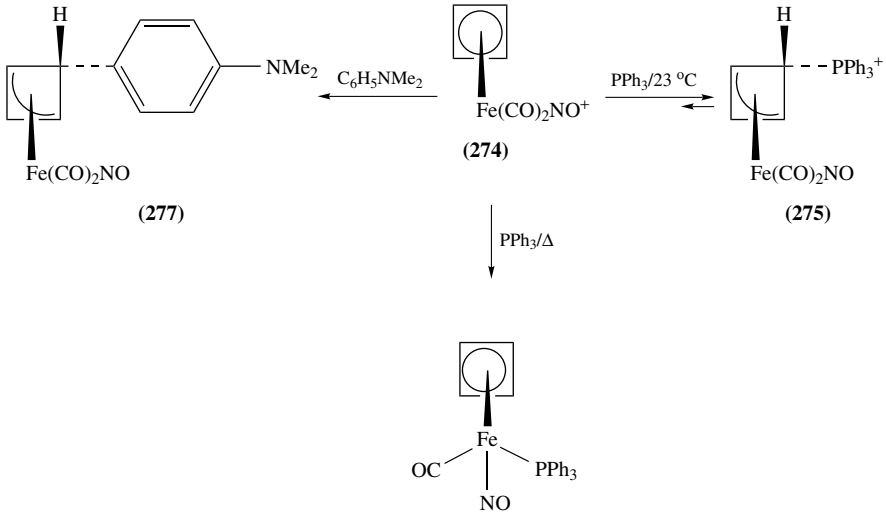


(273) M = Pd, Pt (36)

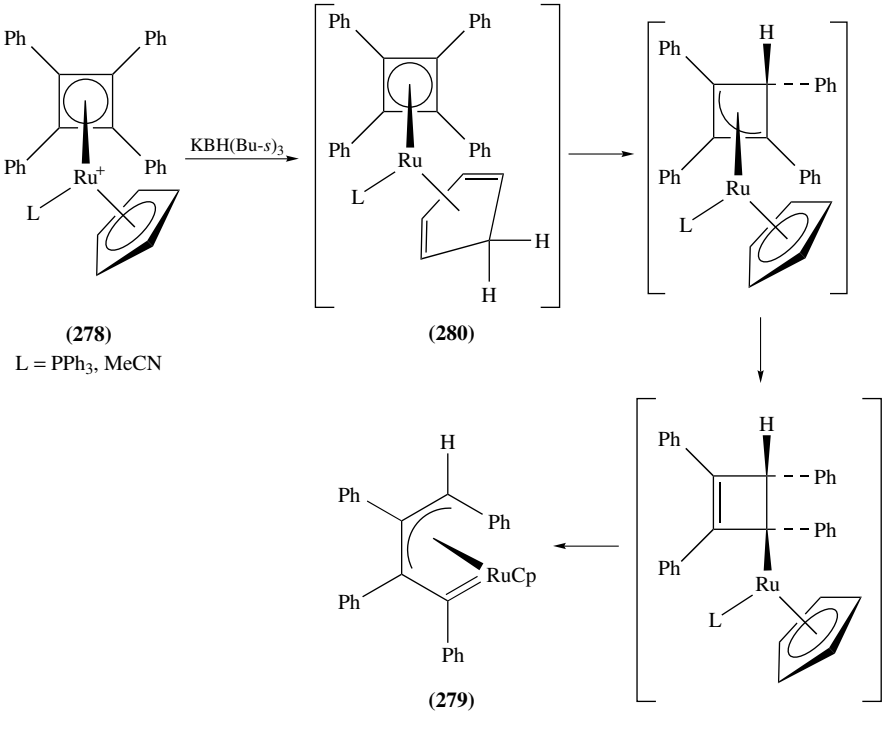
Although the reactivity of cyclobutadiene–metal complexes toward electrophiles has been studied extensively, there is relatively little known about their reactivity with nucleophiles. (Iodocyclobutadiene)$Fe(CO)_3$ reacts with alkoxide, sulfide or cyanide anions via displacement of the iodine. In the presence of palladium catalysts, (iodocyclobutadiene) $Fe(CO)_3$ undergoes coupling reactions with stannylalkynes to generate alkynylcyclobutadiene complexes[247]. Cyclobutadiene palladium- and platinum- chloride dimers **273** are reported to react with oxygen nucleophiles; the product is an *exo*-alkoxy-η^3-cyclobutenyl-metal species. This reaction is reversible upon addition of acid (equation 36)[248]. The (cyclobutadiene)$Fe(CO)_2NO^+$ cation **274** undergoes reaction with tertiary phosphines at 23 °C to form *exo*-phosphonium-η^3-cyclobutenyl iron complexes **275** (Scheme 73)[249]. This nucleophilic addition is reversible and, under more vigorous thermal conditions, the reaction proceeds via carbonyl substitution to yield the phosphine coordinated cation **276**. Reaction of **274** with *N*,*N*-dimethylaniline gives the η^3-cyclobutenyl iron complexes **277**.


Me
H
O
(269)
R = CH2OCH2C≡CMe
CAN
R
Fe(CO)3
(268)
Me
hν
R = Me, CO2Me, OEt
Me
R
R = CH2OCH2CH=CHPr-n
CAN
hν
Me
O
(271)
n-Pr
O
(270)
R
Me
R
Me
Me
R

SCHEME 72



SCHEME 73



SCHEME 74

Exo attack of the nucleophile on both **273** and **274** were unambiguously determined by crystal structure analysis.

Reaction of (tetraphenylcyclobutadiene)RuCpL$^+$ cations **278** with KBH(Bu-*s*)$_3$ gave product **279** from opening of the cyclobutadiene ring (Scheme 74)[250]. These reactions are believed to proceed via hydride attack on the cyclopentadienyl ligand to give **280**. Evidence for the intermediacy of **280** was obtained by NMR spectroscopy when L = P(OMe)$_3$. Migration of the hydride to the *endo* face of the cyclobutadiene would give a η^3-cyclobutenyl ruthenium species which undergoes ring opening to the final product.

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CHAPTER **12**

Reduction of dienes and polyenes

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I. INTRODUCTION

Reduction of dienes and polyenes has attracted much attention since it is important from both practical and theoretical aspects. In these reactions the major interest is the selective reduction of a double bond in the presence of another. In general, saturation of all the multiple double bonds of nonaromatic compounds can be carried out with any of the catalysts which are suitable for low-pressure reductions or with some reducing chemicals.

The selective partial hydrogenation of polyenes is interesting from both preparative and commercial points of view. Success depends on the nature of the polyene as well as on a careful choice of catalyst and conditions.

There are several industrial processes in which reduction of dienes and polyenes is involved. The three most well known ones are the following: the hydrotreating of pyrolysis gases and gasoline[1], the hydrogenation of fats and fatty oils[2] and the hydrogenation of nitrile-butadiene rubber[3]. In all of these processes selectivity is a key issue. For example, in the purification of ethylene and propylene from acetylene and diene traces, the selectivity of the Pd catalyst influences the yield of the olefinic products. Similarly, the selectivity of the hydrogenation of fatty oils towards *cis* oleic acid containing glycerides determines basically the quality and value of the saturated products.

Besides these processes, several reduction methods or hydrogenation technologies of dienes and polyenes are used for the fine chemicals industry.

II. METHODS OF REDUCTION

A. Catalytic Hydrogenation

The olefinic C=C double bond is easy to reduce, under mild conditions, with most of the hydrogenation catalysts, with noble metals, with different forms of nickel as heterogeneous catalysts, with Rh, Pt, Co complexes and with Ziegler catalysts as homogeneous catalysts. In the hydrogenation of dienes and polyenes the selectivity is the most important issue, i.e. how can one double bond be saturated with retention of the other(s). When high selectivity is required, homogeneous catalysts are used. Nevertheless, as known, their separation from the reaction mixture is a difficult task.

In the industrial processes for the hydrogenation of dienes and polyenes, heterogeneous catalysts are used in most cases, although their selectivity is not perfect.

1. Homogeneous catalyzed hydrogenation of dienes and polyenes

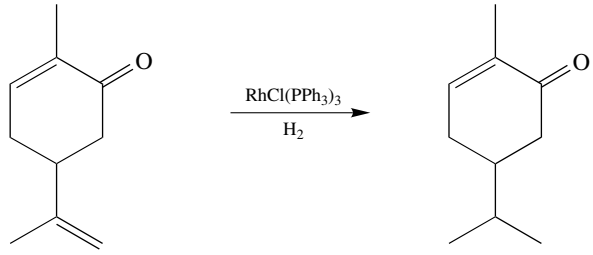
The hydrogenation of olefins with soluble metal complexes has been studied extensively[4,5]. This intensive study seems anomalous because soluble catalysts are seldom used for olefin hydrogenation in industry and in organic synthesis. The importance of homogeneous catalysts is great in asymmetric reactions (L-Dopa, Dual herbicide synthesis) where the high stereoselectivity of optically active catalysts is the major advantage.

Another potential use of homogeneous hydrogenation catalysts is the hydrogenation of dienes and trienes to monoolefins, where they display high specificity. Such an example is the conversion of the easily available butadiene dimers and trimers to polymer intermediates[6].

The hydrogenation of unsaturated polymers like polyisoprene is based on the mobility of a soluble catalyst in the reaction medium. In the hydrogenation of such unsaturated polymers the soluble catalyst brings its active site to the C=C bonds in the polymer chain. In contrast, a heterogeneous catalyst requires that the polymer chain unfold to gain access to a catalytically active site on the surface of a metal particle.

For practical hydrogenation of olefins four classes of metal complexes are preferred: (a) Rh complexes, the $RhCl(PPh_3)_3$, the so-called Wilkinson catalyst and the $[Rh(diene)-(PR_3)_2]^+$ complexes, (b) a mixture of Pt and Sn chlorides, (c) anionic cyanocobalt complexes and (d) Ziegler catalysts, prepared from a transition metal salt and an alkylaluminum compound.

The Wilkinson catalyst reduces external double bonds much faster than the internal ones as in the hydrogenation of carvone (equation 1)[7].



(1)

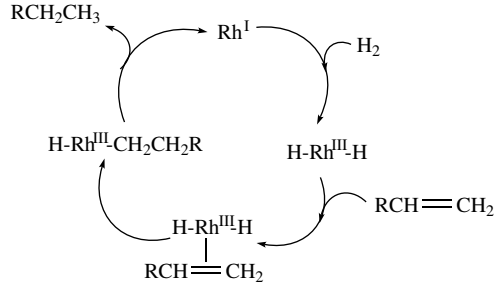
As this catalyst is slow in the hydrogenation of internal olefins, the closely related $[Rh(diene)-(PR_3)_2)]^+$ catalysts are useful with highly substituted olefins, for example in asymmetric hydrogenations[8].

The Pt–Sn complexes were studied extensively in the hydrogenation of vegetable oils to remove excessive unsaturation[9].

For hydrogenation in water with an inexpensive catalyst, solutions containing cobalt salts and excess cyanide are useful[10,11]. The catalysts are selective for conjugated C=C bonds and are relatively unreactive with unconjugated dienes such as 1,5-cyclooctadiene.

The Ziegler-type systems are useful for the hydrogenation of unsaturated polymers, so they have industrial application[12].

The mechanism of olefin hydrogenation is rather simple: the olefin and the H_2 are brought together as ligands in the coordination sphere of the metal and a rearrangement of the H–M-olefin complex to a metal-alkyl is followed by hydrogenolytic cleavage of the M–C bond (Scheme 1). The catalysts differ in the mode of cleaving H_2 to form the metal-hydride ligand and in the mechanism of cleavage of the metal-alkyl bond to form alkane. The Rh, Pt–Sn and Co based catalysts differ in the H_2 cleavage mechanism[13].



SCHEME 1

The Rh complex undergoes oxidative addition while activating hydrogen. With the anionic Pt catalyst the process occurs by heterolytic cleavage of hydrogen (equation 2)[14].

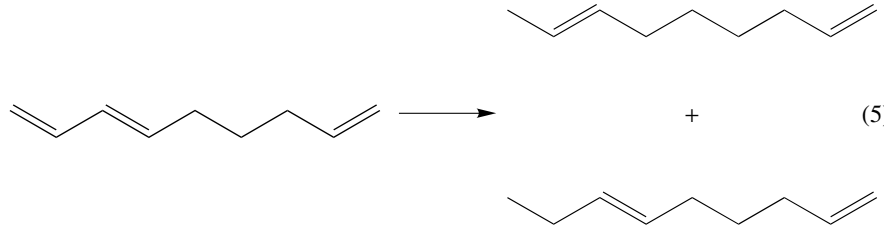
$$H_2 + [Pt(SnCl_3)_5]^{3-} \rightleftharpoons H^+ + [HPt(SnCl_3)_4]^{3-} + SnCl_3^- \quad (2)$$

The third major mechanism is based on homolytic cleavage of the dihydrogen molecule by metal–metal (Co) bonded species or by a paramagnetic complex (equations 3 and 4)[15].

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \quad (3)$$

$$2[Co(CN)_5]^{3-} \rightleftharpoons [Co_2(CN)_{10}]^{6-} \xrightarrow{H_2} 2[HCo(CN)_5]^{3-} \quad (4)$$

A practical example for polyene hydrogenation is the reduction of 1,5,9-cyclododecatriene to cyclododecene. The starting compound is a readily available butadiene trimer; it can be converted to cyclododecene, the precursor of dodecanedioic acid and laurolactam, two commercial polyamide intermediates. The two soluble catalysts, which are superior in selectivity compared with the Pd/Al_2O_3 catalyst used in the industrial process, are $[Co(CO)_3(PBu_3)$ and $NiI_2(PPh_3)_2]$, which are prepared from nonprecious metals. These catalysts effect partial hydrogenation of either conjugated or unconjugated dienes and trienes[14,16–21]. Another group of catalysts, $[Co(CN)_5]^{3-}$, [Cr(CO)(methyl benzoate)], $Cr(CO)_6$, $[Cr(CO)_2(C_2H_5)_2]_2$, hydrogenate only conjugated dienes and trienes (equation 5)[10,22].

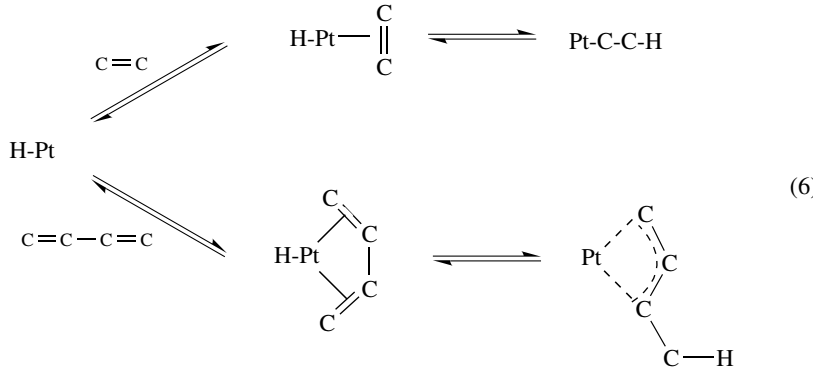


(5)

The major distinction between the two classes of catalysts is that the members of the former group are olefin isomerization catalysts, while the cobalt cyanide and the chromium catalysts are not[23–25].

The isomerization catalysts are hydride complexes, and they can convert the unconjugated dienes or polyenes to conjugated systems through double-bond migration. This process occurs by an M–H addition–elimination process.

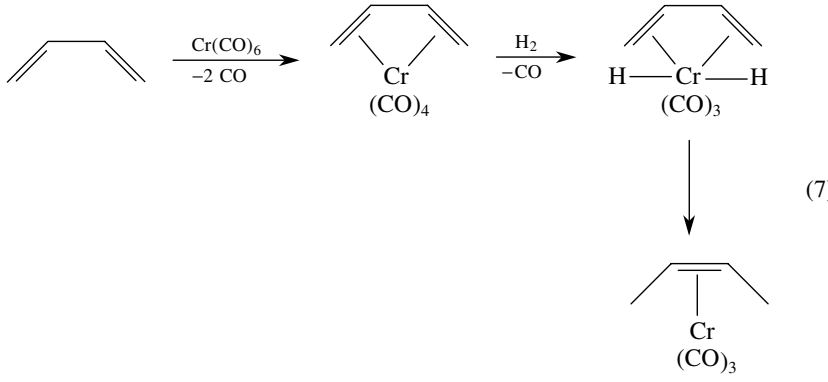
The selectivity for hydrogenation of dienes in the presence of monoolefins arises from the exceptional stability of π-allyl complexes. In the case of Pt catalysts the reactions shown can compete with one another (equation 6)[14]. The second pathway is favored, especially when the olefin or diene must compete with excess ligands (phosphine, CO, $SnCl_3^-$) for a coordination site. This is why the diene is almost completely hydrogenated before the concentration of olefin increases to the point that the olefin gains access to the catalyst. A similar phenomenon can be responsible for selectivity in hydrogenation of dienes with heterogeneous catalysts.



(6)

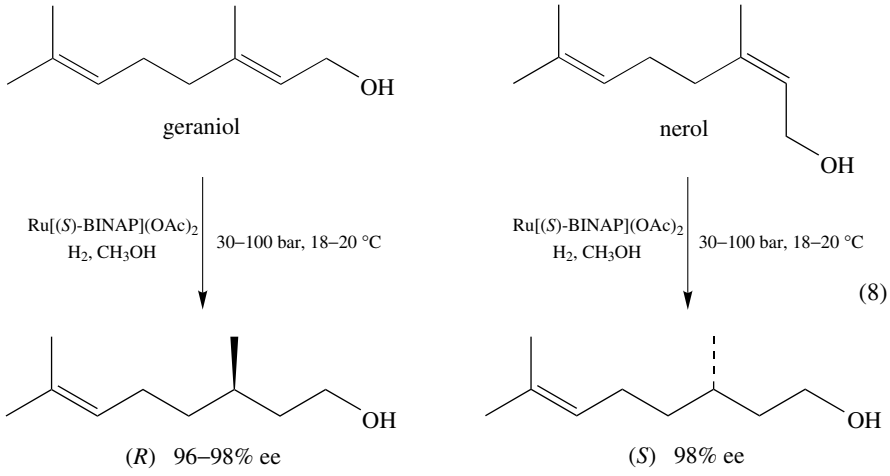
The $Cr(CO)_6$ and $Cr(CO)_3$(arene) catalysts hydrogenate conjugated dienes by 1,4-addition of hydrogen. The diene coordinates in a *cisoid* configuration (equation 7)[23]. This

proposal is supported by the high selectivity for 1,4-addition and the *cis* conformation of the olefinic product.



(7)

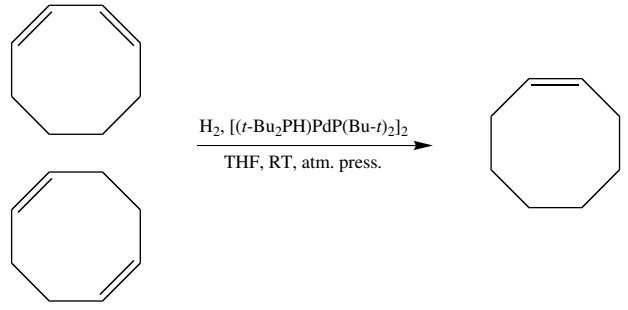
A characteristic example for the application of homogeneous catalysts in enantioselective and regioselective hydrogenation of dienic compounds is the hydrogenation of geraniol and nerol to citronellol with Ru-BINAP catalyst (equation 8)[26,27]. The high enantiomeric excesses (96–98%), the nearly quantitative yields (>95%) and the very low catalyst/substrate ratio (1 : 50000) are attractive attributes of this process.



(8)

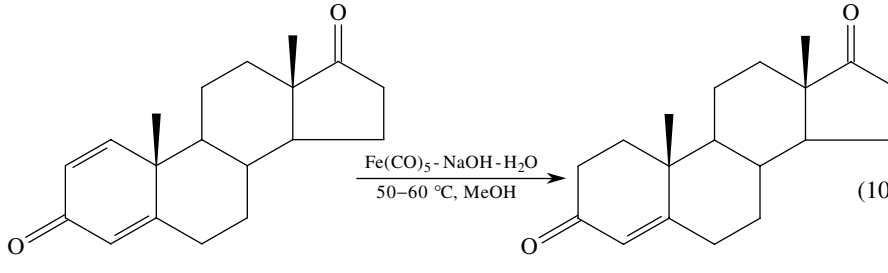
Besides the catalysts mentioned in the introductory part of this topic, other catalytic systems were used successfully in diene hydrogenation. An example is $NiH(PPh_3)(AlCl_4)$, which hydrogenated 1,4-cyclohexadiene to cyclohexene in toluene at 40 °C[28].

A selective hydrogenation of conjugated dienes was carried out with a Pd complex which was preactivated with oxygen. Besides the conversion of dienes with good selectivity (98%), diene esters, ketones and nitro compounds were also hydrogenated with fairly good selectivities (equation 9)[29].



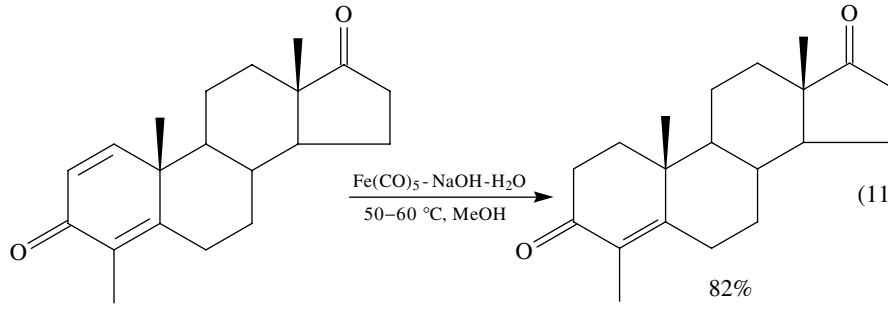
(9)

The iron carbonyl complex $[Fe(CO)_5]$ in basic media hydrogenated steroidal dienes selectively (equations 10–12)[30].



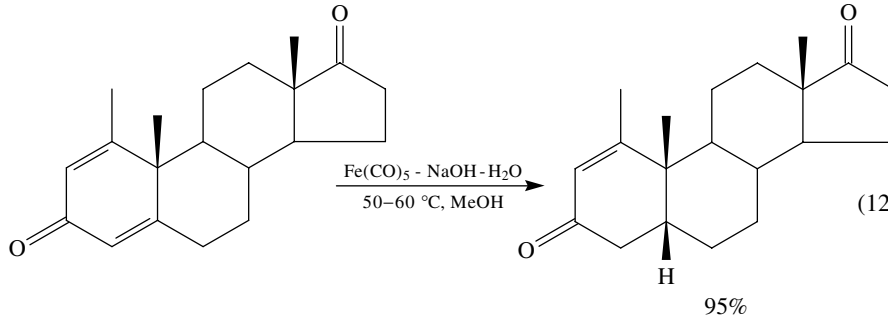
(10)

85%



(11)

82%



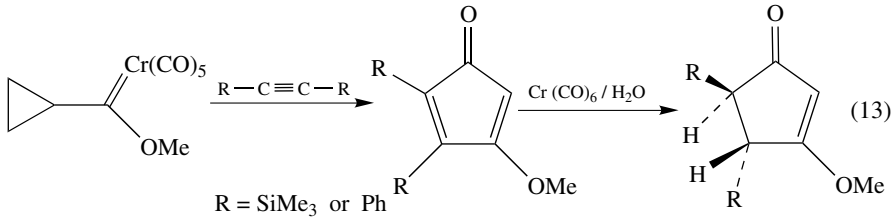
(12)

95%

Low melting tetraalkylammonium salts of $SnCl_3^-$ and $GeCl_3^-$ anions are convenient solvents for some homogeneous catalytic reactions of olefins. These salts, when fused, dissolve up to 7% $PtCl_2$ to give deep red solution which catalyze among other reactions the hydrogenation of 1,5,9-cyclododecatriene with considerable selectivity to cyclododecene at 150 °C and 100 bar hydrogen pressure. The catalytic solution of $PtCl_2$ in $[(C_2H_5)_4N][SnCl_3]$ appears to contain $SnCl_3^-$ complexes of platinum, including the known $[Pt(SnCl_3)_5]^{3-}$ and $[HPt(SnCl_3)_4]^{3-}$ anions[14].

There were several attempts to use homogeneous catalysts in the hydrogenation of fatty acid esters. Pt, Pd and Mo complexes were investigated. The monoene selectivity and the activity of Pt catalysts were good, but their separation from the product remained an unsolved problem. They were active in a double-bond migration reaction which, however, was accompanied by the disadvantageous *cis–trans* isomerization[9,31].

An interesting example is the stereoselective reduction of a cyclopentadienone derivative with a chromium carbonyl itself without hydrogen (equation 13)[32].



(13)

2. Heterogeneous catalyzed hydrogenation of dienes and polyenes

For the hydrogenation of dienes and polyenes the most frequently applied catalysts are heterogeneous metal catalysts. Their advantage is the high reaction rate, good selectivity under optimized conditions and the easy separation.

For olefin hydrogenation Horiuti and Polányi[33] proposed a scheme, which is generally being accepted and which accounts for two aspects of this reaction, i.e. double-bond migration and *cis–trans* isomerization. The elementary steps of this scheme are the following: the dissociative adsorption of hydrogen, the diadsorption of olefin and the addition of one hydrogen atom to the olefin, forming a so called 'half-hydrogenated species'. If this undergoes a configurational change, *cis–trans* isomerization may occur. Transformation of the monoadsorbed species to form a different diadsorbed species may also occur, resulting in double-bond migration. (Monoadsorbed and diadsorbed mean attachment to the catalyst surface by one and two covalent bonds, respectively.) Migration and isomerization are favored by a low hydrogen concentration at the surface and diminished by high hydrogen availability at the surface.

Catalysts differ in their ability to promote double-bond migration and *cis–trans* isomerization, in their thermodynamic and mechanistic selectivities in diene hydrogenation and in their tendencies to catalyze 1,2-, 3,4-, or 1,4-addition[34].

The reason for the selectivity is that dienes are adsorbed with strengths comparable to those of alkynes. The large selectivities that various metals show in the hydrogenation of allene (propadiene), 1,3-butadiene and 1,4-pentadiene are similar to those observed with alkynes. Pd is again outstanding in diene hydrogenation, its behavior being similar to that shown in the hydrogenation of alkynes. However, the hydrogenation of dienes is a more complex process, and the relative amounts of isomeric alkenes vary considerably from one metal to another, and with the reaction conditions due to varying amounts of 1,2- and 1,4-addition[35,36].

The mechanistic studies were carried out mainly with butadiene and two mechanisms were suggested depending first of all on the *trans/cis* ratio of the formed 2-butene. On Pd and sometimes on Co catalysts the *trans/cis* ratio is high and the mechanism is based on formating of *syn*- and *anti*-π-allyl intermediates which cannot interconvert on the surface. On other metals, where the *trans/cis* ratio is about unity, the intermediates are π-alkenes or σ-alkyls that may interconvert more freely[36].

The hydrogenation of butadiene is structure-sensitive on Pd and Rh but lacks particle-size dependence in the case of platinum. The strong complexation of the diene to atoms of low coordination number is a possible explanation for this phenomenon where it occurs[37,38].

Three factors determine the activity and selectivity in the hydrogenation of alkadienes[39]: (a) the particle size through the effect of complexation of reactants to active sites containing low coordination number atoms, (b) the particle size, through self-poisoning by carbonaceous residues, and (c) with palladium, a particle-size effect through the solubility of hydrogen and the formation of the unselective β-PdH derivatives.

The selectivity of metal catalysts improves in some reactions with alloying; for example the alumina-supported Pd–Cu catalyst hydrogenates butadiene to 1-butene with 99% selectivity, i.e. the isomerization is less than 1%. The explanation is that hydrogen adsorption decreased on the Cu-containing catalysts[40]. Similarly, better selectivities were observed with a polymer anchored Pd, or a Pd–Co catalyst in the gas-phase hydrogenation of butadiene and cyclopentadiene in a hollow-fiber reactor[41,42] and in the liquid-phase hydrogenation of 1,5-hexadiene with Pd–Ag catalyst[43].

The intermetallic compounds $CePd_3$ and $ZrPd_3$ exhibited higher selectivity for butene formation than Pd. On Pd the hydrogen and butadiene are adsorbed on similar sites, whereas on the intermetallic compounds different sites may be involved in these adsorption processes[44].

Another explanation for the selectivity of Pd in reduction to 1-butene is the phenomenon of self-poisoning. Carbonaceous materials and oligomers are formed on the catalyst surface. Butadiene, due to its high adsorption ability, is able to be adsorbed on metallic sites in the presence of the oligomers. However, *n*-butenes could not compete with the oligomers. A large quantity of hydrocarbonaceous deposit decreases the surface fugacity of the diene due to hindrance of transport and in consequence enhances the overhydrogenation of diene[45,46].

Recently, silica supported nickel–boron catalyst was tested in the hydrogenation of cyclopentadiene and was found to be selective in giving cyclopentene[47].

The liquid-phase hydrogenation of dienes and polyenes is also an extensively studied topic. The behavior of metals in such reactions is similar to that in the gas-phase reactions, i.e., Pd is the most selective catalyst.

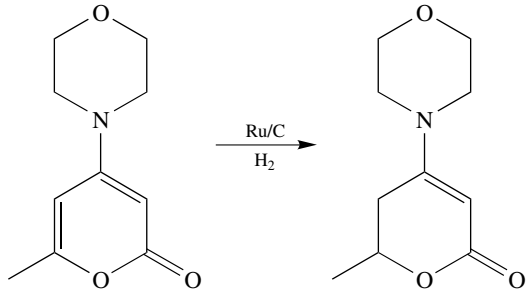
In the industrial scale of hydrogenation of fats and oils, the most frequently used catalysts are Ni based. The 20–30% Ni is supported on silica. When partial hydrogenation is needed, the temperature applied is between 140 and 200 °C and the pressure between 4 and 10 bar. The total hydrogenation requires higher temperature and pressure (200 °C, 20 bar). Nickel is not a perfect catalyst due to its relative low activity and also due to the formation of Ni-soaps. Recently, a colloidal Pd catalyst was applied successfully in a two-phase system for this type of hydrogenation, at room temperature and atmospheric pressure. The complete conversion of multiunsaturated compounds could be achieved during 15–45 minutes. In dimethylformamide as the second phase solvent, 92% monoene yield with a 70/30 *cis/trans* ratio could be produced[48].

Recently, Ir/Al_2O_3 catalyst was tested in the hydrogenation of linoleic acid at 140 °C and 300 torr hydrogen pressure. The Δ-12 double bond showed the highest reactivity in the reduction process[49].

In the hydrogenation of 1,3-pentadiene the selectivity sequence is the following[50]:

$$Pd > Rh > Ru \cong Pt > Ir.$$

An exception is the hydrogenation with Ru/C catalyst shown in equation 14[51]. Another exception is the Pd-catalyzed hydrogenation of 1,3-cyclohexadiene, where benzene and cyclohexane are formed[52].

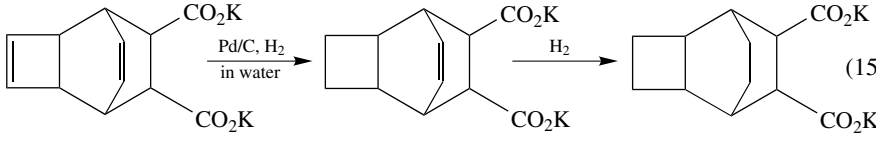


(14)

In order to increase the selectivity in diene hydrogenation, low-temperature basic additives and the use of less polar solvents may help. In special cases, treatment of the catalysts with the salts of heavy metals (Zn, Cd, Pb) can be the method used to modify the activity and selectivity[53]. Rh and Ir catalysts could be selectively poisoned with CO-containing hydrogen, in order to saturate 1,3-butadiene to 1-butene without isomerization[54].

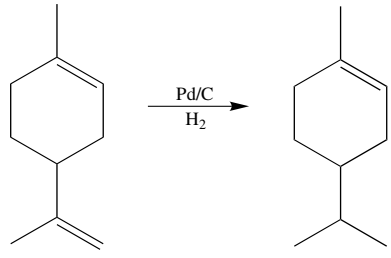
Iron introduced into Pd/Al_2O_3 catalyst by controlled surface reaction promoted the activity of the catalyst in the liquid-phase hydrogenation of isoprene. When Fe was introduced by impregnation or coimpregnation, it had an opposite effect[55].

The hydrogenation of the double bond is facilitated by steric strain (equation 15)[53].



(15)

It is generally observed that the less hindered double bond in a diolefin is preferentially hydrogenated as found in the reaction of limonene (equation 16)[56].

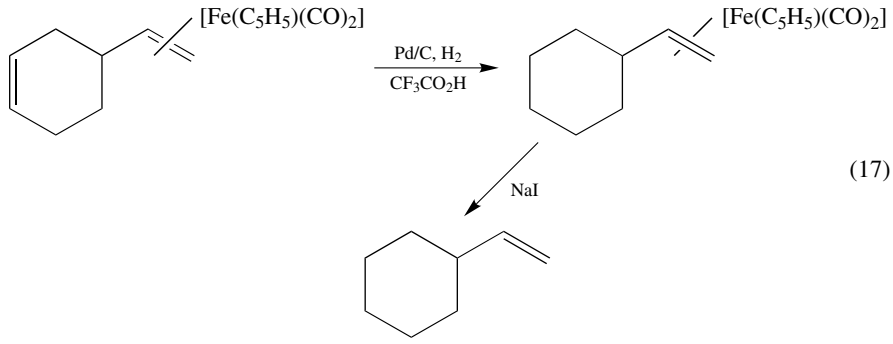


(16)

In most cases during the hydrogenation of dienes and polyenes there is an easily observed decrease in the rate of hydrogenation after the uptake of one mole of hydrogen. When this decrease is not easily detectable, it is worthwhile to stop the reaction after

the uptake of one mol hydrogen, because it may enable one to prepare successfully the half-hydrogenated product in a fairly good yield.

An interesting method is to protect one double bond by addition of cyclopentadienyl dicarbonyl iron during hydrogenation and afterwards to regenerate the product (equation 17)[57].



(17)

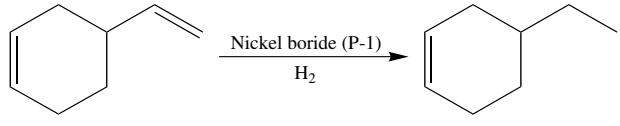
Not only metals but some oxide catalysts are active in diene hydrogenation: ZnO modified by $Sn(CH_3)_4$ afforded 1-butene in hydrogenation of butadiene at room temperature[58]. Reduced and sulfided molibdena on alumina catalyst hydrogenated butadiene and cyclohexadiene selectively[59]. When the transition metal complex $Mo(CO)_6$ was encapsulated in NaY zeolite cages, it converted *trans*-1,3-pentadiene to *cis*-2-pentene and 1,4-pentadiene to *cis*-1,3-pentadiene at 150 °C[60]. $Cr(CO)_3$ encaged in LiX or NaX zeolite was efficient and selective in butadiene hydrogenation to *cis*-2-butene[61].

Copper, gold and Pt/TiO_2 catalysts were tested in the hydrogenation of norbornadiene. When the latter catalyst is thermally treated at high temperature, strong metal support interaction takes place and the catalyst adsorbs a negligible amount of hydrogen. The common characteristic of these catalysts is that they cannot activate hydrogen, but the diene hydrogenation is rather fast. A plausible explanation is that the surface olefin–metal complex is directly involved in activating the molecular hydrogen[62].

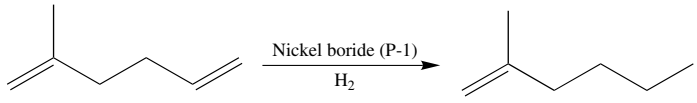
Catalysts formed by reacting nickel(II) acetate with NaH or $NaBH_4$ can be applied as hydrogenation catalysts in selective hydrogenations of dienes[63–65].

In aqueous medium, the reduction of nickel(II) acetate with $NaBH_4$ produces nickel boride[66]. This fine black precipitate, designated P-1 nickel, is a more active catalyst than Raney nickel for double-bond hydrogenations. The P-1 nickel catalyst produces less double-bond migration than standard Raney nickel, it is not pyrophoric and is more readily prepared than Raney nickel.

P-1 nickel can also be used for the selective hydrogenation of dienes. For instance, 4-vinylcyclohexene was hydrogenated with high selectivity (98%) to 4-ethylcyclohexene (equation 18), whilst 2-methyl-1-hexene was obtained with 93% selectivity from 2-methyl-1,5-hexadiene over it (equation 19)[66].

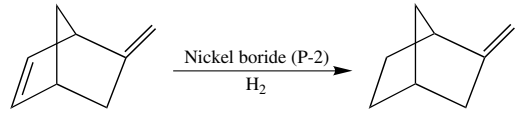


(18)



(19)

In ethanol nickel(II) acetate treated with $NaBH_4$ produces a nearly colloidal black suspension[63]. Variation of the solvent in the preparation of the nickel catalyst results in an amorphous nickel boride catalyst[67,68]. This P-2 nickel catalyst is much more sensitive to the double-bond structure[69,70]. In the hydrogenation of the strained double bonds of norbornadienes, P-2 nickel shows high selectivity (95%) and low isomerization characteristics (equations 20 and 21).



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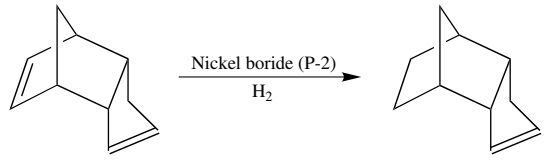


(21)

A complex reducing agent was prepared from NaH, RONa and nickel(II) acetate[64,65]. This catalyst (referred to as Nic), similarly to the P-1 and P-2 nickel catalysts, is a selective catalyst in diene reductions. The reactive parts of Nic are metal hydrides[71] and the key step in the hydrogenation is the formation of M−H bonds. The sodium salt of the alcohol added plays an important role as an activating agent in reductions using Nic. Whereas P-1 and P-2 nickels are selective and sensitive to the double-bond structure and show a rather low propensity toward isomerization, Nic has no propensity toward disproportionation.

B. Chemical Reduction

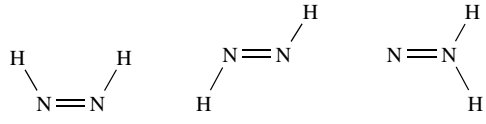
For the chemical reduction of dienes and polyenes diimide, ionic hydrogenating agents, metal hydrides containing reducing agents and alkali metals are used. The regioselectivity and the stereoselectivity can be different in these reductions depending on the nature of reagents.

1. Reduction by diimide

In the 1960s diimide was recognized as a new reducing agent in the reduction of double bonds[72−76].

Since diimide exists as a transient intermediate and cannot be isolated under normal conditions, procedures for reduction by diimide necessarily involve generation of the reagent *in situ*[74,75,77]. Diimide can be generated by (i) oxidation of hydrazine, (ii) acid decomposition of azodicarboxylate salts and (iii) thermal or base-catalyzed decomposition of substituted benzenesulfonyl hydrazides.

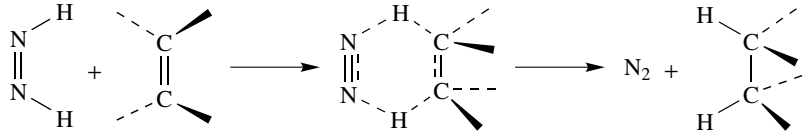
Diimide has three isomers: *cis*- and *trans*-diimide as well as 1,1-diimide (aminonitrene) (Figure 1)[77−80]. Although *trans*-diimide is the only isolated and characterized diimide, *cis*-diimide must be formed as a reactive intermediate in the reduction system[72,77].



cis-diimide *trans*-diimide 1,1-diimide

FIGURE 1

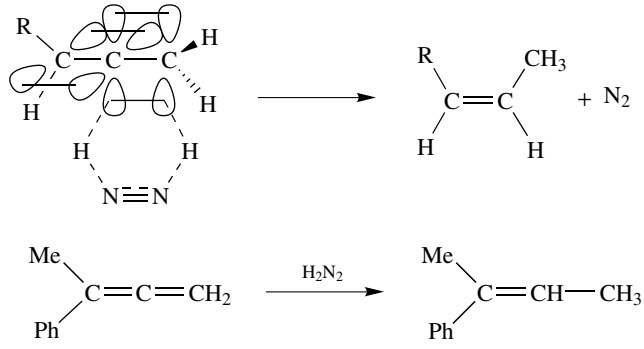
Transfer of hydrogen occurs exclusively in a *syn* manner and it has been concluded that the reduction of a multiple bond by diimide involves a synchronous transfer of a pair of hydrogens to a single face of the carbon–carbon double bond via a six-membered cyclic transition state to give a *syn* adduct (equation 22)[77,81].



(22)

Diimide can act as both a hydrogen acceptor and donor, undergoing disproportionation as a side-reaction which produces a considerable amount of nitrogen gas. From a practical point of view the occurrence of this disproportionation reaction requires the use of an excess of the diimide precursor.

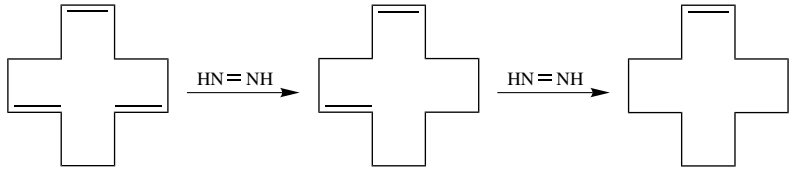
The reduction of dienes by diimide depends on the nature of the substitution of the diene. Several studies of relative reactivity have been carried out and they indicated that an increasing degree of alkyl substitution on the double bond results in decreasing reactivity[82]. In the case of allenes, the reduction of the less substituted allenic double bonds and the formation of the thermodynamically less stable *cis* olefin can be explained by the steric control of the approach of the diimide (equation 23)[83].



(23)

In the reduction of phenylallenes it was found that the phenyl group inhibits sterically the *cis* coplanar approach of diimide, while in alkylallenes the alkyl group activates electronically the remote double bond[81].

In general, *trans* double bonds are more reactive than *cis* double bonds, and diimide reduction is not accompanied by migration or by *cis–trans* isomerization of the double bonds (equation 24)[77].



(24)

It was shown that conjugated dienes are more reactive than monoenes in their reduction by diimide[84]. According to the data of Table 1, conjugation increases the relative reactivity in reduction of dienes (k_{rel}) compared with the reduction of monoenes, but the more substituted double bond is less reactive.

2. Ionic hydrogenation

Ionic hydrogenation reactions[85] involve the use of a hydrogenating pair consisting of a proton donor and a hydride ion donor. The ionic hydrogenation is based on the principle that the carbenium ion formed by the protonation of the double bond abstracts a hydride ion from the hydride source.

The hydrogenating pair consisting of a proton source and a hydride ion source has to meet several requirements[86]. The proton donor must be sufficiently acidic to protonate the carbon–carbon double bond of the substrate to form a carbocation, but not so acidic as to protonate the hydride source. The intermediate carbocation must be electrophilic enough to abstract a hydride ion from the hydride source, but it should not react with any other nucleophile source in the reaction system, including the conjugate anion of the proton donor. In these respects the pairs involving trifluoroacetic acid and organosilanes proved to be the most useful. The donating ability of organosilanes in ionic hydrogenation reactions is a function of the substituents on the silicon atom, and it decreases in the following sequence[87–89]:

$$Et_3SiH > (n\text{-}C_8H_{17})_3SiH > Et_2SiH_2 > Ph_2SiH_2 > Ph_3SiH > PhSiH_3.$$

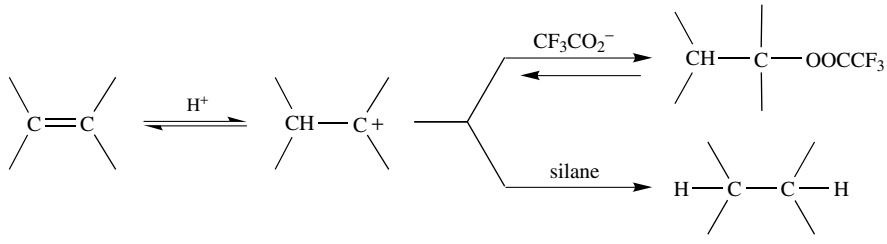
The ionic hydrogenation of unsaturated carbon–carbon bonds proceeds according to Scheme 2.

The rate-determining step in ionic hydrogenation is the protonation of the C=C bond[90]. The unsaturated substrate must be capable of forming a stable carbocation by protonation with CF_3CO_2H which strongly limits the application of this reaction. Unsaturated compounds which are branched at the alkenic carbon atom can be easily reduced[86,91], but unbranched compounds are not reduced under conditions of ionic hydrogenation reaction[91,92].

TABLE 1. Relative reactivities[a] in the reduction of dienes by diimide

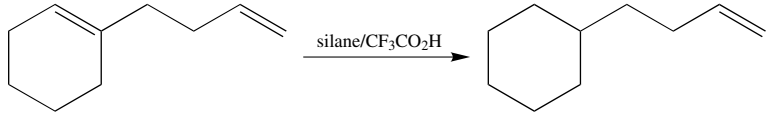
Dienes	k_{rel}
Cyclohexene	1.0
1,3-Cyclohexadiene	47.4
1,4-Cyclohexadiene	2.8
2-Methyl-1,3-butadiene	13.6
2,3-Dimethyl-1,3-butadiene	3.1
2,5-Dimethyl-2,4-hexadiene	0.5

[a]Relative to cyclohexene.



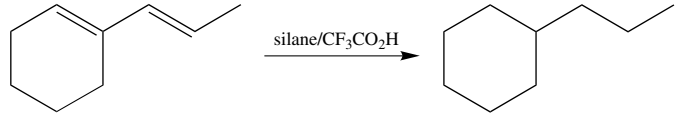
SCHEME 2

In a nonconjugated diene, where the C=C bonds are separated by two or more methylene groups, only the double bond containing a branched carbon atom is reduced (equation 25)[85].



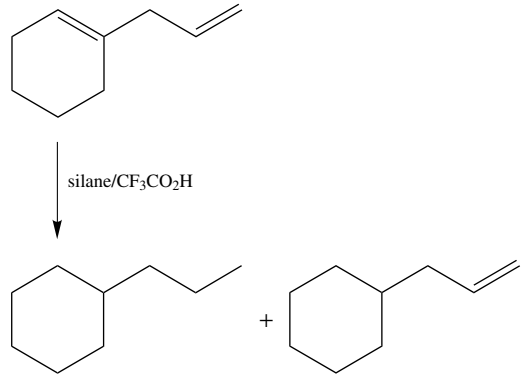
65% (25)

In a conjugated diene, where one of the carbon atoms is branched, both alkenic bonds are hydrogenated in the trifluoroacetic acid/silane reaction mixture to give the corresponding saturated hydrocarbon (equation 26)[85].



70% (26)

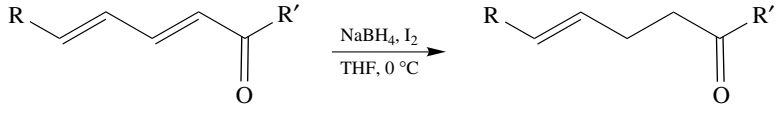
When the alkenic bonds are separated by one methylene group, the branched alkenic bond is mainly reduced but the completely hydrogenated product is also formed (equation 27)[85].



15% 55% (27)

3. Reduction by metal hydrides and dissolving metals

In the reduction of dienes and polyenes, combinations of a metal hydride and transition metal halides can also be used. Sodium borohydride and cobalt(II) halides were applied in the selective reduction of unsaturated carbon–carbon double bonds[93]. $LiAlH_4$, in the presence of Zr^{IV}-, Ti^{IV}- or V^{IV}-halides, is a selective reducing agent of dienes[94,95]. The following reactions were carried out with sodium borohydride and iodine (equation 28)[96].

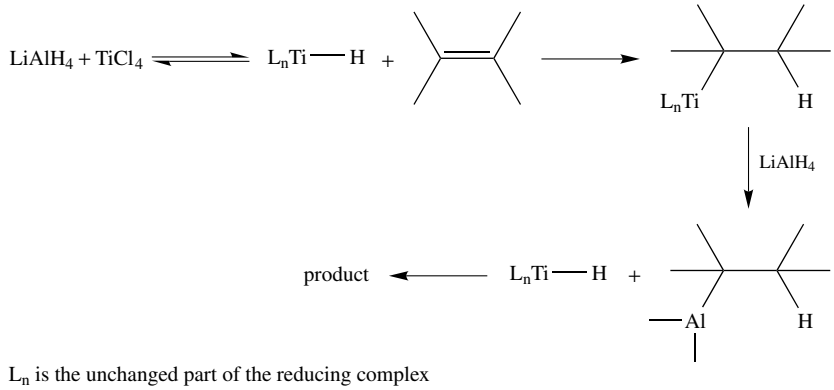


(28)

R	R′
3,4-Methylenedioxyphenyl	Piperidyl, *i*-BuNH
C_5H_{11}	*i*-BuNH

The first step of the reduction by cobalt(II) chloride and $NaBH_4$ involves the production of cobalt hydride species which is capable of exchanging hydrogen ligands with the medium. The second step is a hydrometallation reaction followed by a reductive cleavage of the carbon-cobalt bond. The hydrocobaltation seems to be reversible, as indicated by deuterium label incorporation[93].

Titanium tetrachloride is a very effective catalyst for the addition of $LiAlH_4$ or alane to the olefinic double bond. The mechanism of this reaction involves intermediate transition metal hydrides, as in the case of reaction of $NaBH_4$ and Co^{II}-salts. The hydrotitanation of the double bonds is probably followed by a rapid metal exchange reaction (Scheme 3)[94].



L_n is the unchanged part of the reducing complex

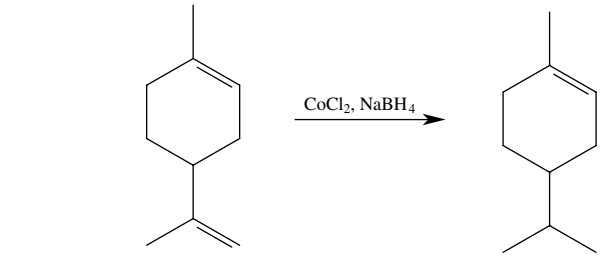
SCHEME 3

The combination of Co^{II}-salts with $NaBH_4$ is a selective reducing agent of a disubstituted side-chain olefinic double bond in the presence of a trisubstituted endocyclic double bond, which is demonstrated in the reduction of limonene (equation 29)[93,97].

The selectivity decreases in the following sequence: mono- > di- > tri- and tetrasubstituted alkenes, an order which can be ascribed to the operation of steric effects.

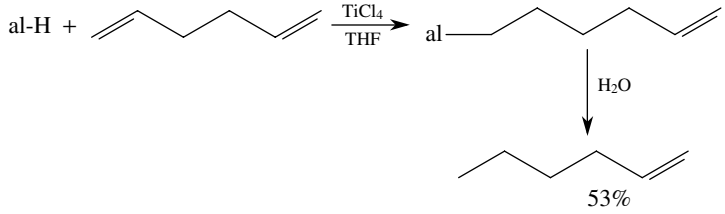
In the reaction of $LiAlH_4$ with nonconjugated dienes in the presence of titanium(IV) or zirconium(IV) chloride, selective reduction of the less hindered double bond was observed

(equation 30)[94,95].

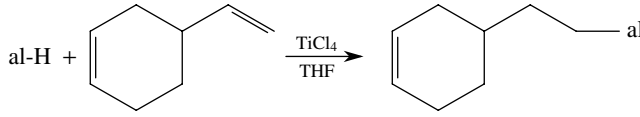


(29)

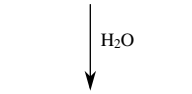
79%



53%



(30)



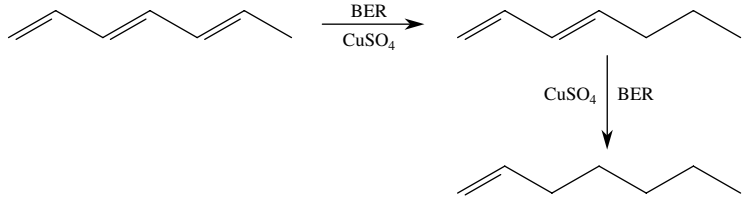
97%

al-H = $LiAlH_4$

The relative rates for reduction of double bonds are in the following order:

$$RHC{=}CH_2 > R'RC{=}CH_2 > RHC{=}CHR'.$$

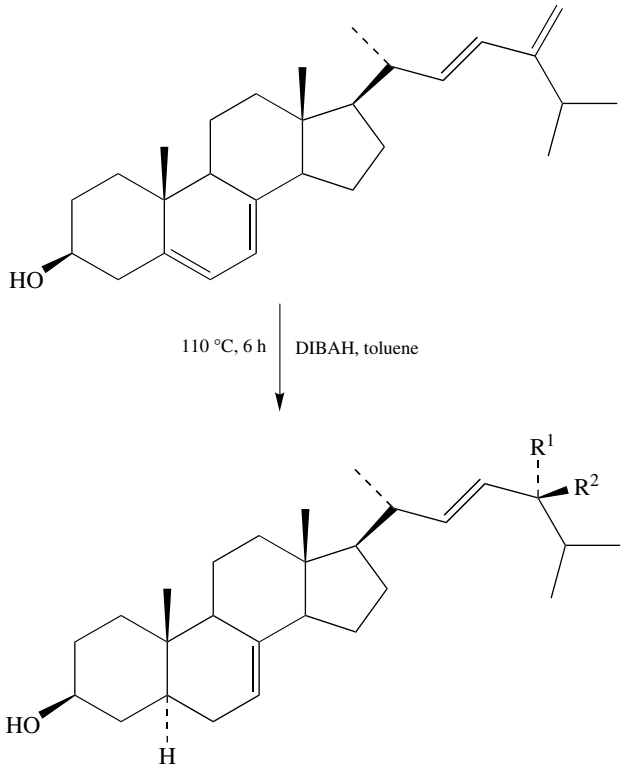
A special mild reducing agent called BER is prepared by treating an anion exchange resin with aqueous $NaBH_4$. Addition of $CuSO_4$ allows selective reductions of dienes and polyenes (equation 31)[98].



(31)

The reduction of conjugated dienes by dissolving metals is not extensively reported. This method appears to be nonselective, giving rise to a mixture of the expected olefins and polyolefins as by-products[99].

Recently, diisobutylaluminium hydride (DIBAH) was found to be a selective reducing agent in the reduction of steroidal 5,7 and 22,24(28) dienes (equation 32)[100].



(32)

R^1 = Me, R^2 = H

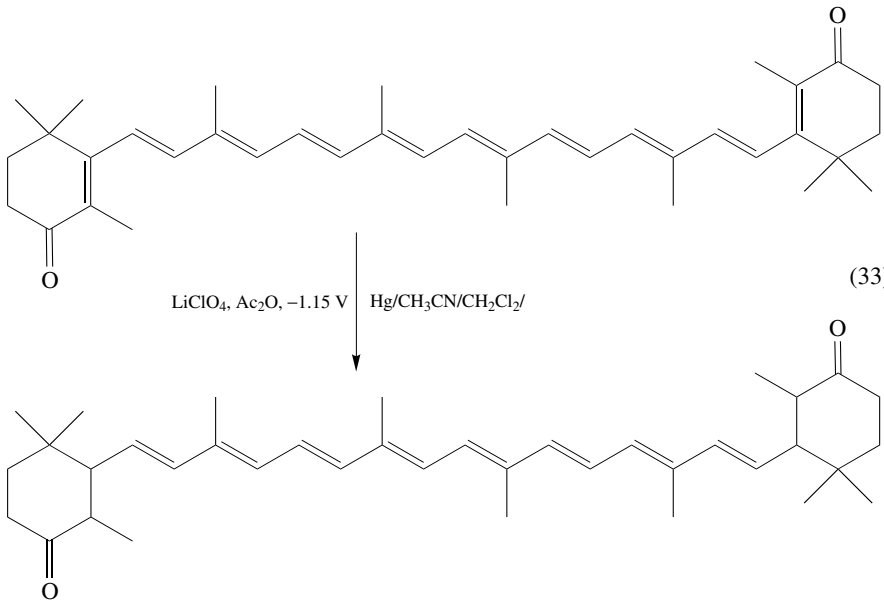
R^1 = H, R^2 = Me

C. Electrochemical Reduction

The electrocatalytic reduction of dienes, like that of monoenes, is difficult when the double bond is not activated. Polyolefins with isolated double bonds cannot be reduced on mercury cathode, while double bonds conjugated to another π-system can be reduced.

The reduction is usually made in a multi-compartment electrochemical cell, where the reference electrode is isolated from the reaction solution. The solvent can be water, alcohol or their mixture. As organic solvent *N*,*N*-dimethylformamide or acetonitrile is used. Mercury is often used as a cathode, but graphite or low hydrogen overpotential electrically conducting catalysts (e.g. Raney nickel, platinum and palladium black on carbon rod, and Devarda copper) are also applicable.

It is possible to get 4,4′-dioxo-5,5′,6,6′-tetrahydrocarotene by reduction of 4,4′-dioxo-β-carotene at a mercury cathode (equation 33)[101].

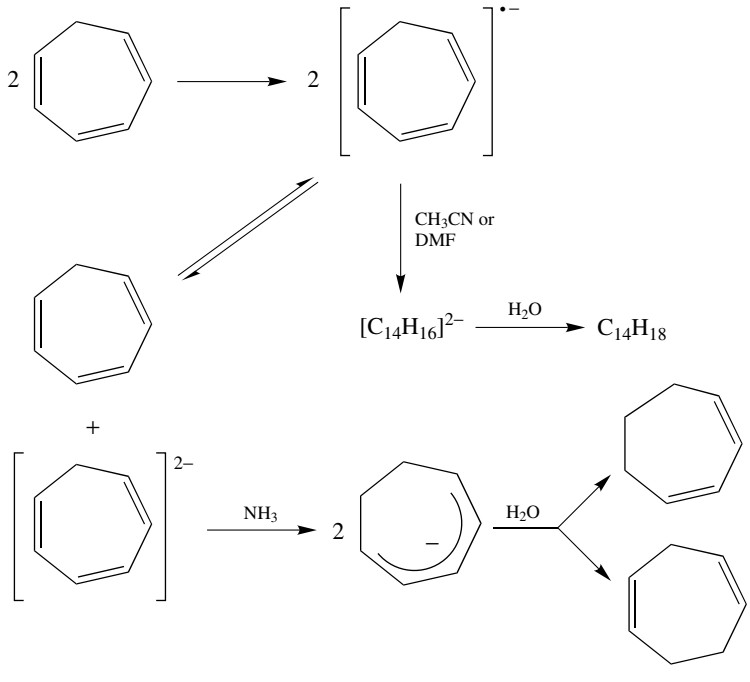


(33)

Cyclooctatetraene was reduced electrochemically to cyclooctatetraenyl dianion. In DMF the product is mostly (92%) 1,3,5-cyclooctatriene at −1.2 V. If the potential is lowered the main product is 1,3,6-cyclooctatriene. Previous experiments, in which the anion radical was found to be disproportionated, were explained on the basis of reactions of the cyclooctatetraene dianion with alkali metal ions to form tightly bound complexes, or with water to form cyclooctatrienes. The first electron transfer to cyclooctatetraene is slow and proceeds via a transition state which resembles planar cyclooctatetraene[102].

The reduction of cycloheptatriene was studied in aprotic solvents at a platinum electrode. A reversible wave at −2.5 V for the production of the radical anion was observed in ammonia containing 0.1 M KI. Quasi-reversible or irreversible reduction was observed in acetonitrile and in *N*,*N*-dimethylformamide (equation 34)[103].

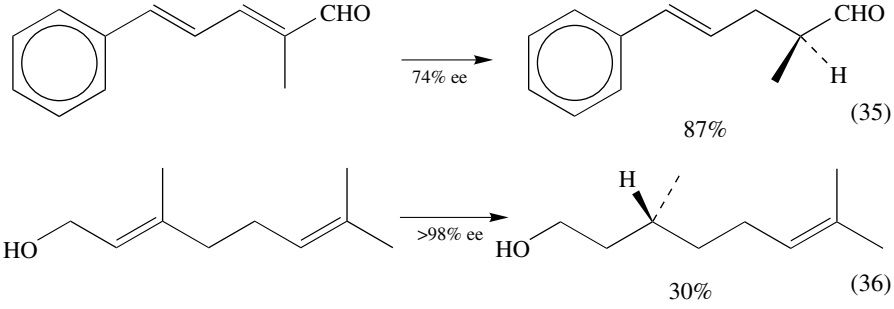
Soybean oil can be hydrogenated electrocatalytically at a moderate temperature, without an external supply of pressurized H_2 gas. In the electrocatalytic reaction scheme, atomic hydrogen is produced on an active Raney nickel powder cathode surface by the electrochemical reduction of water molecules from the electrolytic solution. The concentration of the hydrogen in the catalyst metal surface can easily be controlled by adjusting the applied current (or electric potential), which may lead to improved product selectivity; the catalyst will be cathodically polarized during reactor operation, resulting in less corrosion and lower concentrations of nickel ion contaminants in the oil product; since only a little free hydrogen gas is present, the risk of explosion and fire is reduced. The adsorbed hydrogen then reacts with triglycerides to form the hydrogenated product. The electrohydrogenated oil is characterized by a high stearic acid content and a low percentage of total *trans* isomers, as compared with that produced in a traditional hydrogenation process[104].

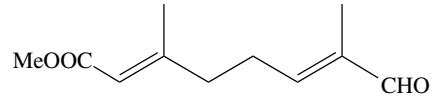


D. Enzymatic Reduction

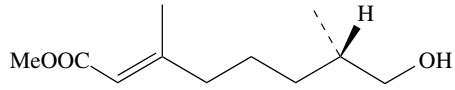
Besides the most widely used catalytic reductions of dienes and polyenes there are some other ways to saturate the C=C double bonds in these molecules. One of these rarely used methods is the enzymatic or microbial reduction. In the presence of bacteria and fungi the reactions progress just as over any classical catalysts.

Several catalysts are used in the field of microbial reductions. The common features of these catalysts are the high selectivity and their use only on a laboratorial scale. They are applied, for example, in the stereoselective synthesis of pharmaceutical intermediates. The reductions are exclusively selective either in the hydrogenation of the C=C double bond or in that of other reducible groups. One of the most widely used catalysts is baker's yeast. In the following hydrogenations, which are catalyzed by *Saccharomyces cerevisiae*, high enantioselectivities were achieved (equations 35–38)[105–108].



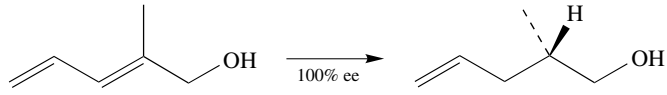


>97% ee



35%

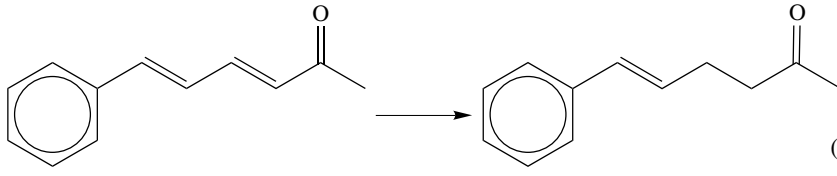
(37)



25–30%

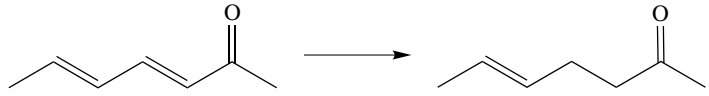
(38)

Baker's yeast can also be used in the saturation of α,β-unsaturated ketones. The reactions described share the following features: (i) remote double bonds are not hydrogenated, (ii) the reaction rate is affected by substitution on or near the double bond and (iii) after a prolonged reaction time reduction of the oxo group can also take place (equations 39 and 40)[109].

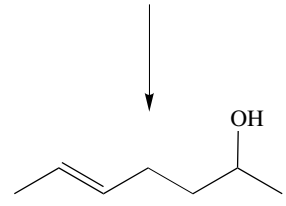


75%

(39)



60%

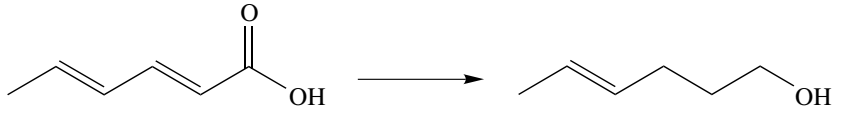


60%

(40)

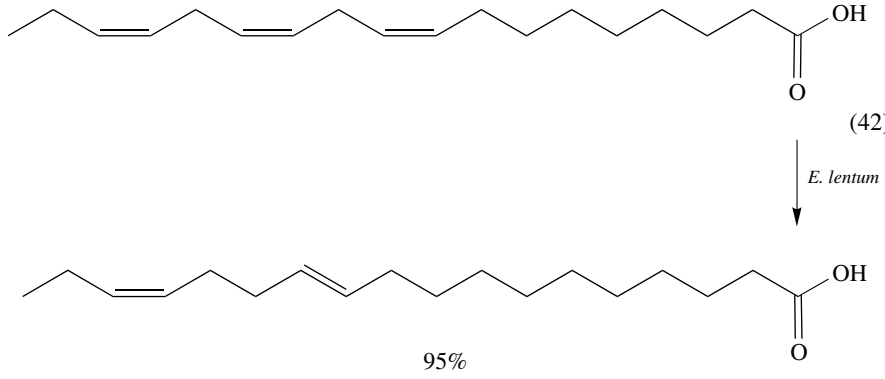
Fungi are capable of producing *trans*-4-hexenol from sorbic acid (equation 41)[110]. This bioconversion comprises two reaction steps. First, the carboxy function is reduced

to alcohol and then the saturation of the α,β-double bond proceeds. The remote double bond remains unchanged. The hydrogenation of sorbic acid can be performed with *Mucor sp.* A-73, as well as with other fungi belonging to the genera *Penicillinum*, *Rhizopus*, *Trichoderma*, *Aspergillus*, *Geotrichum* and *Monascus*[111].



90% (41)

Double bonds of other groups of molecules, such as fatty acids, are reduced with *Butyrivibrio fibrisolvens*[112,113] or *Eubacterium lentum*[114,115]. Under anaerobic conditions *B. fibrisolvens* is able to hydrogenate linoleic acid to octadecenoic acid[112]. This is a multistep reduction, in which isomerization and hydrogenation take place consecutively. α-Linolenic acid was also isomerized with *B. fibrisolvens* to produce a conjugated trienoic acid (9-*cis*,11-*trans*,15-*cis*-octadecatrienoic acid) which was hydrogenated to a nonconjugated *cis–trans* dienoic acid[113]. *Eubacterium lentum* can regioselectively hydrogenate at the 9-position of linoleic, α-linolenic and γ-linolenic acids. Thus, α-linolenic acid ($\Delta^{9,12,15}$) was reduced to 11-*trans*,15-*cis*-octadecadienoic acid with 95% yield (equation 42)[114,115].



(42)

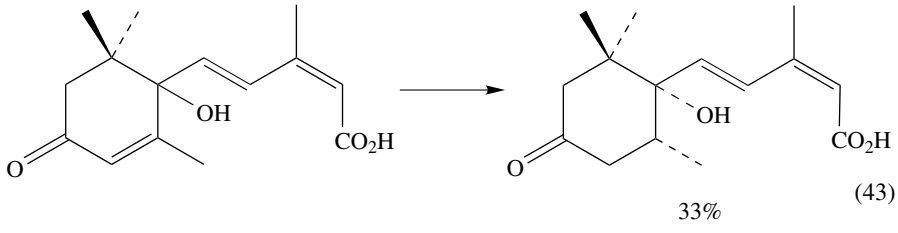
95%

The hydrogenation of the monoterpenes (−)- and (+)-carvone was studied extensively. Several microorganisms were used in these reductions. They catalyzed the production of all possible stereoisomers, but some of them only in small quantities. The distribution of the products depended on the catalyst applied[116].

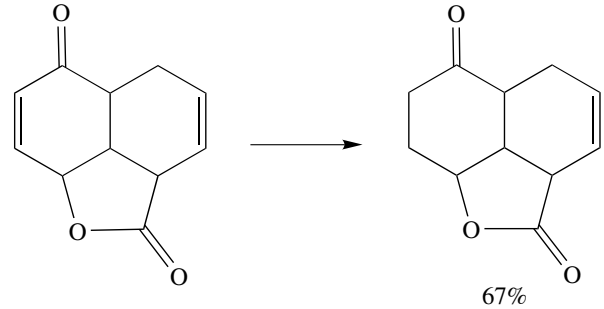
Finally, there are some examples for reduction of various compounds, which are of biochemical interest. Racemic abscisic acid was reduced with *Aspergillus niger* affording (−)-(1′*S*,2′*R*)-2′,3′-dihydroabscisic acid with >95% ee (equation 43)[117].

The reduction of Woodward's lactone with *Saccharomyces cerevisiae* produced an intermediate which is used for the preparation of hypotensive alkaloids (equation 44)[118].

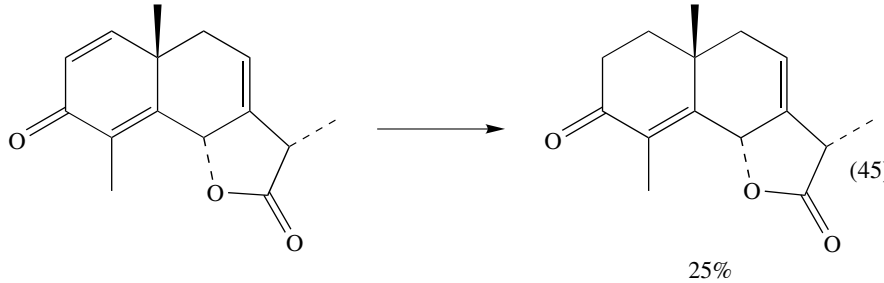
α-Santonin, a sesquiterpene lactone, was reduced with *Pseudomonas cichorii S* (equation 45)[119].



33% (43)



67% (44)



25% (45)

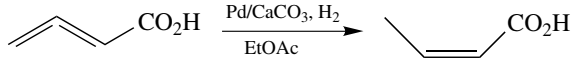
III. REDUCTION OF DIENES AND POLYENES WITH DIFFERENT STRUCTURES

A. Allenes

Allenes are reduced in two distinct stages. In the first stage, the major products are olefins, accompanied by a small amount of the alkane, while in the second stage the olefins produced are reduced to alkanes. The selectivity of reduction varies with the metal[34], and for allene itself at various temperatures it decreased in the following series of metals:

$$Pd > Rh \approx Pt > Ru > Os \gg Ir.$$

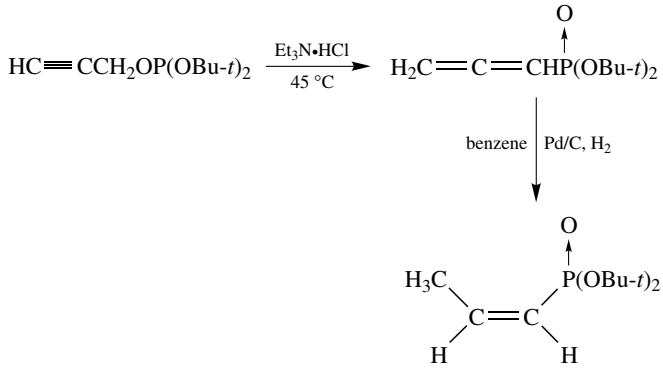
Allenes with terminal double bonds are selectively reduced in the terminal position, whereas internal allenes afford a mixture of the corresponding olefins[120]. Some hydrogenations resulted in the *cis* alkene derivative (equation 46)[121].



(46)

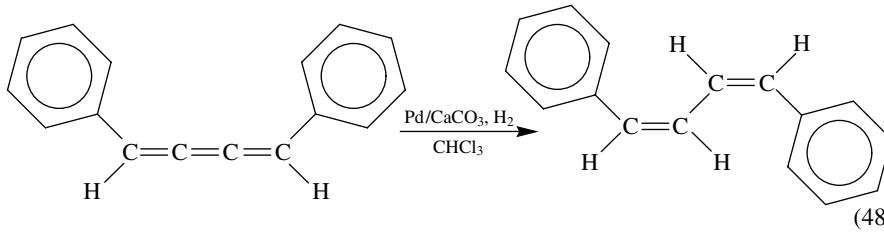
Similarly, 1,2-cyclononadiene in methanol with 10% palladium on carbon catalyst gave *cis*-cyclononene[122]. The *cis* isomer is not necessarily the primary product of allene hydrogenation, since the initially formed *trans* isomer is rapidly isomerized under the reaction conditions. Bond and Sheridan showed that allene resembles acetylene in its ease of hydrogenation[123]. They suggested that it is selectively adsorbed and held more strongly by the catalyst than 1-propene. Allene was selectively hydrogenated with Pd, Pt and Ni in the presence of 1-propene without its further reduction.

An example of the synthetic use of allene hydrogenation is the preparation of the antibiotic phosphonomycin (equation 47)[124].



(47)

In the reduction of trienes, only the central double bond was hydrogenated (equation 48)[125]. The product was a *cis*,*cis*-1,3-butadiene derivative. Similar results were obtained in the hydrogenation of the tetraphenyl derivative with a Pd catalyst modified by lead[126].



(48)

B. Conjugated Dienes

A conjugated double bond should be more resistant to hydrogenation than an isolated one, because the conjugation energy is included in the energy balance (the heat of hydrogenation is 227 kJ mol^{-1} for 1,3-pentadiene and 255 kJ mol^{-1} for 1,4-pentadiene). In spite of this, conjugated olefins are hydrogenated more easily[127].

Much experience concerning the hydrogenation of conjugated dienes was obtained with butadiene hydrogenation. On Pt single crystals the reaction was found to be structure sensitive; the activity sequence of different planes (marked with Miller's index) is

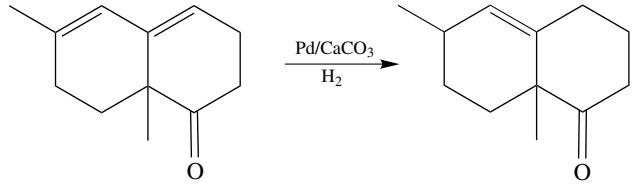
$$(111) < (100) < (110)$$

The $H_2 + D_2$ equilibration reaction was much faster than the diene hydrogenation, so that the rate-limiting step is not the hydrogen dissociation. The Pt behaves as a bifunctional

catalyst, and the hydrogenation and hydrogen exchange reactions do not occur at the same kind of sites. An adsorbed hydrocarbon layer is present on the Pt surface during the hydrogenation. This does not prevent the dissociation of hydrogen but induces geometrical hindrance as well as an electronic effect[128].

In the case of Pd/Al_2O_3 catalysts the morphology of the metal particles is also important because it determines the hydrogenation and isomerization selectivity. On flat metal surfaces isomerization is preferred whereas rough surfaces are more active in hydrogenation[129].

The most disputed question about the hydrogenation of conjugated dienes is whether 1,2- or 1,4-addition takes place as in the following reaction (equation 49)[128].

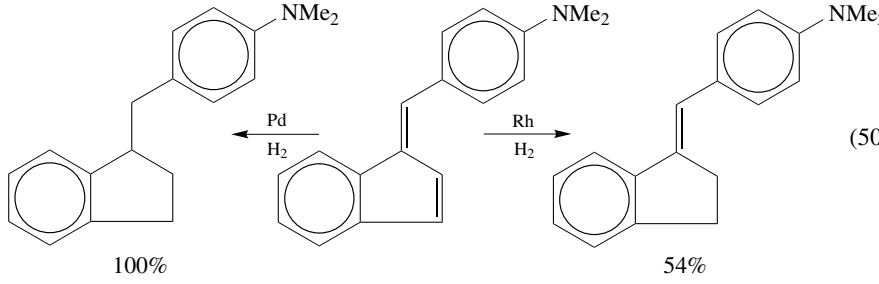


(49)

This is the most dubious in the case of Pd catalysts, which have high activity in isomerization and double-bond migration. From studies of the half hydrogenation and the isomerization of isoprene[130] with Pd, Pt and Ni, the Pd catalyst led to the highest extent of isomerization. From the results of the reduction of isoprene it appears that 1,4-addition as well as 1,2- and 3,4-additions took place, because a significant amount of 2-methyl-2-butene was formed with all catalysts.

Most researchers have found 1,2-addition of hydrogen in C=C hydrogenation of conjugated double bonds[131–134], for example, in the reduction of 1-vinylcyclohexene, 4-methylene-1,2,3-trimethylcyclobutene-3-ol benzoate and some steroid derivatives.

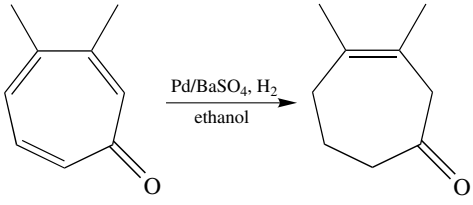
The selectivity of partial hydrogenation depends on the catalyst in the case of a benzylidene indene derivative (equation 50)[135].



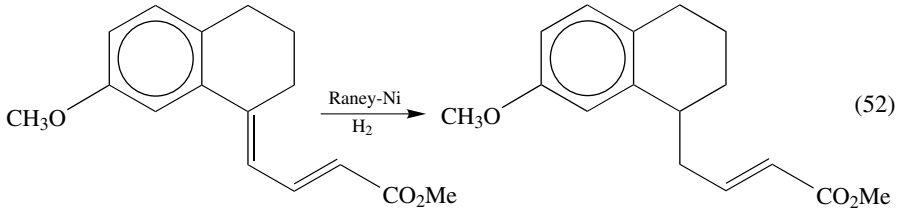
(50)

The reduction of some polyenes is affected by the double bond migration, e.g. when a tetrasubstituted olefin is formed, since it is hydrogenated with difficulty. For example, the reduction of the second double bond was fast, but the reduction ceased after the uptake of two moles of hydrogen (equation 51)[136].

Raney-nickel was found to be selective in the hydrogenation of cyclopentadiene and cyclohexadiene and of their methyl and ethyl derivatives at 0–40 °C and 2–5 bar pressure[137,138]. The skeletal nickel proved to be selective in the semihydrogenation of conjugated polyenic compounds (equation 52)[139].

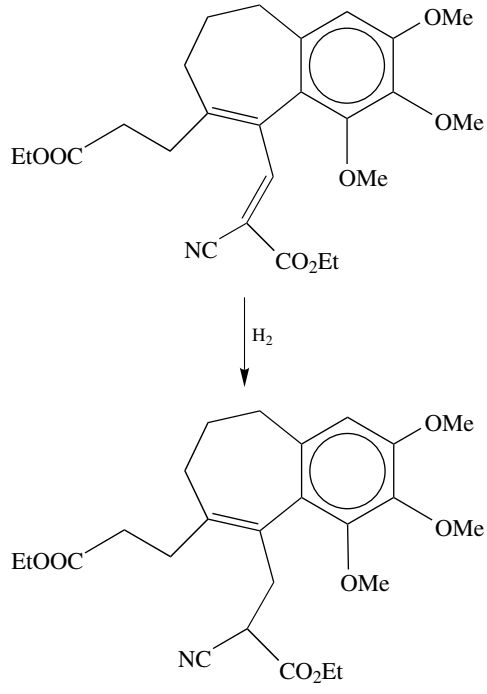


(51)



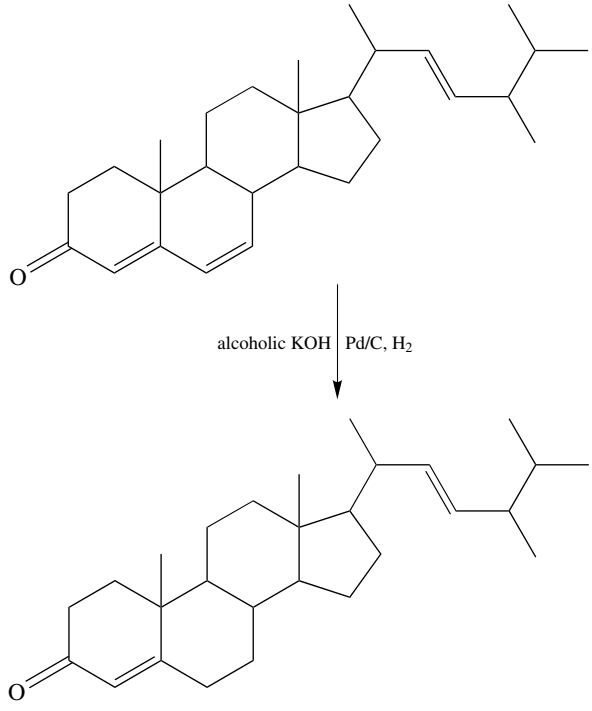
(52)

In the above mentioned reaction, platinum oxide and palladium on barium sulfate showed no perceptible change in the rate of hydrogen uptake. On the other hand, platinum oxide was selective in the hydrogenation of cyclohexa-2,4-diene-1,2-dicarboxylic acid to 1,4,5,6-tetrahydrophthalic acid[140]. A similar result may be the favored reduction of a symmetrical disubstituted double bond over a more hindered trisubstituted bond. The retarding effect of additional substitution is demonstrated in the hydrogenation of a trisubstituted double bond in the presence of a tetrasubstituted double bond (equation 53)[141].



(53)

The selectivity can be increased by addition of alkali (equation 54)[142].

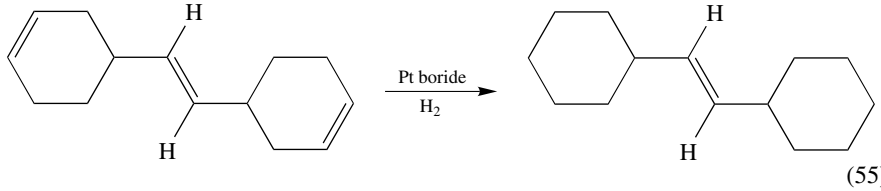


(54)

Another method of increasing the catalyst's selectivity is its poisoning with heavy metals, like lead. This was effective with a Pd catalyst in the hydrogenation of cyclopentadiene, 1,3-cyclohexadiene and cyclooctatriene[143].

C. Isolated Dienes

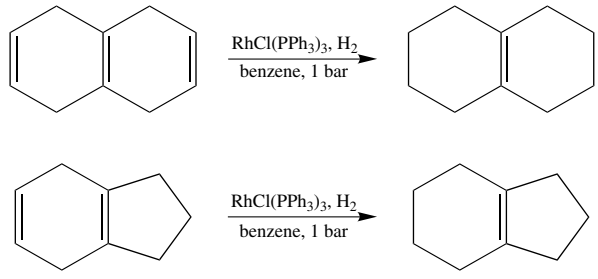
The selectivity in the hydrogenation of isolated double bonds depends on the type of substitution of the unsaturated carbon atoms, as in the reaction in equation 55[144].



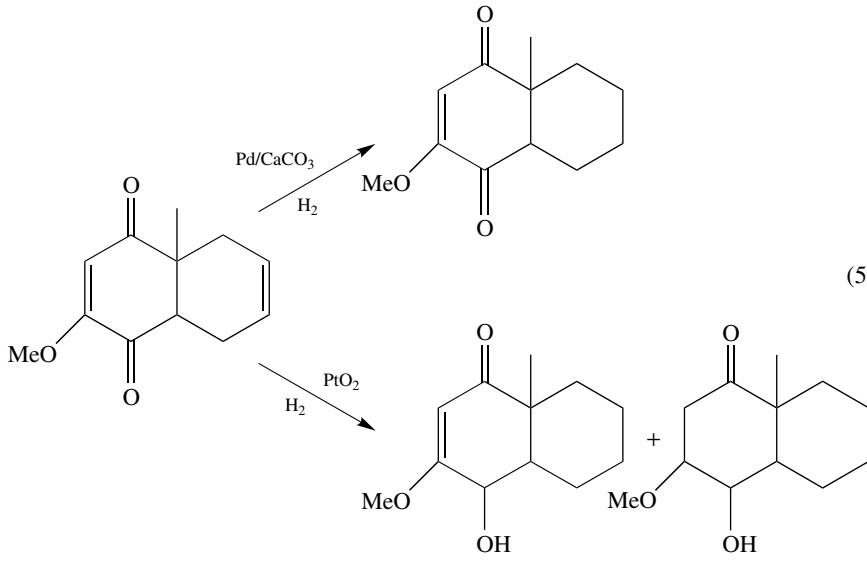
(55)

A similar phenomenon was observed in a homogeneous rhodium complex catalyzed hydrogenation (equation 56)[6].

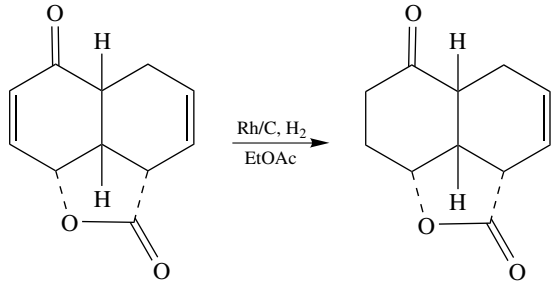
In the case of molecules which have both conjugated and isolated double bonds, the selectivity of the hydrogenation depends on the catalysts and on the nature of the substituents of the unsaturated compound (equations 57 and 58)[145,146].



(56)



(57)

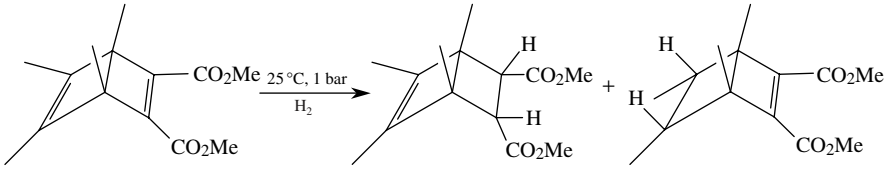


(58)

The selectivity of hydrogenation of dimethyl tetramethylbicyclo[2.2.0]hexa-2,5-diene-5,6-dicarboxylate depends on the catalytically active metal and on the bulk of the ester substituent (equations 59 and 60)[147].

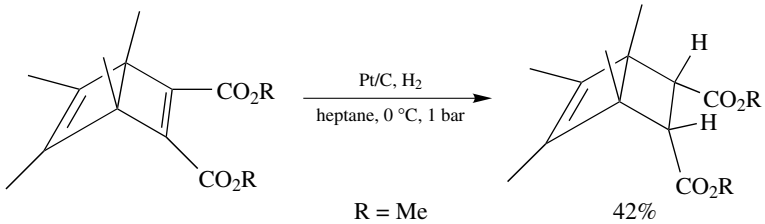
There are other possibilities for selective reduction in the hydrogenation of symmetrically substituted dienes. Raney-nickel afforded 1-alkenes, whereas supported Pd catalysts gave a mixture of 1- and 2-alkenes[148]. A selective reduction of a terminal double bond was carried out in the presence of an endocyclic double bond, which was trisubstituted[149–152].

The ability of Pd to cause isomerization is demonstrated in the reaction of equation 61[153].



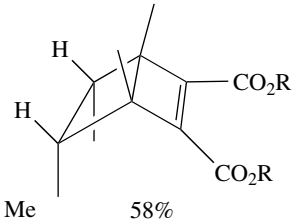
Raney-Ni	100%	0%
Pd/C	85%	15%
Ru/C	66%	34%
Rh/C	52%	48%
Pt/C	47%	53%
Os	32%	68%

(59)



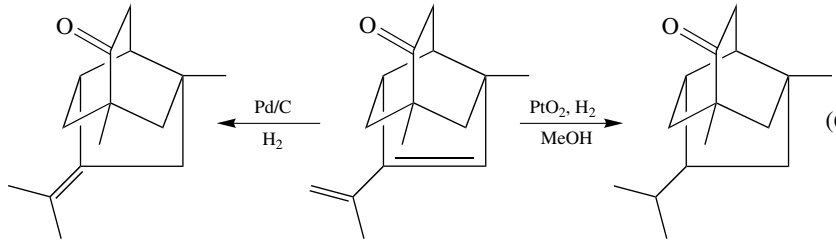
R = Me 42%
R = *t*-Bu 5%

+



R = Me 58%
R = *t*-Bu 95%

(60)

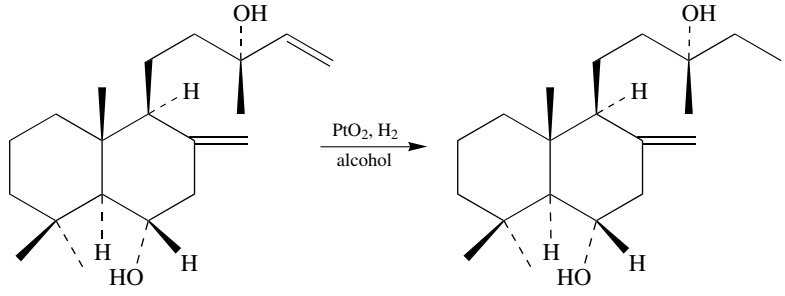


(61)

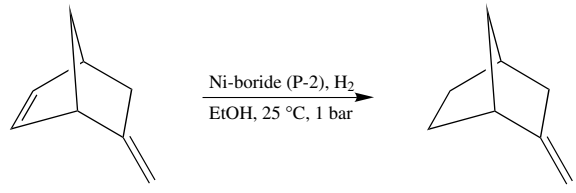
Preferential reduction of a monosubstituted double bond in the presence of an unsymmetrically disubstituted double bond is shown in equation 62[154].

Ring strain can also exert an important influence on the regioselectivity: the hydrogenation of 5-methylenenorbornene over a Ni-boride catalyst (P-2) resulted in preferential

saturation of the strained endocyclic double bond, although the exocyclic double bond seems to be more accessible (equation 63)[63].

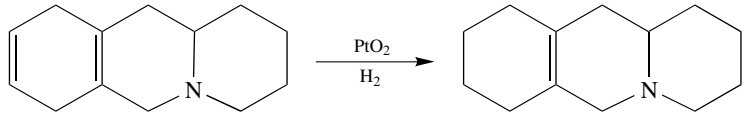


(62)



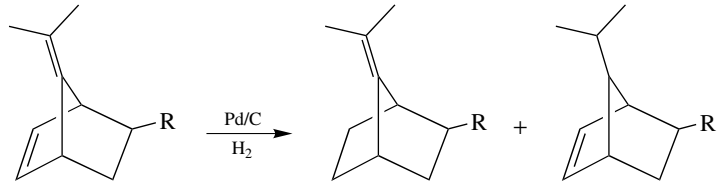
(63)

The hydrogenation of a symmetrically disubstituted double bond is favored over that of a tetrasubstituted one (equation 64)[155–157].



(64)

Selective reduction of dienes may be influenced by the substituents, which can change the substrate orientation during adsorption on the catalyst surface (equation 65)[158]. It has to be mentioned that this effect worked only if low amounts of catalyst were used; at higher amounts the selectivity decreased.

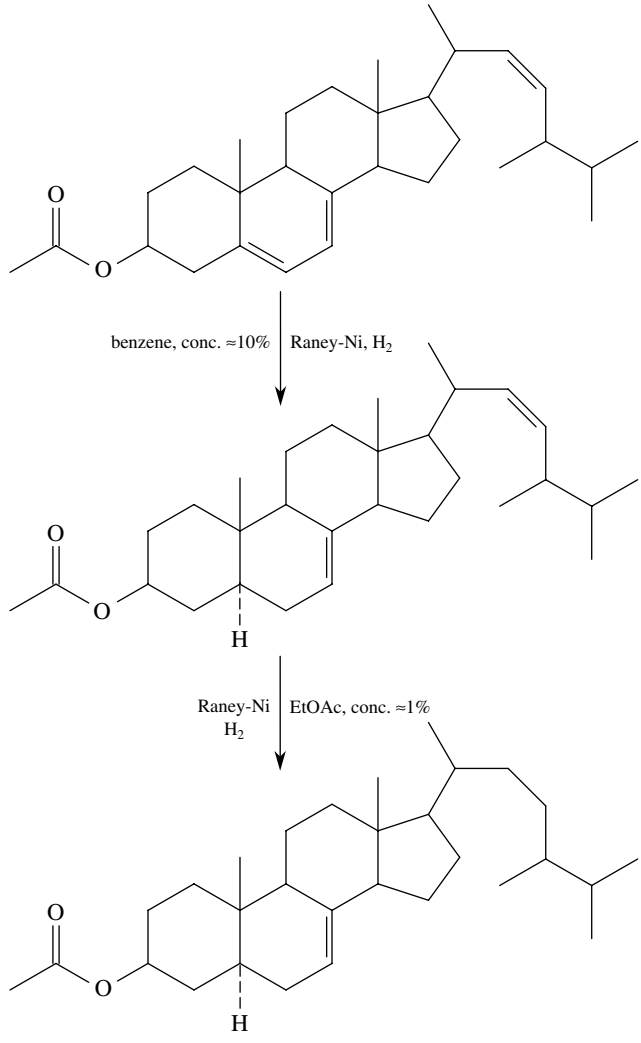


(65)

R = =O	70%	30%
R = –OH	60%	40%
R = –OAc	95%	5%
R = –OTs	>95%	–

The solvent can be an important factor in determining the outcome of hydrogenation as demonstrated by the reduction of a steroid compound (equation 66)[159,160]. At 100 °C

only the saturated compound is produced.



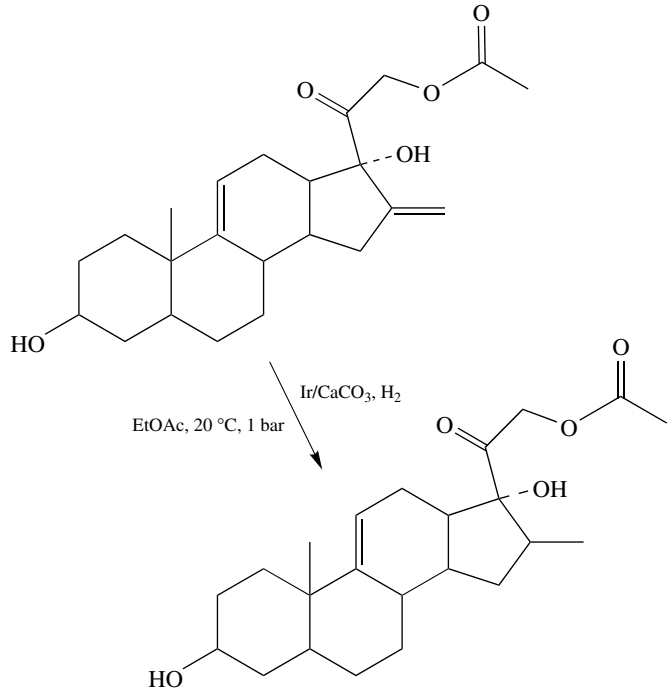
(66)

An iridium catalyst was used in the selective hydrogenation of a steroid compound, where the exocyclic double bond was saturated in the presence of an endocyclic one (equation 67)[161].

D. Polymeric Compounds

Reduction is an important method for polymer modification resulting in a variety of useful elastomers and thermoplastics with unique structures and properties. Reduction also offers a convenient synthetic route to polymers with special monomer sequences, which are inaccessible, difficult or too expensive to prepare by conventional polymerization

methods. The saturated elastomers have good resistance to oxidative and thermal degradation, excellent resistance to oils and fluids at elevated temperatures, low permeability to gases, and better processibility as compared with the unsaturated elastomers[162].



(67)

The aim of the reduction of polymeric compounds is the complete saturation of the substrate, which is different from the usual practice of the hydrogenation of dienes and polyenes, where the incomplete reduction, i.e. a selective reduction, is the main goal.

The reduction can be carried out with stoichiometric reducing agents and by homogeneous or heterogeneous catalytic hydrogenation. A problem in the selectivity in these reactions is the presence of highly coordinating functionalities such as nitrile, carbonyl, amino, hydroxyl, halogen, etc.

The reduction of polymers can be carried out by using a diimide, generated *in situ*. The precursor for diimide can be *p*-toluenesulfonyl hydrazide (TSH), the reaction temperature is between 110–160 °C and the solvents are high boiling aromatic compounds. Possible side-reactions are *cis–trans* isomerization of 1,4-dienes, attachment of hydrazide fragments to the polymer, degradation and cyclization of the polymer.

In the heterogeneous catalytic hydrogenations the polymers, such as the copolymers and homopolymers of styrene, butadiene, isoprene and acrylonitrile, are in solution. The solvents can be cyclohexane, tetrahydrofuran, hexane, acetone, methyl ethyl ketone or methyl isobutyl ketone, the catalytically active metals (Pt, Pd, Ru, Rh, Ni) are supported, the temperature is usually up to 240 °C and the pressure range is from atmospheric to 50 bar. The major advantage of heterogeneous hydrogenation is the easy separation of the catalyst, but the reaction has several disadvantages, such as slow reaction rate, high temperature and pressure, and high catalyst concentration.

The homogeneous hydrogenation catalysts for polymer saturation can be classified into two types: Ziegler-type (Ni, Co, Fe, Ti, Zr based) and noble metal (Rh, Ru, Pd) catalysts.

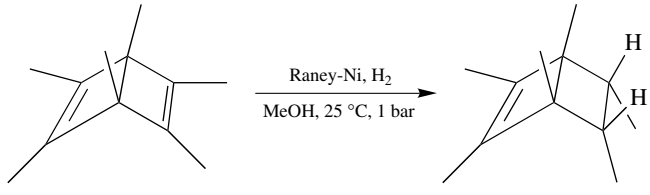
The Ziegler-type catalysts contain also a metal-alkyl, like triethylaluminum. They work usually at moderate temperature and pressure. The most active catalysts for polymer hydrogenation are the noble metal complex catalysts, and they can also be used for reduction of elastomers in the latex phase. The most difficult task is the removal of the catalyst from the reaction mixture. The methods used are based on extraction, adsorption, absorption or on their combination.

The hydrogenated products are nitrile rubber, with good heat resistance, and styrene–butadiene–styrene copolymer, with high tensile strength, better permeability and degradation resistance.

E. Stereoselectivity

In heterogeneous catalytic hydrogenations suprafacial (*cis*) addition of hydrogen would be expected, as the transfer of hydrogen atoms from the catalyst surface to the reactant is usually assumed. However, in some Pt catalyzed reactions antarafacial (*trans*) addition of hydrogen is also observed. The ratio of diastereomeric products formed is determined by the chemisorption equilibrium of the surface intermediates and by the relative rates of hydrogen entrance to the different unsaturated carbon sites. Both effects are influenced by steric factors.

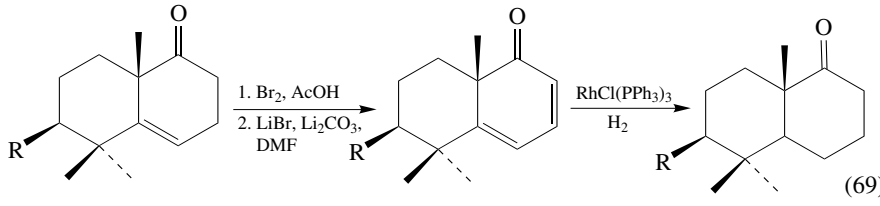
The hydrogenation of hexamethylbicyclo[2.2.0] hexa-2,5-diene over Raney-nickel gives, by *exo* addition, the more strained product. Consequently, it seems that *exo* addition is favored in small bicyclic compounds over the *endo* addition (equation 68)[163].



(68)

α-Hydrogenation of alkenic steroids, which is often observed, plays an important role in many synthetic routes to the steroid skeleton[145,164].

The stereoselective synthesis of tetrahydronaphthalenones was carried out via homogeneous hydrogenation. The reduction at 2 bar hydrogen pressure gave the saturated product in good yield (equation 69)[165].

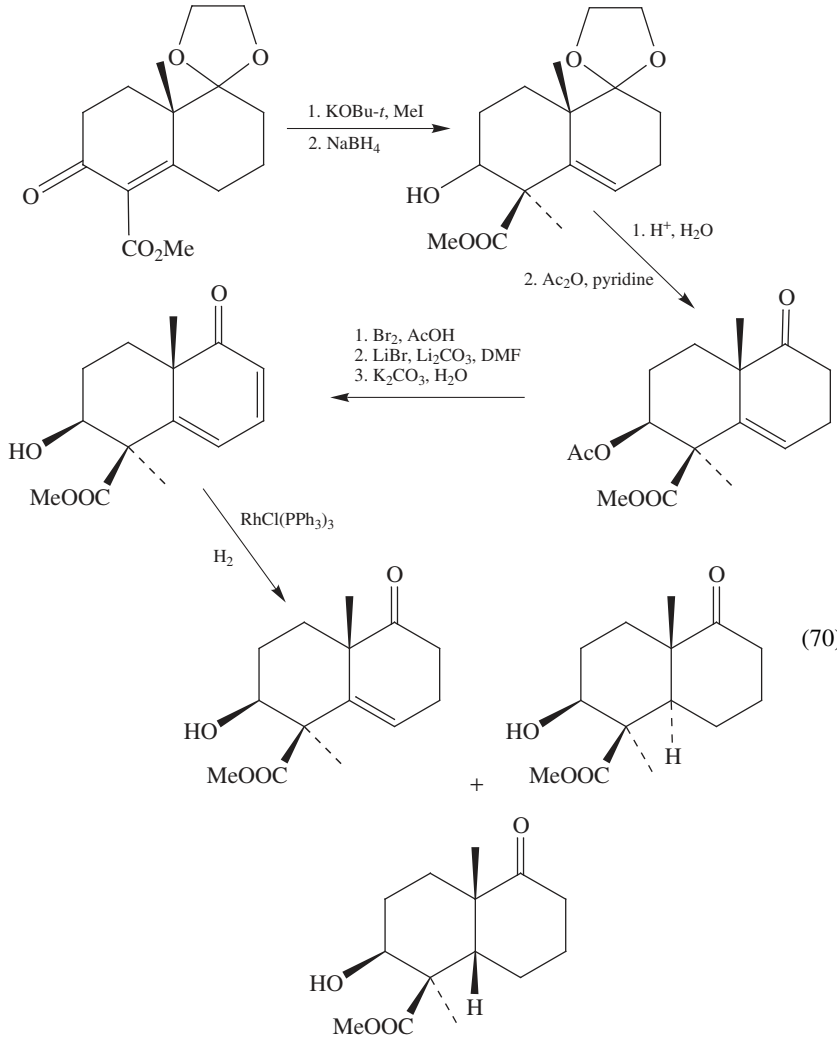


R = H, OAc

(69)

The hydrogenation of the keto ester resulted in the corresponding saturated and half hydrogenated compound, depending on the pressure. Above 5 bar hydrogen pressure the

cis keto ester became a minor product (equation 70)[165].



(70)

Pressure, bar	%	%	%
2	37		63
3.2	62		38
3.9	80		20
4.3	87		13
5	73	<1	27
10.7	70	10	20
16.5	30	30	40

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