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Organometallic Chemistry of Vinylidene and Related Unsaturated Carbenes

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Contents

Michael Bruce was born in London and educated at Lincoln College, Oxford. He worked first at the CSIRO's Division of Plant Industry in Canberra, Australia, on plant cell-division initiators, and returned to Bristol, England, in 1965 to study with Professor Gordon Stone. After seven years on the faculty, he took up the chair in inorganic chemistry at the University of Adelaide, South Australia, where he has been the Angas Professor of Chemistry since 1982. His main interests are in complexes containing M–C(sp) or M–C(sp^2) bonds and in metal cluster chemistry. He was elected to the Australian Academy of Sciences in 1989.

I. Abbreviations

acac	acetylacetonate
chiraphos	(*S*,*S*)-$Ph_2PCHMeCHMePPh_2$
cod	1,5-cyclooctadiene
cypenphos	*trans*-1,2-bis(diphenylphosphino)cyclopentane
dmpz	3,5-dimethylpyrazolyl
dppe	$Ph_2PCH_2CH_2PPh_2$
dppee	$CH_2{=}C(PPh_2)_2$
dppm	$CH_2(PPh_2)_2$
dtc	S_2CNEt_2
nbd	norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)
prophos	$Ph_2PCH_2CHMePPh_2$
pz	pyrazolyl
tcne	$C_2(CN)_4$
thf	tetrahydrofuran
tmp	2,2′,6,6′-tetramethylpiperidine
tol	*p*-tolyl
tpp	*meso*-tetraphenylporpinato(2−)
ttp	*meso*-tetra-*p*-tolylporphinato(2−)

II. Introduction

The stabilization of transient species by coordination to transition metals has enabled their chemistry to be studied and their behavior as intermediates to be modeled and understood. For many years, it has been popular to extend this modeling to surface chemistry, by using metal cluster complexes as the analogues. Considerable progress has been made in determining reaction pathways and mechanisms, for example, of the reduction of carbon monoxide and related reactions.

During the last 10 years or so, the chemistry of unsaturated carbenes, such as vinylidene, allenylidene, and their derivatives, coordinated to one or more metal atoms, has been explored. In general, these ligands form a series C_nH_2; for $n = 1$, methylene, complexes of the parent ligand, and particularly substituted derivatives are well known and have been reviewed on several occasions.[1] The chemistry of CCH_2 (vinylidene) has been developing rapidly, and while no examples of complexes containing $CCCH_2$ (propadienylidene) have been described, several substituted derivatives are known. To a lesser extent, the free molecules have also been obtained and studied, either in a matrix, or by suitable trapping reactions.

The importance of vinylidenes in the overall chemistry of two-carbon ligands has become evident and it is now opportune to summarize progress that has been made. This review surveys the rapidly developing organometallic chemistry of these species. It supplements an earlier review of the synthesis, structures, and chemistry of mono-, bi-, tri-, and tetranuclear metal complexes.[2] Some mention of binuclear complexes occurs in a survey of systems containing bridging hydrocarbon groups,[3] while a brief account of reactions of alkynes at electron-rich metal centers[4] concentrates on rhenium chemistry. More recently, a review of this chemistry has appeared in the Russian literature.[5] It is appropriate in this article to give a reminder of the salient points of vinylidene chemistry; otherwise, the literature has been covered to the end of 1989. This review will not discuss heterovinylidenes, such as ketenylidenes or aza- and phospha-vinylidenes; the chemistry of the former and their metal complexes (particularly clusters) has been reviewed recently.[6,7]

III. Vinylidene and Related Unsaturated Carbenes

A. Vinylidene

1. Generation and Trapping of Vinylidenes

Vinylidene, $H_2C{=}C{:}$, is the simplest unsaturated carbene, and is tautomeric with ethyne, $HC{\equiv}CH$. The organic chemistry of unsaturated carbenes has been summarized in two excellent reviews by Stang.[8] In solution, vinylidenes have been generated from primary vinyl halides and LiR, by the base-induced decomposition of *N*-nitrosooxazolidones, and from vinyl triflates and $KOBu^t$. The latter reactions have been demonstrated by the stereochemical addition of $CCMe_2$ to olefins, which is stereospecific for *cis*- and *trans*-2-butene and 98% stereoselective for *cis*- and *trans*-2-methoxy-2-butene. In the presence of dimethyl– or diethyl–acetylenes polymers were produced via methylenecyclopropenes, detected below −20 °C as the sole products. The latter were trapped with $HClO_4$ as cyclopropenium salts and showed the formation of the dialkylvinylidenes. Trapping experiments with substituted styrenes showed that the electrophilic properties of CCR_2 are comparable to those of dihalocarbenes.

Early reports described singlet C_2 obtained from a carbon arc in a high vacuum, which reacted with RCH_2D to give $RCD{=}C{=}CH_2$ via an alkylcarbene–vinylidene pair followed by coupling.[9] In the presence of acetone, hydrogen abstraction gave CCH_2 which isomerized to ethyne. With cyclopropane, C_2 gave CCH_2, cyclopropene (which isomerized to allene), and the coupled product methylenecyclopropane.[10]

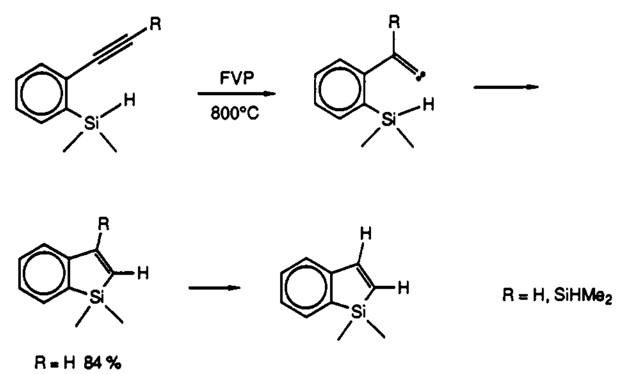
Kinetic and trapping experiments with ethyne/benzene and ethyne/toluene mixtures pyrolyzed at >820 K and studied by modulated beam dynamic mass spectrometry have given evidence for the fast equilibrium preceding carbene addition to the aromatic ring.[11]

$$HC{\equiv}CH \rightleftharpoons H_2C{=}C{:}$$

Thus, straight pyrolysis has an activation energy of 155 (8) kJ mol^{-1}; the reaction gives firstly vinylethyne and then benzene. In the presence of benzene, peaks at $m/z = 78 + 26n$ (n = 1,2,3,4) correspond to polyvinylbenzenes; with toluene, methylstyrene isomers were found. The reactions were described by a series of steps involving insertion/addition of vinylidene into the aromatic C–H bonds.

Flash vacuum pyrolysis (FVP) of a tetrafluoroanthracene at 600 °C gave $HC{\equiv}^{13}CD$, which rearranged

SCHEME 1

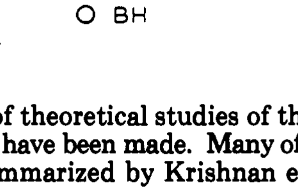


at 700 °C to give $DC\equiv{}^{13}CH$ without appreciable intermolecular H/D exchange: it was proposed that this process occurred via intermediate vinylidene species.[12] Thermal intramolecular scrambling in $H_2C={}^{13}CDCD={}^{13}CH_2$ requires a discrete symmetrical intermediate resembling CCH_2. Similarly, FVP of silyl-substituted phenylethynes gave silaindenes via thermally induced acetylene–vinylidene rearrangements, the vinylidene inserting into a Si–H bond to complete the cyclization (Scheme 1).[13]

The long-lived triplet state ($^3B_2$) of vinylidene was produced by 1,1-elimination of HCl from vinyl chloride induced by flash photolysis in helium; it was detected by its characteristic 137-nm absorption.[14] Quenching in helium gave ethyne. Vacuum UV photolysis of ethyne or ethene gave triplet CCH_2 in quantum yields of 0.4 and 0.75, respectively. Spectroscopic, thermochemical, and kinetic data have been reported.[14]

Difluorovinylidene is the principal primary photoproduct obtained by the triplet Hg photosensitization of $CF_2{=}CHF$, and reacts with C—H bonds to give 1,1-difluoro-1-alkenes, and with C=C bonds to give difluoromethylenecyclopropanes.[15]

Protonation (12 N H_2SO_4) of $[NMe_4][Fe(\eta\text{-}C_5H_5)(\eta^5\text{-}HCB_9H_9CC_2H)]$ afforded the unusually stable dark red zwitterionic vinylidene 1, which could be deprotonated by $NaBH_4$ or LiMe.[16] Addition of HX (X = Cl, Br) to 1 gave $Fe(\eta\text{-}C_5H_5)\{\eta^5\text{-}HCB_9H_9CC(X)Me\}$.



(1) ● C or CH
○ BH

2. Theory

A multitude of theoretical studies of the ethyne/vinylidene system have been made. Many of the ab initio studies were summarized by Krishnan et al.,[17] and a detailed account was also given by Osamura et al.;[18] CCH_2 is either a very shallow minimum or a saddle point with an extremely short lifetime as a result of quantum mechanical tunneling.[18-20] Skell's trapping experiments suggested a lifetime of 10^{-10} M s.[10] Vinylidene is considered to be the effective transition-state structure for the degenerate exchange of the two H atoms on the C_2H_2 surface. The activation energy for this process is ca. 188 kJ mol^{-1}; the barrier to tautomerization of CCH_2 to C_2H_2 is between 4 and 21 kJ mol^{-1}.[21] The calculated geometries and energies relative to C_2H_2 of the $^1A_1$, $^3B_2$, and $^3A_2$ states are shown in Figure 1; the $^3B_2$ triplet state has a much higher barrier to isomerization than singlet CCH_2.[22-24]

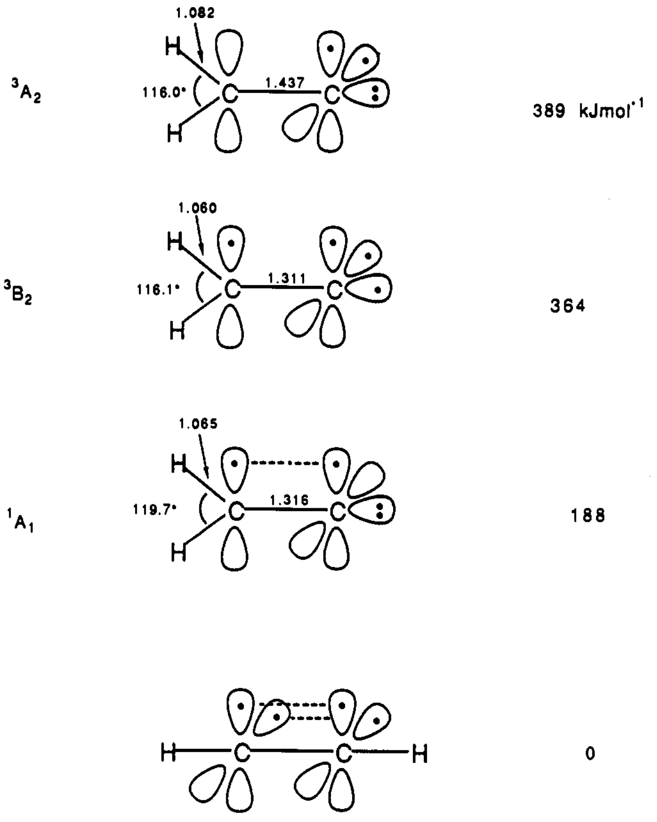


Figure 1. Calculated geometries and relative energies of C_2H_2 isomers.

The difluoro species has also been examined. Ab initio calculations on the isomerization $C_2F_2 \rightarrow F_2CC$ show that the vinylidene is 152 kJ mol^{-1} above the alkyne, with E_a = 569 kJ mol^{-1}.[25]

Several observations of H_2CC^- have been described; theoretical calculations have predicted electron affinities of ca. 0 and −1.8 eV for H_2CC and HC_2H, respectively.[26] The long-lived H_2CC^- anion (ΔH_f 372–423 kJ mol^{-1}) can be generated from reaction of O atoms with ethyne;[19,27] the electron is in a nonbonding orbital on the carbene carbon, leading to partial saturation of the C=C double bond.[28] This species can also be generated on MgO surfaces.[29] The ion of m/z 44 produced by resonant dissociative electron attachment to *cis*-CHF=CHF has been ascribed the $CCHF^-$ structure.[26]

The $^2A_1$ and $^2B_2$ states of H_2CC^+ are almost degenerate and lie about 47.7 kJ mol^{-1} above neutral vinylidene.[30]

B. Propadienylidene and Higher Species, H_2C_n ($n \geq 3$)

Propadienylidene (allenylidene, vinylidenecarbene, or ethylidenecarbene), H_2CCC, has been obtained by photolysis of cyclopropenylidene, from pyrolysis of di-*tert*-butyl 2-cyclopropene-1,1-diperoxycarboxylate. In an argon matrix, propargylene (ethynylcarbene),

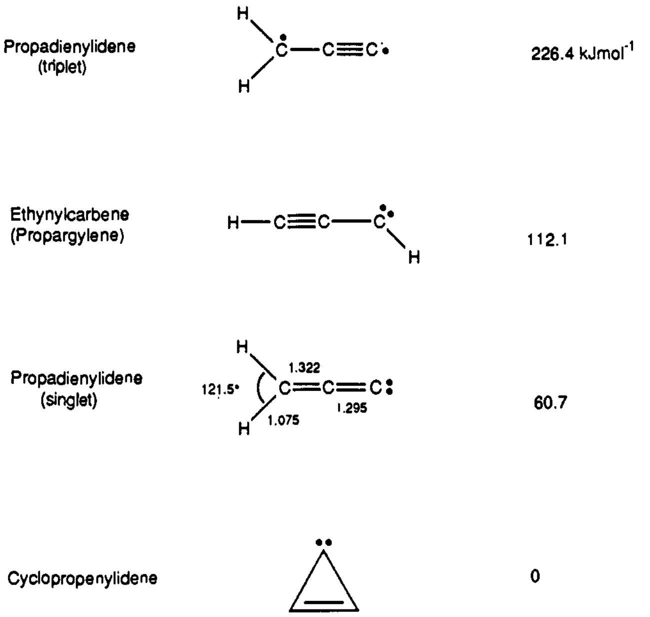


Figure 2. Calculated geometries and relative energies of C_3H_2 isomers.

CH(C≡CH), is formed first (75% conversion after 2.5 h) which with further irradiation for 20 h gives propadienylidene.[31] The latter was identified from its calculated IR spectrum. Irradiation at shorter wavelengths (254 nm) results in rapid reversion to propargylene.

Theoretical studies have shown the ground state of H_2CCC to be a singlet, with the triplet state lying some 201 kJ mol^{-1} higher.[20,32] Cyclopropenylidene is the most stable C_3H_2 isomer and has been detected in space;[33] H_2CCC is more stable than propargylene by 50–67 kJ mol^{-1}. The triplet states are much higher in energy, the most stable being propargylene, with triplet H_2CCC being 102.5 kJ mol^{-1} higher still.[34] The zwitterion $H_2C^+C{\equiv}C^-$ is an important contributor to the structure. The geometries and relative energies of these species are shown in Figure 2.

The latest example of chemical generation and trapping of an unsaturated carbene is that of $CCCCCHBu^t$, obtained from $H_2C_2C_2CHBu^t(OSO_2Me)$ and $KOBu^t$ in 1,2-dimethoxyethane at −62 °C.[35] Slow warming to room temperature in the presence of trapping agents such as C_2Me_4 or $SiHEt_3$ afforded the corresponding addition (isolated as a cyclodimer) and insertion products, respectively.

The higher cumulenyl carbenes require increasing numbers of singlet and triplet configurations to describe their structures, and their stabilization by charge separation is most effective with odd-numbered carbon chains. For H_2C_n (n = 2–5), singlet ground states have been predicted.[20,32] Interestingly, the energy difference between the two C_4H_2 isomers [CCH(C≡CH) (ethynylvinylidene) and H_2CCCC (Figure 3)] and HC_2C_2H is about the same as that between H_2CC and HC_2H.[32]

IV. Mononuclear Vinylidene Complexes

A. Preparative Methods

Several methods have been employed for the preparation of mononuclear vinylidene complexes: (i) from 1-alkynes via a formal 1,2-hydrogen shift; (ii) by addition of electrophiles to metal alkynyl complexes; (iii) by deprotonation of carbyne complexes; and (iv) by formal dehydration of acyl complexes. In addition, alkenes, preformed vinyl complexes, and disubstituted alkynes have been used as precursors in a variety of transformations. Finally, transfer of vinylidene ligands between metal centers and modification of existing vinylidene ligands are reactions which deserve further investigation. Table 1 lists mononuclear vinylidene complexes reported during the period of this review.

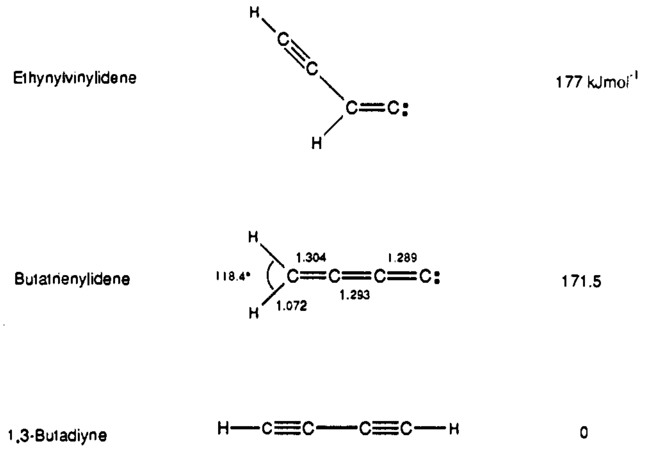


Figure 3. Calculated geometries and relative energies of C_4H_2 isomers.

1. From 1-Alkynes

The 1,2-hydrogen shift undergone by many 1-alkynes on reaction with certain transition metal complexes has proved to be a useful entry into vinylidene complexes. This ready rearrangement has been shown to be preceded by an η^2- to η^1-alkyne slippage (section VIII.A). For d^6 metal complexes, the η^2-alkyne complex is destabilized by a repulsive 4e interaction between the filled $\pi_\perp$ orbital of the alkyne and a filled $d_\pi(t_{2g})$ metal orbital.[36] The relative stability of the vinylidene over the alkyne complex increases with increasing electron density at the metal center.

The cationic alkyne complex $[Mo(\eta\text{-}HC_2Bu^t)(PMe_2Ph)_2(\eta\text{-}C_5H_5)]^+$ was converted to $[Mo(CCHBu^t)(CO)(PMe_2Ph)_2(\eta\text{-}C_5H_5)]^+$ under CO (1 atm, 20 °C). This reaction is notable as the first example of alkyne/vinylidene tautomerism on a d^4 metal.[37]

The $Mo(\eta\text{-}C_7H_7)$ group is isoelectronic with the often-used $Ru(\eta\text{-}C_5H_5)$ group, so that it is not surprising that heating $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ with HC_2Ph in refluxing acetone for 10 days afforded $[Mo(CCHPh)(dppe)(\eta\text{-}C_7H_7)][PF_6]$, albeit in only 7% yield.[38] A better route to larger quantities of this complex is from $[Mo(\eta\text{-}PhMe)(\eta\text{-}C_7H_7)][PF_6]$, dppe, and HC_2Ph in acetone; the product, however, contains a paramagnetic impurity. Deprotonation (NaOMe or proton sponge) gave the corresponding neutral phenylacetylide complex. A red solution containing the phenylvinylidene complex was also obtained from $MoCl(dppe)(\eta\text{-}C_7H_7)$ and HC_2Ph in methanol; the phenylacetylide was obtained in 51% yield after the addition of NaOMe. Protonation of the acetylide with HBF_4 gave the vinylidene (33%), while the corresponding *tert*-butyl complex was not characterized, but was deprotonated to the acetylide in 35% yield with $KOBu^t$.

1-Alkynes reacted directly with *fac*-$W(CO)_3(dppe)(thf)$ to give *mer*-$W(CCHR)(CO)_3(dppe)$ in 65–70% yield. This alkyne/vinylidene isomerization is catalyzed by water, and in its presence, yields of 96% were obtained (R = Ph).[39-42] The strong trans influence of the vinylidene group leads to a small J_{WP} of about 145–155 Hz. Spectroscopic data suggest the formation of an intermediate *fac*-η-alkyne adduct. The mixed CCMePh complex was obtained by further alkylation with $[Me_3O]^+$ to give the phenylethylcarbyne complex, which was then deprotonated with alumina.

Propiolic aldehyde acetals displaced Et_2O from $Mn(OEt_2)(CO)_2(\eta\text{-}C_5H_5)$ to give the η^2-alkyne complexes; deprotonation/protonation cycles with LiBu and H_2O, respectively, gave the red vinylidenes $Mn\{CCCH(OR)_2\}(CO)_2(\eta\text{-}C_5H_5)$ [$(OR)_2$ = $(OMe)_2$, $(OEt)_2$, $O(CH_2)_3O$].[43] Manganese complexes derived from 1,4-diethynylbenzene have been obtained from $Mn(thf)(CO)_2(\eta\text{-}C_5H_5)$. Initially the reaction gave a mixture of the mono- and binuclear η^2-alkyne complexes, which were isomerized by treatment with LiPh.[44] The mononuclear derivative (71%) is a red oil, unstable in air; it could be converted to several other related complexes by conventional reactions on the uncomplexed ethynyl group (Scheme 2). The binuclear complex was obtained in 40% yield.

Displacement of N_2 from *trans*-$ReCl(N_2)(dppe)_2$ by excess HC_2R (R = Et, Bu^t, Ph, CO_2Me, CO_2Et, $C_6H_{10}OH$-1, $SiMe_3$) occurred readily in refluxing thf to give *trans*-$ReCl(CCHR)(dppe)_2$.[45,46] The vinylidene ligand occupies a site opposite the strongest net electron donor, Cl, in these electron-rich complexes.

Chromatography (SiO_2) of the reaction products from $\{Fe(CO)_2[P(OMe)_3]_2\}_2(\mu\text{-}N_2)$ and $HC_2CH(OR)_2$ [R = Me, Et; $(OR)_2$ = $O(CH_2)_3O$] afforded $Fe\{CCH(CHO)\}(CO)_2\{P(OMe)_3\}_2$; the same complex was also obtained directly from the N_2 complex and HC_2CHO.[47] The IR spectrum indicated the presence of *cis*- and *trans*-$\{P(OMe)_3\}_2$-*cis*-$(CO)_2$ isomers; the trans isomer is found in the solid state.

Smooth formation of $[Fe(CCHR)(dppe)(\eta\text{-}C_5H_5)]^+$ from the bromo complex, alkyne, and NH_4PF_6 was reported;[48] alternatively, the reaction between the iodo complex, alkyne, and $TlBF_4$ in dichloromethane was reported to give an 80% yield of the CCHMe complex.[49] A variety of new iron and ruthenium complexes containing chiral tertiary phosphine ligands have been described in the course of a study of the influence of chirality at the metal atom on diastereomeric equilibria.[50] In the case of (*S*,*S*)-$RuCl(chiraphos)(\eta\text{-}C_5H_5)$, the conversion to the phenylvinylidene by reaction with HC_2Ph in refluxing MeOH was neither stereospecific nor stereoselective; in addition, 10–15% methoxy(benzyl)carbene complex was obtained.[51] This reaction may proceed via a 16 e intermediate, such as $[Ru(PP)(\eta\text{-}C_5H_5)]^+X^-$, or via a five-coordinate alkynyl/hydride complex. Under milder conditions (2–3 h/room temperature), the configuration at the metal remained unchanged.[49,50] Low-temperature ^{31}P NMR spectra showed the presence of two diastereoisomers.

The formation of the intermediate η^2-alkyne complex, and its rearrangement to the corresponding η^1-vinylidene, has been observed in the ruthenium series.[52] Ethyne or propyne reacted with $RuCl(PMe_3)_2(\eta\text{-}C_5H_5)$ in methanol to give $[Ru(\eta^2\text{-}HC_2R)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ (R = H, Me). The propyne derivative rearranged to $[Ru(CCHMe)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ in MeOH or MeCN (half-life 5.5 min at 40 °C in MeCN; $\Delta H^{\ddagger}$ 97.9 (1.1) kJ mol^{-1}, $\Delta S^{\ddagger}$ 1.6 (4.0) J K^{-1} mol^{-1}). The ethyne complex is more stable, with half-life >5 h at 60 °C; the parent vinylidene was obtained from HC_2SiMe_3.

In studies of the chemistry of $Os(CO)(PR_3)(\eta\text{-}C_5Me_5)$ complexes, reactions of the iodo complex with HC_2Bu^t or HC_2Ph in the presence of $AgBF_4$ gave the corresponding vinylidene cations; the phenylvinylidene rapidly afforded the phenylacetylide by deprotonation when filtered through Celite in air.[53] The $CCHBu^t$ complex was stable toward this workup. The tricarbonyl cation was isolated from similar reactions of $OsI(CO)_2(\eta\text{-}C_5Me_5)$.

Protonation of $RuCl(C_2Ph)(PMe_3)(\eta\text{-}C_6Me_6)$ (HBF_4 in Et_2O) afforded the corresponding phenylvinylidene cation.[54]

Reactions between $RhCl(PPr^i_3)_2$ and 1-alkynes gave *trans*-$RhCl(\eta^2\text{-}HC_2R)(PPr^i_3)_2$ (**2**, R = H, Me, Ph; Scheme 3), which slowly equilibrate with $RhHCl(C_2R)(PPr^i_3)_2$ (**3**) in benzene or thf at room temperature; the latter complexes are very air sensitive and were not isolated.[55] In pyridine, $RhHCl(C_2R)(py)(PPr^i_3)_2$ (**4**) were formed; these readily lost pyridine in hydrocarbon solvents to give *trans*-$RhCl(CCHR)(PPr^i_3)_2$ (**5**).[56] The latter complexes were also formed by the quantitative rearrangement of the η^2-alkyne complexes **2** on heating in hexane (2 h/50 °C).[55] The alkyne/vinylidene isomerization may proceed by an intermolecular route, as also found for the iridium complex.

The reactions of **4** with NaC_5H_5 are complex, a mixture of $Rh(\eta^2\text{-}HC_2R)(PPr^i_3)(\eta\text{-}C_5H_5)$ (**6**) and $Rh(CCHR)(PPr^i_3)(\eta\text{-}C_5H_5)$ (**7**) being obtained, the relative proportions which depend on R; for R = H, no alkyne complex was formed.[55,57] Vinylidene **7** (R = H) was also formed in the reactions between **4** (R = H) and NaC_5H_5; after 2 min, only air-sensitive *trans*-$Rh(C_2R)(py)(PPr^i_3)_2$ (**8**) was isolated. Dehydrochlorination of **4** by $C_5H_5^-$, acting as a base, gave C_5H_6 which then reacted with **8** to give **9** and pyridine. In the presence of water, $RhH(C_2R)(PPr^i_3)(\eta\text{-}C_5H_5)$ (**10**) was formed and isomerized only slowly to **7**.[58]

Reactions between $RhCl(PPr^i_3)_2$ and HC_2CO_2Me at 0 °C gave square-planar *trans*-$RhCl(\eta\text{-}HC_2CO_2Me)(PPr^i_3)_2$; at 60 °C, isomerization to the vinylidene occurred.[59] Similar reactions with HC_2Bu^t at −30 °C afforded isomeric *trans*-$RhCl(\eta\text{-}HC_2Bu^t)(PPr^i_3)_2$ and $RhHCl(C_2Bu^t)(PPr^i_3)_2$ (9/91) which on heating gave the vinylidene complex. Both alkyne complexes gave only the vinylidenes $Rh(CCHR)(PPr^i_3)(\eta\text{-}C_5H_5)$ (R = Bu^t, CO_2Me) in reactions with NaC_5H_5.

The related alkyne–iridium complexes obtained from HC_2R (R = H, Me, Ph) gave 80–90% yields of thermally stable vinylidene complexes after heating for 36 h in refluxing toluene; the intermediate hydrido–phenylethynyl complex was isolated in 95% yield from the reaction in pentane at −10 °C.[56] While several rhodium complexes can be obtained from terminal alkynes and $RhCl(PPr^i_3)_2$ (which, although unstable, can be isolated free of excess tertiary phosphine), the analogous iridium complexes cannot be so obtained. An alternative approach is to use the dihydride $IrH_2Cl(PPr^i_3)_2$. This reacts with HC_2CO_2Me to give the hydrido–alkynyl complex with elimination of dihydrogen; heating in refluxing benzene for 24 h converts this smoothly into the corresponding vinylidene.[60] In refluxing toluene,

TABLE 1. Mononuclear Vinylidene Complexes, $L_nM(CCRR')$

ML_n	ion	R	R′	color	$\delta(C_\alpha)$	$\delta(C_\beta)$	ref
$TaH(\eta\text{-}C_5H_5)_2$		H	H		354	109	85
$Cr(CO)_2(\eta\text{-}C_6H_6)$		Me	Me	red	312.5	133.7	89
$Cr(CO)_2(\eta\text{-}C_6H_6)$		Ph	Ph	red	327.7	131.7	89
$Cr(CO)_2(\eta\text{-}C_6H_3Me_3)$		Me	Me	red			89
$Cr(CO)_2(\eta\text{-}C_6H_3Me_3)$		Ph	Ph	red			89
$Cr(CO)_2(\eta\text{-}C_6Me_6)$		Me	Me	red			89
$Cr(CO)_2(\eta\text{-}C_6Me_6)$		Ph	Ph	red			89
$Mo(CO)_2\{(pz)_3BH\}$	NR_4^+	CN	CN				79
$Mo(CO)_2\{(pz)_3BH\}$	NR_4^+	CN	CO_2Et		299.9	123.9	79
$Mo(CO)_2\{(pz)_3BH\}$	NR_4^+	CO_2Et	CO_2Et				79
$Mo(CO)_2\{(dmpz)_3BH\}$	Li^+	H	H	red			80
$Mo(CO)_2\{(dmpz)_3BH\}$	Na^+	H	H	red	349.6	91.4	80
trans-$[Mo(CO)(PMe_2Ph)_2(\eta\text{-}C_5H_5)]^+$	BF_4^- and $CF_3SO_3^-$	H	Bu^t				37
trans-$[Mo(CO)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$	BF_4^-	H	Bu^t				37
$[Mo\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)]^+$	BF_4^-	H	Bu^t				37
$[Mo\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^-$	Li^+	H	Bu^t	deep red	322.8	121.8	369
$MoBr\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$		H	Bu^t	red	326.4	132.7	76
$MoBr\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$		H	Ph	orange-brown	336.5	142.4	77, 78
$MoBr(PEt_3)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$		H	Ph	brown	325.6	143.0	77, 78
$Mo(N_2C_6H_4F\text{-}p)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$		H	Bu^t	dark red	348.6	141.3	76
$[Mo(dppe)(\eta\text{-}C_7H_7)]^+$	PF_6^-	H	Ph	orange-red	372.8	120.0	37, 38
$W(CO)_5$		Me	Bu^t	deep green oil	376	128	62
$W(CO)_5$		Et	Bu^t	deep green oil	382	134	62
$W(CO)_2\{(pz)_3BH\}$	NR_4^+	CN	CN				79
mer-$W(CO)_3(dppe)$		H	H	green	332.7	97.2	64
mer-$W(CO)_3(dppe)$		H	Ph	green	336.3	117.7	39, 42
mer-$W(CO)_3(dppe)$		H	CO_2Me	red-orange	328.4	108.8	39
mer-$W(CO)_3(dppe)$		Me	Me	green			64
mer-$W(CO)_3(dppe)$		Me	Ph	green			42, 64
mer-$W(CO)_3(dppe)$		Me	CO_2Me	orange			64
mer-$W(CO)_3(dppe)$		Bu	CO_2Me	orange	333.7	119.8	64
mer-$W(CO)_3(dppe)$		CO_2Me	(*E*)-$C(CO_2Me){=}CHPh$	red	325.5	117.2	144
mer-$W(CO)_3(dppe)$		CO_2Me	(*Z*)-$C(CO_2Me){=}CHPh$	red	326.6	122.3	144
trans-$[W(CO)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$	BF_4^- and $CF_3SO_3^-$	H	Ph				37
trans-$[W(CO)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$	PF_6^- and $CF_3SO_3^-$	Me	Ph				37
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$CH(OMe)_2$	bright red			43
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$CH(OEt)_2$	bright red			43
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$\overline{CHO(CH_2)_3O}$	bright red			43
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$C(OH)Bu^t_2$	pale red			342
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	CO_2Me	orange-brown			342
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$C_6H_4C_2H\text{-}p$	red oil			44
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$C_6H_4CBr{=}CH_2\text{-}p$	light red			44
$Mn(CO)_2(\eta\text{-}C_5H_5)$		Me	$COBu^t$	orange-red			342
$Mn(CO)_2(\eta\text{-}C_5H_5)$		Me	CO_2Me	orange			342
$Mn(CO)_2(\eta\text{-}C_5H_5)$		I	$CH(OMe)_2$	green		96.2	104
$Mn(CO)_2(\eta\text{-}C_5H_5)$		I	$CH(OEt)_2$	green		97.0	104
$Mn(CO)_2(\eta\text{-}C_5H_5)$		I	$\overline{CHO(CH_2)_3O}$	green		88.8	104
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$O(SiMe_2C_2SiMe_2OSiMe_2{-})_2$					103
$\{Mn(CO)_2(\eta\text{-}C_5H_5)\}_2$		H	$C_6H_4\text{-}p$	red			44
$Mn(CO)_2(\eta\text{-}C_5H_4Me)$		Me	Me	red	387.1	122.3	89
$Mn(CO)_2(\eta\text{-}C_5H_4Me)$		Ph	Ph	orange-red	395.7	129.9	89, 90
$Mn(CO)(PMePh_2)(\eta\text{-}C_5H_4Me)$		Me	Me	red	383.0	117.5	89
$Mn(CO)(PMePh_2)(\eta\text{-}C_5H_4Me)$		Ph	Ph	red	381.4	116.9	89
$Mn(CO)\{P(OPh)_3\}(\eta\text{-}C_5H_4Me)$		Me	Me	red			89
$Mn(CO)\{P(OPh)_3\}(\eta\text{-}C_5H_4Me)$		Ph	Ph	red			89
trans-$ReCl(dppe)_2$		H	Et	dark brown			45, 46
trans-$ReCl(dppe)_2$		H	Bu^t	red	296.9	26.1	46
trans-$ReCl(dppe)_2$		H	$C_6H_{10}OH\text{-}1$	dark brown			46
trans-$ReCl(dppe)_2$		H	CO_2Me	dark red		98.4	46
trans-$ReCl(dppe)_2$		H	CO_2Et	brown-red	284.7	98.6	45, 46
trans-$ReCl(dppe)_2$		H	Ph	red		125	45, 46
trans-$ReCl(dppe)_2$		H	$SiMe_3$	brown-green			46
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	$CF_3SO_3^-$	H	H	burnt orange	329.9	113.8	82, 83
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	$CF_3SO_3^-$	H (*ac*)	Me	honey-yellow	328.5	126.0	82, 83
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	$CF_3SO_3^-$	H (*sc*)	Me	honey-yellow	329.7	125.3	82, 83
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	$CF_3SO_3^-$	H (*ac*)	Ph	golden yellow	332.2	124.6	82, 83
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	$CF_3SO_3^-$	H (*sc*)	Ph	golden yellow	335.6	127.0	82, 83
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	$CF_3SO_3^-$	H (*ac*)	$1\text{-}C_{10}H_7$	yellow	332.9		83
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	PF_6^- and $CF_3SO_3^-$	H (*sc*)	$1\text{-}C_{10}H_7$	yellow	336.3		83
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	FSO_3^-	Me	Me	light brown	327.9	136.8	82, 83
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	FSO_3^-	Me	Ph (*ac*)	brown	334.2	141.2	82, 83
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	FSO_3^-	Me	Ph (*sc*)	brown	330.9	140.0	82, 83
$Fe(CO)_2\{P(OMe)_3\}_2$		H	CHO	yellow	328.4	129.7	47

TABLE 1 (Continued)

ML_n	ion	R	R′	color	$\delta(\mathrm{C}_\alpha)$	$\delta(\mathrm{C}_\beta)$	ref
$\mathrm{Fe(CO)_2\{P(OMe)_3\}_2}$		$\overline{\mathrm{CHO(CH_2)_3O}}$	(dimer)	orange			47
$[\mathrm{Fe(CO)(PMe_2Ph)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	H	H	lime-green			81
$[\mathrm{Fe(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	H	H	yellow-gold	372.4	107.1	81
$[\mathrm{Fe(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	Me	Me	peach			81
$[\mathrm{Fe(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	Ph	dark blue			66
$[\mathrm{Fe(CO)(PCy_3)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	H	H	lime-green			81
$[\mathrm{Fe(CO)\{P(OMe)_3\}}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{CF_3SO_3^-}$	H	H	yellow			141
$[\mathrm{Fe(CO)\{P(OMe)_3\}}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{CF_3SO_3^-}$	Me	Me	peach			141, 142
$[\mathrm{Fe(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	H	H				67
$[\mathrm{Fe(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	H	Ph				48
$[\mathrm{Fe(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	Ph				67
$[\mathrm{Fe(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Et	Ph				67
$[\mathrm{Fe(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	$\mathrm{CH_2Ph}$	Ph				67
$[\mathrm{Fe(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	$\mathrm{C_7H_7}$	Ph	buff-orange			70
$[\mathrm{Fe(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	Me	(dimer)	deep red-purple	360.2		122
$[\mathrm{Fe(dppe)}(\eta\text{-}\mathrm{C_5Me_5})]^+$	$\mathrm{PF_6^-}$	H	Ph	brown			136
$[\mathrm{Fe(chiraphos)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	H	Me	yellow-orange	358.6		48, 51
$[\mathrm{Fe(chiraphos)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	H	Ph	light brown	355		48, 51
$[\mathrm{Fe(cypenphos)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	H	Me	yellow	361.5		48, 51
$[\mathrm{Fe(cypenphos)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	H	$\mathrm{Bu^t}$	red	364.0		48, 51
$[\mathrm{Fe(cypenphos)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	H	Ph	brown	368		48, 51
Fe(tpp)		$\mathrm{C_6H_4Cl}\text{-}p$	$\mathrm{C_6H_4Cl}\text{-}p$	red			98
$[\mathrm{Ru(PMe_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	H	H	yellow	343.9	92.7	52
$[\mathrm{Ru(PMe_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	H	Me	yellow	347.9	103.4	52
$[\mathrm{Ru(PMe_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$[\mathrm{M(CO)_3}(\eta\text{-}\mathrm{C_5H_5})]^-$ (M = Cr, Mo, W)	H	Me	yellow			65
$[\mathrm{Ru(CNBu^t)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	Ph	pink			68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$ and $\mathrm{I^-}$	Me	Me	orange		117.5	67, 68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	Et				67
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	Bu				67
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	$\mathrm{(CH_2)C_2H}$	orange			68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$ and $\mathrm{Br^-}$	Me	$\mathrm{CH_2Ph}$	orange			67, 68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	$\mathrm{C_7H_7}$	orange	352.4	125.2	70
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$ and $\mathrm{I^-}$	Me	Ph	pink	353.7	125.3	67, 68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	$\mathrm{C_6H_4F}\text{-}p$	buff			68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{I^-}$	Me	$\mathrm{C_6F_5}$	orange			68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	$\mathrm{N_2Ph}$	red-orange			71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	Me	$\mathrm{N_2C_6H_3Me_2}\text{-}3,4$	orange			71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	$\mathrm{N_2C_6H_4NO_2}\text{-}p$	red			71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	$\mathrm{N_2C_6H_3Cl_2}\text{-}2,4$	orange		118.4	71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	Me	$\mathrm{N_2C_6H_4OMe}\text{-}p$	maroon			71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{I_3^-}$	Me	I	dark olive-green	325.9		72
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Et	Et				67
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Et	Bu				67
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Et	$\mathrm{CH_2Ph}$				67
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Et	Ph				67
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Pr	$\mathrm{C_7H_7}$	buff			70
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	$\mathrm{CH_2CH{=}CH_2}$	Ph	orange		117.7	68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$ and $\mathrm{Br^-}$	$\mathrm{CH_2C_2H}$	Ph	brown			68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	$\mathrm{(CH_2)_3Br}$	Ph	pink			68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	$\mathrm{CH_2Ph}$	Ph	pink	349.0		67, 68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	$-\mathrm{(CH_2)_4}-$					67
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Bu	$\mathrm{CH_2Ph}$				67
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	$\mathrm{C_7H_7}$	Ph	rose-pink	347.0	132.7	69, 70
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	$\mathrm{C_7H_7}$	$\mathrm{C_6F_5}$	orange	337.3	122.3	70
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Ph	$\mathrm{N_2Ph}$	red	362.0	122.2	69, 71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	Ph	$\mathrm{N_2C_6H_3Me_2}\text{-}3,4$	orange		125.4	69, 71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	Ph	$\mathrm{N_2C_6H_4NO_2}\text{-}p$	maroon			69, 71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	Ph	$\mathrm{N_2C_6H_3Cl_2}\text{-}2,4$	red			69, 71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	Ph	$\mathrm{N_2C_6H_4OMe}\text{-}p$	orange	364.5	113.7	69, 71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-/SbCl_6^-}$	Ph	$\mathrm{N_2MePh^+}$	orange			71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Ph	$\overline{\mathrm{NNC_6H_4Mn}}\mathrm{(CO)_4}$	purple			71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$ and $\mathrm{SbCl_6^-}$	Ph	Cl	emerald green			72
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{I_3^-}$	Ph	I	green			72
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{Br_3^-}$	$\mathrm{C_6H_4Br}\text{-}p$	Br	green			72
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	$\mathrm{C_6F_5}$	$\mathrm{N_2Ph}$	orange		122.5	71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{BF_4^-}$	$\mathrm{C_6F_5}$	$\mathrm{N_2C_6H_3Me_2}\text{-}3,4$	red			71
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{I_3^-}$	$\mathrm{C_6F_5}$	I	dark green			72
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]_2^{2+}$	$\mathrm{PF_6^-}$	Ph	$-\mathrm{(CH_2)}-$	light brown			68
$[\mathrm{Ru(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})]_2^{2+}$	$\mathrm{PF_6^-}$	Me	$-\mathrm{(CH_2)_2}-$	orange			68
$[\mathrm{Ru(dppm)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{I^-}$	Me	Ph	orange			68
$[\mathrm{Ru(dppm)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	$\mathrm{C_7H_7}$	Ph	orange			70
$[\mathrm{Ru(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	H	Ph	pink			51
$[\mathrm{Ru(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Me	Bu				67
$[\mathrm{Ru(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{I^-}$ and $\mathrm{PF_6^-}$	Me	Ph	pink			67, 68
$[\mathrm{Ru(dppe)}(\eta\text{-}\mathrm{C_5H_5})]^+$	$\mathrm{PF_6^-}$	Et	Ph				67

TABLE 1 (Continued)

ML_n	ion	R	R′	color	$\delta(C_\alpha)$	$\delta(C_\beta)$	ref
$[Ru(dppe)(\eta\text{-}C_5H_5)]^+$	PF_6^-	$(CH_2)_3Br$	Ph	orange			68
$[Ru(dppe)(\eta\text{-}C_5H_5)]^+$	PF_6^-	CH_2Ph	Ph				67
$[Ru(dppe)(\eta\text{-}C_5H_5)]^+$	PF_6^-	C_7H_7	Ph	rose-pink			70
$[Ru(dppe)(\eta\text{-}C_5H_5)]^+$	PF_6^-	Ph	N_2Ph	orange			71
$[Ru(dppe)(\eta\text{-}C_5H_5)]^+$	Br^-	Ph	Br	dark green			72
$[Ru(prophos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	Me (S_{Ru},R_C)	orange	347		49, 51
$[Ru(prophos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	Me (R_{Ru},R_C)	orange	346.6		49, 51
$[Ru(prophos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	Ph (S_{Ru},R_C)	rose-pink	354.7		49, 51
$[Ru(prophos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	Ph (R_{Ru},R_C)	rose-pink	354.3		49, 51
$[Ru(chiraphos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	Bu^t	flesh	349		51
$[Ru(chiraphos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	Ph	rose-pink	354.9		49, 51, 115
$[Ru(cypenphos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	Me	chrome yellow	347		51
$[Ru(cypenphos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	Ph	salmon pink	355		51
$[Ru(cypenphos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	Me	Bu^t				106
$[Ru(cypenphos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	Me	Ph		356.4		106
$[RuCl(PMe_3)(\eta\text{-}C_6Me_6)]^+$	BF_4^-	H	Ph		360	112.6	54
Ru(tpp)		$C_6H_4Cl\text{-}p$	$C_6H_4Cl\text{-}p$	red			98, 100
Ru(ttp)		$C_6H_4Cl\text{-}p$	$C_6H_4Cl\text{-}p$	red			101
$[Os(PPh_3)_2(\eta\text{-}C_5H_5)]^+$	PF_6^-	Me	Ph	pink			68
$[Os(PPh_3)_2(\eta\text{-}C_5H_5)]^+$	PF_6^-	C_7H_7	Ph	red-pink			70
$[Os(PPh_3)_2(\eta\text{-}C_5H_5)]^+$	PF_6^-	N_2Ph	Ph	orange		122.2	71
$[Os(PPh_3)_2(\eta\text{-}C_5H_5)]^+$	I_3^-	I	Ph	dark green			72
$[Os(CO)(PPh_3)(\eta\text{-}C_5Me_5)]^+$	BF_4^-	H	Bu^t	tan	321.2	123.2	53
$[Os(CO)(PPh_3)(\eta\text{-}C_5Me_5)]^+$	BF_4^-	H	Ph	tan			53
$Os(PPr^i_3)(\eta\text{-}C_6H_6)$		H	Ph	yellow	278.3	110.9	86
trans-$RhCl(PPr^i_3)_2$		H	H	dark red	290.6	89.2	55, 56
trans-$RhCl(PPr^i_3)_2$		H	Me	dark red	292.1	98.5	55, 56
trans-$RhCl(PPr^i_3)_2$		H	Bu^t	black	291.7	117.1	59
trans-$RhCl(PPr^i_3)_2$		H	Ph	dark red	295.2	111.7	55, 56
trans-$RhCl(PPr^i_3)_2$		H	CO_2Me	black	283.1	104.4	59
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		H	H	orange	311.4	94.1	57, 58
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		H	Me		311.6	103.6	58
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		H	Bu^t	bright red	299.2	123.5	59
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		H	Ph	orange-red	317.0	116.3	57, 58
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		H	CO_2Me	yellow	313.3	109.4	59
trans-$IrCl(PPr^i_3)_2$		H	H	red	257.6	87.3	56, 60
trans-$IrCl(PPr^i_3)_2$		H	Me	red	260.0	96.9	56
trans-$IrCl(PPr^i_3)_2$		H	Ph	violet	261.9	110.7	56
trans-$IrCl(PPr^i_3)_2$		H	CO_2Me	red-violet			60
trans-$IrCl(PPr^i_3)_2$		H	$SiMe_3$				60
trans-$IrCl(PPr^i_3)_2$		H	C_7H_9[a]	violet	258.8	128.3	102
trans-$IrCl(PMeBu^t_2)_2$		H	C_7H_9[a]	violet oil			102

[a] C_7H_9 = norborn-2-en-5-yl.

HC_2SiMe_3 affords the very proton-sensitive silylvinylidene, which was not isolated pure.

In contrast with the above results, reactions between $[Rh(PMe_3)_4]Cl$ and 1-alkynes in tetrahydrofuran or water gave *cis*-$[RhH(C_2R)(PMe_3)_4]Cl$ (R = various, including CH_2CH_2OH and $CH_2CH_2CO_2H$) by C–H activation and oxidative addition.[61] No migration of H to form the vinylidene was reported (see also section IV.A.2).

2. From Metal Acetylides

Coordination of acetylide anion to a metal center transfers the nucleophilicity from C_α to C_β. Electrophilic attack on the alkynyl C_β atom is charge controlled, while nucleophilic attack on C_α is frontier orbital controlled. Addition of electrophiles to the electron-rich C_β of metal acetylides has been described on many occasions, and is perhaps the best entry into vinylidene complexes for many systems.

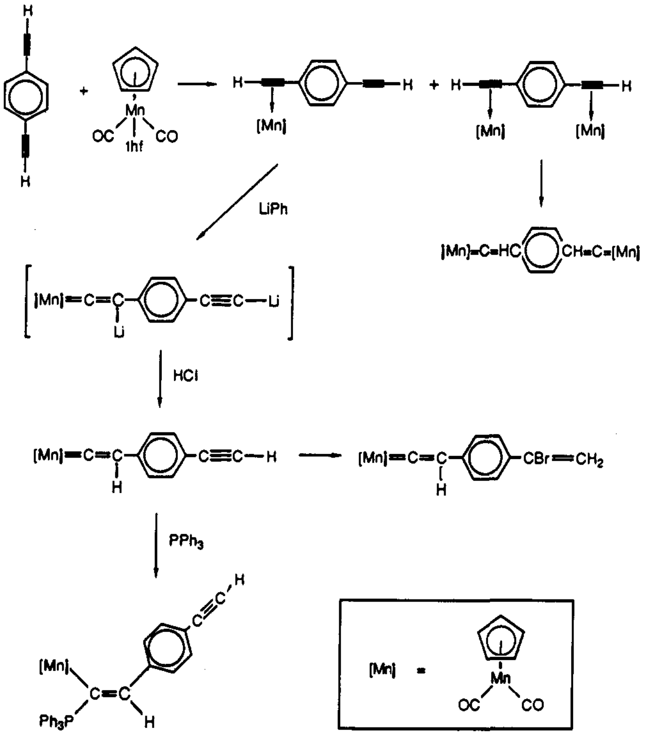
Accordingly, protonation or alkylation of $M(C_2R)(CO)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (M = Mo, W; R = Bu^t, Ph) gave the corresponding vinylidene complexes; the Mo complex is unstable above 0 °C, tautomerizing to the η-alkyne cation with concomitant loss of CO.[37] In contrast, the related vinylidenes $[Mo(CCHBu^t)(L)_3(\eta\text{-}C_5H_5)]^+$ (L_3 = $(CO)(PMe_2Ph)_2$, $\{P(OMe)_3\}_3$) are stable.

Reaction of $[W(C_2Bu^t)(CO)_5]^-$ (from $[WCl(CO)_5]^-$ and LiC_2Bu^t in thf) with $[R_3O]^+$ (R = Me, Et) afforded the neutral $W(CCRBu^t)(CO)_5$ in 40–60% yields as deep green oils.[62] Protonation of $[W(C_2Ph)(CO)_5]^-$ gave the phenylvinylidene, which decomposed at −77 °C.[63] Similar reactions with [*fac*-$W(C_2R)(CO)_3(dppe)]^-$ (R = H, Me, Bu, Ph) (obtained in 60–95% yield from *fac*-$W(CO)_3(dppe)(Me_2CO)$ and alkali metal acetylide) afforded *mer*-$W(CCRR')(CO)_3(dppe)$ (R = H, Ph, R′ = H; R = Me, Ph, R′ = Me).[64] In the acetylides, ion pairing with Li^+ or Na^+ was indicated by spectroscopic [ν(CO)] studies, suggesting a tendency to form the vinylidene tautomer. Treatment of the butylacetylide with CO_2 followed by $[Me_3O]^+$ gave *mer*-$W\{CCBu(CO_2Me)\}(CO)_3(dppe)$, via an intermediate carboxylate. The fac → mer isomerization is intramolecular, as indicated by lack of ^{13}CO exchange during the reaction.

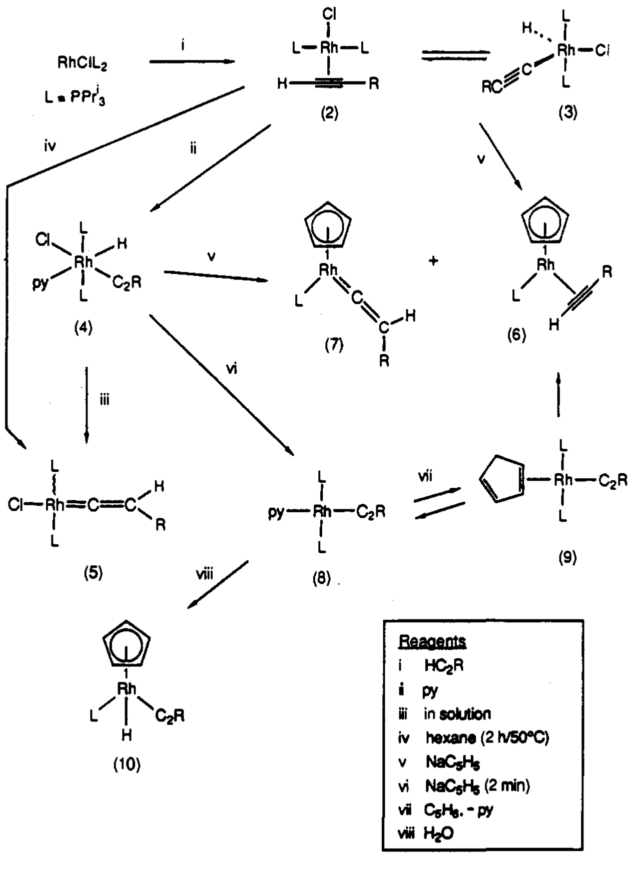
The stereospecificity of protonation or alkylation reactions of $Re(C_2R)(PPh_3)(NO)(\eta\text{-}C_5H_5)$ is discussed in section IV.C.1.

Scheme 4 summarizes the wide variety of substituted vinylidenes obtained from ruthenium acetylide complexes. Iron and ruthenium complexes $M(C_2R)(L)_2(\eta\text{-}C_5H_5)$ are remarkably strong carbon-centered bases; typical pK_a values for the *tert*-butylacetylides in MeCN

SCHEME 2



SCHEME 3



are 13.6 [M = Fe, L_2 = (CO)(PMe_3)] and 20.8 (M = Ru, L = PMe_3).[65] Proton transfer to the iron complex gave two isomers of the *tert*-butylvinylidene complex in 84/16 ratio; $Ru(C_2Me)(PMe_3)_2(\eta\text{-}C_5H_5)$ is protonated by $MH(CO)_3(\eta\text{-}C_5H_5)$ (M = Cr, Mo, W) to give the salts $[Ru(CCHMe)(PMe_3)_2(\eta\text{-}C_5H_5)][M(CO)_3(\eta\text{-}C_5H_5)]$ as yellow powders. The thermodynamic driving force for the protonation is favorable by 26.8 kJ mol^{-1}, but there is a large intrinsic barrier because of electronic and structural rearrangement. NMR measurements of the equilibrium constants showed a lower $\Delta H°$ for the more acidic hydrides, with a negative $\Delta S°$ because of solvation of ionic products.

Alkylation of $Fe(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ with CF_3SO_3Me gave the unstable dark blue methyl(phenyl)vinylidene complex (65%).[66] Alkylation of iron or ruthenium acetylides with alkyl halides has provided a powerful method for the introduction of a wide variety of functional groups. The barrier to rotation of the vinylidene is low, since the $CCMe_2$ complexes show only one Me resonance, and the same CCMeEt complex was obtained from the methyl- or ethylacetylide and iodoethane or -methane, respectively.[67] An internal cyclization was found with 6-chlorohex-1-yne, probably proceeding via intramolecular attack of the acetylide on the terminal C–Cl bond.[67] Extension of this reaction to a variety of halogenated organics has given many disubstituted vinylidene complexes **11** (Scheme 4) containing alkyl, alkenyl, alkyl, and alkynyl substituents.[68]

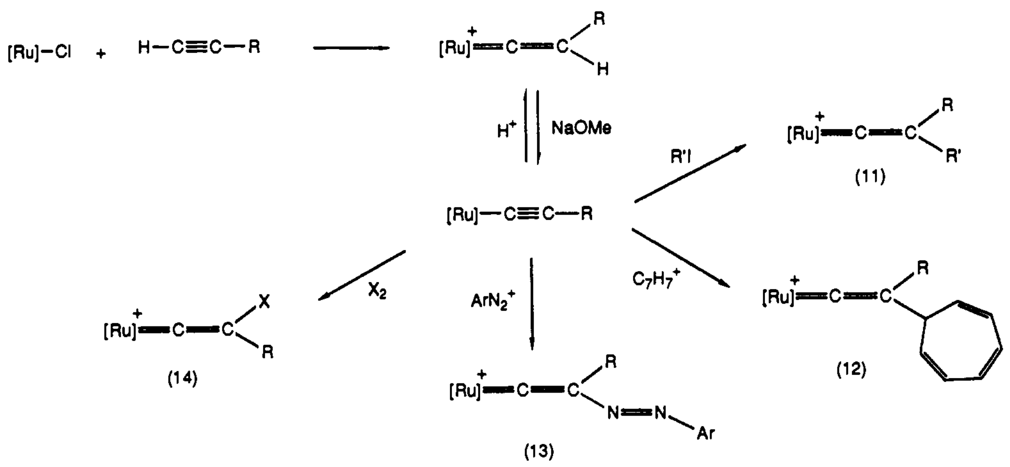
Addition of tropylium cation to a series of ruthenium acetylide complexes afforded the orange cycloheptatrienylvinylidene derivatives **12** (Scheme 4).[69,70] Their reactions are characterized by ready displacement of the C_7H_7 group and formation of the neutral acetylide. Thus, NaOMe gave C_7H_7OMe, and $K[HBBu^s_3]$ gave C_7H_8 as the organic products, while in MeOH, the methoxy(benzyl)carbene complex was formed. Similar reactions of $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ with $[C_7H_7]^+$ gave $[Fe(CO)_3(\eta\text{-}C_5H_5)]^+$ via the vinylidene (detected by FAB mass spectrometry) and thf cations.

Complexes **13** (Scheme 4) containing azovinylindene ligands were prepared by addition of aryldiazonium salts to iron, ruthenium and osmium acetylides. In these complexes, the azo group could be further protonated, alkylated, and entered into cyclometalation reactions, e.g. with $Mn(CH_2Ph)(CO)_5$.[69,71]

Addition of halogens to ruthenium acetylides afforded deep green halovinylidene complexes **14** (Scheme 4); in some cases, halogenation of the phenyl group of a C_2Ph ligand also occurred, for example, in the structurally characterized $[Ru\{CCBr(C_6H_4Br\text{-}p)\}(PPh_3)_2(\eta\text{-}C_5H_5)]Br_3$. A similar complex was obtained indirectly from the reaction between $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ and $[MeCO][SbCl_6]$.[72] These reactions demonstrate the remarkable resistance of the Ru–C(sp) bond toward cleavage.

Protonation of $Rh(C_2Ph)(np_3)$ [np_3 = $N(CH_2CH_2PPh_2)_3$] afforded $[Rh(CCHPh)(np_3)]^+$ (70%), which eliminated H_2 on heating (refluxing thf) to give paramagnetic rhodium(II) derivative $[Rh(C_2Ph)(np_3)]^+$.[73] No interconversion of $[cis\text{-}RhH(C_2R)(L)]^+$ (R = various; L = np_3, pp_3), obtained from $[Rh(L)]^+$ and 1-alkynes, and the isomeric vinylidene complexes, was found. However, the rhodium(I) σ-acetylides were protonated by strong acids in thf to give trigonal-bypyramidal vinylidene complexes, which react with hydride ($NaBH_4$, $LiBHEt_3$) to give alkenyl derivatives. These experiments show that vinylidenes are not formed from 1-alkynes via hydrido–alkynyl complexes on rhodium.[74]

SCHEME 4



[Ru] = $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$

R = Me, Bu^t, Ph, CO_2Me, etc; R' = Me, Pr^i, CH_2Ph, 0.5 CH_2, etc;
Ar = Ph, $C_6H_3Me_2$-3,4, $C_6H_3Cl_2$-2,4, etc; X = Cl, Br, I

3. *By Deprotonation of Carbyne Complexes*

This route to vinylidene complexes is formally the reverse of their protonation (section IV.D). Addition of LiBu to $M(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (M = Mo, W) gave deep red lithium derivatives of an anionic species which can be formulated with the charge on the metal or on C_β:[75]

$$L_nMo^-{=}C{=}CHBu^t \leftrightarrow L_nMo{\equiv}C{-}C^-HBu^t$$

The reaction between $Mo\{C(CH_2Bu^t)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ and CF_3I afforded red $MoI(CCHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ as one product (30%); initial electron transfer from the carbyne HOMO to CF_3I is followed by abstraction of H by the resulting CF_3 radical.[76] Similarly, the reaction between the carbyne complex and $[p\text{-}FC_6H_4N_2][BF_4]$ gave $Mo(CCHBu^t)(N_2C_6H_4F\text{-}p)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$.

In related work, the complex $MoBr(CCHPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ was obtained, with $Mo(CCH_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$, from the reaction between $K[BHBu^s_3]$ and $[Mo(\eta^2\text{-}PhC_2Br)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$. The vinylidene is the major product (39%); the CCMePh complex was obtained from the alkyne cation and $LiCuMe_2$, but reacted further to form the carbyne (43%).[77,78]

The chlorocarbyne complexes $M(CCl)(CO)_2\{(pz)_3BH\}$ (M = Mo, W) reacted with NaCHXY (X, Y = CN, CO_2Et) to give yellow-orange anionic vinylidenes $[Mo(CCXY)(CO)_2\{(pz)_3BH\}]^-$ (**15**).[79] In contrast with the related $CCHBu^t$ complex (see above), these species do not react with water; with HCl or PhCOCl, oxidizing agents such as $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$, $[Ph_2I][PF_6]$ or NaOCl, or $CoCl_2$, the oxametallacarbenes $\overline{Mo\{CHCX{=}C(O)}OEt\}(CO)_2\{(pz)_3BH\}$ (X = CN or CO_2Et) were formed. Addition of electrophiles to **15** (X = CN, Y = CO_2Et) afforded the corresponding carbyne complexes $Mo(CCXYZ)(CO)_2\{(pz)_3BH\}$ (Z = HgCl, HgBr, HgI, Cu, or $N_2C_6H_4NMe_2$). The dicyanovinylidene also forms a stable Cu(I) adduct.

[M] = $M(CO)_2\{(pz)_3BH\}$, M = Mo, W

(15)

The η^2-acyl-molybdenum complexes $Mo(\eta^2\text{-}O{=}CR)(CO)_2\{(dmpz)_3BH\}$ (R = Me, Et) reacted with NaOEt/EtOH to give the carbyne derivatives $Mo(CR)(CO)_2\{(dmpz)_3BH\}$; the methyl complex was deprotonated ($Na[N(SiMe_3)_2]$) to $[Mo(CCH_2)(CO)_2\{(dmpz)_3BH\}]^-$, characterized by NMR and its alkylation (R'I) to $Mo(CCH_2R')(CO)_2\{(dmpz)_3BH\}$ (R' = Me, Et).[80]

4. *From Acyl Complexes*

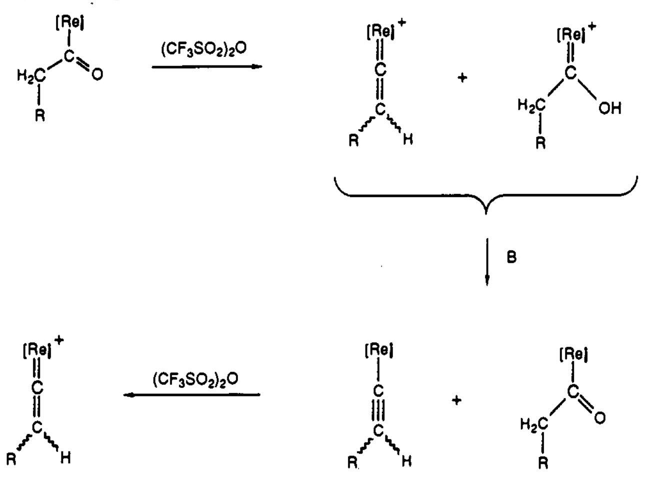
Dehydration of acyl complexes to vinylidenes with triflic anhydride was first achieved by Boland-Lussier and Hughes.[81] Application to the rhenium series resulted in concomitant protonation of the acyl to a stable hydroxycarbene complex by the CF_3SO_3H formed. The vinylidene/hydroxycarbene mixture so obtained was deprotonated [$KOBu^t$ or 2,2,6,6-tetramethylpiperidine (tmp)] to a 1/1 acetylide/acyl mixture. In a second reaction with triflic anhydride, the acetylide is protonated to the same vinylidene formed by dehydration of the acyl (Scheme 5).[82,83] Dehydration of $Fe(COMe)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ ($HBF_4\cdot Et_2O$/triflic anhydride) gave $[Fe(CCH_2)(CO)(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$.[84]

5. *From Vinyl Complexes*

An α-hydrogen shift from a vinyl ligand produces $Ta(H)(CCH_2)(\eta\text{-}C_5Me_5)_2$ in 75% yield when $TaCl_2(\eta\text{-}C_5Me_5)_2$ was treated with vinylmagnesium bromide in thf. The shift was reversed in the presence of CO (1 atm, 60 °C), when $Ta(CH{=}CH_2)(CO)(\eta\text{-}C_5Me_5)_2$ was formed; the vinylidene was reformed on UV irradiation.[85]

A new approach to the formation of M–C multiple bonds has been the elimination of small molecules across the M–C bond. Application to certain vinyl-metal complexes has provided a route to new vinylidene complexes. For example, the osmium acetylide $OsI(C_2Ph)(PPr^i_3)(\eta\text{-}C_6H_6)$ cannot be protonated, but reacts

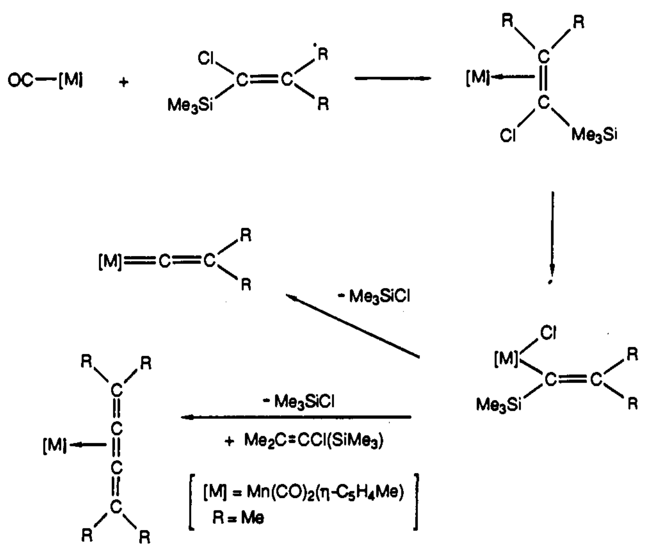
SCHEME 5



[Re] = Re(NO)(PPh$_3$)(η-C$_5$H$_5$)

B = KOBu^t or tmp
R = H, Me, Ph, 1-C$_{10}$H$_7$

SCHEME 6



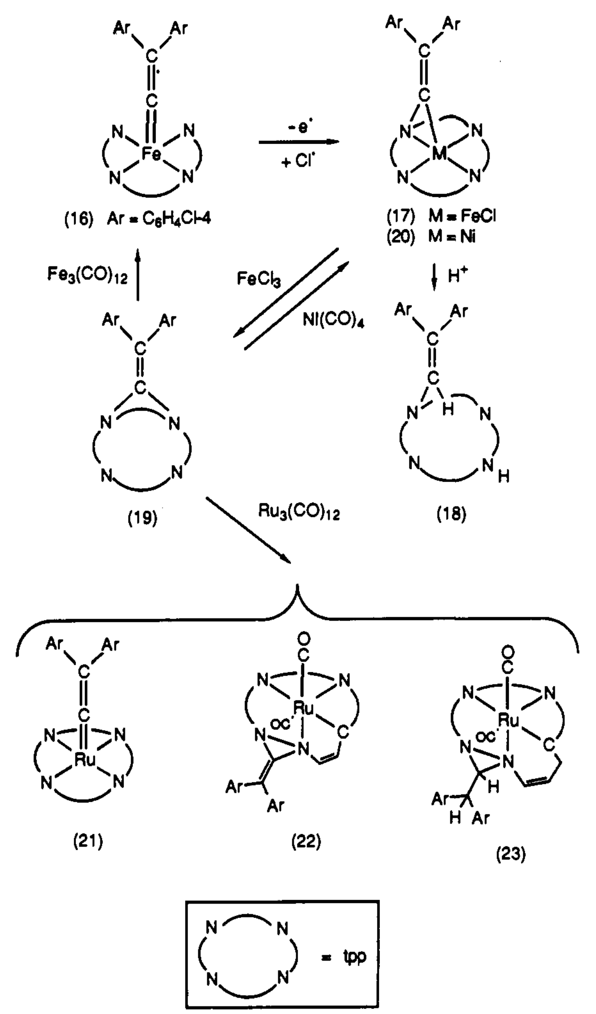
R = Me, Ph
[M] = Cr(CO)$_2$(η^6-Ar), Ar = C$_6$H$_6$, C$_6$H$_3$Me$_3$-1,3,5, C$_6$Me$_6$;
Mn(CO)(L)(η-C$_5$H$_4$Me), L = CO, PMePh$_2$, P(OPh)$_3$'

readily with NaBH$_4$ in methanol to give the hydrido–*E*-vinyl complex. Chlorination (CCl$_4$) or iodination (CH$_2$I$_2$), followed by reaction with LiBu^t at -40 °C, gave a 90% yield of Os(CCHPh)(PPr$^i_3$)(η-C$_6$H$_6$); the methyl complex is much less stable and could not be isolated.[86] The analogous rhodium complex RhCl(*Z*-CH=CHPh)(PPr$^i_3$)(η-C$_5$H$_5$) can be similarly dehydrochlorinated with NEt$_3$. In contrast, the square-pyramidal complexes MCl(CH=CHR)(CO)(PPr$^i_3$)$_2$ (M = Ru, Os) did not give vinylidene complexes on treatment with NEt$_3$ or LiBu.[87]

6. From Olefins

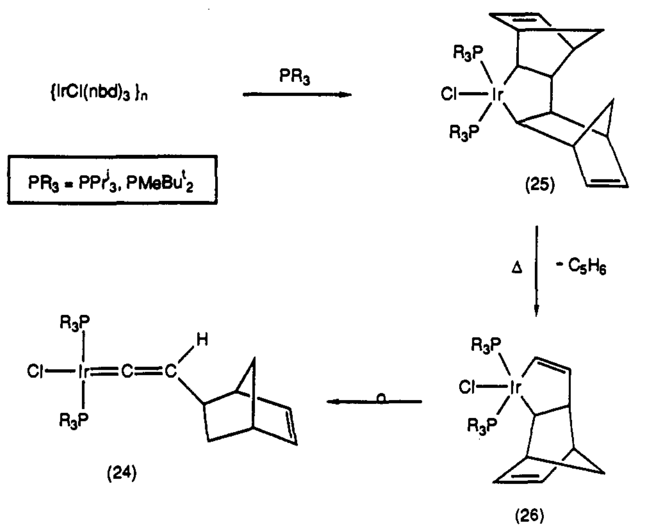
Elimination of chlorosilanes from appropriate metal precursors has provided a novel method to generate metal–element double bonds, including vinylidenes. Thus oxidative addition of α-halogenovinylsilanes to coordinatively unsaturated metal fragments, such as those formed by irradiation of Mn(CO)$_2$(L)(η-C$_5$H$_4$Me) [L = CO, PR$_3$, P(OR)$_3$] or Cr(CO)$_3$(η-arene), gave a series of mono- and di-substituted vinylidene complexes (Scheme 6).[88,89] In the case of Mn{η-CMe$_2$=CBr(SiMe$_3$)}(CO)$_2$(η-C$_5$H$_4$Me), formed as an intermediate, slow conversion to the corresponding CCMe$_2$ complex could be followed. In contrast, the major product from Me$_2$C=CClSiMe$_3$ in thf was the butatriene complex Mn(η^2-Me$_2$C=C=C=CMe$_2$)(CO)$_2$(η-C$_5$H$_4$Me), formed by coupling of CCMe$_2$ residues. In pentane, the vinylidene is the major product.[90] The coupling reaction is reminiscent of the formation of *trans*-Bu^{t}CH=C=C=CHBu^t in the reaction of HC$_2$Bu^t with RuH$_2$(CO)(PPh$_3$)$_3$.[91]

SCHEME 7



In the presence of excess reducing agent [Fe(II), S$_2$O$_4^{2-}$], DDT (1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane) reacted with Fe^{II}(tpp) (tpp = *meso*-tetraphenylporphinato(2-)) to give vinylidene complex **16**.[92] Scheme 7 outlines several reactions, including oxidation to paramagnetic **17**, in which the vinylidene group now bridges the iron atom and a ring nitrogen.[93] This complex reacted with acid to give the *N*-vinylporphyrin **18** and was oxidized (FeCl$_3$ or electrochemically at +0.8 V) to the N,N′-bridged porphyrin **19**.[94] The X-ray structures of **16**[95] and **17**,[93,96] and of the Fe(II) derivative of **18**[97] have been determined.

SCHEME 8



The N,N′-bridged vinylporphyrin **19** reacted with metal carbonyls to break one or both C–N bonds, with incorporation of the metal into the porphyrin. With $Fe_3(CO)_{12}$, vinylidene complex **16** was obtained (90%), while with $Ni(CO)_4$, complex **20**, analogous to the iron derivative **17**, was formed, only one C–N bond being broken.[98] With $Ru_3(CO)_{12}$, three products were isolated, purple $Ru\{CC(C_6H_4Cl\text{-}p)_2\}(tpp)$ (**21**) (40%) and the C-bonded complexes **22** and **23**.[98-100] The latter was also formed by heating **23** in PhCl (85%); the tolyl analogue was produced from DDT and $K_2[Ru(ttp)]$.[101]

Addition of norbornadiene to $\{IrCl(C_8H_{14})_2\}_2$ gave $\{IrCl(nbd)_3\}_n$ which with PPr^i_3 or $PMeBu^t_2$ in C_6H_6 at 50 °C, formed violet, square-planar *trans*-$IrCl\{CCH(C_7H_9)\}(PR_3)_2$ (**24**; Scheme 8) in almost quantitative yield.[102] If the reaction is carried out in pentane/thf mixtures at lower temperatures, a green complex, **25**, containing (probably) the exo,trans,exo isomer of norbornadiene dimer is obtained. This slowly decomposes with the elimination of cyclopentadiene to give metallacyclopentene **26** which then rearranges to the vinylidene complex. The reaction is probably driven by the bulky phosphine ligands, steric congestion in **26** promoting the rearrangement.

7. From Disubstituted Alkynes

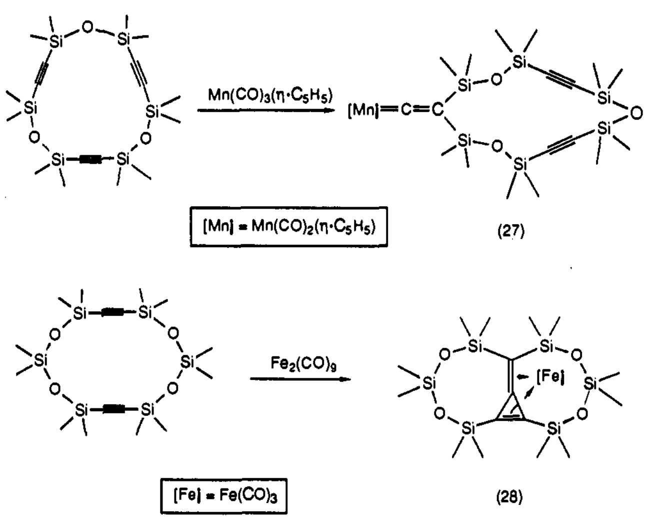
The manganese vinylidene complex **27** (Scheme 9) was obtained from the cyclic silylalkyne illustrated and characterized by X-ray crystallography.[103] The formation of **28** from the reaction between $Fe_2(CO)_9$ with a related diyne may involve an intramolecular addition of an iron–vinylidene derivative (formed by 1,2-migration of the silyl group on one C≡C triple bond) with the second C≡C triple bond.

η-(1-Iodoalkyne)manganese complexes undergo 1,2-halogen shifts to give the corresponding iodovinylidenes, $Mn\{CC(I)CH(OR)_2\}(CO)_2(\eta\text{-}C_5H_5)$ [R = Me, Et; $(OR)_2 = O(CH_2)_3O$], probably via dissociation and readdition of I^-; the iodo complex was structurally characterized.[104]

8. By Vinylidene Ligand Transfer

The reaction between $Rh(CCH_2)(PPr^i_3)(\eta\text{-}C_5H_5)$ and $IrCl(PPr^i_3)_2$ results in transfer of the vinylidene ligand from Rh to Ir in 77% yield, probably via an intermediate binuclear $Rh(\mu\text{-}CCH_2)Ir$ complex. The nature of the rhodium product is unknown.[60] The only previously reported example of this potentially useful reaction is the rather inefficient transfer of CCHPh from manganese to rhenium, proceeding in only 4% yield.[105]

SCHEME 9



9. By Modification of the Vinylidene Ligand

In the ruthenium series, electrophilic addition of CH_2 (from diazomethane) to the C_β–H bond is followed by hydrogen migration to give 50–70% yields of $[Ru(CCMeR)(chiraphos)(\eta\text{-}C_5H_5)]^+$ (R = Bu^t, Ph).[106] An alternative possibility is the formation of MeN_2^+ and methylation of the acetylide complex. This reaction has relevance to the Fischer–Tropsch reaction, since insertion of carbenes into the C–H bond of a vinylidene would give branched chain hydrocarbons, as an alternative to the McCandlish mechanism (see below).

B. Structure and Bonding

1. X-ray Structures

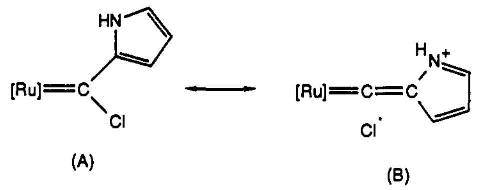
Many vinylidene complexes have been characterized by X-ray structural determinations and the salient features of the vinylidene group geometry are collected in Table 2. In mononuclear complexes, the M=C=C group is essentially linear, the angle at C_α being in the range 167–180°. The C=C bond length is between 1.25 and 1.41 Å, corresponding to a bond order of between two and three, as predicted by theory. The M=C bond is also short and consistent with a bond order of about two. Although the plane of the vinylidene is predicted to be perpendicular to the molecular plane in complexes of the type $M(CCR_2)(L)_2(\eta\text{-}C_5H_5)$,[107] the barrier to rotation is computed to be only ca. 15 kJ mol^{-1}, so that this preference is often overridden by steric effects. In $[Os(CCHBu^t)(CO)(PMe_3)(\eta\text{-}C_5Me_5)]^+$,[53] for example, the torsion angle P–Os–C_β–C differs by 27° from that in the Re cation, the bulk of the C_5Me_5 group directing the Bu^t group toward the CO ligand at the expense of the HOMO/C_α p orbital overlap.[83]

The structure of the pyrrolylcarbene complex $RuCl_2\{CCl(C_4H_4N)\}(CO)(PPh_3)_2$ (A), which contains a planar $RuC(C_4N)$ unit, with an Ru=C=C angle of 139.2°, and a long C–Cl distance [1.826 (13) Å], suggests

TABLE 2. Some Structural Features of Mononuclear Vinylidene Complexes, $ML_n(CCRR')$

ML_n	ion	R	R′	M–C	C–C	M–C–C	ref
$MoBr\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$		H	Ph	1.917 (5)	1.327 (7)	177.9 (5)	77, 78
$MoI\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$		H	Bu^t	1.927 (3)	1.333 (5)	178.2 (3)	76
mer-$W(CO)_3(dppe)$		H	CO_2Me	1.98 (1)	1.30 (1)	173 (1)	39
mer-$W(CO)_3(dppe)$		CO_2Me	$(Z)\text{-}C(CO_2Me){=}CHPh$	1.899 (6)	1.376 (7)	174.4 (5)	144
$[W(CO)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$	PF_6^-	Me	Ph	1.947 (6)	1.330 (9)	177.6 (5)	37
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$C_6H_4CBr{=}CH_2\text{-}p$	1.75 (2)	1.32 (2)	177 (2)	44
$Mn(CO)_2(\eta\text{-}C_5H_5)$		I	$CH(OMe)_2$	1.777 (6)		175.5 (6)	104
trans-$ReCl(dppe)_2$		H	Ph	2.046 (8)	1.31 (2)	166 (1)	45, 46
$[Re(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	$1\text{-}C_{10}H_7$	1.840 (7)	1.39 (2)	178.1 (9)	83
Fe(tpp)		$C_6H_4Cl\text{-}p$	$C_6H_4Cl\text{-}p$	1.689 (3)	1.336 (4)	176.7 (3)	95
$Fe(CO)_2\{P(OMe)_3\}_2$		H	CHO	1.749 (5)	1.335 (7)	177.6 (4)	47
$Fe(CO)_2\{P(OMe)_3\}_2$		$\overline{CHO(CH_2)_3O}$	(dimer)	1.778 (9), 1.763 (9)	1.34 (1), 1.35 (1)	176.1 (8), 174.8 (7)	47
$[Fe(dppe)(\eta\text{-}C_5H_5)]^+$	BF_4^-	Me	(dimer)	1.746 (9), 1.766 (9)	1.33 (1), 1.32 (1)	174.9 (7), 170.0 (8)	122
$[Ru(PMe_3)_2(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	Me	1.845 (7)	1.313 (10)	180 (2)	370
$[Ru(PPh_3)_2(\eta\text{-}C_5H_5)]^+$	I^-	Me	Ph	1.86 (1)	1.29 (2)	173 (1)	371
$[Ru(PPh_3)_2(\eta\text{-}C_5H_5)]^+$	BF_4^-	Ph	$N_2C_6H_3Me_2\text{-}3,4$	1.823 (9)	1.34 (1)	169.9 (7)	69, 71
$[Ru(PPh_3)_2(\eta\text{-}C_5H_5)]^+$	I_3^-	Ph	I	1.839 (7)	1.31 (1)	171.0 (7)	72
$[Ru(PPh_3)_2(\eta\text{-}C_5H_5)]^+$	Br_3^-	$C_6H_4Br\text{-}p$	Br	1.85 (1)	1.31 (2)	169.4 (14)	72
$[Ru(dppe)(\eta\text{-}C_5H_5)]^+$	PF_6^-	Ph	C_7H_7	1.848 (9)	1.32 (1)	174.9 (6)	69, 70
$[Ru(prophos)(\eta\text{-}C_5H_5)]^+$	PF_6^-	H	Me	1.84 (1)	1.25 (1)	175 (1)	49
$[Os(CO)(PPh_3)(\eta\text{-}C_5Me_5)]^+$	BF_4^-	H	Bu^t	1.879 (6)	1.28 (1)	175.0 (5)	53
trans-$RhCl(PPr^i_3)_2$		H	Me	1.775 (6)	1.32 (1)	177.9 (6)	55, 56
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		H	Ph	1.83 (2), 1.74 (2)	1.30 (2), 1.41 (2)	175 (2), 173 (1)	57, 58
trans-$IrCl(PPr^i_3)_2$		H	CO_2Me	1.764 (6)			60

that there is a contribution from the vinylidene resonance structure (B):[108]



$[Ru] = RuCl_2(CO)(PPh_3)_2$

2. ¹³C NMR Studies

Table 1 contains ^{13}C NMR data pertaining to the resonances of the two carbon atoms of the $MC_\alpha C_\beta$ unit. As previously observed, C_α is strongly deshielded and resonates in the range δ 258–382 ppm but most commonly around 330 ppm, while the resonance for C_β is found between δ 87–143 ppm. Theoretical studies show that the sign and magnitude of the paramagnetic contributions to nuclear shielding, which are related to differences in energies of filled and unfilled orbitals on C_α, are more significant in determining this chemical shift than the electron-deficient nature of C_α.[375]

3. Theoretical Investigations

The original and much quoted paper of Kostic and Fenske[109] explains many of the physical, structural, and chemical properties of mononuclear vinylidene complexes. The correspondence to a metalla–allene system has also been noted.[110,111] MO calculations predict that addition of electrophiles to vinylidenes will be governed by the significant charge localization on C_β. For example, protonation to form carbyne complexes occurs readily unless the vinylidene is present in a cationic complex:

$$M{=}C{=}CHR + E^+ \rightarrow [M{\equiv}C{-}CH(E)R]^+$$

However, soft electrophiles may attack the metal center; metal basicity dominates in the reactions of an ambident molybdenum complex,[75] and of square-planar rhodium(I) and iridium(I) complexes.[110]

4. Electrochemical Studies

Electrochemical and UV–visible spectroscopic studies of $Mn(CCHPh)(CO)_2(\eta\text{-}C_5H_5)$ and of Mn_2 and MnPt complexes containing μ-CCHPh ligands have shown that coordination of the Mn=C system with the second metal atom results in transfer of the electrophilic center from C_α to Mn or Pt, respectively.[112] The electrochemical reduction potential of the MnPt complex relates to the energy of the $\sigma \rightarrow \sigma^*$ transition of the M–M′ bond. Donor ligands on the platinum increase the Mn–Pt bond strength, while the Pt → μ'-CO donor interaction has the opposite effect.

The complexes *trans*-$ReCl(CCHR)(dppe)_2$ (R = Bu^t, Ph) undergo single-electron reversible oxidations at −0.26 and −0.16 V (vs SCE), respectively, followed by an irreversible process at ca. 1.0 V.[113] The results confirm the electron richness of the metal fragment and allow an ordering of ligands in terms of π-acceptor–σ-donor power:

$$CCH_2Bu^t > CNR > CNH_2 > C{=}CHPh > C{=}CHBu^t$$

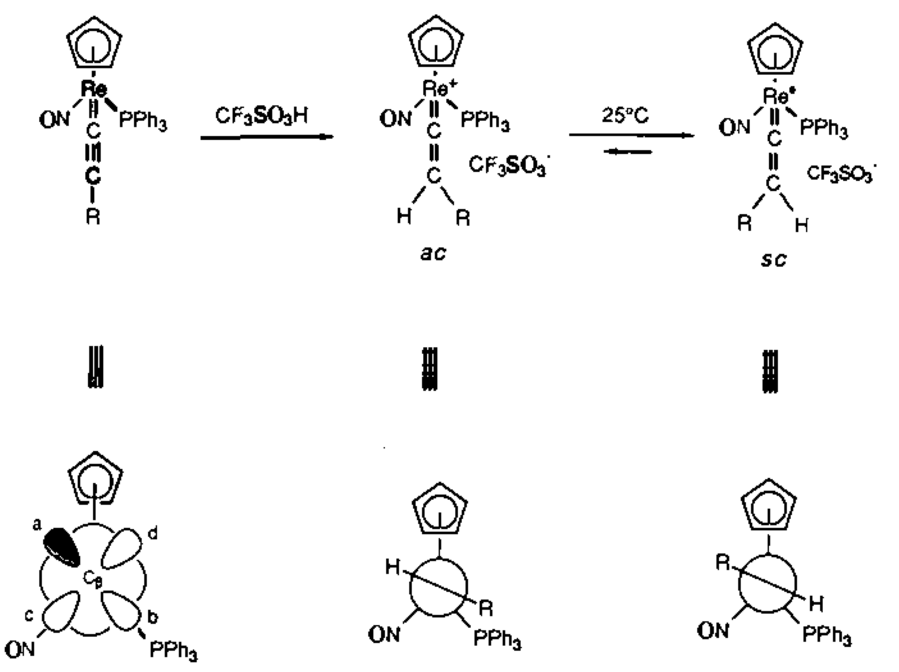
Although poor net electron acceptor ligands, vinylidenes are much better acceptors at Re (strongly electron releasing) than are carbenes at Cr, for example.

C. Stereochemical Aspects of Vinylidene Complexes

1. Rhenium Complexes

High diastereomeric excesses have been found in the products obtained by nucleophilic attack on C_α in rhenium carbene complexes of the type $[Re(CHR)(NO)(PPh_3)(\eta\text{-}C_5H_5)]^+$, because the HOMO of the metal fragment overlaps with the p acceptor orbital in the carbene. Similarly, chiral rhenium vinyl complexes

SCHEME 10



SCHEME 11

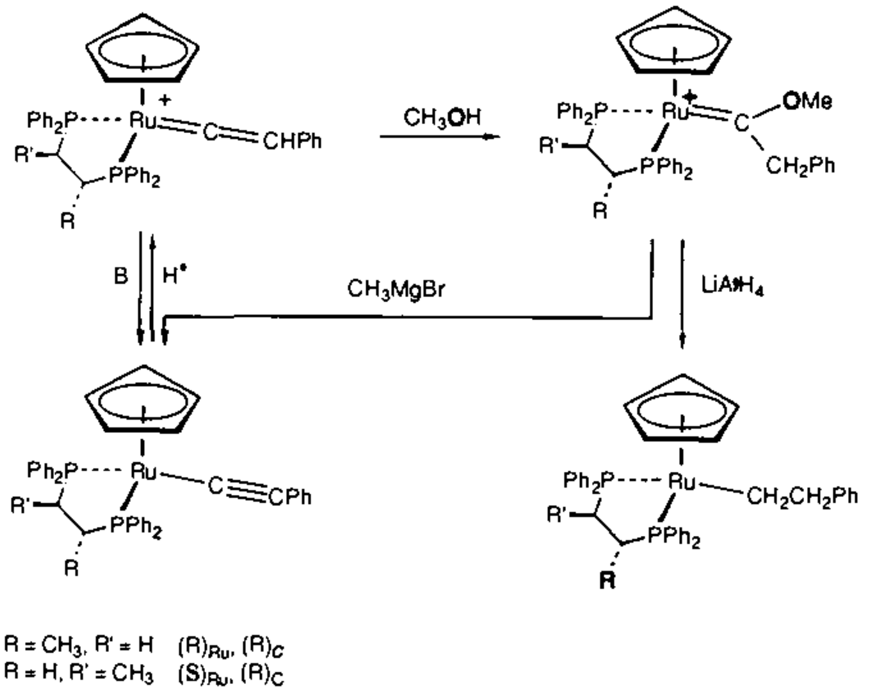


TABLE 3. Diastereomeric Composition of Iron and Ruthenium Vinylidene Complexes, $[M(CCHR)(PPh_2CHR'CHR''PPh_2)(\eta\text{-}C_5H_5)]^+$ at 160 K[51]

R	R'	R''	absolute configuration	diastereomeric ratio M = Fe	diastereomeric ratio M = Ru
Ph	H	Me	$(R)_{Ru},(R)_C$		78/22
Ph	Me	H	$(S)_{Ru},(R)_C$		>90/10
Me	H	Me	$(R)_{Ru},(R)_C$		50/50
Me	Me	H	$(S)_{Ru},(R)_C$		90/10
Ph	Me	Me	(*S*,*S*)	86/14	50/50
Me	Me	Me	(*S*,*S*)	55/45	
Bu^t	Me	Me	(*S*,*S*)		65/35
Ph	$-(CH_2)_3-$		(*S*,*S*),(*R*,*R*)	>90/10	>90/10
Me	$-(CH_2)_3-$		(*S*,*S*),(*R*,*R*)	>90/10	90/10
Bu^t	$-(CH_2)_3-$		(*S*,*S*),(*R*,*R*)	>90/10	

undergo stereospecific electrophilic attack at C_β to give carbene derivatives. Similar behavior has been found with the related vinylidene complexes; those containing two different substituents were obtained as kinetic and thermodynamic isomers.[82,83] If the entering electrophile is smaller than the acetylide substituent, the kinetic product (synclinal, *sc*, isomer) will be less stable than the thermodynamic (anticlinal, *ac*) isomer. In general, slow isomerization to an equilibrium *sc*/*ac* mixture occurred at room temperature over 24 h.

Deprotonation of the vinylidenes with $KOBu^t$ or tmp gave the corresponding acetylides in 53–93% yields. Initial protonation (CF_3SO_3H) gave the *ac* isomer as kinetic product, which isomerized to the *ac*/*sc* equilibrium mixture after 24 h (Scheme 10). In the transition state, the electrophile approaches C_β from the direction opposite to the bulky PPh_3 ligand. Methylation proceeded similarly, the two methyl resonances being readily distinguishable. Use of CD_3SO_3F gave the mixed CH_3/CD_3 product, which initially showed only one Me resonance, but on warming, the second isomer was formed.

The high degree of reaction asymmetry conferred on the cylindrical C≡C triple bond of the acetylide was rationalized by transmission of the rhenium chirality through the bond leading to only one of the four acetylide orbitals, that anti to the bulky PPh_3 ligand [a; Scheme 10] being sterically favored. If the entering electrophile is smaller than the acetylide substituent R, the kinetic isomer should not be the thermodynamic isomer.

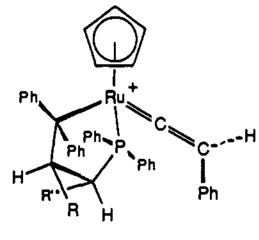
Electrophilic attack on the acetylide generates a new C_β stereogenic center via an atom with more than four valences to give an unprecedented 1,3-asymmetric induction. By the same token, Reger's stereospecific addition of $[CuMe_2(CN)]^{2-}$ to the iron–methyl(phenyl)vinylidene[66] should give the *sc* or *E* isomer. In fact, the *Z* isomer is obtained, probably because of facile isomerization and the use of less hindered nucleophiles. The 84/16 isomer mixture formed by protonation of $Fe(C_2Bu^t)(CO)(PMe_3)(\eta\text{-}C_5H_5)$[65] reflects the same stereodifferentiation.

Detailed kinetic studies of the isomerization reaction suggests that it proceeds by simple bond rotation;[83] it is independent of the anion, with $\Delta G^\ddagger_{110^\circ} > 75$ kJ mol^{-1}. Irradiation at −78 °C gave a 50/50 photostationary state, which returned to the thermal equilibrium point after warming. Photolysis leads to excited species with formal Re–C_α single bonds. Comparison with data for other vinylidenes suggest that isomerization is more facile for iron and ruthenium complexes ($\Delta G^\ddagger$ 33–42 kJ mol^{-1}), suggesting that the electronic barrier is much less in these complexes. Activation parameters for the isomerization of vinylidenes are similar to those found for carbenes. The simplistic explanation that the lesser steric component is balanced by the electronic component is not possible because of the extra $C_\alpha{=}C_\beta$ unsaturation which leads to other complex interactions.

2. Ruthenium Complexes

Consiglio's group has made extensive studies of the stereochemistry of transformation of chiral ruthenium complexes.[50] They used the metal/ligand combination $Ru(LL)(\eta\text{-}C_5H_5)$ (LL = chiraphos, cypenphos), and the relationships involving vinylidenes that have been established are shown in Scheme 11. The reactions are stereospecific at the metal atom under mild conditions. The S_{Ru},R_C or R_{Ru},R_C configurations were assigned by ^{31}P NMR studies.

The vinylidene complexes exist as equilibrium mixtures of diastereomers (Table 3), as first shown in the iron system; an AB ^{31}P NMR spectrum was found.[114] The barrier to rotation is about 38–43 kJ mol^{-1} and is independent of the phosphine ligand, but depends on the vinylidene substituent, so that it is fast at 150 K for the Bu^t complex. Epimerization of the vinylidene observed on heating probably occurs via η^2-alkyne complexes, as found with analogous olefin complexes. Differences in diastereomer population arise for steric reasons, the substituents being in a chiral pocket formed by the *P*-phenyl groups. Similarly, a 2/1 ratio of the rotational conformers of (*S*,*S*)-[Ru(CCHPh)(chiraphos)(η^5-C_9H_7)]$^+$ was present at 80 °C; the difference from the η-C_5H_5 complex again being ascribed to the different environment of the *P*-phenyl groups.[115] For complexes **29a–c** the asymmetric induction is 0, 56, and >80%, respectively; in the latter two cases, the induction is *stereogenic*, while in the former the ruthenium is *chirotopic*.[51]



(29) a R = R' = Me
b R = Me, R' = H
c R = H, R' = Me

Asymmetric induction is higher for iron than for ruthenium, (cf. the predominance of S_{Fe} (86/14) over the S_{Ru} (50/50) configuration for chiraphos complexes), and larger for S_{Ru} than for R_{Ru} complexes; the smaller pocket formed with cypenphos leads to higher asymmetric induction compared with chiraphos.[51] The absolute configuration at the metal is influenced mainly by the phosphine ligands, although it was not possible to determine whether the configuration of the vinylidene is influenced by the configuration at the metal.

The λ–δ stereoisomer interconversion of the RuPCCP chelate rings is rapid on the NMR time scale. Only the δ form of the chiraphos complex, with *S* absolute configuration of the two carbon atoms, is found as two diastereomeric rotamers. No interconversion of the diastereomers of the prophos complex occurs, only one species being found at low temperatures.

D. Reactions of Coordinated Vinylidenes

As mentioned above, a theoretical study of vinylidene complexes by Kostic and Fenske[110] identified the electron deficiency at C_α and the localization of electron density in the M=C double bond and on C_β (the HOMO). Chemical reactivity is thus oriented toward electrophiles at both the M=C bond and at C_β and toward nucleophiles at C_α. Vinylidene complexes are related to other η^1-carbon-bonded ligands (Scheme 12). Many of these reactions are stereospecific with retention of configuration at the metal atom.[49,50]

1. Reactions with Electrophiles

Protonation of the vinylidene ligand at C_β to form a carbyne occurs readily unless the ligand is present in a cationic complex. However, with more electron-rich metal centers, addition to the M=C bond gives an η^2-allene– or heteroketene–metal complexes.

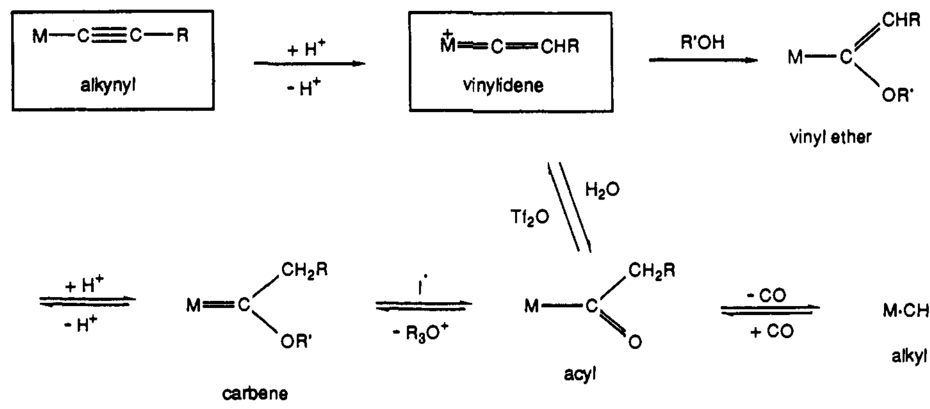
Double electrophilic addition to metal acetylides was reported in the tungsten series with W(CCRR')(CO)$_5$ (R = Bu^t, R' = Me, Et).[62] Protonation with CF_3SO_3H in dichloromethane at −70 °C and addition of MeI gave *trans*-WI{CHRR')}(CO)$_4$; proton addition probably goes via an undetected carbyne cation, such as [W{C(CHRR')}(CO)$_5$]$^+$, or a tetracarbonyl containing a weakly coordinated CF_3SO_3 group. A single-pot synthesis of the carbyne derivatives was achieved by reacting [NEt$_4$][W(C_2R)(CO)$_5$] (R = Bu^t, Ph) with excess CF_3SO_3H in the presence of [NMe$_4$]I to give 50–60% yields of *trans*-WI{C(CH$_2$R)}(CO)$_4$.[62]

Protonation (HBF$_4$·OMe$_2$) of W(CCHPh)(CO)$_3$(dppe) (reversed on alumina or by 1,8-bis(dimethylamino)-naphthalene) gave [W{C(CH$_2$Ph)}(CO)$_3$(dppe)]$^+$ which decarbonylated in refluxing CH_2Cl_2 (24 h) to give the coordinatively unsaturated dicarbonyl complex; with halide this gave *trans*-WX{C(CH$_2$Ph)}(CO)$_2$(dppe) (X = F, Cl, Br, I).[39] The dicarbonyl readily adds ligands such as CO, PMe$_3$, acetone, and water. Bidentate ligands, such as dialkyldithiocarbamates, also add with concomitant coupling of carbyne and carbonyl ligands to give W(η^2-OC=CCH$_2$Ph)(CO)(dppe)(dtc). Methylation with [Me$_3$O]$^+$ then gave the η^2-alkyne complex [W(η^2-MeOC≡CCH$_2$Ph)(CO)(dppe)(dtc)][BF$_4$]; protonation gave an unstable hydroxyalkyne complex which was not isolated.[42] These reactions overall demonstrate the two-carbon coupling reaction:

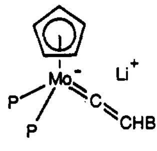
$$\mathrm{M{\equiv}CR + CO \rightarrow M(RC{=}C{=}O) \rightarrow M(RC{\equiv}COR')}$$

The lithium complex Li[Mo(CCHBu^t){P(OMe)$_3$}$_2$(η-C_5H_5)] (**30**) reacts with many electrophiles to form carbyne complexes Mo{C(CHBu^{t}R)}{P(OMe)$_3$}$_2$(η-C_5H_5) (R = Me, CH_2CH_2OH, CH_2OEt, COBu^t, SiMe$_3$, SMe) by selective attack at C_β.[75] Both "hard" and "soft" nucleophiles add to the carbon center, probably because

SCHEME 12

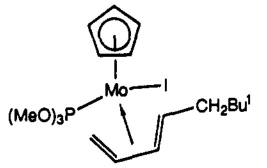


of steric effects. In one case ($CH_2{=}CHCH_2Cl$), attack at the metal was also found, and this became the predominant mode with $CH_2{=}CHCH_2I$; the product was $MoI(\eta^4\text{-}CH_2{=}CHCH{=}CHCH_2Bu^t)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$ (**31**).[75]



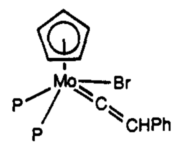
P = P(OMe)$_3$

(30)



(31)

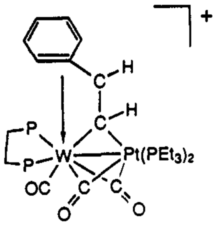
Protonation of $MoBr(CCHPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**32**) gave $[MoBr\{C(CH_2Ph)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$ (77%), containing Mo(VI), which could be reduced to the neutral carbyne $Mo\{C(CH_2Ph)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ with magnesium amalgam.[77,78] Excess triflic acid protonated *trans*-$Mo(C_2Bu^t)(CO)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ via the vinylidene to give *trans*-$[Mo(CCH_2Bu^t)(OTf)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$.[37]



P = P(OMe)$_3$

(32)

Addition of the Pt–H bond in $[PtH(OCMe_2)(PEt_3)_2]^+$ to *mer*-$W(CCHPh)(CO)_3(dppe)$ occurs regiospecifically across the W=C bond to give the orange, fluxional $\mu\text{-}\sigma,\eta^4$-styryl complex $[PtW\{\mu\text{-}CH{=}CHPh)(CO)_3(PEt_3)_2(dppe)]^+$ (**33**) (72%). In solution, the styryl group is bonded as shown, but in the $CHCl_3$ solvate, the aryl group is not coordinated to tungsten.[116]

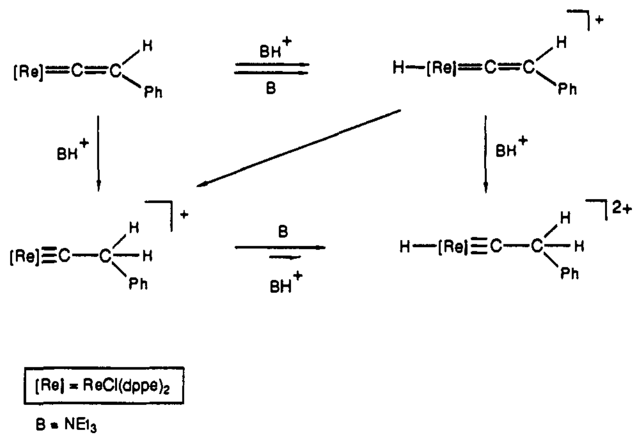


(33)

Protonation ($HBF_4{\cdot}OEt_2$) of *trans*-$ReCl(CCHR)(dppe)_2$ (R = Bu^t, Ph) gave the corresponding carbyne complexes *trans*-$[ReX(CCH_2R)(dppe)_2][BF_4]$ (X = Cl, F), the latter being formed by Cl/F exchange.[117] Stopped-flow methods have shown that protonation with $[NHEt_3]^+$ can occur by three routes involving (a) a slow, direct protonation of the vinylidene ligand or (b) a fast addition of H^+ to the metal (or the Cl atom) followed by either an intramolecular 1,3-proton shift from Re to C_β, or by further protonation to give a hydrido–carbyne complex, of which the metal center is deprotonated by base (Scheme 13).[118] Protonation at the metal center deactivates the vinylidene ligand toward addition of a proton.

Protonation of $Rh(CCH_2)(PPr^i_3)(\eta\text{-}C_5H_5)$ with CF_3CO_2H, HCl, or HI gave $RhX(CH{=}CH_2)(PPr^i_3)(\eta\text{-}C_5H_5)$ (X = CF_3CO_2, Cl, or I); addition of a second molecule of HCl to the chloro complex gave the 2-chloroethyl derivative.[119] The kinetically preferred *Z* isomer of the vinyl, formed first, rearranges in polar solvents to the thermodynamic *E* isomer. Halide exchange with NaI gave the iodo complex. The methylvinylidene complex gave a 62/38 mixture of *Z*/*E* isomers which was independent of anion and solvent. Excess acid resulted in cleavage of the Rh–C bond and formation of $RhX_2(PPr^i_3)(\eta\text{-}C_5H_5)$ (X = Cl, CF_3CO_2). The *Z*-styryl complex partially isomerized with NEt_3 in benzene at 50 °C, with 75% regeneration of the vinylidene. Conversion of $Rh(CCHBu^t)(PPr^i_3)(\eta\text{-}C_5H_5)$ to $Rh(CH{=}CHBu^t)\{OC(O)CF_3\}(PPr^i_3)(\eta\text{-}C_5H_5)$ was achieved by addition of CF_3CO_2H.[59]

SCHEME 13



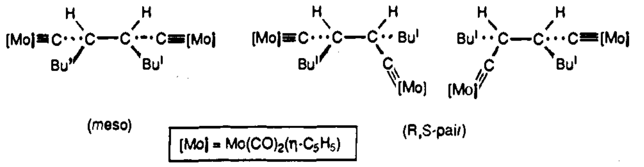
While protonation of the molybdenum or tungsten vinylidene complexes described above afforded the corresponding carbyne complexes by attack on C_β, metal basicity dominates in the square-planar iridium(I) complexes, $Ir(CCHR)(Cl)(PPr^i_3)_2$ (R = H, Me, Ph).[111] These undergo electrophilic addition to the metal to give the cationic hydrido–vinylidenes $[IrHCl(CCHR)(PPr^i_3)_2]^+$. These transformed rapidly (seconds) to the carbyne complexes $[Ir(CCH_2R)(Cl)(PPr^i_3)_2]^+$. However, the solid products obtained from nitromethane solution contain an equilibrium mixture of carbyne/hydrido–vinylidene cations. Addition of NaH regenerated the vinylidene, while excess NaH gave $IrH_5(PPr^i_3)_2$.

Reactions of diazomethane with $Rh(CCHR)(PPr^i_3)(\eta\text{-}C_5H_5)$ (R = H, Me, Ph) in the presence of $CuSO_4$ at 0 °C resulted in stereoselective addition of CH_2 to the Rh=C bond and formation of the allene complexes $Rh(\eta^2\text{-}CH_2{=}C{=}CHR)(PPr^i_3)(\eta\text{-}C_5H_5)$, in which the substituents L_nRh/R are cis.[110,120]

Addition of S, Se, or Te directly to $Rh(CCHR)(PPr^i_3)(\eta\text{-}C_5H_5)$ gave the corresponding thio-, seleno-, or telluroketene complexes $Rh(\eta^2\text{-}E{=}C{=}CHR)(PPr^i_3)(\eta\text{-}C_5H_5)$ (E = S, Se, Te) in 50–90% yields.[110,120,121] The tellurium complex slowly decomposes in benzene at room temperature to give back the vinylidene with deposition of tellurium. The complexes obtained from the unsubstituted vinylidene were the first derivatives of $CH_2{=}C{=}E$ to be obtained. Similarly, reactions of $Rh(CCHR)(PPr^i_3)(\eta\text{-}C_5H_5)$ (R = Bu^t, CO_2Me) with S_8 afforded the corresponding $\eta^2\text{-}S{=}C{=}CHR$ complexes, which were methylated (CF_3SO_3Me) to $[Rh(\eta^2\text{-}MeS{=}CCHR)(PPr^i_3)(\eta\text{-}C_5H_5)]^+$.[60]

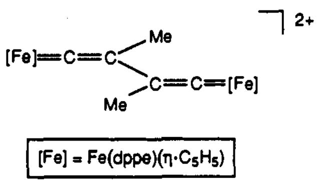
2. Oxidation

Reactions of the molybdenum complex **30** with one-electron oxidants ($[Fe(\eta\text{-}C_5H_5)_2]^+$, CuI) afforded the coupled bis-carbyne complexes **34** as meso and the *RS* pair.[75] Similar oxidative couplings have been found in



(34)

the reaction between [Fe(CCHMe)(dppe)(η-C$_5$H$_5$)]$^+$ and PhIO in MeCN, which afforded [Fe$_2$(μ-C$_4$Me$_2$)(dppe)$_2$(η-C$_5$H$_5$)$_2$]$^{2+}$ (**35**; 77%),[122] and the aerial oxidation of [Ru{CCH(SiMe$_3$)}(PMe$_3$)$_2$(η-C$_5$H$_5$)]$^+$, which gave the related C$_4$(SiMe$_3$)$_2$ complex.[123] The X-ray structure of **35** showed that the 1,3-butadien-1,4-diylidene ligand had the s-trans conformation at the C–C bond.[122] The oxidation of the phenylvinylidene analogue was achieved with Cu(OAc)$_2$ in MeOH. The suggested mode of formation is given in Scheme 14. The related binuclear complex {Fe(CO)$_2$[P(OMe)$_3$]$_2$[CC(R)$^-$]}$_2$ (R = CHO(CH$_2$)$_3$O) was obtained from the μ-N$_2$ complex and ClC$_2$CHO(CH$_2$)$_3$O.[47]



(35)

3. Reactions with Nucleophiles

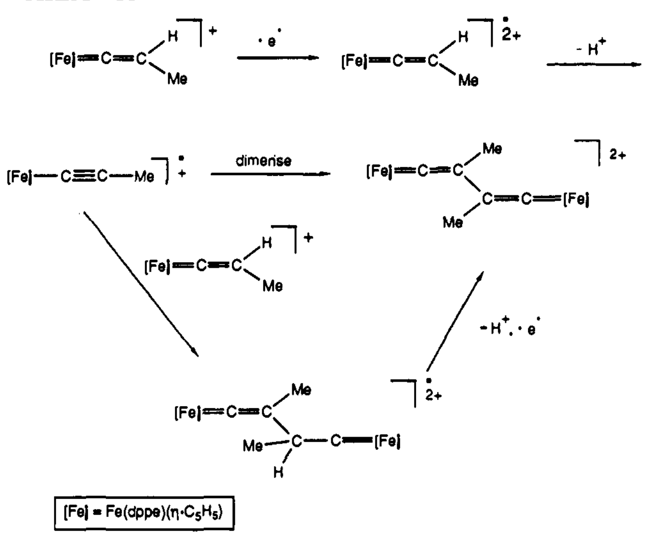
The further reactions of the vinylidene **32** with K[BHBu$^s_3$] and LiCuPh$_2$ to form the corresponding carbyne complexes was envisaged to proceed by an S$_N$2′ mechanism via attack of the nucleophile on C$_β$ of an intermediate η^2-bromoalkene complex, followed by loss of bromide: the η^2-vinyl complex may be an intermediate.[77,78] The ready loss of the α-bromine atom recalls the easy hydrolysis of a related platinum–chlorovinyl complex, which was related to the long C–Cl bond found in the latter complex.[124]

Attack of PEt$_3$ on the molybdenum complex **32** occurs at the metal atom, resulting in displacement of a P(OMe)$_3$ ligand. Excess PEt$_3$ or K[BHBu$^s_3$] gave a low yield of the mixed ligand carbyne complex, formed by PEt$_3$ attack on the bromine followed by H$^+$ abstraction from the solvent.[77,78]

Isocyanides reacted with Mn(CCHPh)(CO)$_2$(η-C$_5$H$_5$) to give the reactive ketenimines Mn(NR=C=C=CHPh)(CO)$_2$(η-C$_5$H$_5$) (R = Bu^t, Cy, CH$_2$Ph), which added H$_2$O or NHEt$_2$ to give complexes containing cinnamic acid amides and CHPh=C=C=C(NEt$_2$)(NHCy), respectively. These reactions were used to synthesize the olefins by displacement of the latter from manganese by N donors.[125]

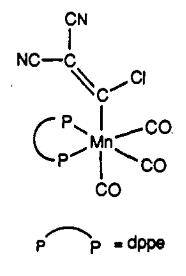
The chemistry of the manganese complexes Mn(CCHR)(CO)$_2$(η-C$_5$H$_5$) had already been shown to involve addition of bases to C$_α$,[126] although substitution of CO at the metal center was also known. Addition of tertiary phosphines (PPh$_2$R′) to Mn(CCHR)(CO)$_2$(η-C$_5$H$_5$) afforded Mn{C(PPh$_2$R′)=CHR}(CO)$_2$(η-C$_5$H$_5$) [R = Ph, R′ = Me, Ph; R′ = Ph, R = Me, CBu$^t_2$(OH)]. Exchange of more basic for less basic phosphines was shown for PMePh$_2$, although the complex Mn{C(PMePh$_2$)=CHPh}(CO)$_2$(η-C$_5$H$_5$) dissociates in polar solvents.[127] The original reaction of Mn(η-HC$_2$CO$_2$Me)(CO)$_2$(η-C$_5$H$_5$) with PPh$_3$ in pentane was described as giving a red 1/1 adduct in 85% yield which was thought to be Mn{C(PPh$_3$)=CH(CO$_2$Me)}(CO)$_2$(η-C$_5$H$_5$).[128] An attempt to add PPh$_3$ directly to the vinylidene gave instead a brown isomer. An X-ray crystallographic study of the red complex showed that a new π → σ rearrangement had occurred to give the zwitterionic complex Mn$^-${C(CO$_2$Me)=CH(P$^+$Ph$_3$)}(CO)$_2$(η-C$_5$H$_5$), also formulated as the carbene ylid Mn{C(CO$_2$Me)CH=PPh$_3$}(CO)$_2$(η-C$_5$H$_5$). Orange Mn{C(CO$_2$Me)CH=PPh$_2$(CH$_2$)$_2$PPh$_2$}(CO)$_2$(η-C$_5$H$_5$) was obtained similarly in 60% yield.[129] The earlier formation of Mn(CCHPh)(CO)(PPh$_3$)(η-C$_5$H$_5$) by addition of PPh$_3$ to the dicarbonyl is now shown to proceed via initial formation of Mn{C(PPh$_3$)=CHPh}(CO)$_2$(η-C$_5$H$_5$).[127] Similar reactions between Mn(η^2-C$_2$H$_2$)(CO)$_2$(η-C$_5$R$_5$) (R$_5$ = H$_5$, H$_4$Me, Me$_5$) and PR′$_3$ (R′ = Me, Et) gave 1/1 adducts formulated as Mn{CH=CH(PR′$_3$)}(CO)$_2$(η-C$_5$R$_5$) which readily rearranged to the vinylidene ylids Mn$^-${C(P$^+$R′$_3$)=CH$_2$}(CO)$_2$(η-C$_5$R$_5$).[130]

SCHEME 14

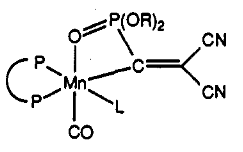


Rhenium vinylidenes reacted with nucleophiles, e.g. PMe$_3$, to give Re$^-${C(P$^+$Me$_3$)=CMe$_2$}(NO)(PPh$_3$)(η-C$_5$H$_5$). This reaction is stereospecific, attack of the nucleophile occurring anti to the bulky PPh$_3$ ligand.[83]

The complex *fac*-Mn{CCl=C(CN)$_2$}(CO)$_3$(dppe) (**36**) was earlier reported to react with P(OPr^i)$_3$ under irradiation to give the chelate phosphonato complex **37** (L = CO).[131] Similar complexes were obtained from the reaction between **36** and a mixture of (RO)$_2$P(O)H (R = Me, Et) and LiBu^t, followed by irradiation, while irradiation of **36** with P(OR)$_3$ (R = Me, Et) afforded the

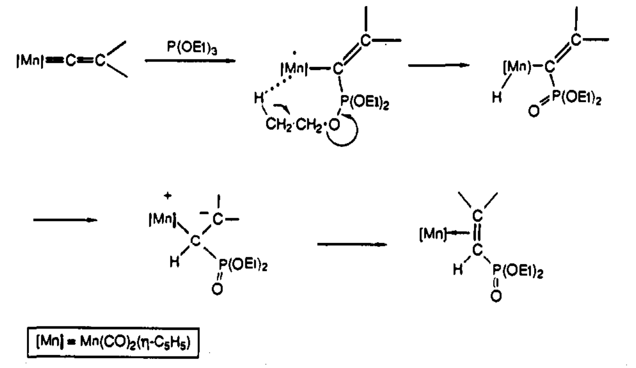


(36)

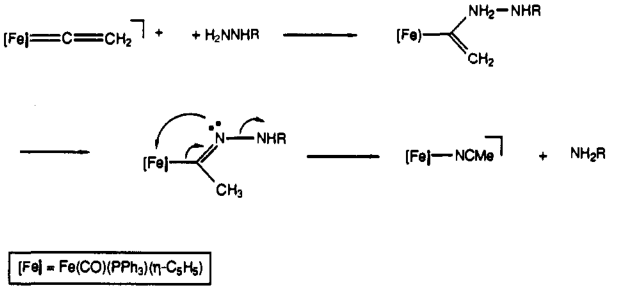


(37)

SCHEME 15



SCHEME 16



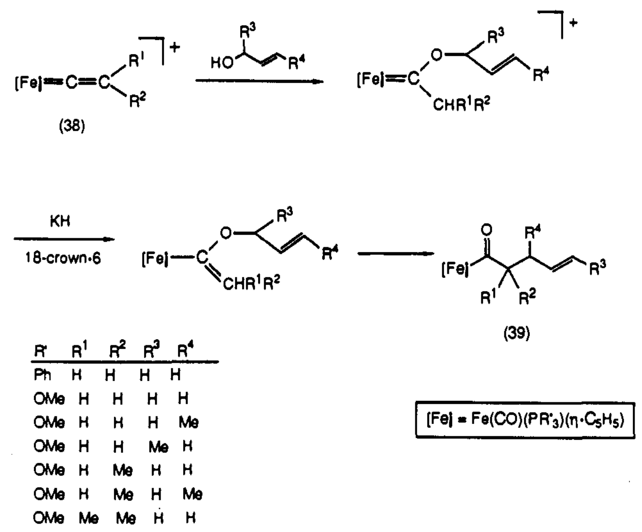
monocarbonyls **37** (L = $P(OR)_3$). The Russian group has found that a novel variant of this Arbuzov reaction occurs when $Mn(CCHPh)(CO)_2(\eta\text{-}C_5H_5)$ is treated with $P(OR)_3$ (R = Et, Ph).[132] In cyclohexane, the olefin complexes $Mn\{\eta^2\text{-}CHPh{=}CHP(O)(OR)_2\}(CO)_2(\eta\text{-}C_5H_5)$ are formed in quantitative yields; they were also obtained in reactions of the manganese complex with $Pt\{P(OR)_3\}_4$. The mechanism shown in Scheme 15 was suggested.[133] With $PPh(OEt)_2$, $Mn\{\eta^2\text{-}CHPh{=}CHPPh(O)(OEt)\}(CO)_2(\eta\text{-}C_5H_5)$ was obtained as a mixture of isomers, while similar compounds were formed from $\overline{P(OCHMeCHMeO)}(SiMe_3)$ and $\overline{P\{O(CH_2)_3O\}}Bu$. Subsequent reactions with CO, PPh_3, or $P(OPh)_3$ gave up to 98% free styryl phosphonate.[134]

Ready deprotonation of the vinylidenes (basic alumina) formed from terminal alkynes was again demonstrated for several iron and ruthenium complexes, including products from $FeCl(dppe)(\eta\text{-}C_5H_5)$, $[Fe(NCMe)(dppe)(\eta\text{-}C_5H_5)]^+$, $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, or $RuCl(dppe)(\eta\text{-}C_5Me_5)$ with HC_2R (R = Ph or Bu^t).[135,136] In MeOH, the reactions between $FeCl(dppe)(\eta\text{-}C_5H_5)$ and C_2H_2 or HC_2SiMe_3 gave the parent vinylidene complex, but the reaction with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ gave 75% $[Ru\{CMe(OMe)\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ by rapid addition of MeOH to the vinylidene.[67]

Attack on $Fe(CCMeR)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (R = Me, Ph) by carbon-based nucleophiles delivered by $Li_2[Cu(CN)R_2]$ or SPh^- readily gave the corresponding vinyl complexes. Addition of $Li_2[Cu(CN)Me_2]$ to the methy(phenyl)vinylidene gave a quantitative yield of $Fe(CMe{=}CMePh)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (Z/E isomer ratio 93/7).[66]

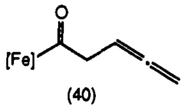
Reactions between $[Fe(CCH_2)(CO)(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$ and hydrazines afforded $[Fe(NCMe)(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ by a facile organometallic Beckman rearrangement of an intermediate hydrazine complex (Scheme 16); with $p\text{-}MeC_6H_4SO_2NHNH_2$, the sulfonamide was also isolated (84%).[84]

SCHEME 17



R'	R1	R2	R3	R4
Ph	H	H	H	H
OMe	H	H	H	H
OMe	H	H	H	Me
OMe	H	H	Me	H
OMe	H	Me	H	H
OMe	H	Me	H	Me
OMe	Me	Me	H	H

Claisen rearrangement of iron (allyloxy)carbene complexes was observed in the reaction of the vinylidene–iron complex **38** (Scheme 17) with allylic alcohols. Treatment of the initial products with KH in the presence of 18-crown-6 afforded the acyl complexes **39** in 10–60% yields.[137] In the same type of reaction, propargyl alcohol afforded the allenyl–acyl complex **40**, which readily isomerized to the butadienyl–acyl **41**.



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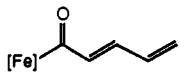
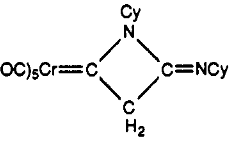


(41)

[Fe] = Fe(CO){P(OMe)3}(η-C5H5)

4. Cycloaddition Reactions

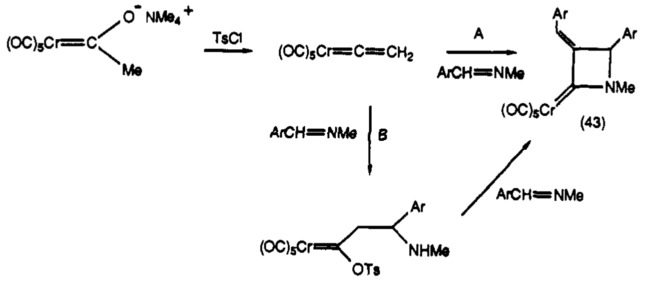
The intermediacy of $Cr(CCH_2)(CO)_5$ in the reaction of $Cr\{C(OH)Me\}(CO)_5$ with CyN=C=NCy was used to explain the formation of complex **42**, by subsequent cycloaddition of the carbodiimide to the vinylidene.[138]



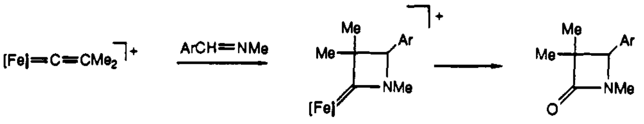
(42)

This reaction has been exploited for β-lactam synthesis, taking advantage of the ready conversion of $R_2C{=}[Cr(CO)_5]$ to $R_2C{=}O$ with certain oxidizing agents. Thus, vinylidenes are ketene surrogates, and their potent electrophilic nature allows their use in synthesis. The chromium vinylidene was generated from $[NMe_4][Cr\{C(O)Me\}(CO)_5]$ and tosyl chloride and reacted with benzylideneimines to give **43** (25%), which in turn were converted to the β-lactams by reaction with PhIO or pyridine N-oxide in 87–100% yields.[139] The reaction was postulated to proceed via cycloaddition of the imine to the vinylidene (route A, Scheme 18), although a possible alternative is reaction via the open

SCHEME 18



SCHEME 19

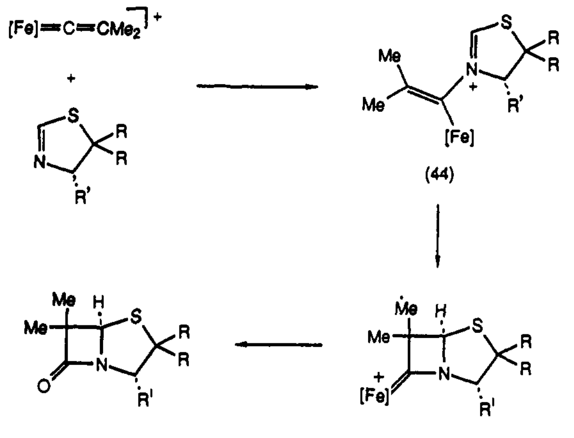


[Fe] = Fe(CO)(PR$_3$)(η-C$_5$H$_5$)

R = Ph, OMe

Ar = Ph, C$_6$H$_4$Me-3 or -4, (E)-CH=CHPh

SCHEME 20



[Fe] = Fe(CO){P(OMe)$_3$}(η-C$_5$H$_5$)

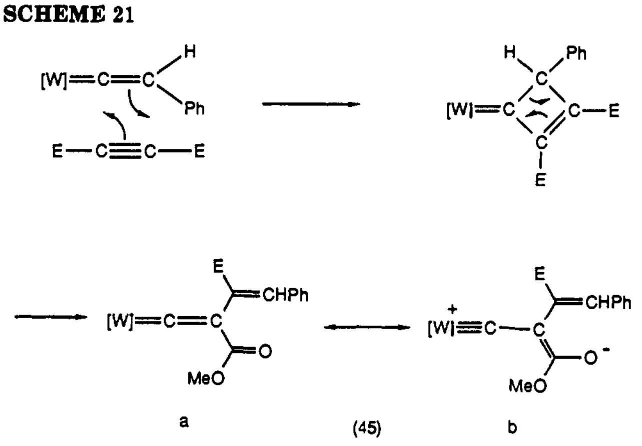
R, R^1 = H, H; H, CO$_2$Et; Me, CO$_2$Me

system, obtained in MeOH, followed by cyclization (route B).

Similar reactions were found with the cationic iron systems derived from [Fe(CO)(PR$_3$)(η-C$_5$H$_5$)]$^+$ (R = Ph, OMe).. Cycloaddition of benzylideneimines gave the corresponding azetidinylidene complexes, which could be oxidized (PhIO) to β-lactams in moderate yield (Scheme 19).[140,141] Low diastereomeric selectivity was found, apparently as the result of stepwise reactions which allow time for E/Z isomerization of the intermediates to occur.

Extension to sulfur-containing heterocycles (Scheme 20) gave mono and bicyclic intermediates with part of the penicillin framework.[142] In these cases, E/Z isomerization of the intermediate **44** cannot occur, so that there is considerable facial selectivity in the formation of the final C–C bond. Final oxidation of the heterocyclic iron carbene complexes was achieved with [NBu$_4$][NO$_2$] in dichloromethane under pressure.

SCHEME 21



[W] = mer-W(CO)$_3$(dppe)

E = CO$_2$Me

The reaction between Cr(OEt$_2$)(CO)$_5$ and HC$_2$CO$_2$Me gave the three complexes Cr(η^2-HC$_2$CO$_2$Me)(CO)$_5$, Cr[CCH(CO$_2$Me)CH=C(CO$_2$Me)](CO)$_5$, and Cr{CC(CO$_2$Me)CH=CH(CO$_2$Me)}(CO)$_5$, the former rearranging to an undetected vinylidene and adding a second molecule of alkyne.[143] Similar reactivity between W(CCHPh)(CO)$_3$(dppe) and C$_2$(CO$_2$Me)$_2$ afforded the Z and E isomers of W{CC(CO$_2$Me)C(CO$_2$Me)=CHPh}(CO)$_3$(dppe) (**45a**), formed by ring opening of an intermediate cyclobutenylidene complex formed by cycloaddition of the alkyne to the C=C double bond of the vinylidene (Scheme 21).[144] Irradiation of the kinetic Z isomer gave a 1/8 mixture of the Z and E isomers. Structural data on the Z isomer suggest a significant contribution from the carbyne form (**45b**).

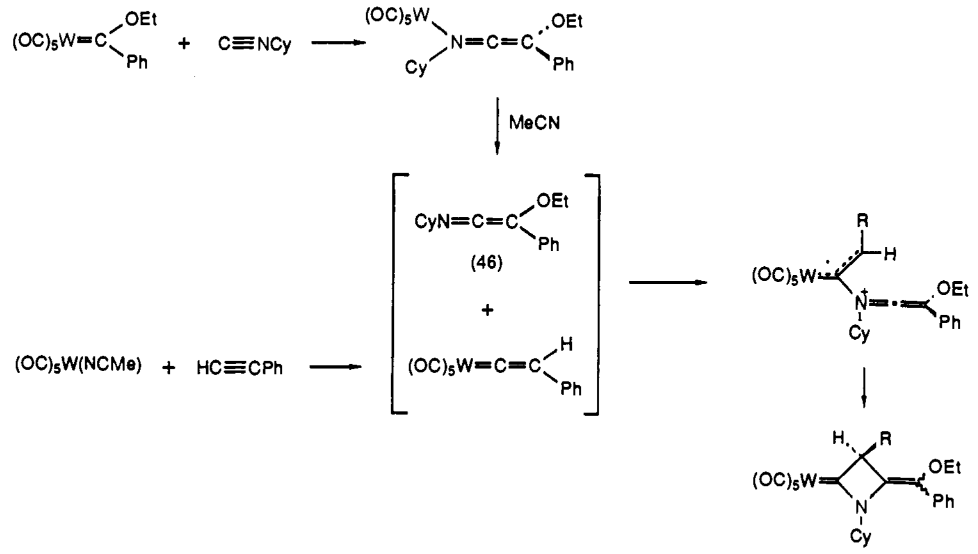
Three-component reactions between 1-alkynes, cyclohexyl isocyanide, and W{C(OEt)Ph}(CO)$_5$ afforded azetidinylidene complexes via a tungsten vinylidene complex formed from the 1-alkyne (Scheme 22).[145] Subsequent attack of **46**, formed from the carbene complex and the isocyanide, and liberated in acetonitrile solution, gave an intermediate which cyclized to the heterocyclic product.

The [2 + 3]-cycloaddition of benzoyl azide to M(CCHR)(PPr$^i_3$)(η-C$_n$H$_n$) (R = Me, Ph; M = Rh, n = 5; M = Os, n = 6) gave metallocyclic complexes **47** (68–72%).[146,147] Both phenyl derivatives have the Z configuration; the methyl–rhodium complex exists as a 10/3 Z/E isomer mixture in diethyl ether, but 10/8 in acetone. The metallacycles are formed by addition of benzoylnitrene to the M=C bond, followed by ring-opening and subsequent cyclization of the dipolar intermediate. The Z/E isomerization may occur via a ring-opened intermediate. Phenyl azide and Rh(CCHPh)(PPr$^i_3$)(η-C$_5$H$_5$) gave almost quantitatively the red ketenimine complex Rh(η^2-PhNC=CHPh)(PPr$^i_3$)(η-C$_5$H$_5$) (**48**) (85%); this reaction resembles that of CH$_2$N$_2$ (above).[148]

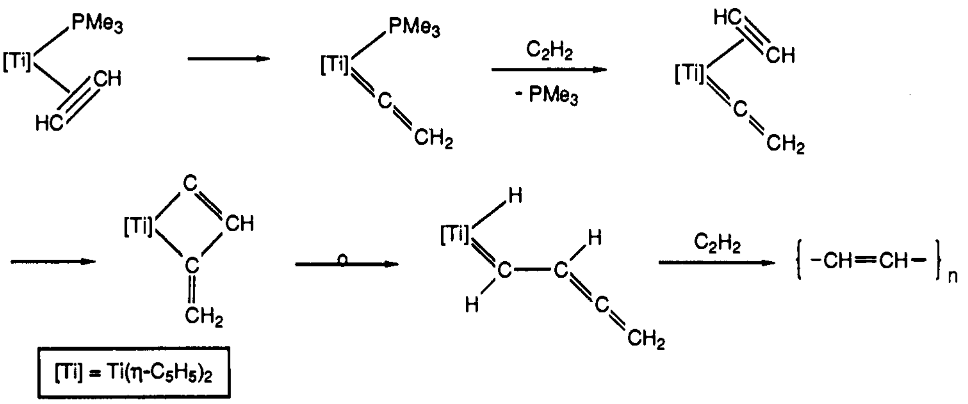
5. Displacement of Vinylidene Ligands

In MeCN, the salts [Ru(CCHMe)(PMe$_3$)(η-C$_5$H$_5$)][M(CO)$_3$(η-C$_5$H$_5$)] (M = Cr, Mo, W) disproportionate on heating to give [Ru(NCMe)(PMe$_3$)$_2$(η-C$_5$H$_5$)]$^+$ and

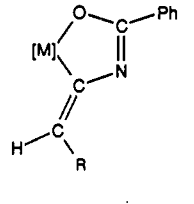
SCHEME 22



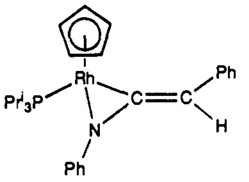
SCHEME 23



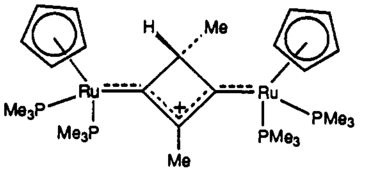
the intensely orange cation **49**, independently synthesized from an equimolar mixture of the vinylidene and parent acetylide in 73% yield.[65] In acetonitrile, the vinylidenes (as PF_6 salts) cleanly transformed into the corresponding acetonitrile cations and the 1-alkyne.[52]



(47) [M] = $Rh(PPr^i_3)(\eta\text{-}C_5H_5)$
$Os(PPr^i_3)(\eta\text{-}C_6H_6)$
R = H, Me, Ph



(48)



(49)

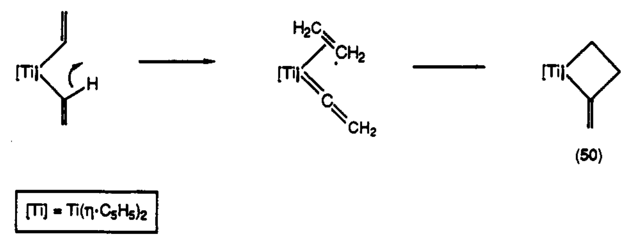
E. Reactions in Which Vinylidenes Complexes Have Been Implicated

Ethyne reacts with $Ti(PMe_3)_2(\eta\text{-}C_5H_5)_2$ to give, first, dark purple $Ti(C_2H_2)(PMe_3)(\eta\text{-}C_5H_5)_2$ and with excess ethyne, $Ti(C_4H_4)(\eta\text{-}C_5H_5)_2$, together with black *trans*-polyacetylene. The latter is formed catalytically, but the titanacyclopentadiene is not a catalyst. It is suggested that the η^2-ethyne complex isomerizes to the vinylidene, after which replacement of PMe_3 by ethene gives the alkyne–vinylidene complex which can rearrange to an allenyl derivative; insertion of ethyne then leads to polyacetylene (Scheme 23).[148] The reaction is not found with substituted alkynes, which reactions favor formation of the metallacycle.

The titanacycle complex **50** was obtained from $TiCl_2(\eta\text{-}C_5H_5)_2$ and $LiCH{=}CH_2$ in a reaction suggested to proceed by metal-centered coupling of vinylidene and ethene ligands formed by H-transfer between vinyl groups (Scheme 24).[149] Substituted complexes (**51**, Scheme 25) were obtained from titanacyclobutanes and 1,1-disubstituted allenes; in turn these gave good to excellent yields of substituted allenes when treated with ketones.[150] The mechanism supposes the intermediacy of a vinylidene–titanium complex and is supported by unpublished work demonstrating the formation of $Ti(CCMe_2)(PMe_3)(\eta\text{-}C_5H_5)_2$ in the reaction between (**51**, $R^2 = R^3 =$ Me) and PMe_3.[150b]

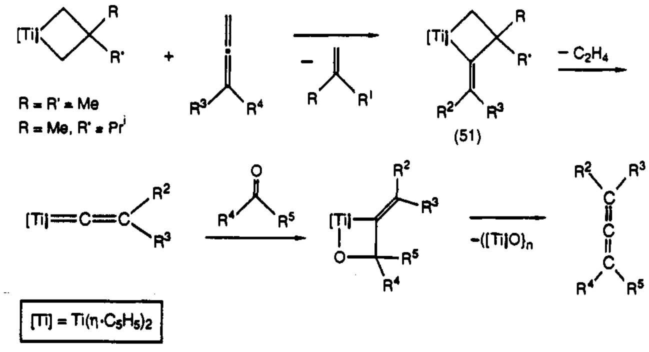
Vinylidene complexes have been proposed as intermediates in the reactions of chromium or manganese η-ethyne complexes with PMe_3 to give $M\{C(PMe_3)CH_2\}(CO)_2(L)$ (M = Cr, L = $\eta\text{-}C_6H_3Me_3$; M = Mn, L = $\eta\text{-}C_5H_5$); with Cr, phosphines with larger substituents (PEt_3, PBu_3) added to C_β to give $Cr\{CHCH(PR_3)\}(CO)_2(\eta\text{-}C_6H_3Me_3)$. A similar reaction with $NHMe_2$

SCHEME 24



[Ti] = Ti(η-C5H5)2

SCHEME 25



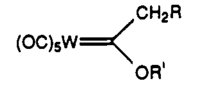
[Ti] = Ti(η-C5H5)2

$R^2 = R^3$ = H, Me, Ph; R^4, R^5 = various

afforded $Cr\{C(NMe_2)Me\}(CO)_2(\eta\text{-arene})$.[151]

The kinetics of phenylethyne polymerization by a $W\{C(OMe)Ph\}(CO)_5$ initiator[152] were originally interpreted in terms of an intermediate of the type $Ph(MeO)C{=}CPhCH{=}W(CO)_4$.[153] More recently, alkyne polymers were obtained by irradiation of hydrocarbon solutions containing $W(CO)_6$ and 1-alkynes; with acetylene, irradiation was required only for the initiation of the reaction. The suggested intermediacy of a vinylidene complex was supported by the reaction between $W(CCMeBu^t)(CO)_5$ and HC_2Ph; no reaction occurred at room temperature for 22 h, but irradiation caused a color change from green to red and the deposition of phenylethyne polymer. Irradiation of the vinylidene complex in MeCN caused spectral changes consistent with the formation of *cis*-$W(CCMeBu^t)(NCMe)(CO)_4$, which reacted with but-2-yne to give the η^2-alkyne complex. After addition of a trace of HC_2Ph, photoinduced polymerization of the but-2-yne occurred after an induction period of 30–40 min.[63]

Irradiation of $W(CO)_6$ or $W(CO)_4(cod)$ in the presence of ethyne or HC_2SiMe_3, in dichloromethane or hexane, followed by treatment with MeOH on silica, afforded $W\{C(OMe)Me\}(CO)_5$ in 32% yield.[154] Other combinations of alkynes (HC_2R) and alcohols (R'OH) gave related products (52); 4-hydroxybutyne gave the cyclic carbene $W\{\overline{CO(CH_2)_2CH_2}\}(CO)_5$. These results point



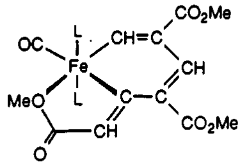
$(OC)_5W{=}C(CH_2R)(OR')$

R = H; R' = Me, $CH_2CH{=}CH_2$

(52)

to a common intermediate of the type $W(CCHR)(CO)_5$. Protonation (HBF_4) of $WH_2(C_2R)(dppe)_2$ (R = Ph, CO_2Me) gave $WF\{CH(CH_2Ph)\}(dppe)_2$ and $WF(CCH_2CO_2Me)(dppe)_2$, respectively.[155]

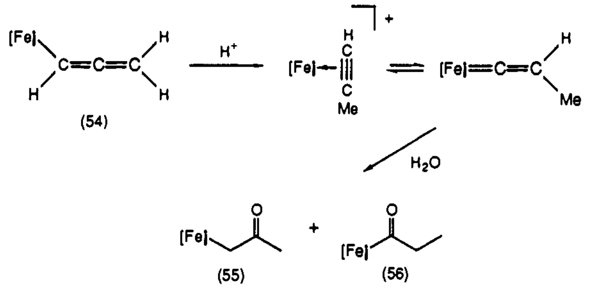
In general, alkynes react with $\{Fe(CO)_2[P(OMe)_3]_2\}_2(\mu\text{-}N_2)$ to give $Fe(\eta^2\text{-}R^1C_2R^2)(CO)_2\{P(OMe)_3\}_2$, which for C_2H_2 and HC_2Ph reversibly convert to the hydrido–acetylide.[156] With HC_2CO_2Me, the initial η^2-alkyne complex reacts with excess alkyne, presumably via the very reactive vinylidene $Fe\{CCH(CO_2Me)\}(CO)_2\{P(OMe)_3\}_2$, to give **53** by successive head-to-tail insertions (or possibly cycloaddition to the vinylidene?), followed by chelation via other ester CO groups.



(53) L = $P(OMe)_3$

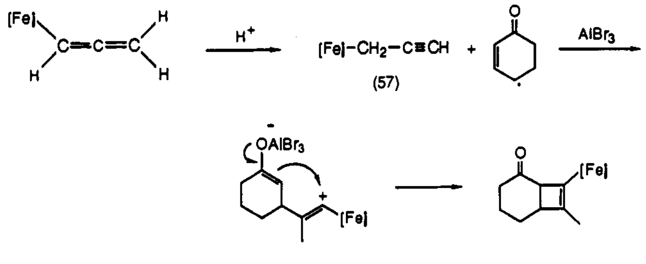
Protonation of $Fe(CH{=}C{=}CH_2)(CO)_2(\eta\text{-}C_5H_5)$ (**54**), followed by reaction with water, gave a 2/1 mixture of the ketone **55** and the propionyl **56** complexes, formation of which can be envisaged via the η^2-alkyne and vinylidene cations, respectively (Scheme 26).[157] Similar stabilized carbonium ions, obtained from the isobutylene cation and terminal alkynes, react with EtOH

SCHEME 26



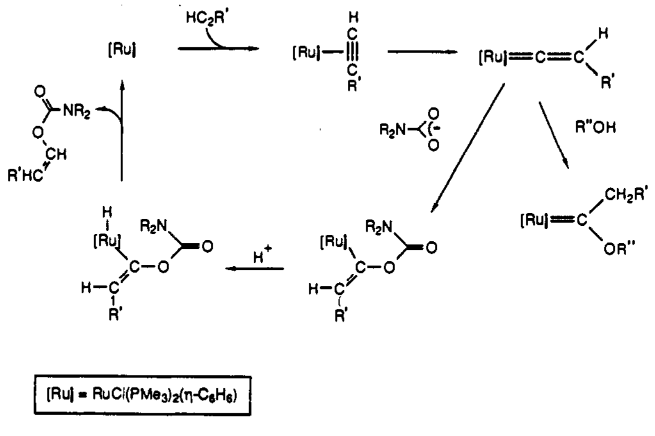
[Fe] = $Fe(CO)_2(\eta\text{-}C_5H_5)$

SCHEME 27



[Fe] = $Fe(CO)_2(\eta\text{-}C_5H_5)$

SCHEME 28



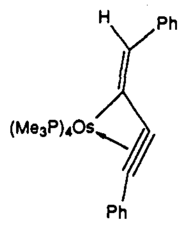
[Ru] = $RuCl(PMe_3)_2(\eta\text{-}C_6H_6)$

to give the corresponding vinyl complexes, while addition of water gave acyl derivatives; protonation afforded the ethoxycarbene derivatives. In EtOD, only one D atom adds to the carbon adjacent to the oxonium center.[158] Methyl propiolate gave the vinyl derived from the η^2-alkyne complex. In contrast, vinylidene intermediates are not implicated in the reactions of the isobutylene cation with phenylethyne to give 2-phenylnaphthalene.[159] The formal [2 + 2]-cycloaddition reactions of **57** with cyclohexenone have been suggested to proceed via a vinylidene cation (Scheme 27).[160]

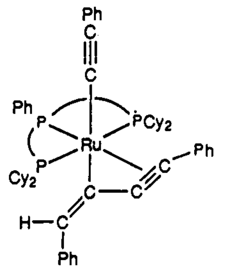
Several ruthenium complexes, including $RuCl_2(PR_3)(\eta\text{-}C_6Me_6)$, are catalyst precursors for the addition of carbamates to 1-alkynes to give vinylcarbamates in 55–60% yields.[161] The reaction is assumed to proceed via a vinylidene intermediate, and although no reaction occurs in nonpolar solvents, this has been trapped with alcohols as the corresponding alkoxycarbene complex (Scheme 28). The yields are decreased in the presence of NEt_3 as a result of deprotonation of the vinylidene. A byproduct is the corresponding ene-yne RCH=CHC≡CR. Reactions of the PMe_3 complex with 1-alkynes in MeOH in the presence of NH_4PF_6 have given $[Ru\{C(OMe)CH_2R\}(PMe_3)(\eta\text{-}C_6Me_6)]^+$ (R = Ph, Bu^t); the PMe_2Ph complex from HC_2Ph was also prepared. With HC_2SiMe_3, the methyl(methoxy)carbene complex was isolated, probably because of ready hydrolysis of the C–Si bond with formation of the parent vinylidene,[162] while with HC_2CH_2OH, the cyclic carbene complex $RuCl\{\overline{CO(CH_2)_2C}H_2\}(PMe_3)(\eta\text{-}C_6Me_6)$ was isolated.[54]

A vinylidene complex has been suggested as an intermediate in the photosensitized reductive cleavage of ethyne to methane on a pentammine–ruthenium(II) complex.[163]

Oxidation of *cis*-$Os(C_2Ph)_2(PMe_3)_4$ with Ag^+ ion gave a 64% yield of complex **58**, containing a C_4Ph_2 ligand formed by coupling of the two phenylacetylide groups.[164] In the suggested mode of formation, electron and proton transfer to one of the acetylide units forms a vinylidene which then undergoes an intramolecular coupling reaction with the second acetylide. Parallels are drawn with the dimerization of ethyne on $[Cu(NH_3)_2]^+$, of phenylethyne by Wilkinson's complex, and the oxidative coupling of copper(I) acetylides. The related complex **59** was obtained from HC_2Ph and RuH_4(cyttp) (cyttp = $PPh\{(CH_2)_3PCy_2\}_2$).[165]



(58)



$Cy_2P\text{-}PPh\text{-}PCy_2 = PhP\{(CH_2)_3PCy_2\}_2$

(59)

A general route to **60** from the maleoyl–cobalt complex **61** and 1-alkynes (Scheme 29) has been described.[166] The intermediate is formed from the dioxocyclobutene and $CoCl(PPh_3)_3$, followed by reaction with dimethylglyoxime and treatment with $AgBF_4$ in acetonitrile. Lower yields were obtained when electron-withdrawing substituents are present, while 1/1 mixtures of double bond stereoisomers were obtained with asymmetric cyclobutene precursors. Complexes similar to **61** with pyridine in place of PPh_3 gave quinones; the retardation of the overall reaction by PPh_3 allows the slower alkyne → vinylidene isomerization to occur and results in the observed products.

The formation of **62** in 83% yield from the reaction between $\{RhCl(cod)_2\}_2$ and HC_2Bu^t in the presence of $AgPF_6$ is envisaged to proceed by the linking of three alkynes via an intermediate vinylidene derivative (Scheme 30).[167] Treatment of (**62**) with acetonitrile afforded 1,3,6-tri-*tert*-butylfulvene quantitatively, together with $[Rh(NCMe)_2(cod)]^+$.

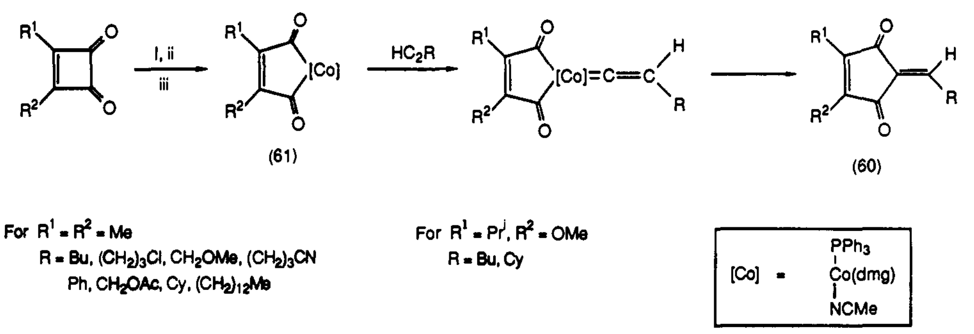
Rhodium(I) complexes are active catalysts for the formation of **63** from phenylethyne and 3-butenoic acid (Scheme 31), which reaction is envisaged to proceed via an intermediate vinylidene–rhodium complex.[168] Subsequent insertion of the unsaturated molecule gives a four-membered metallocycle, which can transform by an internal hydrogen transfer to the phenylhexadienoate precursor, or enlarge by insertion of further alkyne or alkene to give **64**–**66**.

2-Aryl- and 2,2-diaryl-1,1-dibromoethenes gave the corresponding butatrienes in reactions with $Ni(PPh_3)_4$ (from $NiBr_2(PPh_3)_2$ and zinc in benzene); the reaction was accelerated in the presence of $[NEt_4]I$.[169] Similarly, with an active nickel reagent (from NiI_2, Li, and naphthalene) a variety of products were formed also consistent with the generation of diarylvinylidene (Scheme 32); reactions carried out in the presence of diarylalkynes gave hexaarylfulvenes.[170] Isolation of trimers of Ar_2CC suggest the Ar_2CC → ArCCAr rearrangement occurs via aryl group migration. Cyclooligomerization of dialkylbutatrienes to [4]- and [6]-radialenes occurs on Ni(0) complexes derived from $NiBr_2(PR_3)_2$ (R = Bu, Ph) and activated Zn in benzene, thf, or dmf. Likely mechanisms involve hydrogenative debromination or dimerization of Ar_2CC formed by reductive elimination of $NiBr_2(PPh_3)_2$ from a bromovinyl–nickel intermediate. The formation of the intermediate butatrienes from dihaloethenes may involve either dehalogenation of a 2,3-dihalo-1,3-butadiene (as found with the manganese system)[90] or coupling of vinylidene intermediates at the nickel(0) center.[171]

Other examples of the cyclization of nickel methylenecarbenoids generated from 1,1-dihalogenoethanes and activated nickel (from NiI_2, Li powder, and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl as electron carrier in thf under sonification) to [3]-, [4]-, and [5]-radialenes have been described.[172] Precursors included 2-aryl-1,1-dibromopropenes (aryl = Ph, *p*-C_6H_4Cl, *p*-C_6H_4CN), $CMe_2{=}CBr_2$, and fluorene derivatives. The reaction between **67** and **68** in the presence of activated Ni gave the mixed [3]-radialene (**69**) (10%), perhaps by addition of the intermediate vinylidene to the triene (Scheme 33).

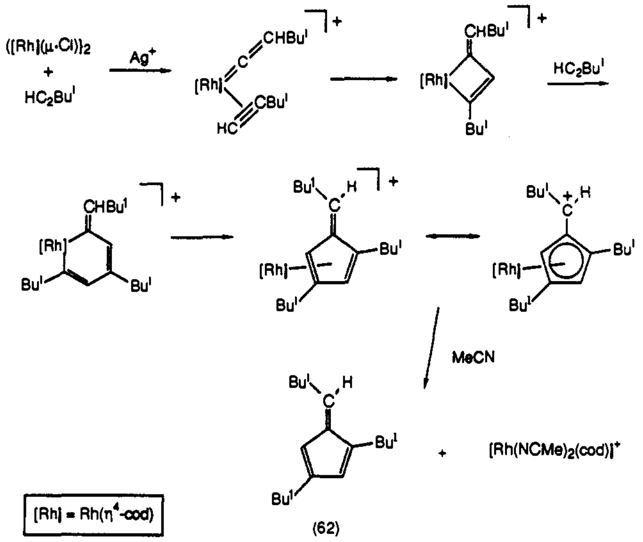
Coupling of 1,1-diphenyl-2,2-dibromoethene via the lithium cuprate(I) complex $LiCu(CBr{=}CPh_2)_2$ gave tetraphenylbutatriene, together with octaphenyl[4]radialene, via oligomerization of the ate complex and reductive elimination of CuBr from **70**.[173] [4]- and [5]-radialenes were obtained by warming the ate complex from $Me_2C{=}CBr_2$, LiBu and Cu(I) complexes;

SCHEME 29[a]

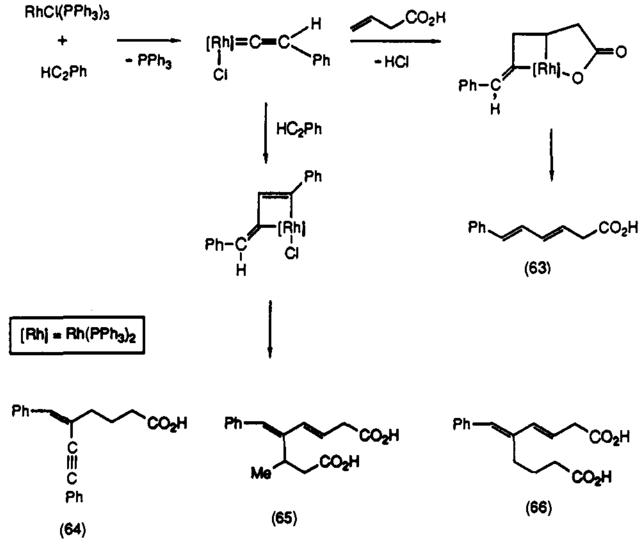


[a] Reagents: (i) $CoCl(PPh_3)_3/C_6H_6$; (ii) dimethylglyoxime/MeCN; (iii) $AgBF_4$/MeCN.

SCHEME 30



SCHEME 31



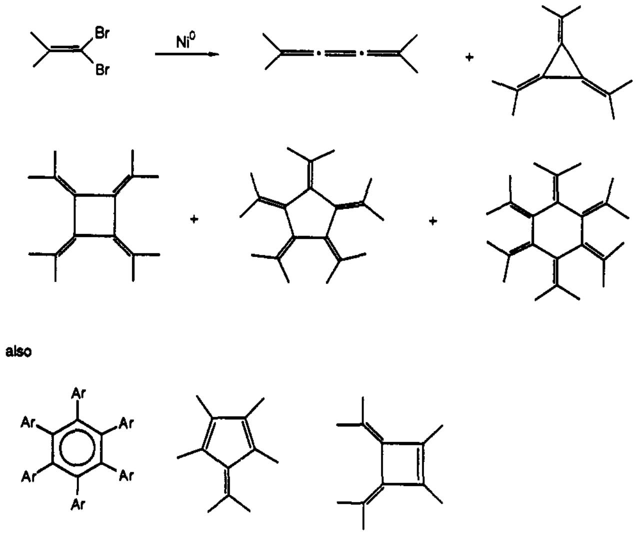
their formation may involve the intermediacy of Me_2CC.[174]

Reactions between (Z)-$BCl_2CEt{=}CEtBCl_2$ and $(Me_3Sn)_2C{=}CMe_2$ afforded the diboron heterocycle 71 by elimination of $SnClMe_3$ (Scheme 34).[175]

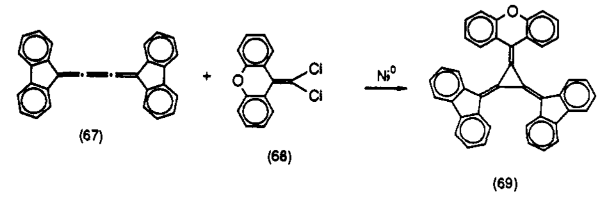
V. Binuclear Vinylidene Complexes

The chemistry of binuclear metal complexes containing vinylidene ligands bridging the two metal centers has largely concentrated on their preparation, with the notable exception of the elegant studies of Casey,

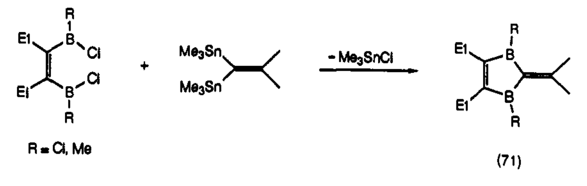
SCHEME 32

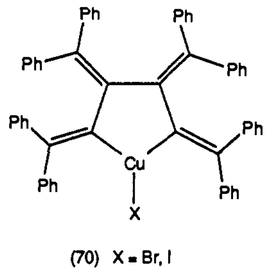


SCHEME 33



SCHEME 34





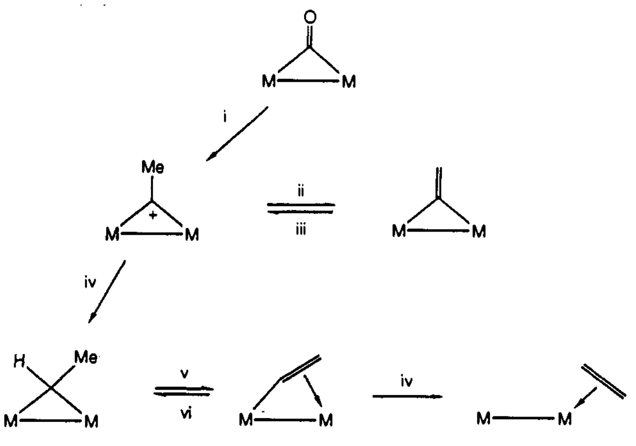
(70) X = Br, I

TABLE 4. Homobinuclear Complexes $\{ML_n\}_2(\mu\text{-X})(\mu\text{-CCRR}')$

ML_n	X	R	R′	color	$\delta(C_\alpha)$	$\delta(C_\beta)$	ref
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	H	purple			81
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$CH(OMe)_2$	red			43
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$CH(OEt)_2$	red			43
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$\overline{CHO(CH_2)_3O}$	red			43
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	CHO	dark red			43
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	CO_2Me	red-violet			342
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	Ph		284.2	146.4	226
$Mn(CO)_2(\eta\text{-}C_5H_4Me)$		H	H	red	289.2		181
$Fe(CO)_3$	PPh_2	Ph	$NHMe_2$	yellow			189
$Fe(CO)_3$	PPh_2	Ph	$NHEt_2$	yellow			189
$Fe(CO)_3$	PPh_2	$C_6H_4OMe\text{-}p$	$NHEt_2$	yellow			189
$Fe(CO)_3$	PPh_2	H	$PHCy_2$	yellow			191
$Fe(CO)_4$		F	F	yellow			186
$Fe\{(PMe_2CH_2)_3SiMe\}$	$(H)_2$	H	H	green	290.3	118.5	188
$Fe(\eta\text{-}C_5H_5)$	CO, dppe	H	H	green-brown	297.1	123.6	257
$Fe(\eta\text{-}C_5H_5)$	CO, dppm	H	H	green			257
$Fe(\eta\text{-}C_5H_5)$	CO, dppm	H	$CH{=}CH(CN)$ (*Z* + *E*)	green	329.8	150.6 (*E*), 152.0 (*Z*)	255b
$Fe(\eta\text{-}C_5H_5)$	CO, dppm	H	$C(CN){=}C(CN)_2$	violet	379.0	140.1	257
$Fe(\eta\text{-}C_5H_5)$	CO, dppe	H	$C(CN){=}C(CN)_2$	violet	378.5	141.0	257
$Fe(CO)(\eta\text{-}C_5H_5)$	CO	H	$CH{=}CH(CN)$ (*Z*)	red-purple	303.3	150.4	255b
$Fe(CO)(\eta\text{-}C_5H_5)$	CO	H	$C(CN){=}CH(CN)$ (*Z*)	orange	307.7	136.4	255b
$Fe(CO)(\eta\text{-}C_5H_5)$	CO	Me	$CH{=}CH(CN)$				255b
$Fe(CO)(\eta\text{-}C_5H_5)$	CO	Pr^i	$CH{=}CH(CN)$ (*E*)	red-purple	300.2	153.1	255b
$Ru(CO)(\eta\text{-}C_5H_5)$	CO	H	H	yellow	250.1, 244.1[a]	123.0	259
$Co(CO)(\eta\text{-}C_5H_5)$		H	H	deep red	247.8	125.7	203
$Co(CO)(\eta\text{-}C_5Me_5)$		Me	Me	black-green			206
$Rh(\eta\text{-}C_5H_5)$	$C_4HBu^t(CF_3)_2CO$	H	Bu^t	yellow			212
$Rh(CO)(\eta\text{-}C_5Me_5)$		Me	Me	dark red	232.1	127.6	205, 206
$Rh(CO)(\eta\text{-}C_5Me_5)$		$-(CH_2)_5-$		red oil			205, 206
$Rh(CO)(\eta^5\text{-}C_9H_7)$		H	H	red			204
Rh(CO)	$(dppm)_2$	H	H	blue			209
Rh(CO)	$(dppm)_2$	H	Bu^t	blue			209
Rh(CO)	$(dppm)_2$	H	Ph	purple			207–209
Rh(CO)	$(dppm)_2$	H	$PMePh_2$	purple			209
Rh(CO)	$(dppm)_2$	H	PPh_3	purple			209
NiCl	$(dppm)_2$	H	H	purple-red			213
NiBr	$(dppm)_2$	H	H	red			213
NiI	$(dppm)_2$	H	H	deep purple			213
Ni(NCS)	$(dppm)_2$	H	H	orange			213
PdCl	$(dppm)_2$	H	H	yellow			215
PdCl	$(dppm)_2$	Cl	Cl	yellow-white			214–216
PdCl	$(mdppm)_2$[b]	H	H	deep yellow			215
PdCl	$(dppm)_2$	Cl	Cl	orange			216
PdBr	$(dppm)_2$	H	H	yellow			214, 215
PdI	$(dppm)_2$	Cl	Cl	orange			216
PdI	$(dppm)_2$	H	H	deep yellow			214, 215
Pd(NCS)	$(dppm)_2$	H	H	cream			215
$Pd(O_2CMe)$	$(dppm)_2$	H	H	orange			215
$Pd(C_2Ph)$	$(dppm)_2$	H	H	orange			214, 215
$Pd\{C_2(tol)\}$	$(dppm)_2$	H	H	orange			215
$Pd\{C_2CMe_2(OH)\}$	$(dppm)_2$	H	H	orange			215
$[Pd\{CN(tol)\}]^{2+}BPh_4^-$	$(dppm)_2$	H	H	pale yellow			215

[a] $\delta(C_\alpha, \mu\text{-CO})$. [b] mdppm = $CHMe(PPh_2)_2$.

SCHEME 35[a]



[a] Reagents: (i) LiMe, 2 H^+, − H_2O; (ii) LiMe, NEt_3 or H_2O; (iii) H^+; (iv) H^-; (v) $[CPh_3]^+$, − H^-.

Knox, and others on the iron and ruthenium systems described in detail below. The vinylidene complexes occupy a central position in respect to related complexes containing CO, CMe, CHMe, C_2H_4, and vinyl ligands (Scheme 35). The chemistry will be discussed according to the element involved; there are also several reports of complexes containing two different metals. These complexes feature in a review of hydrocarbyl-bridged binuclear complexes.[3]

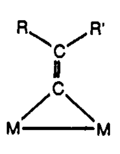
Synthetic methods are generally based on addition of an electrophile to a μ-acetylide or by generation of a vinylidene fragment from α,α-dihalo-olefins in the presence of a potential or actual binuclear systems. Other methods include addition of a metal hydride across the C≡C bond of a metal acetylide and addition of appropriate metal–ligand fragments to mononuclear vinylidene complexes. Tables 4–6 collect reported binuclear μ-vinylidene complexes with some spectroscopic

TABLE 5. Heterobinuclear Complexes $\{ML_m\}\{M'L'_n\}(\mu\text{-}X)(\mu\text{-}CCRR')$

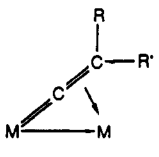
ML_m	X	$M'L'_n$	R	R′	color	$\delta(C_\alpha)$	$\delta(C_\beta)$	ref
$Cr(CO)_2(\eta\text{-}C_6H_6)$	CO	$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	H	H	deep red	285.0	120.3	229, 230
$W(CO)_5$		$Pt(dppm)$	H	H	yellow	241.3	125.9	220
$W(CO)_4$	dppm	$Pt(CO)$	H	H	yellow	254.4	123.9	220
$W(CO)_3(\eta\text{-}C_5H_5)$		$[Pt(PEt_3)_2]^+PF_6^-$	H	Ph	brown			218
$Mn(CO)(\eta\text{-}C_5H_5)$	CO	$Rh(CO)(acac)$	H	Ph		290.6	132.4	225
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$Fe(CO)_4$ (*E*)	H	CO_2Me	red			223
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$Fe(CO)_4$ (*Z*)	H	CO_2Me	dark red			223
$Mn(CO)(\eta\text{-}C_5H_5)$	CO	$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	H	H	deep red	278.9	121.5	229, 230
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$Pt(PPh_3)_2$	H	Ph	yellow	264.3	141.3	226
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$Pt\{P(OEt)_3\}_2$	H	Ph	orange	259.8	141.1	226
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$Pt\{P(OPr^i)_3\}_2$	H	Ph	yellow	259.5	141.4	228
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$Pt\{P(OPh)_3\}_2$	H	Ph	orange			226
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$Pt(CO)(PPh_3)$	H	Ph	red-orange	260.5	146.3	226
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$Pt(CO)\{P(OPr^i)_3\}$	H	Ph	yellow			228
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$Pt(PPh_3)\{P(OPr^i)_3\}$	H	Ph	orange	260.0	140.3	228
$Fe(CO)_3$	CO	$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	H	H	deep red	250.6	124.7	229, 230
$Fe(CO)_3$	CO	$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	H	Me	deep red	248.4	130.5	230
$Fe(CO)_3$	CO	$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	H	Ph	deep red	238.8	140.0	230
$Fe(CO)_2(PMe_3)$	CO	$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	H	Me	deep blue			230
$Fe(CO)(\eta\text{-}C_5H_5)$	CO	$Fe(CO)(\eta\text{-}C_5Me_5)$	H	Bu	red	274.5, 272.1[a]		239
$Fe(CO)(\eta\text{-}C_5H_5)$	CO	$[Pt(PEt_3)_2]^+PF_6^-$	H	Ph	orange-red			218
$Os(PPr^i_3)(\eta\text{-}C_6H_6)$		CuCl	H	Ph	yellow			86
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		CuCl	H	H	orange-red	274.1		210
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		CuCl[b]	H	H	red			210
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		CuCl	H	Me	red			210
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		CuCl	H	Ph	red			210
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$		$Cu(\eta\text{-}C_5H_5)$	H	H	dark red			210
NiCl	$(dppm)_2$	PdCl	H	H	red			213
NiCl	$(dppm)_2$	PdCl	Cl	Cl	orange			213
NiCl	$(dppm)_2$	PtCl	Cl	Cl	orange			213
$Ni(C_2Ph)(PEt_3)_2$		$[Pt(PEt_3)_2]^+PF_6^-$	H	Ph	brown			218
PdCl	$(dppm)_2$	PdI	Cl	Cl	orange			216
$Pd(C_2Ph)(PEt_3)_2$		$[Pt(PEt_3)_2]^+PF_6^-$	H	Ph	brown			218
$PtCl(PEt_3)$		$PtCl(PEt_3)_2$	H	Ph	orange			219
$PtCl(PEt_3)$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	orange-red			219
$PtBr(PEt_3)$		$PtBr(PEt_3)_2$	H	Ph	pale orange			219
$PtBr(PEt_3)$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	orange-red			219
$PtI(PEt_3)$		$PtI(PEt_3)_2$	H	Ph	orange			219
$PtI(PEt_3)$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	red			219
$Pt(NCS)(PEt_3)$		$Pt(NCS)(PEt_3)_2$	H	Ph	pale orange			219
$Pt(NCS)(PEt_3)$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	red-orange			219
$Pt(SPr^i)(PEt_3)$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	bright yellow			219
$Pt(SPh)(PEt_3)$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	dark purple			219
$Pt(SC_6Cl_5)(PEt_3)$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	red-orange			219
$[Pt(PEt_3)_2]^+PF_6^-$		$Pt(C_2H)(PEt_3)_2$	H	H	orange			218
$[Pt(PEt_3)_2]^+PF_6^-$		$Pt(C_2H)(PEt_3)_2$	H	Me	red			218
$[Pt(PEt_3)_2]^+PF_6^-$		$Pt(C_2Me)(PEt_3)_2$	H	Me	orange			218
$[Pt(PEt_3)_2]^+PF_6^-$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	red			217
$[Pt(PEt_3)_2]^+PF_6^-$		$Au(PEt_3)$	H	Ph	deep brown			218
$[Pt(PEt_3)_2]^+PF_6^-$		$Au(PPh_3)$	H	Ph	amber			218

[a] $\delta(C_\alpha, \mu\text{-}CO)$. [b] Polymeric form.

details. The majority of these complexes contain the vinylidene ligand bridging the two metals in a more or less symmetrical fashion, in a μ-2σ(2e) arrangement (C); a few complexes contain the side-on, μ-σ,η^2(4e) system (D). Tables 7 and 8 summarize available structural data.



(C)



(D)

A. Homometallic Complexes

1. Molybdenum and Tungsten

The first example of a side-on bonded vinylidene ligand (or μ-σ,η^2(4e)-CCH_2), analogous to side-on CO, was prepared by UV irradiation of a mixture of $\{Mo(CO)_2(\eta\text{-}C_5Me_5)\}_2$ and ethyne, when air-stable blue-black **72** (Scheme 36) was formed in 40% yield.[176] Similar complexes were later obtained from the ambident anion **73** formed by addition of lithium acetylides to $\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2$ or to its η^5-indenyl analogue, or by deprotonation of μ-alkyne–Mo_2 complexes with LiBu.[177] Reaction of the anions with MeOH resulted in protonation to the dark purple μ-σ,η^2-vinylidenes **74**, obtained in 80% yield. The vinylidenes rearrange to the μ-alkyne complex within 12 h at room temperature in solution, or in 2 weeks as a solid. Methylation of the anion gave the CCMePh complex **75** (dark blue, 85%), although if the reaction was carried out in tetrahydrofuran,

TABLE 6. Complexes Containing μ-σ,η^2-CCRR′ Ligands

ML_m	$M'L'_n$	R	R′	color	$\delta(C_\alpha)$	$\delta(C_\beta)$	ref
$Mo(CO)_2(\eta\text{-}C_5H_5)$	$Mo(CO)_2(\eta\text{-}C_5H_5)$	H	H		329.5	40.0	179
$Mo(CO)_2(\eta\text{-}C_5H_5)$	$Mo(CO)_2(\eta\text{-}C_5H_5)$	H	Ph	dark purple	333.2	66.1	177
$Mo(CO)_2(\eta\text{-}C_5H_5)$	$Mo(CO)_2(\eta\text{-}C_5H_5)$	Me	Me	blue-black	342.9	79.8	178
$Mo(CO)_2(\eta\text{-}C_5H_5)$	$Mo(CO)_2(\eta\text{-}C_5H_5)$	Me	Ph	dark blue	340.7	78.9	177
$Mo(CO)_2(\eta\text{-}C_5H_5)$	$Mo(CO)_2(\eta\text{-}C_5H_5)$	$(CH_2)_4OMe$	Ph	blue	338.7	83.8	177
$Mo(CO)_2(\eta\text{-}C_5Me_5)$	$Mo(CO)_2(\eta\text{-}C_5Me_5)$	H	H	blue-black	337.3	45.3	176, 177
$W(CO)_2(\eta\text{-}C_5H_5)$	$W(CO)_2(\eta\text{-}C_5H_5)$	Me	Me	deep blue	315.2		178
$Mn(CO)_2(\mu\text{-dppm})$	$Mn(CO)_2$	H	Bu^t			84.8	183
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	$RhCl(PPr^i_3)$	H	H	orange-red			110, 210
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	$RhCl(PPr^i_3)$	H	Ph				110
$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	H	H	red	310.4		110, 210

TABLE 7. Some Structural Features of Binuclear Complexes $\{ML_n\}_2(\mu\text{-X})(\mu\text{-CCRR}')$

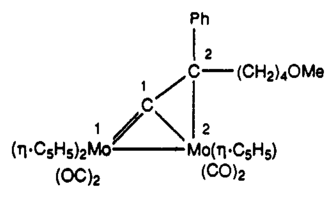
ML_n	X	R	R′	M–M′	M–C	M′–C	C–C	ref
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	CHO	2.753 (1)	1.945 (4)	1.949 (4)	1.347 (5)	43
$Mn(CO)_2(\eta\text{-}C_5H_5)$		H	$\overline{CHO(CH_2)_3O}$	2.748 (1)	1.983 (3)	1.954 (4)	1.329 (5)	43
$Fe(CO)_3$	PPh_2	H	$PHCy_2$	2.550 (2)	1.969 (7)	1.956 (7)	1.322 (9)	191
$Fe(CO)_4$		F	F	2.674 (1)	1.954 (4)	1.956 (4)	1.288 (6)	186
$Fe(CO)(\eta\text{-}C_5H_5)$	CO	H	$C(CN){=}C(CN)_2$	2.503 (1)	1.874 (3)	1.888 (3)	1.358 (5)	256
$Fe(CO)(\eta\text{-}C_5H_5)$	CO	CH_2Ph	Ph	2.510 (1)	1.944 (2)	1.936 (2)	1.326 (3)	372
$Fe\{(PMe_2CH_2)_3SiMe\}$	$(H)_2$	H	H	2.428 (1)	1.920 (8)	1.928 (8)	1.35 (1)	188
$Ru(CO)(\eta\text{-}C_5H_5)$	CO	H	H	2.696 (1)	2.033 (7)	2.026 (7)	1.326 (11)	259
$Co(CO)(\eta\text{-}C_5H_5)$		H	H	2.500 (1)	1.886 (1)	1.882 (1)	1.312 (2)	203
Rh(CO)	$(dppm)_2$	H	Ph	3.011 (1)	2.063 (7)	2.051 (7)	1.329 (9)	207, 208
$Rh(\eta\text{-}C_5H_5)$	$C_4HBu^t(CF_3)_2CO$	H	Bu^t	2.625 (2)	2.00 (2)	1.98 (2)	1.32 (3)	212
$Rh(CO)(\eta\text{-}C_5Me_5)$		Me	Me	2.684 (0)	1.978 (1)	2.043 (1)	1.318 (2)	206
$Rh(CO)(\eta^5\text{-}C_6H_7)$		H	H	2.691 (1)	1.982 (3)	1.988 (3)	1.304 (5)	204
Ni(SCN)	$(dppm)_2$	H	H	2.840 (4)	1.871 (7)	1.885 (7)	1.134 (9)	213
PdCl	$(dppm)_2$	Cl	Cl	3.248 (2)	1.96 (1)	2.01 (2)	1.30 (2)	216

TABLE 8. Some Structural Features of Heteronuclear Complexes $\{ML_m\}\{M'L'_n\}(\mu\text{-X})(\mu\text{-CCRR}')$

ML_m	X	$M'L'_n$	R	R′	M–M′	M–C	M′–C	C–C	ref
$Mo(CO)_2$		$[Mn(CO)(\eta\text{-}C_5H_5)]_2$	H	CO_2Me^a	2.964 (1)	1.909 (2)	2.110 (2)	1.346 (3)	222
$W(CO)_4$		$Mn(CO)_2(\eta\text{-}C_5H_5)$	H	CO_2Me^b	2.994 (1)	1.903 (5)	2.130 (5)	1.337 (7)	222
$W(CO)_5$		Pt(dppm)	H	H	2.774 (1)	2.198 (8)	2.012 (9)	1.363 (13)	220
$Mn(CO)(\eta\text{-}C_5H_5)$	CO	$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	H	H	2.667 (1)	1.901 (3)	2.056 (3)	1.294 (6)	229, 230
$Mn(CO)_2(\eta\text{-}C_5H_5)$		$Fe(CO)_4$	H	CO_2Me	2.703 (4)	1.95 (1)	1.94 (1)	1.30 (2)	223
$Fe(CO)_3$	CO	$Rh(PPr^i_3)(\eta\text{-}C_5H_5)$	H	H	2.604 (1)	1.936 (3)	2.011 (3)	1.320 (5)	229, 230
$NiCl^c$	$(dppm)_2$	$PdCl^c$	Cl	Cl	3.091 (4)	1.937 (8)	1.937 (8)	1.290 (14)	213
$PtCl(PEt_3)$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	2.711 (1)	2.068 (14)	1.909 (12)	1.35 (2)	219
$PtBr(PEt_3)$		$PtBr(PEt_3)_2$	H	Ph	2.682 (1), 2.687 (1)	2.05 (2), 2.09 (2)	1.94 (2), 1.85 (1)	1.38 (2), 1.34 (2)	219
$PtI(PEt_3)$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	2.721 (1)	2.099 (9)	1.900 (9)	1.347 (13)	219
$Pt(PEt_3)_2$		$Pt(C_2Ph)(PEt_3)_2$	H	Ph	2.750 (2)	2.10 (2)	1.93 (2)	1.33 (3)	217

[a] Bridges Mn–Mo bond. [b] Bridges Mn–W bond. [c] Disordered Ni/Pd.

ring-opening of the solvent afforded **76**, characterized by an X-ray structure. The formation of these complexes was rationalized on the basis of a rotation of the symmetrically bound vinylidene ligand to relieve steric strain, with formation of the Mo=C bond to relieve the electronic unsaturation.[177] On heating in toluene at 50 °C, **74** underwent a 1,3-H shift to give a μ-σ,η^3-$CHCPhCH_2$ complex.



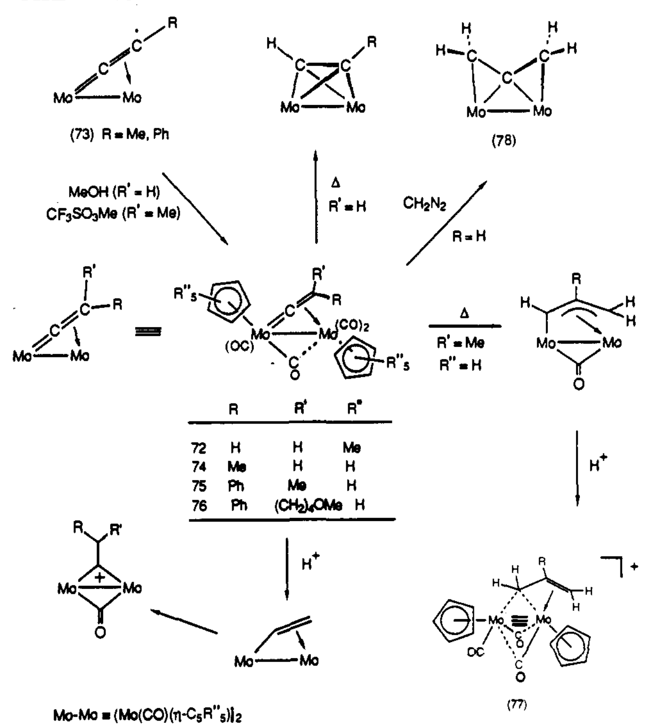
(76)

$Mo^1\text{·}Mo^2$	3.120(1)
$Mo^1\text{-}C^1$	1.909(5)
$Mo^2\text{-}C^1,C^2$	2.179(5), 2.443(6)
$C^1\text{-}C^2$	1.380(7)
$Mo^1C^1C^2$	168.5(4)

The dynamic process occurring in these complexes was revealed by the low-temperature NMR study of the μ-σ,η^2-$CCMe_2$ complexes, obtained from $\{M(CO)_2(\eta\text{-}C_5H_5)\}_2$ (M = Mo, W) and LiC_2Me, followed by methylation with CF_3SO_3Me. This procedure gave a separable mixture of the red μ-alkyne and deep blue μ-vinylidene complexes. Barriers to rearrangement were measured from both the Me and Cp resonances as $\Delta G^{\ddagger}_{Tc}$ 61 (2) (Me) and 59 (2) (Cp) kJ mol^{-1} for Mo; the values for the W complex were experimentally the same.[178]

Protonation of **72** with CF_3CO_2D afforded $\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CD{=}CH_2)\{OCO(O)CF_3\}$, whereas the μ-CCD_2 complex gave the corresponding μ-$CH{=}CD_2$ derivative with CF_3CO_2H, showing that protonation of C_α occurred, the $CF_3CO_2^-$ anion adding to the resulting cationic vinyl.[179] A similar reaction occurred with **72** (R = Me),[176] but with $HBF_4\text{·}OEt_2$, the cationic μ-allyl **77** was obtained; the same complex was formed by protonation ($HBF_4\text{·}OEt_2$ or CF_3SO_3H) of $\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\sigma,\eta^3\text{-}CHCMeCH)$ (which was formed[177] by heating **72** (R = Me) in hexane for 4 h).[179] Protonation

SCHEME 36



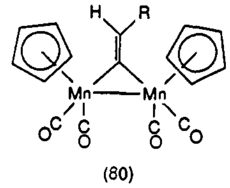
at C_α is followed by H transfer from one of the Me groups via the metal and an agostic Mo(μ-H)C interaction. Transfer to carbon forms the asymmetric allyl attached via a 3c–2e bridge across the Mo≡Mo bond and η^2-coordination to one Mo atom.

In these complexes the unsaturation rests in the Mo=C bond, diazomethane reacting to form the same μ-allene complex **78** as that obtained from the unsaturated Mo_2 complex and allene. Reaction with CF_3CO_2H (but not with $HBF_4 \cdot OEt_2$) affords initially the μ-σ,η^2-vinyl, and with excess acid, the μ-CHMe cation.[176]

Related 1,2-H shifts may occur in the reactions of μ-alkyne–Mo_2 complexes with $PClPh_2$ to give the phospha-allene complexes **79** (Scheme 37).[180]

2. Manganese

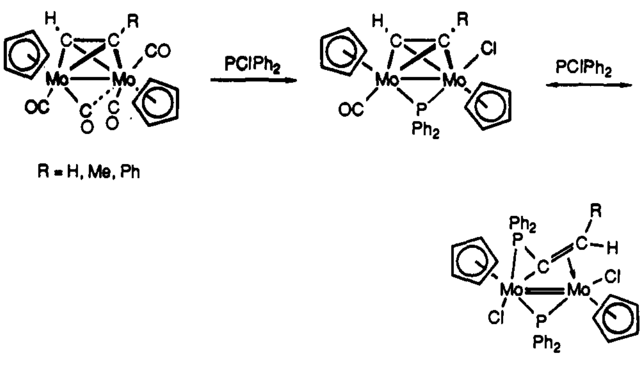
Treatment of Mn(η-C_2H_2)$(CO)_2$(η-C_5H_5) with NEt_3 afforded $Mn_2(\mu\text{-}CCH_2)(CO)_4(\eta\text{-}C_5H_5)_2$ (**80**, R = H).[181] The phenyl complex **80** (R = Ph) does not react with PPh_3 between 20–80 °C, but on UV irradiation afforded Mn(CCHPh)$(CO)_2$(η-C_5H_5) and $Mn(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$.[126] Protonation (HX) of **80** (R = Ph, CO_2Me)



(80)

gave unstable μ-carbyne complexes $Mn_2(\mu\text{-}CCH_2R)(CO)_4(\eta\text{-}C_5H_5)_2$ which were not isolated. Free rotation of the CH_2R groups occurred as was shown by the equivalence of the C_5H_5 groups.[182] Related complexes were obtained from propiolaldehyde acetals and excess $Mn(OEt_2)(CO)_2(\eta\text{-}C_5H_5)$.[43] Chromatography ($SiO_2$) resulted in the formation of $Mn_2\{\mu\text{-}CCH(CHO)\}(CO)_4(\eta\text{-}C_5H_5)_2$, containing the complexed aldehyde. The two $Mn(CO)_2(\eta\text{-}C_5H_5)$ moieties take up a *transoid* configuration.

SCHEME 37



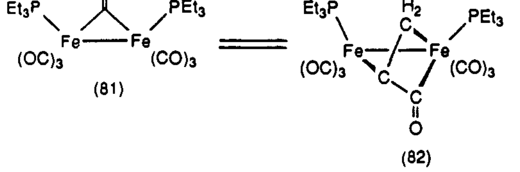
The complex $Mn_2(\mu\text{-}H)_2(\mu\text{-}dppm)(CO)_6$ reacted with HC_2Bu^t to give a small amount of $Mn_2(\mu\text{-}CCHBu^t)(\mu\text{-}dppm)(CO)_6$, the hydrido–acetylide being the major product.[183]

3. Iron, Ruthenium, and Osmium

Comparison of the X-ray structures of the two complexes $Fe_2(\mu\text{-}CX)(CO)_8$ (CX = CH_2, CCH_2) shows that in the former, the Fe–Fe bond [2.507 (1) Å] is strengthened by overlap of the e″ MO (the HOMO) with the μ-ligand orbitals; there are also two μ-CO ligands in this molecule. In the μ-vinylidene, there are no bridging CO groups, and no resulting MO to stabilize the antibonding e″ MO of the diiron system. Consequently, in this complex the Fe–Fe bond [2.635 (3) Å] is weaker.[184] Earlier calculations for coordinatively unsaturated $Fe_2(\mu\text{-}CCH_2)(CO)_6$ indicated that the anti-van't Hoff geometry, in which the CH_2 plane is perpendicular to the Fe_2C plane, is stabilized by the diiron unit.[165]

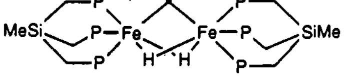
The first difluorovinylidene complex was prepared from $CF_2(COCl)_2$ and $[Fe_3(CO)_{11}]^{2-}$: yellow $Fe_2(\mu\text{-}CCF_2)(CO)_8$ was obtained in 25% yield.[186] The short C=C bond length (1.288 Å) and FCF angle (106.2°) show the pronounced effect of the fluorine atoms.

The dinitrogen complex $\{Fe(CO)_3(PEt_3)\}_2(\mu\text{-}N_2)$ reacted with C_2H_2 to give the μ-CCH_2 derivative **81**, detected by NMR methods, which is in equilibrium with the μ-CH_2CCO complex **82**, isolated in 5% yield at low temperatures.[187]



(81) (82)

Green complex **83** was obtained in 50–60% yields either from the reaction between Fe(η-C_6H_6)(tmps) [tmps = $MeSi(CH_2PMe_2)_3$] and ethene (50 °C/7 atm), or by reduction of $[\{Fe(tmps)\}_2(\mu\text{-}Cl)_3][BPh_4]$ with sodium amalgam under ethene (1.5 atm/2 days).[188] The

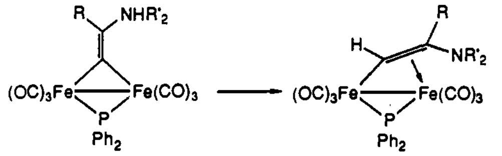


(83)

X-ray structure shows the symmetrical μ-vinylidene ligand and two μ-H atoms bridging the two iron atoms;

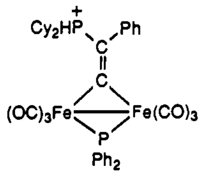
formal electron counting does not require there to be an Fe–Fe bond, but the short separation between the Fe atoms [2.428 (1) Å] suggests that there is significant interaction between them. The vinylidene ligand has a greater trans influence than H. This dissociation of ethene into 2H + CCH_2 models the proposed first step in the chemisorption of ethene on the Pt(111) surface (see section IX).

Addition of amines to $Fe_2(\mu\text{-}PPh_2)(\mu\text{-}C_2R)(CO)_6$ gave three types of adduct, including the yellow zwitterionic vinylidene complexes, $Fe_2(\mu\text{-}PPh_2)\{\mu\text{-}CCR(NHR'_2)\}(CO)_6$ (84; R = Ph, R′ = Me, Et; R = C_6H_4OMe-p, R′ = Et); on warming, isomerization to red $Fe_2(\mu\text{-}PPh_2)\{\mu\text{-}CHCR(NR'_2)\}(CO)_6$ (85) occurred.[189] This conversion occurred more readily with bulky amines ($NHPr^i_2$, $NHCy_2$). NMR studies revealed that competitive reversible addition of NHR'_2 to C_β gave 84, while irreversible addition of the N–H bond across the C≡C triple bond gave 85, eventually as the sole product. This reaction was extended to survey the Fe, Ru, and Os triad (for R = Ph, R′ = Et).[190]



(84) (85)

The reaction between $PHCy_2$ and $Fe_2(\mu\text{-}PPh_2)(\mu\text{-}C_2Ph)(CO)_6$ gave bright yellow 86 (90%), in which similar addition of the secondary phosphine to C_β has produced the μ-CCPh($PHCy_2$) ligand.[191] A ^{31}P NMR study of this and related complexes has been reported.[192] These reactions, which give complexes containing trigonal carbon bridges, contrast with the addition of $P(OEt)_3$, which gave $Fe_2(\mu\text{-}PPh_2)\{\mu\text{-}C[P(OEt)_3]CPh\}(CO)_6$, with a two-carbon bridge,[193] and also with the addition of PMe_2Ph to $Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_{10}$, which afforded $Os_3(\mu\text{-}H)\{\mu\text{-}CHCH_2(PMe_2Ph)\}(CO)_{10}$, containing a tetrahedral carbon bridge.[194,195]

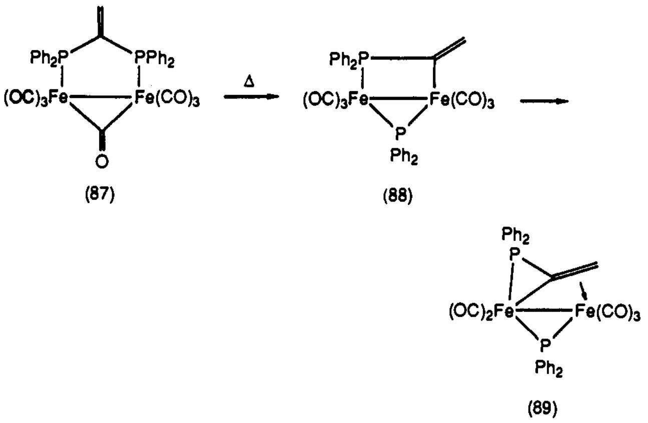


(86)

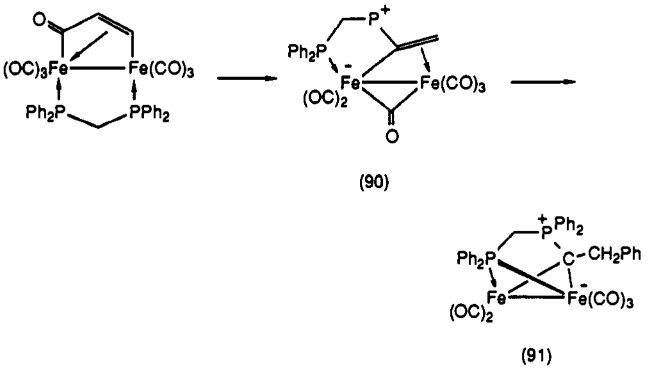
Cleavage of P–C(sp^2) bonds in $CH_2{=}C(PPh_2)_2$ (dppee) occurred readily on heating $Fe_2(\mu\text{-}dppee)(\mu\text{-}CO)(CO)_6$ (87; Scheme 38) in refluxing heptane, with concomitant loss of CO; the phospha-allene complex 88 so formed rearranged to the phosphavinyl 89 on UV irradiation.[196] A vinylidene-related ligand is also found in the isomerization of $Fe_2(\mu\text{-}dppm)(\mu\text{-}CHCHCO)(CO)_5$ [from $Fe_2(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_6$ and C_2H_2] at 90 °C in solution; complex 90 (Scheme 39) was formed, in a reaction where CCH_2 formally inserts into the P–Fe bond.[197] This may occur by intramolecular attack of the P atom on a carbon of the CHCHCO unit, followed by H migration and breaking of the C–CO bond. A further slow reaction resulted in quantitative isomerization to 91.

The thioketene complex 92 reacted with the free thioketene to give the dark brown 93 in 72% isolated yield (Scheme 40).[198] The X-ray structure shows that cleavage of the C=S bond has occurred to give a bridging dithiolato ligand, while the sulfur-free vinylidene resulting has displaced PPh_3 from one of the iron atoms [Fe–C 1.79 (1), C–C 1.30 (2) Å, Fe–C–C 177 (1)°].

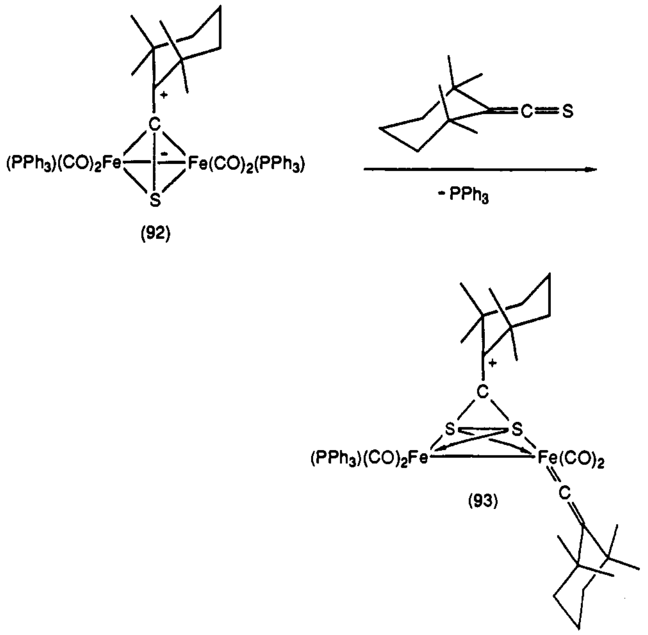
SCHEME 38



SCHEME 39



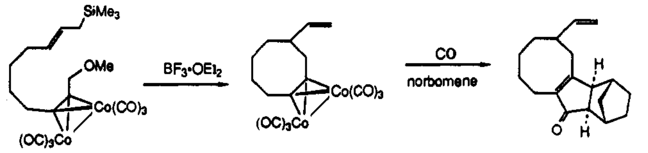
SCHEME 40



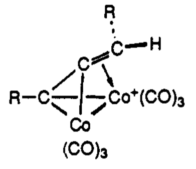
4. Cobalt and Rhodium

It has been known for many years that $Co_2(CO)_6$-complexed propargylic alcohols react with strong acids (HPF_6, HBF_4) to form stabilized carbocations, which are isolobal with the $Co_3(CO)_9$-stabilized species of Seyferth (section VI.B.4). Reactions of the dinuclear

SCHEME 41



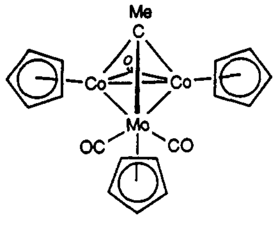
cations with nucleophiles afford alkylated products (the Nicholas reaction).[199] Recent modifications of this reaction have been designed to extend its usefulness to species containing acid-sensitive functional groups. One such approach has been to add a Lewis acid ($BF_3{\cdot}Et_2O$) to a 1/1 mixture of the dicobalt complex and the nucleophile.[200] High levels of diastereoselection for syn-alkylated products formed in intermolecular reactions were achieved. The results are rationalized in terms of the transition-state model **94**, where the intermediate is a *cis*-allyl cation equivalent. The organic product can be isolated by treatment of the reaction mixture with Me_3NO or $Fe(NO_3)_3$; where protection with $SiMe_3$ groups was employed, concomitant removal of the protecting group can be achieved by using $[NBu_4]F$. In some reactions, complexed cycloalkynes are formed (Scheme 41). These cannot be displaced by Me_3NO, the complexes following different reaction pathways still to be elucidated. The products can be further elaborated by the Pauson-Khand reaction to give a method for the intramolecular construction of medium-sized rings.[201]



(94)

The formation of $Co_3(\mu\text{-}CR)(CO)_9$ (R = $CMe{=}CH_2$, $CHMe_2$) by reaction of $Co_2(CO)_8$ with Me_2CCO was explained by the interaction of an intermediate $Co_2(\mu\text{-}CCMe_2)(\mu\text{-}CO)(CO)_6$ with $Co_2(CO)_8$ or $CoH(CO)_4$, respectively.[202]

The radical anion $Na[\{Co(CO)(\eta\text{-}C_5H_5)\}_2]$ reacted with $Br_2C{=}CH_2$ to give the deep red $Co_2(\mu\text{-}CCH_2)(CO)_2(\eta\text{-}C_5H_5)_2$ in 48% yield.[203] Protonation ($HBF_4{\cdot}Et_2O$) gave the alkylidyne complex, in contrast with the analogous rhodium complex, which is protonated at the Rh–Rh bond.[204] Hydrogenation (3–4 atm, C_6D_6, 60 °C) gave the μ-CHMe complex, obtained in only 43% yield because of subsequent slow conversion to ethane. Addition of $MoH(CO)_2(L)(\eta\text{-}C_5H_5)$ (L = CO, PPh_3, PMe_3) (but not the Cr or W analogues) or $MnH(CO)_5$ to the dicobalt complex afforded the heteronuclear clusters **95** and **96**, respectively. A kinetic study of the molybdenum reaction showed that H-atom transfer from Mo to C_β gives a caged radical pair, stabilized by the dimetal center. This collapses to an intermediate which then loses 2 CO to form the cluster. It is concluded that the reaction can only proceed for hydrides with a critical M–H bond strength, since those with strong M–H bonds will not react because H transfer to give the radical intermediate cannot occur, while those with weak M–H bonds hydrogenate the vinylidene C=C double bond.



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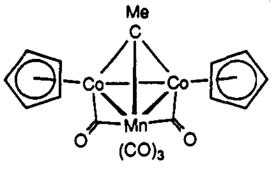
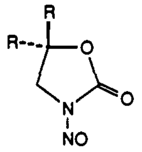
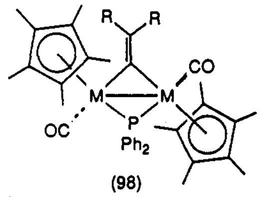


(96)

The well-known synthesis of μ-methylene complexes from diazomethanes and compounds containing multiple metal–metal bonds has been adapted to the preparation of μ-vinylidene derivatives. Although $N_2{=}C{=}CR_2$ are unstable, they can be generated in situ from cyclic nitrosourethanes **97**. Accordingly, addition of LiOEt to **97a** or **97b** in the presence of $\{M(\mu\text{-}CO)(\eta\text{-}C_5Me_5)\}_2$ at −50 °C afforded low yields of $M_2(\mu\text{-}CCR_2)(CO)_2(\eta\text{-}C_5H_5)_2$ [**98**, M = Co, R = Me, black-green; M = Rh, R = Me; R,R = $(CH_2)_5$, deep red].[205,206] Some of the μ-methylene complex was also obtained. The vinylidene group is symmetrically bonded to the two metal atoms.

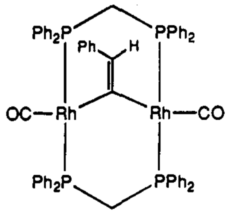


(97) a R = Me
b RR = $(CH_2)_5$

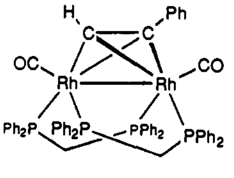


(98)

Reactions of HC_2Ph with $Rh_2(\mu\text{-dppm})_2(CO)_3$ afforded the fluxional vinylidene $Rh_2(\mu\text{-CCHPh})(\mu\text{-dppm})_2(CO)_2$ (**99**) by an associative reaction, and the alkyne complex $Rh_2(\mu\text{-}HC_2Ph)(\mu\text{-dppm})_2(CO)_2$ (**100**) from the dicarbonyl intermediate formed by CO dissociation.[207,206] The vinylidene is the thermodynamic isomer, slow isomerization of **100** to **99** occurring on heating in benzene at 80 °C ($t_{1/2}$ ~27 h). These studies established that the μ-alkyne complex does not lie on the reaction path of the metal-promoted alkyne-to-vinylidene isomerization, which is a bimolecular process between the tricarbonyl and the alkyne, with C–H bond activation occurring in or before the rate-determining step. High yields of the vinylidene were obtained by using a 10-fold excess of the alkyne at 25 °C. Reaction of **99** with CO gave a labile CO adduct, with a color change from intense purple to pale yellow, which was reversed on heating. The vinylidene complexes were also obtained from the corresponding μ-acetylide complexes and $Li[BHEt_3]$; the deep blue *tert*-butyl complex

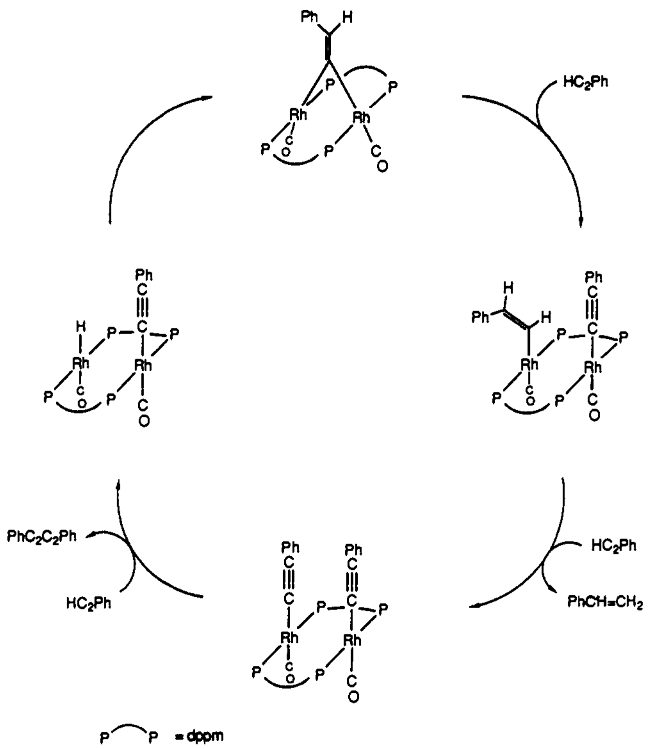


(99)



(100)

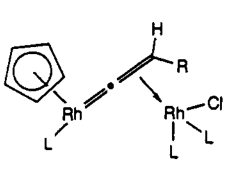
SCHEME 42



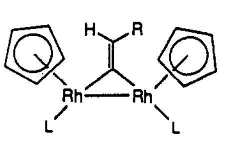
was oxidized by O_2 to regenerate the red μ-C_2Bu^t complex.[209] Addition of $PRPh_2$ (R = Me, Ph) to the μ-C_2H complex gave μ-$CCH(PRPh_2)$ derivatives.

The vinylidene complex **99** catalyzed the disproportionation of HC_2Ph to a mixture of PhC_2C_2Ph and $PhCH{=}CH_2$, together with about 10% of a 1/1 mixture of (*E*) and (*Z*)-$PhC_2CH{=}CHPh$; Scheme 42 shows a possible mechanism for this reaction.[208] Hydrogenation of HC_2Ph to styrene also occurs in the presence of **99**, **100** also being present during the reaction; labeling studies indicated unusual reactivity patterns for the proposed intermediates and a definitive mechanism has still to be established.

Addition of $RhCl(PPr^i_3)_2$ to $Rh(CCH_2)(PPr^i_3)(\eta$-$C_5H_5)$ gave the orange μ-vinylidene complex $(\eta$-$C_5H_5)(PPr^i_3)Rh(\mu$-η^1,η^2-$CCH_2)RhCl(PPr^i_3)_2$ (**101**), which with NaC_5H_5 afforded $(\eta$-$C_5H_5)(PPr^i_3)Rh(\mu$-$CCH_2)Rh(PPr^i_3)(\eta$-$C_5H_5)$ (**102**); protonation of the latter ($HBF_4{\cdot}Et_2O$) gave a μ-vinyl derivative, which regenerated **101** on treatment with KOH.[110,210] Warming **101** in benzene to 50 °C gave **103** by coupling of the CCHR ligand with one of the PPr^i_3 ligands via oxidative addition of the latter to one metal atom; similar compounds were obtained directly from $Rh(CCHR)(PPr^i_3)(\eta$-$C_5H_5)$ (R = Me, Ph) and $RhCl(PPr^i_3)_2$. This reaction may be related to the formation of the binuclear complexes $Co_2(\mu$-σ,η^3,P-$MeCC_6H_4PPh_2)(\eta$-$C_5H_4R)_2$ from $(\eta$-$C_5H_4R)Co(PPh_3)_2$ (R = H, COMe, CO_2Me) and C_2H_2, via addition of $(\eta$-$C_5H_4R)Co$ to an intermediate $(\eta$-$C_5H_4R)(PPh_3)Co(\mu$-$CCH_2)Co(\eta$-$C_5H_4R)$ (Scheme 43).[211]

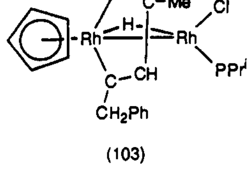


(101)



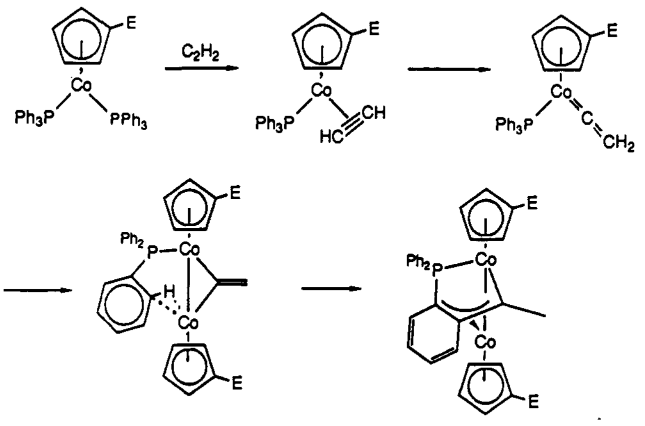
(102)

L = PPr^i_3

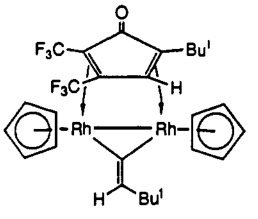


(103)

SCHEME 43



One of six complexes isolated from the reaction between HC_2Bu^t and $Rh_2(CO)\{C_2(CF_3)_2\}(\eta$-$C_5H_5)_2$ in hexane for 6 days was the crystallographically characterized **104**.[212] This yellow complex appears to isomerize during chromatography either by switching of the H and Bu^t groups, or by flipping of the μ-cyclopentadienone ligand.



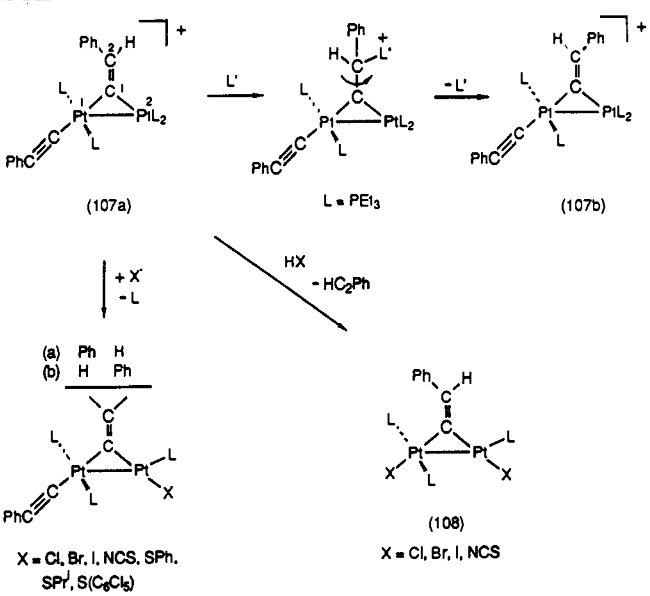
(104)

5. Nickel, Palladium, and Platinum

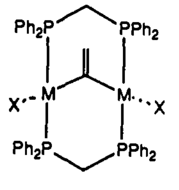
Red-purple $Ni_2(\mu$-$CCH_2)(\mu$-$dppm)_2Cl_2$ (**105**; M = Ni, X = Cl) was obtained in 38% by double oxidative addition of 1,1-dichloroethene to $Ni(cod)_2$ in the presence of dppm, or in 74% yield from $NiCl(CCl{=}CH_2)(PPh_3)_2$, $Ni(cod)_2$, and dppm.[213] It is thermally very stable, decomposing above 200 °C, and undergoes ready halide replacement by Br, I, or SCN; no replacement by alkyl or aryl groups could be effected, however. An impure cationic complex, $[Ni_2(\mu$-$CCH_2)(\mu$-$dppm)_2(Me_2CO)_2][PF_6]_2$, was formed from the chloro complex and $TlPF_6$.

Analogous dipalladium complexes **105** (M = Pd) were obtained from $Pd(PPh_3)_4$ or from $Pd(dba)_2$, dppm, and $CH_2{=}CX_2$ (X = Cl, Br),[214,215] or from $\{Pd(\mu$-$dppm)Cl\}_2$ and C_2I_2.[216] Ready exchange of Cl for Br, I, or SCN occurred in acetone, while TlOAc afforded $Pd_2(\mu$-$CCH_2)(\mu$-$dppm)_2(OAc)_2$. Complex **105** (M = Pd) reacted with $LiC_2(tol)$ to give the orange acetylide, and with (tol)NC to give the dication $[Pd_2(\mu$-$CCH_2)(\mu$-$dppm)_2(CNtol)_2]^{2+}$; other acetylides were prepared from **105** (M = Pd), HC_2R [R = Ph, tol, $CMe_2(OH)$], and $TlPF_6$. A related μ-$CCCl_2$ compound was obtained from $Pd(PPh_3)_4$, $PdCl(CCl{=}CCl_2)(PPh_3)_2$, and dppm, while the μ-$CHMe(PPh_2)_2$ derivative was formed as a single isomer, probably **106**; only **105** (M = Pd) was isolated

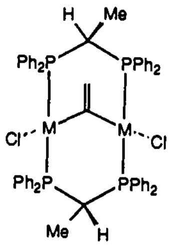
SCHEME 44



from the reaction with $CH(SiMe_3)(PPh_2)_2$. Protonation ($HBF_4{\cdot}OEt_2$) of **105** (M = Pd) gave two intermediates which changed within minutes to an asymmetric (NMR) μ-CMe complex, possibly containing *cis*-dppm ligands.



(105)

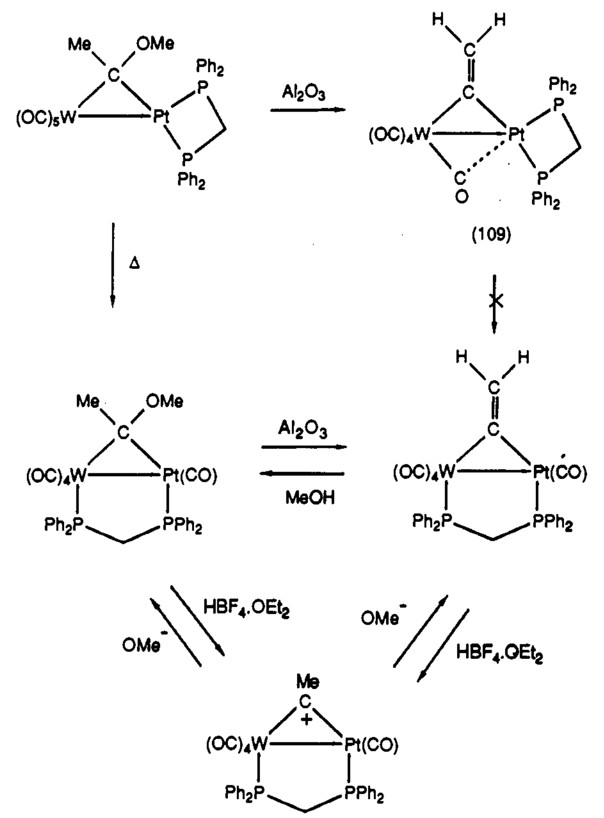


(106)

1,2-Addition of a metal hydride across the C≡C triple bond of a metal acetylide has been used to produce bridging vinylidene ligands, the first example of this reaction being applied to the synthesis of **107** from *trans*-$Pt(C_2R)_2(PEt_3)_2$ (R = H, Me, Ph) and [*trans*-$PtH(OCMe_2)(PEt_3)_2$][BF_4].[217,218] Other applications of this reaction to the synthesis of heterodimetallic species are described in section V.B. Initial displacement of acetone by the acetylide, followed by a hydrogen atom shift from platinum to C_β, is the likely mechanism. The orange to red Pt_2 complexes were obtained in 40–70% yield. Two isomeric forms were obtained which interconverted, perhaps via addition of a trace of PEt_3 to C_β allowing rotation around the C–C bond of the resulting μ-ethylidyne group (Scheme 44).

Replacement of one PEt_3 ligand in the Pt_2 complex by halide, pseudohalide, or RS^- occurred readily (54–75%), while protic acids (HX) reacted to give HC_2Ph and the corresponding Pt_2X_2 derivatives **108** (46–76%).[219] Addition of HBF_4 or HPF_6 to **107**, followed by LiBr, also gave the Pt_2Br_2 complex. In these complexes, the μ-CCHPh ligand can take up two positions **107a** or **107b**; the products from nucleophilic substitution on either **107a** or **107b** all have configuration **108a**, but it was noted that **107b** reacted at a quarter of the rate of the other isomer. Complexes formed by elimination of HC_2Ph are found as isomeric mixtures.

SCHEME 45



Preliminary theoretical studies of **107** showed that the HOMO is primarily vinylidene Ph and μ-C in character, with the LUMO (only 0.36 eV above the HOMO) mainly having acetylene Ph character.[219] Neither has more than 4% Pt character. The net atomic charges for the $Pt^1(\mu\text{-}C^1C^2)Pt^2$ system are as follows: C^1, 0.26; C^2, −0.09; Pt^1, −1.07; Pt^2, −1.18. The Pt^1Pt^2 interatomic population is −0.467, indicating that there is no formal metal–metal bond. Similarities between the electronic structures of **107** and $[Pt_2(H_2P_2O_5)_4]^{4-}$ are apparent, and preliminary studies of the photophysics and photochemistry of **107** were made.[219] A red-orange luminescence (λ_{max} 696 nm) is emitted from **108** (X = Cl) in an EtOH/MeOH matrix at 77 K when excited (410 nm).

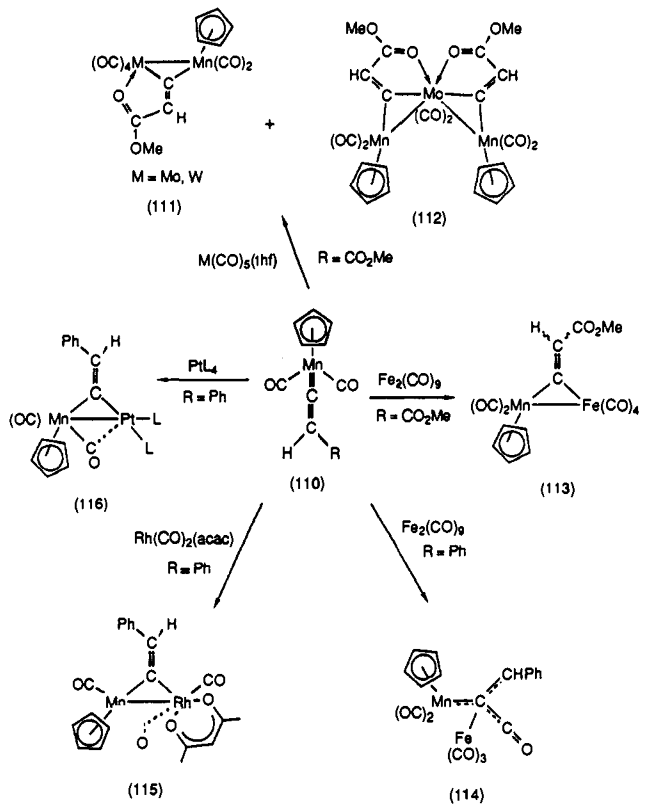
The photochemical reactivity observed for **108** included its acting as a catalyst for the dehydrogenation of Me_2CHOH to acetone, with formation of an (unidentified) Pt–H species. Irradiation of a mixture of **107** and MeI resulted in its conversion to the $Pt_2I(C_2Ph)$ (33%) and Pt_2I_2 (25%) complexes, but the reaction does not proceed thermally.[219]

B. Heterometallic Complexes

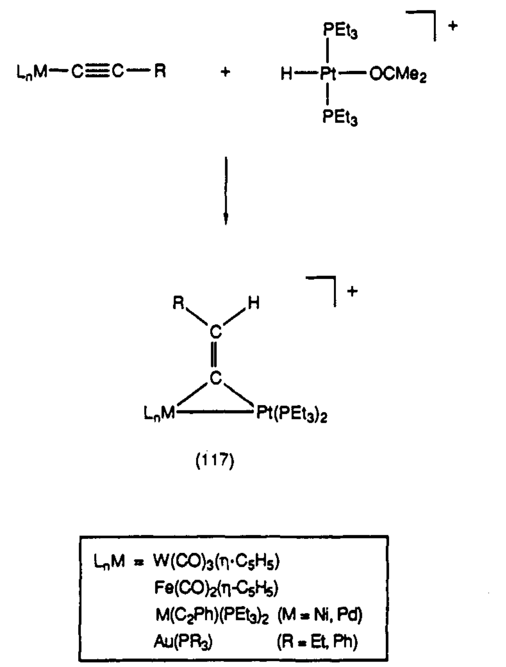
Chromatography of PtW{μ-C(OMe)Me}$(CO)_5$(dppm) on basic alumina afforded PtW(μ-CCH_2)$(CO)_5$(dppm) (**109**; Scheme 45), in which the Pt–W bond is asymmetrically bridged by the CCH_2 ligand and one of the CO groups.[220] An isomeric complex was obtained from the same precursor by thermal isomerization, conversion to the cationic μ-CMe complex with $HBF_4{\cdot}OEt_2$, and deprotonation with $K[BHBu^s_3]$ or NaOMe; some **109** is also reformed with the latter.

Reactions of the manganese–vinylidene complexes **110** with various transition metal substrates have given

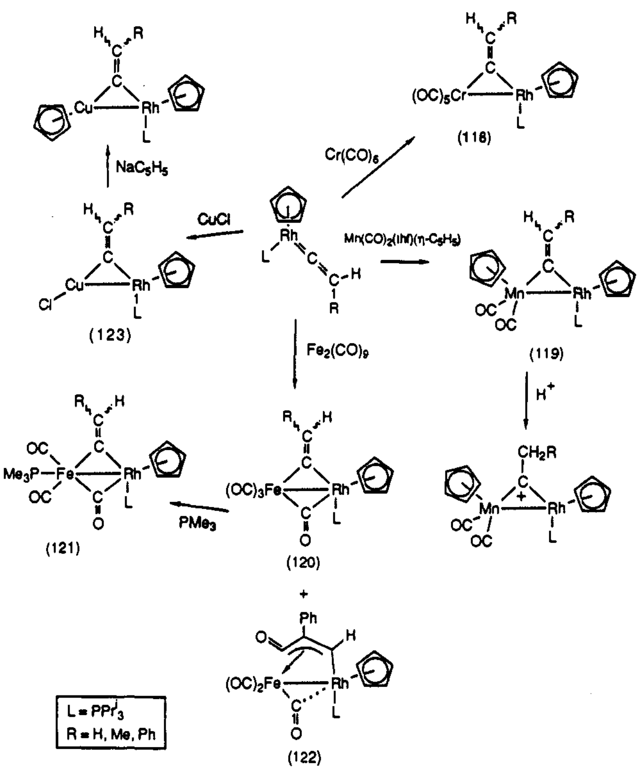
SCHEME 46



SCHEME 47



SCHEME 48



several interesting bimetallic derivatives (Scheme 46). With $M(CO)_5(thf)$ (M = Mo, W) dark brown bi- and trinuclear complexes **111** and **112** containing chelating vinylidene ligands were obtained; the ester oxygen coordinates to the group 6 metal.[221,222] The *E* and *Z* isomers of the Mn–Fe complex **113** were similarly prepared; they interconvert via protonation/deprotonation reactions, with formation of the μ-carbyne intermediate in which free rotation of the CH_2R group can occur (cf. Scheme 44).[223] In contrast, **110** (R = Ph) afforded **114**, formulated as containing a mangana–trimethylenemethane ligand bonded to an $Fe(CO)_3$ group.[224] With $Rh(CO)_2(acac)$, the Mn–Rh derivative **115** was obtained; reaction with PPh_3 gave $Rh(CO)(PPh_3)(acac)$ and **110** (R = Ph).[225]

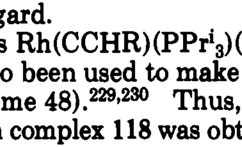
The reactions between **110** (R = Ph) and PtL_4 [L = PPh_3, $P(OEt)_3$, $P(OPh)_3$] or $Pt(\eta^2\text{-stilbene})(PPh_3)_2$ afforded the binuclear Mn–Pt complexes **116**.[127,226] These complexes are yellow-orange, with relative stabilities $P(OEt)_3 < P(OPh)_3 < PPh_3$. Comparison of the μ-CCHPh complexes with the μ-C(OMe)(C_6H_4Me-4) complexes of Stone et al.[227] showed that the vinylidene ligand was more electron-withdrawing than the carbene. They show a tendency to exchange the ligands at platinum; for example, in benzene, CO or $P(OR)_3$ exchanged for one of the PPh_3 ligands. Good yields of the CO complex can be obtained in reactions with $Co_2(CO)_8$, perhaps via an intermediate in which the vinylidene bridges the two metals. One of the CO groups is semibridging to balance the strong electron withdrawal by the vinylidene ligand.[127,226]

A mixture of mono- and disubstituted (on Pt) complexes was obtained from **110** (R = Ph) and $P(OPr^i)_3$; in the former, the phosphite is cis to the vinylidene ligand.[228] The complexes are air-stable yellow-orange compounds; the proportion of disubstituted complex increases with increasing amount of phosphite reactant. The exchange is reversed by treating the disubstituted complex with PPh_3. The first ligand to be replaced is trans to the vinylidene group. With $Co_2(CO)_8$, a mixture of the carbonyl–phosphine and carbonyl–phosphite complexes was obtained from the monosubstituted complex. Slow disproportionation of the latter to the bisphosphine and bisphosphite complexes occurred on standing. A byproduct from the reaction of **110** with $Pt\{P(OR)_3\}_4$ is the olefin complex $Mn(CO)_2\{\eta^2\text{-CHPh=CHP(O)(OR)}_2\}(\eta\text{-}C_5H_5)$[127,226] (see section IV.D.3).

The mixed Ni–Pd complex $NiPd(\mu\text{-}CCH_2)(\mu\text{-dppm})_2Cl_2$ (**105**; MM = NiPd) was obtained from a reaction of the chloro(chlorovinyl)nickel derivative with $Pd(PPh_3)_4$; with $Pd(dba)_2$ or $Pt(PPh_3)_4$, the dichlorovinylidene complexes $NiM(\mu\text{-}CCCl_2)_2(\mu\text{-dppm})_2Cl_2$ (M = Pd and Pt, respectively) were formed in low yield.[213]

Addition of the Pt–H bond in $[PtH(OCMe_2)(PEt_3)_2]^+$ across the C≡C bonds in alkynyl–transition metal complexes (see above) is a general approach to the synthesis of heterometallic μ-vinylidene complexes **117** (Scheme 47).[218] These compounds were obtained in 30–75% yields and were characterized by NMR spectroscopy, the vinylidene proton resonance being most useful in this regard.

The complexes $Rh(CCHR)(PPr^i_3)(\eta\text{-}C_5H_5)$ (R = H, Me, Ph) have also been used to make heterobimetallic complexes (Scheme 48).[229,230] Thus, with $Cr(CO)_3(\eta\text{-}C_6H_6)$, the Cr–Rh complex **118** was obtained, while with $Mn(thf)(CO)_2(\eta\text{-}C_5H_5)$, the Mn–Rh derivative **119** was formed. Protonation ($HBF_4\cdot OEt_2$) of the latter gave the dark blue μ-CMe cation. With $Fe_2(CO)_9$, the Fe–Rh complex **120** was formed, together with a trinuclear Fe_2Rh derivative; again, protonation gave μ-alkylidyne cations, while PMe_3 substituted a CO group on iron (**121**). The isomeric $(\eta\text{-}C_5H_5)(Pr^i_3P)Rh(\mu\text{-}\eta^1,\eta^3\text{-}CHCPhCO)Fe(CO)_3$ (**122**) was also characterized.[231] Addition of CuCl to $Rh(CCHR)(PPr^i_3)(\eta\text{-}C_5H_5)$ (R = H, Me, Ph) gave the orange-red to red μ-CCHR complexes **123**; their chirality is shown by the Pr^i resonances.[110,210] The $\mu\text{-}CCH_2$ complex can be obtained as a second, less-soluble form, perhaps a dimer or polymer. Both forms react with NaC_5H_5 to give $(\eta\text{-}C_5H_5)(Pr^i_3P)Rh(\mu\text{-}CCH_2)Cu(\eta\text{-}C_5H_5)$ as a dark air-sensitive oil. A similar reaction with $Os(CCHPh)(PPr^i_3)(\eta\text{-}C_6H_6)$ gave $CuOs(\mu\text{-}CCHPh)(Cl)(PPr^i_3)(\eta\text{-}C_6H_6)$ (**124**) in almost quantitative yield.[86]



(124)

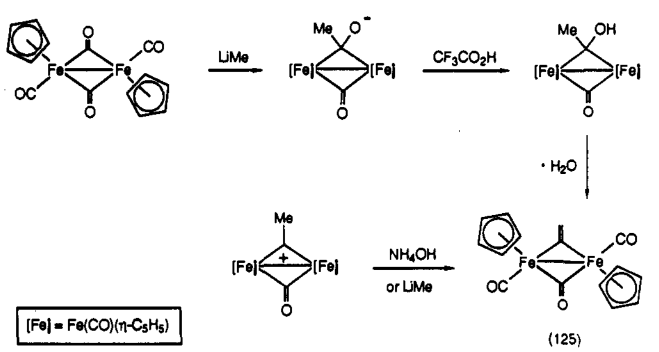
C. Complexes $\{M(CO)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CO)(\mu\text{-}CCRR')$ (M = Fe, Ru)

1. Iron

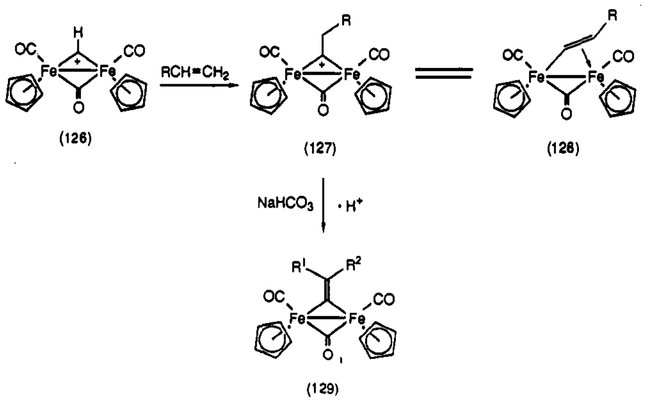
Binuclear iron complexes containing bridging vinylidene ligands (Table 9) have proved to be important intermediates and to have a fascinating chemistry. Some related chemistry of the ruthenium analogues has also been developed.

(*a*) *Synthesis.* The parent complex, $\{Fe(CO)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CO)(\mu\text{-}CCH_2)$ (**125**), was first described in 1980,[232] being obtained from reactions of LiMe with $\{Fe(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)\}_2$ followed by protonation (Scheme 49). Deprotonation of the related μ-CMe cation also afforded **125**.[233] Generally, these complexes have been prepared by hydrocarbation of alkenes with $[\{Fe(CO)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CO)(\mu\text{-}CH)]^+$ (**126**) followed by rapid deprotonation (aqueous $NaHCO_3$) of the μ-alkylidyne cations **127** so formed (Scheme 50).[234–239] The μ-alkylidene complexes are in rapid equilibrium with μ-σ,π-vinyl complexes **128**, but only the former are deprotonated rapidly.[240] Formation of the μ-vinyl complexes is favored by sterically demanding substituents on the olefin and hence lower yields of the μ-vinylidenes were obtained from the more hindered olefins.[238,239] The μ-vinyl can be deprotonated to a μ-β-hydroxycarbene or μ-vinylcarbene complex.

SCHEME 49

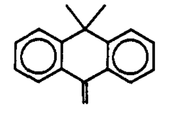


SCHEME 50



Monosubstituted alkenes $CH_2{=}CHR$ (R = Me, Ph, Bu^t) and **126** gave **129** (R^1 = H, R^2 = Et, CH_2Ph, CH_2Bu^t, respectively) after deprotonation. For **127** (R = Pr), thermal isomerization to **128** (R = Pr) occurred at elevated temperatures; only the former is selectively deprotonated to **129** (R^1 = H, R^2 = Pr).[238] The reaction between *cis*-2-butene and **126** gave a 2.3/1.5/1.0 mixture of **127** (R = CHMeEt) and isomers of the μ-CH=CMeEt complex (Scheme 51). Deprotonation of the former resulted in complete conversion to **129** (R^1 = Me, R^2 = Et). Protonation of the latter regenerated the equilibrium mixture of cations. When **126**-d_1 was used, the product was **129** (R^1 = Me, R^2 = CHDMe).

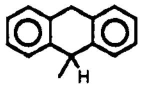
Vinylcyclopropane and vinyl acetate gave only the μ-vinyl complexes and hence the μ-vinylcarbene. Detailed studies of the steric effects on the position of the μ-alkylidyne/μ-vinyl equilibrium have been made.[239] Of interest is the comparison between $CH_2{=}CPh_2$ and the planar **130**, where only the latter formed a μ-alkylidyne which could be deprotonated to the μ-vinylidene.



(130)

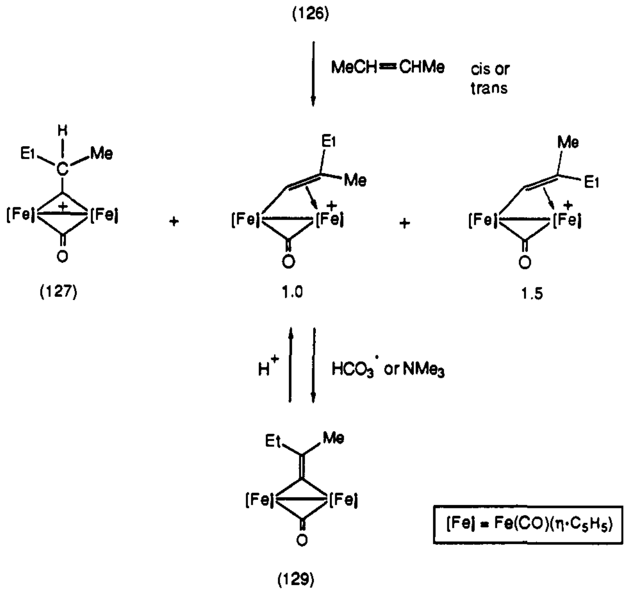
μ-Vinylcarbyne complexes **131** were formed in high yield by allylic hydride abstraction from μ-vinylidene complexes with $[CPh_3]^+$ (Scheme 52).[241] The reaction is reversed by addition of $[NEt_4][FeH(CO)_4]$, which acts as a source of H^-. Addition of nucleophiles at the remote vinyl carbon in **131** is an alternative route to μ-vinylidene complexes **132**.[242] The addition is regiose-

TABLE 9. Binuclear Iron Vinylidenes, $\{Fe(CO)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CO)(\mu\text{-}CCRR')$

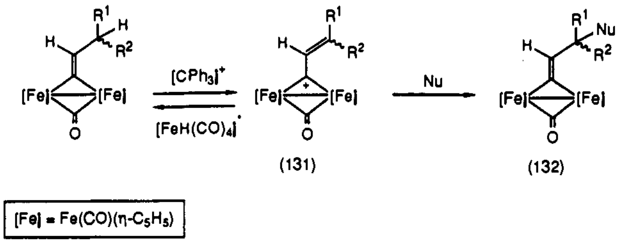
R	R′	$\delta(C_\alpha, \mu\text{-}CO)$	$\delta(C_\beta)$	ref
H	H (*cis*, *trans*)	276.7, 279.2	125.8, 125.4	232b, 233
H	Me	269.8, 266.5	133.6	234b, 251
H	Et	273.0, 265.8	142.9	234b
H	Pr	271.4, 262.3	140.6	234b
H	$CHMe_2$	271.4, 263.6	149.0	234b
H	Bu	269.8, 265.4	140.7	234b
H	CHMeEt	274.5, 264.8, 264.5[a]		239
H	Bu^t	271.8, 260.7	153.6	242
H	CH_2CHMe_2	271.5, 266.4	139.7	264
H	CH_2Bu^t	269.5, 266.6	137.6	234b
H	CH_2Ph	270.6, 267.8	139.1	234b
H	CH_2CH_2Ph	271.1, 266.8	143.6	234b
H	CH_2CO_2Et	270.4, 270.1		253
H	CH_2OEt	274.0, 270.3	137.8	242
H	CHMe(tol)	271.8, 264.3; 271.9, 263.7[a]	135.0	242
H	$CH(tol)_2$	271.4, 266.1		242
H	$CH(tol)\{CH(CO_2Et)_2\}$	270.8, 269.1; 270.8, 268.4[a]	139.7; 139.3[a]	242
H	$CMeCH_2(tol)$	271.2, 261.7		242
H	$CMe_2\{CH(CO_2Et)_2\}$	269.8, 262.8	150.3	242
H	CH=CHMe	283.8, 272.3		241
H	CH=CH(CN)	304.8, 266.7	150.8	255a
H	$C(CN)=C(CN)_2$	342.6, 259.6		256
H	$CH(^+NMe_2)$	355.7, 261.1	137.0	242
H	$CHEt(^+PMe_3)$	277.7, 267.0; 277.5, 267.3[a]	130.0	241, 242
H	CHO	319.5, 265.7	148.8	242
H	CO_2Et	304.5, 267.4	133.3	245
H				239
Me	Me			251
Me	Et	272.1, 259.5		238
Me	$CHMe_2$	270.3, 258.1		239
Me	CH_2Ph	274.2, 262.7		238
Me	$CH_2(tol)$	271.2, 261.7		264
Me	CO_2Me	295.2, 268.4	137.7	245
Pr	CH_2CO_2Et	265.9, 270.9	141.5	245
	$-(CH_2)_4-$	270.2, 253.0		238, 241
	$-(CH_2)_3CHMe-$	275.2, 255.1, 254.0[a]		239
	$-(CH_2)_5-$	270.5, 256.0		238

[a] Minor isomer.

SCHEME 51



SCHEME 52

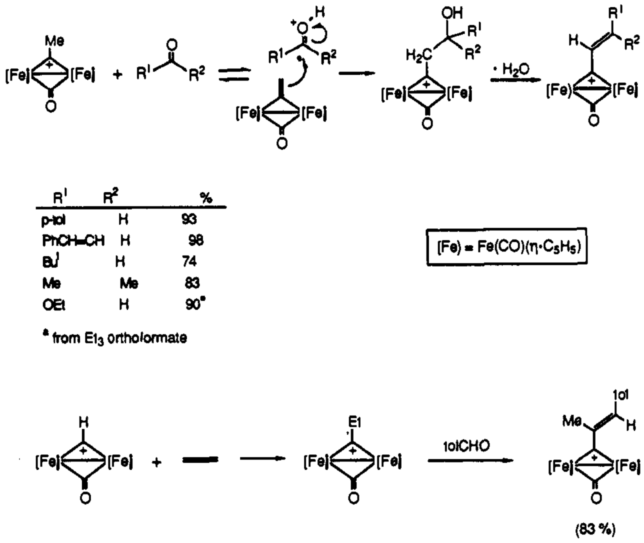


lective and has been observed with $LiC_6H_4Me\text{-}p$, $NaCH(CO_2Et)_2$, LiMe, hydride (from $[FeH(CO)_4]^-$), and PMe_3; with the $\mu\text{-}CCH{=}CMe_2$ complex, addition to give the μ-CCHCHR(Nu) complexes is favored over deprotonation (which would give the $\mu\text{-}CCHCMe{=}CH_2$ derivative).

Reaction of **127** (R = H) with NaN_3 gave EtCN (19%) and **125** (57%); the amount of nitrile was increased by working in CF_3CO_2H (39%) or by using Me_3SiN_3 (24%), while the yield of **125** dropped below 7%.[243] A 56/44 mixture of alkylidyne and vinylidene was obtained from the reaction between **127** (R = H) and N_2O.

Condensation of cationic μ-carbyne complexes with aldehydes, acetone, or ortho esters also afforded μ-vinylcarbyne complexes via attack of the intermediate vinylidenes (formed by deprotonation of the μ-carbyne by the aldehyde, etc.) on the C-electrophile (Scheme 53).[244] Addition to aldehydes probably proceeds via deprotonation, subsequent attack of the $\mu\text{-}CCH_2$ complex on the protonated aldehyde and elimination of water. The vinyl ether carbyne complex **133** exchanges OEt for NMe_2 in a reaction with $HNMe_2$ at −78 °C

SCHEME 53



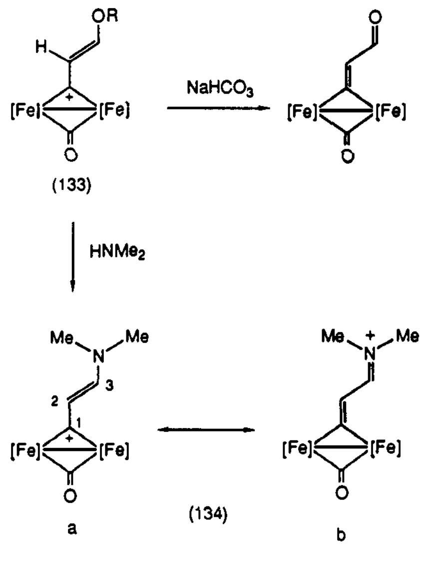
R¹	R²	%
p-tol	H	93
PhCH=CH	H	98
Bu^t	H	74
Me	Me	83
OEt	H	90^a

^{a} from Et$_3$ orthoformate

[Fe] = Fe(CO)(η-C$_5$H$_5$)

(83%)

SCHEME 54



(133)

a (134) b

C^1-C^2 1.377(10) C^2-C^3 1.391(11) C^3-N 1.295(9) Å

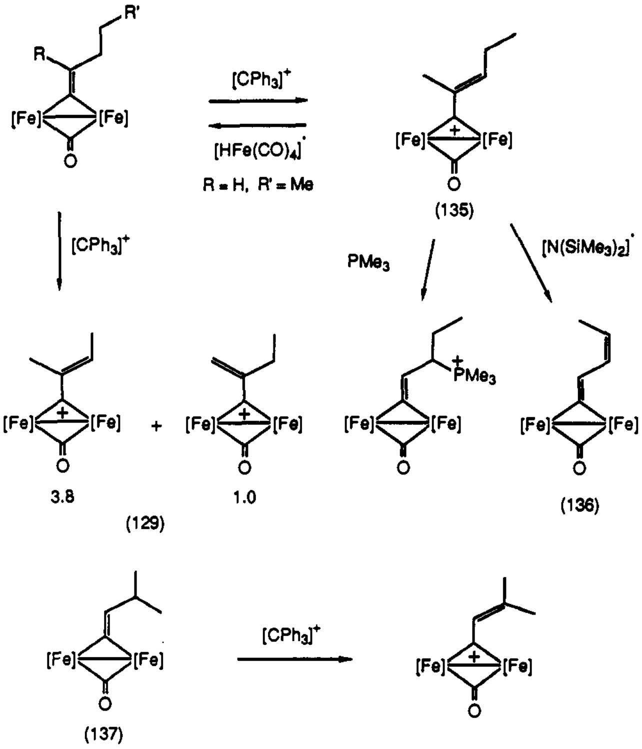
[Fe] = Fe(CO)(η-C$_5$H$_5$)

(Scheme 54).[242] ^{1}H and ^{13}C NMR studies showed contributions from both resonance forms, the carbyne **134a** and the vinylidene **134b**. Similar exchange of OEt for O occurred on reaction with aqueous NaHCO$_3$.

Reaction of vinylcarbyne **135** with [N(SiMe$_3$)$_2$]$^-$ gave a 3.8/1 mixture of cis/trans isomers of the butadienylidene complex **136**, while PMe$_3$ adds to Cγ also to produce a mixture of stereoisomers (Scheme 55). Related complexes were formed by loss of the secondary or tertiary H, e.g. from **137**. The μ-CCMeEt complex gave a 3.8/1 mixture of isomers of **129** by exclusive loss of the secondary allylic H.[241]

Related reactions with cationic complexes derived from **126** and diazoalkanes afforded the substituted μ-vinylidene complexes.[245] Thus, the μ-alkenyl from **126** and N$_2$CH(CO$_2$Et) decomposes above −20 °C to give a mixture containing **129** (R^1 = H, R^2 = CO$_2$Et) (23%); the analogous complex (as a 6/1 *E*/*Z* isomeric mixture) from N$_2$CMe(CO$_2$Me) gave **129** (R^1 = Me, R^2 = CO$_2$Me) (40%) after reaction with NMe$_3$. Prolonged (10 days) reaction between **127** (R = H, Pr) and N$_2$CH(CO$_2$Et) gave low yields of **129** (R^1 = R, R^2 = CH$_2$CO$_2$Et), probably by attack of the μ-vinylidene complex on N$_2$C$^+$H$_2$(CO$_2$Et), followed by deprotonation of the resulting μ-alkylidyne complex. The μ-vinyl reacted with increasing excesses of CH$_2$N$_2$ (up to 40 equiv) to give as successive insertion products the μ-CCHMe, μ-CCMe$_2$, and μ-CCMeEt complexes.[245]

SCHEME 55



(135)

(129)

(136)

(137)

[Fe] = Fe(CO)(η-C$_5$H$_5$)

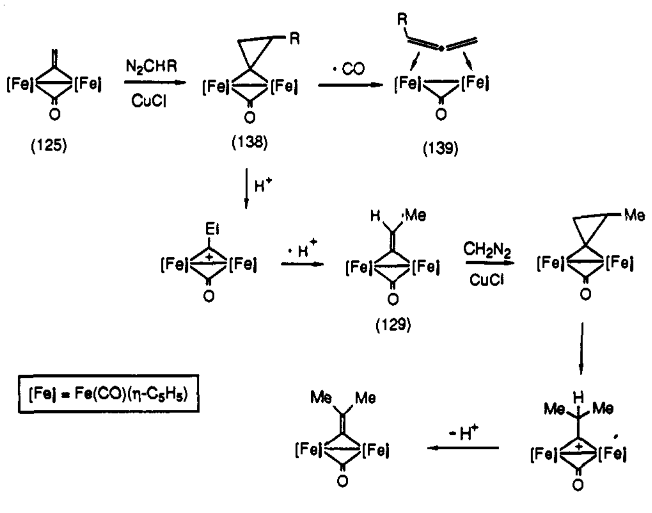
Addition of CO to **126** gave the acylium cation [{Fe(CO)(η-C$_5$H$_5$)}$_2$(μ-CO)(μ-CHCO)]$^+$; this reacted with excess Li$_2$[CuMe$_2$(CN)] to give the μ-CCMe$_2$ complex (32%), probably by addition of Me$^-$ to the initially formed μ-CHC(O)Me complex to give the anionic μ-CHC(O$^-$)Me$_2$ derivative, followed by protonation at oxygen and elimination of water.[246]

Nucleophilic addition of Br$^-$ to **126** gave the μ-bromocarbene derivative, which reacted with CH$_2$=CMe$_2$ to give the μ-CCHCHMe$_2$ derivative (16%), probably by reaction of **126** generated by ionization of Br$^-$, followed by deprotonation (NMe$_3$).[247]

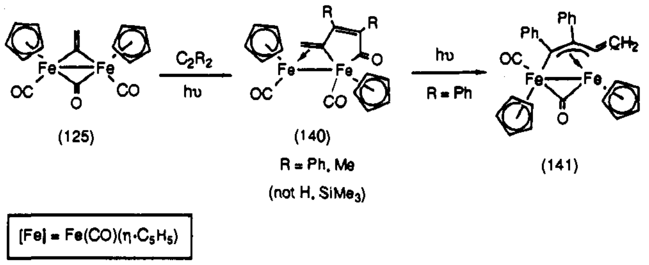
The mixed complex {Fe(CO)(η-C$_5$H$_5$)}{Fe(CO)(η-C$_5$Me$_5$)}(μ-CO)(μ-CCHBu) was obtained (61%) by deprotonation of the μ-C(CH$_2$)$_4$Me complex formed by addition of 1-pentene to the corresponding μ-CH$^+$ cation.[239] The bis-C$_5$Me$_5$ complex does not react.

(*b*) *Reactions*. The gas-phase basicity of **125** has been determined by FT MS as similar to that of NEt$_3$ (proton affinities: **125**, 232.5; NEt$_2$, 232.3 kcal mol^{-1}).[248] This high value can be related to the interaction of the $\pi_\perp$ orbital of the Fe(μ-C)Fe framework with an empty π_y orbital of the μ-C$^+$Me group (see below). Decomposition of collisionally activated [{Fe(CO)(η-C$_5$H$_5$)}$_2$(CO)(CCH$_2$)]$^+$ proceeded via sequential loss of three CO groups to [{Fe(C$_5$H$_5$)}$_2$C$_2$H$_2$]$^+$, which then afforded [Fe$_2$C$_{10}$H$_{10}$]$^+$, [FeC$_{12}$H$_{12}$]$^+$, and [FeC$_{10}$H$_{10}$]$^+$ by elimination of C$_2$H$_2$, Fe, and FeC$_2$H$_2$, respectively.

SCHEME 56



SCHEME 57



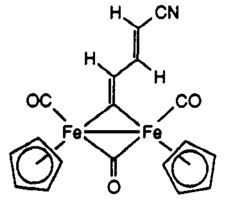
Reversible protonation of **125** to the μ-CMe cation was first demonstrated by Pettit[233] and Stone.[232] Protonation of substituted vinylidenes afforded the same alkylidene cations from which the vinylidenes were derived (Scheme 51).[234,235] Alkylation ($[Me_3O][BF_4]$) of the μ-$CCMe_2$ complex slowly formed the cationic μ-CBu^t alkylidyne derivative (36%) by addition at C_β.[245]

The CuCl-catalyzed reaction of CH_2N_2 with **125** afforded the cyclopropenylidene complex **138** (Scheme 56);[249] the equilibrium 6/1 mixture of red cis and purple trans isomers, which slowly interconvert in solution, rearranges on heating (100 °C) or photolysis to the μ-allene complex **139** (R = H).[250] Protonation (HBF_4 or CF_3SO_3H) of **138** gave the μ-CEt cation, which was deprotonated to **129** (R^1 = H, R^2 = Me).[251] Repetition of this series of reactions gave exclusively the μ-$CCMe_2$ complex, with none of the linear isomeric μ-CCHEt derivative being found. This contrasts with the situation in the Fischer–Tropsch reaction: selective attack of H^+ at the less-branched C atom occurred. These observations contradict the McCandlish mechanism for chain growth,[252] which suggested that vinylidene, perhaps formed by combination of surface carbide with methylene, itself reacts further with methylene to give a cyclopropenylidene. Alternative modes of ring-opening then result in either linear or branched growth. The relative stabilities of the carbonium ions involved in this process suggest that linear growth would be favored.

Related reactions between $N_2CH(CO_2Et)$ and **125** gave three products (Scheme 56).[253] In the presence of CuI, the cyclopropenylidene **138** (R = CO_2Et) was obtained (60%), which on photolysis gave the μ-allene **139** (R = CO_2Et) (45%), also obtained directly by photolyzing a mixture of **135** and the diazo compound. Later studies demonstrated the direct formation of the μ-allene complexes by photolysis of the reaction mixtures; only with $CH(SiMe_3)N_2$ was replacement of the μ-vinylidene by μ-$CHSiMe_3$ found. In the presence of HBF_4, ring-opening of **138** (R = CO_2Et) gave **129** (R^1 = H, R^2 = CH_2CO_2Et) via initial addition of H^+ to the ester CO group.[253]

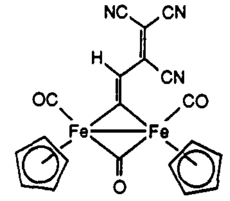
While no reaction occurred with HC_2R (R = H, Ph, CO_2Me, CF_3 or $SiMe_3$), thermal or photochemical insertion of C_2R_2 (R = Me, Ph) into one of the Fe–C bonds of the μ-CCH_2 complex occurred, the highest yield of the metallacyclopentenones **140** being obtained under CO (Scheme 57).[254] Further irradiation of the phenyl derivative in the absence of CO resulted in decarbonylation to the μ-σ,η^3-allylic complex **141**. Several possible mechanisms for the rearrangement of the initially formed η^2-alkyne complex to the products were discussed.

Complex **125** reacted with HC_2CN by insertion of the alkyne into a C(sp^2)–H bond to give purple $\{Fe(CO)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CO)\{\mu\text{-}CCHCH{=}CH(CN)\}$ (**142**), formed as a separable 1.4/1 mixture of *E*/*Z* isomers.[255] Similar complexes were obtained from the μ-CCHMe and μ-$CCHPr^i$ derivatives. There is no reaction between **142** and CO, even upon UV irradiation. Addition of $HBF_4{\cdot}OEt_2$ afforded a μ-alkylidyne complex, which rapidly decomposed, while $Li[BHEt_3]$ gave a stable anionic species, thought to contain a μ-organovinylalkylidene ligand.[255]



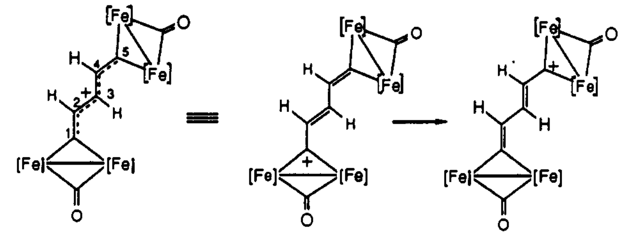
(142)

Tetracyanoethene and **125** gave the orange-red buta-1,3-dienylidene complex **143** with elimination of HCN. ESR studies of the reaction mixture after mixing indicated the presence of radical species, including $[tcne]^{\bullet-}$ and the radical $Fe\{N{=}C^{\bullet}C(CN){=}C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)$, the reaction proceeding via successive electron transfer steps.[256] Insertion into the vinylic C–H bond probably occurs by C–C bond formation between the electron-rich vinyl carbon and the electron deficient alkyne carbon, followed by a 1,3-H shift. Substitution of CO by dppm occurs in refluxing toluene to give $\{Fe(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CO)(\mu\text{-}dppm)\{\mu\text{-}CCHCH{=}CH(CN)\}$. A similar complex was obtained (60%) from tcne and $\{Fe(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CCH_2)(\mu\text{-}CO)(\mu\text{-}dppe)$ [from **125** and dppe in toluene]; its deep violet color (λ_{max} 539 nm) is associated with the presence of both the electron-rich metal system and the tricyanobutadienyl group.[257]



(143)

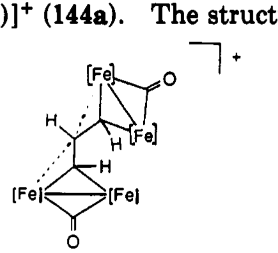
Coupling between **125** and the ethoxyvinylcarbyne cation occurred with elimination of EtOH to give the pink-brown tetra-iron complex **144** (84%), which is fluxional. The X-ray study showed the symmetrical attachment of the bridging ligand, which can be rationalized by the valence tautomers shown.[258] Electrophilic addition of **125** to **126**, followed by a 1,2-H shift, gave the blue-black cation $[\{Fe_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2\}_2(\mu\text{-}C_3H_3)]^+$ (**144a**). The structure is best described as containing an allylic cation with two in-plane iron substituents syn to the central CH, with the other iron atoms above and below the allyl plane. These interact strongly with the terminal C atoms, but only weakly with the central C atom.[264]



Fe-C[1] 1.859, 1.894(8), Fe-C[5] 1.855, 1.884(8), C[1]-C[2] 1.355(11), C[4]-C[5] 1.373(11) Å

[Fe] = Fe(CO)(η-C$_5$H$_5$)

(144)



[Fe] = Fe(CO)(η-C$_5$H$_5$)

(144a)

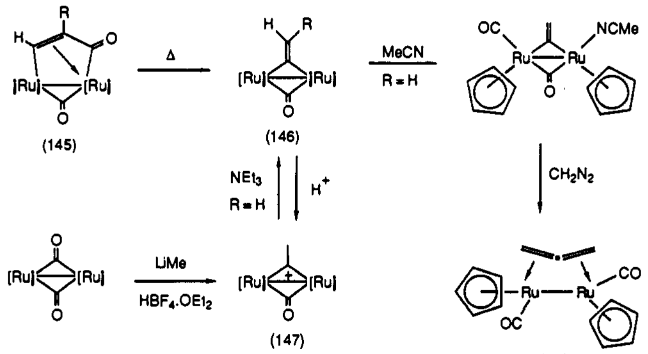
Displacement of the vinylidene ligands from a variety of μ-vinylidene–diiron complexes was achieved by photolysis under hydrogen, when mixtures of the corresponding alkanes and alkenes were obtained. Reactions with $SiHMe_3$ gave the $SiMe_3$-substituted olefin in a reaction that was inhibited by CO. These reactions probably proceed via an intermediate such as $\{Fe(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CO)_2(\mu\text{-}CCRR')$.[253b]

2. Ruthenium

In the ruthenium series, the alkyne–CO adducts $\{Ru(CO)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CO)\{\mu\text{-}C(O)CHCR\}$ (**145**) are fluxional below 100 °C, but in refluxing toluene they underwent C–C bond cleavage to give μ-CCHR complexes **146**.[259] The reaction was slow, requiring a day for completion and gave cis/trans mixtures for R = H (63%, 1.2/1) and R = Ph (20%, 1/1). A one-pot synthesis of the parent vinylidene complex in 77% yield was achieved by treating $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2$ with LiMe, followed by $HBF_4\cdot OEt_2$, then deprotonation with water or NEt_3 (Scheme 58). The reaction is assumed to proceed via a concerted ring-opening to give a terminal vinylidene complex. Protonation ($HBF_4\cdot OEt_2$) of **146** gave the methylcarbyne complex **147**. Detailed procedures for the synthesis of a variety of $\{Ru(CO)(\eta\text{-}C_5R_5)\}_2(\mu\text{-}CO)(\mu\text{-}L)$ complexes (R = H, Me), including L = CCH_2, have been given.[260]

Irradiation of **146** in MeCN resulted in displacement of CO by MeCN; addition of CH_2N_2 gave the red μ-η^3-allene complex **148** in 10% yield.[261] Details of the synthetic procedures required for these and related complexes have been given.[262]

SCHEME 58



[Ru] = Ru(CO)(η-C$_5$H$_5$)

3. Structure and Bonding

The X-ray structures of the μ-CCH_2 complexes (Table 7) show that the CH_2 group is coplanar with the M_2C unit, thereby maximizing overlap of the vinylidene π-acceptor orbital with the filled orbitals of the metal framework. An extended Huckel MO study of the diiron complex showed that three MO's of the Fe_2 framework are directed at the bridging site.[263] There are strong interactions of the vinylidene $3a_1$ and $2b_1$ orbitals with the 22a′ and 18a″ orbitals of the dimer framework (Figure 4) leading to coplanarity of the CH_2 group with the Fe_2C unit, as found in the X-ray structure of the analogous ruthenium complex.[259] The $1b_2$ orbital scarcely interacts with the dimer framework. The $\pi_\perp$ system is localized on C_α and C_β, and the C–C π-bond is relatively unaffected by coordination to the Fe_2 system. Thus, thermal reactions proceed as with the olefin, e.g. addition of CH_2, but the primary photochemical process is cleavage of the Fe–C and Fe–Fe bonds, so that in these reactions, again e.g. with CH_2, coupling occurs with the vinylidene ligand. Similarly, alkynes photochemically insert into the Fe–C bond.

The X-ray structure of **134** revealed similar C–C distances in the vinylidene moiety together with a short C–N bond, indicating contributions from tautomers **134a** and **134b** (Scheme 54).[264] Likewise, observation of two isomers of the ethoxyvinylcarbyne cation indicate restricted rotation about the C–O bond of the vinyl ether. These and related results suggest that the planar vinylcarbyne ligand remains in conjugation with the electron-deficient μ-carbyne atom throughout rotation of the vinylcarbyne ligand.[265] The solid-state structures established the coplanar arrangements and MO calculations showed that conjugation can be preserved during rotation because of the orthogonal p orbitals on the μ-carbyne carbon, which result in a low rotational barrier to the entire vinylcarbyne ligand. Alternatively, it can be considered as stabilization of a perpendicular C═C double bond by the diiron unit, as calculated earlier[185] for $Fe_2(\mu\text{-}CCH_2)(CO)_6$ (section V.A.3).

VI. Polynuclear (Cluster) Complexes Containing Vinylidene Ligands

Cluster complexes containing vinylidene ligands have been prepared by the following routes: (a) deprotona-

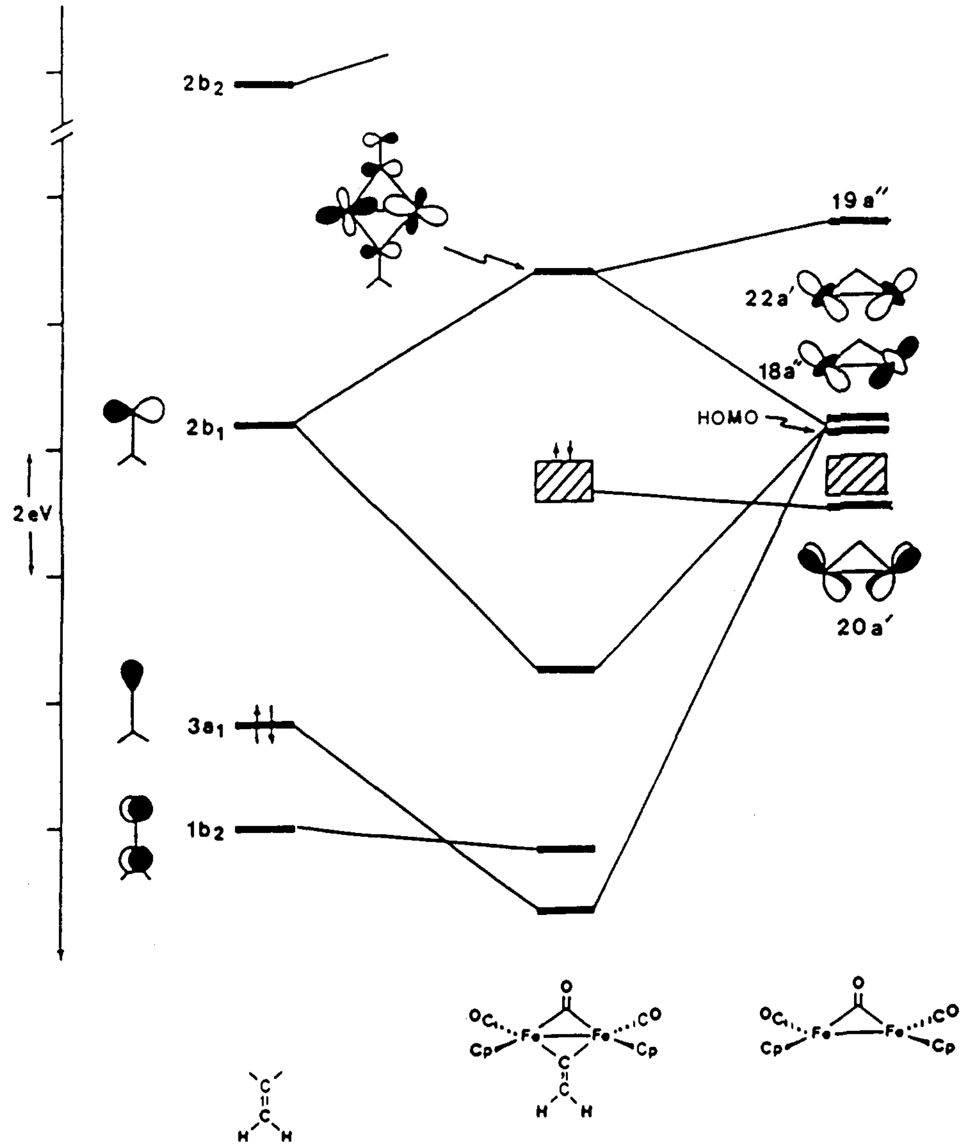
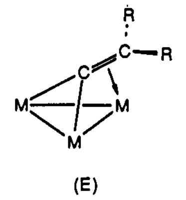
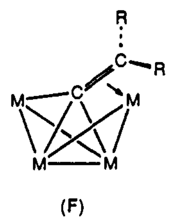


Figure 4. Molecular orbital diagram of *cis*-$\{Fe(CO)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CO)(\mu\text{-}CCH_2)$ (adapted from ref 263).

tion of a cluster-bound alkylidyne; (b) reactions of μ-CO ligands with organolithium reagents, followed by alkylation; (c) from 1-alkynes or 1-haloalkynes with cluster complexes; (d) alkylation of ketenylidene ligands; (e) reactions of mono- or binuclear vinylidene complexes with reactive metal precursors to build up the cluster. Examples of compounds containing terminal or μ-vinylidene ligands are known, but the majority of complexes contain the ligand coordinated to three (E) or four (F) metal atoms:



(E)



(F)

Tables 10 and 11 collect reported examples of cluster complexes containing vinylidene ligands together with selected NMR data. Tables 12 and 13 summarize the structural data for μ_3- and μ_4-vinylidene complexes and the metal frameworks to which they are attached.

Multi-site bonded vinylidenes are postulated on theoretical or mechanistic grounds as intermediates in the formation of alkylidynes from alkenes and alkynes adsorbed on metal surfaces (see section IX.A). Vinylidenes interacting with up to four metal atoms are conceivable intermediates in elementary processes involved in the production of hydrocarbons from simpler molecules. Nucleophilic addition to cluster-bound vinylidene would increase the number of reactions observed for these species. As the number of metal atoms increases, the electronic nature of C_α and C_β exhibits a reversal in character (umpolung), so that on a Co_3 cluster, for example, these atoms are nucleophilic and electrophilic, respectively.

A. Complexes Containing Terminal or μ-Bridging Vinylidenes

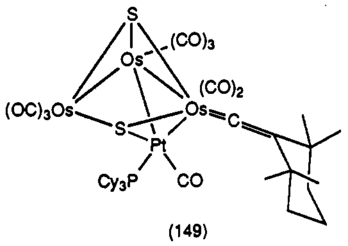
As with the binuclear iron complex **93** (section V.A.3), the sterically hindered thioketene $C_6H_6Me_4CCS$ reacts

TABLE 10. Homometallic Cluster Complexes Containing μ_3-CCRR′ Ligands

cluster	R	R′	color	$\delta(C_\alpha)$	$\delta(C_\beta)$	ref
$Fe_3(CO)_9$	OMe	CH=NCy[a]	brown	302.0	128.7	279
$Fe_3(CO)_9$	Pr^i	$OPPh_2$[a]	brown-green	264.2	145.4	278
$Fe_3(\mu\text{-}CO)(CO)_9$	H	H	green	292.3	74.5	272
$Fe_3(\mu\text{-}CO)(CO)_9$	H	H	red	250.1	75.1	275
$Fe_3(\mu\text{-}CO)(CO)_9$	H	Et	green	287.8	105.1	277
$Fe_3(\mu\text{-}CO)(CO)_9$	H	Pr	green oil	285.8	101.9	277
$Fe_3(\mu\text{-}CO)(CO)_9$	H	Bu	green oil	285.6	102.3	277
$Fe_3(\mu\text{-}CO)(CO)_9$	H	Ph	green	274.1	102.7	277
$Fe_3(\mu\text{-}CO)(CO)_9$	H	CH_2OMe	green oil	288.2	95.2	277
$Fe_3(\mu\text{-}CO)(CO)_9$	H	$SiMe_3$	brown-green oil	292.0	96.7	277
$[Fe_3(\mu\text{-}H)(CO)_9]^-$	H	H	red	254.3	72.9	271, 272
$[Fe_3(\mu\text{-}H)(CO)_9]^-NHEt_3^+$	H	H	red-brown			270
$[Fe_3(\mu\text{-}H)(CO)_9]^-PPh_4^+$	H	Pr	dark red	280.4		273
$[Fe_3(\mu\text{-}H)(CO)_9]^-PPh_4^+$	H	Ph	dark brown	278		273
$[Fe_3(\mu\text{-}H)(CO)_9]^-PPh_4^+$	H	COMe	dark brown	293.0		273
$[Fe_3(\mu\text{-}H)(CO)_9]^-PPh_4^+$	H	CO_2Me	dark red	294.0		273
$[Fe_3(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]^-PPh_4^+$	H	Bu^t	dark green	232.6		274
$Fe_3(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_6$	H	H	dark green	274	95.6	196
(*asym*, *sym* isomers)				305.7	141.3	
$Ru_3(\mu_3\text{-}CO)(CO)_9$	Me	OMe	orange-yellow	214.2	149.8	280
$Ru_3(CO)_9$	Pr^i	PPh_2[b]	green-brown	254.9	100.3	278
$[Ru_3(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_3]^+BF_4^-$	H	H	orange			284
$Os_3(\mu\text{-}H)_2(CO)_9$	H	Pr^i	yellow	201.7	103.3	294
$Os_3(\mu\text{-}H)_2(CO)_9$	H	OEt	pale yellow			290, 294
$Os_3(\mu\text{-}H)_2(CO)_9$	$-(CH_2)_3-$					295, 296
$Os_3(\mu\text{-}H)(\mu\text{-}Br)(CO)_9$	H	Ph				293
$[Co_3(CO)_9]^+FSO_3^-$	H	Pr^i		272.0	131.6	300
$[Pt_3(\mu\text{-}dppm)_3]^+PF_6^-$	H	H	yellow	252.1	86.8	303

[a] Bridges Fe–Fe bond. [b] Bridges Ru–Ru bond.

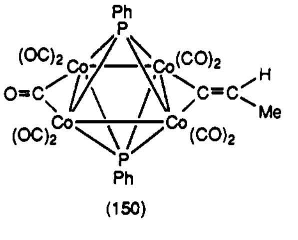
with $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$ to give red complex **149** as the major product (45%).[266] In this case, two sulfur atoms have transferred to the cluster; the initial tetrahedral Os_3Pt core has opened to a spiked triangular skeleton, the vinylidene being attached to an Os atom [Os–C, 1.90 (1); C–C, 1.29 (2) Å; Os–C–C 175 (1)°].



(149)

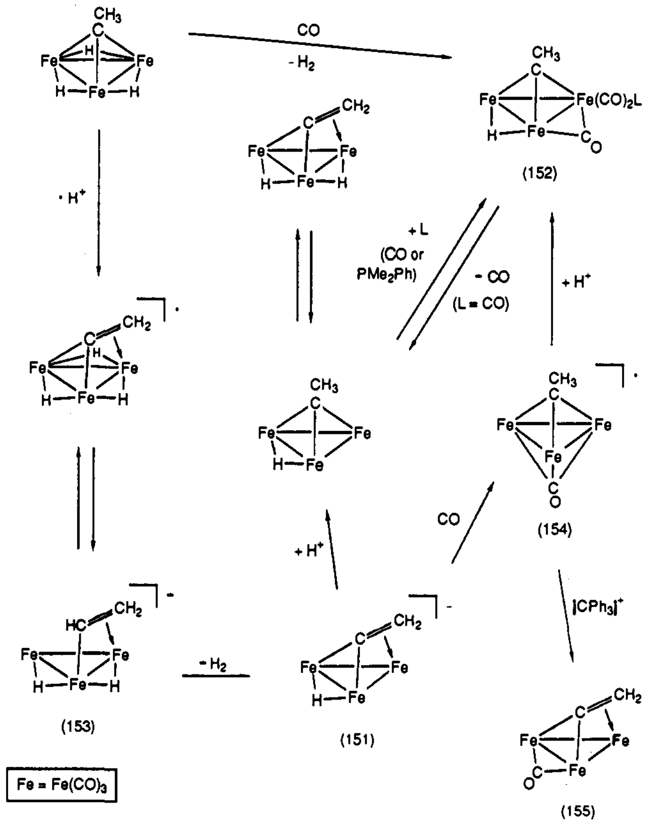
The complex $Mo\{[\mu\text{-}CCHC(O)OMe]Mn(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)_2$ (**112**) (section V.B) was obtained from $Mn\{CCH(CO_2Me)\}(CO)_2(\eta\text{-}C_5H_5)$ and excess $Mo(CO)_5(thf)$.[222]

Nucleophilic addition of LiMe to a bridging CO in $Co_4(\mu_4\text{-}PPh)(\mu\text{-}CO)_2(CO)_8$ afforded the acyl anion, which with trifluoroacetic anhydride forms the dark burgundy vinylidene complex **150**, probably via an intermediate $\mu\text{-}CMe\{OC(O)CF_3\}$ complex, which decomposed on workup with elimination of CF_3CO_2H. The CCHMe ligand bridges a Co–Co edge [Co–C, 1.928 (2); C–C 1.355 (6) Å]. This is a general reaction, for example, addition of LiBu and the anhydride gave the μ-CCHPr complex in 60% yield in a one-pot synthesis.[267] The reaction parallels the acid-induced elimination of ROH from Fischer-type carbene complexes.



(150)

SCHEME 59



B. μ_3-Vinylidenes

1. Iron

Relationships established between vinylidene, vinyl, and alkylidyne iron clusters are illustrated in Scheme

TABLE 11. **Heterometallic Cluster Complexes Containing μ_3-CCHR Ligands**

cluster	MM′[a]	R	color	ref
$Au_2Ru_3(CO)_9(PPh_3)_2$	RuRu	Bu^t	deep red	314
$CoFeMo(CO)_8(\eta\text{-}C_5H_5)$	CoMo	H	green-brown	308
$CoFeMo(CO)_8(\eta\text{-}C_5H_5)$	CoMo	Me	black	308, 316
$CoFeMo(CO)_8(\eta\text{-}C_5H_5)$	CoMo	Bu^t	brown	308
$CoFeMo(CO)_8(\eta\text{-}C_5H_5)$	CoMo	Ph	dark red	308
$CoFeNi(CO)_6(\eta\text{-}C_5H_5)$	CoNi	H	green	308
$CoFeNi(CO)_6(\eta\text{-}C_5H_5)$	CoNi	Me	black	308
$CoFeNi(CO)_6(\eta\text{-}C_5H_5)$	CoNi	Bu^t	brown	308
$CoFeNi(CO)_6(\eta\text{-}C_5H_5)$	CoNi	Ph	black	308
$CoFeW(CO)_6(\eta\text{-}C_5H_5)$	CoW	H	black	308
$CoFeW(CO)_8(\eta\text{-}C_5H_5)$	CoW	Me	black	308
$CoFeW(CO)_8(\eta\text{-}C_5H_5)$	CoW	Bu^t	black	308
$CoFeW(CO)_8(\eta\text{-}C_5H_5)$	CoW	Ph	black	308
$CoMoOs(CO)_8(\eta\text{-}C_5H_5)$	CoMo	H	red	319
$CoMoRu(CO)_8(\eta\text{-}C_5H_5)$	CoMo	H	red-brown	308
$CoMoRu(CO)_8(\eta\text{-}C_5H_5)$	CoMo	Me	red	308
$CoMoRu(CO)_8(\eta\text{-}C_5H_5)$	CoMo	Bu^t	dark red	308
$CoMoRu(CO)_8(\eta\text{-}C_5H_5)$	CoMo	Ph	orange	308
$CoNiRu(CO)_6(\eta\text{-}C_5H_5)$	CoNi	H	brown	308
$CoNiRu(CO)_6(\eta\text{-}C_5H_5)$	CoNi	Me	dark brown	308, 316
$CoNiRu(CO)_6(\eta\text{-}C_5H_5)$	CoNi	Bu^t	red-brown	308
$CoNiRu(CO)_6(\eta\text{-}C_5H_5)$	CoNi	Ph	brown	308
$CoOsW(CO)_8(\eta\text{-}C_5H_5)$	CoW	H	red	319
$CoRuW(CO)_8(\eta\text{-}C_5H_5)$	CoW	H	red	308
$CoRuW(CO)_8(\eta\text{-}C_5H_5)$	CoW	Bu^t	red	308, 316
$Co_2Fe(CO)_9$[b]	CoCo	H	brown	309
$Co_2Fe(CO)_9$	CoCo	Ph	brown	316
$Co_2Fe(CO)_9$	CoCo	$OC(O)CCo_3(CO)_9$	brown	310
$Co_2Fe(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2$	CoCo	H	black	308
$Co_2Fe(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2$	CoCo	Me	black	308
$Co_2Fe(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2$	CoCo	Bu^t	green-brown	308
$Co_2Fe(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2$	CoCo	Ph	green-brown	308
$Co_2Ru(CO)_9$	CoCo	H	red	311, 312b
$Co_2Ru(CO)_9$	CoCo	Me	bright red	312b
$Co_2Ru(CO)_9$	CoCo	Bu^t	dark red	312a
$Co_2Ru(CO)_9$	CoCo	Ph	dark red	311, 312b
$Co_2Ru(CO)_8(PMe_3)$	CoCo	H	red	320
$Co_2Ru(CO)_8(PMe_2Ph)$	CoCo	Me	red	320
$Co_2Ru(CO)_8(PMe_2Ph)$	CoCo	Ph	red	320
$Co_2Ru(CO)_7(PMe_3)_2$	CoCo	H	brown	320
$Co_2Ru(CO)_7(PMe_2Ph)_2$	CoCo	Ph	brown	320
$FeMnPt(CO)_6\{P(OPr^i)_3\}$[c]	MnPt	Ph		317
$FeNi_2(CO)_3(\eta\text{-}C_5H_5)_2$	NiNi	H	black	308
$FeNi_2(CO)_3(\eta\text{-}C_5H_5)_2$	NiNi	Me	green	308
$FeNi_2(CO)_3(\eta\text{-}C_5H_5)_2$	NiNi	Bu^t	black	308
$FeNi_2(CO)_3(\eta\text{-}C_5H_5)_2$	NiNi	Ph	black	308
$FeW_2(CO)_7(\eta\text{-}C_5H_5)_2$[d]	FeW	H	purple	306
$Fe_2Rh(\mu\text{-}CO)_2(CO)_3(PPr^i_3)(\eta\text{-}C_5H_5)$	FeFe	H	green	230
$Fe_2Rh(\mu\text{-}CO)_2(CO)_3(PPr^i_3)(\eta\text{-}C_5H_5)$	FeFe	Me	green	230
$Fe_2Rh(\mu\text{-}CO)_2(CO)_3(PPr^i_3)(\eta\text{-}C_5H_5)$	FeFe	Ph	green	230
$Re_2W_2(\mu\text{-}H)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)_2$[e]	ReW	H	red	305

[a] MM′ bond bridged by CCHR. [b] $\delta(C_\beta)$ 79.5. [c] Two isomers (1/1.5): $\delta(C_\alpha)$ 297.5, 311.8; $\delta(C_\beta)$ 92.7, 93.6. [d] $\delta(C_\alpha, C_\beta)$ 264.8, 80.7. [e] $\delta(C_\alpha, C_\beta)$ 238.7, 78.0.

59.[268,269] Deprotonation (KOAc or NEt_3) of $Fe_3(\mu\text{-}H)_3(\mu_3\text{-}CMe)(CO)_9$ gave $[Fe_3(\mu\text{-}H)(\mu_3\text{-}CCH_2)(CO)_9]^-$ (**151**) quantitatively at 25 °C. The reaction was accompanied by loss of H_2 and was reversed by addition of acid under H_2 (70%). Conversion of the trihydrido cluster to $Fe_3(\mu\text{-}H)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_9$ (**152**, L = CO) (40%) occurs in 5 h at 60 °C under CO. Addition of CO to the μ_3-CCH_2 anion was followed by migration of cluster-bound hydride to give the μ_3-CMe complex, and finally protonation to **152** (L = CO).[270] Labeling studies showed that the proton attacks the vinylidene in the anion with high selectivity (albeit with some scrambling), opening the Fe–Fe bond and allowing coordination of H_2 at the unique iron atom. Protonation/deprotonation of the alkyl group precedes addition/elimination of H_2 from the metal cluster; substituted methyl systems (Et, Pr, CH_2Ph) showed a steric effect on the reaction rate. Rapid elimination of H_2 from an intermediate with two terminal H atoms is consistent with a kinetic isotope effect favoring D_2 elimination.[269,270]

An intermediate μ-$CH{=}CH_2$ anion **153** was proposed, formed by transfer of metal-bound hydride to carbon. It can be trapped by Lewis bases, e.g. CO, to give $Fe_3(\mu\text{-}H)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_9$ (**152**, L = CO). The facile reaction of **151** with CO may proceed via an intermediate analogous to **154**; addition of PMe_2Ph to **151**, followed by protonation, gave only one isomer of **152** (L = PMe_2Ph). The reactions demonstrate the importance of the stabilization of the vacant coordination site by the $C{=}CH_2$ double bond and the nonthermal generation of intermediates which do not differ much in energy, allowing a number of competitive, consecutive reaction pathways to be available to cluster complexes.

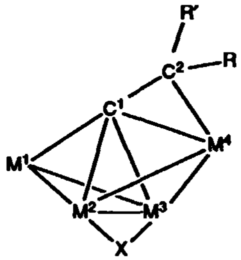
Rearrangement of $[Fe_3(\mu\text{-}CMe)(CO)_{10}]^-$, which is

TABLE 12. Some Structural Features of Cluster Complexes Containing μ_3-CCRR′ Ligands

cluster	MM′[a]	R	R′	M^1–M^2	M^1–C^1	M^2–C^1	M^3–C^1	M^3–C^2	C^1–C^2	tilt[b]	ref
(a) Homometallic											
$Fe_3(CO)_9$		OMe	CH=NCy[c]	2.675 (1)	1.939 (5)	1.823 (5)	1.981 (5)	2.458 (7)	1.391 (7)		279
$Fe_3(CO)_9$		Pr^i	$OPPh_2$[c]	2.586 (1)	1.853 (3)	1.945 (3)	1.982 (3)	2.230 (3)	1.388 (5)		278
$Fe_3(\mu\text{-}CO)(CO)_9$		H	Ph	2.562 (1)	1.917 (2)	1.909 (2)	2.009 (2)	2.288 (2)	1.378 (3)		277
$Fe_3(\mu\text{-}CO)(CO)_9$		H	H	2.547 (1)	1.877 (6)	1.901 (6)	1.966 (6)	2.194 (6)	1.399 (9)		275
$[Fe_3(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]^-PPh_4^+$		H	Bu^t	2.578 (1)	1.955 (4)	1.913 (4)	2.013 (3)	2.294 (4)	1.378 (5)		274
$Fe_3(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_6$ (*asym* isomer)		H	H	2.557 (1)	1.881 (7)	1.984 (8)	2.063 (7)	2.302 (8)	1.35 (1)	38.6	196
$Ru_3(CO)_9$		Pr^i	PPh_2[d]	2.733 (1)	1.921 (5)	2.182 (5)	2.126 (5)	2.340 (5)	1.408 (7)		278
$Ru_3(\mu_3\text{-}CO)(CO)_9$		Me	OMe	2.793 (1)	2.056 (2)	2.066 (2)	2.161 (2)	2.782 (2)	1.387 (3)	63	280
$Ru_3(\mu\text{-}H)_2(CO)_9$		Me	Ph	2.821 (1)	2.057 (5)	2.019 (6)	2.167 (4)	2.500 (4)	1.379 (8)		283
$Os_3(\mu\text{-}H)_2(CO)_9$		H	OEt	2.883 (1)	2.01 (2)	2.06 (2)	2.21 (2)	2.43 (2)	1.39 (2)		291
$Os_3(\mu\text{-}H)_2(CO)_9$		$-(CH_2)_3-$		2.897 (1)	2.05 (1)	2.09 (1)	2.21 (1)	2.40 (1)	1.38 (2)	19	296
$Os_3(\mu\text{-}H)(\mu\text{-}Br)(CO)_9$		H	Ph	2.883 (1)	2.16 (1)	2.05 (2)	2.27 (1)	2.34 (2)	1.37 (2)		293
(b) Heterometallic											
$Au_2Ru_3(CO)_9(PPh_3)_2$	RuRu	H	Bu^t	2.918 (2)	2.10 (2)	2.04 (1)	2.19 (1)	2.42 (2)	1.41 (2)		314
$CoRuW(CO)_6(\eta\text{-}C_5H_5)$	CoW	H	Bu^t	2.723 (3)	1.95 (1)	2.01 (1)	2.10 (1)	2.35 (2)	1.29 (2)	45.1	308, 316
$Co_2Fe(CO)_9$	CoCo	H	$OC(O)\text{-}CCo_3\text{-}(CO)_9$	2.490 (1)	1.856 (5)	1.868 (4)	1.983 (4)	2.221 (5)	1.362 (7)		310
$Co_2Ru(CO)_9$	CoCo	H	Bu^t	2.489 (1)	1.901 (7)	1.893 (7)	2.099 (8)	2.405 (8)	1.37 (1)	47.2	312
$Co_2Ru(CO)_9$	CoCo	H	Ph	2.513 (1)	1.93 (1)	1.92 (1)	2.07 (1)	2.40 (1)	1.25 (1)	50.2	312b
$Co_2Ru(CO)_8(PMe_2Ph)$(*Ru-P*)	CoCo	H	Me	2.491 (1)	1.88 (1)	1.87 (1)	2.13 (1)	2.36 (1)	1.39 (1)		320
$FeW_2(CO)_7(\eta\text{-}C_5H_5)_2$	WW	H	H	3.030 (1)	2.04 (1)	2.07 (2)	1.96 (2)	2.21 (2)	1.43 (3)		306
$Fe_2Rh(\mu\text{-}CO)_2(CO)_3(PPr^i_3)(\eta\text{-}C_5H_5)$	FeFe	H	H	2.558 (1), 2.552 (1)	1.858 (6), 1.869 (8)	1.927 (8), 1.932 (6)	2.183 (6), 2.166 (8)	2.219 (6), 2.212 (8)	1.37 (1), 1.36 (1)		230
$Re_2W_2(\mu\text{-}H)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)_2$	ReW	H	H	2.923 (1)	2.03 (2)	2.19 (1)	2.18 (2)	2.41 (2)	1.41 (2)		305

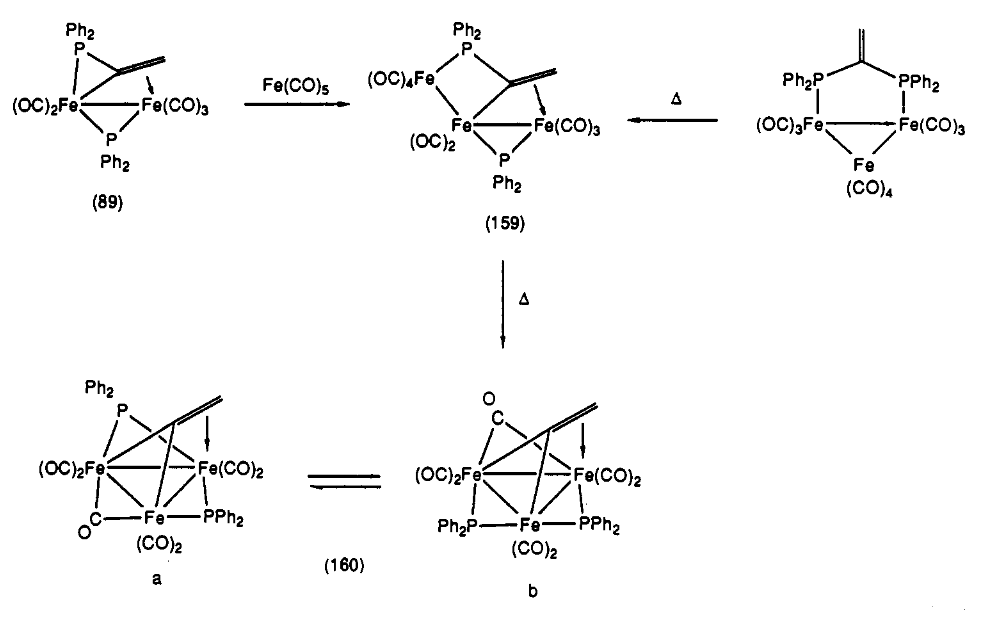
[a] MM′ bond bridged by CCHR. [b] Angle of C_α–C_β vector with M_3 plane. [c] Bridges Fe–Fe bond. [d] Bridges Ru–Ru bond.

TABLE 13. Some Structural Features of Complexes Containing μ_4-CCHR Ligands



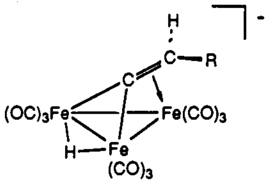
complex	M^1	$M^2M^3M^4$	R′	M^1–C^1	M^2–C^1	M^3–C^1	M^4–C^1	M^4–C^2	C^1–C^2	ref
218	Mo	$MoRe_2$	C_6H_4	2.17 (2)	2.10 (2)	2.01 (2)	2.23 (2)	2.27 (3)	1.48 (3)	328
215	$Ru(CO)_3$	$Ru(CO)_3$	PPh_2	2.175 (4)	2.014 (3)	2.162 (4)	2.187 (4)	2.175 (4)	1.436 (5)	285
216	$Os(CO)_3$	$Os(CO)_3$	Ph	2.17 (1)	2.22 (1)	2.19 (1)	2.12 (1)	2.23 (1)		326
221	$Ni(\eta\text{-}C_5H_5)$	$Ru(CO)_3$	Bu^t	1.834 (8)	2.156 (8)	2.176 (9)	2.159 (8)	2.23 (1)	1.44 (1)	374
222	Pt(dppe)	$Fe(CO)_3$	Ph	2.100 (8)	1.955 (7)	1.965 (7)	1.971 (8)	2.173 (7)	1.42 (1)	333
224	Pt(dppe)	$Ru(CO)_3$	Bu^t	2.12 (1)	2.12 (1)	2.14 (1)	2.12 (1)	2.30 (1)	1.39 (2)	334
225	Pt(dppe)	$Ru(CO)_3$	Bu^t	2.092 (6)	2.155 (7)	2.112 (7)	2.089 (6)	2.278 (7)	1.40 (1)	334

SCHEME 60



formed from $[Fe_3(\mu\text{-}H)(CO)_{11}]^-$ and ethyne at room temperature, occurs by migration of the proton to the cluster to give **151** (72%). The reaction occurs in refluxing acetone; the immediate reversal under CO is in marked contrast with the corresponding osmium system.[271] The ethylidyne anion gave green $Fe_3(\mu_3\text{-}CCH_2)(\mu\text{-}CO)(CO)_9$ (**155**) with $[CPh_3]^+$, a complex also obtained by heating $Fe_3(\mu\text{-}H)(\mu\text{-}CMe)(CO)_{10}$ in methylcyclohexane.[269] Hydrogen reacts with the anionic vinylidene cluster to give traces of ethane and ethene, together with $[Fe_3(\mu_3\text{-}COEt)(CO)_9]^-$; the neutral complex gave EtOPr by hydrogenation and coupling of the resulting two CR fragments.[272]

In acetone, alkynes reacted with $[Fe_3(\mu\text{-}H)(CO)_{11}]^-$ to give $[Fe_3(\mu\text{-}H)(\mu_3\text{-}CCHR)(CO)_9]^-$ (**156**; R = Ph, Pr, CO_2Me, COMe) as dark brown or dark red solids.



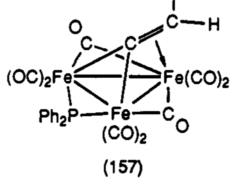
(156)

Initial formation of $[Fe_3(\mu_3\text{-}CCH_2R)(CO)_{10}]^-$ probably occurs; heating the vinylidene under CO (20 atm) gave the alkylidyne complexes, which on refluxing in acetone, reformed the vinylidenes.[273] At higher temperatures (refluxing 2-methoxyethanol), the acetylide anions $[Fe_3(\mu_3\text{-}C_2R)(CO)_9]^-$ (R = Pr, Ph) were formed, thus completing the transformation

$$RC{\equiv}CH \rightarrow RCH_2C{\equiv} \rightarrow RCH{=}C{=} \rightarrow RC{\equiv}C{-}$$

on the Fe_3 cluster, earlier demonstrated for the Ru and Os analogues.

Similarly, the reaction between $Ph_2PC_2Bu^t$ and $[PPh_4][Fe_3(\mu\text{-}H)(CO)_{11}]$ gave dark green $[PPh_4][Fe_3(\mu_3\text{-}CCHBu^t)(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$ (**157**), formed by P–C(sp) bond cleavage and H migration from the cluster.[274]

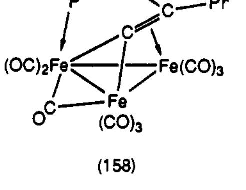


(157)

Reactions between $Fe_3(CO)_{12}$ and LiBu or LiPh, followed by $[OMe_3][BF_4]$, gave $Fe(\mu_3\text{-}CCH_2)(\mu\text{-}CO)(CO)_9$ (**155**) (2–6%); the major products were $Fe_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}$ (34%) and $Fe_3(\mu_3\text{-}COMe)_2(CO)_9$ (15%).[275] This reaction was first reported in 1975;[276] the green vinylidene complex, then described as a $\mu\text{-}C_2H_2$ complex, has now been crystallographically characterized. It probably results from the reductive dimerization of two CO groups on the cluster; this is supported by the above results, and by its formation from $Fe_3(\mu_3\text{-}COMe)_2(CO)_9$ and $Li[BHEt_3]$, followed by protonation (20%). Irradiation of **155** under H_2 gave $Fe_3(\mu\text{-}H)(\mu_3\text{-}CMe)(CO)_{10}$ and $Fe_3(\mu\text{-}H)_3(\mu_3\text{-}CMe)(CO)_9$; with *E*-cyclooctene, dark green $Fe_3(\mu_3\text{-}CCH_2)(\mu\text{-}CO)(CO)_8(C_8H_{14})$ was formed.

Reactions between 1-bromoalkynes and $[NHEt_3][Fe_3H(CO)_{11}]$ gave the vinylidenes $Fe_3(\mu_3\text{-}CCHR)(\mu\text{-}CO)(CO)_9$ (R = Ph, CH_2OMe, $SiMe_3$, Et, Pr, Bu) in 17–51% yields; no reaction was found with BrC_2Bu^t, and the complex (R = CH_2NMe_2) was thermally unstable.[277]

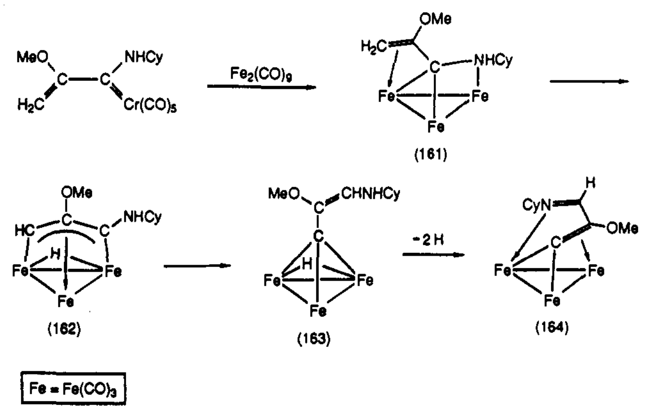
Isomerization of $Ph_2P(O)C_2Pr^i$ occurred in the reaction with $Fe_2(CO)_9$ (12 h, 24 °C) to give brown-green $Fe_3\{\mu_3\text{-}CCPr^i(OPPh_2)\}(CO)_9$ (**158**), together with the allene derivative $Fe_2\{\mu\text{-}Ph_2P(O)CH{=}C{=}CMe\}(CO)_6$.[278]



(158)

Further reaction of **89** (section V.A.3) with $Fe(CO)_5$ gave the trinuclear derivative **159**, which on heating underwent the second P–C(sp^2) bond cleavage to give

SCHEME 61



the vinylidene complex **160**.[196] In solution, this compound exists as the two isomers shown, in which the μ_3-CCH_2 group rotates around the Fe_3 core (NMR). The solid-state structure corresponds to **160b**. The stepwise fragmentation of the dppee ligand occurs more rapidly on the Fe_3 center, the conversion $Fe_3(\mu\text{-dppee})(CO)_{10} \rightarrow$ **159** $\rightarrow$ **160** (Scheme 60) being accompanied by opening and closing of the triangular Fe_3 core.

Transmetalation of the vinylcarbene ligand in $Cr\{C(NHCy)C(OMe){=}CH_2\}(CO)_5$ with $Fe_2(CO)_9$ afforded the four Fe_3 clusters **161**–**164** (Scheme 61), which are related by oxidative addition of the CH_2 group in **161** to the cluster to give **162**, a 1,3-hydrogen transfer (to give **163**) and finally loss of two hydrogens to give the vinylidene **164**.[279]

2. Ruthenium

A series of transformations has related μ_3-ketenylidene clusters to derivatives containing the μ_3-CCMe(OMe) ligand (Scheme 62),[280–282] and these reactions reflect the stabilization of vinylidenes by the $Ru_3(CO)_9$ cluster. Thus, methylation and carbonylation of the ketenylidene dianion **165** gave the acetyl anion **166**, whose NMR and structural parameters suggested a contribution from the $C{=}C(O^-)Me$ valence isomer **166b**. In solution, the equilibrium

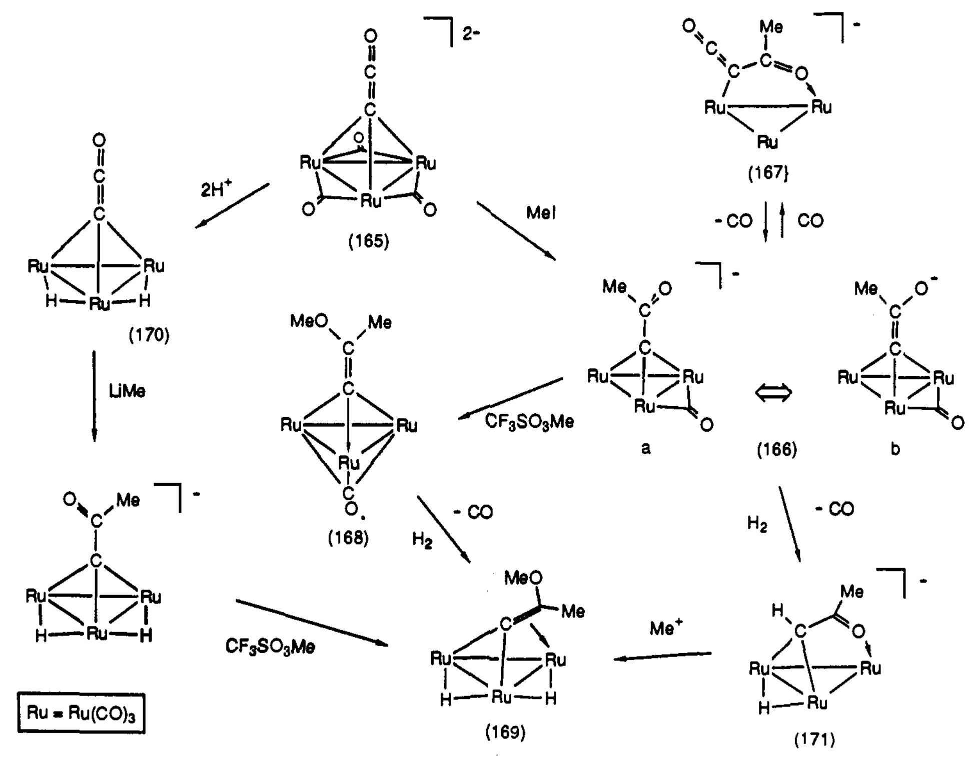
$$[Ru_3]\{\mu_3\text{-}CC(O)Me^-\} + CO \rightleftharpoons [Ru_3]\{\mu_3\text{-}C({=}C{=}O)CMe{=}O\}$$

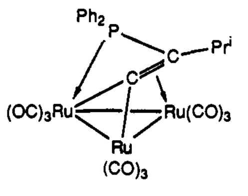
exists but the acylketenylidene **167** could not be isolated; labeling studies showed the CO added to the μ_3-CC(O)Me comes from the cluster.[281] Further methylation converted **166** to $Ru_3\{\mu_3\text{-}CCMe(OMe)\}(\mu_3\text{-}CO)(CO)_9$ (**168**). This complex contains a nearly planar capping CCR_2 group inclined at 63° to the Ru_3 plane; however, the Ru–C_β distance [2.782 (2) Å] precludes the strong bonding interaction normally found in vinylidenes of type E. An intermediate form between E and a 4e/3-center attachment probably exists. This conclusion is supported by ^{13}C NMR data, with C_α and C_β resonating at δ 214.2 and 149.8, respectively, compared with values of δ 168.7 and 192.8 found for the dihydro analogue **169**. The latter derivative was obtained by successive attack of Me^- and Me^+ on $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCO)(CO)_9$ (**170**) or by addition of H_2 to **166** (to give the μ_3-CHC(O)Me complex **171**) followed by methylation. Cleavage of the C_α-Ru(3) bond gave a μ-CCR_2 group on a 46e cluster, and the facile H_2/CO exchange suggests that this coordinatively unsaturated isomer is readily accessible.

Ready cleavage of the P–C(sp) bond in $Ru_3(CO)_{11}\{PPh_2(C_2Pr^i)\}$ occurred at 10 °C to give $Ru_3(\mu_3\text{-}C_2Pr^i)(\mu\text{-}PPh_2)(CO)_9$; after 48 h at 24 °C further alteration to greenish-brown $Ru_3\{\mu_3\text{-}CCPr^i(PPh_2)\}(CO)_9$ (**172**) had occurred, accompanied by several other binuclear and cluster complexes.[278] Isomerization of the phosphinoalkyne occurs by an oxidative addition/intramolecular reductive coupling sequence.

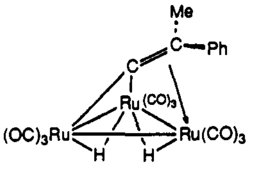
Coupling between styrene and the carbide atom in $Ru_4C(\mu\text{-}H)(CO)_{12}$ gave the yellow trinuclear complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCMePh)(CO)_9$ (**173**).[283] •

SCHEME 62



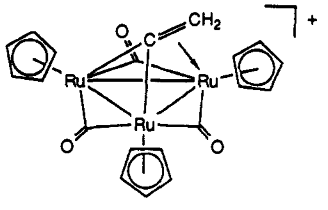


(172)



(173)

Oxidation ($AgBF_4$) of $Ru_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3$ occurred stepwise to give the mono- and dications; the latter was deprotonated to the reactive cationic vinylidene $[Ru_3(\mu_3\text{-}CCH_2)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3]^+$ (**174**). With $NaBH_4$ or LiMe, the μ_3-CMe or μ_3-CEt complexes were obtained.[284]



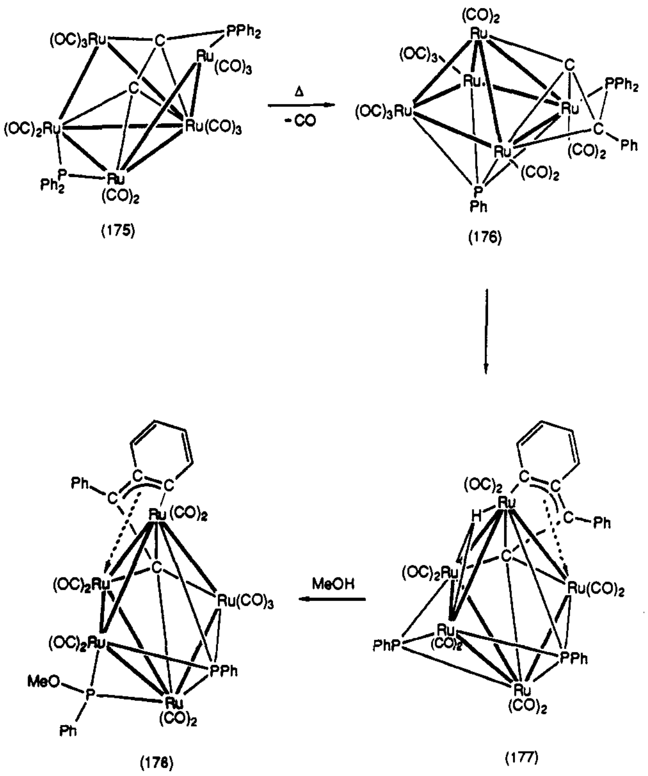
(174)

An interesting series of pentanuclear vinylidene clusters has been obtained from the phosphino-acetylide complex $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**175**) (Scheme 63). Simple heating of **175** in refluxing toluene gave **176**, containing a vinylidene ligand formed by migration of a phenyl group from the μ-PPh_2 ligand to C_β. Further alteration occurred by migration of the second PPh group to the cluster; the resulting $CCPh_2$ group was metalated concomitantly to give the μ_3-$CCPh(C_6H_4)$ ligand found in **177**. This complex reacted with MeOH to give **178**. In both cases, the C and P atoms have been incorporated into the cluster to give pentagonal bipyramidal C_2PRu_5 skeletons.[286]

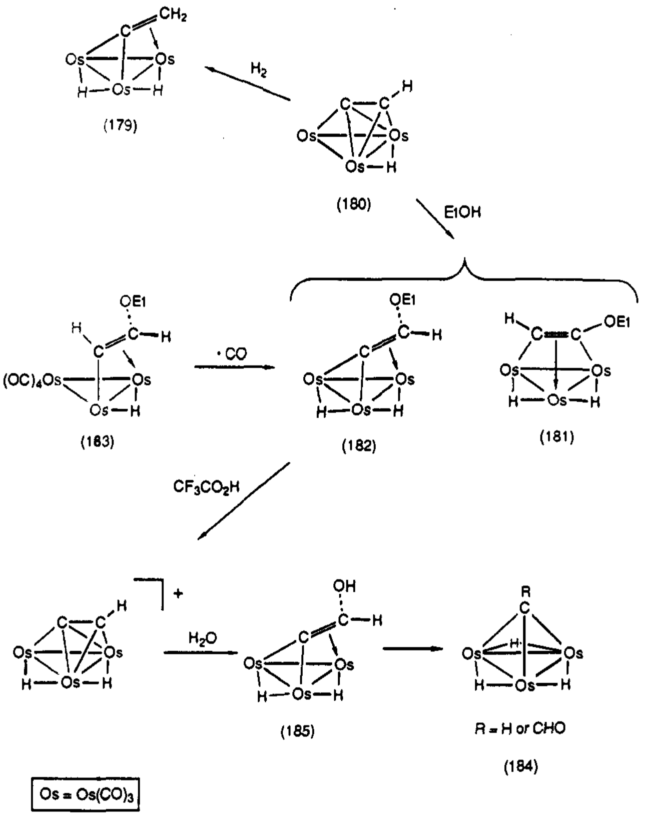
3. Osmium

Early work showed that the vinylidene $Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCH_2)(CO)_9$ (**179**; Scheme 64) could be obtained from **180** by hydrogenation and from related μ_3-CMe and μ-CH=CH$_2$ complexes by pyrolysis.[287,288] Deprotonation of **179** gave the anion $[Os_3(\mu\text{-}H)(\mu_3\text{-}CCH_2)(CO)_9]^-$, isolated as the [ppn]$^+$ salt. For **179**, ^{1}H NMR spin-lattice relaxation studies showed that the T_1 times are determined by efficient dipolar interactions with nearby ^{1}H nuclei in an intramolecular process; no difference in T_1 for the different hydrido resonances was found: both have a T_1 of 4.3 s at 20 °C.[289]

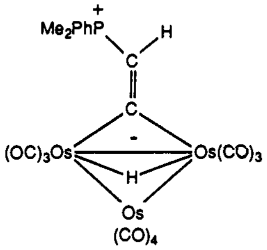
SCHEME 63



SCHEME 64

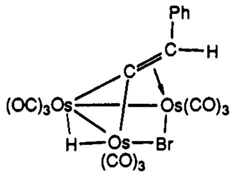


Several other vinylidene complexes have been obtained from **179**.[290,291] Thus, addition of EtOH proceeds mainly (78%) at C_α to give **181** (as with pyridine, NH_3, or $NHEt_2$) but also afforded 21% $Os_3(\mu\text{-}H)_2\{\mu_3\text{-}CCH(OEt)\}(CO)_9$ (**182**). Thermal decarbonylation of **183** gave 67% of **182** and 7% of **181**. The μ_3-CCH(OEt) ligand is asymmetrically bonded to the Os_3 cluster; the ^{1}H NMR spectrum shows the presence of two isomers (by H position) which undergo intramolecular conversion. Rapid enantiomerization also occurs at a similar rate, probably by rotation of the vinylidene on the cluster (ΔG ca. 47 kJ mol^{-1}). Addition of CF_3CO_2H to **182** gave $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_2H)(CO)_9]^+$, which reacted with water to give $Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_9$ (**184**, R = H). In the presence of acid, the μ_3-formylmethylidyne cluster **184** (R = CHO) was also formed, probably by rearrangement of the hydroxyvinylidene **185**.[291] The methyl analogue of complex **182** was obtained as a minor product in the reaction between $Os_3(\mu\text{-}H)_2(CO)_{10}$ and neat $MeOCH{=}CH_2$, being formed by C–O bond cleavage; the major product is $Os_3(\mu\text{-}H)\{\mu\text{-}CHMe(OMe)\}(CO)_{10}$, an alkyl stabilized by O coordination and obtained as a mixture of two isomers.[292] The vinylidene is the major product from the reaction in thf at 90 °C and is also formed with other products when the alkyl is heated in hydrocarbon solvents. Reactions between PMe_2Ph and $Os_3(\mu_3\text{-}HC_2H)(CO)_9$ or $Os_3(\mu\text{-}H)(\mu\text{-}C_2Ph)(CO)_{10}$ gave the yellow zwitterionic vinylidenes **186** (R = H, Ph), the tertiary phosphine adding to C_β. The H and $CCR(PMe_2Ph)$ ligands bridge an Os–Os edge [Os–Os 2.802 (1), Os–C 2.096, 2.103 (10), C–C 1.356 (13) Å].[293]



(186)

The hydrido–vinylidene complex **187** was prepared by decarbonylation and rearrangement of $Os_3(\mu\text{-}Br)(\mu\text{-}CH{=}CHPh)(CO)_{10}$ in refluxing toluene.[294] The open Os_3 cluster has the nonbonded Os–Os vector bridged by the vinylidene and halogen moieties. As with **182** hydride migration between the two Os–Os bonds occurs. Under hydrogen, $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CCH_2Ph)(CO)_9$ was formed, while with C_2Ph_2, dehydrogenation to $Os_3(\mu\text{-}Br)(\mu_3\text{-}C_2Ph)(CO)_9$ occurred. These reactions demonstrate stepwise dehydrogenation of vinyl to vinylidene and acetylide.



(187)

Pyrolysis of the μ-carbyne complex **188**, obtained from $Os_3(\mu\text{-}H)_2(CO)_{10}$ and 3,3-dimethylcyclopropene, afforded a mixture of the vinylidene **189** and vinyl **190** (Scheme 65).[295] Reaction occurs via H transfer first to the carbyne C atom to give the intermediate vinyl derivative, and then to the cluster on prolonged heating to give up to 59% of **189**, together with 31% of **190**, and 10% of $Os_3(\mu\text{-}H)_2(CO)_{10}$; **189** was obtained directly from **188** by photolysis (87%). Two geometric isomers of **189** did not interconvert at room temperature in solution. The overall sequence μ-carbyne → μ-vinyl → μ-vinylidene is a model for hydrocarbon rearrangements on metal surfaces.

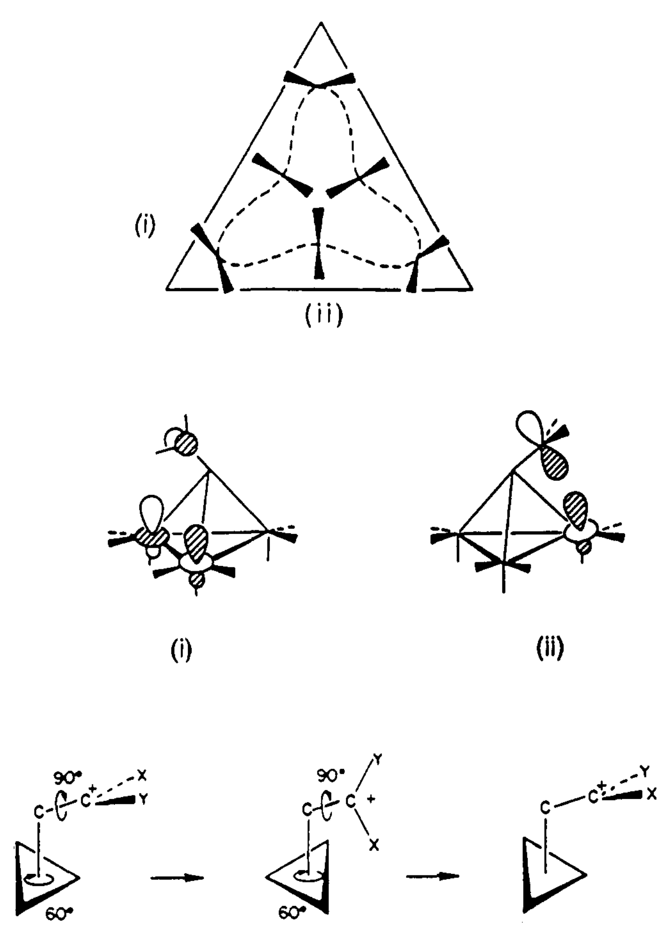
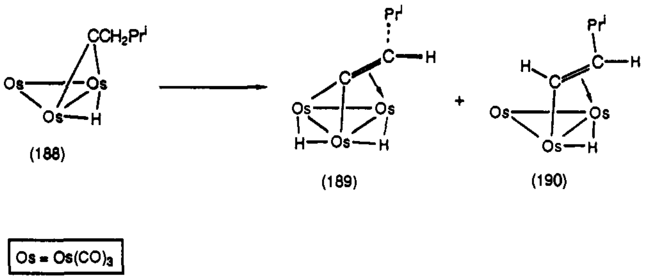
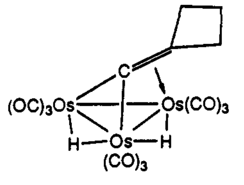


Figure 5. Conformations of $[Co_3(\mu_3\text{-}CCHR)(CO)_9]^+$, showing stationary points, i and ii, and rotation of CCHR group during isomerization (from refs 300 and 301).

SCHEME 65



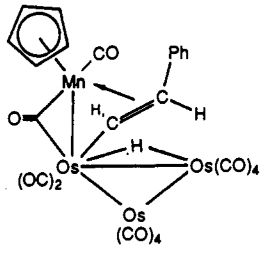
Methylenecyclobutane reacted with $Os_3(CO)_{12}$ to give the vinylidene **191** by oxidative addition of the methylene C–H bonds to the cluster.[296] Protonation afforded the trihydride, for which the single proton resonance showed two sets of $J(^1H\text{–}^{187}Os)$ coupling constants, consistent with the carbenium ion structure and rapid rotation of the tilted vinylidene ligand around the cluster.[296a,297]



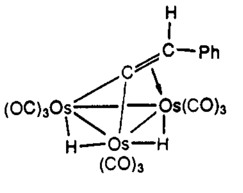
(191)

The reaction between $Mn(CCHPh)(CO)_2(\eta\text{-}C_5H_5)$ and $Os_3(\mu\text{-}H)_2(CO)_{10}$ gave as the major product dark red

$MnOs_3(\mu\text{-H})(\mu\text{-CH=CHPh})(CO)_{12}(\eta\text{-}C_5H_5)$ (**192**), isolated in 60% yield. Rapid decomposition in octane (120 °C/1 h) to $Os_3(\mu\text{-H})_2(\mu_3\text{-CCHPh})(CO)_9$ (**193**), $Os_3(\mu\text{-H})(\mu\text{-CH=CHPh})(CO)_{10}$, and $Os_3(\mu\text{-H})_2(\mu_3\text{-HC}_2\text{Ph})(CO)_9$ occurred.[298,299]



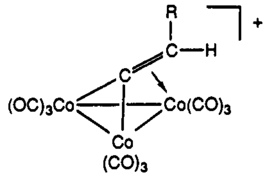
(192)



(193)

4. Cobalt

High-field ^{13}C NMR studies of $[Co_3(\mu_3\text{-CCHR})(CO)_9]^+$ suggested a structure in which the vinylidene ligand bends over one of the metal atoms; diastereotopic Me groups in the $\mu_3\text{-CCHPr}^i$ complex **194** confirm this finding, and unambiguously exclude the upright position.[300] Complex **194** was obtained by protonation of $Co_3(\mu_3\text{-CCH=CMe}_2)(CO)_9$ with FSO_3H. At −65 °C, the Me resonance is split into two peaks (ΔG^* 43.9 (4) kJ mol^{-1} at coalescence, −52 °C). Theoretical calculations have shown that there are two stationary points i and ii (Figure 5); the former has C^+ bending toward the Co with the σ-plane bisecting the H–C–H angle, while the latter has the CH_2 bending toward the Co–Co bond and lying in the σ-plane.[301] The ground state is i, isomerization occurring via ii, a saddle-point. The NMR results are consistent with i being the most stable. The cation is viewed as a bevel gear system which is electronically driven. The gearing is by a disrotatory controlled rotation about two axes via ii, so that the C^+ interacts with the metal framework.[302]



(194)

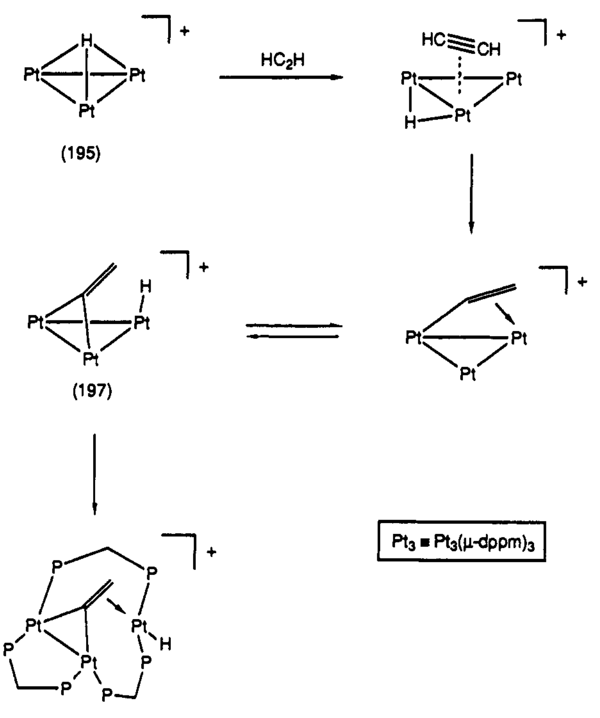
5. Platinum

Modeling of reactions on a Pt(111) surface has been achieved with the cluster $[Pt_3(\mu_3\text{-H})(\mu\text{-dppm})_3]^+$ (**195**) (Scheme 66). With C_2H_2 at −80 °C, an adduct was obtained in which the bonding of the ethyne was not fully defined; the ethyne is probably weakly bound and fluxional. Attempted isolation of this complex gave instead the vinylidene **196**, a 46e cluster.[303] A detailed study using ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR with HC≡CH, $H^{13}C{\equiv}^{13}CH$, and DC≡CD was carried out. H/D scrambling is consistent with the processes

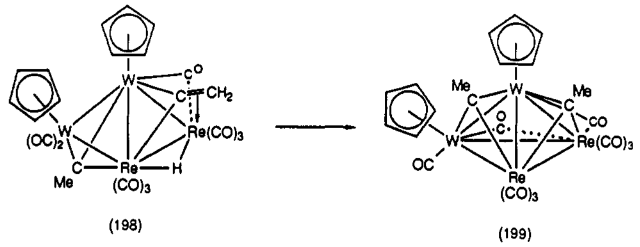
$$Pt_3(CH{=}CH_2) \rightleftharpoons Pt_3H(CCH_2) \rightleftharpoons Pt_3(CCH_3)$$

although the latter complex is not formed by isomerization of the vinylidene, as found on the surface. Excess ethyne reacted with **195** to give $[Pt_3(\mu_3\text{-C}_2H_2)(\mu\text{-CH=CH}_2)(\mu\text{-dppm})_3]^+$, in which H–H scrambling occurs within the vinyl group but not the ethyne.[304] This process, which is proposed to occur via a short-lived $\mu\text{-CCH}_2$ intermediate **197**, is closely related to processes occurring during chemisorption of ethyne on the Pt(111) surface (section IX.A). Stoichiometric amounts of ethyne reacted with the Pt_3 cluster to give **196**, although this complex failed to react with excess ethyne. It was thought that a rapid equilibration occurs via the sequence shown in Scheme 66.

SCHEME 66



SCHEME 67

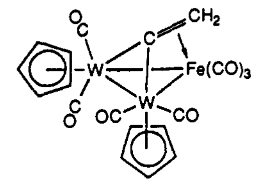


6. Heterometallic Complexes

(*a*) *Bimetallic Derivatives.* The red 62e cluster $W_2Re_2(\mu_3\text{-CCH}_2)(\mu_3\text{-CMe})(\mu\text{-CO})(CO)_8(\eta\text{-}C_5H_5)_2$ (**198**) is one of the products from the reaction between $W({\equiv}CMe)(CO)_2(\eta\text{-}C_5H_5)$ and $Re_2(\mu\text{-H})(\mu\text{-CH=CHBu})(CO)_8$. The metal core is nearly planar, with the vinylidene attached to the WRe_2 triangle.[305] A second product is brown $W_2Re_2(\mu_3\text{-CMe})(\mu\text{-CO})_2(CO)_7(\eta\text{-}C_5H_5)_2$ (**199**), related to **198** by an H-atom shift from the cluster framework to the vinylidene C_β; partial rearrangement occurs on heating **198** in thf. The proposed mechanism of formation of **198** is shown in Scheme 67.

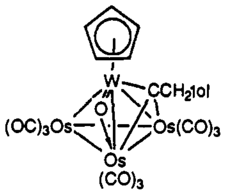
The purple FeW_2 cluster **200** was obtained as the major product (18%) from the reaction between $W({\equiv}CMe)(CO)_2(\eta\text{-}C_5H_5)$ and $Fe_2W(\mu_3\text{-CC}_6H_4Me\text{-}p)(CO)_9(\eta\text{-}C_5H_5)$; the products included two other FeW_2 clusters with μ-CR and $\mu\text{-C}_2R_2$ (R = $C_6H_4Me\text{-}p$) ligands. The vinylidene ligand in **200** is derived from the CMe group.

Coordination to Fe lengthens the C=C double bond to 1.43 (3) Å.[306]

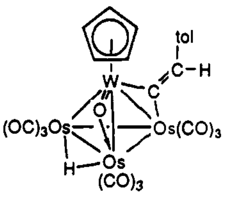


(200)

The Os_3W oxo cluster **201** is converted into the vinylidene **202** by heating in refluxing toluene under N_2.[307] The reaction may proceed via a 4e → 2e → 4e transformation of the μ-oxo group, which allows oxidative addition of the C–H bond to the cluster.

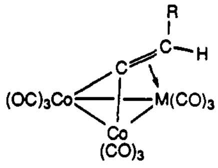


(201)

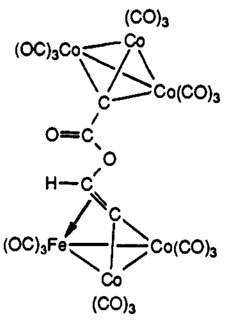


(202)

Many cobalt–iron μ_3-vinylidene clusters **203** have been obtained from $Co_2(\mu\text{-}HC_2R)(CO)_6$ (R = H, Me, Bu^t, Ph) and $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$; in general, the μ_3-alkyne complex was formed first, but isomerized on heating.[308] The parent vinylidene cluster, $Co_2Fe(\mu_3\text{-}CCH_2)(CO)_9$, was formed in refluxing thf.



(203) M = Fe
(205) M = Ru



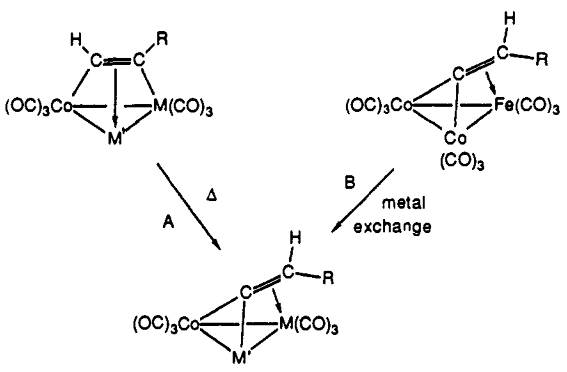
(204)

The reaction between $[PPh_4][Fe_2(\mu\text{-}CH{=}CH_2)(CO)_7]$ and $Co_2(CO)_8$ gave a mixture of $[PPh_4][Co_2Fe(\mu_3\text{-}CMe)(CO)_9]$ and $CoFe(\mu\text{-}CH{=}CH_2)(CO)_7$. In refluxing hexane, the latter is converted to $Co_3(\mu_3\text{-}CMe)(CO)_9$ and the brown vinylidene cluster $Co_2Fe(\mu\text{-}CCH_2)(CO)_9$, in which C_α bridges the two cobalt atoms while the C=C bonds to the iron.[309] A third product is brown $CoFe_2(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_9$. In this reaction, conversion of the vinyl ligand to vinylidene and CMe is a function of the stabilization of these ligands by Co_2Fe and $CoFe_2$ cores, respectively.

The major product **204** from the reaction between $[PPh_4][FeH(CO)_4]$ and $[Co_3(\mu_3\text{-}CCO)(CO)_9][PF_6]$ results from coupling of the latter with $[Co_2Fe(\mu_3\text{-}CCHO)(CO)_9]^-$, formed in situ by hydride addition and metal exchange in $[Co_3(\mu_3\text{-}CCO)(CO)_9]^-$; attack of the aldehydic oxygen on C_β of the μ_3-CCO ligand has direct analogues in its organic chemistry.[326] In **204**, the two cluster cores are joined by the vinylidene ester ligand μ_3-CCH{OC(O)C}.

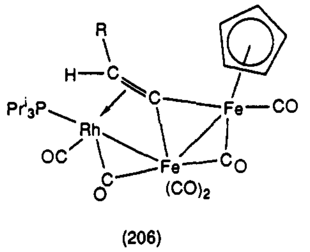
Reactions between $Co_2Ru(CO)_{11}$ and HC_2R (R = H, Me, Bu^t, Ph) gave the μ_3-alkyne complexes as the first product (90%) at 5–15 °C, which rearranged in boiling hexane (hours) to the red μ_3-vinylidene complexes **205** (80%).[311,312] Both complexes were characterized crystallographically for R = Bu^t, from which it could be seen that the conversion is associated with a gradual inclination of the C=C bond with respect to the M_3 plane. There is a slight extension of the C–C bond from 1.34 to 1.37 Å. In contrast with the μ_3-alkyne complexes, the vinylidenes have static structures, with C_α bridging the Co–Co bond and the C=C double bond being attached asymmetrically to Ru.

SCHEME 68

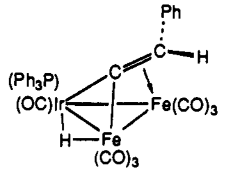


Roule	R	Me	M'	Composition
A	Me	Ru	Ni(η·C_5H_5)	1/1
A	Bu^1	Ru	Ni(η·C_5H_5)	1/1
A	Bu^1	Ru	$Mo(CO)_2$(η·C_5H_5)	1
A	Bu^t	Ru	$W(CO)_2$(η·C_5H_5)	1
B	Me	Fe	Ni(η·C_5H_5)	1/1
B	Ph	Fe	Ni(η-C_5H_5)	1/1
B	Bu^i	Fe	Ni(η-C_5H_5)	1/1
B	Me	Fe	$Mo(CO)_2$(η·C_5H_5)	1/3·1/4
B	Ph	Fe	$Mo(CO)_2$(η·C_5H_5)	1/3·1/4
B	Bu^1	Fe	$Mo(CO)_2$(η·C_5H_5)	1
B	Me	Fe	$W(CO)_2$(η·C_5H_5)	1/3·1/4
B	Ph	Fe	$W(CO)_2$(η·C_5H_5)	1/3·1/4
B	Bu^1	Fe	$W(CO)_2$(η·C_5H_5)	1

Small quantities of the Fe_2Rh clusters **206** (R = H, Me, Ph) were obtained from $Rh(CCHR)(PPr^i_3)(\eta\text{-}C_5H_5)$ and $Fe_2(CO)_9$; the η-C_5H_5 group had transferred from Rh to Fe.[230] The iridium–iron cluster $Fe_2Ir(\mu_3\text{-}C_2Ph)(CO)_8(PPh_3)$ was converted to the hydrido–alkyne complex by H_2 or $K[BHBu^s_3]/H_3PO_4$; heating in refluxing toluene (1.5 h) resulted in isomerization to the hydrido–vinylidene $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}CCHPh)(CO)_8(PPh_3)$ (**207**).[313]



(206)



(207)

The reaction between $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ and $[\{Au(PPh_3)\}_3O]^+$ gave complexes containing $AuRu_3$ (9%), Au_2Ru_3 (16%), and Au_3Ru_3 (3%) clusters. The second of these contains a trigonal-bipyramidal core with a μ_3-C=CHBu^t ligand **208**.[314] In contrast the

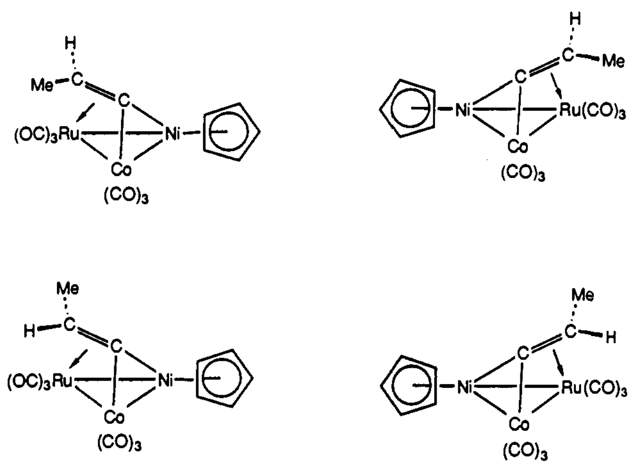
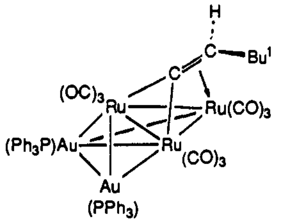


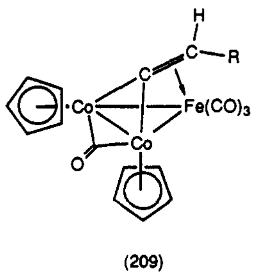
Figure 6. Isomers of $CoNiRu(\mu_3\text{-}CCHMe)(CO)_6(\eta\text{-}C_5H_5)$.

complex obtained from H_2 contains a $\mu_3\text{-}HC_2Bu^t$ ligand.[315]



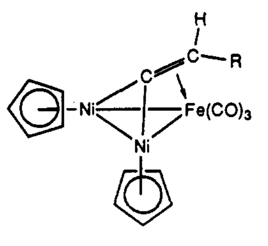
(208)

(*b*) *Trimetallic Complexes.* Few diastereoselective transformations have been accomplished on metal cluster complexes. For this reason, the transformations of bimetallic to trimetallic μ_3-vinylidene clusters by metal-exchange reactions are of interest. Complexes **203** and **205** readily enter into these reactions and many complexes containing CoFeM or CoRuM (M = Mo, W, Ni) cores have been prepared by Vahrenkamp and coworkers (Scheme 68).[308,316] For M = $Ni(\eta\text{-}C_5H_5)$, the impure vinylidene was obtained from the μ_3-alkyne for R = H and Me; the Bu^t complex was better obtained from the Co_2Ru-vinylidene. In the CoMoRu series, metal exchange was followed by ligand rearrangement, although CoMoRu–alkyne complexes could also be obtained from the vinylidene precursor. In the Co_2Fe series, vinylidene complexes were best obtained from vinylidene precursors; the FeCoNi–CCH_2 derivative could not be obtained pure. The higher lability of **203** resulted in transfer of $\eta\text{-}C_5H_5$ groups (to give **209**) or double exchange (to give **210**) in reactions with $Ni(\eta\text{-}C_5H_5)$ precursors.



(209)

R = H, Me, Bu^t, Ph

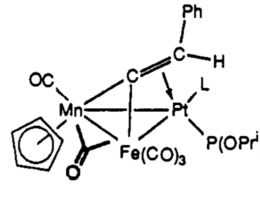


(210)

R = H, Me, Bu^t, Ph

These trimetallic clusters are chiral and isomeric possibilities are shown in Figure 6; the μ_3-vinylidene ligand has two chiral centers (C_α and C_β) and isomerization of the μ_3-alkyne may afford two isomers. The observed stereoselectivity (by NMR) in the metal-exchange and isomerization reactions ranged from 0 to 100%. The molecular structure of the derivative with the bulkiest groups (Bu^t and W) showed minimal steric hindrance (between Bu^t and C_5H_5 hydrogens), suggesting that the observed stereoselectivity is not steric in origin, although the influence of other factors (kinetic, electronic) is not clear.

The reaction between $Fe_2(CO)_9$ and $MnPt(\mu\text{-}CCHPh)(CO)_2\{P(OPr^i)_3\}_2(\eta\text{-}C_5H_5)$ (**116**) afforded the trimetallic derivative **211**.[317] Two isomers were formed;



(211)

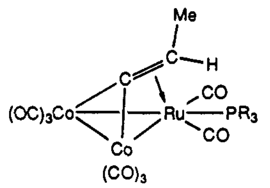
L = CO, $P(OPr^i)_3$

a 14 ppm difference in C_α chemical shifts suggests that this atom may bridge the Mn–Fe and Mn–Pt bonds in the two isomers.

7. Reactivity of μ_3-Vinylidene Clusters

The conversion of μ_3-alkylidyne complexes to μ_3-vinylidenes by loss of H_2 has been found to occur spontaneously for $Co_2Fe(\mu\text{-}H)(\mu_3\text{-}CMe)(CO)_9$ and, in the presence of acid, for $Fe_3(\mu\text{-}H)(\mu_3\text{-}CMe)(CO)_9$; some metal exchange reactions of $Co_3(\mu_3\text{-}CCH_2R)(CO)_9$ have also given μ_3-vinylidene complexes. Hydrogenation of $Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCH_2)(CO)_9$ to $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CMe)(CO)_9$ was reported as long ago as 1973.[318] A survey of the reactivity of heterometallic clusters in this reaction showed that, while the relative stabilities of the HC_2R, CCHR and CCH_2R ligands vary, the vinylidene is the most stable on trinuclear clusters.[319] Thus for Co_2Ru, the μ_3-CMe complex is unknown and is unstable on the Co_2Fe cluster. Both $\mu_3\text{-}CCH_2$ and μ_3-CMe ligands are found for CoFeMo and CoRuM (M = Mo, W), the equilibrium for the CoMoRu derivatives being sensitive to H_2 pressure.

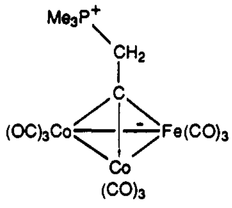
Substitution of CO by PR_3 in $Co_2Ru(\mu_3\text{-}CCHR')(CO)_9$ is kinetically controlled at Co, but thermally induced migration of the phosphine gave the more stable isomer **212**. This isomerization occurs less readily down the series PMe_3 > PMe_2Ph > $PMePh_2$ > PPh_3.[320] The Ru-substituted complexes were also obtained by isomerization of the corresponding μ_3-alkyne derivatives. Complexes **212** were formed as 1/1 isomeric mixtures with alternative conformations of the CCHR′ ligand.



(212)

C_β in cluster-bound vinylidenes is highly electrophilic, particularly in the cation $[Co_3(\mu_3\text{-}CCH_2)(CO)_9]^+$, in accord with the formulation as a cluster-stabilized carbonium ion.[321] The isoelectronic neutral Co_2Fe-

(μ_3-CCH_2)$(CO)_9$ is considerably less reactive toward nucleophiles. However, addition of PMe_3 to C_β below 0 °C gave zwitterionic **213**, isosteric with Co_3(μ_3-CCH_2SiMe_3)$(CO)_9$, in a reaction which competes with CO substitution at Co.[322] The latter reaction predominates at elevated temperatures. Increasing the bulkiness of the tertiary phosphine has the same effect, the adduct being increasingly labile with PMe_2Ph and $PMePh_2$, and not formed at all with PPh_3. The corresponding Co_2Ru complex reacts by CO substitution alone.



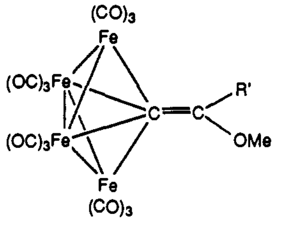
(213)

C. μ_4-Vinylidenes

1. Homometallic Complexes

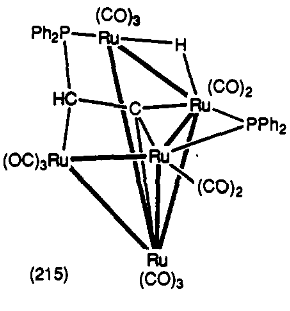
The hypothetical complex Fe_4(μ_4-CCH_2)$(CO)_{12}$ has been studied by molecular graphics in a survey which considered the steric effects of C(sp^2)- and C(sp^3)-bonded substituents to the cluster carbon atom.[323] It was concluded that the latter would have considerable interaction with the CO groups on Fe, the CCH_3 derivative lying 50 kT higher than $C{=}CH_2$, for example. It is significant that all derivatives of the Fe_4C system isolated so far contain C(sp^2).

Oxidation of the anion $[Fe_4C(CO)_{12}]^{2-}$ with Ag^+ afforded $Fe_4C(CO)_{13}$, which under CO gives Fe_4(μ_4-CCO)$(CO)_{12}$; in the absence of other reagents, Ag^+ oxidation affords Fe_3(μ_3-CCO)$(CO)_9$.[324] Addition of Li[$BHEt_3$], alcohols, or secondary amines to $Fe_4C(CO)_{13}$ afforded the anions $[Fe_4\{\mu_4\text{-}CC(O)R'\}(CO)_{12}]^-$ (R′ = H, OR, or NHR, respectively), while alkyl halides and the dianion $[Fe_4C(CO)_{12}]^{2-}$ gave $[Fe_4\{\mu_4\text{-}CC(O)R'\}(CO)_{12}]^-$.[325] Further alkylation ($[Me_3O]^+$) of these anions produced the neutral vinylidenes $Fe_4\{\mu_4\text{-}CCR'(OMe)\}(CO)_{12}$ (**214**).



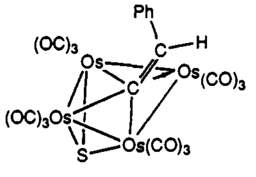
(214)

Addition of H_2 to **175** initially gave **215** containing the μ_5-$CCHPPh_2$ ligand.[285] Further stepwise addition resulted in conversion to the μ_4-CCH_2PPh_2 alkylidyne and finally cleavage of the C_α–C_β bond to give a cluster carbide and $PMePh_2$.

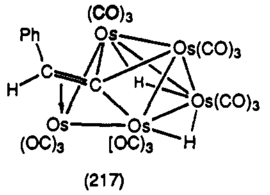


(215)

Phenylethyne reacted with Os_4(μ_3-S)$(CO)_{12}$ in hexane at 55–60 °C over 12 h to give the complexes Os_4(μ_4-CCHPh)(μ_3-S)$(CO)_{12}$ (**216**, 46%) and Os_4(μ_4-η^3-$SCPh{=}CH_2$)$(CO)_{12}$ (27%), which are not interconvertible.[326] In **216**, the vinylidene ligand is on the opposite side of the Os_4 rhombus to the sulfur. The analogous reaction with HC_2CO_2Me gave only the vinylidene complex. One of the two major products from the reaction between phenylethyne and Os_5(μ-H)$_2$$(CO)_{15}$ is the yellow μ_4-vinylidene **217**, in which the Os_5 cluster has the wing-tip bridged butterfly conformation.[327]



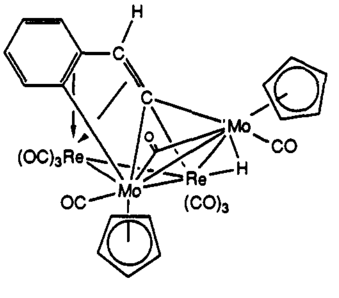
(216)



(217)

2. Heterometallic Complexes

The reaction between Re_2(μ-H)(μ-C_2Ph)$(CO)_8$ and $\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2$ gave black-green Mo_2Re_2(μ-H)$\{\mu_4\text{-}CCH(C_6H_4)\}$($\mu$-CO)$(CO)_7$($\eta$-$C_5H_5$)$_2$ (**218**), formed by decarbonylation and isomerization of the initially formed Mo_2Re_2(μ_4-HC_2Ph)(μ-CO)$_2$$(CO)_8$($\eta$-$C_5H_5$)$_2$.[328] Unusually, the phenyl group has been cyclometalated during the reaction.

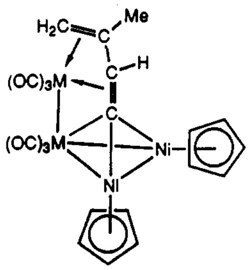


(218)

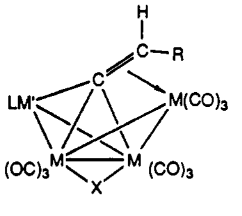
Reaction of $[Fe_3(\mu_3\text{-}CMe)(\mu_3\text{-}CO)(CO)_9]^-$ and $\{RhCl(CO)_2\}_2$ in the presence of $TlBF_4$ gave an anion which was protonated to the green tetranuclear complex **219** (Chart 1); a higher yield (26%) was obtained from $[Fe_3(\mu\text{-}H)(\mu\text{-}CCH_2)(CO)_9]^-$. The phenylvinylidene afforded the analogous Fe_3Rh complex in 84% yield, while the anion was isolated as the $[PPh_4]^+$ salt in 50% yield.[329] Tested as catalysts, no specific activity was associated with the iron over that found for $Rh_4(CO)_{12}$ in hydroformylation, whereas the iron "poisoned" the rhodium in attempted hydrogenation of olefins, isomerization being favored.

The complexes $M_2Ni_2\{\mu_4\text{-}CCH(CMe{=}CH_2)\}(CO)_6(\eta\text{-}C_5H_5)_2$ (**220**; Chart 1) have been prepared from Ni_2(μ-$HC_2CMe{=}CH_2$)(η-C_5H_5)$_2$ and $M_3(CO)_{12}$ (M = Fe,[330] Ru[331]); the isomeric μ_4-alkyne–iron derivative was also obtained, while the $NiRu_3$ complex **221** was also formed in the reaction with $Ru_3(CO)_{12}$. Complexes **220**, with the unsaturated side chain coordinated to the M atom, can also be considered as allylic alkylidyne derivatives. The $NiRu_3$ complex **221** reacts with olefins to give several products including species formed by coupling

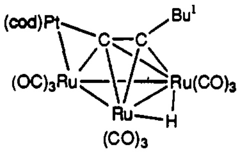
CHART 1



(220) M = Fe, Ru



	M	M'L	X	R
(219)	Fe	$Rh(CO)_2$	H	H, Ph
(221)	Ru	$Ni(\eta\text{-}C_5H_5)$	H	Bu^t
(222)	Fe	Pt(dppe)		Ph
(224)	Ru	Pt(dppe)		Bu^t



(223)

of the $=CHBu^t$ group with $=CRR'$ derived from the olefins ("olefin metathesis") and of the $C=CHBu^t$ moiety with $=CH_2$.[332] Products are also obtained from oligomerization (with or without dehydrogenation), C–C bond cleavage, and hydrogenolysis reactions, but none are formed by addition of the vinylidene across a C=C double bond.

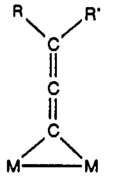
Treatment of $MnPt(\mu\text{-}CCHPh)(\mu\text{-}CO)(CO)(dppe)(\eta\text{-}C_5H_5)$ with $Fe_2(CO)_9$ gave the Fe_3Pt complex **222** in 91% yield, in which the attachment of the vinylidene ligand to the cluster is unusually asymmetric; the Mn fragment was found as $Mn(CO)_3(\eta\text{-}C_5H_5)$ (58%).[333]

Isomeric orange hydrido–alkynyl (30%) and red vinylidene (63%) complexes were obtained from $PtRu_3(\mu\text{-}H)(\mu_4\text{-}C_2Bu^t)(CO)_9(cod)$ (**223**) and dppe.[334] Facile reversible isomerization of the acetylide to the vinylidene (**224**) occurred, with a first-order rate constant, *k*, of 1.8×10^{-3} min^{-1}. The reaction is an intramolecular H migration, with concomitant conversion of the core from spiked-triangular to butterfly. The facile conversion, when compared with several stable hydrido–alkynyl complexes, was explained in terms of electron donation by the ligands ($\mu_{3,4}$-alkynyl, 5, vs μ-η^2-alkynyl, 3; $\mu_{3,4}$-vinylidene, 4, vs μ-η^2-vinylidene, 2), so that the $\mu_{3,4} \rightarrow \mu_{3,4}$ (or $\mu \rightarrow \mu$) conversion involves a formal loss of 2e, to be recouped by M–M bond formation (addition of a 2e ligand does not appear to be effective). Protonation ($HBF_4 \cdot Et_2O$) of **224** gave $[PtRu_3(\mu\text{-}H)(\mu_4\text{-}CCHBu^t)(CO)_9(dppe)]^+$ in which the hydride bridges the hinge Ru(1)–Ru(2) bond; in the latter barriers to CO exchange are higher than those in **224**. In contrast, protonation of **223** occurred at C_α to give the μ_4-HC_2Bu^t complex.

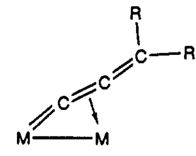
VII. Allenylidene Complexes

The previous review[2] described several complexes containing CCCRR' ligands, usually obtained by elimination of water or alcohols from intermediate carbene or vinylidene complexes or by deoxygenation of propargylate anions. This aspect of unsaturated carbene chemistry has been explored relatively little. Table 14 summarizes the allenylidene complexes which have been described during the period of this review.

Whereas mononuclear complexes contain an approximately linear MCCC unit, with the two C_γ substituents predicted to take up a configuration orthogonal to that of related vinylidene complexes, binuclear complexes may contain the unsaturated carbene bridging in two modes, μ-σ,σ (2e) (G) or μ-σ,η^2 (4e) (H) (side-on):



(G)



(H)

Some structural details of mono- and binuclear allenylidene complexes are given in Table 15.

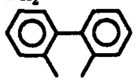
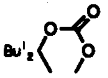
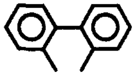
A. Synthesis

Reactions between deprotonated $HC_2CR_2(OH)$ ($R_2 = Ph_2$, 2,2'-biphenylyl) and $M(CO)_6$ (M = Cr, W) gave $[M(C{\equiv}CCR_2O)(CO)_5]^{2-}$ which was deoxygenated with $COCl_2$ to deep blue $M(CCCR_2)(CO)_5$. These complexes are thermally unstable; the tungsten derivatives rearrange in solution to red binuclear $W_2(\mu\text{-}CCCR_2O)(CO)_{10}$. The C_3 ligand is characterized by ν(CCC) at ca. 1925 (terminal) or 1370 cm^{-1} (bridging).[335]

Addition of $LiC{\equiv}CCMe{=}CH_2$ to $\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2$ (M = Mo, W) gave a separable mixture of dark green $M_2(\mu\text{-}\sigma,\eta^2\text{-}CCCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2$ (**225**) (Scheme 69) and $M_2(\mu\text{-}HC_2CMe{=}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2$.[178] The allenylidene was obtained in 50% yield and was formed by protonation of an anionic intermediate on the alumina column. Site exchange occurs slowly with this complex, in contrast with the side-on coordinated vinylidene complexes mentioned above (section V.A.1). The X-ray structure of the Mo complex showed that the Mo–C distances were shorter than those found in the vinylidene. The C_3 fragment is kinked [angles at C_α 167.2 (2), C_β 144.5 (3)°]. The ^{13}C NMR spectra contained resonances at δ 287.7 or 260.2 (C_α for Mo and W), 149.4 or 146.1 (C_β), and 148.9 or 145.6 (C_γ).

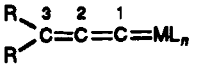
Details of the synthesis of $Mn(CCCBu^t_2)(CO)_2(\eta\text{-}C_5H_5)$ (90%) from the reaction of $Mn(\eta^2\text{-}HC_2CO_2Me)(CO)_2(\eta\text{-}C_5H_5)$ with $LiBu^t$, followed by treatment of the resulting $Li_2[Mn\{C_2CBu^t_2(O)\}(CO)_2(\eta\text{-}C_5H_5)]$ with $COCl_2$ have been given.[336] Manganese and rhenium allenylidene complexes were prepared from $M_2(CO)_{10}$ either by reaction with $[C_2CBu^t_2O]^{2-}$ directly to give the intermediate carbene complex, or by reaction of the $M_2(CO)_9(NMe_3)$ (from the carbonyl and Me_3NO) with the acetylenic dianion.[337] The re-

TABLE 14. Allenylidene Complexes

ML_n		R_2	color	$\delta(C_\alpha, C_\beta, C_\gamma)$	ν(CCC)	ref
		(a) Mononuclear				
$Cr(CO)_5$		Pr^i_2	red		1933	143
$Cr(CO)_5$		Bu^t_2	dark red		1930	143
$Cr(CO)_5$		Ph_2	deep blue		1930	335
$Cr(CO)_5$			red-violet		1920	335
$W(CO)_5$		Pr^i_2	red		1933	143
$W(CO)_5$		Bu^t_2	dark red		1925	143
$W(CO)_5$		Ph_2	blue		1920	335
$Mn(CO)_2(\eta\text{-}C_5H_5)$		Cy_2				342
$Re_2(CO)_9$		Bu^t_2	red-brown		1927	338
$Fe(CO)_4$		Bu^t_2	black	257.6, 189.2, 171.5	1924	339
$Fe(CO)_4$			black	243.4, 151.5, 131.0	1961	339
$[Ru(PMe_3)_2(\eta\text{-}C_5H_5)]^+PF_6^-$		Ph_2	orange-brown	295.8, 216.0, 153.8	1926	340
$[RuCl(PMe_3)(\eta\text{-}C_6Me_6)]^+PF_6^-$		Ph_2	violet		1940	341
		(b) Binuclear				
$Mo(CO)_2(\eta\text{-}C_5H_5)$		Me_2[a]	dark green	287.7, 149.4, 148.9		178
$W(CO)_5$		Ph_2	red		1866	335
$W(CO)_5$			red		1879	335
$W(CO)_2(\eta\text{-}C_5H_5)$		Me_2[a]	dark green	260.2, 146.1, 145.6		178
$Mn(CO)_4$	CO	Bu^t_2	red		1907, 1848	338
$Mn(CO)_2(\eta\text{-}C_5H_5)$		Ph_2		339.3, 105.9, 204.1		223
$Fe(CO)_4$		Bu^t_2	red	201.6, 145.5, 128.8	1886	339
$Fe(CO)(\eta\text{-}C_5H_5)$	CO, dppm	$(CN)_2$	green	176.0, 199.3, 40.4	1835	257
$Fe(CO)(\eta\text{-}C_5H_5)$	CO, dppe	$(CN)_2$	green	173.1, 201.2, 39.5	1837	257
$Mn(CO)_2(\eta\text{-}C_5H_5)$ $Fe(CO)_4$		Ph_2	violet	333.3, 106.6, 201.1		223

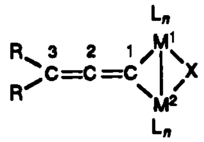
[a] $\mu\text{-}\sigma,\eta^2\text{-}CCCMe_2$.

TABLE 15. Structual Features of Allenylidene Complexes



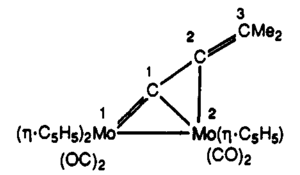
$R_2C^3{=}C^2{=}C^1{=}ML_n$

ML_n	R	$M\text{-}C^1$	$C^1\text{-}C^2$	$C^2\text{-}C^3$	MC^1C^2	$C^1C^2C^3$	ref
$Mn(CO)_2(\eta\text{-}C_5H_5)$	Cy	1.806 (6)	1.252 (8)	1.342 (8)			342
$Fe(CO)_4$	$\text{-}CBu^t_2OC(O)O\text{-}$	1.803 (5)	1.255 (6)	1.315 (6)	177.9 (5)	177.2 (5)	339
$[Ru(PMe_3)_2(\eta\text{-}C_5H_5)]^+PF_6^-$	Ph	1.884 (5)	1.255 (8)	1.329 (9)	175.9 (5)	175.1 (7)	340



ML_n	μ-X	R	$M^1\text{-}M^2$	$M^1\text{-}C^1$	$M^2\text{-}C^1$	$C^1\text{-}C^2$	$C^2\text{-}C^3$	$C^1C^2C^3$	ref
$W(CO)_5$		Ph	3.15 (6)	2.19 (4)	2.22 (4)	1.28 (4)	1.32 (4)	177 (2)	335
$Mn(CO)_4$	CO	Bu^t	2.739 (2)	2.06 (1)	2.06 (1)	1.27 (2)	1.39 (2)	178.4 (9)	338
$Fe(\eta\text{-}C_5H_5)$	CO, dppe	CN	2.515 (1)	1.916 (6)	1.937 (6)	1.258 (5)	1.345 (6)	173.8 (5)	257

sulting binuclear anionic complexes (Scheme 70) were treated with $COCl_2$ to give **226** or **227** in low yields.



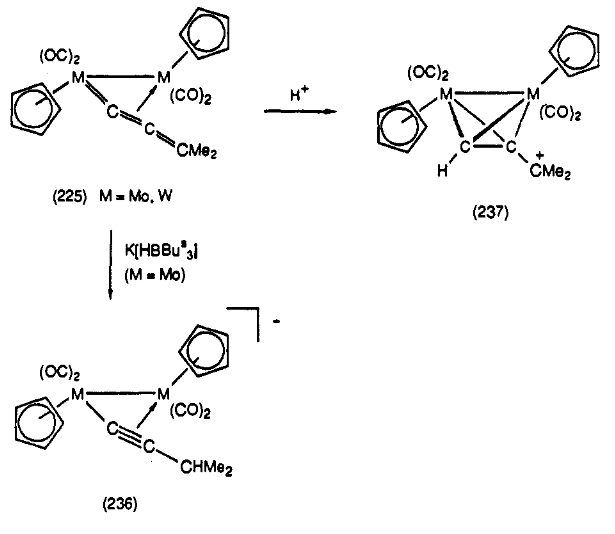
(226)

$Mo^1\cdot Mo^2$	3.145(1)	$C^1\text{-}C^2$	1.336(3)
$Mo^1\text{-}C^1$	1.912(3)	$C^1\text{-}C^2$	1.348(4)
$Mo^2\text{-}C^1$	2.209(3)	MoC^1C^2	167.2(2)
$Mo^2\text{-}C^2$	2.240(3)	$C^1C^2C^3$	144.5(3)

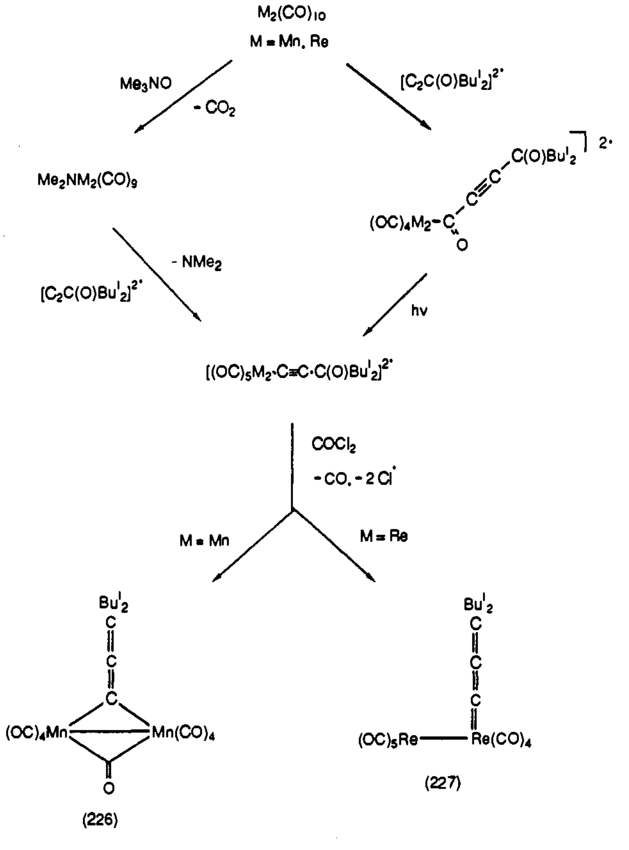
The major products are the acetylides $M(C_2CBu^t_2OH)(CO)_5$, also obtained directly from $MCl(CO)_5$, and the lithio derivative. The unusual difference in structure between the manganese and rhenium complexes is attributed to the heavier metal forming stronger bonds to terminal carbene and CO ligands.

Similar reactions with $Fe(CO)_5$ afforded a series of mono- and polynuclear allenylidene complexes (Scheme 71).[338] Those containing the $CCCBu^t_2$ ligand are formed from the mononuclear complex **228** by successive addition of $Fe(CO)_4$ moieties, and the red binuclear derivative **229** was also formed by reaction of $Fe(CCCBu^t_2)(CO)_4$ with $Fe_2(CO)_9$. The black trinuclear complex **230** shows an interesting equilibrium between

SCHEME 69

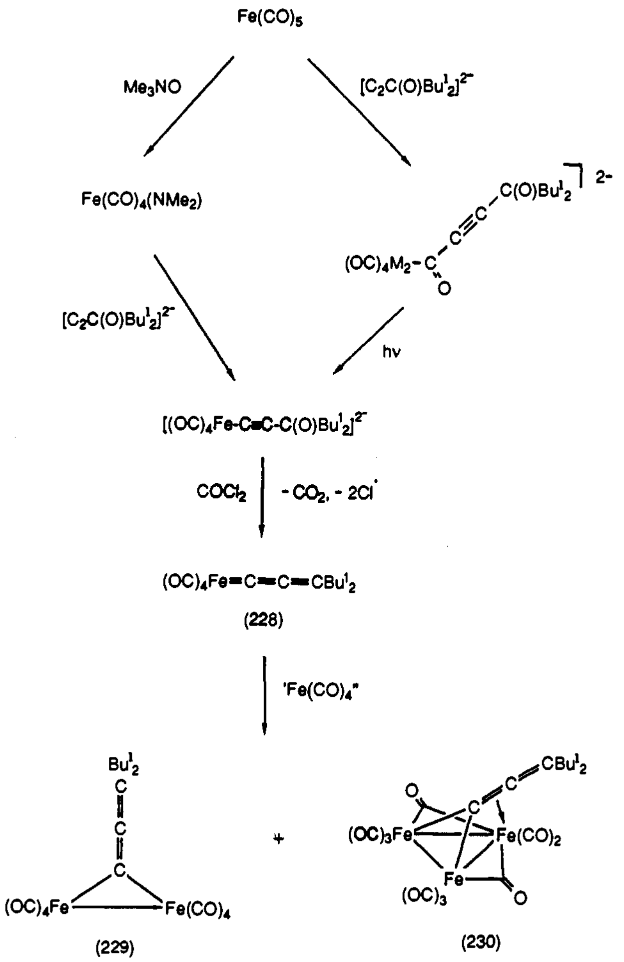


SCHEME 70

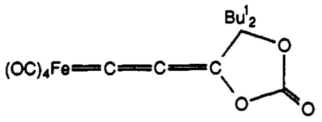


μ_2- and μ_3-CCCBu$^t_2$ ligands, with concomitant change of a μ-CO group to a terminal position. Also isolated was **231** containing the 2-oxo-1,3-dioxolan-4-ylidene ligand, which was formed by an intramolecular cyclization of the intermediate alkynylacyl complex. The crystal structure shows that the carbene occupies an equatorial coordination site, in agreement with its strong π-acceptor powers; the Fe–C distance is 1.803 Å.

SCHEME 71



Reactions between {Fe(η-C_5H_5)}$_2$(μ-CCH_2)(μ-CO)(μ-PP) (PP = dppe, dppm) and tcne gave the μ-CCH{C(CN)=C(CN)$_2$} complexes (section V.C.2) and green {Fe(η-C_5H_5)}$_2${μ-CCC(CN)$_2$}(μ-CO)(μ-PP) (**232**).[257] The C=C=C system has short (1.258 Å) and normal (1.345 Å) C=C bonds, the former involving the μ-C atom. The unusual conversion of CCH_2 to an allenylidene occurs with elimination of $CH_2(CN)_2$.



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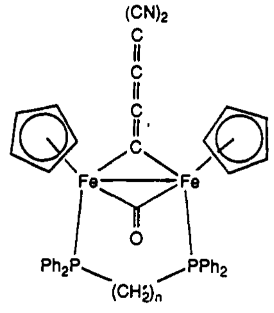
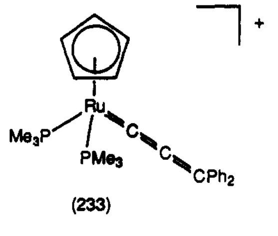


(232) n = 1, 2

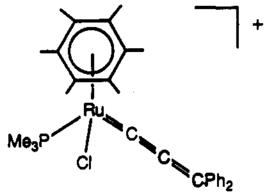
The hydroxy-alkyne $HC_2CPh_2(OH)$ reacted with RuCl(PMe_3)$_2$(η-C_5H_5) to give **233** in 76% yield by dehydration of an intermediate vinylidene complex.[339]



(233)

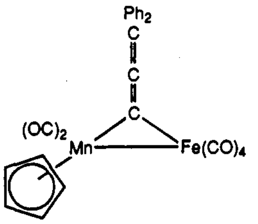
The related Fe(dppe)(μ-C_5H_5) acetylide also undergoes a spontaneous dehydration. The ligand is essentially linear and undergoes rapid rotation; in the solid state, the CPh_2 group lies approximately (dihedral 10.6°) in the plane which contains Ru, C_α, and the midpoint of the C_5 ring, as predicted. It is as good a π-acid as CO, but weaker than CCH_2. In the ^{13}C NMR spectrum, C_α, C_β, and C_γ are found at δ 195.8, 216.0, and 153.8 ppm, respectively.

The reactions of $RuCl_2(PMe_3)(\eta$-$C_6Me_6)$ with $HC_2CR_2(OH)$ in MeOH in the presence of NH_4PF_6 gave $[RuCl\{C(OMe)CH_2CH_2OMe\}(PMe_3)(\eta\text{-}C_6Me_6)]^+$ (for R = H) or $[RuCl\{C(OMe)CH{=}CR_2\}(PMe_3)(\eta\text{-}C_6Me_6)]^+$ [for R = Me, Ph; $R_2 = (CH_2)_5$], via the corresponding allenylidene intermediates.[340] The 1-methoxyethyl cation was also prepared from HC_2CH_2X (X = Cl, OMe) in similar reactions. The violet $CCCPh_2$ cation **234** was isolated after short reaction times (69% after 20 min); the high reactivity of the arene–ruthenium complex again contrasts with that of the corresponding cyclopentadienyl species.



(234)

The violet binuclear heterometallic complex **235** was obtained from $Fe_2(CO)_9$ and $Mn(CCCPh_2)(CO)_2(\eta$-$C_5H_5)$.[223]



(235)

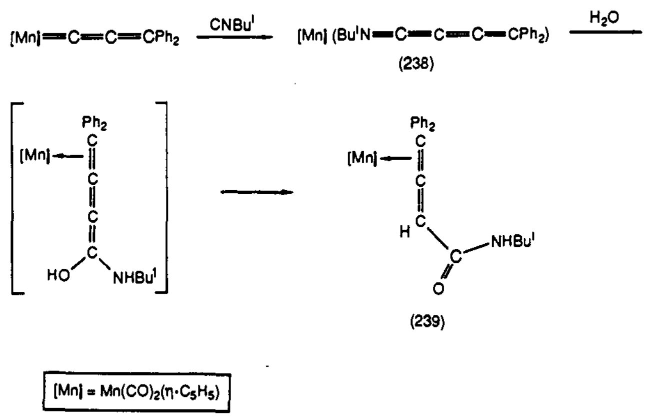
B. Reactivity

MO calculations on $Mn(CCCPh_2)(CO)_2(\eta$-$C_5H_5)$ showed that C_α and C_γ are electrophilic centers and that C_β is nucleophilic; experimentally, it is found that hard bases (such as MeO^-, Me_2N^-) add to C_α and soft bases (PR_3) to C_γ.[107,341,342] The methoxyvinyl complex is more stable than the phosphine ylid. The μ-σ,η^2 (4e) allenylidene **226** undergoes nucleophilic attack at C_γ and electrophilic attack at C_α.

Treatment of **225** (Scheme 69) with $K[BHBu^s_3]$ in tetrahydrofuran at −78 °C gave an anion **236** identical with that obtained from LiC_2Pr^i and $\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2$,[343] i.e. kinetically controlled regioselective attack on C_γ occurs. Both Mo and W allenylidenes were protonated at C_α with $HBF_4{\cdot}OEt_2$ to give $[M_2(\mu\text{-}HC_2CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]^+$ (**237**); these complexes were also obtained directly by protonation of $M_2(\mu\text{-}HC_2CMe{=}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2$. The cations are isolobal with the cationic propargyl–$Co_2(CO)_6$ and $Co_3(\mu_3\text{-}CCH_2)(CO)_9$ complexes.

Protonation of $Mn(CCCR_2)(CO)_2(\eta$-$C_5H_5)$ (R = Bu^t, Ph) with HX (X = Cl, BF_4, CF_3SO_3) gave the orange cationic vinylcarbyne complexes $[Mn({\equiv}CCH{=}CR_2)(CO)_2(\eta\text{-}C_5H_5)]^+$; the electrophile has added to C_β. The very short Mn–C bond found in the phenyl complex indicates some contribution from the Mn=C=CH-C^+Ph_2 canonical form.[182] The earlier report[341] of addition of PR_3 to C_γ of the manganese complexes (R = Bu^t, Ph) has been corrected by X-ray characterization of $Mn\{C(PPh_3)CCPh_2\}(CO)_2(\eta\text{-}C_5H_5)$;[130] this finding is in accord with the similar reaction of $Cr(CCCPr^i_2)(CO)_5$.[143]

SCHEME 72



Insertion of $CNBu^t$ into the Mn–C_α bond of $Mn(CCCPh_2)(CO)_2(\eta$-$C_5H_5)$ proceeds more slowly than for the vinylidenes (section IV.D.3) to give an intermediate cumulenimine complex **238** (Scheme 72).[125] This was treated with water to give the η^2-allene complex **239**, formed by rearrangement of the η^2-butatriene (not isolated).

VIII. Isomerization of 1-Alkynes to Vinylidenes on Metal Centers

Two possible mechanisms for the isomerization of 1-alkynes to vinylidenes on metal centers have been considered: (i) oxidative addition of the 1-alkyne to the metal center to give a hydrido–alkynyl complex, which then isomerizes by a 1,3-hydrogen shift from the metal to C_β; and (ii) approach of the metal to C_α while the hydrogen atom concomitantly bends down and then toward C_β, a pathway which was first indicated by extended Huckel MO studies. It seems likely that both mechanisms may operate, dependent on the nature of the metal and associated ligands.

The alkyne–vinylidene rearrangement is promoted by an unfavorable 4e-2-center d_π–π conflict in d^6 complexes because octahedral d^6 complexes have no vacant d orbitals.[36] The dominant π-acceptor orbital on C_α thus finds filled d orbitals of similar energy and extension in all orientations. The isomerization is rarely observed in d^4 complexes[37] which, like the d^2 configuration, favor the formation of η^2-alkyne complexes. The alkyne is a better ligand for high oxidation state metal complexes with vacant metal d_π orbitals.

An important contribution to this discussion was the paper by Silvestre and Hoffmann,[344] who performed extended Huckel MO calculations to define the 1,2-hydrogen shift. They noted that the reaction has been reported under mild conditions for mono- and polynuclear complexes, but not for binuclears. The transition-state geometry was optimized, and for ethyne, the

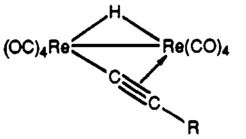
E_a of 318 kJ mol^{-1} is overestimated by ca. 1.0 eV. As negative charge builds up on C_β, positive charge develops on C_α, so that the hydrogen migrates as a proton.

A. Mononuclear Systems

In mononuclear systems, interaction of the alkyne or vinylidene involves forward donation from filled π_σ and σ orbitals with the metal 3a′ level, and back-donation from the metal a″ orbital to π_σ^* (C_2H_2) or $\pi_\parallel^*$ (CCH_2). On coordination the thermodynamic stabilities of acetylene and vinylidene are reversed (by 146 kJ mol^{-1}). The more electronegative transition metals form the more stable vinylidene complexes.

The synchronous interconversion has E_a 230 kJ mol^{-1}: the concerted 1,2-shift is not efficiently catalyzed by the metal. Following the organic analogy of the conversion of corner-protonated cyclopropene to a methylvinyl cation isomer, the isomerization is considered to involve an η^1-alkyne complex, i.e. there is slippage prior to the hydrogen shift. The η^1-isomer is ca. 37.5 kJ mol^{-1} above the η^2-isomer, but the E_a is only ca. 121 kJ mol^{-1}. Figure 7 shows the topology of the change and includes the transition state for addition of H^+ to MC_2R; at all stages there is substantial electron density on the metal. There is a difference in speed of movement of ML_n and of H* around C_α, with a slight tendency for H to join to the metal rather than to C_α; distortion of the M–C_α–C_β backbone ultimately leads to the oxidative addition product, but no symmetrical M–H–C systems develop.

Calculations of electron density changes indicate that donor groups near C_β would stabilize the η^1-alkyne geometry; the off-center slippage is similar to nucleophilic addition to an η^2-olefin complex. The CCH_2 unit is stabilized even in the transition state. By the isolobal analogy, the H can be replaced by $AuPR_3$, $Mn(CO)_2(\eta\text{-}C_5H_5)$, or SnR_3; if an M–M bond is present, the μ-σ,π-alkynyl-Re_2 complexes **240**, which interconvert σ and π bridging modes, also provide an analogy. The effect of ligands is such that while electronegative weak σ-donors push a_1 down, they also stabilize the η^2-alkyne complex; enhanced π-acceptor ligands should send the d_{yz} orbital down in energy.

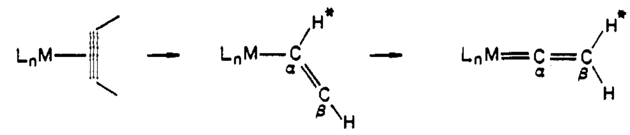


(240)

The alternative pathway of oxidative addition to give a hydrido–alkynyl complex, followed by a 1,3-shift of hydrogen to C_β was considered. This requires bending of the metal acetylide; calculations show that the energy expenditure to promote migration from the metal to C_β is prohibitive. The examples known (from Werner's work, see above, section IV.A.1) are rather slow and presumably proceed in a nonconcerted fashion.

B. Binuclear Systems

In a model binuclear Pt system, the μ-vinylidene is 21 kJ mol^{-1} above the μ-2σ-HC_2H isomer; while the two types of complex are well known, the isomerization is energetically unlikely. Dihaloalkynes have been reported to give binuclear vinylidene complexes, but no intermediate η^2-alkyne complexes were detected.[345]



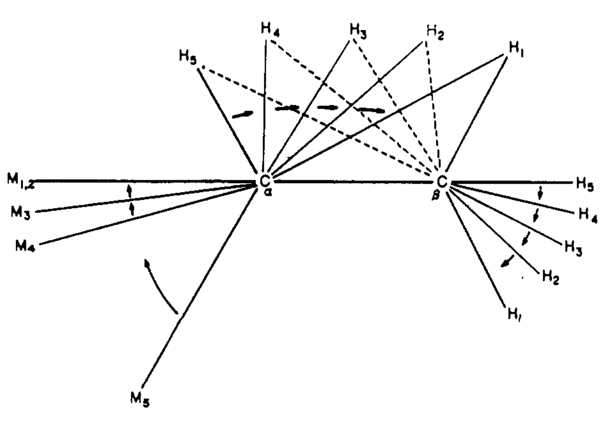


Figure 7. Calculated trajectories of H shift and M–C bending during isomerization of C_2H_2 to CCH_2 at a metal center (reprinted from ref 344; copyright 1985 Verlag Helvetica Chimica Acta).

The formation of binuclear vinylidene complexes usually occurs via the combination of mononuclear vinylidenes with organometallic fragments in the reaction mixture. The formation of a binuclear vinylidene from a hydrido–acetylide complex appears to be more feasible. This is equivalent to a [2 + 2]-addition, or the insertion of the C=C into the M–H bond. Several examples are known in the platinum series (see sections V.A.5 and V.B). This reaction probably proceeds via coordination of the alkynyl to the metal bearing the hydride, followed by 1,2-addition of the M–H bond across the C≡C bond, and formation of a M–M bond by donation of an electron pair from d^{10} Pt to d^8 Pt. The polarization requires a weak donor on Pt_1 and a strong σ-donor trans to C_α on Pt_2.

C. Trinuclear Systems

For trinuclear systems, the energy of transition state (route a, Figure 8) is very high because of the loss of the strong interaction resulting from two electrons entering an M–M antibonding orbital. An alternative mechanism (route b) involves rotation of the alkyne to bisect the M–M bond, oxidative addition of the C–H bond to the cluster, pivoting of the acetylide, and migration of H to C_β. This process is favored by the μ-H atom, i.e. a small barrier in the vicinity of C_β, and the tendency of the acetylide to act as a μ_3-5e donor. Supporting this are actual structures and the thermal isomerization of an Os_3 cluster.[346] A theoretical study of CCH_2^+ on a $Co_3(CO)_9$ cluster has also been given from which it was deduced that the electron-deficient C_β atom bends toward one Co atom (section VI.B.4).[301]

Structural studies have shown the extent of the movement of the C_2 fragment during the conversion

$$\underset{1°}{\mu_3\text{-HCCR}} \rightarrow \underset{19°}{\mu_3\text{-CCR}} \rightarrow \underset{50°}{\mu_3\text{-CCHR}} \rightarrow \underset{90°}{\mu_3\text{-CCH}_2\text{R}}$$

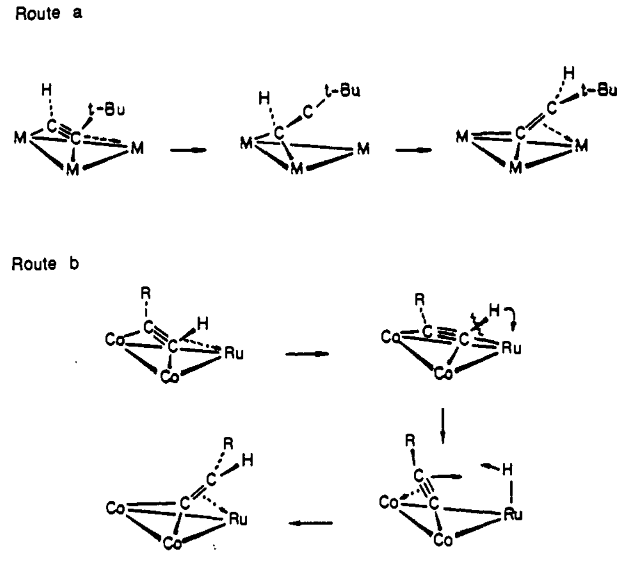


Figure 8. Two possibilities for isomerization of C_2H_2 to CCH_2 on a trinuclear metal cluster (reprinted from ref 344; copyright 1985 Verlag Helvetica Chimica Acta).

(angles are inclination of CC vector to the M_3 plane) C_β lifting up from the M_3 plane so that for μ_3-CCH_2R, the C_α–C_β bond is nearly perpendicular. A parallel is found in the conversion of the corresponding nitrogen containing molecules studied by Kaesz and co-workers.[347] These changes in coordination allow mobility

$$\underset{2^\circ}{\mu_3\text{-HN=CR}} \rightarrow \underset{21.5^\circ}{\mu_3\text{-N}\equiv\text{CR}} \rightarrow \underset{45.3^\circ}{\mu_3\text{-N=CHR}} \rightarrow \underset{90^\circ}{\mu_3\text{-NCH}_2\text{R}}$$

of the multiple bond while the functional part (C_α or N) remains in one location on the core (or metal surface).

IX. Vinylidenes on Metals

A. On Surfaces

Extensive investigations of the changes taking place after adsorption of C_2H_2 on a Pt(111) surface, using a variety of physical techniques including high-resolution IR, electron energy loss (EELS), low-energy electron diffraction (LEED), and NMR methods, have shown that isomerization to CCH_2 occurs readily.[348-354] These changes and the further dehydrogenation to CH_n and finally to adsorbed carbon, are depicted in Figure 9.[355]

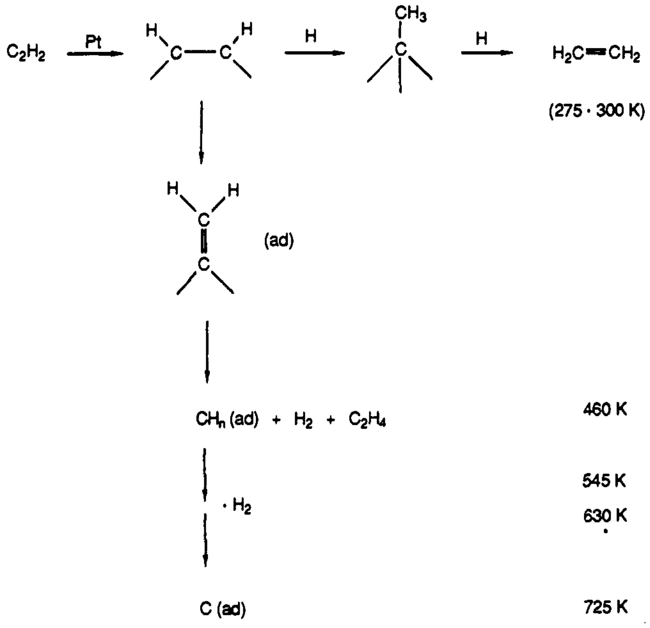


Figure 9. Formation of adsorbed C/H species on a Pt surface.

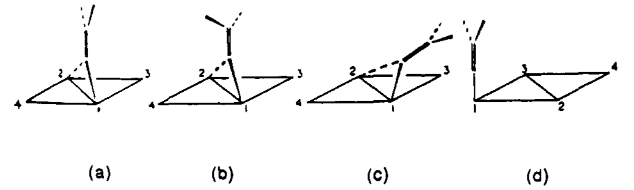


Figure 10. Various geometries of CCH_2 on a metal surface: (a) 2σ (parallel); (b) 2σ (perpendicular); (c) 2σ (bent); (d) σ (linear) (from ref 358).

Several theoretical treatments have been given which have concluded that the vinylidene is relatively stable. Extended Huckel and empirical force field calculations of CCH_2 (and also of CCHF and CCF_2) on Pt clusters[356] have been supplemented by considering the suprafacial 1,2-H shift on a Pt_{16} cluster model[357] and by a more extensive study of CCH_2 chemisorbed on a four-layer surface.[358] The latter considered four orientations of the C_2 fragment on the surface (Figure 10) and concluded that the 2σ (parallel) geometry a is strongly bound by both σ and π interactions, while the 2σ (perpendicular) b geometry is less strongly attached. In molecular complexes, it is the former that is favored, the π-bond determining the conformation. The 2σ (bent) geometry c, in which the C=C double bond bends toward a third atom, is less favorable than the upright ones, although this apparent lack of correspondence with experimental results may be a consequence of the method. Finally, the σ (linear) geometry d is reinforced by backbonding interactions with adjacent Pt atoms, but is ca. 1.5 eV higher than the other conformations, because more surface atoms are involved in the bonding. In general, bonding within the CCH_2 fragment and within the surface are both weakened.

In recent years, many other reports of the detection of vinylidene on metal surfaces have appeared. These have mainly involved chemisorption of ethyne, but dehydrogenation of ethene has also been observed. The results are relevant to the mechanism of isomerization and of dehydrogenation of hydrocarbon species on metal surfaces. For example, electron energy loss spectra of mixtures of CO and H_2 on an Fe(110) surface gave evidence for C_2, CH, and possibly CCH_2 (characterized by energy loss at 1190 cm^{-1}).[359]

Adsorption of ethene on Ru(001) with ordered p(2 × 2) and p(1 × 2) overlayers of oxygen atoms has been studied by high-resolution EELS, thermal desorption mass spectrometry and LEED.[360] On clean Ru(001), a di-σ-bonded C_2H_4 complex is formed, but in the presence of the oxygen atoms, a π-ethene complex forms; above 240 K, it is fully desorbed from the Ru(001)–p(1 × 2) surface, but only one-third is desorbed from Ru(001)–p(2 × 2). At 250 K, formation of CCH_3 with desorption of H_2 (25%) is found. At 350 K, quantitative conversion to CCH_2 is seen, again with evolution of H_2 (25%); at 400 K, decomposition to CH, surface C, and H_2 (25%) is found, while above 500 K, CH forms surface C and H_2 (25%). No CCH or CH_2 was found. In contrast, on an Ru(001) surface, which favors sp^3 species, ethyne forms CCH, which is converted to CH at 360 K, and to surface C and H_2 between 500–700 K. The vinylidene species were identified by comparison of their IR ν(CC) and $\delta(CH_2)$ modes with those assigned for an Os_3 cluster complex. A lower ν(CC) is found as a result of π-donation to the Ru because of tilting of the vinylidene relative to the surface normal. Rehydrogenation occurs under H_2, CCH_2 being regenerated at 350 K.[361]

Vinylidene is an intermediate in the formation of CCH_3 from H + C_2H_2 on Pd(III), and CCH_2 has been tentatively identified from H + C_2H_2 on Pt(III). Various studies of the decomposition of η-C_2H_4 on Pt(111)/O have been interpreted as giving CCH_2 at 325 K. Similarly, annealing the low-temperature phase of ethyne adsorbed on platinum at 350 K is proposed to give CCH_2.[346] The thermal evolution and decomposition of C_2H_4 on a Pt(111) surface shows that stable CHMe coexists with CCH_2, so that it was proposed[350] that the isomerization occurred via vinylidene:

$$C_2H_4 \rightarrow CCH_2 + 2H \rightarrow CHCH_3$$

These transformations have been modeled on $Pt_3(\mu\text{-dppm})_3$ clusters (section VI.B.5).

B. In Matrices

The ESR of the sodium–ethyne complex, prepared by photoirradiation of sodium atoms in an argon matrix containing 1% ethyne were interpreted in terms of formation of the adduct $Na^+/^-CCH_2$. Sodium complexation reduces the barrier to ethyne isomerization by forming this anion.[362] A strong bond to Al is predicted [$AlCCH_2$ is 84 kJ mol^{-1} below (Al + C_2H_2)].[363] However, the ESR spectrum of the species formed from Al atoms and ethyne at liquid He temperatures[364] was interpreted as the species $AlCH{=}CH^{\bullet}$, although it was also suggested that the 17 kJ barrier might be sufficient to preclude the 1,2-H shift at 4 K.[365]

Codeposition of nickel atoms with ethyne in an Ar matrix at 12 K gave $Ni(\eta^2\text{-}C_2H_2)$ which was converted to $Ni(CCH_2)$ on photolysis ($\lambda > 400$ nm); irradiation between 280–360 nm reversed the process. Reaction with H_2 decreased the intensity of the IR bands, but no Ni–C_2H_4 complex was formed.[366]

LCAO/SCF MO calculations of possible modes of coordination of Cu^+ to C_2H_2 and CCH_2 showed the most stable gas-phase complex to be $[Cu(\eta\text{-}C_2H_2)]^+$, with ΔH_f 96.6 kJ mol^{-1} (from Cu^+ and C_2H_2).[367] All adducts are stable with respect to Cu^+ and C_2H_2 in the ground state. The barrier to isomerization of $[Cu(CCH_2)]^+$ to $[Cu(\eta\text{-}C_2H_2)]^+$ is 89.87 kJ mol^{-1}, with the positive charge localized on Cu. The reaction of gold atoms with ethyne in an adamantane matrix at 77 K gave bent $AuCCH_2$; the deuterio species was also identified.[368] The variable-temperature ESR spectrum showed inversion between two equivalent structures at a rate comparable with the frequency of the β-hydrogen hyperfine coupling constant; 35% of the 6s spin density was on the gold atom. The species are formed by an initial rapid 1,2-shift of hydrogen in the vinyl $AuCH{=}CH$. Phenylethyne appears to give $AuCH{=}C^{\bullet}Ph$ rather than AuCCHPh.

X. Prognosis

The organometallic chemistry of vinylidenes has exhibited strong growth over the past decade and these species are now widespread as ligands in both mono- and polynuclear complexes. However, there is still a need to develop other routes to vinylidenes with selected substituents; one example is the lack of a general synthesis of fluorinated derivatives, although the preparation of uncomplexed CCF_2 was reported during the assembly of this survey.[376] Undoubtedly, the application of vinylidene complexes to organic synthesis will increase and, as we learn more about their chemistry, further examples of their intermediacy in reactions catalyzed by transition metals will emerge. Again, a new development is the involvement of vinylidene intermediates in the polymerization of alkynes.[377]

The propensity of vinylidenes to interact with more than one metal atom and the reactivity thus conferred on them will make the chemistry of cluster-bound species an area of much growth in the future. Particularly, the ability of clusters to facilitate multicomponent reactions will result in much interesting chemistry. Heteroatom analogues (CCO, CBH_2, etc.) are destined to play an important role in developing our knowledge of the reactivity of cluster-bound molecules. These and related species are also likely to be detected in various environments on metal surfaces.

Another area which may be expected to develop rapidly is the chemistry of higher members of the C_nH_2 series ($n \geq 3$). The high degree of unsaturation and alternating degree of electrophilicity of the C atoms in the unsaturated chain will ensure that much new and interesting chemistry will be discovered, once the synthetic approaches to these molecules have been defined.

All in all, and in spite of the claim that the "final chapter" may have been written (from the theoretical point of view, at least),[378] one would expect to see continuing expansion of this exciting area of chemistry over the next decade, with the emphasis shifting from preparation and structural characterization to studies of reactivity and synthetic utility.

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