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Transition Metal Complexes Containing Allenylidene, Cumulenylidene, and Related Ligands

Michael I. Bruce

Department of Chemistry, University of Adelaide, Adelaide, South Australia 5005

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Contents

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Michael Bruce graduated from the University of Oxford, England, and completed his Ph.D. in 1967 under Gordon Stone's guidance at the University of Bristol. There, he then took up a faculty position until moving to Australia in 1974 as Professor Inorganic Chemistry at the University of Adelaide, where he has been Angas Professor of Chemistry since 1982. His research interests center on the chemistry of unsaturated carbene ligands, all-carbon molecules, and metal clusters. He is a Fellow of the Australian Academy of Science, the Royal Society of Chemistry, and the Royal Australian Institute of Chemistry, whose H. G. Smith Medal and Burrows Award he received in 1989. He has been a Visiting Professor at the Universities of British Columbia; Cambridge; Neuchátel, Rennes; and Louis Pasteur, Strasbourg; and CNRS, Toulose. His extramural interests include to photography and bush-walking.

I. Introduction

The current intense interest in complexes containing highly unsaturated carbon chains arises from their potential to form molecular wires[1-3] and other nanoelectronic devices,[4,5] as possible components of two- or three-dimensional carbon networks[6,7] and as likely monomers for the preparation of novel polymers related to polyacetylene.[8-11] Current extensions of the chemistry of conjugated diyne and polyyne complexes of transition metals have also resulted in further discoveries of novel unsaturated carbene complexes.

The first carbene complex was discovered in 1964 by Fischer and Maasböl.[12] Since that time, the chemistry of these species has become enormously diversified, with applications in organic synthesis, catalysis, and elsewhere.[13,14] Conceptually, a series of higher unsaturated carbenes can be envisaged, which are closely related to more familiar heterocumulenic ligands (Figure 1).

Vinylidenes are tautomers of 1-alkynes and are formed by a formal 1,2-shift of the alkyne hydrogen from C(1) to C(2):

$$\mathrm{H{-}C{\equiv}C{-}H} \rightarrow \mathrm{:C{=}CH_2} \qquad (1)$$

While in the free state the lifetime of the vinylidene is extremely short ($\sim 10^{-10}$ s),[15] the formation and stabilization of vinylidenes at a transition metal center was first reported in 1966, when one product from the reaction between $Fe_2(CO)_9$ and diphenylketene was shown to be the binuclear complex $Fe_2(\mu\text{-}C{=}CPh_2)(CO)_8$.[16,17] A mononuclear dicyanovinylidene−molybdenum complex was described six years later.[18] The importance of metal-stabilized vinyl cations in the chemistry of cationic platinum alkyne complexes was discussed in a review by Chisholm and Clark.[19] Vinylidene complexes have been reviewed several times since then.[20-24] The development of applications of vinylidene complexes has been much slower than for carbenes, although there are now several examples of organic reactions proceeding via actual or proposed intermediate complexes.[25] As unsaturated species, they also have an as yet unrealized potential for polymerization.

The stabilization of unsaturated carbenes by coordination to a transition metal center is achieved by use of the lone pair of electrons on carbon in formation of a dative carbon-to-metal donor bond. Some degree of back-bonding from metal to carbon ligand may further strengthen this bond. Stabilization of allenylidenes by two heteroatom substituents is indicated by the resonance structures shown in Figure 2 and strongly dipolar characteristics are expected, particularly when heteroatoms are present.

The first allenylidene complexes were described simultaneously by the groups of Fischer[26] and Berke[27] in 1976, who obtained them from the reactions of Lewis acids (BF_3, $AlEt_3$) with amino−vinylcarbene complexes, whereby EtOH was eliminated:

$$\mathrm{M(CO)_5\{{=}C(OEt)CH{=}CPh(NEt_2)\} + EX_3 \rightarrow M(CO)_5\{{=}C{=}C{=}CPh(NEt_2)\}}$$
$$[\mathrm{M = Cr, W;\ EX_3 = BF_3\ (Cr),\ AlEt_3\ (W)}] \qquad (2)$$

What is now the most general method of preparation, the spontaneous dehydration of hydroxymethylvinylidene ligands derived from substituted 2-propyn-1-ols on electron-rich metal centers, was first demonstrated by Selegue in 1982, who made $[Ru({=}C{=}C{=}CPh_2)(PMe_3)_2Cp]^+$.[28] Many octahedral complexes containing d^6 metal centers have been prepared, while more recently, there has been considerable development of the chemistry of square-planar allenylidene complexes of Rh(I) and Ir(I) (d^8), which show a distinctly different chemistry.

$M{=}CR_2$	$M{=}C{=}CR_2$	$M{=}C{=}C{=}CR_2$	...	$M{=}(C)_n{=}CR_2$
carbene	vinylidene	allenylidene		
$M{-}C{=}NR$	$M{=}C{=}C{=}NR$	$M{=}C{=}C{=}C{=}NR$	...	$M{=}(C)_n{=}NR$
isocyanide	azavinylidene			
$M{-}C{\equiv}O$	$M{=}C{=}C{=}O$	$M{=}C{=}C{=}C{=}O$	...	$M{=}(C)_n{=}O$
carbonyl	ketenylidene			

Figure 1.

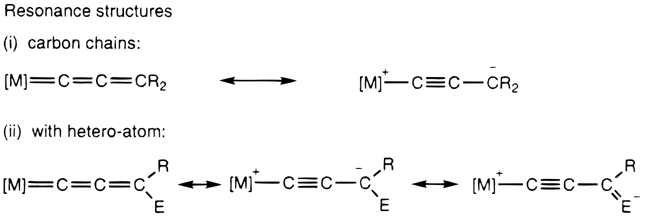


Figure 2.

Complexes containing higher members of this series of ligands are much rarer. Butatrienylidene has been stabilized in a ruthenium cluster complex[29] and at the time of writing, the longest chains which have been structurally characterized are the pentatetraenylidene ligands found in *trans*-$[RuCl(=C=C=C=C=CPh_2)(dppe)_2][BF_4]$[30] and *trans*-$IrCl(=C=C=C=C=CPh_2)(PPr^i_3)_2$.[31] Isolation of other pentatetraenylidene complexes has been taken as evidence for the intermediate formation of heptahexaenylidenes.[32]

Previous general surveys have been given in 1983[22] and 1991;[23] specific accounts of the chemistry of ruthenium,[33,34] rhodium,[21,35] and binuclear allenylidene complexes[36,37] have also been given. The following review summarizes the state of our knowledge as at June 1998. The ligands themselves, which are known to coordinate to mononuclear metal centers, to bridge two metal atoms, and to adopt a variety of coordination modes in metal clusters, are briefly described. This is followed by a discussion of methods of synthesis of mononuclear complexes, which are then surveyed by Periodic Group. Their properties and reactions are discussed, as are their uses in organic synthesis. This is followed by a description of the syntheses and properties of bi- and polynuclear complexes. The review concludes with a summary of reactions in which unsaturated carbene complexes can reasonably be supposed to be intermediates and a brief account of some complexes containing related ligands.

A Note about Nomenclature. Formal nomenclature of the ligands is based on the “enylidene” of the longest carbon chain present, although the trivial name “allenylidene” will be used here for the C_3 species, although the terms propadienylidene and vinylidenecarbene have also been used.

II. The Ligands

Unsaturated carbenes are extremely reactive and are considered to be important intermediates. The presence of a lone-pair (or two unpaired electrons) on the terminal carbon atom enables them to be stabilized by coordination to a transition metal center. The synthesis, nature (spin multiplicity), and reactions of the free unsaturated carbenes have been surveyed;[38] they are expected to be electrophilic and no intramolecular rearrangements have been reported.

Although vinylidene itself has an extremely short lifetime, both experimental and theoretical studies confirm that higher unsaturated carbenes are considerably more stable. Several of them have been detected in interstellar cold molecular clouds (such as TMC-1) and circumstellar environments (as around the carbon-rich star IRC +10216). Indeed, some have speculated that the “diffuse interstellar bands” originate in part from these molecules.[39] The identifications of these molecules are supported by microwave spectroscopy and structural calculations: the geometries of $:C(=C)_n=CH_2$ calculated at the MP2 level are given in Table 1 and show interesting variations in distances and angles which have been related to C−C bond alternation (C=C=C vs C−C≡C) in even- and odd-numbered chains.[40]

In the laboratory, the free ligands have been generated by subjecting mixtures of ethyne or buta-1,3-diyne with He or Ne to DC discharges ($:C=C=CH_2$;[41] $:C=C=C=CH_2$[42]), or flash vacuum pyrolysis (fvp) or photolysis (or a combination thereof) of suitable precursors, trapped in cold matrixes and identified from their microwave or IR spectra. Several members of the series $R_2C=(C=)_nC:$ have been generated from appropriate acetylenic vinyl triflates ($n = 0$,[43] 2[44]), $HC{\equiv}CCClMe_2$ ($n = 1$),[45] $HC{\equiv}CC{\equiv}CCHClMe$ ($n = 3$),[46] or a diynyl mesylate ($n = 3$)[47] by treatment with strong bases, such as $KOBu^t$ (Scheme 1). The cumulenes can be trapped by reactions with olefins, particularly C_2Me_4, or by self-dimerization and rearrangement reactions, and the products identified by conventional means. Other trapping agents include secondary amines or Group 14 hydrides (by insertion into N−H or E−H bonds, respectively).[48]

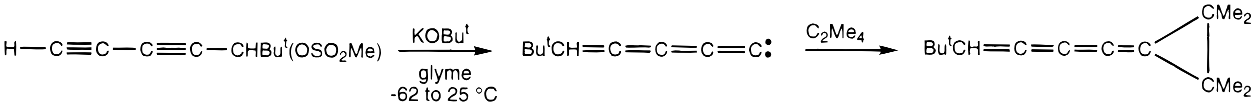
Many theoretical studies substantiate the isolation and characterization of these reactive species, particularly by using calculated IR frequencies. Of interest are the relative energies of the various C_nH_2 isomers. Ab initio calculations predict a triplet ground state for $:CH_2$, but in general, although an increasing number of singlet and triplet configurations are available to the higher cumulenes, the higher unsaturated carbenes $:C_nH_2$ ($n = 2-7$) are predicted to have singlet ground states.[49−51] In some cases, contributions from zwitterionic forms have

Table 1. Calculated Geometries of $:C=(=C)_nCH_2$ ($n = 1-8$) (Data Ref 40)[a]

n	C(1)−C(2)	C(2)−C(3)	C(3)−C(4)	C(4)−C(5)	C(5)−C(6)	C(6)−C(7)	C(7)−C(8)	C(8)−C(9)	C(9)−C(10)	H−C(n+1)	HCH
1	1.292	1.333								1.084	116.59
2	1.290	1.299	1.311							1.080	119.26
3	1.290	1.309	1.270	1.328						1.084	117.08
4	1.287	1.304	1.275	1.287	1.317					1.084	118.82
5	1.289	1.309	1.269	1.301	1.271	1.329				1.083	117.26
6	1.289	1.307	1.271	1.294	1.279	1.285	1.320			1.082	118.45
7	1.289	1.309	1.268	1.301	1.270	1.301	1.271	1.329		1.083	117.38
8	1.288	1.308	1.269	1.298	1.273	1.293	1.281	1.284	1.321	1.082	118.25

[a] C−C, C−H distances are in angstroms; HCH angles, in degrees.

Scheme 1



been evaluated; stabilization of cumulene carbenes by charge separation ($H_2C^+—C≡C^-$) is most effective with odd numbers of carbon atoms.[50]

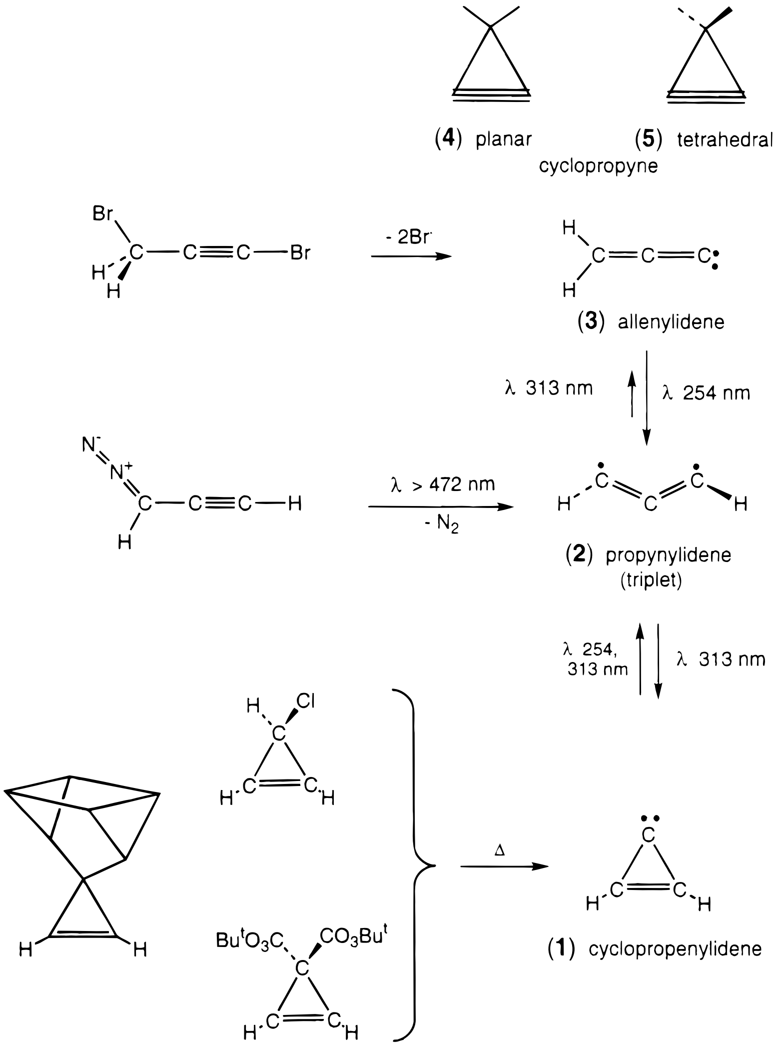
While these values have little consequence in the derivative transition metal chemistry, the fact that stable complexes can be obtained is yet another indication of the use of metal centers to stabilize reactive organic molecules and intermediates.

A. Individual C_nH_2 Species

1. $n = 3$

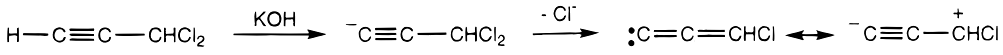
The lowest energy C_3H_2 species is cyclopropenylidene (**1**; Scheme 2), which has been generated from the quadricyclane derivative shown,[52] by fvp of the perester 3,3-(CO_3Bu^t)$_2$-cyclopropene at 480 °C[53] or from 3-chlorocyclopropene.[54] Photolysis (λ 254 nm) of **1** in an Ar matrix at 12 K gave triplet propynylidene (**2**),[55] which can also be obtained by long-wavelength photolysis of diazopropyne ($\lambda > 472$ nm, at 8 K).[56] After 20-h irradiation at 313 nm, **2** gave propadienylidene (allenylidene), :C=C=CH_2 (**3**); partial reversion to **1** also occurred. Singlet **3** has ν(CCC) at 1940.6 cm^{-1}. This species has been detected and the structure determined by microwave spectroscopy among the products of a DC discharge through ethyne/carbon monoxide/helium mixtures[41,57] and later in TMC-1 and possibly in IRC +10216.[58] Irradiation at 254 nm results in a rapid (2 h) back-reaction to **2**, which is reversed with 313-nm radiation.[53,59] A ^{13}C-labeling study of the automerization and isomerization of **3** clarified these relationships between the open and closed C_3H_2 isomers.[60] Comparison of three isomers of C_3H_2, obtained by flash pyrolysis of the precursors shown in a supersonic molecular beam at 1700 °C for 10−50 μs, has given ΔH_f values of 114, 129, and 136 kJ mol^{-1}, for **1**, **2**, and **3**, respectively.[54]

Scheme 2



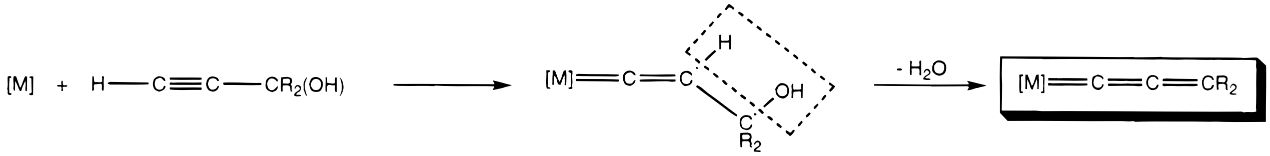
Relative energies: **1** (0.0) < **2** (41.0) < **3** (55.2) < **4**, **5** (212.1 kJ mol^{-1}) (ref. 55)

Scheme 3



$$H{-}C{\equiv}C{-}CHCl_2 \xrightarrow{KOH} {}^{-}C{\equiv}C{-}CHCl_2 \xrightarrow{-\,Cl^-} :C{=}C{=}CHCl \longleftrightarrow {}^{-}C{\equiv}C{-}\overset{+}{C}HCl$$

Scheme 4



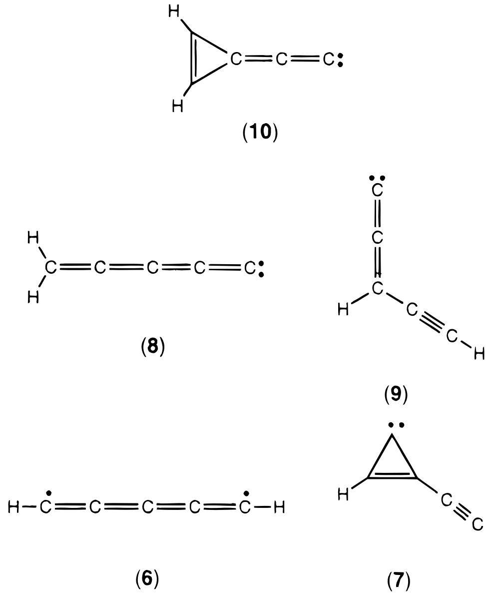
The relative energies of these isomers have been calculated and the complex IR and visible absorption spectra have been assigned.[61,62] Calculations at various levels consistently give **1** as the most stable isomer, with **2** and various forms of **3** as the next most stable forms, and cyclopropyne [planar (**4**) or tetrahedral (**5**)] at considerably higher energies.[55]

Several substituted allenylidenes have been described. Chloroallenylidene ($:C{=}C{=}CHCl$) has been generated by elimination of HCl from 3,3-dichloropropyne and powdered KOH under phase-transfer catalysis conditions (Scheme 3).[63] It can be trapped by olefins (di- and tetramethylethenes) to give chlorovinylidenecyclopropanes. Fvp of polychlorocyclopropenes has given mono- and dichlorocyclopropenylidenes. Irradiation of these matrix isolated species has given $:C{=}C{=}CHCl$ and $:C{=}C{=}CCl_2$, respectively.[64]

A similar route was used to prepare $:C{=}C{=}CF_2$ from 1-chloro- (or 1,2-diiodo-) 3,3-difluorocyclopropene.[65] The ν(CCC) values for $:C{=}C{=}CF_2$, $:C{=}C{=}CHCl$ and $:C{=}C{=}CCl_2$ are 2025, 1968, and 1977 cm^{-1}, respectively.[64,65]

2. $n = 4$

Passage of a discharge through ethyne/helium mixtures enabled detection and structure determination of C_4H_2 by microwave spectroscopy;[42,66] it was later found in IRC +10216 and TMC-1.[67] Ab initio calculations on $:C{=}C{=}C{=}CH_2$ confirmed the singlet state as lowest lying, having the same stability as $:C{=}CH(C{\equiv}CH)$. The difference between the two C_4H_2 isomers and $HC{\equiv}CC{\equiv}CH$ is about the same as between $C{=}CH_2$ and $HC{\equiv}CH$:[50] $HC{\equiv}CC{\equiv}CH$ (0) < $:C{=}C{=}C{=}CH_2$ (171.5) < $:C{=}CH(C{\equiv}CH)$ (177 kJ mol^{-1}).



Relative energies: **6, 7** (0.0) < **8, 9** (63) < **10** (84 kJ/mol)

Figure 3. Isomers of C_5H_2.

3. $n = 5$

Free $:C{=}C{=}C{=}C{=}CH_2$ was detected in mixtures obtained by pulsed discharge on a supersonic molecular beam containing ethyne or (better) buta-1,3-diyne in Ne or Ar.[68] Calculations at three levels of theory show HCCCCCH (**6**) and ethynylcyclopropenylidene (**7**) to be the most stable isomers, followed by $:C{=}C{=}C{=}C{=}CH_2$ (**8**) and ethynylallenylidene (**9**), cyclopropylidenevinylidene (**10**) being least stable (Figure 3).[69]

4. $n = 6$

FT microwave spectroscopy has been used to detect C_6H_2 in a similar experiment,[68] and it has also been detected in the interstellar molecular cloud TMC-1.

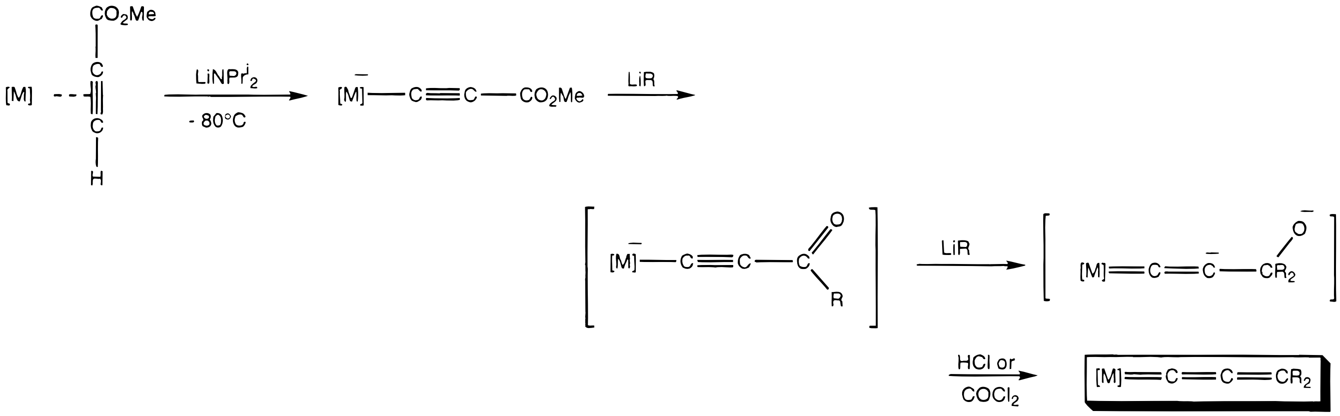
III. Syntheses of Allenylidene and Cumulenylidene Complexes

A. Complexes Containing Propadienylidene (Allenylidene), $:C{=}C{=}CR_2$

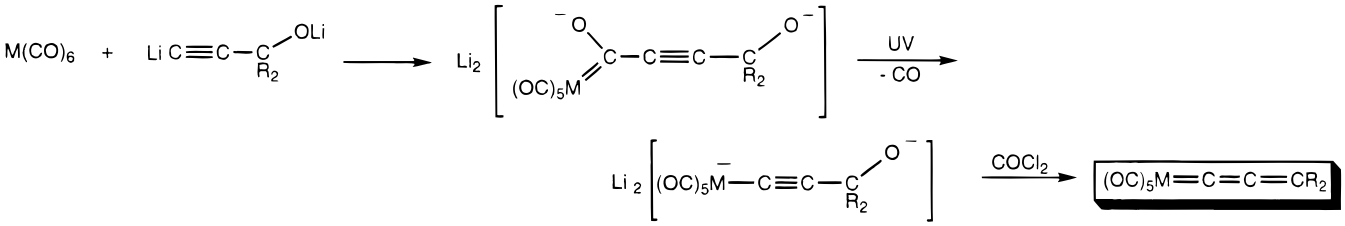
The general synthetic strategy for metal complexes of allenylidenes involves the introduction of a preformed C_3 skeleton containing a leaving group or molecule. The latter is often lost spontaneously, as with the dehydration of 2-propyn-1-ols. Four routes have some general utility. Trapping of the intermediate unsaturated carbene complex can occur in the presence of suitable nucleophiles, such as alcohols, when the next lower vinylogue is obtained, or PR_3, when zwitterionic phosphonium complexes are formed. In some cases, the complexes are unstable, undergoing spontaneous polymerization.

(i) By Loss (Often Spontaneous) of H_2O or ROH from Suitable Carbene or Vinylidene Precursors. The latter can be obtained from (usually substituted) propargylic alcohols (Scheme 4).[70−84] Other examples require help, for example, acid catalysis, in the dehydration step.[85−93] This method was first employed for a ruthenium complex,[28] but has found widespread application with other elements. Alkoxide elimination from alkoxy−alkenyl carbene complexes also leads to allenylidenes.[27,94−96]

Scheme 5



Scheme 6



In the mass spectra of hydroxyalkyl–vinylidenes, dehydration of M^+ occurred, although this reaction could not be carried out in vitro:[97]

$$[\mathrm{Mn}\{\mathrm{CCHCBu}^{t}{}_{2}(\mathrm{OH})\}(\mathrm{CO})_2(\mathrm{C}_5\mathrm{H}_5)]^+ \rightarrow [\mathrm{Mn}(\mathrm{CCCBu}^{t}{}_{2})(\mathrm{CO})_2(\mathrm{C}_5\mathrm{H}_5)]^+ \quad (3)$$

(ii) A Related Reaction Generates the Hydroxy Group by Attack of Organolithiums on η^2-Alkyne Complexes Containing Ester Groups, e.g. $HC\equiv CCO_2Me$. Deprotonation (with LDA or excess LiR) is followed by loss of H_2O or ROH, promoted by base (dbu) or $COCl_2$ (Scheme 5).[88,97,98]

Nonallenylidene ligands may also be formed by complex addition, cyclization, or polymerization side reactions.[37]

(iii) Reactions of Dilithio Derivatives of Substituted 2-Propyn-1-ols [$LiC\equiv CCR_2(OLi)$] with Metal Carbonyls [Usually $M(CO)_6$ or $M(CO)_5(thf)$][99–107] and Subsequent Loss of Oxo or Alkoxy Groups (Scheme 6). Initial formation of an intermediate thought to be $Li[(OC)_5M{=}C(O^-)C{\equiv}CCMe_2O^-]$ is followed by decarbonylation (UV irradiation) and treatment with $COCl_2$ at −80 °C[99,108] or base (dbu)[99] to give the allenylidene. Related chemistry is known in Groups 7 and 8. Again, these reactions are not always straightforward and several different types of products derived from subsequent cyclization and addition reactions have been obtained.

(iv) Some Allenylidene Complexes Have Been Obtained in Reactions Designed to Yield Higher Unsaturated Carbenes. If these reactions are carried out in MeOH (as solvent) or in the presence of a nucleophile, addition of the alcohol (or nucleophile) to C(3) may occur to give the derived allenylidene:[32,109–111]

$$[\mathrm{M}]{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{CR}_2 + \mathrm{MeOH} \rightarrow [\mathrm{M}]{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{C}(\mathrm{OMe})\mathrm{CH}{=}\mathrm{CR}_2 \quad (4)$$

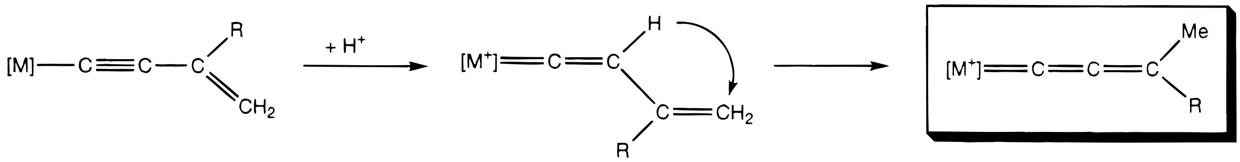
In addition to these routes, a few allenylidene complexes have been obtained by addition of electrophiles (usually the proton) to conjugated enynyl complexes (Scheme 7).[112,113]

B. Complexes Containing Higher Cumulenylidenes

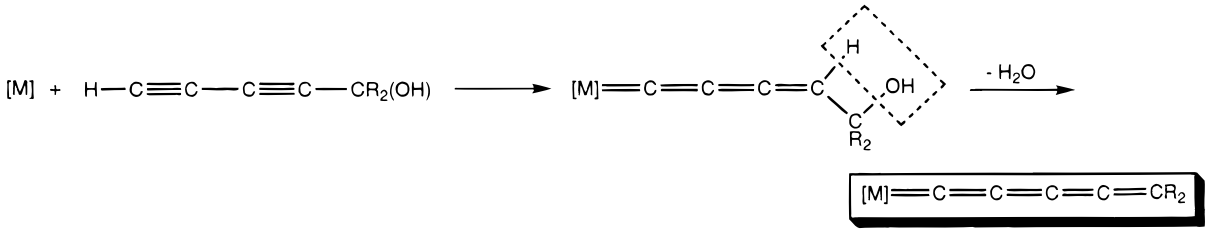
The most common approach to these complexes has been to introduce additional unsaturation into the alkyne derivatives used in methods i–iv above. Thus, dehydration of diynols may give pentatetraenylidenes (Scheme 8).[30,114]

However, many of these reactions have been carried out in alcohol solvents, resulting in addition to C(3) and formation of the corresponding vinylallenylidenes [see method iv, above]. In some cases, protection of the OH group by conversion to $OSiMe_3$, for example, enables the reaction to be carried out stepwise, via the intermediate vinylidene.[115]

Scheme 7



Scheme 8



IV. Mononuclear Complexes Containing Allenylidene and Cumulenylidene Ligands

The following discussion surveys the known allenylidene complexes by Periodic Group. Table 2 lists the known examples, together with their characteristic IR and NMR parameters.

A. Titanium

Lithiation of 3,3-diphenylcyclopropene results mainly in ring opening to give $Li_2C{=}C{=}CPh_2$; the dilithiocyclopropene is also present (ratio 86/14). Reaction with $TiCl_2Cp_2$ in the presence of PMe_3 gave $Ti({=}C{=}C{=}CPh_2)(PMe_3)Cp_2$ (**11**; Scheme 9) in 70% yield.[116]

B. Chromium, Molybdenum, and Tungsten

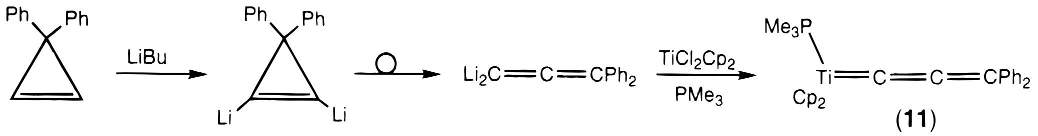
The majority of Group 6 allenylidenes have been obtained by method iii.[86,99,104,105,108,117] Direct reactions between $M(CO)_5(thf)$ (M = Cr, W) and the propynol proceeded via the η^2-alkyne complex to give the vinylidene, which then lost water to give the allenylidenes.[86] The complexes are generally thermally unstable, but the presence of electron-donating substituents on the aryl groups allows crystalline compounds to be isolated. Polycyclic systems, such as those with $CR_2 = C(C_6H_4)_2O$ or $C(C_6H_4)_2$ have also been obtained. The alkyl complexes are less stable, isopropyl derivatives being polymeric solids, but the *tert*-butyl complexes are sublimable solids.[104]

Some side products are obtained. For example, reaction of the chromium complex obtained from $HC{\equiv}CCMe_2(OH)$ with MeCOCl gave the bicyclic allenylidene (**12**; Scheme 10).[101]

The analogous tungsten system gave a cyclic carbene (**13**; Scheme 11) with HCl.[101]

The dianion $[Cr\{C{\equiv}CCMe_2(O)\}(CO)_5]^{2-}$ could not be deoxygenated with $COCl_2$. Instead, treatment wih

Scheme 9



Scheme 10

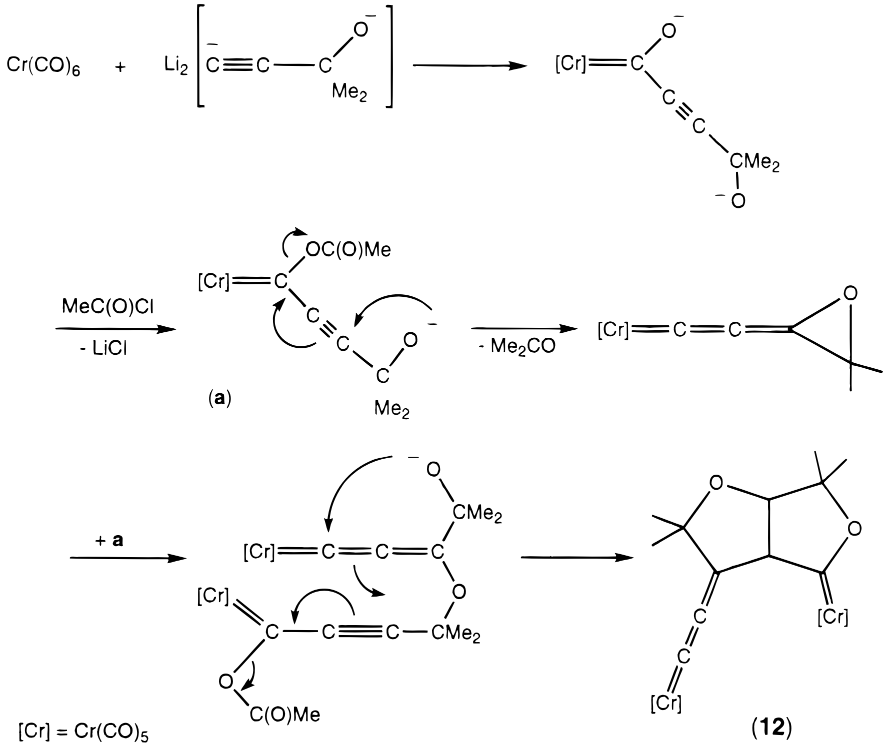


Table 2. Mononuclear Allenylidene Complexes, $[\{L_nM\}{=}C(1){=}C(2){=}C(3)R^1R^2][X]_n$

					yield,		^{13}C NMR^a			
ML$_n$	R^1	R^2	[X]$_n$	color	%	ν(CCC)	C(1)	C(2)	C(3)	ref
Group 4										
Ti(PMe$_3$)Cp$_2$	Ph	Ph		dark violet	71	1870	264.9 (PC 31.4)	168.3 (PC 7.8)	94.0 (PC 13.2)	116
Group 6										
Cr(CO)$_5$	CH=C(NMe$_2$)$_2$	NMe$_2$		yellow	96	2020	170.9	110.6	162.4	118
Cr(CO)$_5$	Pr^i	Pr^i		red		1933				104
Cr(CO)$_5$	CMe$_2$(OEt)	NHPr		orange	41	2190	230.09	114.97	162.35	95
Cr(CO)$_5$	CMe$_2$(OEt)	NHPr^i		orange	86		231.16	115.20	160.75	95
Cr(CO)$_5$	CMe$_2$(OEt)	NHCy		orange	67		228.07	114.63	160.74	95
Cr(CO)$_5$	CMe$_2$(OEt)	NMe$_2$			13					95
Cr(CO)$_5$	CMe$_2$(OEt)	NEt$_2$		red	75	2079	229.34	122.40	158.77	95
Cr(CO)$_5$	CMe$_2$(OEt)	NPr$^i{}_2$			68					95
Cr(CO)$_5$	CMe$_2$(OEt)	N(CH$_2$CH=CH$_2$)$_2$			64					95
Cr(CO)$_5$	CMe$_2$(OEt)	N(CH$_2$Ph)$_2$			74					95
Cr(CO)$_5$	CMe$_2$(OSiMe$_3$)	NMe$_2$		orange	12		230.58	121.59	160.38	95
Cr(CO)$_5$	c-Pr	NHCy		orange	47	2082	220.67	110.97	161.12	95
Cr(CO)$_5$	c-Pr	NMe$_2$								95
Cr(CO)$_5$	c-C$_3$H$_4$OEt	NHCy		orange	11		225.74	111.58	158.84	95
Cr(CO)$_5$	c-C$_3$H$_4$OEt	NMe$_2$			13					95
Cr(CO)$_5$	c-C$_3$H$_4$OEt	N(CH$_2$Ph)$_2$		orange	45	2200	237.86	125.02	154.77	95
Cr(CO)$_5$	Bu^t	Bu^t		dark red		1930				104
Cr(CO)$_5$	Bu^t	NMe$_2$			8					95
Cr(CO)$_5$	Bu^t	N(CH$_2$Ph)$_2$		orange	71		237.49	125.67	169.15	95
Cr(CO)$_5$	C$_5$Me$_4$O$_2$ [Cr(CO)$_5$]			deep yellow	36	1933				101
Cr(CO)$_5$	Ph	Ph		black	58	1930	334.2	142.0	156.2	99,105
Cr(CO)$_5$	Ph	NMe$_2$		maroon	64	1988	230.2	153.1	125.3	26,120
Cr(CO)$_5$	Ph	NPr$^i{}_2$			53					95
Cr(CO)$_5$	Ph	NMePh		violet	60	1978	243.6	150.2	129.5	120
Cr(CO)$_5$	Ph	NEtPh		violet	53	1977	240.0	150.9	129.3	120
Cr(CO)$_5$	tol	tol		black	51	1931	327.1	139.7	157.4	99
Cr(CO)$_5$	C$_6$H$_4$NMe$_2$-4	C$_6$H$_4$NMe$_2$-4		black	77	1920	261.0	136.3	153.5	86,99
Cr(CO)$_5$	C$_6$H$_4$OMe-4	C$_6$H$_4$OMe-4		black	44	1934	313.9	135.5	163.4	86,99
Cr(CO)$_5$	(C$_6$H$_4$)$_2$					1920				105
Cr(CO)$_5$	(C$_6$H$_4$)$_2$O			black	70	1938	290.6	135.1	169.3	86, 99
Cr(CO)$_5$	NMe$_2$	NMe$_2$		yellow	64	2014	185.9	106.5	151.7	118
Cr(CO)$_5$	indolinyl			violet	73	1974	239.0	144.3	125.8	120
W(CO)$_5$	CH=C(NMe$_2$)$_2$	NMe$_2$		yellow	96	2025	170.3	108.3	150.1	118
W(CO)$_5$	Pr^i	Pr^i		red		1933				104
W(CO)$_5$	Bu^t	Bu^t		dark red		1925				104
W(CO)$_5$	Ph	Ph		black	38	1923	302.5	145.0	155.5	86,99,105
W(CO)$_5$	Ph	NMe$_2$		red-violet	32		198.9 (WC 102.5)	121.3 (WC 26.9)	157.5 (WC < 5)	26
W(CO)$_5$	Ph	OEt		violet	10	in ν(CO)	245.3	191.1	154.0	96
W(CO)$_5$	tol	tol		black	37	1927	295.0	142.9	157.6	86,99
W(CO)$_5$	C$_6$H$_4$NMe$_2$-4	C$_6$H$_4$NMe$_2$-4		blue	46	1907	259.2	147.9	161.0	86,99
W(CO)$_5$	C$_6$H$_4$OMe-4	C$_6$H$_4$OMe-4		black	44	1926	273.4	137.8	157.8	86,99
W(CO)$_5$	NMe$_2$	NMe$_2$		yellow	67	2018	173.0 (WC 133.2)	105.0 (WC 24.7)	152.4	118
Group 7										
Mn(CO)$_2$Cp	Bu^t	Bu^t		red-brown	89.5	1922	331.18	167.51	213.61	27,103
Mn(CO)$_2$Cp	CH$_2$Ph	CH$_2$Ph		orange-red	25	1922	382.4	140.2		103
Mn(CO)$_2$Cp	Ph	Ph		red-violet	43	1909	304.5	139.8	223.3	103
Mn(CO)$_2$Cp	Cy	Cy		red-brown	42	1925	323.4	169.5	202.3	103
Group 8										
Fe(CO)$_4$	Bu^t	Bu^t			12	1924	257.61	189.15	171.48	107
Fe(CO)$_4$	CBu^{t}OC(O)O			black	18	1961	243.39	151.54	131.03	107
Fe(CO)$_2$(PEt$_3$)$_2$	Bu^t	Bu^t		brown oil	65	n.f.	242.6 (PC 50)	200.2 (PC 9)	139.3 (PC 12)	122
Fe(CO)$_2$(PEt$_3$)$_2$	Ph	Ph		dark green oil	67	n.f.	224.5 (PC 56)	208.1 (PC 10)	118.7 (PC 11)	122
Fe(CO)$_2${P(OMe)$_3$}$_2$	Me	Bu^t		dark red	17	n.f.	248.9 (PC 67)	201.4 (PC 11)	138.4 (PC 11)	122
Fe(CO)$_2${P(OMe)$_3$}$_2$	Bu^t	Bu^t		dark brown	73	1865	253.9 (PC 70)	202.9 (PC 11)	152.8 (PC 12)	122
Fe(CO)$_2${P(OMe)$_3$}$_2$	Ph	Ph		green black oil	38	1868	230.3 (PC 74)	209.5 (PC 12)	126.7 (PC 13)	122
Fe(dppe)Cp	Ph	Ph	?		77	1926	289.5 (PC 37.2)	228.4	151.6	90

Table 2. (Continued)

ML$_n$	R^1	R^2	[X]$_n$	color	yield, %	ν(CCC)	^{13}C NMR^a			ref
							C(1)	C(2)	C(3)	
			Group 8 (Continued)							
trans-Ru(dppm)$_2$	$CH{=}CPh_2$	OMe	[BF$_4$]$_2$	violet	76	1958	233.68 (PC 14.3)	138.93 (PC 1.6)	164.96	111
trans-RuCl(dppm)$_2$	H	$CH{=}CHPh$	PF$_6$	red	77	1947	315.15 (PC 14.5)	220.37 (PC 2.7)	149.85	72,140
trans-RuCl(dppm)$_2$	H	Ph	PF$_6$	red	93	1943	216.0	151.0	142.2	246
trans-RuCl(dppm)$_2$	H	Ph	PF$_6$	red	84	1938	323.08 (PC 14.4)	217.31 (PC 2.7)	150.86	72,140
trans-RuCl(dppm)$_2$	H	C_6H_4Cl-4	PF$_6$	red	73	1950	323.24 (PC 14.5)	220.27 (PC 2.7)	148.28 (PC 2.2)	72,140
trans-RuCl(dppm)$_2$	H	C_6H_4F-4	PF$_6$	red	68	1950	321.25 (PC 14.4)	215.88 (PC 2.7)	148.41	140
trans-RuCl(dppm)$_2$	H	$C_6H_{4O}Me$-4	PF$_6$	red	70	1943	308.37 (PC 14.1)	200.78 (PC 2.6)	149.92	72,140
trans-RuCl(dppm)$_2$	Me	Me	PF$_6$	green	79	1964	322.69 (PC 13.9)	199.85 (PC 2.3)	173.33	77,140
trans-RuCl(dppm)$_2$	$CH{=}CPh_2$	OMe	BF$_4$	red	39	1955				111
trans-RuCl(dppm)$_2$	$CH{=}CPh_2$	OMe	PF$_6$	red	65	1952	252.76 (PC 13.5)	150.18 (PC 2.2)	155.71	111
trans-RuCl(dppm)$_2$	$C_2H_4CH{=}CH_2$	NMe$_2$	PF$_6$	green	51	1995	202.09 (PC 13.9)	118.73	156.91	152
trans-RuCl(dppm)$_2$	Ph	Ph	BF$_4$		63	1924				140
trans-RuCl(dppm)$_2$	Ph	Ph	PF$_6$	dark red	89	1928	306.72 (PC 14.5)	208.94 (PC 2.5)	161.88	77,140
trans-RuCl(dppm)$_2$	C_6H_4Cl-4	C_6H_4Cl-4	PF$_6$	red	88	1921	307.33 (PC 14.3)	213.92	156.63	77,140
trans-RuCl(dppm)$_2$	C_6H_4F-4	C_6H_4F-4	PF$_6$	violet	69	1939	304.64 (PC 14.3)	208.51 (PC 4.0)	157.22 (PC 2.2)	140
trans-RuCl(dppm)$_2$	2-$C_6H_4CPh{=}CH$		BF$_4$	violet	30	1934				111
trans-RuCl(dppm)$_2$	2-$C_6H_4CPh{=}CH$		PF$_6$	violet	64	1934	316.13 (PC 14.6)	234.07 (PC 3.3)	158.82 (PC 2.2)	77,111
trans-RuCl(dppm)$_2$	(2-C_6H_4)$_2$		PF$_6$	violet	69	1939	312.02 (PC 14.9)	218.10 (PC 2.7)	155.46 (PC 1.8)	140
trans-RuCl(depe)$_2$	$C_2H_4CH{=}CH_2$	NMe$_2$	PF$_6$		35	1979	211.09 (PC 13.7)	117.89	155.40	152
trans-RuCl(dppe)$_2$	H	$C_6H_4CH(OH)C{\equiv}CH$	PF$_6$	violet	78		320.70 (PC 14)	221.89 (PC 2)	151.65	143
trans-RuCl(dppe)$_2$	H	$C_6H_4C{=}C{=}C{=}$[*trans*-RuCl(dppe)$_2$]	(PF$_6$)$_2$	violet	52		326.86 (PC 15)	241.33 (PC 3)	152.01	143
trans-RuCl(dppe)$_2$	H	$C_4H_2SCH(OH)C{\equiv}CH$	PF$_6$		41					143
trans-RuCl(dpe)$_2$	H	$C_4H_2SC{=}C{=}C{=}$[*trans*-RuCl(dppe)$_2$]	(PF$_6$)$_2$		49					143
trans-RuCl(dppe)	Ph	Ph	PF$_6$	deep red	77	1923	308.57 (PC 14.2)	215.90 (PC 2.5)	161.47 (PC 1.4)	84
trans-RuCl(dppe)	C_6H_4Cl-4	C_6H_4Cl-4	PF$_6$	deep red	84		308.33 (PC 14.4)	220.84 (PC 2.7)	(n.g.)	84
trans-RuCl(dppe)	C_6H_4F-4	C_6H_4F-4	PF$_6$	deep red	81		305.88 (PC 13.9)	215.07	(n.g.)	84
trans-Ru($C{\equiv}CPh$)-(dppe)$_2$	Ph	Ph	PF$_6$	deep blue	60	1921	316.58 (PC 14)	213.21 (PC 2)	162.31	140
trans-Ru($C{\equiv}CC_6H_4NO_2$-4)(dppe)$_2$	H	$C_6H_4CH(OH)C{\equiv}CH$	PF$_6$		79					143
trans-Ru($C{\equiv}CC_6H_4NO_2$-4)(dppe)$_2$	H	$C_6H_4C{=}C{=}C{=}$[*trans*-Ru($C{\equiv}CC_6H_4NO_2$-4)-(dppe)$_2$]	PF$_6$	blue-black	61					143
cis-RuCl(κ^2-*P*,*O*-$PPr^i{}_2C_2H_4OMe$)$_2$	Ph	Ph	OTf	red	29	1930	304.6 (PC 18.5)	220.3	154.6	144
cis-RuCl(κ^2-*P*,*O*-$PPr^i{}_2C_2H_4OMe$)$_2$	Ph	C_6H_4Me-2	OTf	red	38	1930	308.3 (PC 18.0)	222.0	155.0	144

Table 2. (Continued)

							^{13}C NMR[a]			
ML$_n$	R^1	R^2	[X]$_n$	color	yield, %	ν(CCC)	C(1)	C(2)	C(3)	ref
				Group 8 (Continued)						
RuCl(np$_3$)	CH=CPh$_2$	OMe	BPh$_4$	deep red	66	1955	252.90 (PC 95.7, 16.2)	n.s.	159.19	78
RuCl(np$_3$)	CH=CPh$_2$	OMe	PF$_6$	red	46	1955	253.08 (PC 95.5, 18.5)	143.90 (PC 25, 1)	159.04	78
RuCl(np$_3$)	Ph	Ph	PF$_6$	violet	55	1933	323.81 (PC 96.7, 17.8)	205.94 (PC 26.3)	167.82	78
RuCl$_2$(CNBu^t)(PPr$^i_2$CH$_2$CO$_2$Me)$_2$	Ph	Ph		lilac	75	1970	323.3 (PC 16.2)	225.8 (PC 2.5)	146.7	71
RuCl$_2$(PPr$^i_2$CH$_2$CO$_2$Me){κ^2-*P*,*O*-PPr$^i_2$CH$_2$C(O)OMe}	Ph	Ph		deep red	68	1915	306.2 (PC 16.5)	249.0 (PC 3.8)	147.7 (PC 1.9)	71
RuCl$_2$(PPr$^i_2$CH$_2$CO$_2$Me){κ^2-*P*,*O*-Pr$^i_2$CH$_2$C(O)OMe}	Ph	C$_6$H$_4$Me-2		red	68	1885	311.0 (PC 16.6)	242.2 (PC 4.1)	147.8 (PC 1.9)	71
RuCl$_2$(py)(PPr$^i_2$CH$_2$CO$_2$Me)$_2$	Ph	Ph		violet	62	1908	304.5 (PC 15.8)	247.9 (PC 3.0)	147.0	71
Ru(acac)$_2$(PPh$_3$)	Ph	Ph		deep red	58	1890	292 (PC 22.1)	239.2 (PC 2.0)	143.1	145
RuCl(PPh$_3$)Cp*	Ph	Ph		red	22	1879	300.0	224.0	146.5	134
RuCl{PPr$^i_2$CH$_2$C(O)Me}Cp*	Ph	Ph		red	18	1865	269.82 (PC 22.6)	232.79	167.72	80
Ru(CO)(PPh$_3$)(η^5-C$_9$H$_4$Me$_3$)	Ph	Ph	BF$_4$	violet	65−85		289.29 (PC 15.9)	183.62 (PC 1.8)	166.94	133
Ru(PMe$_3$)$_2$Cp	Ph	Ph	PF$_6$	orange-brown	76	1926	295.8	216.0	153.8	28
Ru(PPh$_3$)$_2$Cp	H	C≡C[Ru(PPh$_3$)$_2$Cp]	BF$_4$	blue	61	1881	228.5 (PC 21.7)	168.5	133.1	150
Ru(PPh$_3$)$_2$Cp	H	CH=C=[Ru(PPh$_3$)$_2$Cp]	(BF$_4$)$_2$	purple	76		282.4 (PC 19.2)	191.1	138.0	150
Ru(PPh$_3$)$_2$Cp	Me	C$_4$H$_3$NMe	BF$_4$	deep blue	91	1951	256.0 (PC 20)	166.7	141.0	109,130
Ru(PPh$_3$)$_2$Cp	Me	C$_4$H$_3$NMe	PF$_6$	deep blue	75	1948	256.7 (PC 20)	167.4	146.0	109,130
Ru(PPh$_3$)$_2$Cp	Me	NPh$_2$	BF$_4$	yellow	66	1997	218.9 (PC 21)	153.0	145.4	109,130
Ru(PPh$_3$)$_2$Cp	Me	NPh$_2$	PF$_6$	yellow	64	1988	219.2 (PC 21)	153.0	145.4	109,130
Ru(PPh$_3$)$_2$Cp	C$_5$H$_5$Me$_2$[Ru(PPh$_3$)$_2$Cp]		PF$_6$	deep blue	77	1975	277.1	151.4	142.4	76,129
Ru(PPh$_3$)$_2$(η^5-C$_9$H$_7$)	H	Ph	PF$_6$	red	63	1936	301.39 (PC 18.7)	212.16	142.70	83
Ru(PPh$_3$)$_2$(η^5-C$_9$H$_7$)	Me	Ph	PF$_6$	purple	55	1934	292.88 (PC 19.1)	202.47	156.93	83
Ru(PPh$_3$)$_2$(η^5-C$_9$H$_7$)	Ph	Ph	PF$_6$	violet	72	1933	290.90 (PC 18.6)	208.44	156.59	83,132
Ru(PPh$_3$)$_2$(η^5-C$_9$H$_7$)	C$_{12}$H$_8$		PF$_6$	violet	83	1932	291.39 (PC 18.1)	211.17	150.02	83
Ru(PPh$_3$)$_2$(η^5-C$_9$H$_7$)	C$_{13}$H$_{20}$		PF$_6$	orange	55	1952	304.48 (PC 19.4)	191.07	186.83	74
Ru(PPh$_3$){PPh$_2$CH$_2$C(O)Bu^t}Cp	Ph	Ph	PF$_6$	dark green	82	1938	294.4 (PC 18)	207.0	161.2	131
Ru(PPh$_3$){PPh$_2$CH$_2$C(O)Bu^t}(η^5-C$_9$H$_7$)	Ph	Ph	PF$_6$	dark violet	75	1932	290.2 (PC 17.9)	205.7	156.5	131
Ru(PPh$_3$)$_2${[O(EtO)$_2$P]$_3$CoCp}	Me	Ph	PF$_6$	red	55	1932	311.8 (PC 26.4)	151.8	220.7	146
Ru(dppm)(η^5-C$_9$H$_7$)	Ph	Ph	PF$_6$	violet	76	1935	290.26 (PC 16.8)	202.25	155.54	83,132

Table 2. (Continued)

ML_n	R^1	R^2	$[X]_n$	color	yield, %	ν(CCC)	^{13}C NMR^a C(1)	C(2)	C(3)	ref
Group 8 (Continued)										
Ru(dppm)(η^5-C_9H_7)	$C_{12}H_8$		PF_6	violet	72	1952	290.77 (PC 16.3)	205.24	148.05	83
Ru(dppm)(η^5-$C_9H_4Me_3$)	Ph	Ph	BF_4	violet	65−85					133
Ru(dippe)Cp	Me	Me	BPh_4	brown	63	1996				127
Ru(dippe)Cp	Me	Ph	BPh_4	brown	80	1936	285.24 (PC 17.2)	150.53	141.92	127
Ru(dippe)Cp	$C_5H_5Me_2$-[Ru(dippe)Cp]		BF_4	blue		1972	271.12 (PC 11.1)	186.7	149.05	127
Ru(dippe)Cp*	Me	Me	BPh_4	brown	80−85	1936	288.34 (PC 17.1)	199.0	153.52	127
Ru(dippe)Cp*	Me	Ph	BPh_4	brown	80−85	1915	271.04 (m)	209.21	147.90	127
Ru(dippe)Tp	Me	Ph	BPh_4	dark red-brown	78	1973	312.9 (PC 17.2)	205.1	156.3	136
Ru(dippe)Tp	$C_5H_5Me_2$-[Ru(dippe)Tp]		BPh_4	dark blue	50	1941				136
Ru(dppe)Cp	H	$CH{=}C{=}$[Ru(dppe)Cp]	$(BF_4)_2$	purple	74	1953, 1881	281.1 (PC 19.6)	188.9	132.8	150,151
Ru(dppe)Cp	H	$C{\equiv}C$[Ru(dppe)Cp]	BF_4	blue	86	1881	225.6 (PC 20.9)	163.1	128.4	150
Ru(dppe)(η^5-C_9H_7)	Ph	Ph	PF_6	violet	75	1943	292.84 (PC 19.2)	203.54	157.32	83,132
Ru(dppe)(η^5-C_9H_7)	$C_{12}H_8$		PF_6	violet	74	1936	293.99 (PC 18.4)	207.59	149.86	83
RuCl(PMe_3)(η-C_6Me_6)	$CH{=}CPh_2$	NPh_2	PF_6	red-brown	53	2010	213.04 (PC 33.0)	121.02	152.10	138
RuCl(PMe_3)(η-C_6Me_6)	$CH{=}CPh_2$	OEt	PF_6	violet	45	2000	231.20 (PC 28.6)	133.55	161.13	138
RuCl(PMe_3)(η-C_6Me_6)	$CH{=}CPh_2$	OPr^i	PF_6	violet	57	2000	229.0 (PC 30.5)	131.88	161.12	110,138
RuCl(PMe_3)(η-C_6Me_6)	Ph	Ph	PF_6	violet	69	1940				79,82
RuCl(PMe_3)(η-C_6Me_6)	Ph	Fc	PF_6	violet	45	1965	243.26 (PC 30.5)	169.40	154.70	75,82
RuCl(PEt_3)(η-C_6Me_6) (2 diastereomers)	$CH{=}CPh_2$	OCHMeEt	PF_6	violet	59	1972	229.97 (PC 26.8); 229.15 (PC 27.5)	134.04; 133.83	161.08; 161.05	138
RuCl(PMe2Ph)(η-C_6Me_6)	$CH{=}CPh_2$	NPh_2	PF_6	violet	47	1997	210.37 (PC 32.3)	120.68	150.16	138
RuCl(PMe_2Ph)(η-C_6Me_6)	$CH{=}CPh_2$	OPr^i	PF_6	violet	38	1974	227.99 (PC 28.8)	132.13	161.40	110,138
RuCl(PMe_2Ph)(η-C_6Me_6) (2 diastereomers)	$CH{=}CPh_2$	OCHMeEt	PF_6	violet		1961	227.49 (PC 28.7); 227.26 (PC 29.4)	130.88; 130.73	161.65; 161.63	138
RuCl($PMePh_2$)(η-C_6Me_6)	$CH{=}CPh_2$	NPh_2	PF_6	red-brown	81	2010	210.62 (PC 32.2)	122.75	150.85	110
RuCl(PPh_3)(η-C_6Me_6)	Ph	Ph	PF_6	dark green	81	1965	288.30 (PC 29.1)	191.04	167.38	82
$Ru_2(\mu$-$Cl)_3(PPh_3)_2$	Ph	Ph	PF_6	violet	84	1930	310.8 (PC 19.7)	217.8	158.7	84
$Ru_2(\mu$-$Cl)_3(PPh_3)_2$	C_6H_4Cl-4	C_6H_4Cl-4	PF_6	violet	64	1924	309.8 (PC 19.9)	220.55	154.1	84
$Ru_2(\mu$-$Cl)_3(PPh_3)_2$	C_6H_4F-4	C_6H_4F-4	PF_6	violet	59					84
Os{C[C(O)OMe]$=CH_2$-}(CO)(PPr^i_3)$_2$	Ph	Ph	BF_4	dark red	94	1954	279.3 (PC 9.1)	197.9	156.0	147

Table 2. (Continued)

ML_n	R^1	R^2	$[X]_n$	color	yield, %	ν(CCC)	^{13}C NMR^a			ref
							C(1)	C(2)	C(3)	
				Group 8 (Continued)						
cis-$OsCl(CO)\{C[C(O)OMe]=CH_2\}(PPr^i_3)_2$	Ph	Ph		purple	16	1954	284.1 (PC 11.0)	221.6	135.4	147
trans-$OsCl(CO)\{C[C(O)OMe]=CH_2\}(PPr^i_3)_2$	Ph	Ph		purple	40	1961	268.0 (PC 10.1)	232.5	139.3	147
trans-$OsCl(dppm)_2$	H	Ph	PF_6	dark red	88	1940	230.0	147.9	144.4	246
$OsCl(PPr^i_3)Cp$	Ph	Ph		green	100	1874	225.1 (PC 15.2)	238	129.1	137
$OsI(PPr^i_3)Cp$	Ph	Ph		brown	64	1872	234.1 (PC 14.3)	243.3	132.0	137
$Os(PPh_3)_2(\eta^5\text{-}C_9H_7)$	Ph	Ph	PF_6	purple	55	1908	336.41	218.76	149.12	83
$Os(PPh_3)_2(\eta^5\text{-}C_9H_7)$	$C_{12}H_8$		PF_6	purple	39	1922	340.55	281.58	147.13	83
				Group 9						
trans-$RhCl(PPr^i_3)_2$	H	Ph		yellow	67	1875	223.95 (PC 17.1)	250.02 (PC 7.0)	151.66	87,92
trans-$RhCl(PPr^i_3)_2$	Me	Ph		red		1885				87
trans-$RhCl(PPr^i_3)_2$	Pr^i	Pr^i				1889				87
trans-$RhCl(PPr^i_3)_2$	$C_{12}H_8$			deep red	91	1875	(n.a.)	(n.a.)	151.84	87
trans-$Rh(NCO)(PPr^i_3)_2$	Ph	Ph		red	95	1892	255.2 (RhC 60.4; PC 17.1)	233.5 (RhC 15.1; PC 6.0)	159.9	153
$Rh(AsPr^iC_2H_4OMe)Cp$	Ph	Ph		turquoise oil	66	1908	225.73 (RhC 68.4)	209.25 (RhC 15.9)	165.33	149
$Rh(AsPr^iC_2H_4OMe)Cp$	Ph	$C_6H_4Me\text{-}2$		turquoise-blue oil	68	1912	227.52 (RhC 67.7)	207.85 (RhC 16.0)	163.18	149
trans-$Rh(N_3)(PPr^i_3)_2$	Bu^t	Ph		green	quant	1885	255.0 (PC 17.1; RhC 62.4)	244.6 (PC 6.0; RhC 15.1)	140.5	153
trans-$Rh(N_3)(PPr^i_3)_2$	Ph	Ph		red	quant	1870	233.7 (PC 17.1; RhC 62.4)	244.6 (PC 6.0; RhC 15.1)	140.5	153
trans-$Rh(N_3)(PPr^i_3)_2$	$C_6H_4OMe\text{-}4$	$C_6H_4OMe\text{-}4$		violet	quant	1885	235.0 (PC 17.1; RhC 61.4)	228.4 (PC 6.0; RhC 15.1)	142.0	153
trans-$Rh(OH)(PPr^i_3)_2$	Ph	Ph					221.8 (PC 18.2)	247.4 (PC 5.8)	129.7	154
trans-$Rh(OPh)(PPr^i_3)_2$	Ph	Ph					229.8 (PC 18.4)	251.6 (PC 5.7)	136.3 (PC 2.2)	154
trans-$Rh\{OC(O)Me\}(PPr^i_3)_2$	Ph	Ph					204.8 (PC 17.8)	245.0 (PC 7.0)	134.8 (PC 2.5)	154
trans-$RhCl(AsPr^iC_2H_4OMe)_2$	Ph	Ph		red	79	1875	220.25 (RhC 58.6)	248.35 (RhC 13.4)	154.32	149
trans-$RhCl(AsPr^iC_2H_4OMe)_2$	Ph	$C_6H_4Me\text{-}2$		red	89	1877	221.51 (RhC 58.8)	246.94 (RhC 13.4)	153.62	149
trans-$IrCl(PPr^i_3)_2$	Ph	Ph		dark red	72, 91	1875	199.3 (PC 13.4)	249.7 (PC 3.9)	138.7 (PC 2.5)	155

[a] *J*(XC) in parentheses; resonances are singlets otherwise.

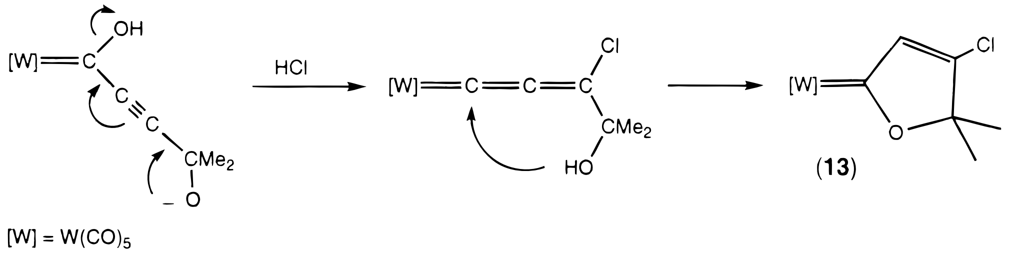
$MeCOCl/PPh_3$ resulted in formation of vinylidene **14** (Scheme 12).[106]

Related reactions of $M(CO)_5(thf)$ (M = Cr, W) with $[C{\equiv}CC(NMe_2)_3]^-$ gave $[M\{C{\equiv}CC(NMe_2)_3\}(CO)_5]^-$ which with $BF_3{\cdot}OEt_2$ gave yellow air-stable $M\{=C=C=C(NMe_2)_2\}(CO)_5$ in good yield.[118] No further reaction occurred with an excess of $NHMe_2$.

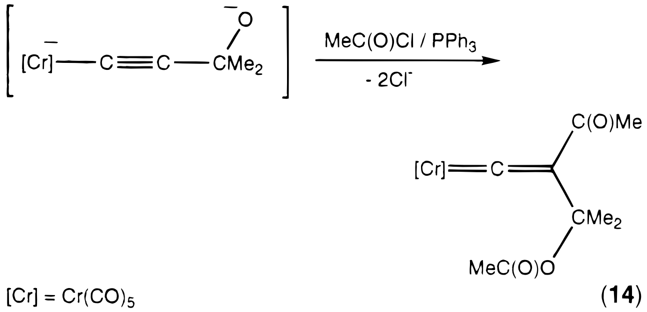
Reactions of $M\{=C(OEt)C{\equiv}CPh\}(CO)_5$ (M = Cr, W) with ethoxide gave a mixture of $M\{=C=C=CPh(OEt)\}(CO)_5$ and (*E*/*Z*)-$M\{=C(OEt)CH=CPh(OEt)\}(CO)_5$ (Scheme 13); the Cr complexes decomposed readily under the reaction conditions.[96]

A variety of ethoxy(alkynyl)carbene complexes $Cr\{=C(OEt)C{\equiv}CR\}(CO)_5$ [R = Bu^t, c-$C_3H_4(OEt)$, CMe_2-

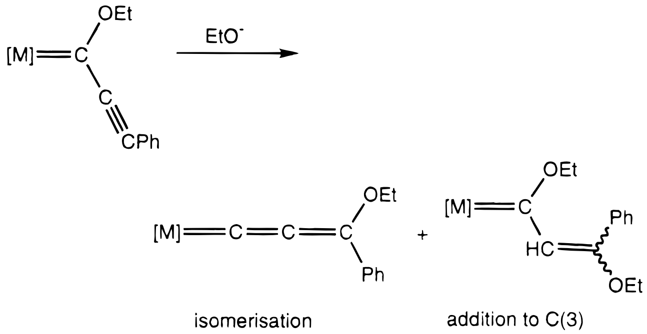
Scheme 11



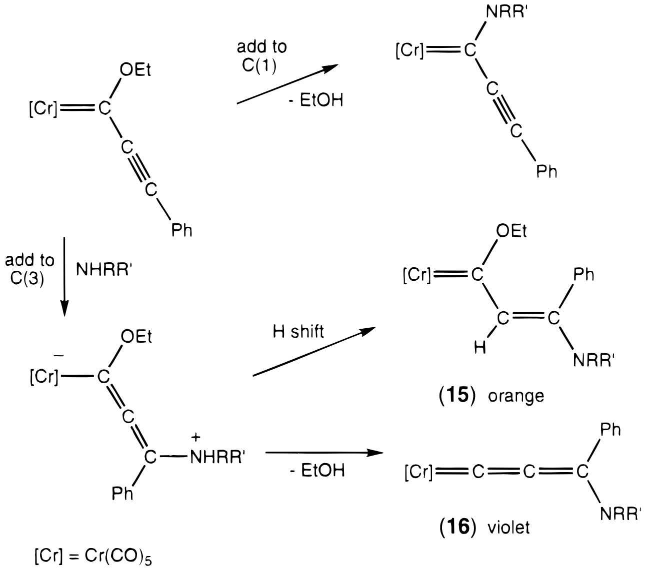
Scheme 12



Scheme 13



Scheme 14



(OEt), $SiMe_3$] react with secondary amines NHR'_2 (R' = Me_2, Et_2, Pr^i_2, $CH_2CH{=}CH_2$, CH_2Ph; R'_2 = HPr^n, HPr^i, HCy) in Et_2O to give Michael adducts $Cr\{{=}C(OEt)CH{=}CR(NR'_2)\}(CO)_5$ and the allenylidenes as byproducts $Cr\{{=}C{=}C{=}CR(NMe_2)\}(CO)_5$.[94,95] The $SiMe_3$-substituted isomers are obtained in approximately equal amounts. Factors affecting the formation of the allenylidene include the size of the substituents R and R' (increased yield with increased bulk, which promotes loss of EtOH), the basicity of the amine (increased yields with increasing basicity), and reaction temperature (higher yields with higher temperatures). In some cases, higher yields of the allenylidenes were obtained from reactions of the carbene complexes [R = Ph, c-Pr, Bu^t, $CMe_2(OEt)$] with lithium amides, $LiNR'_2$. The same complexes were obtained from reactions of $Cr\{{=}C(OEt)CH{=}C(NEt_2)CMe_2(OEt)\}(CO)_5$ with LiR (R = NEt_2, tmp, Bu^t), while D_2O gave the d^1 complex. Secondary amines also react, again bulky groups giving allenylidenes $Cr\{{=}C{=}C{=}CR(NR'_2)\}(CO)_5$ [R = Ph, R' = Pr^i; R = $CMe_2(OEt)$, R' = $CH_2CH{=}CH_2$, CH_2Ph].

Note that the reaction between $Cr\{C(OEt)C{\equiv}C(SiMe_3)\}(CO)_5$ and $NHMe_2$ at room temperature was shown be a 57/43 mixture of $Cr\{C(NMe_2)C{\equiv}C(SiMe_3)\}(CO)_5$ and $Cr\{C(OEt)CH{=}C(NMe_2)(SiMe_3)\}(CO)_5$; the ethynylcarbene complex is formed quantitatively at −100 °C.[119] Consequently, the structure of the secondary allenylidene $Cr\{{=}C{=}C{=}CH(NMe_2)\}(CO)_5$ originally reported[94] is reassigned as $Cr\{{=}C(NMe_2)C{\equiv}C(SiMe_3)\}$. Similar reactions of $Cr\{{=}C(NMe_2)C{\equiv}CPh\}(CO)_5$ with $NHEt_2$ gave a 59/41 mixture of $Cr\{{=}C{=}C{=}CPh(NEt_2)\}(CO)_5$ and $Cr\{{=}C(NMe_2)CH{=}CPh(NEt_2)\}(CO)_5$ (E/Z = 3.5:1).[87]

Three competing paths for aminolysis of ethoxy(alkynyl)carbene complexes involve substitution at C(1) and addition to C(3) followed by either H-shift to form 2-aminoethenylcarbene complexes (**15**) or elimination of EtOH to give 3-aminoallenylidene complexes (**16**) (Scheme 14).[95]

Conversion of **15** to **16** can be achieved by reaction of the former with $AlCl_3$ in CS_2/CH_2Cl_2 (Scheme 15; for R,R' = Me_2; Me,Ph; Et,Ph; indolinyl).[120]

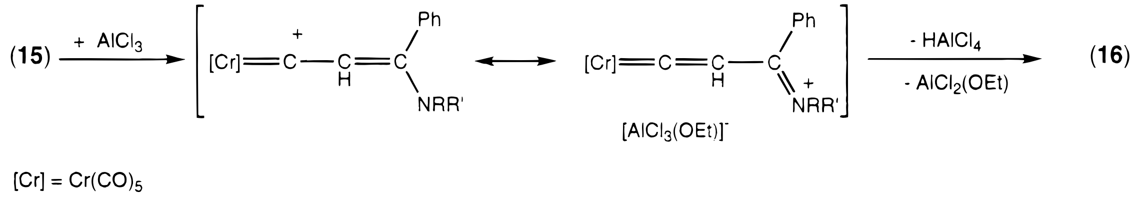
The product is formed as a 3/2 mixture of stereoisomers, which undergo slow interconversion by hindered rotation around the C=N bond (Scheme 16).[120]

Vinylallenylidenes are formed by nucleophilic addition to C(3) of $M\{{=}C{=}C{=}C{=}C{=}C(NMe_2)_2\}(CO)_5$, e.g., the addition of $NHMe_2$ gives $M\{{=}C{=}C{=}C(NMe_2)CH{=}C(NMe_2)_2\}(CO)_5$.[118]

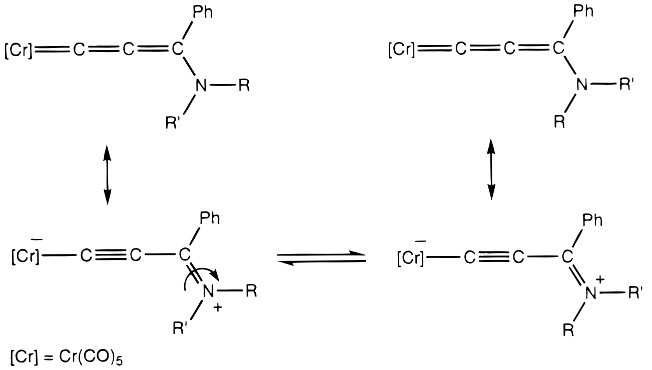
C. Manganese

Deprotonation of η^2-1-alkyne carboxylic esters with excess LiR (R = Bu^t, Cy, Ph, CH_2Ph), followed by deoxygenation with HCl or $COCl_2$ gave the allenylidenes $Mn({=}C{=}C{=}CR_2)(CO)_2Cp$ (method ii; tested synthetic procedure in ref 121).[103,121] In essence, this reaction is closely related to those involving addition of the ynol dianions to $M(CO)_6$ (above). Similar

Scheme 15



Scheme 16



reactions with LiMe give $[Mn(=C=C-CMe_2O)(CO)_2Cp]^{2-}$, which loses Me_2CO to form $[Mn(C\equiv C)(CO)_2Cp]^{2-}$. Further reaction with LiMe gave only polymeric products, but neutralization with MeOTf gave $Mn(C=CMe_2)(CO)_2Cp$ (Scheme 17).[103]

D. Iron, Ruthenium, and Osmium

1. Iron

Reactions of deprotonated $HC\equiv CCBu^t_2(OH)$ with $Fe(CO)_4(NMe_3)$ gave mixtures of mono- and polynuclear complexes, from which $Fe(=C=C=CBu^t_2)(CO)_4$ and $Fe\{=C=C=CCBu^t_2OC(O)O\}(CO)_4$ (**17**) were isolated. The latter is formed by cyclization of an intermediate acylethynyl complex (Scheme 18).[107]

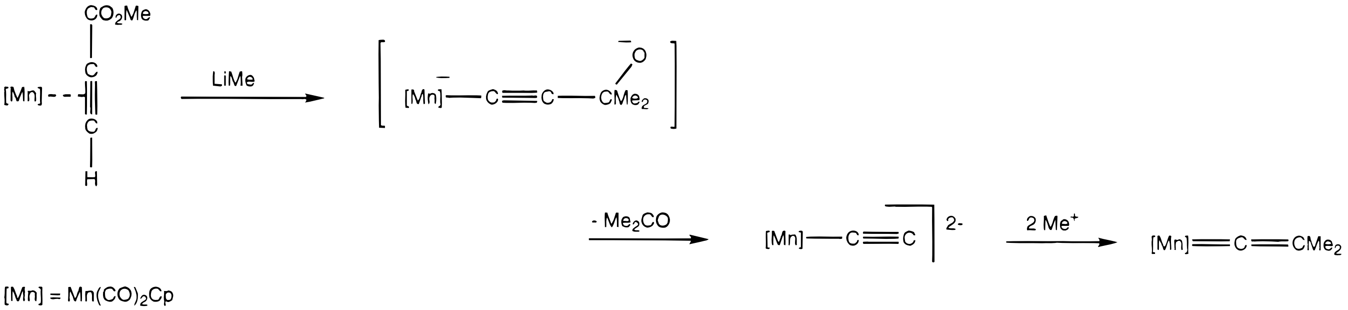
The mixture of dinitrogen complexes $N_2\{Fe(CO)_2(PEt_3)_2\}_n$ (n = 1, 2) is a source of the electron-rich $Fe(CO)_2(PEt_3)_2$ fragment. Oxidative addition of propynols gave hydridoalkynyl complexes which on deprotonation with LiBu and treatment with MeCOCl at −60 °C gave $Fe\{=C=C=CR_2)(CO)_2(PEt_3)_2$ (R = Bu^t, Ph).[122] Similarly, $Na[FeI(CO)_2\{P(OMe)_3\}_2]$ is a source of the $Fe(CO)_2\{P(OMe)_3\}_2$ fragment and reacts with $HC\equiv CCR^1R^2(OH)$ to give the corresponding vinylidenes, which on alumina or silica dehydrate to give either allenylidenes or vinylvinylidenes. The former are formed with $R^1 = R^2 = Bu^t$, Ph and $R^1 = Bu^t$, R^2 = Ph. The diphenyl complex was formed directly if $HC\equiv CCPh_2(OAc)$ was used.[122]

The photoreaction between $[Fe(CO)(dppe)Cp]^+$ and $HC\equiv CCPh_2(OH)$ (>280 nm, 12 h, CH_2Cl_2) gave $[Fe(=C=C=CPh_2)(dppe)Cp]^+$; analogous reactions with 2-methyl-3-butyn-2-ol and 1-ethynylcyclohexanol were unsuccessful.[90] The intermediate hydroxyvinylidene complex can be obtained from FeCl(dppe)Cp.[28]

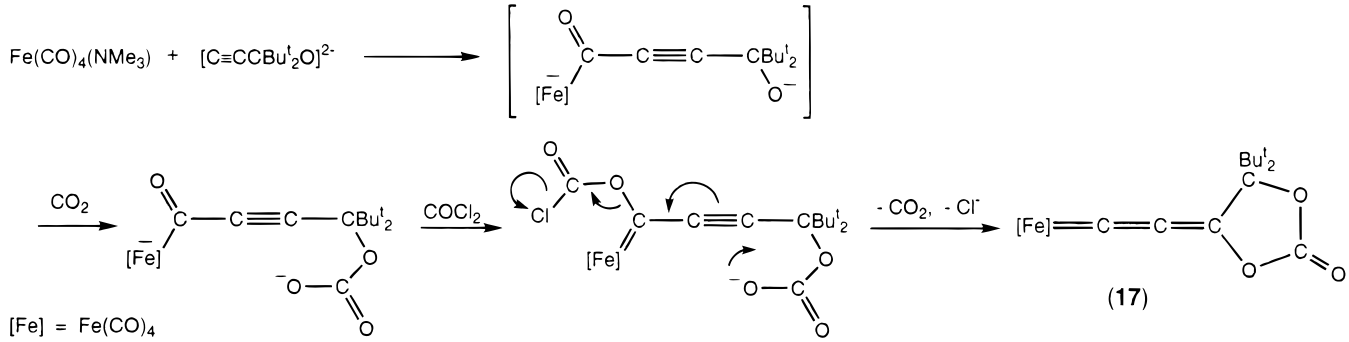
2. Ruthenium and Osmium

The most general synthesis of these complexes is the activation of propyn-1-ol derivatives toward spontaneous dehydration by ruthenium. Intermediacy of allenylidene complexes explains formation of frequently observed alkenylcarbene complexes or dimeric products (section IX.B). The most common metal−ligand combinations are $MCl(PR_3)_2Cp$ (M =

Scheme 17



Scheme 18



Ru; R = Ph; Cp = Cp, Cp*, $\eta^5-C_9H_7$; M = Os, R = Ph, Cp = $\eta^5-C_9H_7$),

$RuCl_2(PR_3)(\eta$-arene) (R = Me; arene = C_6H_6, mesitylene, C_6Me_6), *trans*-$RuCl_2(PP)_2$ (PP = dppm, dppe), and $RuCl_2(L_n)$ [L_n = $N(C_2H_4PPh_2)_3$, np$_3$; $PPr^i{}_2CH_2CH_2OMe$]. It is noticeable that the dehydration of the hydroxyvinylidene is either inhibited or prevented altogether by strongly electron-releasing systems, such as $Ru(\eta-C_5R_5)$, in contrast to the more electron-poor $Ru(\eta$-arene) analogues, thereby allowing the isolation of several examples. The indenyl group is also more electron-releasing than C_6Me_6.[83] The arene−ruthenium system has greater electrophilicity and smaller bulk than $[RuCl(dppe)_2]^+$.[123]

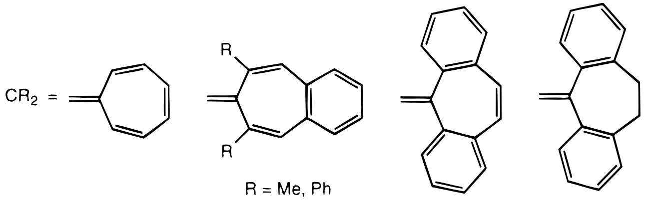
a. Derivatives of $M(L)_2(\eta-C_mR_n)$ (M = Ru, Os; C_mR_n = Cp, Cp*, $\eta^5-C_9H_7$, $\eta^5-C_9H_4Me_3$). The solvated complex $[Ru(OCMe_2)(CO)(PPr^i{}_3)Cp]^+$ reacts with $HC{\equiv}CCPh_2(OH)$ to give $[Ru(=C=C=CPh_2)(CO)(PPr^i{}_3)Cp]^+$; $HC{\equiv}CCH_2(OH)$ and 1-ethynylcyclohexanol give the related hydroxycarbenes $[Ru\{=C(OH)CH=CR_2\}(CO)(PPr^i{}_3)Cp]^+$ [R_2 = H_2, $(CH_2)_5$], possibly by reaction of an intermediate allenylidene (not detected) with H_2O.[124] The latter reaction contrasts with that of $[Os(CO)(PPr^i{}_3)Cp]^+$ with ethynylcyclohexanol, which gives the vinylvinylidene $[Os\{=C=CH(\text{cyclohex-1-enyl})\}(CO)(PPr^i{}_3)Cp]^+$.[125]

The first allenylidene complex was obtained from $RuCl(PMe_3)_2Cp$ and $HC{\equiv}CCPh_2(OH)$, when brown $[Ru(=C=C=CPh_2)(PMe_3)_2Cp]^+$ was obtained;[28] the $(PPh_3)_2$[126] and dippe[127] analogues have been obtained similarly. They are formed by dehydration of (unobserved) intermediate hydroxyvinylidenes, formed by a 1,2-H shift in the alkyne.

Strongly polarized ruthenium allenylidene complexes (**18**) have been obtained by using the ethynylhydroxycycloheptatrienes and their mono- and dibenzo derivatives in the classical reaction.[128] 1-Ethynylcycloheptatriene afforded the alkynyl complex directly, but this could not be further transformed to the allenylidene with $[CPh_3]^+$. Instead, the ethynyltropylium cation was treated with $Na[OSiMe_3]$ to give an isomeric mixture of the ethynyl silyl ethers, which gave $[Ru(=C=C=C_7H_6)(PPh_3)_2Cp]^+$ directly. Combination of the strong electron donor $Ru(PPh_3)_2Cp$ and strong electron acceptor tropylium groups at each end of the unsaturated C=C=C chain results in their having NLO properties, with large SHG efficiencies [section V.B.iii].

$[Ru(=C=C=CR_2)(PPh_3)_2Cp]^+$

(**18**)



Allenylidene complexes are also obtained by reactions of aprotic nucleophiles with the butatrienylidene complex $[Ru(=C=C=C=CH_2)(PPh_3)_2Cp]^+$.[109,129,130] Thus, with $NHPh_2$, the structurally characterized $[Ru\{=C=C=CMe(NPh_2)\}(PPh_3)_2Cp]^+$ is formed, while with *N*-methylpyrrole, $[Ru\{=C=C=CMe(pyr)\}(PPh_3)_2Cp]^+$ was obtained.

Complexes containing the hemilabile ligand $PPh_2CH_2C(O)Bu^t$ such as $[Ru(PPh_3)\{\kappa^2\text{-}P,O\text{-}PPh_2CH_2C(O)Bu^t\}(L)]^+$ (L = Cp, $\eta^5-C_9H_7$) react with $HC{\equiv}CCPh_2(OH)$ to give $[Ru(=C=C=CPh_2)(PPh_3)\{PPh_2CH_2C(O)Bu^t\text{-}P\}(L)]^+$. In ROH (R = Me, Et), these complexes react with K_2CO_3, adding OR to C(3) to form $Ru\{C{\equiv}CCPh_2(OR)\}(PPh_3)\{PPh_2CH_2C(O)Bu^t\text{-}P\}(L)$; in thf, deprotonation of the enolized $PPh_2CH_2C(O)Bu^t$ ligand is followed by attack at C(1) to give the chelate complex $Ru\{C(CHCOBu^t)PPh_2\}=C=CPh_2\}(PPh_3)(L)$ in a diastereoselective reaction.[131] With acidic alumina, the allenylidene $[Ru(=C=C=CPh_2)\{\kappa^2\text{-}P,O\text{-}PPr^i{}_2CH_2C(O)OMe\}Cp^*]^+$ is obtained directly from $RuCl\{PPr^i{}_2CH_2C(O)OMe\}Cp^*$ and $HC{\equiv}CCPh_2(OH)$; acidic alumina also induces isomerization of the vinylidene.[80]

A series of indenyl−Ru and −Os complexes have been obtained from $MCl(L)_2(\eta^5-C_9H_7)$ [M = Ru, Os; L = PPh_3 (**19**); L_2 = dppm (**20**), dppe (**21**)] and $HC{\equiv}CCR_2(OH)$ [R_2 = Ph_2, $C_{12}H_8$ (2,2′-biphenyldiyl)] in MeOH with $NaPF_6$.[83,132] With $HC{\equiv}CCMePh(OH)$, complexes **20** or **21** gave mixtures of $[Ru(=C=C=CMePh)(LL)(\eta^5-C_9H_7)]^+$ and $[Ru\{=C=CH(CPh=CH_2)\}(LL)(\eta^5-C_9H_7)]^+$, the latter being formed by combination of the OH group with a methyl H atom. For **19** (R = Ph), these complexes could be separated by chromatography on silica gel. However, deprotonation of the mixture (K_2CO_3/CH_2Cl_2) gave the enynyl complexes in good yield.

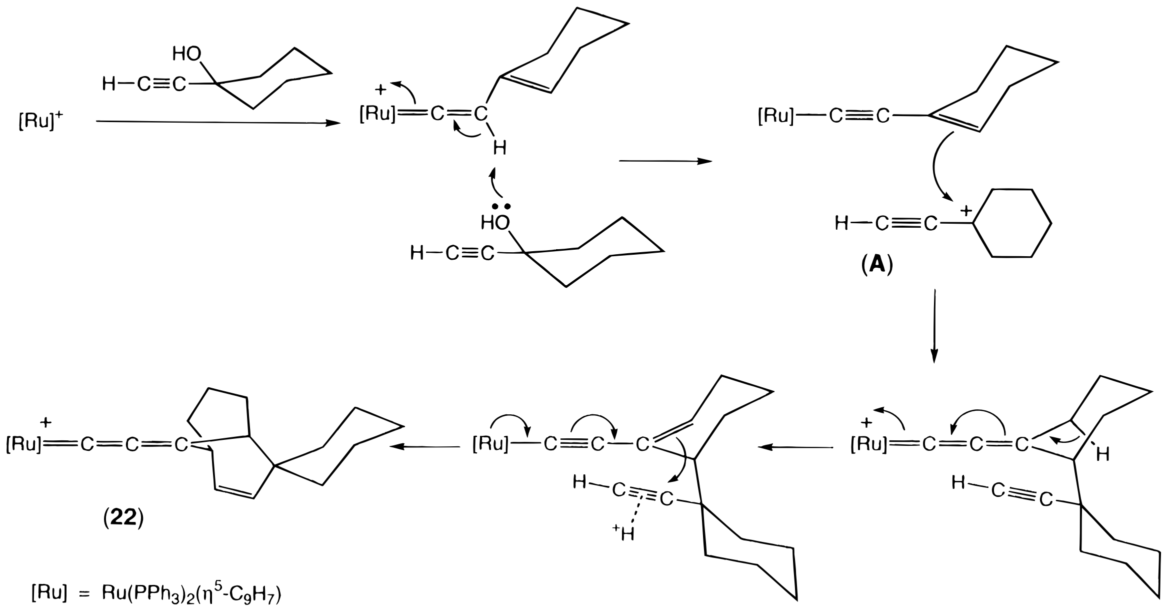
Reactions with $HC{\equiv}CCHPh(OH)$ gave the *secondary* allenylidenes $[Ru(=C=C=CHPh)(LL)(\eta^5-C_9H_7)]^+$ by ready elimination of MeOH from the intermediate $[Ru\{=C=CHCHPh(OMe)\}(LL)(\eta^5-C_9H_7)]^+$ which could be detected by ^{31}P NMR.[71] Only $[Ru\{=C(OMe)CH=CHPh\}(LL)(\eta^5-C_9H_7)]^+$ was obtained from **20** or **21**, by addition of MeOH to the allenylidene. Evidently, small steric differences in PR_3 control stabilization of the allenylidene. With 2-propyn-1-ol, the vinylidene $[Ru\{=C=CHCH_2(OH)\}(PPh_3)_2(\eta^5-C_9H_7)]^+$ is stable to dehydration, while the dppm complex gives $[Ru\{=C(OMe)CH=CH_2\}(dppm)(\eta^5-C_9H_7)]^+$.[83]

Formal addition of 2 equiv of 1-ethynylcyclohexanol to $RuCl(PPh_3)_2(\eta^5-C_9H_7)$ and double dehydration gave the unusual allenylidene complex **22** (Scheme 19). The initial product is the expected vinylidene, but reaction with a second molecule of the cyclohexanol and rearrangement gives the observed product. The key step is formation of carbocation **A** which is rapidly trapped by $Ru\{C{\equiv}C(\text{cyclohex-1-enyl})\}(PPh_3)_2(\eta^5-C_9H_7)$; intramolecular cyclization then gives **22**.[74]

A series of allenylidene complexes containing substituted η^5-indenyl ligands, $[Ru(=C=C=CPh_2)(L)(L')(\eta^5\text{-}C_9H_4Me_3\text{-}1,2,3)]^+$ [LL′ = (CO)(PPh_3), (CO)($PPr^i{}_3$), dppm] has been obtained from reactions of $RuBr(L)(L')(\eta^5-C_9H_4Me_3)$, $AgBF_4$, and $HC{\equiv}CCPh_2(OH)$ in CH_2Cl_2.[120]

Three examples of neutral allenylidene complexes in the ML_2Cp series have been made. The reaction of $RuCl(L)_2Cp^*$ [L = PPh_3;[134] L_2 = $PPr^i{}_2CH_2C(O)OMe$[80]] with $HC{\equiv}CCPh_2(OH)$ in benzene affords $RuCl(=C=C=CPh_2)(L)_2Cp^*$, the latter requiring the presence of basic alumina. The similar reaction of

Scheme 19

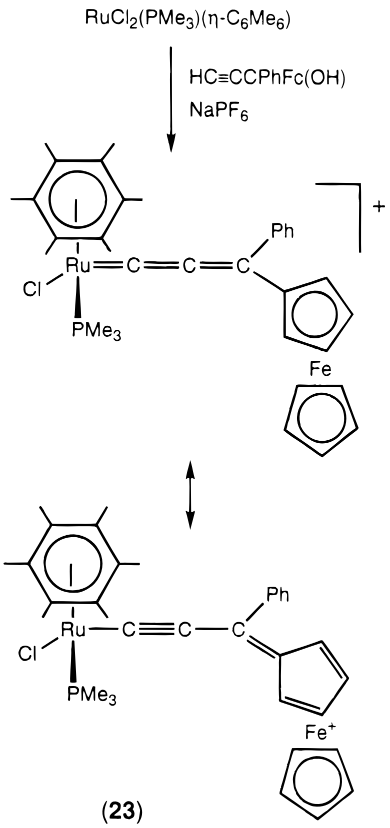


$OsCl(PPr^i_3)_2Cp$ gave the violet alkyne complex $OsCl\{\eta^2-HC_2CPh_2(OH)\}(PPr^i_3)Cp$, which was converted into green $OsCl(=C=C=CPh_2)(PPr^i_3)Cp$ at 85 °C.[137] Exchange of Cl for I occurred on treatment with KI in methanol.

b. Derivatives of $Ru(PR_3)_2Tp$ [$Tp = HB(pz)_3$]. The $HB(pz)_3$ ligand (Tp) has steric and electronic properties similar to those of Cp. Conventional reactions of RuCl(dippe)Tp with $HC≡CCMePh(OH)$ in the presence of $Na[BPh_4]$ gave $[Ru(=C=C=CMePh)(dippe)Tp]^+$, which was deprotonated to $Ru(C≡CCPh=CH_2)(dippe)Tp$.[136]

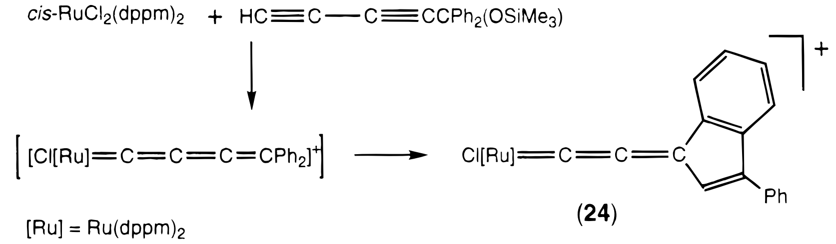
c. Derivatives of $RuCl(PR_3)(\eta$-arene). With $RuCl_2(PR_3)(\eta$-arene), activation of $HC≡CCMe=CH_2$ and $HC≡CCR_2(OH)$ [CR_2 = CHMe, CMe_2, CPh_2, $C(CH_2)_5$] gave the corresponding alkoxy(vinyl)carbene complexes, $[RuCl\{=C(OR')CH=CR_2\}(PR_3)(\eta\text{-arene})]^+$, as a result of the strong electron-accepting nature of this metal−ligand combination, which activates the short-lived allenylidene intermediates toward nucleophilic attack at C(1).[82,112,113,137] Rapid (10 min) formation of violet $[RuCl(=C=C=CPh_2)(PMe_3)(\eta-C_6Me_6)]^+$ from the dichloride and $HC≡CCPh_2(OH)$ in MeOH is followed by a slow (24 h) addition of MeOH to the allenylidene to give red $[RuCl\{=C(OMe)CH=CPh_2\}(PR_3)(\eta-C_6Me_6)]^+$.[79] With $HC≡CCH_2(OH)$, attack occurs at both C(1) and C(3) to give $[RuCl\{=C(OMe)CH_2CH_2OMe\}(PR_3)(\eta-C_6Me_6)]^+$ via $[RuCl\{=C=CHCH_2(OMe)\}(PR_3)(\eta-C_6Me_6)]^+$. The PMe_3 and PPh_3 complexes were used to prepare $[RuCl(=C=C=CPh_2)(PR_3)(\eta-C_6Me_6)]^+$ from $HC≡CCPh_2(OH)$ in slow reactions which were quenched with Et_2O after the appearance of the violet color. In contrast, the ferrocenyl derivative $[RuCl(=C=C=CPhFc)(PMe_3)(\eta-C_6Me_6)]^+$ (**23**) is stable toward MeOH addition; the cyclopentadienylidene tautomer is considered to make an important contribution to the bonding (Scheme 20).[75,82]

Scheme 20



Reactions between $RuCl_2(PMe_{3-n}Ph_n)(\eta-C_6Me_6)$ (n = 0−2) and $HC≡CC≡CPh_2(OX)$ (X = H, $SiMe_3$) in alcohols (R′OH) gave $[RuCl\{=C=C=C(OR')CH=CPh_2\}(PR_3)(\eta-C_6Me_6)]^+$ (R′ = Et, Pr^i); with $NHPh_2$ in CH_2Cl_2, $[RuCl\{=C=C=C(NPh_2)CH=CPh_2\}(PR_3)(\eta-C_6Me_6)]^+$ was formed. Slow elimination of $SiMe_3(OH)$ is followed by addition of the alcohol or amine to C(3) of the initial deep blue intermediate, probably $[RuCl(=C=C=C=C=CR_2)(PR_3)(\eta-C_6Me_6)]^+$.[110,138] The alkenylallenylidene complexes are stabilized by electron-releasing heteroatom groups on C(3), so that reactions with $HC≡CC≡CPh_2(OSiMe_3)$ in $NHPh_2$ (pK_a 0.79) gave $[RuCl\{=C=C=C(NPh_2)CH=CPh_2\}(PR_3)(\eta-C_6Me_6)]^+$.[110,123,138] The reactions strongly correlate with the pK_a of the amine: with more basic amines, e.g.,

Scheme 21



$NHPr^i_2$ (pK_a 10.96), NEt_3 (11.01) or NH_2Bu^t (10.83), only $RuCl\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}(PR_3)(\eta\text{-}C_6Me_6)$ were obtained. The latter are inert to both Pr^iOH and $NHPh_2$. The η^2-alkyne complex $[RuCl\{\eta^2\text{-}HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}(PR_3)(\eta\text{-}C_6Me_6)]^+$ can be deprotonated with $NHPr^i_2$.

This reaction allows the generation of chiral C(3) atoms in the allenylidene. In (±)-butan-2-ol, the PEt_3 complex $[RuCl\{{=}C{=}C{=}C(OCHMeEt)CH{=}CPh_2\}(PEt_3)(\eta\text{-}C_6Me_6)]^+$ formed as two diastereoisomers in approximately equal amounts. Two diastereomers of the PMe_2Ph complex (3/2 ratio) were obtained when pure (+)-butan-2-ol was used.[138]

d. Derivatives of $RuCl_2(PP)_2$ (PP = dppm, dppe). Reactions of *cis*-$RuCl_2(dppm)_2$ and $HC{\equiv}CCR_2(OH)$ (R = Me, Ph, C_6H_4Cl-4) gave *trans*-$[RuCl({=}C{=}C{=}CR_2)(dppm)_2]^+$ in high yield; cis/trans isomerization proceeds via dissociation of Cl^- and isomerization of the resulting 16-electron (16-e) intermediate,[77,139] which is sterically protected by the dppm phenyl groups. These compounds are stable to addition of MeOH, but NaOMe adds to C(3) to give *trans*-$RuCl\{C{\equiv}CCPh_2(OMe)\}(dppm)_2$, which is converted back to the allenylidene with $[CPh_3]^+$. The lability of the Cl ligand in *trans*-$RuCl(C{\equiv}CPh)(dppe)_2$ enabled reactions with $HC{\equiv}CCPh_2(OH)$ to proceed readily in NEt_3, in the presence of $NaPF_6$, to give *trans*-$Ru(C{\equiv}CPh)({=}C{=}C{=}CPh_2)(dppe)_2$.[139]

Similarly, a series of *secondary* allenylidene complexes, *trans*-$[RuCl({=}C{=}C{=}CHR)(dppm)_2]^+$ [R = C_6H_4X-4 (X = H, F, Cl, OMe), $CH{=}CHPh$], was obtained from $HC{\equiv}CCHR(OH)$ in CH_2Cl_2, but $HC{\equiv}CCHMe(OH)$ gave the vinylvinylidene *trans*-$[RuCl({=}C{=}CHCH{=}CH_2)(dppm)_2]^+$.[72,140] With 2-propyn-1-ol, only *trans*-$[RuCl\{{=}C{=}CHCH_2(OH)\}(dppm)_2]^+$ is formed, this complex being resistant to dehydration. In MeOH, there is no addition to C(1), the only product obtained after 67 h at room temperature being *trans*-$[RuCl\{{=}C{=}CHCH_2(OMe)\}(dppm)_2]^+$.[141]

The reaction of $HC{\equiv}CCMe{=}CH_2$ with *cis*-$RuCl_2(dppm)_2$ gave *trans*-$[RuCl({=}C{=}C{=}CMe_2)(dppm)_2]^+$ by a 1,4-migration of a proton via a vinylidene (method v).[77,140]

Reactions of *trans*-$RuCl\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}(dppm)_2$ [from $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ in the presence of $NaPF_6$ in NEt_3 (40%) or $Bu_3SnC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ in the presence of NH_4PF_6 (30%)] with excess $HBF_4{\cdot}OEt_2$ in MeOH gave violet *trans*-$[RuCl\{{=}C{=}C{=}C(OMe)CH{=}CPh_2\}(dppm)_2][BF_4]$ by addition of MeOH to C(3) of an intermediate *trans*-$[RuCl({=}C{=}C{=}C{=}C{=}CPh_2)(dppm)_2]^+$.[30,111,142] Similarly, protonation of *trans*-$Ru\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}_2(dppm)_2$ gave the first example of a bis-allenylidene complex, [*trans*-$Ru\{{=}C{=}C{=}C(OMe)CH{=}CPh_2\}_2(dppm)_2][BF_4]_2$, which was obtained as violet crystals.[111] In these reactions, successive elimination of $SiMe_3(OH)$ and addition of MeOH occurred.

In CH_2Cl_2, reactions between *cis*-$RuCl_2(dppm)_2$, $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ and $NaPF_6$ gave the indenylidene complex **24** (Scheme 21). This compound was also obtained from *trans*-$RuCl\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}(dppm)_2$ and $HBF_4{\cdot}OEt_2$ or $HPF_6{\cdot}OEt_2$ in CH_2Cl_2. Apparent intramolecular ortho substitution of one phenyl group in a putative pentatetraenylidene intermediate by the electrophilic C(3) and H transfer to C(4) occurs.[77,111]

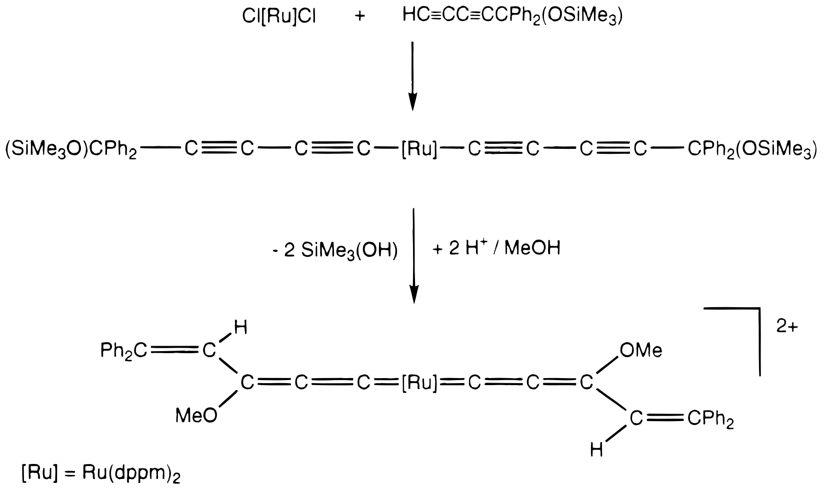
Reactions of *cis*-$RuCl_2(dppe)_2$ with 1,4-$\{HC{\equiv}CCH(OH)\}_2C_6H_4$ in the presence of $NaPF_6$ were slow, but pretreatment of the dichloride with $NaPF_6$ in CH_2Cl_2 to give $[RuCl(dppe)_2]^+$ (**25**), followed by addition of the diyne, gave violet *trans*-$[RuCl\{{=}C{=}C{=}CHC_6H_4CH(OH)C{\equiv}CH\}(dppe)_2]^+$. Further reaction with **25** in CH_2Cl_2 over 5 days gave the binuclear dication [1,4-$\{$*trans*-$RuCl({=}C{=}C{=}CH)_2(dppe)_2\}_2C_6H_4]^{2+}$, also formed from two eq 2 and the diyne directly.[143] Similar complexes were obtained from 2,5-$\{HC{\equiv}CCH(OH)\}_2C_4H_2S$ and starting from *trans*-$RuCl(C{\equiv}CC_6H_4NO_2\text{-}4)(dppe)_2$.

The bis-diynyl complex *trans*-$Ru\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}_2(dppm)_2$ was formed when an excess of the diyne was used in $NHPr^i_2$ solution in the presence of $NaPF_6$ (24%). With $HBF_4{\cdot}OEt_2$ this formed the bis-vinylallenylidene complex *trans*-$[Ru\{{=}C{=}C{=}CC(OMe){=}CPh_2\}_2(dppm)_2]^{2+}$ (Scheme 22).[3]

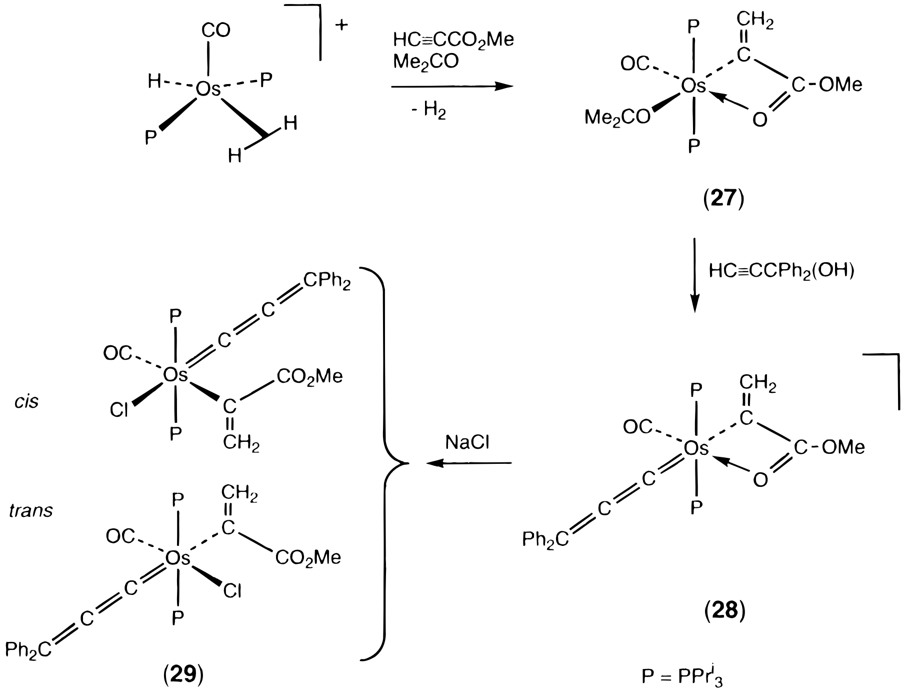
e. Other Ruthenium and Osmium Complexes. The deep red complexes $RuCl_2({=}C{=}C{=}CPhR)\{\kappa^2\text{-}P,O\text{-}PPr^i_2CH_2C(O)OMe\}(PPr^i_2CH_2CO_2Me\text{-}P)$ [R = Ph (**26**), tol] were obtained by heating $RuCl_2\{{=}C{=}CHCPhR(OH)\}\{\kappa^2\text{-}P,O\text{-}PPr^i_2CH_2C(O)OMe\}(PPr^i_2CH_2CO_2Me\text{-}P)$ [from $RuCl_2\{\kappa^2\text{-}P,O\text{-}PPr^i_2CH_2C(O)OMe\}_2$ and $HC{\equiv}CPhR(OH)$] in toluene. With HCl, **26** gave *trans*-$RuCl_2({=}CClCH{=}CPh_2)\{PPr^i_2CH_2C(O)OMe\text{-}P\}_2$, while other ligands (CO, $CNBu^t$, py) displaced the remaining O atom to form *trans*-$RuCl_2({=}C{=}C{=}CPh_2)(L)(PPr^i_2CH_2CO_2Me\text{-}P)_2$. There was no reaction between **26** and MeOH.[71] The complex *trans*-$RuCl_2(PPr^i_2C_2H_4OMe)_2$ is inert to $HC{\equiv}CCPhR(OH)$, but in the presence of AgOTf, slowly reacts to form *trans*-$[RuCl({=}C{=}C{=}CPhR)(PPr^i_2C_2H_4OMe)_2]^+$, isolated by chromatography on acidic alumina.[144] Other complexes containing the *O*-donor ligands are $Ru({=}C{=}C{=}CPh_2)(acac)_2(PPr^i_3)$[145] and $Ru({=}C{=}C{=}CMePh)(PPh_3)_2\{[O(EtO)_2P]_3CoCp\}$.[146]

Allenylidenes have also been obtained from $RuCl_2(np_3)$ [$np_3 = (PPh_2C_2H_4)_3N$] and $HC{\equiv}CCPh_2(OH)$: the complex $[Ru({=}C{=}C{=}CPh_2)(np_3)]^+$ is stable in MeOH, from a combination of steric hindrance provided by the np_3 ligand and the electron-releasing properties

Scheme 22



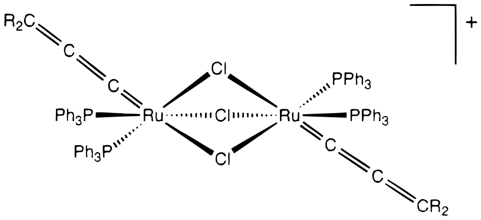
Scheme 23



of the Ru(np$_3$) fragment.[78] In MeOH, the diyne HC≡CC≡CCPh$_2$(OH) gave [Ru{=C=C=C(OMe)CH=CPh$_2$}(np$_3$)]$^+$, also obtained from HC≡CC≡CCPh$_2$(OSiMe$_3$).

Treatment of [OsH(η-H$_2$)(CO)(PPr$^i_3$)$_2$]$^+$ with methyl propiolate in acetone afforded the alkenyl complex **27**, which on further reaction with HC≡CCPh$_2$(OH) gave the allenylidene **28**. Reaction with NaCl in methanol gave *cis*- and *trans*-OsCl(CO){C(CO$_2$Me)=CH$_2$}(=C=C=CPh$_2$)(PPr$^i_3$)$_2$ (**29**) (Scheme 23).[147]

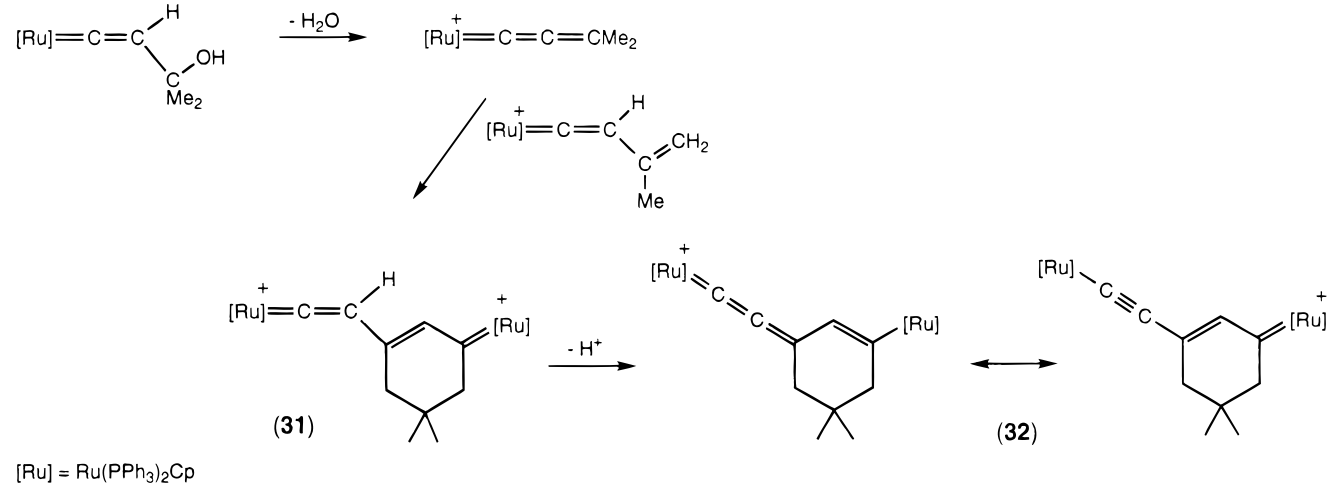
Binuclear complexes **30** were obtained from RuCl$_2$(PPh$_3$)$_3$ and HC≡CCAr$_2$(OH) (Ar = C$_6$H$_4$X-4, X = H, F, Cl); the Ph derivative was also obtained in low yield from [Ru$_2$(μ-Cl)$_3$(PPh$_3$)$_6$]$^+$. The first reaction probably proceeds via the 16-e RuCl$_2$(=C=C=CAr$_2$)(PPh$_3$)$_2$ which dimerizes with loss of chloride. Substitution of PPh$_3$ by dppe gave [RuCl(=C=C=CPh$_2$)(dppe)$_2$]$^+$, also obtained from *cis*-RuCl$_2$(dppe)$_2$ and the propyn-1-ol.[84]



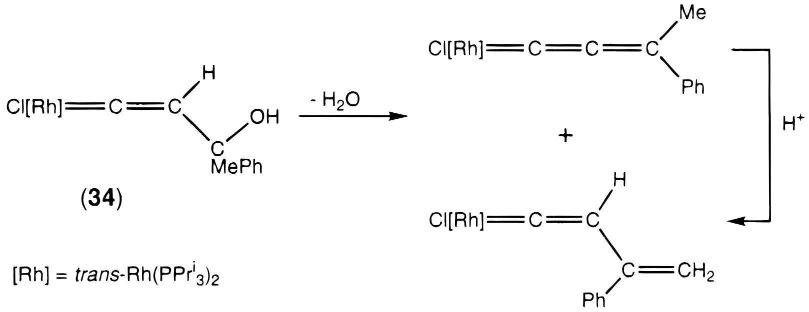
(**30**) R = Ph, C$_6$H$_4$Cl-4, C$_6$H$_4$F-4

The reaction between RuCl(PPh$_3$)$_2$Cp and HC≡CCMe$_2$(OH) does not proceed in the usual way. Instead, the deep purple dinuclear compound **31** is formed and can be deprotonated to blue-violet **32** (Scheme 24).[76] The same compound is formed by protonation of Ru(C≡CCMe=CH$_2$)(PPh$_3$)$_2$Cp, via a

Scheme 24



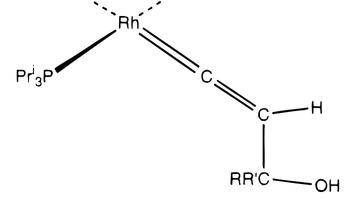
Scheme 25



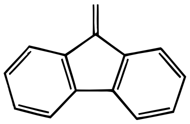
deep blue intermediate, probably $[\mathrm{Ru}(=\mathrm{C}=\mathrm{C}=\mathrm{CMe}_2)(\mathrm{PPh}_3)_2\mathrm{Cp}]^+$, which reacts with a second molecule of the vinylidene.[76,129] Analogous compounds are formed with $\mathrm{HC{\equiv}CCMe_2(OH)}$ and $\mathrm{RuCl(dippe)L}$ (L = Cp,[127] Tp[136]): initially, a red binuclear cation is formed, which can be deprotonated to the deep blue vinylallenylidene.

E. Rhodium and Iridium

A wide range of allenylidene complexes of rhodium have been prepared from variously substituted 2-propyn-1-ols, via the vinylidenes *trans*-$\mathrm{RhCl\{=C=CHCRR'(OH)\}(PPr^i_3)_2}$ [R = Ph, R′ = H (**33**), Me (**34**), Bu^t, Ph, *o*-tol; RR′ = $\mathrm{C_{12}H_8}$ (**35**), $\mathrm{Pr^i_2}$ (**36**)].[35,87] Treatment of **34** or **36** with alumina gave vinylvinylidenes. However, with neutral alumina, **34** gave a 9/1 mixture of *trans*-$\mathrm{RhCl(=C=CHCPh=CH_2)(PPr^i_3)_2}$ and *trans*-$\mathrm{RhCl(=C=C=CMePh)(PPr^i_3)_2}$; the latter is converted to the vinylvinylidene by acid (Scheme 25).



CRR′ = CHPh (**33**), CMePh (**34**), CPr$^i_2$ (**36**)



(**35**)

Similarly, *trans*-$\mathrm{RhCl(=C=C=CPr^i_2)(PPr^i_3)_2}$ gives *trans*-$\mathrm{RhCl(=C=CHCPr^i{=}CMe_2)(PPr^i_3)_2}$. Experimentally, conversion to the allenylidene can be best achieved in the presence of acidic alumina in benzene.[87] These products are formed via hydroxy–vinylvinylidenes, which are the only products from RR′ = HMe, $\mathrm{Me_2}$.[91] For R′ = Me, dehydration can be directed to give either the allenylidene (as above) or, in the presence of a trace of $\mathrm{CF_3CO_2H}$ or on acidic alumina, the thermodynamically favored isomeric vinylvinylidene, *trans*-$\mathrm{RhCl(=C=CHCPh=CH_2)(PPr^i_3)_2}$.[21] On neutral alumina, **33** gave *trans*-$\mathrm{RhCl(CO)(PPr^i_3)_2}$, probably by attack of $\mathrm{H_2O}$ or $\mathrm{OH^-}$ at C(1). However, dehydration of **33** could be achieved with a catalytic amount of HCl or $\mathrm{CF_3CO_2H}$. A one-pot synthesis from $\mathrm{\{RhCl(C_8H_{14})_2\}_2}$, $\mathrm{PPr^i_3}$, and the alkynol, followed by treatment with alumina, gives 70–75% yields.[87]

Treatment of $\mathrm{\{RhCl(PPr^i_3)_2\}_2}$ with $\mathrm{HC{\equiv}CCRR'X}$ (X = OH, OMe, Cl, $\mathrm{NH_2}$) gave η^2-alkyne, hydrido–alkynyl, or vinylidene complexes, according to reaction conditions; however, for R = R′ = Ph, X = OH, this treatment affords *trans*-$\mathrm{RhCl(=C=C=CPh_2)(PPr^i_3)_2}$.[91]

1,2-Migration of $\mathrm{SnPh_3}$ groups has been found in the reactions of $\mathrm{RC{\equiv}CSnPh_3}$ with rhodium complexes. Extending this approach, the reaction of $\mathrm{SnPh_3\{C{\equiv}CCHPh(OH)\}}$ with $\mathrm{RhCl(PPr^i_3)_2}$ gave *trans*-$\mathrm{RhCl\{=C=C(SnPh_3)CHPh(OH)\}(PPr^i_3)_2}$ which with $\mathrm{CF_3CO_2H}$ gave *trans*-$\mathrm{RhCl(=C=C=CHPh)(PPr^i_3)_2}$ (perhaps via the hydroxy–vinylidene).[92] The $\mathrm{CH_2}$-

(OH) compound did not give the parent allenylidene, but instead, *trans*-RhCl{=C=CHCH$_2$(OH)}(PPr$^i_3$)$_2$.

Various substituted 2-propyn-1-ols react with Rh(η-C$_3$H$_5$)(PPr$^i_3$)$_2$ to give alkynyl/vinylidene or alkynyl/enyne complexes. With Rh(η^3-CH$_2$Ph)(PPr$^i_3$)$_2$, HC≡CCR$_2$(OH) (R = Me, Ph, Pr^i) gives *trans*-RhH{C≡CCR$_2$(OH)}$_2$(PPr$^i_3$)$_2$ which isomerizes to *trans*-Rh{C≡CCR$_2$(OH)}{=C=CHCR$_2$(OH)}(PPr$^i_3$)$_2$.[137] In the presence of chloride, the diphenyl compounds are converted by alumina into *trans*-RhCl(=C=C=CPh$_2$)(PPr$^i_3$)$_2$ and *trans*-RhCl(η^2-Ph$_2$C=C=C=C=C=CPh$_2$)(PPr$^i_3$)$_2$. Formation of the allenylidene occurs via alkyne, hydrido−alkynyl, and vinylidene intermediates.

The complex RhCl(κ^2-*P*,*O*-PPr$^i_2$C$_2$H$_4$OMe)(PPr$^i_2$C$_2$H$_4$OMe-*P)* reacts with 2-propyn-1-ols to give vinylidenes. On alumina, *trans*-RhCl(=C=C=CPh$_2$)(PPr$^i_2$C$_2$H$_4$OMe-*P)*$_2$ was obtained from the diphenyl complex, but treatment of *trans*-RhCl{=C=CHCMe$_2$(OH)}(PPr$^i_2$C$_2$H$_4$OMe-*P)*$_2$ with a catalytic amount of CF$_3$CO$_2$H gave only *trans*-RhCl(=C=CHCMe=CH$_2$)(PPr$^i_2$C$_2$H$_4$OMe-*P*)$_2$.[148] Similarly, RhCl(η-C$_2$H$_4$)(AsPr$^i_2$C$_2$H$_4$OMe)$_2$ reacts with HC≡CCRR′(OH) to give the vinylidene, which is dehydrated on alumina to the allenylidenes *trans*-RhCl(=C=C=CRR′)(PPr$^i_2$C$_2$H$_4$OMe)$_2$. With NaCp, conversion to Rh(=C=C=CRR′)(AsPr$^i_2$C$_2$H$_4$OMe)Cp occurs.[149]

The lower reactivity of iridium complexes requires the use of different precursors. The reaction between IrH$_2$Cl(PPr$^i_3$)$_2$ and HC≡CCPh$_2$(OH) gives IrCl(=C=C=CPh$_2$)(PPr$^i_3$)$_2$.[35] Square-planar Ir(OMe)(diene)(PR$_3$) (diene = cod, tfbb, R = Cy; diene = tfbb, R = Pr^i) reacts with HC≡CCPh$_2$(OH) to give Ir{C≡CCPh$_2$(OH)}(diene)(PR$_3$) which loses water on treatment with HBF$_4$·OEt$_2$ to give [Ir(=C=C=CPh$_2$)(diene)(PR$_3$)]$^+$.[93] The reactions may proceed by direct protonation of the OH group of the hydroxyalkynyl complex, or by spontaneous dehydration of the analogous hydroxyvinylidene complex.

F. Complexes Containing Butatrienylidene Ligands, :C=C=C=CR$_2$

Known examples of mononuclear complexes containing higher cumulenylidene ligands are listed in Table 3.

Attempts to produce a butatrienylidene by reaction of Ru{C≡CC(O)Pr^i}(PPh$_3$)$_2$Cp with (CF$_3$CO)$_2$O gave a complex structurally identified as Ru{C≡CC(OCOCF$_3$)=CMe$_2$}}(PPh$_3$)$_2$Cp and claimed [on the basis of a large $J_{PC(1)}$ and its subsequent chemistry] to resemble [Ru(=C=C=C=CMe$_2$)(PPh$_3$)$_2$Cp]$^+$ trapped by attachment of CF$_3$CO$_2^-$ to C(3) (Scheme 26).[156]

The reaction between [Ru(thf)(PPh$_3$)$_2$Cp]$^+$ and buta-1,3-diyne affords a cationic species which is assumed to be [Ru(=C=C=C=CH$_2$)(PPh$_3$)$_2$Cp]$^+$ from its mode of preparation (1,4-H migration in reactions of HC≡CC≡CH with [Ru(thf)(PPh$_3$)$_2$Cp]$^+$) and subsequent

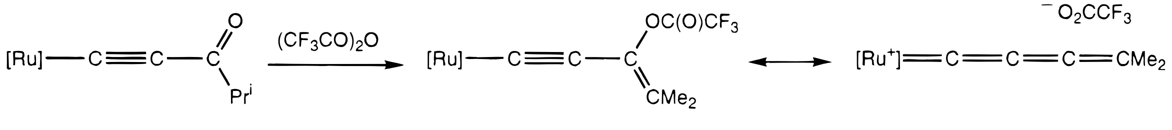
Table 3. Mononuclear Pentatetraenylidene Complexes, [{L$_n$M}=C(1)=C(2)=C(3)=C(4)=C(5)R^{1}R^2][X]

ML$_n$	R^1	R^2	color	yield, %	ν(CCCCC)	^{13}C NMR, δ(C)	ref
Cr(CO)$_5$ (**a**)	NEt$_2$	CMe=C(NMe$_2$)$_2$	orange	65	2149, 2000	δC(1) 175.3; δC(2,3,4), =CMe 55.8, 87.3, 94.7, 102.2; δC(5), C(NMe$_2$)$_2$ 147.0, 154.0	158
Cr(CO)$_5$	NMe$_2$	NMe$_2$	orange	42	2140, 1998	δC(1) 174.1; δC(2,3,4) 99.5, 95.7, 49.6; δC(5) 155.0	118
W(CO)$_5$	NMe$_2$	CMe=C(NMe$_2$)$_2$	yellow	61	2148, 2001	δC(1) 175.2; δC(2,3,4), =CMe 58.3, 87.4, 93.9, 102.5; δC(5), C(NMe$_2$)$_2$ 136.4, 146.7	158
W(CO)$_5$	NMe$_2$	CH=C(NMe$_2$)$_2$	yellow	5	2161, 2145, 2003	δC(1) 170.4; δC(2,3,4,5) 56.0, 92.7, 93.8, 142.9, 149.8	32
W(CO)$_5$ (**b**)	NMe$_2$	NMe$_2$	orange	36	2140, 1999	δC(1) 153.8 (J_{WC} 102.6); δC(2) 94.6 (J_{WC} 25.6); δC(3,4) 99.5, 52.1; δC(5) 154.8	118
trans-RuCl(dppe)$_2$ [BF$_4$ salt] (**c**)	Ph	Ph	deep blue	70	2024, 1918	δC(1) 316.35 (J_{PC} 14.6); δC(2) 206.7 (2.6); δC(3) 167.63 (2.3); δC(4) 160.25 (2); δC(5) 165.44 (s)	30
trans-RhCl(PPr$^i_3$)$_2$	Ph	Ph	deep violet oil	58	1962, 1860	δC(1) 205.25 (J_{RhC} 67.4, J_{PC} 17.8); δC(2) 246.13 (J_{RhC} 16.5, J_{PC} 6.4); δC(3) 197.78 (J_{RhC} 1.3, J_{PC} 3.8); δC(4) 141.41 (J_{PC} 3.5); δC(5) 156.07 (J_{PC} 1.9)	114
trans-IrCl(PPr$^i_3$)$_2$ (**d**)	Ph	Ph	copper brown	80	1960, 1856	δC(1) 186.70 (J_{PC} 13.9); δC(2) 245.45 (4.0); δC(3) 133.70 (3.3); δC(4) 209.61 (3.2); δC(5) 161.74 (1.5)	31

Molecular Structures

complex	M−C(1)	C(1)−C(2)	C(2)−C(3)	C(3)−C(4)	C(4)−C(5)	M−C(1)−C(2)	C(1)−C(2)−C(3)	C(2)−C(3)−C(4)	C(3)−C(4)−C(5)	ref
a	2.041(6)	1.219(8)	1.379(8)	1.209(9)	1.433(8)	175.4(6)	177.1(7)	178.8(7)	180.0(10)	158
b	2.144(6)	1.223(9)	1.361(9)	1.192(9)	1.399(9)					118
c	1.891(9)	1.25(1)	1.30(1)	1.24(1)	1.36(1)	179(1)	178(1)	179(1)	178(1)	30
d	1.834(5), 1.821(5)	1.261(6), 1.278(6)	1.296(6), 1.279(6)	1.259(6), 1.249(6)	1.344(6), 1.343(6)	176.8(4), 173.8(5)	175.8(5), 175.6(5)	177.1(5), 178.9(6)	174.8(5), 177.6(6)	31

Scheme 26



[Ru] = Ru(PPh$_3$)$_2$Cp

reactions (see below).[130,157] This intermediate has also been obtained by direct protonation of $Ru(C{\equiv}CC{\equiv}CH)(PPh_3)_2Cp$:[129]

$$[Ru(thf)(PPh_3)_2Cp]^+ + HC{\equiv}CC{\equiv}CH \rightarrow [Ru({=}C{=}C{=}C{=}CH_2)(PPh_3)_2Cp]^+ \quad (5)$$

Similar arguments were used to support the formation of [*trans*-$RuCl({=}C{=}C{=}C{=}CH_2)(dppm)_2]^+$ in the reaction between buta-1,3-diyne and *cis*-$RuCl_2(dppm)_2$.[152]

G. Complexes Containing Pentatetraenylidene Ligands, :C=C=C=C=CR$_2$

These ligands are generally obtained from pentadiynols and their derivatives.[123,138] The formation of allenylidene complexes by supposed addition of nucleophiles (usually solvent methanol) to intermediate pentatetraenylidenes has been suggested on several occasions.

1. Chromium, Molybdenum, and Tungsten

Treatment of $M(CO)_5(thf)$ (M = Cr, W) with $LiC{\equiv}CC{\equiv}CC(NMe_2)_3$ [from LiBu and $SiMe_3C{\equiv}CC{\equiv}CC(NMe_2)_3$] gave $[M\{C{\equiv}CC{\equiv}CC(NMe_2)_3\}(CO)_5]^+$ which with $BF_3{\cdot}OEt_2$ gave orange $M\{{=}C{=}C{=}C{=}C{=}C(NMe_2)_2\}(CO)_5$ (cf., allenylidenes, above).[118] Of six possible resonance structures (Figure 4), the ylidic ones are the most important contributors.

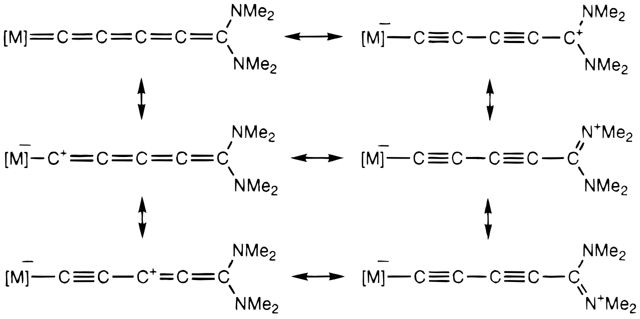


Figure 4.

Desilylation of $SiMe_3C{\equiv}CC{\equiv}CC{\equiv}CC(NMe_2)_3$ with LiBu, followed by addition of $W(CO)_5(thf)$ and $BF_3{\cdot}OEt_2$, gave a mixture of yellow $W\{{=}C{=}C{=}C{=}C{=}C(NMe_2)CH{=}C(NMe_2)_2\}(CO)_5$ and $W\{{=}C(C{\equiv}CSiMe_3)CBu{=}C{=}C{=}C(NMe_2)_2\}(CO)_5$.[32,158] The former is considered to be formed by addition of $NHMe_2$ to the undetected heptahexaenylidene complex $W\{{=}C{=}C{=}C{=}C{=}C{=}C{=}C(NMe_2)_2\}(CO)_5$ (see below).

2. Ruthenium

Deep blue [*trans*-$RuCl({=}C{=}C{=}C{=}C{=}CPh_2)(dppe)_2]^+$ was obtained from the reaction of the electron-rich *cis*-$RuCl_2(dppe)_2$ with $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$, via *trans*-$RuCl\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}(dppe)_2$ which eliminated $CPh_3(OH)$ with $[CPh_3]^+$.[30]

Attempts to obtain pentatetraenylidenes from $RuCl_2(PMe_3)(\eta\text{-}C_6Me_6)$ and $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ in MeOH gave a mixture of the allenylidene $[RuCl\{{=}C{=}C{=}C(OMe)CH{=}CPh_2\}(PMe_3)(\eta\text{-}C_6Me_6)]^+$ with the methoxycarbene $[RuCl\{{=}C(OMe)CH{=}C{=}C{=}CPh_2\}(PMe_3)(\eta\text{-}C_6Me_6)]^+$,[123] by addition of MeOH to an intermediate $[RuCl({=}C{=}C{=}C{=}C{=}CPh_2)(PMe_3)(\eta\text{-}C_6Me_6)]^+$ complex. The latter could be stabilized by using aryl groups with electron-releasing substituents. Thus reaction of $RuCl_2(PMe_3)(\eta\text{-}C_6Me_6)$ with $SiMe_3C{\equiv}CC{\equiv}CC(C_6H_4NMe_2\text{-}4)_2(OSiMe_3)$ gave blue $[RuCl\{{=}C{=}C{=}C{=}C{=}C(C_6H_4NMe_2\text{-}4)_2\}(PMe_3)(\eta\text{-}C_6Me_6)]^+$, which is inert to MeOH.[138] The stability arises from mesomeric contributions (Figure 5).

3. Rhodium and Iridium

Treatment of $\{RhCl(PPr^i_3)_2\}_2$ with $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ afforded the corresponding η^2-alkyne complex, which thermally isomerized to the hydridoalkynyl derivative and then to the vinylidene. Reaction of the alkyne complex with pyridine gave $RhHCl\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}(py)(PPr^i_3)_2$, which on treatment with Tf_2O, followed by NEt_3, afforded *trans*-$RhCl({=}C{=}C{=}C{=}C{=}CPh_2)(PPr^i_3)_2$; this complex was also obtained directly from the vinylidene with Tf_2O, followed by NEt_3.[114]

The reaction of $IrCl(coe)(PPr^i_3)_2$ with $SiMe_3C{\equiv}CC{\equiv}CCPh_2(OH)$ gives the η^2-alkyne complex, which on heating is transformed into $IrCl\{{=}C{=}C(SiMe_3)C{\equiv}CCPh_2(OH)\}(PPr^i_3)_2$, but no formation of the pentatetraenylidene complex is found.[155] However, treatment of $IrHCl\{C{\equiv}CC{\equiv}CCPh_2(OH)\}(PPr^i_3)_2$ with triflic anhydride at −78 °C gave an unidentified intermediate which with 2 equiv of NEt_3 afforded *trans*-IrCl-

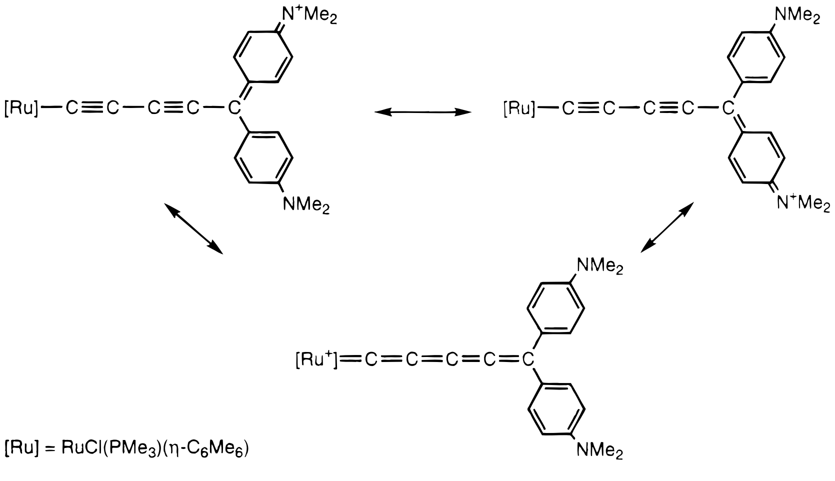


Figure 5.

Table 4. Electrochemical Properties of Allenylidene and Cumulenylidene Complexes

complex	reduction/oxidation waves (V, vs SCE)	ref
$[\{Ru(PPh_3)_2({=}C{=}C{=}CPh_2)\}_2(\mu\text{-}Cl)_3]^+$	+1.394 (irrev ox), −0.946, −0.648 (rev redn)	143
$[\{Ru(PPh_3)_2[{=}C{=}C{=}C(C_6H_4Cl\text{-}4)_2]\}_2(\mu\text{-}Cl)_3]^+$	−0.808, −0.506 (rev redn)	143
$[\{Ru(PPh_3)_2[{=}C{=}C{=}C(C_6H_4F\text{-}4)_2]\}_2(\mu\text{-}Cl)_3]^+$	−0.910, −0.608 (rev)	143
$[\{RuCl(dppe)_2({=}C{=}C{=}CH)\}_2C_6H_4]^+$	−0.281, −0.079 (rev)	84
$[\{RuCl(dppe)_2({=}C{=}C{=}CH)\}_2C_4H_2S]^+$	−0.176, +0.095 (rev)	84
$[\{Ru(C{\equiv}CC_6H_4NO_2\text{-}4)(dppe)_2({=}C{=}C{=}CH)\}_2C_6H_4]^+$	−0.109, +0.082 (rev)	84
trans-$RuCl(C{\equiv}CFc)(dppm)_2$	−0.39 (Fe^{II}/Fe^{III}), +0.37 (Ru^{II}/Ru^{III})	159
trans-$RuCl(C{\equiv}CFc)(dppe)_2$	−0.344 (Fe^{II}/Fe^{III}), +0.377 (Ru^{II}/Ru^{III})	162
trans-$RuCl(C{\equiv}CC{\equiv}CFc)(dppe)_2$	−0.165 (Fe^{II}/Fe^{III}), +0.295 (Ru^{II}/Ru^{III})	162
trans-$Ru(C{\equiv}CFc)(C{\equiv}CPh)(dppm)_2$	−0.327 (Fe^{II}/Fe^{III}), +0.241 (Ru^{II}/Ru^{III})	160, 162
trans-$Ru(C{\equiv}CFc)(C{\equiv}CC_6H_4NO_2\text{-}4)(dppm)_2$	−0.287 (Fe^{II}/Fe^{III}), +0.371 (Ru^{II}/Ru^{III})	160, 162
trans-$Ru(C{\equiv}CFc)(C{\equiv}CAr)(dppm)_2$ (Ar = C_6H_4R, R = 4-Me, 2-NO_2; $C_6H_3Me\text{-}3\text{-}NO_2\text{-}4$)	−0.34 to −0.29 (Fe^{II}/Fe^{III}) 0.22 to 0.33 (Ru^{II}/Ru^{III})	160
trans-$Ru(C{\equiv}CFc)_2(dppm)_2$	−0.40, −0.18 (Fe^{II}/Fe^{III}), +0.45 (Ru^{II}/Ru^{III})	160, 161
trans-$Ru(C{\equiv}CFc)_2(dppe)_2$	−0.364, −0.159 (Fe^{II}/Fe^{III}), +0.534 (Ru^{II}/Ru^{III})	162
trans-$Ru(C{\equiv}CFc)(C{\equiv}CC{\equiv}CFc)(dppe)_2$	−0.300, −0.015 (Fe^{II}/Fe^{III}), +0.460 (Ru^{II}/Ru^{III})	162
trans-$Ru(C{\equiv}CC{\equiv}CFc)(C{\equiv}CC_6H_4NO_2\text{-}4)(dppm)_2$	−0.094 (Fe^{II}/Fe^{III}), +0.318 (Ru^{II}/Ru^{III})	162
trans-$Ru(C{\equiv}CC{\equiv}CFc)_2(dppe)_2$	−0.124, −0.015 (Fe^{II}/Fe^{III}), +0.404 (Ru^{II}/Ru^{III})	162
$\{Fe(\eta\text{-}C_5H_4C_2[$*trans*-$RuCl(dppm)_2]\}_2(\mu\text{-}C_5H_4C_5H_4)$	−0.37, −0.21 (Fe^{II}/Fe^{III}), +0.34, +0.51 (Ru^{II}/Ru^{III})	161
$Ru(C{\equiv}CFc)(dppe)Cp$	−0.03 (Fe^{II}/Fe^{III}), +0.64 (Ru^{II}/Ru^{III})	*a*
$Ru(C{\equiv}CFc)(PPh_3)_2Cp$	+0.03 (Fe^{II}/Fe^{III}), +0.63 (Ru^{II}/Ru^{III})	*a*
trans-$OsCl(C{\equiv}CFc)(dppm)_2$	−0.44 (Fe^{II}/Fe^{III}), +0.21 (Os^{II}/Os^{III})	159
$\{Fe_2(\mu\text{-}dppm)(CO)_2Cp_2\}(\mu\text{-}C{=}C{=}C(CN)_2\}$	−1.898	170

[a] Sato, M.; Shintate, H.; Kawata, Y.; Sekino, M.; Katada, M; Kawata, S. *Organometallics* **1994**, *13*, 1956.

$({=}C{=}C{=}C{=}C{=}CPh_2)(PPr^i{}_3)_2$. This complex is copper brown in the solid state, but gives different colored solutions depending on solvent. The structure indicates a contribution from the zwitterionic form:[31]

$$[Ir]{=}C{=}C{=}C{=}C{=}CPh_2 \leftrightarrow [Ir^+]{-}C{\equiv}CC{\equiv}C{-}C^-Ph_2$$

H. Complexes Containing Heptahexaenylidene Ligands, :C=C=C=C=C=C=CR$_2$

As described above, attempts to form $W\{{=}C{=}C{=}C{=}C{=}C{=}C(NMe_2)_2\}(CO)_5$ resulted instead in ready addition of $NHMe_2$ to C(5) and formation of $W\{{=}C{=}C{=}C{=}C{=}C(NMe_2)CH{=}C(NMe_2)_2\}(CO)_5$.[32]

I. Other Manifestations of Allenylidenes

Several studies of electronic interactions between metal centers in ferrocenyl−alkynyl and −diynyl derivatives have been reported. The CVs of $MCl(C{\equiv}CFc)(dppm)_2$ (M = Ru, Os) show two quasireversible processes, the half-wave potentials for the metal centers being considerably less anodic than those for $MCl_2(dppm)_2$ (Table 4).[159] This is interpreted as indicating that electron donation to M from the Fc group occurs through the C≡C link, with ruthenium being a better acceptor than osmium. Conversely, the half-wave potentials for the Fc centers are more anodic. These data are consistent with contributions from the cyclopentadienylidene (fulvene)−carbene form (Figure 6).

Oxidation of $FcC{\equiv}C\{M(dppm)_2\}C{\equiv}CR$ (R = Ph, $C_6H_4NO_2$-4; M = Ru, Os) with $[FcH]PF_6$ gave air-stable violet or blue-violet monocations, isolated in nearly quantitative yields. These have ν(CCC) bands between 1987 and 1990 cm^{-1}, intermediate between the usual ν(CC) and ν(CCC) regions (2061 and 1940 cm^{-1}, respectively) for this system.[160,161] The oxidations are quasireversible: oxidation potentials Ru^{II}/Ru^{III} show the expected cathodic or anodic shift with donor and acceptor ligands, respectively. Four oxidation states were found for the bis-FcC≡C complex, the Ru^{II}/Ru^{III} potential being anodically shifted:[160]

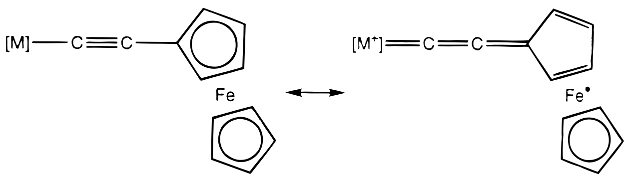


Figure 6.

$$\begin{array}{l} \underset{\text{yellow}}{Fe^{II}{-}Ru^{II}{-}Fe^{II}} \leftrightarrow \underset{\text{blue}}{Fe^{III}{-}Ru^{II}{-}Fe^{II}} \leftrightarrow \\ \qquad\qquad \underset{\text{violet}}{Fe^{III}{-}Ru^{II}{-}Fe^{III}} \leftrightarrow \underset{\text{purple}}{Fe^{III}{-}Ru^{III}{-}Fe^{III}} \end{array}$$

Replacement of Cl by C_2R thus allows more electronic interaction and delocalization between the two metal centers so that the complexes are Robin−Day Class II systems. The rate of electron transfer in the $\{Ru(dppm)_2\}$ series is greater for the bis-acetylide than for the chloro−acetylide complex.[160]

Electronic communication through the C_2 bridges is also found in *trans*-$FcC{\equiv}C\{Ru(PP)_2\}C{\equiv}CFc$ (PP = dppm,[161] dppe[162]). With *trans*-$FcC{\equiv}C\{Ru(dppe)_2\}C{\equiv}CC{\equiv}CFc$, the C_4 bridge does not communicate as effectively as the C_2 bridge, with the Fe^{II}/Fe^{III} potential being greater than found in the bis-alkynyl compound and the Ru^{II}/Ru^{III} potential lower (Table 4).[162] Related observations were made with the biferrocenyl derivative $\{Fe(\eta\text{-}C_5H_4C_2[$*trans*-$RuCl(dppm)_2]\}_2(\mu\text{-}C_5H_4C_5H_4)$.[163]

Substantial stabilization of violet $[RuCl({=}C{=}C{=}CFcPh)(PR_3)(\eta\text{-}C_6Me_6)]^+$ by a contribution from the cyclopentadienylidene (fulvene)−carbene form is suggested by the NMR spectra.[75,82] Replacement of Ph by Fc gives substantial shielding of C(1,2) resonances and inhibits the addition of MeOH.

Table 5. Some Electrochemical Properties of *trans*-RhCl(L)(PPr$^i_3$)$_2$ (Data from Ref 166)

L	$E_{1/2}$ (Rh$^{2+/+}$)	E_L	Rh−C(1), Å
:CPh$_2$	0.49	0.51	1.876(3)
:C=CPh$_2$	1.06	0.83	1.775(6)
:C=C=CPh$_2$	0.84	0.71	1.855(5)
:C=C=C=C=CPh$_2$			[1.834(5)][a]
CO	1.36	0.99	1.770(4)[b]
C$_2$H$_4$	0.94	0.76	

[a] Value for Ir compound. [b] Value for RhCl(CO)(PMe$_3$)$_2$ (from ref 168).

There is only moderate communication via the organic chain between the redox centers in *trans*-Pt(C≡CFc)$_2$(PPh$_3$)$_2$, with $\Delta E°$ 260 mV, considerably greater than that found for FcC≡CC≡CFc ($\Delta E°$ 100 mV).[164,165] Overall, a series of five oxidation states ($-2 \rightarrow +2$) were detected; the transient Pt(I) systems are somewhat stabilized by electron delocalization over the ferrocenyl units.

V. Properties

A. Electronic Properties

The π-acceptor power of the allenylidene ligand in [Ru(=C=C=CPh$_2$)(PMe$_3$)$_2$Cp]$^+$ appears to be less than those of the vinylidene and carbonyl ligands, as indicated by the chemical shift of the Cp group protons[28] or ν(CO) frequencies.[107] Comparison of the oxidation potentials of the complexes *trans*-RhCl(L)(PPr$^i_3$)$_2$ enables a more quantitative assessment of the relative π-acceptor powers of unsaturated carbenes to be obtained.[166] The electron comes from the HOMOs, the relative energies of which depend on the degree of M→L charge transfer, i.e., the π-acceptor abilities of the ligands. With L = :C(=C)$_n$Ph$_2$, for n = 0, 1 and 2, partially reversible oxidation waves were obtained, followed by an irreversible oxidation process at higher potentials. The oxidation product is least stable for $n = 1$. For $n = 4$, only irreversible oxidation was found. The following series of increasing π-acceptor ability was obtained [cf., Table 5, $E_{1/2}$(Rh$^{2+/+}$) and Lever's ligand electrochemical parameters E_L (empirical parameters enabling the prediction of redox couples of a series of complexes by adding contributions from each ligand present)[167] given]:

$$:\mathrm{CPh_2} < :\mathrm{C{=}C{=}CPh_2} \approx :\mathrm{C{=}C{=}C{=}C{=}CPh_2} < :\mathrm{C{=}CPh_2} < \mathrm{CO}$$

This order is consistent with trends in the Rh−C distances and with theoretical results which suggest that vinylidene and CO have a similar degree of π acidity,[169] but differs from the order suggested by the δ_{Cp} values.

B. Spectroscopic Properties

1. Infrared Spectra

The infrared spectra contain characteristic bands for the cumulated C=C=C double bonds, with ν(CCC) bands appearing in the 1800−2100 cm^{-1} region (Table 2); two bands are found for the pentatetraenylidene complexes in this region.

2. UV−Visible Spectra

The UV−visible spectra of several allenylidene and related complexes are listed in Table 6. Many of the complexes are intensely colored, with strong absorptions assigned to intervalence charge-transfer bands in the 500−600-nm region, consistent with the contributions from the canonical forms:

$$[\mathrm{M}]{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{CR_2} \leftrightarrow [\mathrm{M}^-]{-}\mathrm{C}^+{=}\mathrm{C}{=}\mathrm{CR_2} \leftrightarrow [\mathrm{M}^-]{-}\mathrm{C}{\equiv}\mathrm{C}{-}\mathrm{CR_2}^+$$

As R is changed, so the absorptions can be tuned. For example, in the series [Ru(=C=C=C$_7$R$_6$)(PPh$_3$)$_2$Cp]$^+$, the tropylium-acetylide form is favored for R = H, but increasing annelation favors the metallacumulene formulation.[128] As the carbene chain length increases, the LUMO becomes lower in energy, resulting in a bathochromic shift. In mixed-valence systems, such as [Ru{(=C=C=C$_5$H$_4$)FeCp}(C$_2$Ar)(dppm)$_2$]$^+$, bands between 433 and 450, 578−610, and near 1500 nm are present; the latter is assigned to an intervalence charge-transfer absorption.[160]

Strong negative solvatochromism, where the UV−visible λ_{max} moves to shorter wavelength in polar solvents, is found for Group 6 complexes. The λ shift is influenced both by conformational factors and chain length.[158]

3. Nonlinear Optical (NLO) Properties

Nonlinear optical properties have been measured for several derivatives (Table 7). For the Group 6 cumulenylidene complexes, values of the first molecular hyperpolarizability, β, are enhanced by chain lengthening, insertion of a C$_2$ unit resulting in an approximate 4-fold increase. However, insertion of a C$_2$ fragment into the C−N bond gives only slight improvement.[158] There is significant activity and the complexes are transparent to the scattered radiation. Values of β for ruthenium complexes containing cycloheptatrienylidene ligands[128] are smaller than found for related acetylides Ru(C≡CC$_6$H$_4$NO$_2$-4)(PPh$_3$)$_2$Cp ($\beta = 468 \times 10^{-30}$ esu), for the oxidized form of which an allenylidene mesomer can also be written.[171,172]

4. ^{13}C NMR Spectra

Reported NMR data for allenylidene complexes are summarized in Table 2; data are listed as reported in the original papers, although detailed inspection shows that the assignments are not always consistent. Many metal centers also contain tertiary phosphines, with two-, three-, and four-bond J(PC) couplings being found. Appropriate J(MC) coupling constants are also found to metals containing magnetically active nuclei (usually ^{103}Rh or ^{183}W, spin $^1/_2$). These data have been used to identify the resonances of the carbon atoms attached to the metal.

Reference to Table 2 shows that the chemical shifts of the C$_3$ chain nuclei depend on the metal−ligand fragment to which they are attached. Thus, the order

Table 6. UV−Visible Spectra of Allenylidene and Cumulenylidene Complexes

complex	solvent	$\lambda_{\max}$ (log ϵ)	$\Delta\nu$	ref
Cr{$=$C$=$C$=$C(NMe$_2$)$_2$}(CO)$_5$	PhMe	408 (4.208)	2370[a]	118
	CH$_2$Cl$_2$	394 (4.164)		
	EtOH	390 (4.111)		
	dmf	372 (4.072)		
W{$=$C$=$C$=$C(NMe$_2$)$_2$}(CO)$_5$	PhMe	406 (4.091)	2540[a]	118
	CH$_2$Cl$_2$	394 (4.155)		
	EtOH	388 (4.096)		
	dmf	368 (4.089)		
Cr{C$=$C$=$C$=$C$=$C$=$C(NMe$_2$)$_2$}(CO)$_5$	PhMe	510 (4.238)	3980[a]	118
	CH$_2$Cl$_2$	474 (4.262)		
	EtOH	456 (4.260)		
	dmf	424 (4.230)		
W{$=$C$=$C$=$C$=$C$=$C(NMe$_2$)$_2$}(CO)$_5$	PhMe	500 (4.342)	3580[a]	118
	CH$_2$Cl$_2$	466 (4.338)		
	EtOH	450 (4.229)		
	dmf	424 (4.159)		
W{$=$C$=$C$=$C$=$C$=$C(NMe$_2$)CH$=$C(NMe$_2$)$_2$}(CO)$_5$	PhMe	482 (4.074)	3109	32
	CHCl$_3$	464 (4.163)		
	CH$_2$Cl$_2$	442 (4.163)		
	EtOH	436 (4.082)		
	dmf	416 (4.139)		
[{Ru(dppe)Cp*}$_2$(μ-$=$C$=$C$=$CHCH$=$C$=$)]$^{2+}$	CH$_2$Cl$_2$	230 (4.892), 528 (4.623)		150
[{Ru(PPh$_3$)$_2$Cp}$_2${μ-($=$C$=$C$=$CHC$\equiv$C)}]$^+$	CH$_{2Cl2}$	230 (4.833), 600 (4.857)		150, 151
[{Ru(dppe)Cp}$_2${μ-($=$C$=$C$=$CHC$\equiv$C)}]$^+$	CH$_2$Cl$_2$	230 (4.903), 630 (4.763)		150, 151
[Ru($=$C$=$C$=$C$_7$H$_6$)(PPh$_3$)$_2$Cp]$^+$	CHCl$_3$	557	230[b]	128
	MeCN	550		
[Ru($=$C$=$C$=$CC$_{11}$H$_6$Me$_2$)(PPh$_3$)$_2$Cp]$^+$	CHCl$_3$	596	170[b]	128
	MeCN	590		
[Ru($=$C$=$C$=$C$_{11}$H$_6$Ph$_2$)(PPh$_3$)$_2$Cp]$^+$	CHCl$_3$	611	270[b]	128
	MeCN	601		
[Ru{$=$C$=$C$=$C(C$_6$H$_4$)$_2$C$_2$H$_2$}(PPh$_3$)$_2$Cp]$^+$	CHCl$_3$	562	220[b]	128
	MeCN	555		
[Ru{$=$C$=$C$=$C(C$_6$H$_4$)$_2$C$_2$H$_4$}(PPh$_3$)$_2$Cp]$^+$	CHCl$_3$	502	240[b]	128
	MeCN	496		

[a] (PhMe − dmf). [b] (CHCl$_3$ − MeCN).

Table 7. NLO Properties of Allenylidene and Cumulenylidene Complexes

complex	β (10^{-30} esu)	β_0 (calcd) (10^{-30} esu)	ref
Cr{$=$C$=$C$=$C(NMe$_2$)$_2$}(CO)$_5$	21	9.5	158
W{$=$C$=$C$=$C(NMe$_2$)$_2$}(CO)$_5$	25	11	158
Cr{$=$C$=$C$=$C(NMe$_2$)CH$=$C(NMe$_2$)$_2$}(CO)$_5$	22	9	158
Cr{$=$C$=$C$=$C$=$C$=$C(NMe$_2$)$_2$}(CO)$_5$	100	31	158
W{$=$C$=$C$=$C$=$C$=$C(NMe$_2$)$_2$}(CO)$_5$	102	31	158
Cr{$=$C$=$C$=$C$=$C$=$C(NEt$_2$)CMe$=$C(NMe$_2$)$_2$}(CO)$_5$	125	40	158
[Ru($=$C$=$C$=$C$_{11}$H$_6$Me$_2$)(PPh$_3$)$_2$Cp][PF$_6$]	120	19	128
Ru(C$\equiv$CC$_6$H$_4$NO$_2$-4)(PPh$_3$)$_2$Cp	468		171,172

δC(1) > δC(2) > δC(3) is found for complexes containing Ti(PMe$_3$)Cp$_2$, Fe(L)$_2$Cp, Ru(L)$_2$Cp, and Ru(dppm)$_2$ groups, δC(1) > δC(3) > δC(2) for those containing Group 6 M(CO)$_5$, Mn(CO)$_2$Cp, RuCl(L)(η^6-arene), and Rh(L)Cp fragments, and δC(2) > δC(1) > δC(3) for some Rh(PPr$^i_3$)$_2$ complexes. For binuclear complexes, the orders are δC(1) > δC(2) $\approx$ δC(3) and δC(2) $\geq$ δC(1) > δC(3) for Mo$_2$(CO)$_4$Cp$_2$ and Fe$_2$(CO)$_3$Cp$_2$ complexes, respectively.

The metal-bonded carbon generally shows a characteristic low-field resonance ($\delta \approx 250-300$ ppm) for C(1) (cf., vinylidene complexes). The chemical shift is affected by the electron density on the carbon (diamagnetic term) and the HOMO−LUMO gap (paramagnetic term). It has been related to the extent of the mesomeric equilibrium, with the most electron-deficient carbon resonating at lowest field. As an example, in the tropylium complexes mentioned, δC(1) is 235 for the C$=$C$=$C$_7$H$_6$ complex and 297 for the dihydrodibenzo derivative.[128] Values of δC(1) below 250 are often found if electron-donating substituents are present on C(3). For example, progressive replacement of Ph by NMe$_2$ in the series W{$=$C$=$C$=$CPh$_n$(NMe$_2$)$_{2-n}$}(CO)$_5$ results in a decrease in δC(1) and δC(2), which is not so marked for δC(3): the reported values are respectively 302, 145, 156 (n = 2),[86,99] 199, 121,158 (n = 1),[26] and 173, 105, 152 (n = 0).[118] Further detailed studies of the ^{13}C NMR spectra of these and related complexes would be useful.

5. Fluxional Properties

While W{$=$C$=$C$=$CPh(NMe$_2$)}(CO)$_5$ shows two NMe resonances, only one is found for W{$=$C$=$C$=$C(NMe$_2$)$_2$}(CO)$_5$, replacement of Ph by NMe$_2$ leading to a lower rotational barrier about the C(sp^2)-N bond.[118] In W{$=$C$=$C$=$C$=$C$=$C(NMe$_2$)$_2$}(CO)$_5$ the Me groups give rise to two singlets at −90 °C, with coalescence at −83 °C, corresponding to $\Delta G^\ddagger$ of 40 kJ mol^{-1} for rotation about the C(sp^2)−N bond,

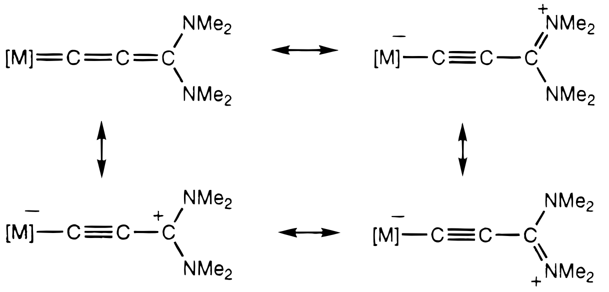


Figure 7.

indicating that W(═C═C═C═C)(CO)$_5$ is a better π acceptor than W(═C═C)(CO)$_5$.

The complex W{═C═C═C═C═C(NMe$_2$)CH═C(NMe$_2$)$_2$}(CO)$_5$ is also fluxional but has a higher rotational barrier. Three processes can be distinguished: fast rotation around each type of C−NMe$_2$ bond and about the C(6)═C(7) alkenyl bond. For the equilibration of the terminal NMe$_2$ groups, $\Delta G^\ddagger$ are 47 and 43 kJ mol^{-1}, while for the former, $\Delta G^\ddagger = 53$ kJ mol^{-1}.[32] These values indicate a strong mesomeric interaction (Figure 7):

The allenylidene ligands in indenylruthenium complexes are either in rapid rotation or locked in the vertical position, which is more stable than the horizontal conformation by 20.0 kJ mol^{-1}. The indenyl benzo groups are cis to the allenylidene (cf., trans for the vinylidene) with atoms C(1−3) not being in the mirror plane; EH MO calculations and overlap analyses have rationalized these structural preferences.[83]

C. Structures

1. Allenylidenes

Structural parameters for several mononuclear allenylidene complexes are summarized in Table 8.

Short M−C(1) distances are found (for Cr, 1.99−2.02 Å; for Ru, 1.84−2.00 Å). In the three-carbon chain, the C(1)−C(2) distances are shorter (1.18−1.27 Å) than the C(2)−C(3) distances (1.35−1.41 Å). These data are consistent with extensive contributions from the alkynyl mesomers, which are further stabilized by positive charges on any heteroatoms which may be present ("push−pull" stabilization):

$$[\mathrm{M}]{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{CR_2} \leftrightarrow [\mathrm{M}^-]{-}\mathrm{C}^+{=}\mathrm{C}{=}\mathrm{CR_2} \leftrightarrow [\mathrm{M}^-]{-}\mathrm{C}{\equiv}\mathrm{C}{-}\mathrm{C}^+\mathrm{R_2}$$

Although the C(1)═C(2) and C(2)═C(3) bond lengths in W{═C═C═C(NMe$_2$)$_2$}(CO)$_5$ are respectively among the shortest and longest in Table 8, comparison shows that replacement of an NMe$_2$ group by Ph has little effect on the degree of bond length alternation.[118] In the bis-allenylidene dication *trans*-[Ru{═C═C═CC(OMe)CH═CPh$_2$}$_2$(dppm)$_2$]$^{2+}$, the Ru−C(1) bond is longer and the C(1)−C(2) bond shorter than found in [Ru(═C═C═CPh$_2$)(PMe$_3$)$_2$Cp]$^+$, suggesting a greater contribution of the alkyne mesomeric form (above) as a result of the presence of the electron-donating OMe group.[142]

In mononuclear complexes, the M═C═C═CR$_2$ systems are close to linear [angles at C(1) and C(2) generally in the range 165−180°]. In contrast with vinylidene complexes, the CPh$_2$ plane is 10.6° out of

Table 8. Structures of Mononuclear Allenylidene Complexes, [{L$_n$M}═C(1)═C(2)═C(3)R^{1}R^2][X]

ML$_n$	R^1	R^2	X	M−C(1)	C(1)−C(2)	C(2)−C(3)	M−C(1)−C(2)	C(1)−C(2)−C(3)	ref
Cr(CO)$_5$	CMe$_2$(OEt)	NHPr^i		2.008(4)	1.204(5)	1.399(5)	179.0(3)	175.0(4)	95
Cr(CO)$_5$	CMe$_2$(OEt)	N(CH$_2$Ph)$_2$		1.993(2)	1.222(2)	1.388(2)	177.2(1)	173.5(2)	95
Cr(CO)$_5$	Ph	Ph		1.931(2)	1.249(3)	1.358(3)	176.7(2)	179.5(3)	99
Cr(CO)$_5$	Ph	NMe$_2$		2.015(1.5)	1.236(2.2)	1.372(2.1)			26
Cr(CO)$_5$	Ph	NMePh		2.007(3)	1.224(5)	1.389(5)	173.7(3)	174.3(4)	120
Cr(CO)$_5$	C$_5$Me$_4$O$_2$[Cr(CO)$_5$]			1.913(7)	1.26(1)	1.359(9)	173.4(6)	174.3(7)	101
W(CO)$_5$	NMe$_2$	NMe$_2$		2.185(8)	1.205(11)	1.386(11)	n.g.	n.g.	118
Mn(CO)$_2$Cp	Cy	Cy		1.806(6)	1.252(8)	1.342(8)	177.9(5)	175.1(6)	102
Fe(CO)$_2${P(OMe)$_3$}$_2$	Bu^t	Bu^t		1.833(4)	1.266(5)	1.344(6)	179.1(2)	177.8(3)	122
trans-Ru(dppm)$_2$	CH═CPh$_2$	OMe	[BF$_4$]$_2$	1.997(7)	1.22(1)	1.39(1)	175.0(7)	171.4(9)	111
trans-RuCl(dppm)$_2$	H	Ph	PF$_6$	1.886(10)	1.254(14)	1.34(2)	177.0(8)	174.1(11)	246
trans-RuCl(dppm)$_2$	C$_2$H$_4$CH═CH$_2$	NMe$_2$	PF$_6$	1.950(4)	1.218(6)	1.372(9)		175.1(6)	152
trans-RuCl(dppm)$_2$	C$_6$H$_4$CPh═CH		BF$_4$	1.85(2)	1.29(3)	1.39(3)	179(2)	177(2)	111
trans-RuCl(dppm)$_2$	C$_6$H$_4$CPh═CH		PF$_6$	1.85(2), 1.67(2)	1.29(3), 1.43(3)	1.39(3), 1.42(3)	179.0(2), 175.0(1)	177.0(2), 172.0(2)	77, 111
cis-RuCl{N(C$_2$H$_4$PPh$_2$)$_3$}	OMe	CH═CPh$_2$	PF$_6$	1.921(5)	1.254(7)	1.369(7)	174.1(3)	170.2(6)	78
cis-RuCl(PPr$^i_2$C$_2$H$_4$OMe)$_2$	Ph	Ph	OTf	1.829(6)	1.259(9)	1.352(9)	170.9(4)	171.8(6)	144
trans-RuCl$_2$(PPr$^i_2$CH$_2$CO$_2$Me){PPr$^i_2$CH$_{2C}$(O)OMe}	Ph	Ph		1.84(1)	1.27(2)	1.34(2)	178(1)	175(1)	71
Ru(CO)(PPh$_3$)(η^5-C$_9$H$_4$Me$_3$)	Ph	Ph	BF$_4$	1.92(1)	1.26(1)	1.35(2)	172(1)	176(1)	133
Ru(PMe$_3$)$_2$Cp	Ph	Ph	PF$_6$	1.884(5)	1.255(8)	1.329(9)	175.9(5)	175.1(7)	28
Ru(PPh$_3$)$_2$Cp	H	C≡C[Ru-(PPh$_3$)$_2$Cp]	BPh$_4$	1.933(8)	1.241(12)	1.364(11)	176.6(8)	166.5(12)	150
Ru(PPh$_3$)$_2$Cp	Me	NPh$_2$	PF$_6$	1.97(1)	1.18(2)	1.41(2)	171(1)	178(2)	109
Ru(PPh$_3$)$_2$(η^5-C$_9$H$_7$)	Ph	Ph	PF$_6$	1.878(5)	1.260(7)	1.353(7)	168.5(5)	168.2(7)	83
Ru(PPh$_3$)$_2$(η^5-C$_9$H$_7$)	C$_{13}$H$_{20}$		PF$_6$	1.889(5)	1.256(7)	1.339(7)	173.6(4)	173.2(5)	74
Ru(PPh$_3$)$_2${[O(EtO)$_2$P]$_3$CoCp}	Me	Ph	PF$_6$	1.86(2)	1.23(2)	1.37(3)	169(1)	177(2)	146
Ru(dippe)Cp	Ph	Ph	BPh$_4$	1.884(5)	1.257(6)	1.338(7)	169.3(4)	175.9(5)	127
Os{C[C(O)OMe]═CH$_2$}-(CO)(PPr$^i_3$)$_2$	Ph	Ph	BF$_4$	1.947(6)	1.250(8)	1.376(9)	173.5(6)	171.2(7)	147
Os(PPh$_3$)$_2$(η^5-C$_9$H$_7$)	Ph	Ph	PF$_6$	1.895(4)	1.265(6)	1.349(7)	169.3(4)	168.0(5)	83
trans-RhCl(PPr$^i_3$)$_2$	Ph	tol		1.855(5)	1.239(8)	1.370(9)	176.0(5)	170.9(1)	87

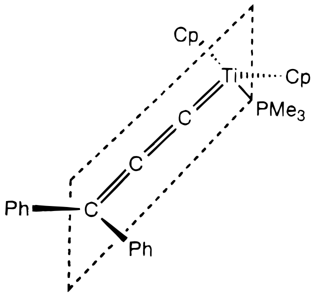


Figure 8.

the Ru−C(1)−C_5 centroid plane in $[Ru(=C=C=CPh_2)(PMe_3)_2Cp]^+$,[28] which is consistent with the metalla-allene formulation and theoretical expectations (see below). The indenyl group in $[M(=C=C=CPh_2)(PPh_3)_2(\eta^5\text{-}C_9H_7)]^+$ (M = Ru, Os) lies over the unsaturated carbene, i.e., cis to it. The trans and cis configurations differ by 7.9 kJ mol^{-1}, with a rotational barrier of 24.7 kJ mol^{-1}. The nature of the unsaturated carbene determines the indenyl conformation and distortion.[83]

The complex $Ti(=C=C=CPh_2)(PMe_3)Cp_2$ is stereochemically rigid, indicating that structure shown in Figure 8 is adopted, with the TiC_3 chain lying in the mirror plane.[116] The rotational barrier about the Ti=C bond is calculated to be 217 kJ mol^{-1}. Only the perpendicular orientation of the CPh_2 group with the $TiCp_2$ unit allows Ti→C(1) back-bonding, thus lowering the rotational barrier to 134 kJ mol^{-1}.[173,174]

2. Other Cumulenylidenes

Structural details for these complexes are included in Table 3. In contrast with the two diphenyl-substituted C_5 complexes, there is a pronounced C=C bond length alternation in $W\{=C=C=C=C=C(NMe_2)_2\}(CO)_5$.[118] There is a π interaction between [M]=C=C=C and substituents at C(3) and a strong mesomeric interaction between $=C(NMe_2)_2$ group and C(3).

VI. Reactions of Mononuclear Allenylidene and Cumulenylidene Complexes

A. General Considerations of Reactivity

1. Theory

Extensive theoretical calculations have rationalized the observed structural details (see above) and the reactivity of these complexes.[101,102] At one level, extended Hückel molecular orbital (EHMO) calculations on carbene complexes in the $M(CO)_2Cp$ series showed alternate vertical and horizontal alignments of metal-bonding orbitals with the substituents, as the empty p orbital on carbon aligns with the metal a″ MO (Figure 9).[169]

Calculated barriers to rotation about the Fe−C bond in $[Fe\{=C(=C)_nH_2\}(CO)_2Cp]^+$ are small:

carbene	vinylidene	allenylidene	
$n = 012$	1	2	
25.9	15.1	11.3	kJ mol^{-1}

For $Mn(=C=C=CH_2)(CO)_2Cp$, the calculated barrier is 13.4 kJ mol^{-1} from the preferred plane of CR_2 in the symmetry plane of the molecule. The NMR data of this and other complexes suggest that rapid rotation is occurring.[27] The low rotational barrier is also responsible for the CRR′ plane not being exactly orthogonal with the ML_2 plane, e.g. in $[Ru(=C=C=CPh_2)(PMe_3)_2Cp]^+$ where the interplanar angle is 10.6°.[28]

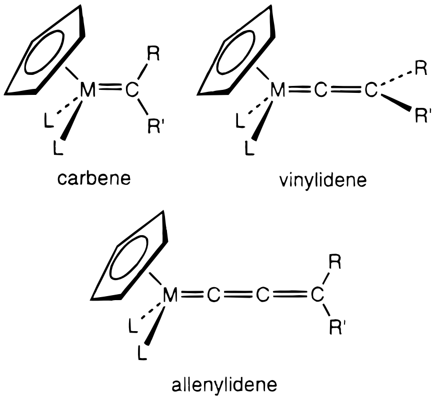


Figure 9.

The EH MO calculations show that there is an alternation of electron density along the unsaturated carbon chain. These studies show that C(1) and odd-numbered carbons are electrophilic centers and that C(2) and even-numbered carbons are electron rich. Nucleophilic attack is often found at C(3) when the metal center is coordinated by bulky ligands which protect C(1). The electrophilicity of the ligand increases as the chain lengthens, as shown particularly for $W\{=(C=C=)_nC(NMe_2)_2\}(CO)_5$, where C(3) and C(5) are most electrophilic for $n = 1$ and 3, respectively.[32] The consequences of this on reactivity are discussed below.

In the model compound $[Ru(=C=C=CH_2)(CO)(PH_3)Cp]^+$, the allenylidene ligand is both a σ donor (0.44-e transferred from the allenylidene HOMO to the metal LUMO) and a π acceptor (0.93-e transferred from the metal HOMO to the allenylidene LUMO).[175] Allenylidene is a stronger π acceptor than σ donor, so that there is a net transfer of 0.45-e to the carbene. The LUMO of the complex is located 60% on the C_3 ligand, with 23, 6, and 31% on C(1), C(2), and C(3), respectively. The net charges are −0.36, −0.13, and −0.05, respectively. Consequently, orbital-controlled nucleophilic attack is expected at C(1) and C(3). The HOMO is 26% on the allenylidene, mainly (20%) on C(2), so that electrophilic attack occurs at this carbon. Similarly, the electrophilicty of C(1) and C(3) in η^5-indenyl complexes show little difference, the LUMO being located on both atoms [C(1) 25%, C(3) 35%]. Both the bulky ligands and the preferred orientation of the benzo portion of the indenyl group sterically protect C(1), so that regiselectivity of attack on C(3) results.[132,176]

The presence of one nucleophilic and two electrophilic centers in the allenylidene ligand makes possible cycloaddition reactions with molecules containing an acidic hydrogen and two nucleophilic centers. Such syntheses have been realized with pyrazoles and pyridine-2-thiol.[177]

2. Nucleophilic Reactions

Nucleophilic reactions of Group 6 allenylidenes at C(1) or C(3) are orbital-controlled, soft nucleophiles attacking C(3) and hard ones attacking C(1). This can also be rationalized by considering the mesomeric forms:

$$[M]{=}C{=}C{=}CR_2 \leftrightarrow [M^-]{-}C^+{=}C{=}CR_2 \leftrightarrow [M^-]{-}C{\equiv}C{-}C^+R_2$$

Distinctions between the reactivity of Group 8 complexes (especially cationic systems), which react predominantly with nucleophiles, and those of square-planar Group 9 systems, which show reactivity toward both electrophiles and nucleophiles, can also be made. Neutral ruthenium complexes without η-Cp or η-arene groups seem to be resistant to attack by nucleophiles.[71]

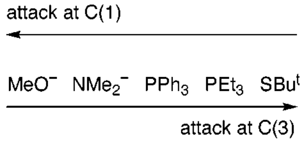
The reactivity of allenylidenes toward nucleophiles is determined by the HOMO–LUMO gap and the relative energies of the lone pairs on the nucleophiles.[89,109,169] Anionic nucleophiles (hard bases, X^-, such as MeO^-, Me_2N^-) generally have low-lying lone pairs which can interact directly with the HOMO and thus tend to attack at C(1). After protonation, the product is a vinylcarbene:

$$[M]{=}C{=}C{=}CR_2 + X^- \rightarrow \{[M]{-}C(X){=}C{=}CR_2\}^- + H^+ \rightarrow [M]{=}CX{-}CH{=}CR_2 \quad (6)$$

In contrast, neutral nucleophiles are generally soft bases with high-lying lone pairs which can add directly to the LUMO centered on C(3) to give substituted acetylides:

$$[M]{=}C{=}C{=}CR_2 + Nu \rightarrow [M]{-}C{\equiv}C{-}CR_2(Nu) \quad (7)$$

Nucleophiles of intermediate energy, such as SR^-, may give products formed by both routes. The following series of reactivities has been established for the manganese complexes:[109]



Such straightforward rationalizations of the reactions with anionic carbon nucleophiles cannot yet be made, the site of attack being dependent both on the nucleophile and on the other ligands present on the metal center. Thus, for $[Ru({=}C{=}C{=}CPh_2)(L)(L')Cp']^+$ (L = CO, L′ = PPr^i_3, Cp′ = Cp), attack of LiMe or LiC≡CPh on C(1) and C(3) is competitive,[175] while for L = L′ = PPh_3, Cp′ = η^5-C_9H_7, regioselective addition at C(3) is found.[132,176]

3. Electrophilic Reactions

Electrophiles react with allenylidene ligands to give carbyne complexes by addition to C(2) (as found with manganese systems):[178]

$$[M]{=}C{=}C{=}CR_2 + E^+ \rightarrow [M^+]{\equiv}C{-}CE{=}CR_2 \quad (8)$$

or to afford allenyl complexes by addition across the metal–C(1) bond (as found for rhodium systems):[35]

$$[M]{=}C{=}C{=}CR_2 + HX \rightarrow X{-}[M]{-}CH{=}C{=}CR_2 \quad (9)$$

4. Ligand Transfer and Coupling Reactions

There has been little success attendant on attempts to transfer the unsaturated carbene ligands from the metal complexes. Only in one case has thermal decomposition of $Mn({=}C{=}C{=}CR_2)(CO)_2Cp$ given the expected hexapentaene [with R = Bu^t, to give $Bu^t{}_2C{=}(C{=}C)_2{=}CBu^t{}_2$].[103]

In rhodium complexes, it has been possible to couple the allenylidene with other ligands (particularly other carbenes), either by migration (insertion) or by intramolecular coupling, to give either σ-bonded functionalized alkynes or η^2-bonded polyene ligands.[35] These reactions may occur even if the two ligands which couple are disposed trans on the metal; these reactions occur in the presence of halide or a coordinating solvent.[135,179] As described below, the coupled products can often be displaced from the metal by CO.

B. Reactions of Allenylidene Complexes

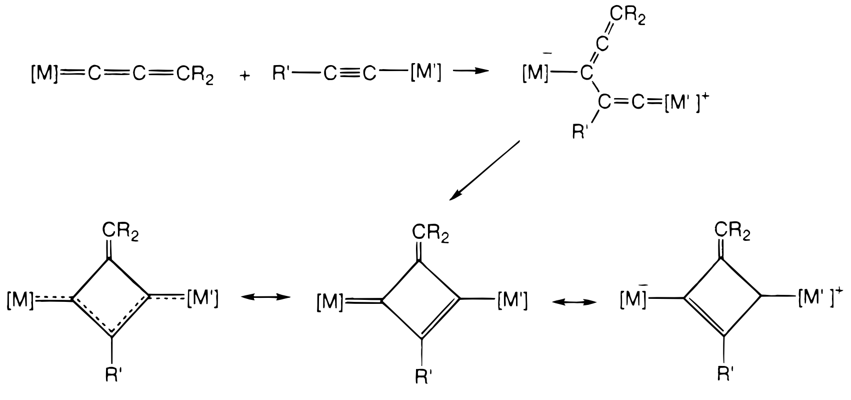
1. Chromium, Molybdenum, and Tungsten

Following the reactions of vinylidene complexes with M–C≡C–R (M = Fe, Ni) systems to give methylenecyclobutane derivatives,[180] analogous allenylidene complexes were found to undergo the same type of cycloaddition reaction to give strongly polar heterobinuclear complexes **34** containing the cyclobutadienylidene fragment (Scheme 27).[117]

In this reaction, selective addition to the 1,2-C=C portion is found with no ring opening, in contrast to ynamines. The rate of addition increased with increasing electrophilicity of the allenylidene C(1) and the nucleophilicity of the alkynyl C(2) atoms.

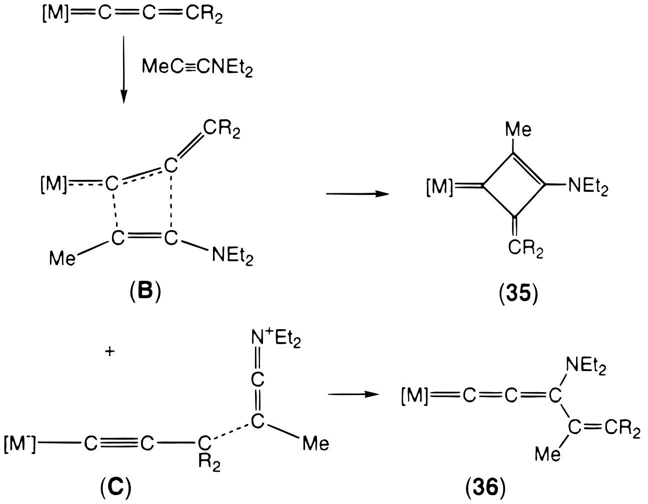
Ynamines $MeC{\equiv}CNEt_2$ react rapidly with the allenylidenes to give inseparable mixtures of the cycloadducts $M\{{=}CCMe{=}C(NEt_2)C{=}C(C_6H_4R\text{-}4)_2\}(CO)_5$ (M = Cr, W; R = H, Me, OMe, NMe_2) (**35**) with the vinylallenylidenes $M\{{=}C{=}C{=}C(NEt_2)CMe{=}C(C_6H_4R\text{-}4)_2\}(CO)_5$ (**36**).[108] Complexes **35** (R = NMe_2) decompose in contact with silica, allowing separation of pure **36** (R = NMe_2); the best separations were achieved by fractional crystallization. The reactions proceed by regioselective [2 + 2] cycloaddition of the alkyne to C(1)=C(2), or by addition to C(2)=C(3) and cycloreversion. No intermediates have been detected in either reaction. The methoxy complexes react faster than the NMe_2 derivatives, while $MeC{\equiv}CNMe_2$ reacts faster than $PhC{\equiv}CNMe_2$. The ratio of products is affected by solvent polarity, cycloaddition being favored in the less polar solvents, but insertion proceeding in $CHCl_2CH_2Cl$. This is consistent with an associative rate-determining step, with a less polar transition state for **35** than for **36**, depicted as **B** and **C**, respectively (Scheme 28).

Scheme 27

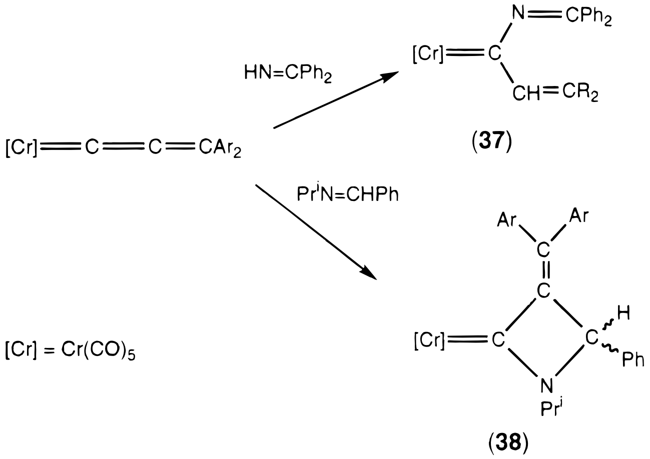


(**34**)

Scheme 28



Scheme 29



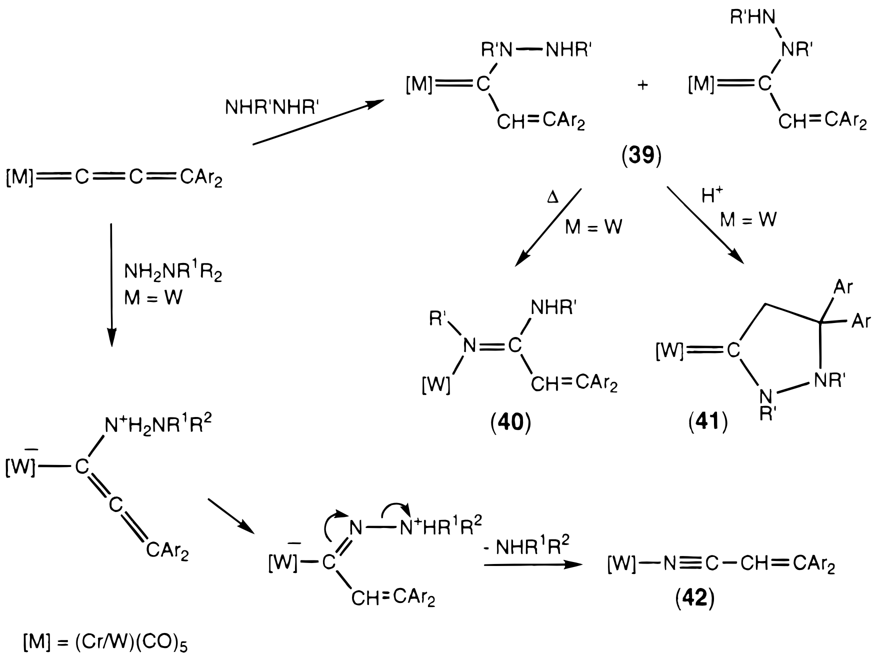
Addition of $\mathrm{NHMe_2}$ to $\mathrm{Cr\{{=}C{=}C{=}CR(NR'_2)\}(CO)_5}$ gives $\mathrm{Cr\{{=}C(NMe_2)CH{=}CR(NR'_2)\}(CO)_5}$ with varying *E*/*Z* ratios.[95] At −70 °C, $\mathrm{M\{{=}C(NEt_2)CH{=}CAr_2\}(CO)_5}$ was obtained from $\mathrm{NHEt_2}$ and the diarylallenylidene, while both *E*/*Z* isomers of $\mathrm{M\{{=}C(NHPh)CH{=}CAr_2\}(CO)_5}$ were obtained with $\mathrm{NH_2Ph}$. No adduct of $\mathrm{Cr\{{=}C{=}C{=}C(C_6H_4NMe_2\text{-}4)_2\}(CO)_5}$ and $\mathrm{NEt_3}$ at C(1) could be isolated. With $\mathrm{NH{=}CR^1R^2}$ ($\mathrm{R^1, R^2 = Ph_2}$; $\mathrm{Bu^t}$, tol) at −25 °C, complexes $\mathrm{M\{{=}C(N{=}CPh_2)CH{=}CR^1R^2\}(CO)_5}$ (**37**) were formed, while with $\mathrm{NPr^i{=}CHPh}$, the azetidinylidene complex (**38**) was formed by addition of N to C(1) and cyclization of the resulting ylide (Scheme 29).[86]

Addition of hydrazines $\mathrm{NHR^1NHR^2}$ to $\mathrm{M({=}C{=}C{=}CAr_2)(CO)_5}$ (M = Cr, W; Ar = $\mathrm{C_6H_4NMe_2\text{-}4}$) gave the vinyl−hydrazino−carbenes $\mathrm{M\{{=}C(NR^1NHR^2)CH{=}CAr_2\}(CO)_5}$ (**39**; M = Cr, $\mathrm{R^1 = R^2 = Me, Pr^i}$; M = W, $\mathrm{R^1 = R^2 = Me, Pr^i, Cy, CH_2Ph}$; $\mathrm{R^1 = Me, R^2 = Ph}$) as *E*/*Z* mixtures except for the isopropyl complexes, which were formed selectively as the *E* conformers (Scheme 30).[86,181] The reactions of the dimethyl compounds are slower than those with $\mathrm{NHEt_2}$. The reaction probably proceeds via initial addition to C(1), followed by rearrangement of the *N*-ylide. On heating, the tungsten complexes rearrange to acrylamidines **40** by concerted migration of $\mathrm{W(CO)_5}$ and NR groups (R = Me, $\mathrm{CH_2Ph}$). Acid-catalyzed cyclization of the tungsten vinylcarbenes gives pyrazolidinylidene complexes **41** (R = Me, $\mathrm{CH_2Ph}$, $\mathrm{Pr^i}$).[181] The unsaturated nitriles $\mathrm{W(NCCH{=}CR_2)(CO)_5}$ (**42**) are also obtained from reactions with $\mathrm{NH_2NR^1R^2}$ ($\mathrm{R^1 = R^2 = H, Me}$; $\mathrm{R^1 = H, R^2 = Ph}$), which proceed by addition to C(1), followed by loss of $\mathrm{NHR^1R^2}$ and 1,2-migration of tungsten from C to N, i.e., an organometallic Beckmann rearrangement.[29]

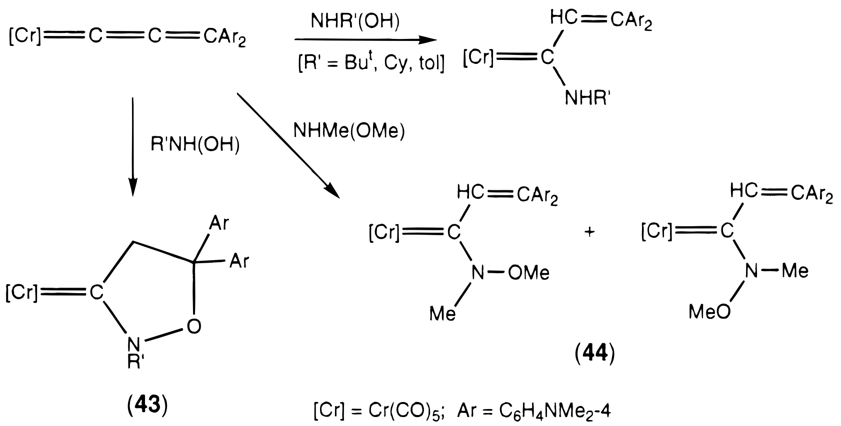
The 4-(dimethylamino)phenyl derivatives $\mathrm{M\{{=}C{=}C{=}C(C_6H_4NMe_2\text{-}4)_2\}(CO)_5}$ (M = Cr, W) react with hydroxylamines to give isoxazolidinylidene complexes **43** by intramolecular attack of the OH group on C(3) of intermediate vinylcarbenes, formed by initial attack of C(1) by the nitrogen (Scheme 31).[182] A byproduct from NHCy(OH) is a mixture of (*E*/*Z*)-$\mathrm{Cr\{{=}C(NHCy)CH{=}C(C_6H_4NMe_2\text{-}4)_2\}(CO)_5}$. Similar products are formed in reactions of NHR′(OH) (R′ = $\mathrm{Bu^t}$, tol) or $\mathrm{NMe_2(OH)}$. With NHMe(OMe), a 1/3.2 *E*/*Z* mixture of $\mathrm{W\{{=}C[NMe(OMe)]CH{=}C(C_6H_4NMe_2\text{-}4)_2\}(CO)_5}$ (**44**) was obtained, of which the *E* form isomerized to *Z* on warming.

Addition of $\mathrm{PPh_3}$ to $\mathrm{M({=}C{=}C{=}CR_2)(CO)_5}$ (M = Cr, W; R = $\mathrm{Pr^i}$; M = Cr, R = $\mathrm{C_6H_4NMe_2\text{-}4}$) gave $\mathrm{M\{C(PPh_3){=}C{=}CR_2\}(CO)_5}$ (Scheme 32) but no adducts were formed with the analogous $\mathrm{Bu^t}$ complexes.[104] Addition of $\mathrm{PR'_3}$ to the chromium series (R = $\mathrm{C_6H_4NMe_2\text{-}4}$) occurs at C(1) ($\mathrm{PR'_3 = PMe_3, PHPh_2}$); the $\mathrm{PHPh_2}$ aduct slowly rearranges to $\mathrm{Cr\{PPh_2(CH{=}C{=}CAr_2)\}(CO)_5}$ (**45**) at room temperature by synchronous migration of the $\mathrm{Cr(CO)_5}$ group from C to P and H migration along the carbon chain. The $\mathrm{PH_2(mes)}$ adduct immediately isomerizes to $\mathrm{Cr\{PH(mes)(C{\equiv}}$

Scheme 30



Scheme 31



$CCHAr_2)\}(CO)_5$ (**46**). Excess $PHPh_2$ reacts with Cr$\{=C=C=C(C_6H_4)_2O\}(CO)_5$ to give the binuclear bismethylenecyclobutane complex (**47**) by chemo-, regio-, and stereoselective dimerization of the allenyldiphenylphosphine complex analogous to **45**.[183]

2. Manganese

a. Nucleophiles. Addition of OMe^- or NMe_2^- (X^-) to $Mn(=C=C=CPh_2)(CO)_2Cp$ gave the anionic allenyl complexes $[Mn\{C(X)=C=CPh_2\}(CO)_2Cp]^-$, which afforded the vinylcarbenes on protonation [i.e., addition of electrophile at C(2)]:[102]

$$[Mn]=C=C=CPh_2 + X^- \rightarrow [[Mn]-C(X)=C=CPh_2]^- + H^+ \rightarrow [Mn]=C(X)CH=CPh_2 \quad (10)$$

An X-ray study corrects the initial report[102] of PPh_3 addition to C(3) for R = Bu^t, Ph, showing that the product is in fact $[Mn\{C(PPh_3)=C=CPh_2\}(CO)_2Cp]^+$;[184] this result is now in accord with the reactions found with chromium complexes (above).[104] For $Mn(=C=C=CPh_2)(CO)_2(\eta\text{-}C_5H_4Me)$ the reaction is reversible (ΔH = 59 kJ mol^{-1} in CS_2) and is solvent and temperature dependent.[102] Exchange of PPh_3 for $PMePh_2$ occurs in nonpolar solvents (pentane), but in polar solvents (thf, Et_2O), it dissociates back to the allenylidene and $PMePh_2$.

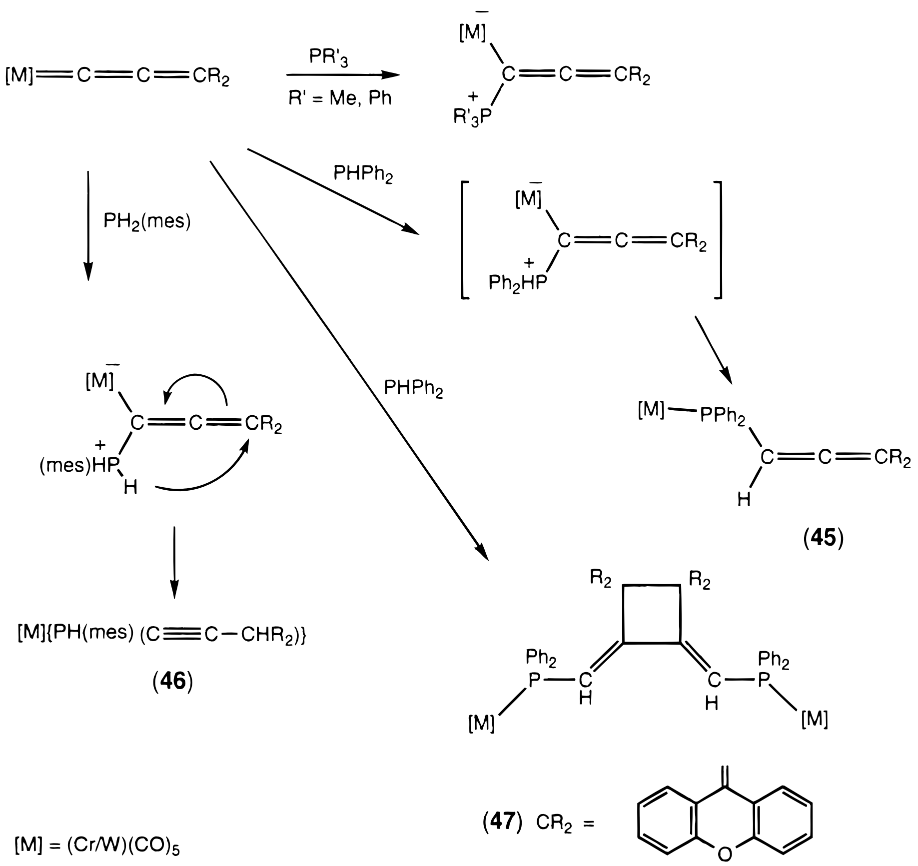
With SBu^{t-}, the C(1) and C(3) adducts were obtained in approximately equal amounts. Protonation of the C(3) adduct gave the vinylidene:

$$[Mn]=C=C=CPh_2 \rightarrow [Mn]-C\equiv C-CPh_2(SBu^t)^- \rightarrow [Mn]=C=CHCPh_2(SBu^t) \quad (11)$$

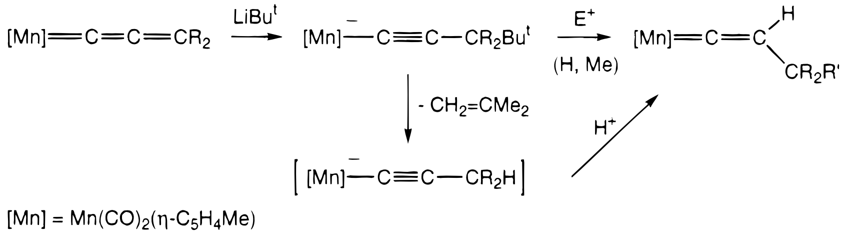
Addition of $LiBu^t$ to $Mn(=C=C=CR_2)(CO)_2(\eta\text{-}C_5H_4Me)$ (R = Bu^t, Ph) occurs at C(3); protonation then gives vinylidenes $Mn(=C=CHCR_2Bu^t)(CO)_2(\eta\text{-}C_5H_4Me)$ (R_2 = Ph_2, HBu^t) and methylation affords $Mn(=C=CMeCPh_2Bu^t)(CO)_2(\eta\text{-}C_5H_4Me)$ via anionic alkynyl complexes (Scheme 33).[185]

In the reaction between $LiBu^t$ and $Mn(=C=C=CBu^t_2)(CO)_2Cp$, elimination of $CMe_2=CH_2$ also occurs

Scheme 32



Scheme 33



and Mn(=C=CH$_2$)(CO)$_2$Cp is isolated in small amounts (<1%) after addition of electrophile.[185] This compound is also obtained by treatment of Mn(η-HC$_2$CO$_2$Me)(CO)$_2$Cp with an excess of LiMe.[103]

b. Electrophiles. Protonation of Mn(=C=C=CR$_2$)(CO)$_2$Cp (R = Bu^t, Ph) gave cationic vinylcarbyne complexes [Mn(≡C−CH=CR$_2$)(CO)$_2$Cp]$^+$ by addition at C(2):[178]

$$[\mathrm{Mn}]{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{CR}_2 \xrightarrow{\mathrm{H}^+} [[\mathrm{Mn}]{\equiv}\mathrm{C}{-}\mathrm{CH}{=}\mathrm{CR}_2]^+ \quad (12)$$

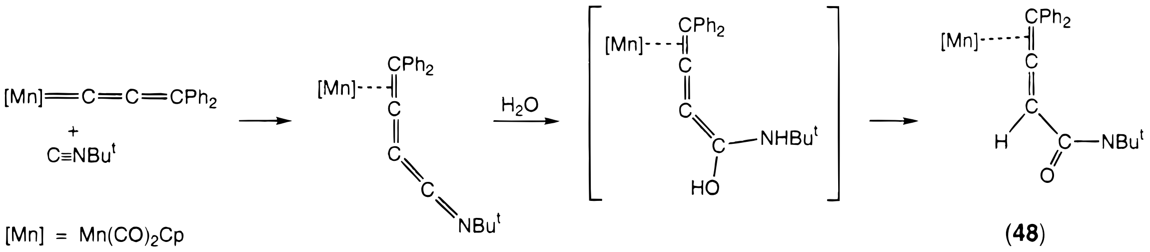
c. Coupling Reactions. Heating Mn(C=C=CBu$^t_2$)(CO)$_2$Cp (100 °C, 1 atm) afforded a 52% yield of Bu$^t_2$C=C=C=C=C=CBu$^t_2$ (identified only by mass spectrometry), possibly by coupling of the released :C=C=CBu$^t_2$.[103] The reaction of CNBu^t with Mn(=C=C=CPh$_2$)(CO)$_2$Cp (a reaction which is slower than for the vinylidene) gives an intermediate Mn(η^2-Bu^{t}N=C=C=C=CPh$_2$)(CO)$_2$Cp which with water gives Mn{η^2-CPh$_2$=C=C=C(OH)(NHBu^t)}(CO)$_2$Cp; this isomerizes to Mn{η^2-CPh$_2$=C=CHC(O)NHBu^t}(CO)$_2$Cp (**48**) (Scheme 34).[186] These reactions hardly proceed with CNR (R = Cy, CH$_2$Ph).

3. Ruthenium and Osmium

a. Nucleophiles. Extensive studies of the reactions of ruthenium−allenylidene complexes have been made in the series [Ru(=C=C=CPh$_2$)(L)(L′)Cp′]$^+$ (L = CO, L′ = PPr$^i_3$, Cp′ = Cp, η^5-C$_9$H$_4$Me$_3$; L = L′ = PPh$_3$, Cp′ = Cp, η^5-C$_9$H$_7$; LL′ = dppm, dppe, Cp′ = η^5-C$_9$H$_7$).[83,124,132,133,175,176] As predicted, reactions with nucleophiles occur mainly at C(3) to give acetylide complexes, although with smaller ligands L, some attack at C(1) is found to give carbene ligands. These reactions are summarized in Schemes 35 and 36. In general, the site of nucleophilic addition depends on steric and electronic properties of L, L′, and the indenyl group; the (CO)(PPh$_3$) combination is less sterically demanding and the allenylidene ligand is more electrophilic.[133]

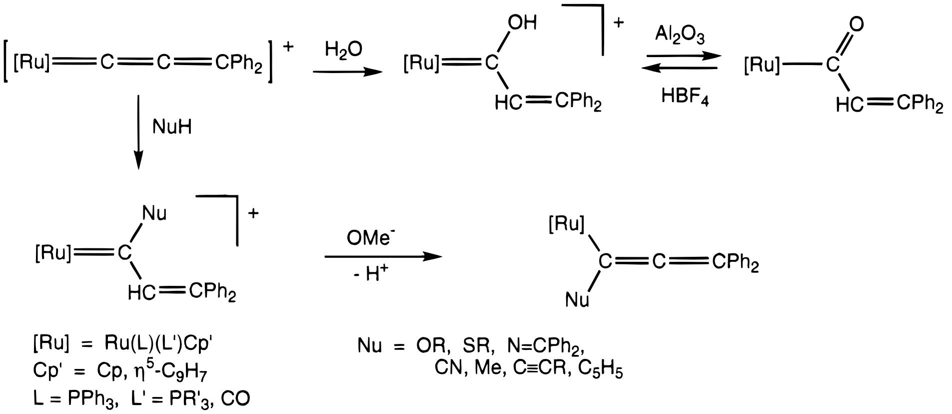
Reactions of [Ru(C=C=CPh$_2$)(CO)(PPr$^i_3$)Cp]$^+$ with neutral nucleophiles, such as water, alcohols, thiols, and imines (NuH), proceed by addition at C(1) to give [Ru{=C(Nu)CH=CPh$_2$}(CO)(PPr$^i_3$)Cp]$^+$; the imine affords the rare azaallenyl ligand (Scheme 36). Subsequent reactions of these adducts have enabled

Scheme 34

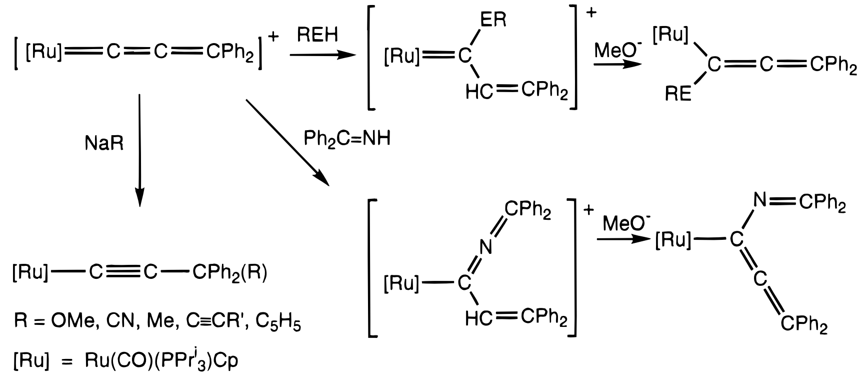


(**48**)

Scheme 35



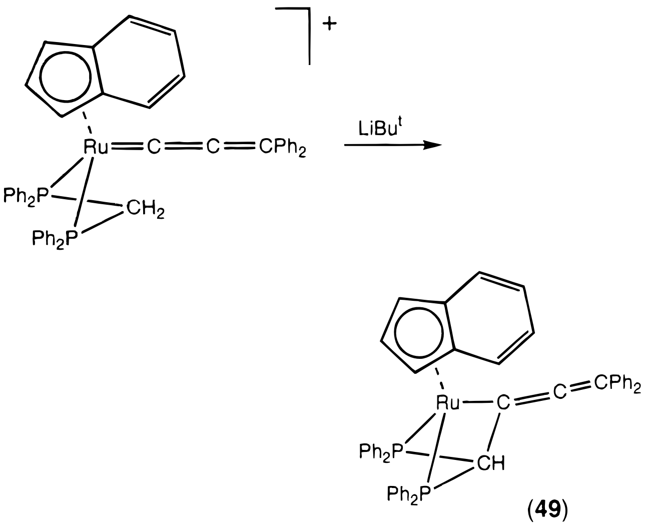
Scheme 36



access to several interesting ligands. Deprotonation, either on alumina or with NaOMe, of the cationic products from neural ligands, generally gives allenyl complexes Ru{C(Nu)═C═CPh$_2$}(CO)(PPr$^i_3$)Cp, although the hydroxycarbene gives the α,β-unsaturated acyl complex.[124]

Complexes with LL′ = (PPh$_3$)$_2$, dppm, or dppe, do not react with methanol. However, uniform addition of alkoxides or carbanions (LiMe, LiC$_5$H$_5$, K[CH$_2$COMe], Na[CH(COMe)$_2$]) to C(3) occurs.[132,133,175] In some cases, such as LiMe or LiC≡CR with the carbonyl-containing complexes, a mixture of products formed by addition to either C(1) or C(3) results;[175] an unstable ammonium cation was formed by addition of NHMe$_2$.[126] Intramolecular cyclization occurs in the reaction of the dppm complex with LiBu^t, the deprotonated dppm attacking C(1) of the allenylidene ligand to give **49** (Scheme 37).[176] The cyclic oxacarbene complex **50** is formed by protonation of the acetone adduct.[175]

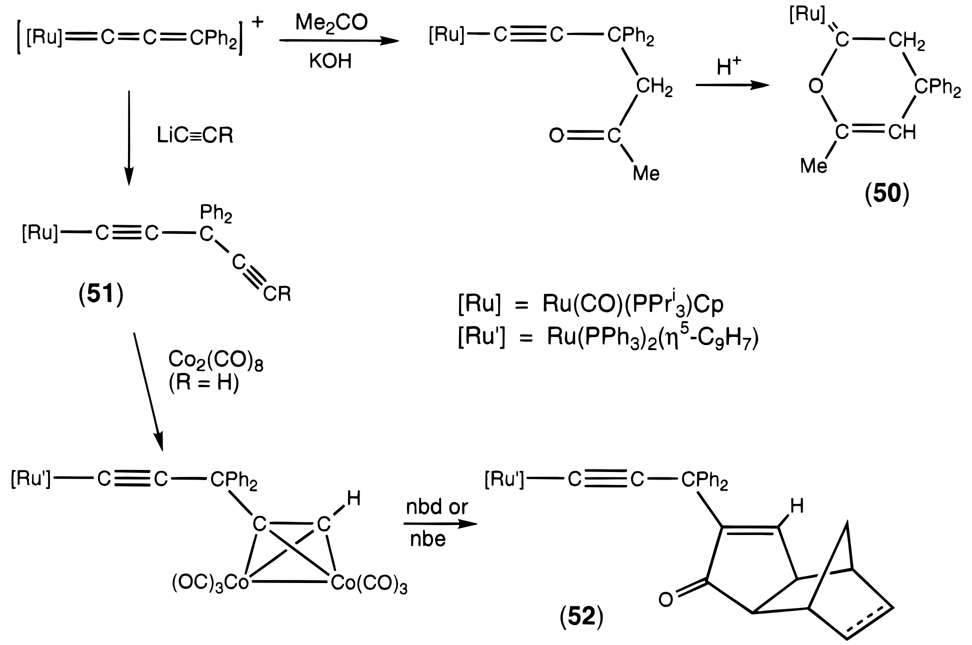
Scheme 37



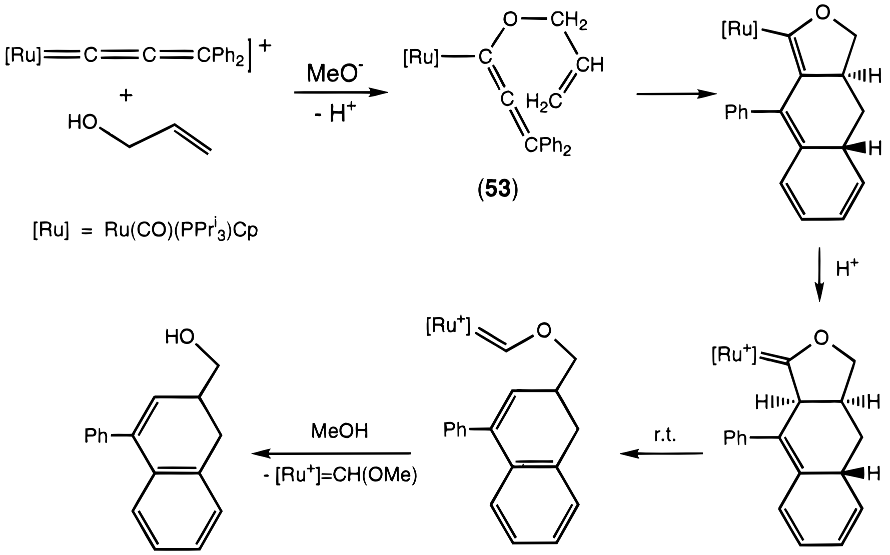
(**49**)

Protonation of the ethynyl complexes generally affords the vinylidenes, although this reaction regenerates the allenylidene with the methoxide and acetylacetonate adducts of the (CO)(PPr$^i_3$) complex. Regioselective attack of HC≡C$^-$ at C(3) in [Ru(═C═C═CPh$_2$)(PPh$_3$)$_2$(η^5-C$_9$H$_7$)]$^+$ gives highly functional-

Scheme 38



Scheme 39



ized alkynyl complexes, Ru{$C{\equiv}CCPh_2(C{\equiv}CR)$}$(PPh_3)_2(\eta^5\text{-}C_9H_7)$ (**51**; R = H, Pr^n, Ph), C(1) being protected by the bulky PPh_3 ligands.[176] The Pauson−Khand reactions between **51** (R = H) and bicyclo[2.2.1]hept-2-ene or -2,5-diene afforded the tricyclic derivatives **52** (Scheme 38).[187]

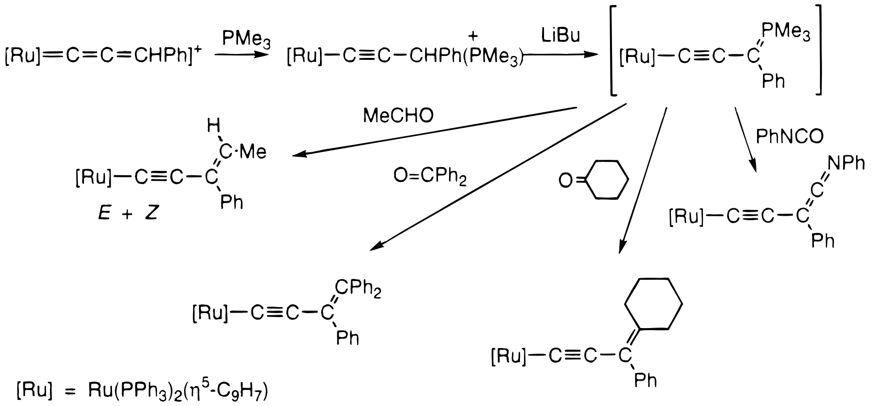
The reaction with allyl alcohol gives the allyloxy carbene [Ru{$=C(OCH_2CH{=}CH_2)CH{=}CPh_2$}(CO)$(PPr^i_3)$Cp $]^+$ which on treatment with NaOMe affords the allenyl complex Ru{$C(OCH_2CH{=}CH_2){=}C{=}CPh_2$}(CO)$(PPr^i_3)$Cp (**53**).[188] Subsequent isomerization and protonation gives tricyclic and dihydronaphthyl derivatives (Scheme 39).

The sites of reactions of phosphorus nucleophiles depend on the size of PR_3, selective addition to C(3) occurring for $PMe_{3-n}Ph_n$ for the $(PPh_3)_2$ complex, and at C(1) for the dppe derivative, while both isomers are formed with the dppm complex.[176] The C(1) adduct is thermodynamically more stable and migratory isomerization to C(1) is found (14 h, room temperature) for the PMe_3 adducts.[132] The secondary allenylidene ligand in the indenyl complexes is stabilized to varying degrees by the associated tertiary phosphine ligands.[176]

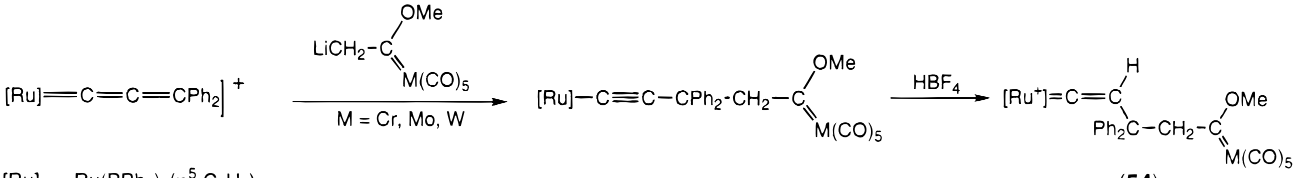
Treatment of Ru{$C{\equiv}CCHPh(P^+Me_3)$}$(PPh_3)_2(\eta^5\text{-}C_9H_7)$ with LiBu gives a dark green complex [probably $Ru(C{\equiv}CCPh{=}PMe_3)(PPh_3)_2(\eta^5\text{-}C_9H_7)$]. Wittig reactions between this species and the appropriate ketones gave $Ru(C{\equiv}CCPh{=}CR_2)(PPh_3)_2(\eta^5\text{-}C_9H_7)$ [$CR_2 = CPh_2$, $C(CH_2)_5$] and (*E*/*Z*)-$Ru(C{\equiv}CCPh{=}CHMe)(PPh_3)_2(\eta^5\text{-}C_9H_7)$ (Scheme 40).[189] Treatment of the PPh_3 adduct of $[Ru({=}C{=}C{=}CHPh)(PPh_3)_2(\eta^5\text{-}C_9H_7)]^+$ with LiBu and $PhC{\equiv}CCHO$ gave (*E*)- and (*Z*)-$Ru(C{\equiv}CCH{=}CHC{\equiv}CPh)PPh_3)_2(\eta^5\text{-}C_9H_7)$.[187]

Of interest is the reaction of the lithiated Fischer carbene complexes at C(3) to give Ru{$C{\equiv}CCPh_2CH_2C(OMe){=}[M(CO)_5]$}$(PPh_3)_2(\eta^5\text{-}C_9H_7)$ M = Cr, Mo,

Scheme 40

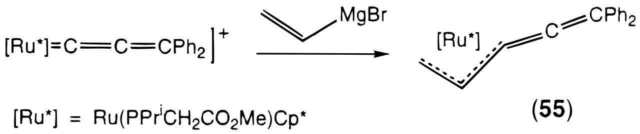


Scheme 41



(**54**)

Scheme 42



(**55**)

W) which could be protonated ($HBF_4{\cdot}OEt_2$) to give **54** (Scheme 41).[189]

Coupling of $RuCl(C{=}C{=}CPPh_2)(PPr^i_2CH_2CO_2Me$-*P*)Cp* with $MgBr(CH{=}CH_2)$ at room temperature gave $Ru(\eta^3$-$CH_2CHC{=}C{=}CPh)(PPr^i_2CH_2CO_2Me$-*P*)-Cp* (**55**) via migratory insertion of allenylidene into a nonisolable vinyl–ruthenium complex (Scheme 42).[80] The facility of this reaction at a relatively well-shielded Ru center probably results from the cis disposition of the vinyl and allenylidene ligands which favors the migration. The alternative possibility, of addition of vinyl to C(1), elimination of chloride and $\eta^1 \rightarrow \eta^3$ rearrangement, was considered unlikely.[190] Attempted reactions of $RuCl(C{=}C{=}CPPh_2)(PPr^i_2CH_2CO_2Me$-*P*)Cp* with MeOH or $NHMe_2$ failed.

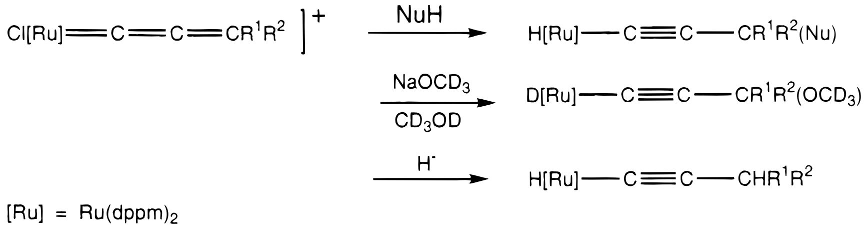
The diphenyl complexes $[RuCl({=}C{=}C{=}CPh_2)(PR_3)(\eta$-$C_6Me_6)]^+$ react with MeOH by attack at C(1) to give $[RuCl\{{=}C(OMe)CH{=}CPh_2\}(PR_3)(\eta$-$C_6Me_6)]^+$. The PPh_3 derivative was isolated in 81% yield.[82]

Attack of alkoxide (OR′) on the cationic allenylidenes *trans*-$[RuCl({=}C{=}C{=}CR_2)(dppm)_2]^+$ occurs at C(3) to give the corresponding acetylides, *trans*-$RuCl\{C{\equiv}CCR_2(OR')\}(dppm)_2$, which reactions are reversed with $[CPh_3]^+$. Secondary allenylidenes react similarly, but the Cl is also replaced by H; $NaOCD_3$/CD_3OD gave *trans*-$RuD\{C{\equiv}CCHPh(OCD_3)\}(dppm)_2$ from *trans*-$[RuCl({=}C{=}C{=}CHPh)(dppm)_2]^+$ (Scheme 43).[8] These reactions involve attack at the metal center, replacing Cl by OMe, followed by elimination of HCHO to give the metal hydrido complex. Addition of hydride (from $NaBH_4$/thf) gave *trans*-$RuCl(C{\equiv}CCHPh_2)(dppm)_2$ (from *trans*-$[RuCl({=}C{=}C{=}CPh_2)(dppm)_2]^+$) or *trans*-$RuCl(C{\equiv}CCH_2Ph)(dppm)_2$ (from the ${=}C{=}C{=}CHPh$ complex).[71]

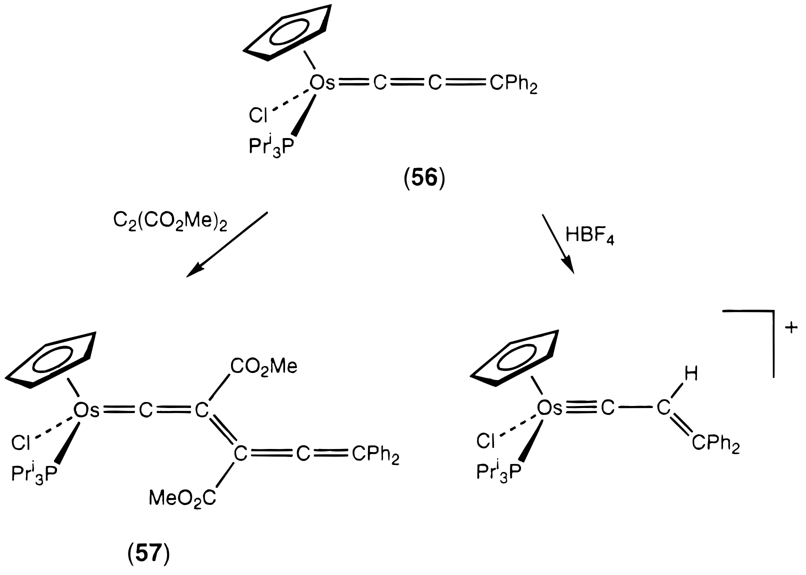
Deprotonation of *trans*-$[RuCl({=}C{=}C{=}CMe_2)(dppm)_2]^+$ with dbu gave *trans*-$RuCl(C{\equiv}CCMe{=}CH_2)(dppm)_2$, i.e., the acetylide corresponding to the precursor $HC{\equiv}CCMe{=}CH_2$.[140] Similarly, $[Ru\{{=}C{=}C{=}C$-$Me(C_4H_3NMe$-$2)\}(PPh_3)_2Cp]^+$ with LiBu affords $Ru\{C{\equiv}CC(C_4H_3NMe$-$2){=}CH_2\}(PPh_3)_2Cp$.[109]

The chelate complex $[Os({=}C{=}C{=}CPh_2)\{C[C(O)OMe]{=}CH_2\}(CO)(PPr^i_3)_2][BF_4]$ (**28**; Scheme 23 above) reacts with LiMe to give $Os(C{\equiv}CCMePh_2)\{C[C(O)OMe]{=}CH_2\}(CO)(PPr^i_3)_2$, which in MeOH is transformed into $Os\{C{\equiv}CCPh_2(OMe)\}\{C[C(O)OMe]{=}CH_2\}(CO)(PPr^i_3)_2$, also formed directly from the allenylidene and NaOMe.[147] In contrast, $OsCl({=}C{=}C{=}CPh_2)(PPr^i_3)Cp$ is inert toward alcohols, acetate, pyrazole, $Ph_2C{=}NH$, and $PHPh_2$. However, addition of $NaBH_4$, followed by MeOH, results in reduction of the C(2)= C(3) double bond to give $OsCl({=}C{=}CHCHPh_2)(PPr^i_3)Cp$.[137]

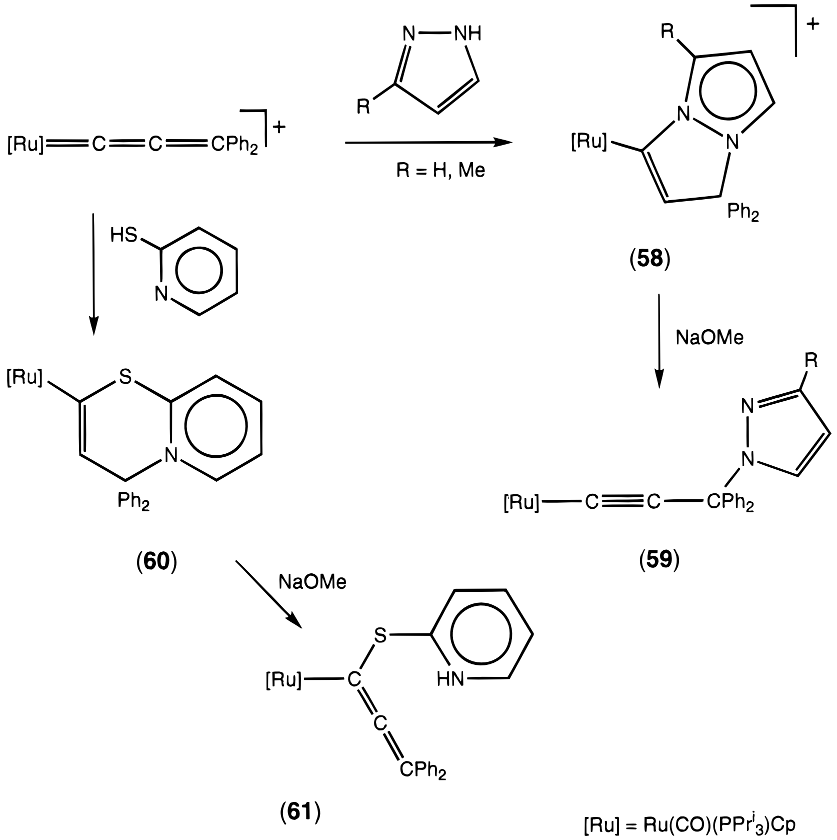
Scheme 43



Scheme 44



Scheme 45

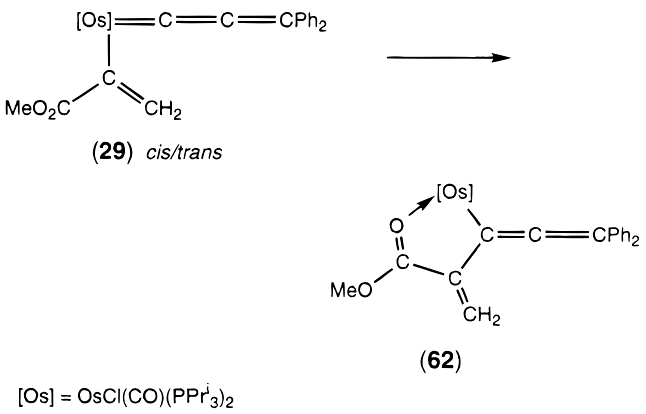


b. Electrophiles. Addition of HCl to $RuCl_2(=C=C=CPh_2)\{\kappa^2\text{-}P,O\text{-}PPr^i_2CH_2C(O)OMe\}(PPr^i_2CH_2CO_2Me\text{-}P)$ occurs at C(1)−C(2) to give the vinylcarbene $RuCl_2(=CClCH=CPh_2)\{\kappa^2\text{-}P,O\text{-}PPr^i_2CH_2C(O)OMe\}(PPr^i_2CH_2CO_2Me\text{-}P)$.[71] Attempts to displace the allenylidene ligand from $[trans\text{-}RuCl(=C=C=CPh_2)(\kappa^2\text{-}P,O\text{-}PPr^i_2C_2H_4OMe)_2]^+$ with CO gave $[RuCl(CO)(\kappa^2\text{-}P,O\text{-}PPr^i_2C_2H_4OMe)_2]^+$ but the fate of the C_3 ligand was not determined.[144]

Protonation ($HBF_4{\cdot}OEt_2$) of $OsCl(=C=C=CPh_2)(PPr^i_3)Cp$ (**56**) forms the cationic carbyne complex $[OsCl(\equiv CCH=CPh_2)(PPr^i_3)Cp]^+$ by addition of a proton at C(2). The electron-deficient alkyne $C_2(CO_2Me)_2$ also reacts readily with **56**, affording the allenylvinylidene $OsCl\{=C=C(CO_2Me)C(CO_2Me)=C=CPh_2\}(PPr^i_3)Cp$ (**57**), probably by cycloaddition to the C(1)=C(2) double bond, followed by ring-opening (Scheme 44).[135]

c. Cycloaddition Reactions. Reactions of $[Ru(=C=C=CPh_2)(CO)(PPr^i_3)Cp]^+$ with pyrazoles have given products formed by cycloaddition to C(1) and C(3), with proton transfer to C(2). Thus the substituted pyrazolo[1,2-*a*]pyrazol-3-yl complexes (**58**; R = H, Me) are obtained in high yields from the corre-

Scheme 46



sponding pyrazoles. With 3-methylpyrazole, the reaction is regioselective. Ring opening occurs on subsequent reaction with methoxide to give the alkynyl complexes (**59**; R = H, Me). Protonation of the former gives back (**58**; R = H) by cleavage of the pyrazolyl group and regeneration of the allenylidene, followed by the cycloaddition. A related reaction is found with pyridine-2-thiol, which forms **60**; deprotonation (NaOMe) also results in ring opening to give the allenyl **61** (Scheme 45).[177] These reactions take advantage of the presence of an electron-rich C(2) to accept the proton and the two electrophilic centers [C(1) and C(3)] which allow the cycloaddition to proceed.

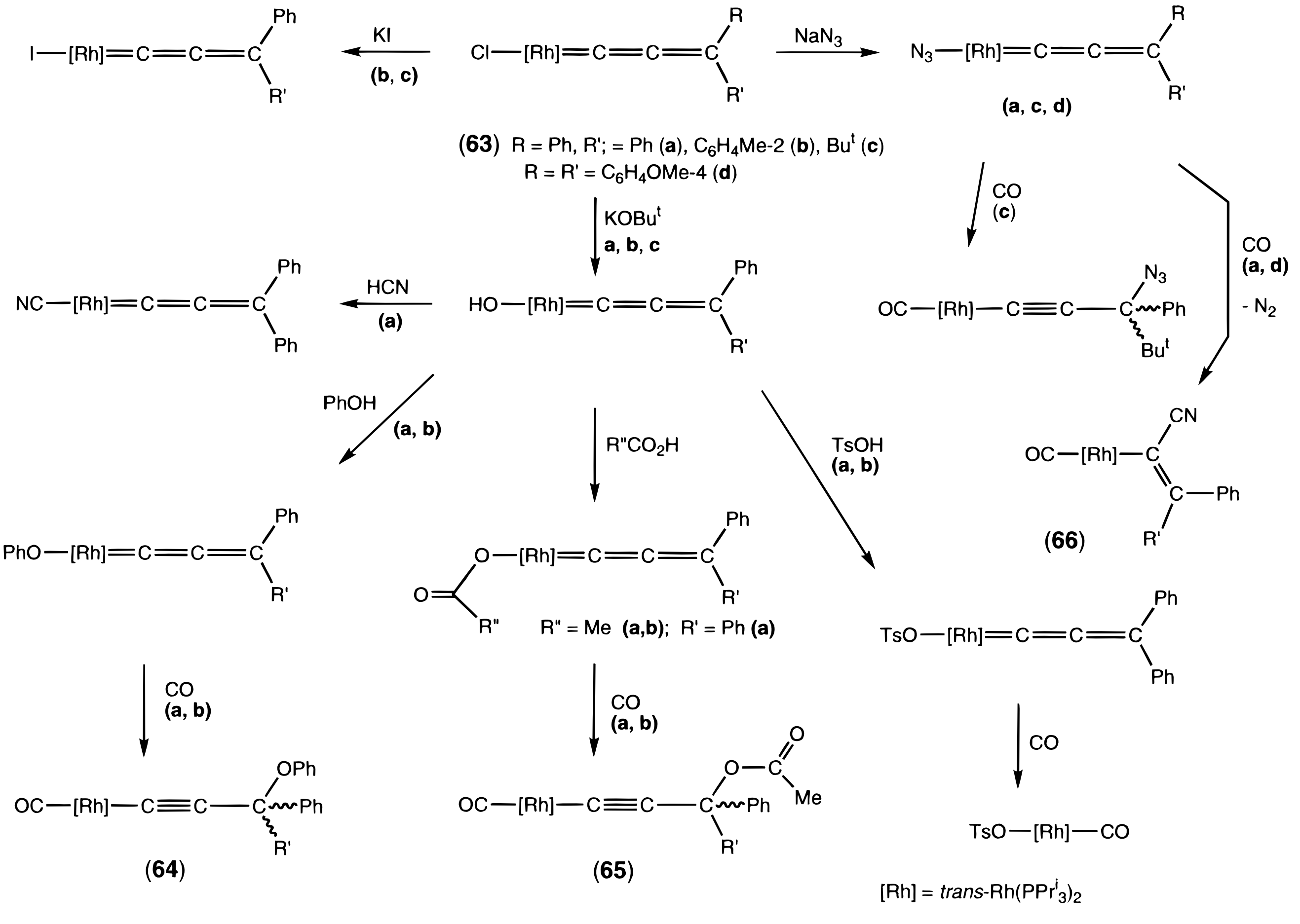
d. Coupling Reactions. Heating the isomeric mixture of alkenyl−allenylidene complex $\mathrm{OsCl\{C(CO_2Me){=}CH_2\}({=}C{=}C{=}CPh_2)(CO)(PPr^i_3)_2}$ (**29**; Scheme 23 above) results in coupling of the unsaturated ligands to form the allenyl complex **62** (Scheme 46).[147]

4. Rhodium and Iridium

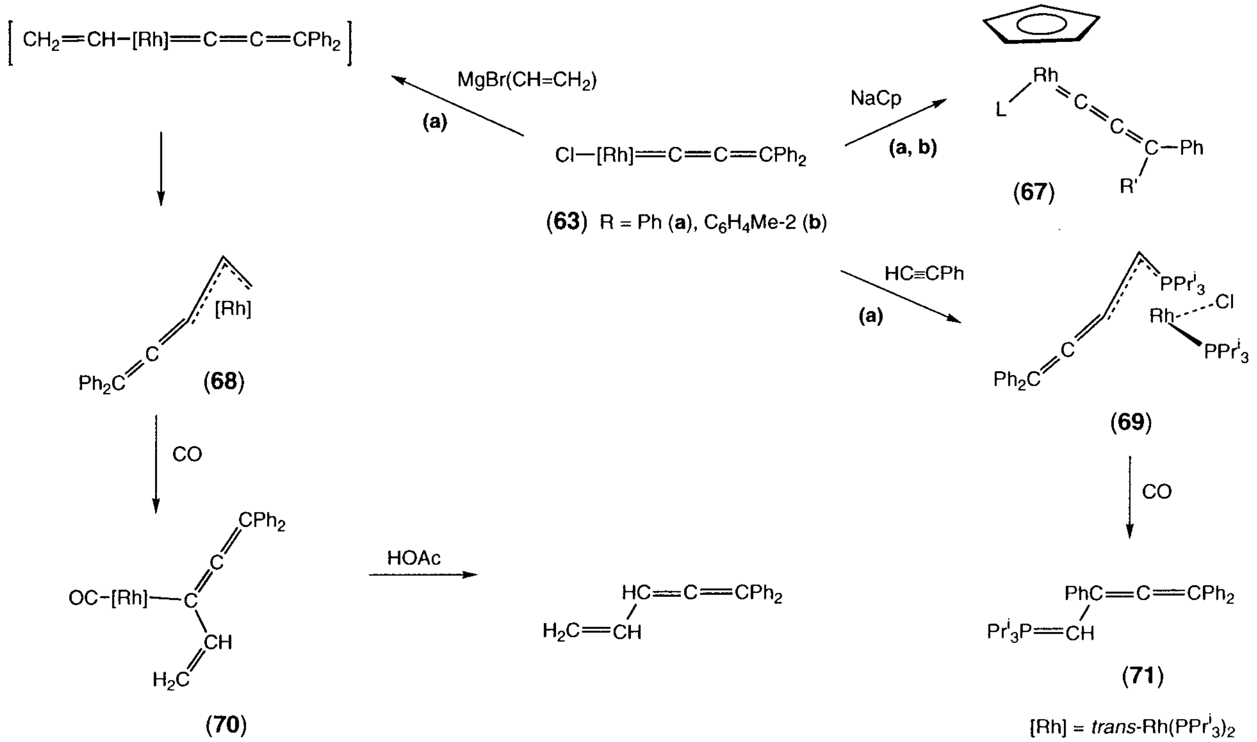
The atom or group trans to a good π-acceptor ligand in square-planar complexes is labilized. Thus, in *trans*-$\mathrm{RhCl({=}C{=}C{=}CPhR)(PPr^i_3)_2}$ [**63**; R = Ph (a), $\mathrm{C_6H_4Me}$-2 (b), $\mathrm{Bu^t}$ (c); Scheme 47] ready replacement of chloride by iodide, hydroxide (using $\mathrm{KOBu^t}$), or azide occurs. In turn, the hydroxy complex can be converted to the analogous cyano, phenoxo, carboxylato, or tosylato derivatives.[35] The Rh−O bond is labile, random exchange of the acetato and phenoxide groups occurring when $\mathrm{Rh\{OC(O)Me\}({=}C{=}C{=}CPh_2)(PPr^i_3)_2}$ and $\mathrm{Rh(OPh)\{{=}C{=}C{=}CPh(C_6H_4Me\text{-}2)\}(PPr^i_3)_2}$ are mixed to give products containing all four possible combinations of the nonphosphine ligands. Carbonylation of complexes with *O*-bonded ligands results in coupling of the two trans-oriented ligands to give **64** or **65**; with the tosylate, replacement of the allenylidene ligand by CO occurs to give $\mathrm{RhCl(CO)(PPr^i_3)_2}$. Heterolytic cleavage of the Rh−O bond does not occur in these reactions, which proceed via five-coordinate 18-electron intermediates.

Reactions of **63** with $\mathrm{NaN_3}$ gave the azido complexes, which react at −60 °C with CO to give $\mathrm{Rh\{C(CN){=}CRR'\}(CO)(PPr^i_3)_2}$ (**66**); in these reactions an $\mathrm{Rh{-}C(N_3){=}C{=}CRR'}$ complex may be an intermediate.[153] With **63c**, the complex $\mathrm{Rh\{C{\equiv}CCPhBu^t(N_3)\}(CO)(PPr^i_3)_2}$ can be isolated. Isocyanato com-

Scheme 47



Scheme 48



plexes are not formed, nor is $Rh(NCO)(=C=C=CPh_2)(PPr^i_3)_2$ converted to **66** under the reaction conditions.

Carbon nucleophiles also substitute the chloride in **63** (Scheme 48), although with RMgX (R = Me, Ph), complex mixtures were obtained: *trans*-$RhR(=C=C=CPh_2)(PPr^i_3)_2$ could not be identified.[35] With NaC_5H_5, $Rh(=C=C=CPhAr)(PPr^i_3)Cp$ (**67**) are formed. In many cases, however, coupling of the allenylidene with the second *C*-bonded ligand occurs, usually so easily that the intermediates cannot be observed. Thus the reaction of **63** with $MgBr(CH=CH_2)$ affords $Rh(\eta^3\text{-}CH_2CHC=C=CPh_2)(PPr^i_3)_2$ (**68**), probably by intramolecular migration of the allenylidene into the Rh–C bond. Coupling of the allenylidene with HC≡CPh similarly afforded the unusual phosphaallyl **69**.[179] Carbonylation of many of these products enables the coupled ligand to be displaced from the rhodium center. In the case of **68**, an initial $\pi \rightarrow \sigma$ rearrangement to **70** occurs, from which the vinylallene $CH_2=CHCH=C=CPh_2$ can be obtained on treatment with acetic acid.[179] The novel ylide $Ph_2C=C=C=CPhCH=PPr^i_3$ (**71**) was obtained from **52** and CO.

Addition of H_2 to **63** slowly gives the η^2-allene complex **72** (Scheme 49).[35,191] The iridium analogue [obtained from $IrH_2Cl(PPr^i_3)_2$ and $HC\equiv CCPh_2(OH)$] also gives the η^2-$CH_2=C=CPh_2$ complex; prolonged reaction gives $MeCH=CPh_2$ and the iridium dihydride.[35] With HCl, oxidative addition forms the five-coordinate allenyl **73** by addition across the Rh=C bond,[35] in contrast to the addition across the C(1)–C(2) bond which occurs with $RuCl_2(=C=C=CPh_2)\{\kappa^2\text{-}P,O\text{-}PPr^i_2C(O)OMe\}\{PPr^i_2C(O)OMe\text{-}P\}$ (see above). Unusually, MeI in the presence of K_2CO_3 acts as a source of the CH_2 group in the formation of $RhI(PPr^i_3)_2\{\eta^2(2,3)\text{-}CH_2=C=C=CPh_2\}$ (**74**) from **63**;[191] diazomethane reacts with **63** to give the η^2-(1,2) isomer (**75**) which isomerizes on heating to the η^2-(2,3) complex **76**.[191] Displacement of the allene from **72** and the butatrienes from **76** occurs rapidly upon their reaction with CO. The rhodium is recovered as $RhCl(CO)(PPr^i_3)_2$. With Cl_2 and **63**, the product is **77**, probably formed by addition of H^+ to the metal center, migration of H to C(1) and addition of Cl^- to the metal, followed by insertion of the allenylidene into an Rh–P bond.

The dialkynyl and hydrido–alkynyl–allenylidene complexes **78** and **79** undergo coupling of the two hydrocarbon fragments on alumina in the presence of chloride ion to give the η^2-(2,3)-hexapentaene complex **80**. The cumulene is again readily displaced by CO.[137] A possible mechanism for this transformation includes the formation of an undetected bis-allenylidene **81**, although an alternative route is dehydration of a coupled alkynyl–allenylidene ligand, as in **82** (Scheme 50). Both pathways would give the η^2-(3,4) isomer (**83**) which is then converted to **80**. This conversion was confirmed by independent synthesis of **83** from the free hexapentaene and $\{RhCl(PPr^i_3)_2\}_2$ at −30 °C; isomerization occurred on warming to 25 °C.[137]

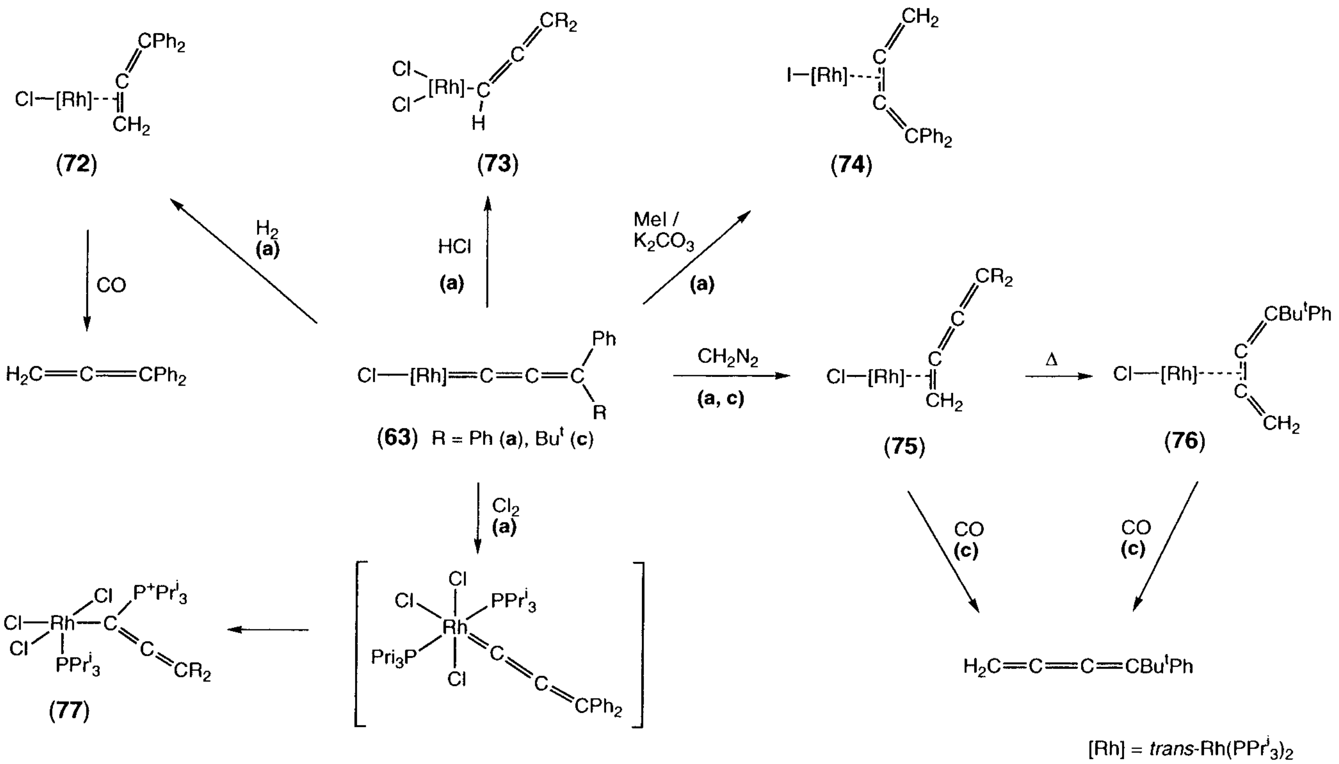
The iridium allenylidene complex is relatively unreactive with HCl and MeI, probably because of the higher kinetic stability of the Ir=C bond.[35]

C. Butatrienylidene Complexes

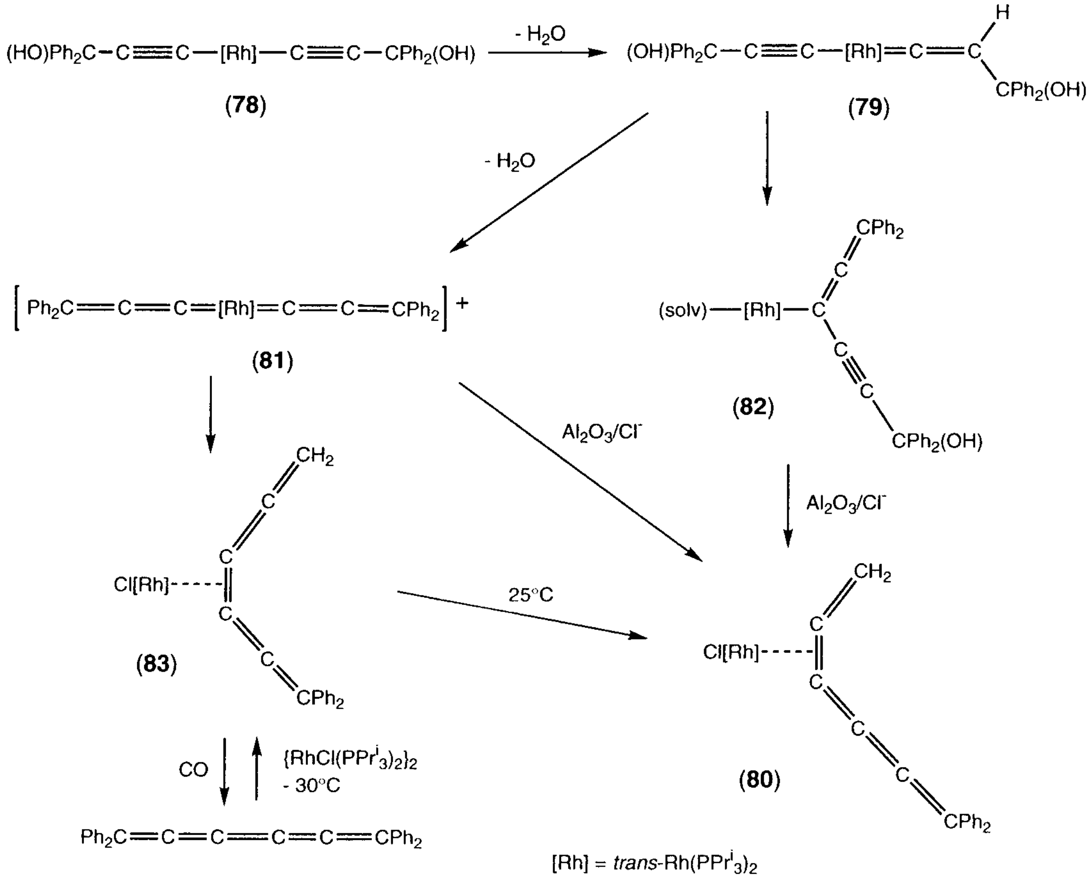
Reactions of $[Ru(=C=C=C=CMe_2)(PPh_3)_2Cp]^+$ with nucleophiles such as MeOH, pyridine, and PR_3 are reported to give $Ru\{C\equiv CC(Nu)=CMe_2\}(PPh_3)_2Cp$.[156] Excess $(CF_3CO)_2O$ gave $[Ru\{=C=C(COCF_3)(OCOCF_3)CMe_2\}(PPh_3)_2Cp][H(CF_3CO_2)_2]$, in which CF_3CO has added to C(2).

The chemistry of the butatrienylidene ligand has been examined briefly using **84**, formed from buta-

Scheme 49

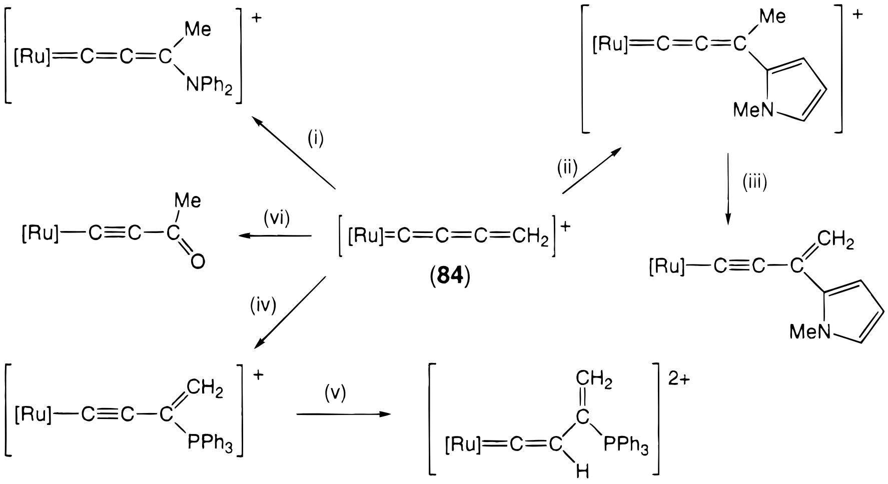


Scheme 50



1,3-diyne and $[Ru(thf)(PPh_3)_2Cp]^+$. The reactions of this complex are critically dependent on the nucleophile (Scheme 51). Attack at C(3) gives the alkenylacetylide; if H migration is possible, this determines the final product. If the nucleophile does not contain a displaceable proton, a cationic adduct is formed. In general, alkenylethynyl complexes are obtained from aprotic nucleophiles, while addition of protic

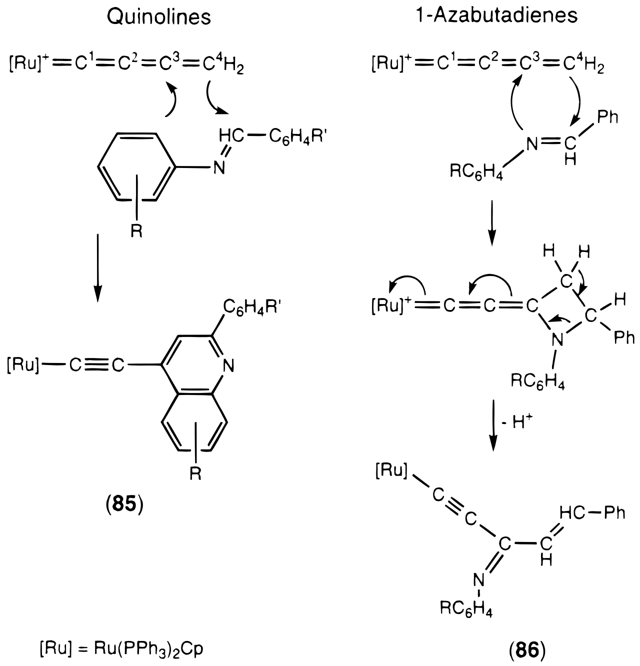
Scheme 51



[Ru] = $\mathrm{Ru(PPh_3)_2Cp}$.

Reagents: (i) $\mathrm{NHPh_2}$; (ii) *N*-methylpyrrole; (iii) LiBu; (iv) $\mathrm{PPh_3}$; (v) $\mathrm{H^+}$; (vi) $\mathrm{H_2O}$.

Scheme 52

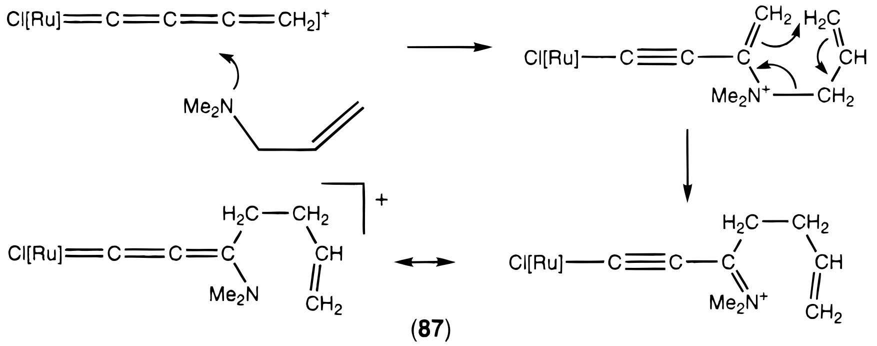


nucleophiles to C(3) is followed by H migration to C(4) to give a methylallenylidene (Scheme 51).[109,130]

Addition of water to **84** gives $\mathrm{Ru\{C{\equiv}CC(O)Me\}(PPh_3)_2Cp}$, probably by initial reaction with C(3), followed by deprotonation. With $\mathrm{NHPh_2}$, addition to C(3) is followed by H migration to C(4) to give $\mathrm{[Ru\{{=}C{=}C{=}CMe(NPh_2)\}(PPh_3)_2Cp]^+}$, which is slowly transformed into $\mathrm{Ru(C{\equiv}CCH{=}CHCl)(PPh_3)_2Cp}$ in $\mathrm{CH_2Cl_2}$.[109,130] Electron-rich *N*-methylpyrrole reacts similarly to give $\mathrm{[Ru\{{=}C{=}C{=}CMe(C_4H_3NMe\text{-}2)\}(PPh_3)_2Cp]^+}$ which can be deprotonated (LiBu) to $\mathrm{Ru\{C{\equiv}CC(C_4H_3NMe\text{-}2){=}CH_2\}(PPh_3)_2Cp}$. Addition of $\mathrm{PPh_3}$ to **84** gives $\mathrm{[Ru\{C{\equiv}CC(PPh_3){=}CH_2\}(PPh_3)_2Cp]^+}$ which can be further protonated to the dicationic phosphonium vinylidene complex $\mathrm{[Ru\{{=}C{=}CHC(PPh_3){=}CH_2\}(PPh_3)_2Cp]^{2+}}$.

Reactions of **84** with aromatic imines have given complexes containing either ethynylquinoline (**85**) or 1-azabuta-1,3-diene ligands (**86**).[157] The polycyclic ligands are obtained by attack of C(4) on the imine CH, followed by electrophilic attack of C(3) on the *o*-carbon of the *N*-bonded aromatic ring (Scheme 52). Dehydrogenation (by excess imine) also occurs in this reaction. The latter products may arise from a [2 + 2] cycloaddition of the imine to the C(3)=C(4) portion of the cumulene, in a reaction analogous to that found for metal acetylides and electron-deficient olefins. The nature of the product is strongly dependent on the substituents on the aromatic rings, formation of the azabutadiene being favored by imines with electron-withdrawing groups on the *N*-aryl group.

Scheme 53



[Ru] = Ru(PP)Cp, PP = dppm, depe

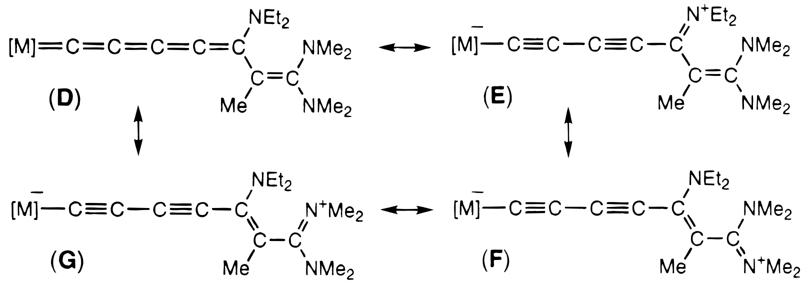
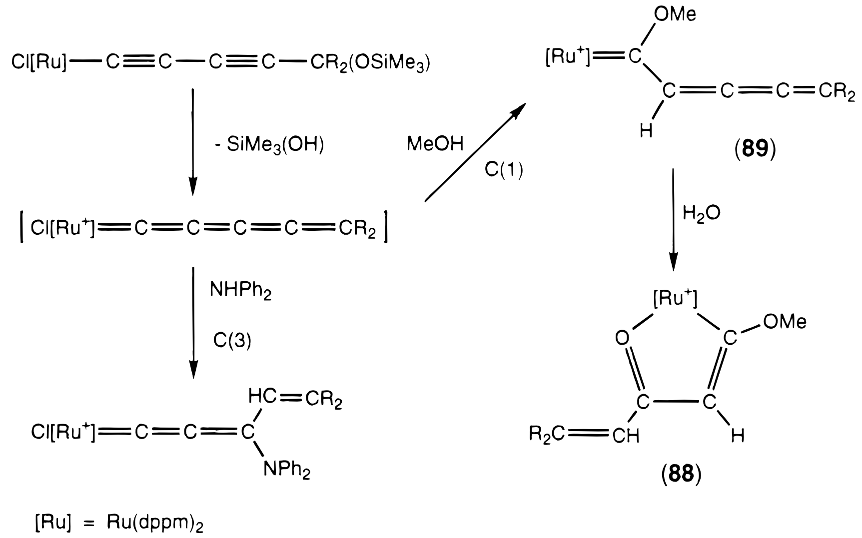


Figure 10.

Scheme 54



Tricyclic products have been obtained with naphthyl-substituted imines.

An intermediate butatrienylidene complex has also been obtained by reaction of *cis*-$RuCl_2(dppm)_2$ with $HC{\equiv}CC{\equiv}CH$ in the presence of $NaPF_6$.[152] This reacts with tertiary amines to give the alkynyl derivatives $[RuCl\{C{\equiv}CC(NR_3){=}CH_2\}(dppm)_2]^+$ (R = Et, Pr). With $NMe_2(CH_2CH{=}CH_2)$, the product is $[RuCl\{{=}C{=}C{=}CNMe_2(CH_2CH_2CH{=}CH_2)\}(dppm)_2]^+$ (**87**), formed by an unusual aza-Cope rearrangement (Scheme 53). Similar chemistry is found with the depe complex. The structure of the cation, with short C(1)−C(2) distance [1.218(6) Å] suggests the imino−alkynyl mesomer predominates.

D. Pentatetraenylidene Complexes

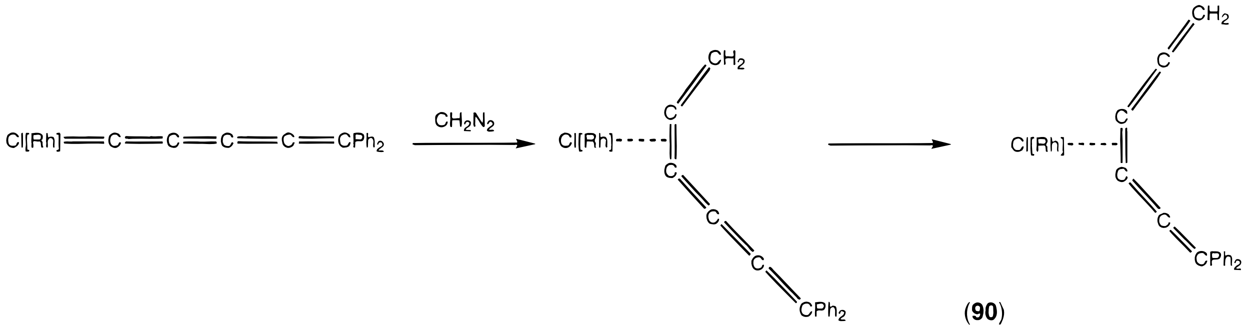
Soft nucleophiles attack C(5) and hard nucleophiles (OMe, NR_2) add to C(3). The reactivity of $M\{{=}C{=}C{=}C{=}C{=}C(NMe_2)_2\}(CO)_5$ (M = Cr, W) is dominated by the electrophilicity of C(3). Addition of $NHMe_2$ occurs rapidly to give yellow $M\{{=}C{=}C{=}C(NMe_2)CH{=}C(NMe_2)_2\}(CO)_5$, which is stable toward further addition.[118]

Addition of $MeC{\equiv}CNEt_2$ to $M\{{=}C{=}C{=}C{=}C{=}C(NMe_2)_2\}(CO)_5$ (M = Cr, W) gave $M\{{=}C{=}C{=}C{=}C(NEt_2)CMe{=}C(NMe_2)_2\}(CO)_5$ as the only products, which are present as mixtures of s-cis/s-trans isomers. The NMR spectra indicated that there is fast rotation around the alkenyl C=C and C−N bonds, with $\Delta G^{\ddagger}$ 64 kJ mol^{-1} for the former process. Structural studies showed the ground state is dominated by the mesomeric dipolar form of the four mesomers **D**−**G** (Figure 10). This reaction proceeds by addition of the alkyne to C(4)=C(5) with cycloreversion of the unobserved intermediate cycloadduct, in an orbitally controlled reaction.[158]

In attempted syntheses of pentatetraenylidenes from $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ and $RuCl_2(PR_3)(\eta\text{-}C_6Me_6)$, slow elimination of $SiMe_3(OH)$ is followed by addition of bulky alcohols or amines to C(3) to give $[RuCl\{{=}C{=}C{=}C(OR'\text{ or }NPh_2)CH{=}CPh_2\}(PR_3)(\eta\text{-}C_6Me_6)]^+$.[110,123] The chelate complex **88** (R = Me, Ph) is formed from $RuCl_2(PMe_2R')(\eta\text{-}C_6Me_6)$ (R′ = Me, Ph) and $HC{\equiv}CC{\equiv}CCR_2(OH)$ in MeOH. With $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$, the methoxycarbene $[RuCl\{{=}C(OMe)CH{=}C{=}C{=}CR_2\}(PMe_2R)(\eta\text{-}C_6Me_6)]^+$ is formed instead. Subsequent reaction with water gives **88**. The reaction is envisaged to proceed via $[RuCl({=}C{=}C{=}C{=}C{=}CR_2)(PMe_2R)(\eta\text{-}C_6Me_6)]^+$ (possibly the observed violet intermediate) which adds MeOH at C(1) and water at C(3) (Scheme 54).[123,192] In dry MeOH, the PMe_3 complex gives only the butatrienyl−carbene complex (**89**).

In the $RuCl(dppe)_2$ system, the reaction of $RuCl\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)(dppe)_2$ with MeOH or $NHEt_2$ (NuH) to give $[RuCl\{{=}C{=}C{=}C(Nu)CH{=}CPh_2\}(dppe)_2]^+$, the intramolecular cyclization to the phenylindenylidene complex **24** (section IV.D.2.d), and the formation of violet $[RuCl\{{=}C{=}C{=}C(OMe)CH{=}CPh_2\}(dppe)_2]^+$ in its reaction with excess $HBF_4{\cdot}OEt_2$ are all taken to demonstrate the electrophilicity of C(3) in an intermediate $[RuCl({=}C{=}C{=}C{=}C{=}CPh_2)(dppe)_2]^+$.[30,111] Similarly, protonation of *trans*-$Ru\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}_2(dppm)_2$ with $HBF_4{\cdot}OEt_2$ in

Scheme 55



(**90**)

[Rh] = *trans*-Rh(PPr$^i_3$)$_2$

methanol afforded the bis-allenylidene complex [*trans*-Ru{═C═C═C(OMe)CH═CPh$_2$}$_2$(dppm)$_2$]$^{2+}$.[111]

Coupling of CH$_2$ (from CH$_2$N$_2$) and the pentatetraenylidene ligand in *trans*-RhCl(═C═C═C═C═CPh$_2$)(PPr$^i_3$)$_2$ gave a new hexapentaene, obtained as two isomers, η^2-(1,2) and η^2-(2,3), of *trans*-RhCl(η^2-CH$_2$═C═C═C═C═CPh$_2$)(PPr$^i_3$)$_2$ (**90**) (Scheme 55).[114]

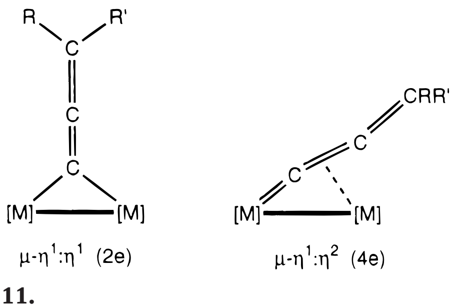
VII. Binuclear Complexes Containing Allenylidene and Cumulenylidene Ligands

The tendency for allenylidene to bridge two bonded metal atoms is so great that in many cases, the binuclear product is formed when the mononuclear complex is sought.[105] Two bridging modes are found for allenylidenes in binuclear complexes: the μ-η^1:η^1-(*2e*) (end-on) and μ-η^1:η^2-(*4e*) (side-on) forms (Figure 11).

The first binuclear allenylidene complexes to be described were the dimanganese complexes obtained by heating Mn(═C═C═CR$_2$)(CO)$_2$Cp (R = Bu^t, Cy, CH$_2$Ph, Ph), or more directly, from their reactions with Mn(OEt$_2$)(CO)$_2$Cp.[193] Known binuclear allenylidene complexes are listed in Table 9; also included are complexes containing two metal atoms not linked by a metal−metal bond. Complexes containing cumulenic carbon chains capped by metal−ligand moieties, {L$_x$M}═C(═C)$_n$═C═{M′L′$_y$}, are discussed in section XI.

A. Syntheses of Binuclear Complexes

Bi- and trinuclear complexes are so rare that general methods of synthesis cannot be said to be available. Some routes are analogous to methods i and iii used for the mononuclear derivatives described above. Binuclear complexes can also be obtained by treatment of the mononuclear derivatives with a source of the metal−ligand fragmentor by heating the mononuclear complexes. Recently attack of alkyllithiums on the bridging C$_2$ ligand in {Fe(CO)$_2$-Cp*}$_2$(μ-C≡C) appears to give some promise of a more general extension.[194]



μ-η^1:η^1 (2e) μ-η^1:η^2 (4e)

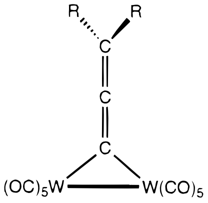
Figure 11.

1. Zirconium

In the reaction between Zr(η-C$_2$H$_4$)(PMe$_3$)Cp$_2$ and 3,3-dimethylcyclopropene, H transfer from the latter to the η-ethene ligand to give ethyl is followed by ring opening to form a μ-C═C═CMe$_2$ ligand, which is asymmetrically bridging in the final product (**91**). However, the NMR spectrum indicates rapid fluxionality at room temperature, with only slight broadening of the CH$_2$ signals at −80 °C. The proposed process (Scheme 56) involves a symmetrical μ-allenediyl (allenylidene) intermediate.[195]

2. Molybdenum and Tungsten

Reactions of W(CO)$_6$ with dilithium ynolates, followed by treatment with COCl$_2$, give first the mononuclear complexes W(═C═C═CR$_2$)(CO)$_5$, which add a W(CO)$_5$ fragment to give red {W$_2$(CO)$_{10}$}(μ-C═C═CR$_2$) [**92**, CR$_2$ = CPh$_2$, C(C$_6$H$_4$)$_2$] in solution.[105]



(**92**)

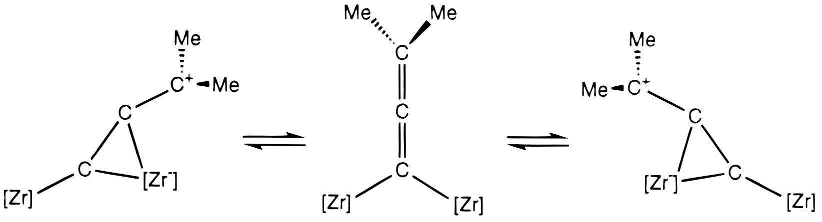
Reactions of LiC≡CCMe═CH$_2$ with {M(CO)$_2$Cp}$_2$ (M = Mo, W; thf, −78 °C) gave dark green {M$_2$(CO)$_4$-Cp$_2$}{μ-η^1:η^2-(*4e*)-C═C═CMe$_2$} (**93**) and {M$_2$(CO)$_4$-Cp$_2$}(μ-η^2-HC$_2$CMe═CH$_2$); the molybdenum-Cp* derivative was also obtained. The former are probably formed by protonation of an anionic intermediate on the alumina column.[196,197] Addition of the mixture to alumina gives only a deep green solution, but fractional crystallization enables the μ-alkyne (9%) and μ-allenylidene complexes (49%) to be separated. In contrast to the normal nucleophilic addition to, or proton abstraction from, C(3) of μ-η^2-propargylium-Mo$_2$ complexes [{Mo$_2$(CO)$_4$Cp$_2$}(μ-η^2:η^3-HC≡CCR^{1}R^2)]$^+$, ethynyl proton abstraction by the soft base LiC≡CCMe═CH$_2$ (only) gave {Mo$_2$(CO)$_4$Cp$_2$}{μ-η^1:η^2-(*4e*)-

Table 9. Binuclear Allenylidene Complexes, $\{L_nM\}\{L'_mM'\}\{\mu\text{-}C(1){=}C(2){=}C(3)R^1R^2\}$

				yield,		^{13}C NMR			
$\{ML_n\}\{M'L'_m\}$	R^1	R^2	color	%	ν(CCC)	δC(1)	δC(2)	δC(3)	ref
$\{ZrEtCp_2(\eta^1)\}\{ZrEtCp_2(\eta^2)\}$	Me	Me				168.6	141.6	75.3	195
$Mo_2(CO)_4Cp_2$	H	H	green	26					85
$Mo_2(CO)_4Cp_2$	H	Me	green	56	1685	291.7, 292.0	156.7, 135.2	158.2, 137.1	85
$Mo_2(CO)_4Cp_2$	H	Et	green	65	1680	292.3, 291.8	156.7, 141.3	153.7, 140.0	85
$Mo_2(CO)_4Cp_2$	H	Fc	green	43	1650	281.9	149.2	137.6	199
$Mo_2(CO)_4Cp_2$	H	1,1′-Fc′	green	38	1650	297.6, 296.4	n.g.	n.g.	199
$Mo_2(CO)_4Cp_2$	Me	Me	deep green	87		287.7	149.4, 148.9		85,197
$Mo_2(CO)_4Cp_2$	Me	Ph	yellow-brown	62	1653	287.2	143.4	142.3	85
$Mo_2(CO)_4Cp_2$	$(CH_2)_5$		green	86	1675	289.5	155.9	147.5	85
$Mo_2(CO)_4Cp^*_2$	Me	Me	green	26		302.5	156.5, 141.9		197
$W_2(CO)_{10}$	Ph	Ph			1866				105
$W_2(CO)_{10}$	$(C_6H_4)_2$				1879				105
$W_2(CO)_4Cp_2$	Me	Me	dark green	48		260.2	146.1, 145.6		197
$Mn_2(\mu\text{-}CO)(CO)_8$	Bu^t	Bu^t	red	7	1907				106
$Mn_2(CO)_4Cp_2$	Bu^t	Bu^t	black-brown	57	1862				193
$Mn_2(CO)_4Cp_2$	CH_2Ph	CH_2Ph	red-violet	82	1887				193
$Mn_2(CO)_4Cp_2$	Ph	Ph	black	76	1873				193
$Mn_2(CO)_4Cp_2$	Cy	Cy		54	1878				193
$Re_2(CO)_9$^{a}	Bu^t	Bu^t	red brown	9	1927				106
$\{Mn(CO)_2Cp\}\{Fe(CO)_4\}$	Ph	Ph	violet	65	1890	333.25	106.61	201.12	203
$Fe_2(CO)_8$	Bu^t	Bu^t	red	92	1886	201.58	145.5	128.78	107
$Fe_2(\mu\text{-}CO)(CO)_2Cp^*_2$	H	H	purple	54		202.3	206.5	77.6 (CH 167)	194,200
$Fe_2(\mu\text{-}CO)(CO)_2Cp^*_2$	H	Bu^t	purple	22		192.3	210.0	109.4 (CH 163)	200
$Fe_2(\mu\text{-}CO)(CO)_2Cp^*_2$	H	Ph	purple	39		193.8	200.6 (CH 10)	97.3 (CH 161)	194,200
$Fe_2(\mu\text{-}CO)(CO)_2Cp^*_2$	Me	Me	purple	29		191.9	206.4	100.9	194,200
$Fe_2(\mu\text{-}CO)(CO)_2Cp^*_2$	Me	Bu	purple	38		192.4	206.2	105.2	194,200
$Fe_2(\mu\text{-}CO)(CO)_2Cp^*_2$	Me	Bu^t	purple	55		191.4	205.1	114.6	200
$Fe_2(\mu\text{-}CO)(CO)_2Cp^*_2$	Me	Ph	purple	78		192.5	197.6	103.3	194,200
$Fe_2(\mu\text{-}CO)(CO)_2Cp^*_2$	Bu	Bu	purple	35		191.5	206.1	111.4	194,200
$Fe_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5Me_4Et)_2$	Me	Bu^t	purple	36		191.8	205.6	111.1	200
$Fe_2(\mu\text{-}dppm)(\mu\text{-}CO)Cp_2$	CN	CN	green	9	1835	176.0 (PC 19)	199.3	40.4	170,201
$Fe_2(\mu\text{-}dppe)(\mu\text{-}CO)Cp_2$	CN	CN	green	17	1837	173.1 (PC 17)	201.2	39.5	170,201
$Ru_2(\mu\text{-}SPr^i)_2ClCp^*_2$	Ph	Ph	violet	88	1941				73
$Ru_2(\mu\text{-}SPr^i)_2ClCp^*_2$	tol	tol	violet	89	1933				73
$Rh_2(\mu\text{-}O_2CMe)_2(CO)_2(PCy_3)_2$-[$BF_4$ salt]	Ph	Ph	dark violet	78	1914	174.2 (PC 36, RhC 52)	181.3 (RhC 6)	134.2	202

[a] Contains terminal allenylidene ligand.

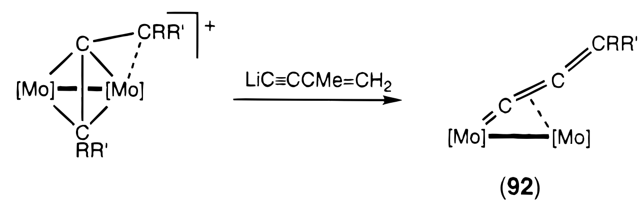
Scheme 56



(**91**)

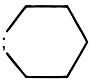
[Zr] = ZrEtCp$_2$

Scheme 57



(**92**)

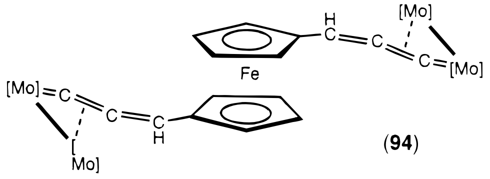
[Mo] = Mo(CO)$_2$Cp

RR' = H$_2$; H, Me; H, Et; Me$_2$; Me,Ph;  ; H, Fc

$CCCR^1R^2\}$ (Scheme 57). The preferred solvent is CH_2Cl_2; other products are formed in thf.[85,198]

For the CMe$_2$ complex, LiC≡CPh was not selective, also producing $\{Mo_2(CO)_4Cp_2\}(\mu\text{-}\eta^2\text{-}HC_2CMe{=}CH_2)$. Allenylidenes with H on C(3) are unstable and have to be kept below −35 °C; the CH$_2$ complex was not fully characterized.[199] The HMe and HEt complexes exist as two diastereomers in solution (3/1 and 1/1, respectively). In the ^{1}H NMR spectra, the degree of deshielding of the terminal H is noteworthy; consideration of the H···CO interaction suggests that it is the proton closest to Mo which is most deshielded.[85]

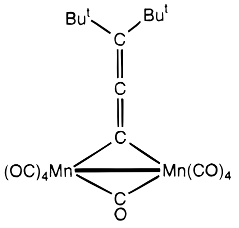
Reaction of $\{Mo(CO)_2Cp\}_2$ with HC≡CCHFc(OH) gave the μ-η^2-alkyne complex; the analogous binuclear complex was obtained from Fc′{CH(OH)C≡CH}$_2$-1,1′ (Fc′ = ferrocene-1,1′-diyl) as two diastereomers. Treatment of both complexes with $HBF_4{\cdot}OEt_2$ gave (μ-HCCC$^+$HFc) cations, in which the C$^+$ center is stabilized mainly by Mo, but with some help from the Fc nucleus. The allenylidenes were obtained by deprotonation with LiC≡CCMe=CH$_2$,[199] or directly from the η^2-alkyne complex by chromatography on silica. The mono-Fc allenylidene is thermally quite stable in solution at room temperature and is formed as one stereoisomer, with the H closest to Mo. The analogous diallenylidene **94** is thermally unstable and is obtained as the *meso* and *rac* diastereomers.



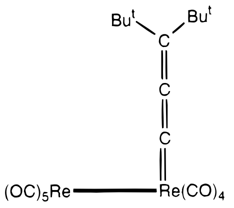
(**94**)

3. Manganese and Rhenium

Binuclear allenylidene complexes are obtained by heating $Mn(=C=C=CR_2)(CO)_2Cp$ (R = Bu^t, Cy, CH_2Ph, Ph), or more directly, by reaction of the mononuclear complex with $Mn(OEt_2)(CO)_2Cp$.[27,103,193] The second equivalent of hydrocarbon ligand is presumably lost as $:C=C=CR_2$ which dimerizes to the hexapentaene, although this has been observed on only one occasion. Binuclear complexes $M_2(CO)_8(C=C=CBu^t_2)$ (M = Mn, Re) were obtained from $M_2(CO)_{10}$ and the dilithium ynolates, but reactions between $MCl(CO)_5$ and $LiC{\equiv}CCBu^t_2(OLi)$ gave only $M\{C{\equiv}CCBu^t_2(OH)\}(CO)_5$.[106] The structures of the two complexes differ, with bridging [Mn(**95**)] and terminal allenylidene ligands [Re(**96**)], respectively. The difference is ascribed to stronger Re−CO(t) bonds.



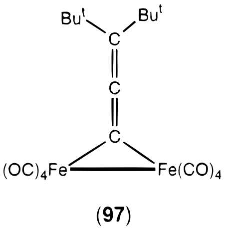
(**95**)



(**96**)

4. Iron and Ruthenium

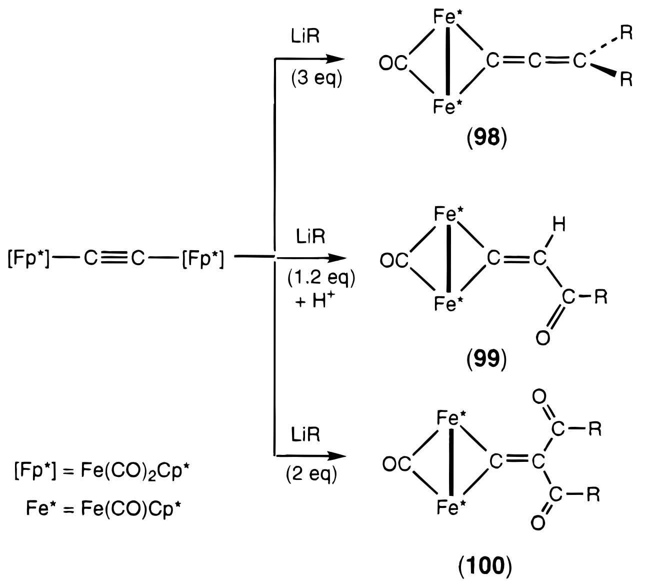
Reactions of $Fe(CO)_5$ with dilithium ynolate gave Fe, Fe_2, and Fe_3 complexes: $\{Fe_2(CO)_8\}(\mu\text{-}C=C=CBu^t_2)$ (**97**) is formed by addition of $Fe(CO)_4$ to the first-formed $Fe(=C=C=CBu^t_2)(CO)_4$.[107]



(**97**)

The nature of the products obtained from reactions of LiR or $Li[BHEt_3]$ with $\{Fe(CO)_2Cp^*\}_2(\mu\text{-}C{\equiv}C)$ depend critically on the stoichiometry and mode of addition (Scheme 58).[194,200] Thus, addition of an an excess of the lithium reagent (in two portions) to a methanol solution provides a one-pot synthesis of the μ-allenylidene complexes, $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)(\mu\text{-}C=C=CR_2)$ (**98**). Addition of stoichiometric amounts of the organolithium affords first $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)(\mu\text{-}C=CHC(O)R^1\}$ (**99**), which on further treatment with the same or different organolithium reagent, gives the μ-allenylidene. In this two-step method, mixed substitution can be achieved and this route also provides the first "parent" compound, $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)(\mu\text{-}C=C=CH_2)$. Diacylvinylidenes $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)\{\mu\text{-}C=C[C(O)R]_2\}$ (**100**)can be obtained by the first route if all of the organolithium reagent is added in one portion. The formation of **98** rather than **100** occurs because of steric repulsion between the μ-ligand and the Cp* methyl groups.

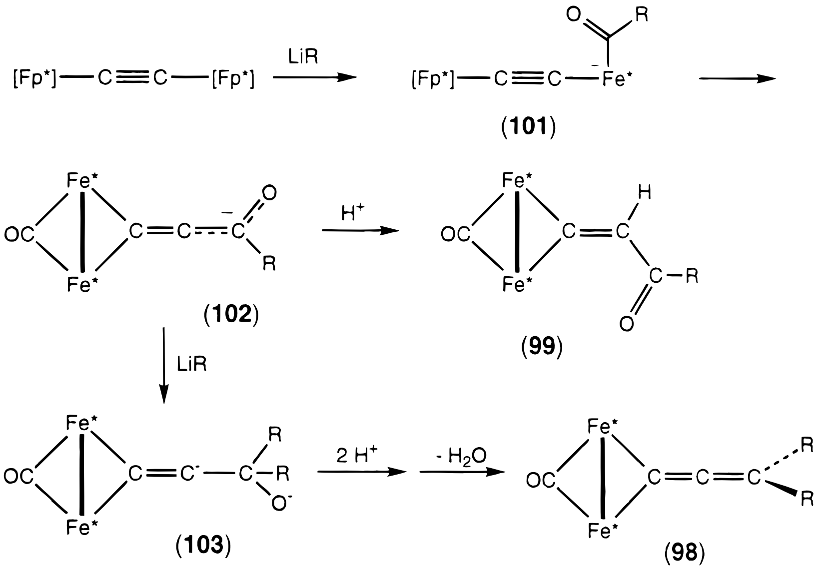
Scheme 58



These reactions are a variant of the propyn-2-ol dehydration. The proposed mechanism of formation is shown in Scheme 59 and involves nucleophilic attack on a CO group of $\{Fe(CO)_2Cp^*\}_2(\mu\text{-}C_2)$ to give anionic acyl **101**, which is converted to the η^2-alkyne by reductive elimination or migratory insertion. Subsequent slippage gives the enolate **102** which can be protonated to give **99**. Further nucleophilic attack on **102** is sluggish, giving the alkoxide dianion **103** (in a two-step reaction via the monoanion), which affords **98** by protonation and loss of water. The latter reaction is controlled by the bulky Cp* group.[194]

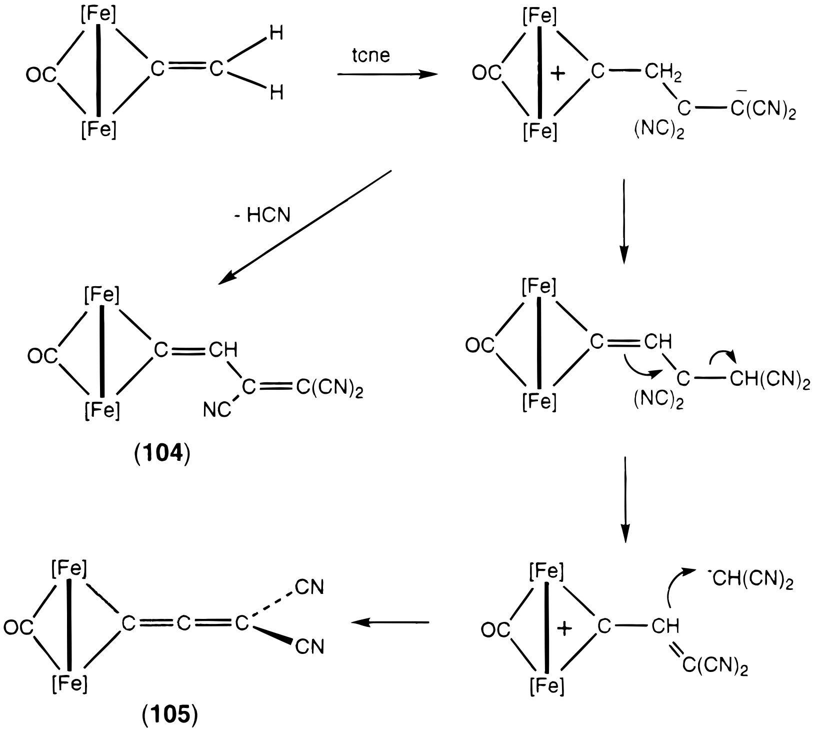
Addition of tetracyanoethene to the carbonyl complex $\{Fe_2(CO)_2Cp_2\}(\mu\text{-}CO)(\mu\text{-}C=CH_2)$ gave the vinylvinylidene $\{Fe_2(CO)_2Cp_2\}(\mu\text{-}CO)\{\mu\text{-}C=CHC(CN)=C(CN)_2\}$ (**104**). In addition, the μ-LL (dppm, dppe) complexes afford the μ-allenylidenes $\{Fe_2(CO)_2Cp_2\}(\mu\text{-}LL)\{\mu\text{-}C=C=C(CN)_2\}$ (**105**) in low yields by elimination of $CH_2(CN)_2$.[170,201] The μ-η^1:η^1-allenylidene ligand in **105** is considered to be a 1,1-dimetalated electron-deficient allene. These reactions have been compared with similar [2 + 2] cycloaddition reactions of vinyl ethers. The likely first step in the reaction is a single electron transfer (SET) via $[tcne]^{\bullet-}$ radical anion. Migration of the β-H atom to CN results in loss of HCN and formation of the tricyanovinylvinylidene complexes. Alternatively, 1,3-H migration results in formation of $CH(CN)_2$ which picks up the proton to give $CH_2(CN)_2$ and the μ-allenylidene (Scheme 60).

Scheme 59



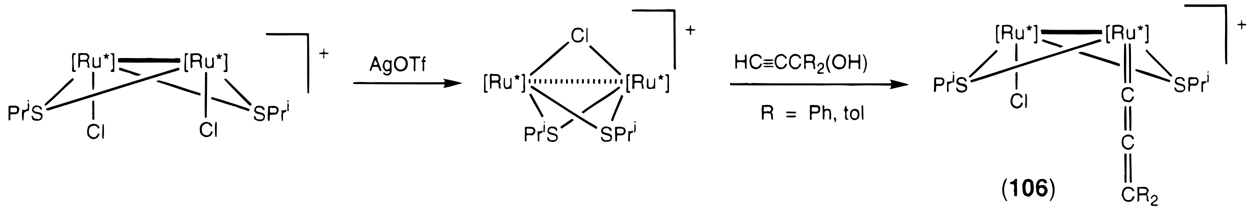
Fp* = $Fe(CO)_2Cp^*$; Fe* = $Fe(CO)Cp^*$

Scheme 60

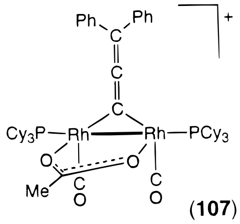


[Fe] = Fe(L)Cp; L = CO, 1/2 dppm, 1/2 dppe

Scheme 61



[Ru*] = RuCp*



(**107**)

Treatment of {Ru(μ-SPr^i)ClCp*}$_2$ with AgOTf and addition of HC≡CCR$_2$(OH) gave Ru$_2$(μ-SPr^i)$_2$Cl(C=C=CR$_2$)Cp*$_2$ (**106**, R = Ph, tol) (Scheme 61).[73]

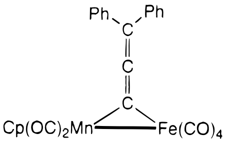
Reactions of [Ru(thf)(L)$_2$Cp]$^+$ (L = PPh$_3$; L$_2$ = dppe) with CH(OH)(C≡CH)$_2$ gave binuclear allenylidene−vinylidene complexes of the type [{Ru(L)$_2$Cp}$_2${μ-(=C=C=CHCH=C=)}]$^{2+}$, probably by dehydration of the intermediate hydroxyvinylidene complexes. Deprotonation with alumina afforded blue [{Ru(L)$_2$Cp}$_2${μ-(=C=C=CHC≡C)}]$^+$.[150,151]

5. Rhodium

The first 30-e binuclear allenylidene was obtained from HC≡CCPh$_2$(OH) and {Rh(μ-O$_2$CMe)(CO)(PCy$_3$)}$_2$; the first-formed fluxional μ-η^1:η^2-acetylide reacts with HBF$_4$·OEt$_2$ to give [Rh$_2$(μ-O$_2$CMe)(μ-η^1:η^1-C=C=CPh$_2$)(CO)$_2$(PCy$_3$)$_2$]BF$_4$ (**107**).[202]

6. Mixed-Metal Derivatives

Addition of an Fe(CO)$_4$ group to Mn(=C=C=Ph$_2$)(CO)$_2$Cp is achieved by reaction with Fe$_2$(CO)$_9$ to give violet {MnFe(CO)$_6$Cp}(μ-η^1:η^1-C=C=CPh$_2$) (**108**).[203]



(**108**)

B. Properties of Binuclear Complexes

1. NMR Spectra

The geometry of binuclear allenylidenes has been correlated with their NMR spectra.[36] Their dynamic behavior includes hydrocarbon migration, rotation about the C−C bond, and internal isomerization of the M$_2$ cluster. Complexes {M$_2$(CO)$_n$}$_2$(μ-C=C=CMe$_2$) (M = Mo, W) show slow site exchange (contrasting with the side-on vinylidene which is fast).[196] The dynamic behavior of {Mo$_2$(CO)$_4$Cp$_2$}(μ-η^1:η^2-C=C=CR^{1}R^2) (R^1 = H, R^2 = Et; R^1 = R^2 = Me, Ph) has been studied, with $\Delta G^\ddagger$ values for the fluxional process ranging between 70 and 80 kJ mol^{-1}. In solution, a 1/1 mixture of isomers (by interchange of R^1, R^2) is found for R^1 = H, R^2 = Et (Scheme 62).[198]

In the ^{13}C NMR spectra of {Fe$_2$(CO)$_2$Cp*$_2$}(μ-CO)(μ-C=C=CR$_2$) (**98**), C(2) is found at the lowest field; C(3) resonates between δ 77 and 114, and C(1) appears between these two resonances.[194] Atom C(3) is even more shielded in the dicyano complexes {Fe$_2$(CO)$_2$Cp$_2$}(μ-LL){μ-C=C=C(CN)$_2$} (**105**; LL = dppm, dppe), having δ ~40.[170,201]

The NMR spectra of [{Ru(L)$_2$Cp}$_2${μ-(=C=C=CHCH=C=)}]$^{2+}$ (L = PPh$_3$; L$_2$ = dppe) indicate that they have a static structure, whereas the μ-C$_5$H derivatives are symmetrical, as shown by single ^{31}P and ^{1}H resonances. The latter have a delocalized structure with contributions from the three tautomers **H**−**J** (Figure 12).[150]

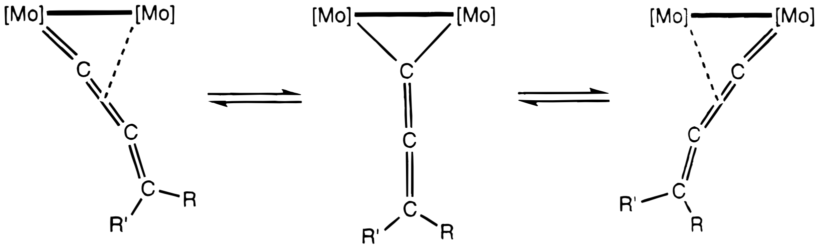
2. Theory

The HOMO/LUMO separation is 0.83 eV for {Mo$_2$(CO)$_4$Cp$_2$}{μ-η^1:η^2-(4e)-C=C=CH$_2$}. Stabilization of π- and σ-type orbitals on C(1) and C(2) by Mo σ-type orbitals leads to the Mo(1)−C(1)C(2) π bond and the Mo(2)−C(1) σ bond. Calculated charges on C(1), C(2), and C(3) are −0.48, −0.02 and −0.19, respectively, so that nucleophilic attack on C(3) is orbital-controlled, while electrophilic attack on C(1) is charge-controlled. Because it is impossible to get simultaneous Mo−Mo π bonding and Mo−C σ overlap, the true transition state for the dynamic process is a μ-2σ system, as proposed for the dynamic process.[198]

In the {Fe$_2$(CO)$_2$Cp*$_2$} complexes, the first HOMO is metal-based and of similar energy to the second, which is a filled p$_y$ orbital on C(2), the site of electrophilic attack. The LUMO has the largest *p* coefficient on C(3).[194] The structural results on {Fe$_2$(CO)$_2$Cp$_2$}(μ-dppe){μ-C=C=C(CN)$_2$} indicate interaction of the allenylidene with the dimetal framework in an extended way as found for other μ-η^1:η^1-allenylidenes.[170]

EH MO calculations on [Rh$_2$(μ-O$_2$CH)(μ-η^1:η^1-C=C=CH$_2$)(CO)$_2$(PH$_3$)$_2$]$^+$ show that the μ-CCCH$_2$ group is a net electron acceptor, with 0.32 e coming from the Rh$_2$ system (compared with 0.25 e from CCH$_2$ in the analogous vinylidene complex). Differences in the role of the C(1) p$_x$ orbital are found: here it is involved in π bonding in the allenylidene. With decreasing electron density on the carbon atoms, nucleophilic attack on the ligand is unlikely.[202]

Scheme 62



$[Mo] = Mo(CO)_2Cp$

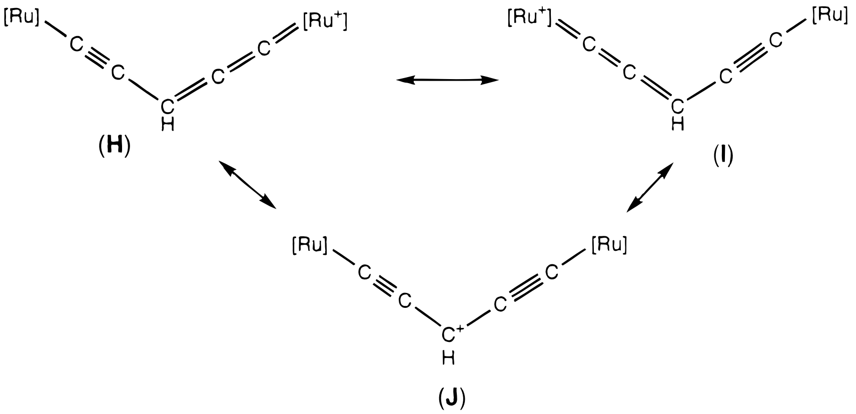


Figure 12.

Table 10. Structures of Binuclear Allenylidene Complexes, $\{L_nM\}\{L'_mM'\}(\mu\text{-}C(1){=}C(2){=}C(3)R^1R^2\}$

$\{ML_n\}\{M'L'_m\}$	R^1	R^2	M−M′	M−C(1)	M′−C(1)	M′−C(2)	C(1)−C(2)	C(2)−C(3)	C(1)−C(2)−C(3)	M−C(1)−M′	ref
$\{ZrEtCp_2\ (\eta^1)\}\{ZrEtCp_2\ (\eta^2)\}$	Me	Me		2.420(4)	2.433(4)	2.245(4)	1.256(5)	1.352(6)	167.8(4)	146.7(2)	195
$Mo_2(CO)_4Cp_2$	$(CH_2)_5$		3.163(2)	1.90(1)	2.20(1)	2.26(1)	1.35(1)	1.33(1)	146(1)		85
$Mo_2(CO)_4Cp_2$	Me	Me	3.145(1)	1.912(3)	2.209(3)	2.240(3)	1.336(3)	1.348(4)	144.5(6)	119.0(2)	197
$W_2(CO)_{10}$	Ph	Ph	3.15(6)	2.23(5)			1.28(4)	1.32(4)	177(2)	90(1)	105
$Mn_2(\mu\text{-}CO)(CO)_8$	Bu^t	Bu^t	2.739(2)	2.06(1)		2.06(1)	1.27(2)	1.39(2)	178.4(9)	83.3(4)	106
$Fe_2(\mu\text{-}dppe)(\mu\text{-}CO)Cp_2$	CN	CN	2.515(1)	1.916(6)		1.937(6)	1.258(5)	1.345(6)	173.8(5)	81.5(2)	170,201
$Fe_2(\mu\text{-}CO)(CO)_2Cp^*_2$	H	H	2.552(1)	1.946(5)	1.937(5)		1.274(7)	1.322(9)	178.1(7)		200
$Fe_2(\mu\text{-}CO)(CO)_2Cp^*_2$	Me	Me	2.562(2), 2.561(2)	1.951(9), 1.95(1)	1.989(9), 1.963(9)		1.26(1), 1.26(1)	1.34(1), 1.38(1)	176(1), 177(1)		194,200
$Fe_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5Me_4Et)_2$	Bu	Bu	2.555(3)	1.94(2)	1.93(1)		1.30(2)	1.27(2)	172(2)		200
$Ru_2(\mu\text{-}SPr^i)_2ClCp^*_2$	tol	tol	2.801(1)	1.94(2)			1.24(2)	1.36(2)	165(2)	*a*	73
$Rh_2(\mu\text{-}O_2CMe)_2(CO)_2(PCy_3)_2$-[BF4 salt]	Ph	Ph	2.723(1)	1.988(10)	1.997(10)	1.30(1)	1.32(1)	174.4(12)			202

[a] Ru(1)−C(1)-C(2) 174(1)°.

3. Structures

Structural data for μ-allenylidene complexes are given in Table 10. The allenylidene ligand in $\{Mo_2(CO)_4Cp_2\}\{\mu\text{-}\eta^1{:}\eta^2\text{-}(4e)\text{-}C{=}C{=}CMe_2\}$ acts as a 4e donor to the Mo_2 system, with bonding to Mo(1) by an Mo═C double bond, and to Mo(2) by a π-type interaction with the C(1)═C(2) double bond. The MoC_3 fragment is kinked, with angles at C(1) and C(2) of 167.2(2) and 144.5(3)°, respectively.[196] Comparison with analogous μ-$\eta^1{:}\eta^1$-vinylidene complexes shows that the Mo(2)−C(2) and C(1)−C(2) distances are shorter.

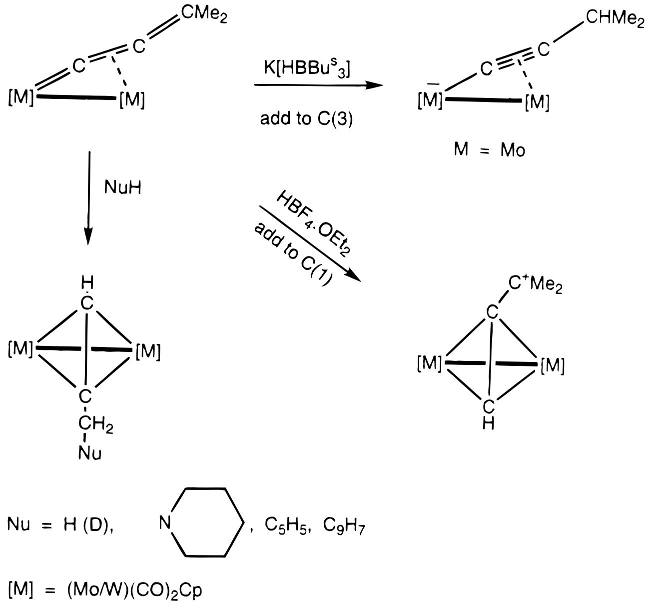
Comparison between appropriate structures shows that reduction in steric repulsion within $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)(\mu\text{-}X)$ (X = CR_2, $C{=}CR_2$, $C{=}C{=}CR_2$) is achieved by stretching and twisting of the μ-X group and by precession of the Cp* ligand.[194] The structural parameters of $\{Fe_2(CO)_2Cp_2\}(\mu\text{-}dppe)\{\mu\text{-}C{=}C{=}C(CN)_2\}$ indicate a C(1)−C(2) bond order between 2 and 3 [1.258(5) Å] and a double bond between C(2) and C(3) [1.345(6) Å].[170] In the solid-state structure of $[\{Ru(L)(L')Cp\}_2\{\mu\text{-}({=}C{=}C{=}CHC{\equiv}C)\}]^+$, the C_5H ligand has a V shape, with the angle at C(3) being 130.3(11)°.[150]

C. Reactions of Binuclear Complexes

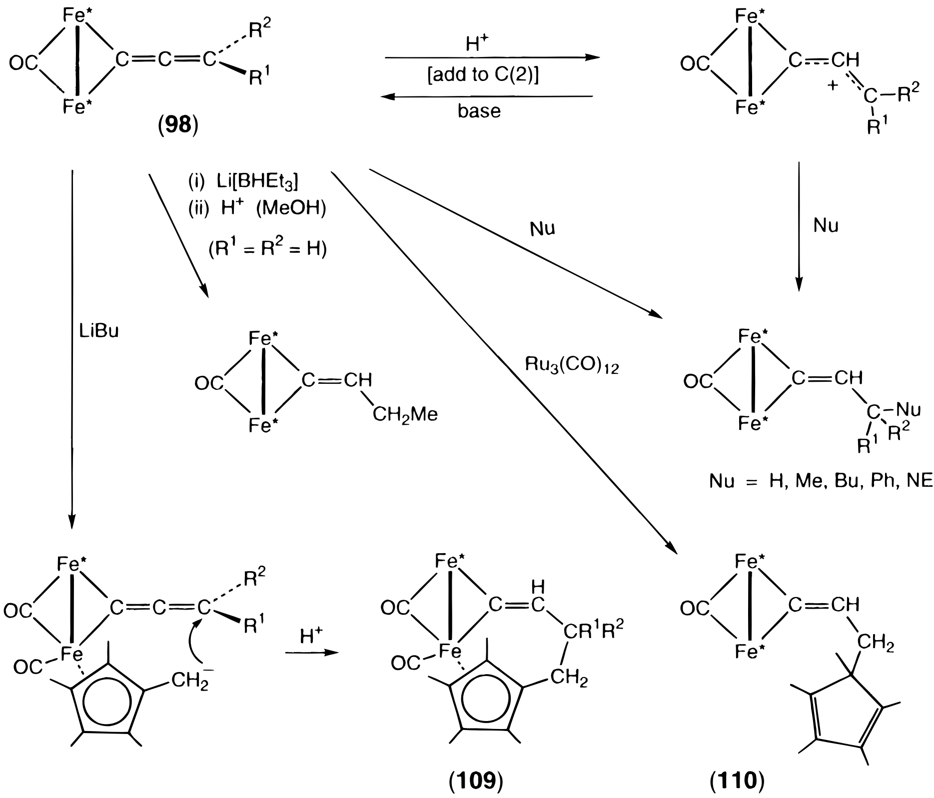
1. Molybdenum and Tungsten

The μ-$\eta^1{:}\eta^2$-(4e) (side-on) allenylidene ligand is regioselectively attacked at C(1) by electrophiles and at C(3) by nucleophiles (the latter kinetically controlled) (Scheme 63).[197,198,204] Protonation of the Mo and W complexes gave dimetal-stabilized propargylium cations $[\{M_2(CO)_4Cp_2\}(\mu\text{-}\eta^2\text{-}HC_2CMe_2)]^+$, also formed by protonation of the μ-$HC_2CMe{=}CH_2$ complex. These cations are isolobal with $[Co_2(\mu\text{-propargylium})(CO)_6]^+$ and $[Co_3(\mu_3\text{-}CCH_2)(CO)_9]^+$. Electron-donating substituents stabilize the propargylium complexes, the normal rearrangement of alkyne to allene being prevented by complexation.[36]

Scheme 63



Scheme 64



The $\{Mo_2(CO)_4Cp_2\}\{\mu\text{-}\eta^1:\eta^2\text{-}(4e)\text{-}C{=}C{=}CMe_2\}$ complex is thermally very unstable in solution, so is prepared in situ, with reactions being carried out <-60 °C. Reaction of this complex with $K[BHBu^s_3]$ (K-Selectride) in thf at −78 °C gave $[\{Mo_2(CO)_4Cp_2\}(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CCHMe_2)]^-$, also obtained from LiC_2Pr^i.[204] Studies of the addition of nucleophiles [to C(3)] have encompassed $LiAlD_4$, LiC_5H_5, LiC_9H_7, and piperidine.[198] The Li salt reactions proceed via an nonisolated violet unstable intermediate $Li[\{Mo_2(CO)_4Cp_2\}(\eta^1:\eta^2\text{-}C{\equiv}CCH_2R)]$. The cyclopentadienyl adduct exists as two isomers (1- and 2-bonded).

2. Iron and Ruthenium

Complexes $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)(\mu\text{-}C{=}C{=}CR_2)$ (**98**) are amphoteric, reacting with electrophiles at C(2) and with nucleophiles at C(3) (Scheme 64). Protonation gives the μ-vinylcarbyne $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)(\mu\text{-}CCH{=}CR^1R^2)]^+$ (R^1, R^2 = H, H; Me, Me; H, Ph), a reaction that can be reversed by lutidine or proton sponge. Similar reactions occur with $\{Fe_2(CO)_2Cp_2\}(\mu\text{-}LL)\{\mu\text{-}C{=}C{=}C(CN)_2\}$ (**105**; LL = dppm, dppe).[170] Subsequent addition of nucleophiles also occurs at C(3) to give $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)(\mu\text{-}C{=}CHCR^1R^2\text{-}Nu)$.[194] However, the bulky Cp* group prevents addition of large electrophiles, such as Me^+ and $[Fp(thf)]^+$, to C(2). Protonation of **98**, followed by addition of nucleophiles [H, Me, Bu, Ph (as $LiCuR_2$), NEt_2] gives $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)(\mu\text{-}C{=}CHCR^1R^2Nu)$. Atom C(1) is sterically protected even though the NMR results show that it is the most electrophilic atom. No reaction occurs between C(3) and cyclopentadienide, the $Fe_2Cp^*_2$ system being quite sterically congested.

Reactions of **98** with nucleophiles are sluggish. Sequential treatment with $Li[BHEt_3]$ and MeOH affords $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2Me)$, perhaps by addition of H^- to C(3) followed by protonation. Similar reactions with LiBu result in deprotonation of a Cp* methyl group and subsequent intramolecular attack of C(3) to give **109** (R = H, Me) after protonation.[194] Treatment of **98** with $Ru_3(CO)_{12}$ affords the vinylidene $\{Fe_2(CO)_2Cp^*_2\}(\mu\text{-}CO)\{\mu\text{-}C{=}CHCH_2C_5Me_5\}$ (**110**).

Complexes $[\{Ru(L)_2Cp\}_2\{\mu\text{-}({=}C{=}C{=}CHC{\equiv}C)]^+$ (L = PPh_3, L_2 = dppe) are gradually oxidized in air to give $[Ru(CO)(L)_2Cp]^+$, as found for analogous ruthenium vinylidene complexes. Attack at C(3) occurred on treatment with $KOBu^t$ in acetone, when $\{Ru(L)_2Cp\}_2\{\mu\text{-}C{\equiv}CCH(CH_2COMe)C{\equiv}C\}$ was obtained.[150,151]

VIII. Cluster Complexes Containing Allenylidene and Cumulenylidene Ligands

Bonding of allenylidene ligands to metal clusters offers the possibilities of attachment to more than two metal centers and of interaction of all three carbons of the unsaturated C_3 fragment with the cluster. Reported examples of allenylidene and cumulenylidene cluster complexes are listed in Table 11.

A. Allenylidene Complexes

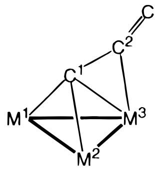
The reaction between $W(C{\equiv}CCMe{=}CH_2)(CO)_3Cp^*$ and $Re_2(CO)_8(NCMe)_2$ gave the μ_3-alkynyl cluster **111**, which on heating with an excess of ROH (R = Me, Et, Ph) in refluxing toluene gave the μ_3-allenylidene clusters **112** (Scheme 65).[205,206]

These compounds contain the unusual $\mu_3\text{-}\eta^1:\eta^2:\eta^3\text{-}(6e)$-allenylidene ligand, which retains some contribution from the C≡C triple bond [C(1)−C(2) 1.27 Å].

Table 11. Cluster Complexes Containing Allenylidene Ligands, $\{M_nL_m\}(=C=C=CR^1R^2)_n$

M_nL_m	R^1	R^2	*n*	color	yield, %	ν(CCC) + ν(CO)	^{13}C NMR	ref
$WRe_2(\mu\text{-}OMe)(CO)_8Cp^*$ (**a**)	Me	Me	1	dark brown	47	2034, 2010, 1974, 1937, 1919, 1901	δC(1) 186.7 (WC 163); δC(2) 140.3 (WC 32); δC(3) 116.1	205,206
$WRe_2(\mu\text{-}OEt)(CO)_8Cp^*$	Me	Me	1	dark brown	57	2031, 2007, 1971, 1929, 1906		205,206
$WRe_2(\mu\text{-}OPh)(CO)_8Cp^*$	Me	Me	1	dark brown	27	2040, 2017, 1976, 1952, 1943, 1920, 1904		205,206
$Fe_3(\mu\text{-}CO)(CO)_9$ (**b**)	Ph	Ph	1	dark green	1.5	n.g.	δC 233.4, 169.1, 122.9	211
$Fe_3(\mu\text{-}CO)(CO)_9$	Me	Bu^t	1	black	17	n.g.		211
$Fe_3(\mu\text{-}CO)_2(CO)_8$	Bu^t	Bu^t	1	black	6	2086, 2064, 2048, 2025, 2004, 1969, 1900, 1868	δC(1) 233.29, C(2) 168.11, C(3) 137.21	107
$Fe_3(CO)_8$ (**c**)	Ph	Ph	2	dark red	27−44	n.g.	δC 293.2, 160.0, 124.3	211
$Fe_3(CO)_8$	tol	tol	2	dark red	34	n.g.	δC 292.5, 158.7, 124.3	211
$Ru_3(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7$ (**d**)	Ph	Ph	1	dark red	55	2059, 2027, 2017, 1999, 1974, 1859	δC(1) 169.16, δC(2) 143.83, δC(3) 113.31	214
$Ru_3(\mu\text{-}H)_2(CO)_9$	Ph	Ph	1	yellow	2	2106, 2094, 2083, 2073, 2063, 2052, 2046, 2033, 2024, 2008, 1988	[δH −20.95]	214
$Ru_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_9$	Ph	Ph	1	yellow	79	2103, 2083, 2062, 2040, 2024, 2017, 1994	[δH −11.13]	213,214
$Ru_3(\mu\text{-}H)(\mu\text{-}OMe)(CO)_9$ (**e**)	Ph	Ph	1	yellow	7	2101, 2082, 2073, 2061, 2051, 2038, 2023, 2019, 1954	[δH −10.80]	214
$Ru_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_7(PPh_3)_2$ (**f**)	Ph	Ph	1	yellow-orange	27	2062, 2043, 2027, 2009, 1998, 1981, 1969, 1963, 1943	[δH −13.16]	214
$Ru_3(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}dppm)(CO)_7$ (**g**)	Ph	Ph	1	orange	56	2063, 2029, 2008, 1996, 1980, 1975, 1944, 1924	[δH −5.56]	214
$Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_9$ (**h**)	Ph	Ph	1	orange	48	2104, 2085, 2062, 2027, 2016, 2014, 2008, 1988	[δH −11.26]	213
$[Os_3(\mu\text{-}H)(CO)_9][OTf]$	H	H	1	unstable			[δH −21.99]	207
$[Os_3(\mu\text{-}H)(CO)_9][OTf]$	Me	Me	1	unstable			[δH −22.99]	207
$AuRu_3(\mu\text{-}H)(CO)_9(PPh_3)$ (**i**)	Ph	Ph	1	yellow	21	2081, 2076, 2060, 2054, 2039, 2028, 2005, 1985, 1979, 1964	[δH −20.47]	214

Molecular Structures (distances in Å, angles in deg)



complex	M(1)−M(2)	M(1)−M(3)	M(2)−M(3)	M(1)−C(1)	M(2)−C(1)	M(3)−C(1)	M(3)−C(2)	C(1)−C(2)	C(2)−C(3)	C(1)−C(2)−C(3)	ref
a	2.559(1)	2.603(1)	2.613(1)	1.917(3)	1.899(3)	2.004(3)	2.119(3)	1.338(4)	1.331(3)		211
b	2.534(1)	2.537(1)	2.537(1)	1.989(3), 1.900(3)	1.948(4), 1.941(4)	1.955(4), 1.935(4)	2.157(3), 2.098(4)	1.334(5), 1.337(5)	1.325(3), 1.336(5)	157.7(4), 152.8(4)	211
c	2.785(1)	2.771(1)	2.758(1)	2.051(9)	2.029(9)	2.150(7)	2.243(8)	1.34(1)	1.35(1)	154.1(8)	214
d	2.847(9)	2.7839(9)	2.8747(9)	2.020(5)	2.079(5)	2.197(5)	2.281(5)	1.328(6)	1.332(7)	153.4(5)	214
e	2.842(3)	2.818(4)	3.315(4)	1.97(2)	2.28(2)	2.20(2)	2.10(1)	1.35(2)	1.31(3)	156(2)	214
f	3.234(1)	2.810(1)	2.920(1)	2.054(9)	2.10(1)	2.20(1)	2.24(1)	1.35(2)	1.36(2)	153(1)	214
g	3.194(2)	2.805(2)	2.904(2)	2.07(1)	2.09(1)	2.16(1)	2.28(1)	1.32(2)	1.37(2)	153(1)	214
h[a]	2.905(5), 2.902(5)[b]	3.374(5), 3.372(5)	2.861(5), 2.869(5)	2.15(4), 2.08(3)	2.07(3), 2.04(3)	2.33(3), 2.33(3)	2.22(3), 2.21(3)	1.32(5), 1.38(4)	1.32(5), 1.36(4)	145(3), 144(3)	213
i	2.891(2)	2.887(2)	2.779(2)	2.07(1)	2.02(1)	2.21(1)	2.29(1)	1.35(2)	1.31(2)	144(2)	214

[a] Values for two independent molecules. [b] H-bridged.

In the formation of **112**, the net change is:

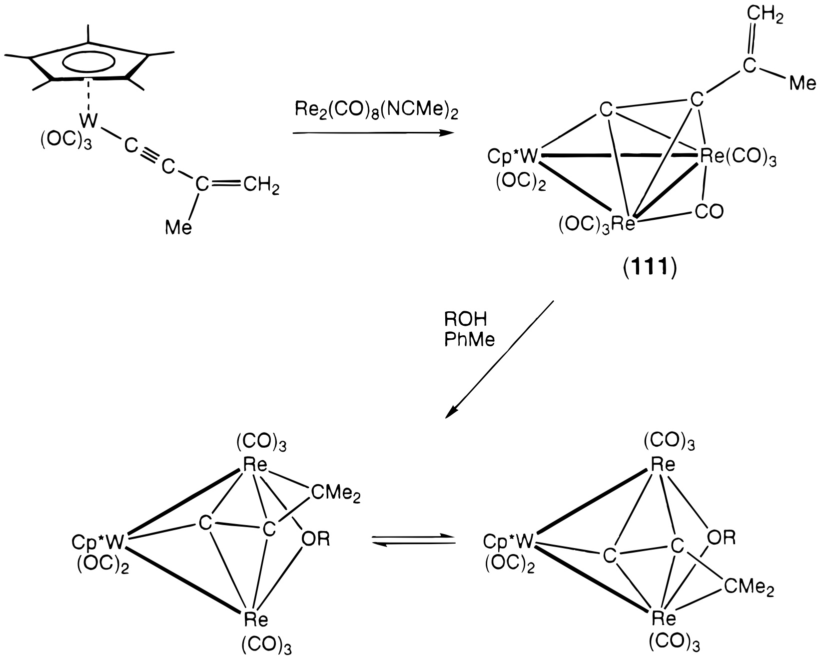
$$\underset{\text{vinylacetylide}}{-C{\equiv}C{-}CMe{=}CH_2} \rightarrow \underset{\text{allenylidene}}{=C{=}C{=}CMe_2} \rightarrow \underset{\text{vinylalkylidyne}}{\equiv C{-}CH{=}CMe_2}$$

The μ_3-(6*e*)-allenylidene ligand can also be considered to be another example of an α-carbonium ion stabilized by interaction with metal centers.[207] The complexes are fluxional by a process which involves movement of the CMe_2 group from one Re atom to the other; for **112** (R = Et), $\Delta G^{\ddagger}$ is 59 kJ mol^{-1}.

Similar reactions of **111** with thiophenol afford $WRe_2(\mu_3\text{-}SPh)(\mu\text{-}SPh)\{\mu\text{-}({\equiv}CCH{=}CMe_2)\}(\mu\text{-}CO)(CO)_6Cp^*$ in a reaction probably going via $Re_2W(\mu_3\text{-}CCCMe_2)(\mu\text{-}SPh)(CO)_8Cp^*$; however, this cluster was not detected, and treatment of **112** with PhSH gave only $WRe(\mu\text{-}SPh)(\mu\text{-}C_2Pr^i)(CO)_5Cp^*$.[208]

Trinuclear iron complexes were formed by addition of $Fe(CO)_4$ units to the mononuclear complexes formed in reactions between $Fe(CO)_5$ and dilithium ynolates. The Fe_3 complex **113** showed a $\mu_2 \leftrightarrow \mu_3$ equilibrium with concomitant shift between CO(t) and CO(br) (Scheme 66).[107] The former is unusual in having only 46 cluster valence electrons.

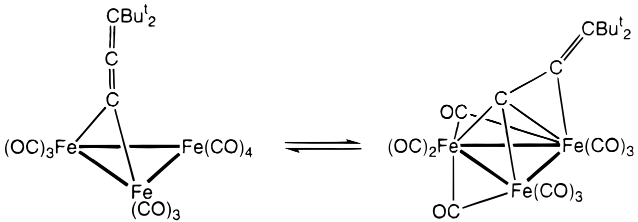
Scheme 65



(**111**)

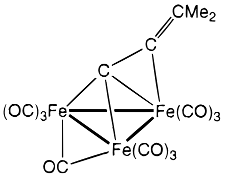
(**112**) R = Me, Et, Ph

Scheme 66



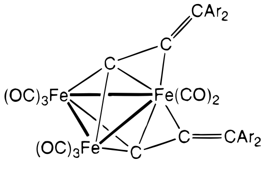
(**113**)

Reactions between $Fe_3(CO)_{12}$ and $HC{\equiv}CCMe_2(OH)$ gave low yields of $Fe_3(\mu_3\text{-}C{=}C{=}CMe_2)(\mu\text{-}CO)(CO)_9$ (**114**) by dehydration (loss of terminal H and the OH group). Several binuclear complexes which do not contain cumulenylidene ligands are also formed.[209] Other prop-2-ynols behave differently, giving di- and trinuclear metallacycles. In contrast with **113**, only one μ-CO ligand is present. Reactions of $HC{\equiv}CCHPh(OH)$ with $Fe_3(CO)_{12}$ gave $Fe_3(\mu_3\text{-}CCCHPh)(\mu\text{-}CO)(CO)_9$ among other products, together with the binuclear derivative $Fe_2\{\mu\text{-}\eta^3{:}O\text{-}CHPhCCHC(OMe)O\}(CO)_6$ (derived from MeOH also present).[210] The allenylidene is formed by the usual dehydration of the prop-2-ynol. Structural features include the allenylidene being held almost perpendicular to the Fe_3 cluster plane. Only C(1) and C(2) are involved in bonding to the cluster. The phenyl ring is coplanar with C(1−3). The asymmetry in attachment of C(1) to Fe(1,3) is reflected in an asymmetry in the μ-CO group which also bridges the Fe(1)−Fe(3) vector. This Fe−Fe separation is the shortest in all three allenylidene−Fe_3 cluster structures. The CCC angles are between 145 and 158°, compared with angles around 174° in binuclear complexes.



(**114**)

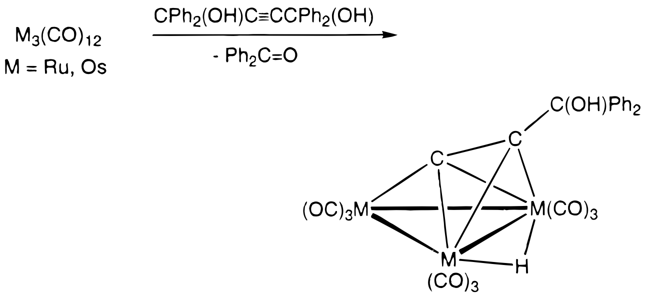
Dark red $Fe_3(\mu_3\text{-}C{=}C{=}CAr_2)_2(CO)_8$ (**115**, Ar = Ph, tol) have been obtained from $Ar_2C{=}C{=}C{=}C{=}C{=}CAr_2$ and $Fe_3(CO)_{12}$. Although the initial reaction gives only low yields (4−7%), reactions of $Fe_3(CO)_{12}$ with the also-formed $Fe_2(\mu\text{-}\eta^3{:}\eta^3\text{-}Ar_2CCCCCCAr_2)(CO)_6$ complexes are a better source of **115**.[211] A cluster-mediated cleavage of the C_6 chain occurs. Related reactions of the C_3 precursors $Br_2C{=}C{=}CR_2$ ($CR_2 = CPh_2$, $CMeBu^t$) with $Fe_3(CO)_{12}$ gave the green monoallenylidene clusters $Fe_3(\mu_3\text{-}C{=}C{=}CR_2)(\mu\text{-}CO)(CO)_9$. In these reactions, some hexapentaene complex is also formed by dimerization of the precursor. Structural studies show that C(1) is tightly attached to the Fe_3 triangle, with C(2) being further away from Fe(1) (although about 0.1 Å closer than found in similar vinylidene clusters).



(**115**)

Reactions between $Ru_3(CO)_{12}$ and propynols result in dehydration by loss of the OH group in combination with an H atom from a substituent.[212] No allenylidene clusters were obtained from $C_2\{CH_2(OH)\}_2$ and $M_3(CO)_{12}$ (M = Ru, Os) or $Ru_4(\mu\text{-}H)_4(CO)_{12}$, nor from $C_2\{CPh_2(OH)\}_2$. Instead, these reactions resulted in either dehydration and H atom transfer from carbon to the cluster to give the $\mu_3\text{-}CH_2{=}C{=}C(CHO)$ ligand, or elimination of Ph_2CO

Scheme 67



(**116**)

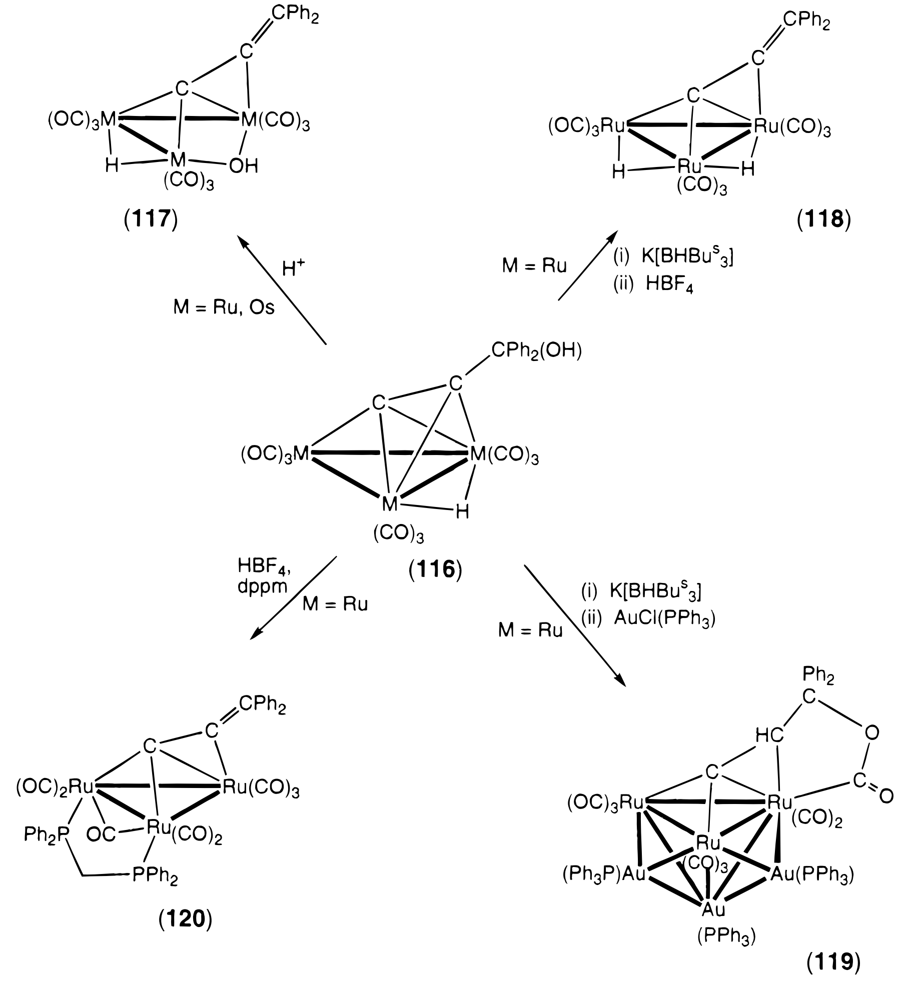
and formation of the hydrido−alkynyl complexes $M_3(\mu\text{-H})\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ (**116**) (Scheme 67).

Migration of OH from carbon to the M_3 cluster occurred on addition of CF_3CO_2H to **116** to form the μ-hydroxy clusters $M_3(\mu\text{-H})(\mu\text{-OH})(\mu\text{-C=C=CPh}_2)(CO)_9$ (**117**) (Scheme 68).[213] The latter form orange crystals, which give intensely orange-red solutions in the presence of acid, possibly containing the hydrido−allenylidene cluster cations $[M_3(\mu\text{-H})(\mu_3\text{-C=C=CPh}_2)(CO)_9]^+$. The Ru_3−allenylidene complexes were isolated if HBF_4 was used;[214] some $Ph_2C=CHCH=CPh_2$ was also formed in the original reaction.[213] Prior treatment of **116** with $K[BHBu^s_3]$, followed by addition of HBF_4, gave the dihydrido−allenylidene cluster **118**.[214] With $AuCl(PPh_3)$, the Au_3Ru_3 cluster **119** was formed, by intramolecular attack of the alkoxide on a cluster-bound CO group.

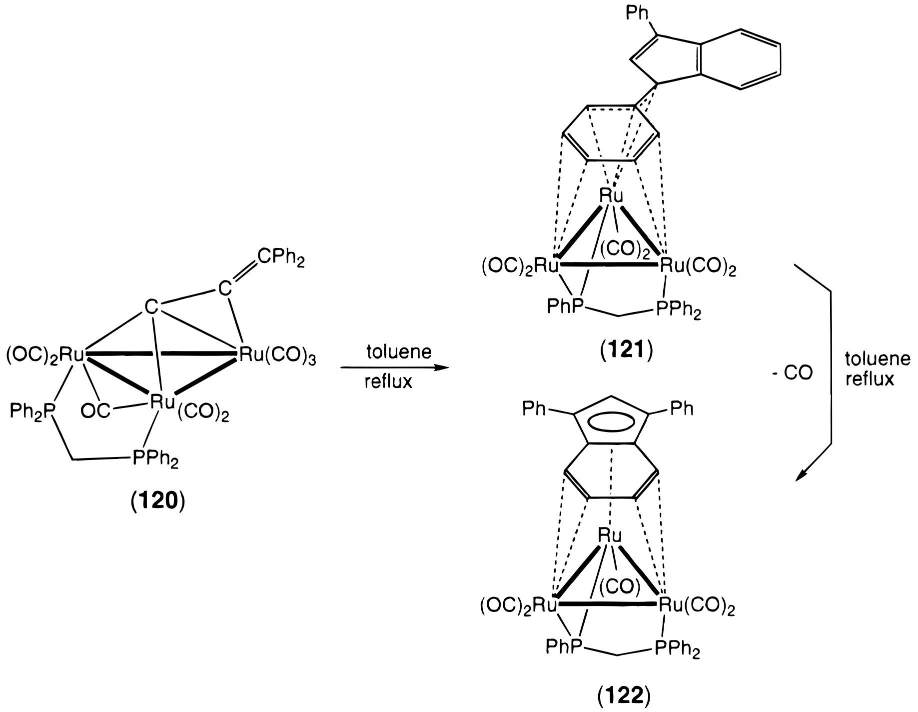
Addition of HBF_4 to **116** in the presence of dppm resulted in formal loss of water and formation of $Ru_3(\mu_3\text{-C=C=CPh}_2)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7$ (**120**). Thermolysis of this complex gave **121** and **122** by loss of CO and migration of a phenyl group from dppm to the allenylidene ligand, with concomitant cyclization to give the 1,3-diphenylindenyl ligand. In the first-formed **121**, this is attached by one of the phenyl groups and adjacent carbon of the five-membered ring, while further loss of CO results in symmetrization of the bonding to give the indenyl group attached by both the five- and six-membered rings in **122** (Scheme 69).[214] This reaction is possibly related to the formation of the indenylidene−ruthenium complex **24** (section IV.D.2.d).

Treatment of the hydroxy-ruthenium cluster **117** with $K[BHBu^s_3]$ and $AuCl(PPh_3)$ gave the hydroxy-free cluster $Ru_3\{\mu\text{-Au}(PPh_3)\}(\mu\text{-H})(\mu_3\text{-C=C=CPh}_2)(CO)_9$ (**123**), which is isolobal with **118**.[214] Substitution of **117** by PPh_3 or dppm occurs at the Ru atoms bridged by the OH group. With alkynes, reactions appear to proceed in two stages, the first leading to **124** by insertion of alkyne into one of the Ru−C σ bonds and transfer of the cluster-bound H atom to the chain, with retention of the hydroxy group. The second molecule of the alkyne then combines with

Scheme 68



Scheme 69



the resulting ligand, loss of water also occurring, to give cluster **125** (Scheme 70).

In the osmium series, protonation (TfOH) of $Os_3(\mu_3$-$C_2R)(CO)_9$ (R = CH_2OH, CMe_2OH, CMe=CH_2) gave $[Os_3(\mu$-H$)(\mu_3$-C=C=$CR'_2)(CO)_9]^+$ (**126**, R′ = H, Me), containing the μ_3-η^3-(6*e*)-allenylidene ligand found in the WRe_2 complexes **112** (Scheme 71).[207] They show similar dynamic behavior with $\Delta G^\ddagger$ 55.6 kJ mol^{-1}. Both complexes are unstable and neither has been isolated pure. At room temperature, the dimethyl complex slowly changes to an isomeric complex, possibly **127**. With PPh_3 at −50 °C, the allenylphosphonium clusters $Os_3(\mu$-H$)\{\mu_3$-C(PPh_3)=C=$CR'_2\}$-$(CO)_9]^+$ (**128**) are formed.

B. Butatrienylidene Complexes

A mixture of isomers of $Ru_5\{\mu_4$-CCCCH$(SiMe_3)\}$-$(\mu_3$-SMe$)(\mu$-SMe$)(\mu$-$PPh_2)_2(CO)_{10}$ (**129**), containing the first example of a cluster-bound butatrienylidene ligand, was obtained by addition of $C_2(SiMe_3)_2$ to Ru_5-$(\mu_5$-$C_2)(\mu$-SMe$)_2(\mu$-$PPh_2)_2(CO)_{11}$; the likely route to the butatrienylidene ligand is isomerization of the partially desilylated alkyne to the vinylidene on the cluster, and coupling with the C_2 unit on the precursor.[29] Conventional desilylation (KOH/MeOH) of **129** afforded the first structurally characterized example of a butatrienylidene ligand in $Ru_5(\mu_4$-$CCCCH_2)(\mu_3$-SMe$)(\mu$-SMe$)(\mu$-$PPh_2)_2(CO)_{10}$ (**130**) (Scheme 72). The $CCCCH_2$ ligand is asymmetrically attached to four of the five Ru atoms in a square face of the open envelope cluster. This cluster seems to be electron-rich (it has 80 cluster valence electrons (cve), two more than expected for an M_5 cluster with six M−M bonds); with one exception, the Ru−Ru separations range between 2.942 and 3.070 Å, consistent with an expansion of the cluster resulting from the extra electrons residing in an orbital with M−M antibonding character. Carbonylation gave a further example of cluster-bound $CCCCH_2$ ligand, this time interacting with all five Ru atoms, in $Ru_5(\mu_5$-$CCCCH_2)(\mu$-SMe$)_2(\mu$-$PPh_2)_2(CO)_{11}$ (**131**). In this complex, the Ru−Ru separations are between 2.830 and 2.943 Å, in agreement with the electron precise cve count of 80.[29]

IX. Allenylidene and Cumulenylidene Complexes as Intermediates, and Related Chemistry

In many cases, reactions designed to give complexes containing unsaturated carbene ligands have resulted in other compounds, many of which can be related to the desired product by virtue of subsequent fast reactions of the unsaturated ligand (usually with solvent). Thus, primary and secondary allenylidenes are implicated in many reactions which afford vinylidenes.[94]

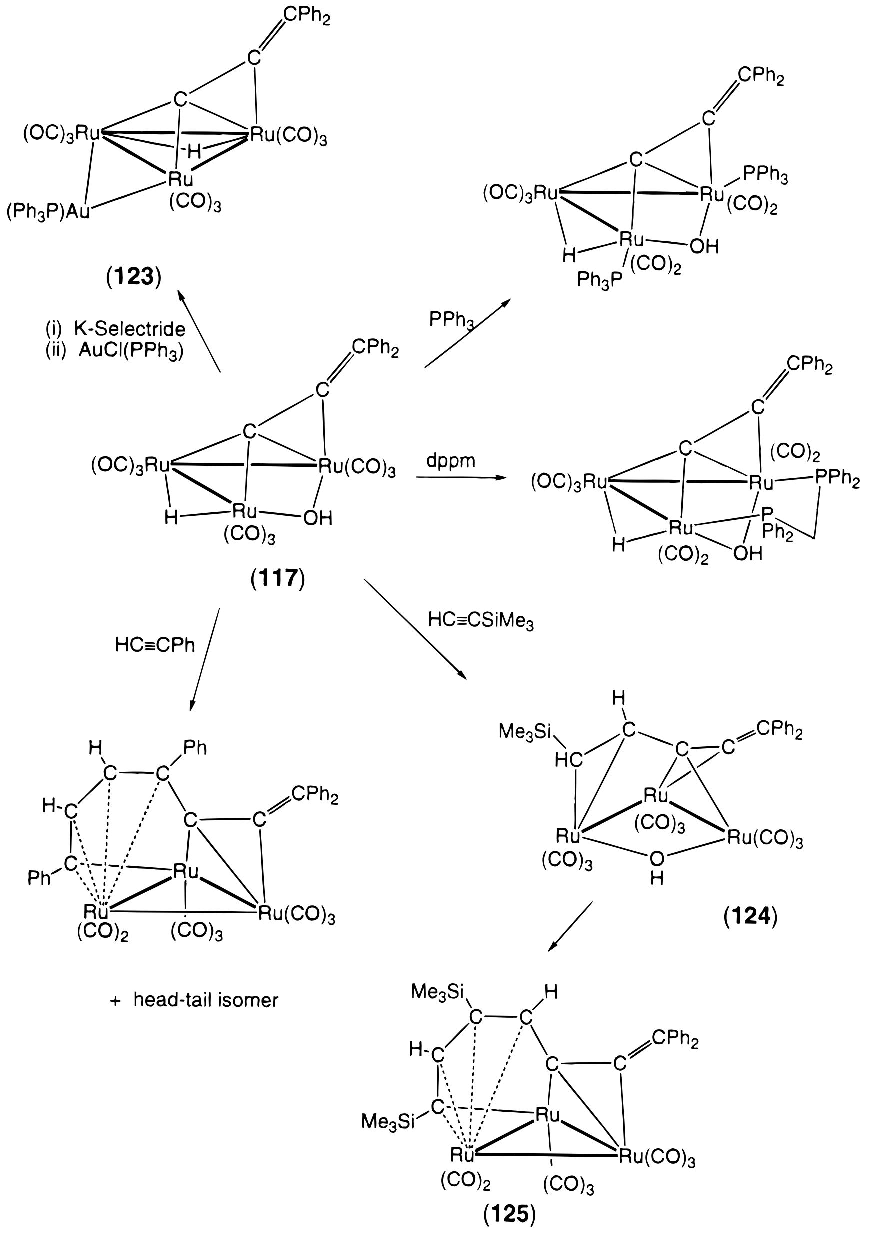
A. Chromium, Molybdenum, and Tungsten

Reactions of $M(CO)_6$ (M = Cr, W) with substituted 2-propyn-1-ols HC≡CCH(OH)(CH=CH)$_n$R [n = 0−2; R = H, Me, Ph (not all combinations)] by irradiation in MeOH−Et_2O gave carbene complexes M{=C(OMe)-{CH=CH(CH=CH)$_n$R}$(CO)_5$, probably via loss of water from intermediate hydroxy−vinylidenes to give allenylidenes which added MeOH at C(1) (Scheme 73).[215]

B. Ruthenium and Osmium

Reactions of $RuCl(PMe_3)_2Cp$ with HC≡CC(OH)-$R'CHR_2$ [$CR'CHR_2$ = cyclopent(hex)enyl, Pr^i] gave $[Ru\{$=C=CHCR′(OH)$CHR_2\}(PMe_3)_2Cp]^+$ which were converted to $[Ru($=C=C=CR′$CHR_2)(PMe_3)_2Cp]^+$ or $[Ru($=C=CHCR′=$CR_2)(PMe_3)_2Cp]^+$ by dehydration across C(3)−C(4).[81] These products suggest that proton transfer to C(4) did not occur, transfer to C(2)

Scheme 70



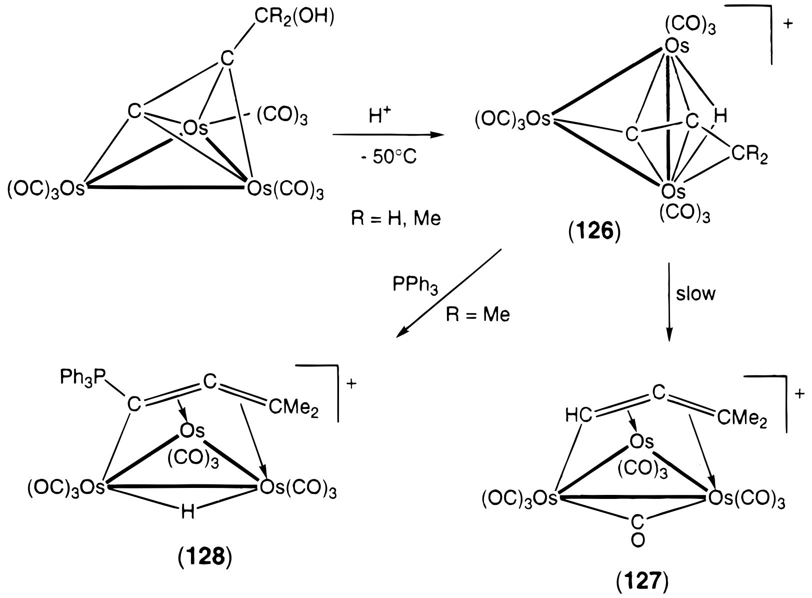
being preferred with the smaller PMe_3 ligand. Deprotonation with NaOMe gives enynyl derivatives; these reacted with CS_2 to give [2 + 2] cycloadducts.

Reactions of $HC{\equiv}CCMe{=}CHCH_2OH$ with $RuCl(PMe_3)_2Cp^*$ gave cyclic carbene complexes; substituted complexes were obtained from (*Z*)-$HC{\equiv}CCMe{=}CHCHR(OH)$ (R = Me, $C{\equiv}CSiMe_3$) (Scheme 74).[216] These reactions likely proceed, not by intramolecular addition of the OH group to the vinylidene (in which case, the *E* and *Z* isomers would be expected to afford different products), but by a related addition of the OH group to C(1) of the intermediate allenylidene, formed by 1,4-migration of the terminal alkyne proton. Subsequent proton transfer to C(2) gives the product directly.

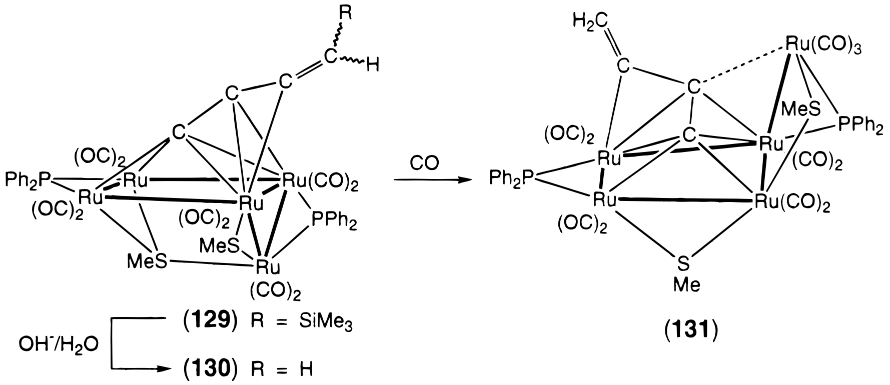
The allenylidene isomers were not detected in the dehydration of 1-ethynyl-1-cycloalkanols, except with $RuCl(PPh_3)_2Cp$ and 1-ethynylcyclopentanol, where IR evidence [ν(CCC) at 1953 cm^{-1}] for an unstable intermediate $[Ru\{{=}C{=}C{=}C(CH_2)_4\}(PPh_3)_2Cp]^+$ was obtained.[81] With $RuCl(L)_2(\eta^5\text{-}C_9H_7)$ (L = PPh_3; L_2 = dppe), the vinylvinylidenes $[Ru\{{=}C{=}CH(cycloalkenyl)\}(L)_2(\eta^5\text{-}C_9H_7)]^+$ (n = 1−3) are obtained.[217] However, in the presence of PPh_3, the reactions between $RuCl(L)_2(\eta^5\text{-}C_9H_7)$ and 1-ethynyl-1-cyclopent(hex)anol gave the corresponding alkynylphosphonio derivatives $[Ru\{C{\equiv}C[C_nH_{2n+1}(PPh_3)]\}](L)_2(\eta^5\text{-}C_9H_7)]^+$ (n = 5, 6), possibly via the allenylidene (Scheme 75). Activation of the propynols clearly depends on their substituents.

Several propargyl compounds, e.g., $HC{\equiv}CCH_2X$ (X = Cl, OH, OMe), $HC{\equiv}CCMe_2(OH)$ or $HC{\equiv}CC(C_5H_{10})(OH)$, react with $RuCl_2(PR_3)(\eta\text{-arene})$ (arene = $C_6Me_nH_{6-n}$, n = 4, 6) to give unsaturated carbenes $[RuCl\{{=}C(OR')CH{=}CR_2\}(PR_3)(\eta\text{-arene})]^+$ by addition of MeOH to intermediate allenylidenes (observed as short-lived violet intermediates).[82,112,113] With $HC{\equiv}CCPh_2(OH)$, deep violet solutions of the allenylidene were obtained, which slowly (24 h) turned red. In CH_2Cl_2, the originally red solution of $RuCl_2(PR_3)(\eta$-

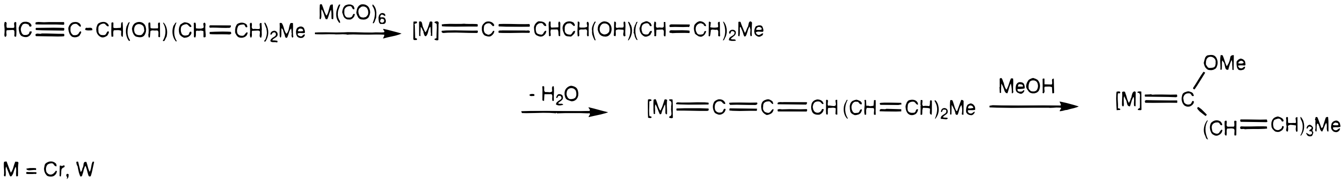
Scheme 71



Scheme 72



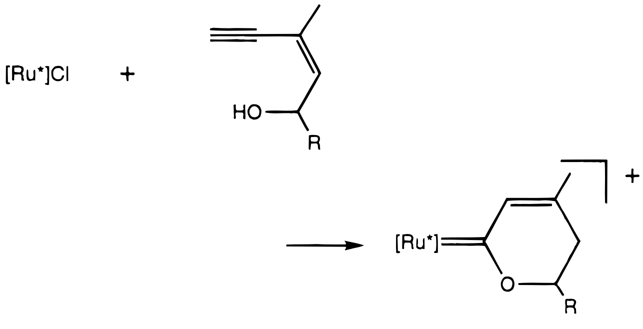
Scheme 73



C_6Me_6) (PR_3 = $PMePh_2$, PMe_2Ph) turned dark blue on addition of the diyne; addition of R′OH resulted in a color change to violet.

With $HC{\equiv}CCH_2(OH)$, the only known example of double addition of MeOH to C(1) and C(3) gave $[RuCl\{{=}C(OMe)CH_2CH_2(OMe)\}(PR_3)(\eta\text{-arene})]^+$.[135] With tertiary and secondary 2-propyn-1-ols $HC{\equiv}CCRR'(OH)$ (R = R′ = Me, Cy, Ph; R = H, R′ = Me, Ph, 2-thienyl), this general route provides a synthesis of the alkoxycarbenes from the related aldehydes, via addition of $LiC{\equiv}CH$ to the aldehydes, and was used to prepare methoxy(di- and trienyl)carbene complexes $[RuCl\{{=}C(OMe)(CH{=}CH)_nR\}(PR_3)(\eta\text{-arene})]^+$ from $HC{\equiv}CCH(OH)(CH{=}CH)_nR$ (R = Me, $n = 1, 2$; R = Ph, $n = 1$).[75,82]

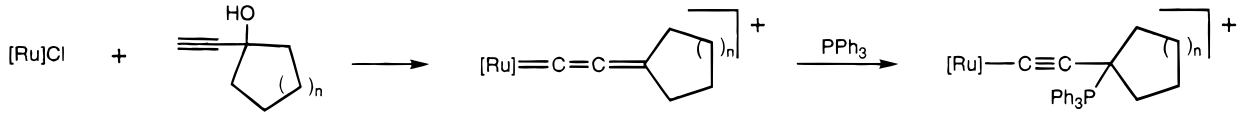
Scheme 74



[Ru*] = Ru(PMe3)2Cp*
R = H, Me, C≡CSiMe3

Reactions of $RuCl_2(PMe_3)(\eta\text{-}C_6Me_6)$ with (*R*,*S*)- and (*S*)-$HC{\equiv}CCH(C_6H_4OMe\text{-}2)(OH)$ in MeOH both afforded the racemic *trans*-alkoxy–alkenyl–carbene complexes $[RuCl\{{=}C(OMe)CH{=}CH(C_6H_4OMe\text{-}2)\}(PMe_3)(\eta\text{-}C_6Me_6)]^+$. Similar reactions with (*S*,*S*)-$Cr(CO)_3\{\eta^6\text{-}2\text{-}MeOC_6H_4CH(OH)C{\equiv}CH\}$ gave the corre-

Scheme 75



[Ru] = Ru(L)$_2$(η^5-C_9H_7),
L$_2$ = (PPh$_3$)$_2$, dppe

sponding carbene complex with a 1/1 ratio of diastereomers. The related $Cr(CO)_3\{\eta^6\text{-}2\text{-}MeC_6H_4CH(OH)C{\equiv}CH\}$ complex gave a 55/45 mixture. The carbene complexes have the *s-cis* conformation, but with $Cr(CO)_3\{\eta^6\text{-}PhCMe(OH)C{\equiv}CH\}$, the *s-trans* isomer was obtained, with a 64/36 ratio of diastereomers. It is considered that these reactions proceed by attack of MeOH at C(1) of the intermediate allenylidene complex.[218] With $HC{\equiv}CCR^1{=}CHR^2$ in MeOH, $RuCl_2(PMe_3)(\eta\text{-}C_6Me_6)$ or $RuCl_2(CNR)(\eta\text{-}C_6Me_6)$ [R = Bu^t, $(CH_2)_4Cl$] affords methoxycarbene complexes $[RuCl\{{=}C(OMe)CH{=}CR^1CH_2R^2\}(L)(\eta\text{-}C_6Me_6)]^+$ (R^1, R^2 = H, Me); with EtOH and R^1, R^2 = H, Me, the ethoxycarbene is formed. Labeling studies indicate that the reactions proceed via an allenylidene intermediate, $[RuCl({=}C{=}C{=}CR^1CH_2R^2)(L)(arene)]^+$.[112,113]

Not all reactions of propargyl alcohols afford allenylidene complexes, even when 1-alkynes give the expected vinylidenes. Hydroxyvinyl complexes $RuCl\{CH{=}CHCR_2(OH)\}(CO)(PPh_3)_2$ were obtained from $RuHCl(CO)(PPh_3)_3$ and $HC{\equiv}CCR_2(OH)$ (R_2 = H_2, Me_2, MeEt, MePh; $CR_2 = C_6H_{10}$); the latter two were dehydrated on alumina to $RuCl(CH{=}CHR')(CO)(PPh_3)_2$ (R' = $CH{=}CHPh$, cyclohexenyl).[219] Reactions of $MHCl(CO)(PPr^i_3)_2$ (M = Ru, Os) with $HC{\equiv}CCR^1R^2(OH)$ gave several products including $MCl\{CH{=}CHCR^1R^2(OH)\}(CO)(PPr^i_3)_2$, $MCl_2({=}CHCH{=}CR^1R^2)(CO)(PPr^i_3)_2$, and $MCl(CHCHCPhO)(CO)(PPr^i_3)_2$, depending on the nature of R^1 and R^2.[220,221] Either $OsH_2Cl_2\{\kappa^2\text{-}P,O\text{-}PPr^i_2CH_2C(O)OMe\}(PPr^i_2CH_2CO_2Me)$ or $OsCl_2\{\kappa^2\text{-}P,O\text{-}PPr^i_2CH_2C(O)OMe\}_2$ react with $HC{\equiv}CCPhR(OH)$ (R = Me, Ph) to give the carbyne complexes $Os({\equiv}CCH{=}CPhR)Cl_2\{\kappa^2\text{-}P,O\text{-}PPr^i_2CH_2C(O)O\}(PPr^i_2CH_2CO_2Me)$ (R = Me, *cis*-Cl_2; R = Ph, *trans*-Cl_2), the former being formed with ester O–Me cleavage. The related complex $OsH_2Cl_2(PPr^i_3)(PPr^i_2C_2H_4NMe_2)$ gave $OsHCl_2({\equiv}CCH{=}CPh_2)(PPr^i_3)(PPr^i_2C_2H_4NMe_2)$ with $HC{\equiv}CCPh_2(OH)$.[222]

Reactions of $OsI_2(PR_3)(\eta\text{-}C_6H_6)$ with $HC{\equiv}CCH_2CHR'(OH)$ in the presence of $AgPF_6$ afford cyclic oxacarbene complexes $[Os({=}CCH_2CH_2CHR'O)(PR_3)(\eta\text{-}C_6H_6)][PF_6]$, probably via vinylidene intermediates.[223] The square-planar 16-e complexes $OsCl(NO)(PR_3)_2$ (PR_3 = PPr^i_3, PPr^i_2Ph) react with $HC{\equiv}CCR'_2(OH)$ (R′ = Me, Ph) to give $OsHCl\{C{\equiv}CCR'_2(OH)\}(PR_3)_2$ (R′ = Me, Ph, R_3 = Pr^i_2Ph; R′ = Ph, R_3 = Pr^i_3). For R′ = Ph, treatment with acidic (HCl) alumina gave allenyl complexes $OsCl_2(CH{=}C{=}CPh_2)(NO)(PR'_3)_2$, but no allenylidenes were detected.[224]

C. Rhodium and Iridium

Attempts to form bis-allenylidene complexes in the $RhCl(PPr^i_3)_2$ series from $Rh(\eta^3\text{-benzyl})(PPr^i_3)_2$ and $HC{\equiv}CCR_2(OH)$ (R = Me, Pr^i, Ph) resulted instead in formation of *trans*-$RhH\{C{\equiv}CCR_2(OH)\}_2(PPr^i_3)_2$.[135] In the presence of NEt_3, these compounds are converted into the alkynyl–vinylidene complexes, the diphenyl complexes being in equilibrium (30/70). Complete conversion requires irradiation in benzene. With alumina in the presence of chloride, coupling of supposed intermediate allenylidene ligands gave the hexapentaene complex as a mixture of η^2-(2,3) and η^2-(3,4) isomers. Allenylidenes were not obtained from enynes and $\{RhCl(PPr^i_3)_2\}_2$: the η^2-enyne or hydrido-enynyl complexes rearrange to vinylidenes. Elimination of H_2O from *trans*-$RhCl\{{=}C{=}CHCHMe(OH)\}(PPr^i_3)_2$ [from $HC{\equiv}CCHMe(OH)$] on acidic alumina gave *trans*-$RhCl({=}C{=}CHCMe{=}CHMe)(PPr^i_3)_2$, protonation of which gave the cationic carbyne *trans*-$[RhCl({\equiv}CCH{=}CMe_2)(PPr^i_3)_2]^+$.[225]

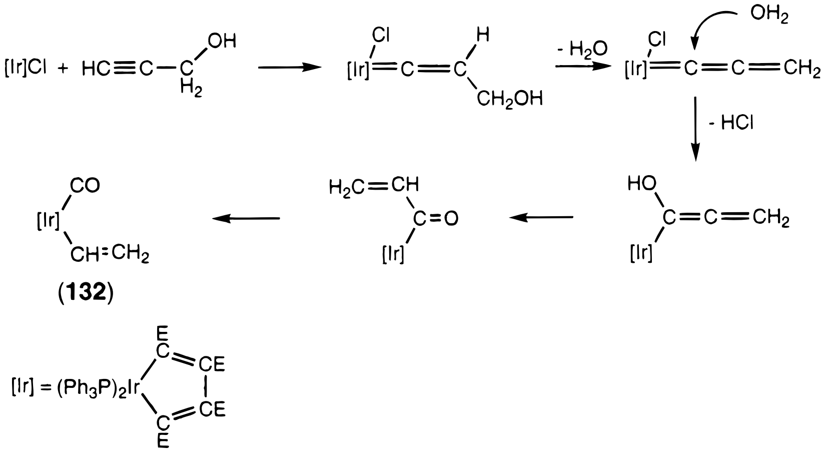
Two routes are suggested for the formation of $IrHCl(CH{=}CHPh)(CO)(PPr^i_3)_2$ from $IrH_2Cl(coe)(PPr^i_3)_2$ and $HC{\equiv}CCHPh(OH)$: one involves an allenylidene intermediate.[155,226] In the case of $HC{\equiv}CCPh_2(OH)$, the allenylidene is obtained from the hydrido–alkynyl either directly, or after irradiation to give the vinylidene, by catalytic dehydration with CF_3CO_2H. Elimination of H_2O is followed by loss of a proton from the resulting $[IrHCl({=}C{=}C{=}CPh_2)(PPr^i_3)_2]^+$. Attempts to form iridium derivatives by reactions of $IrCl(coe)(PPr_3^i)_2$ [from $\{IrCl(coe)\}_2$ and PPr^i_3 in situ] with $HC{\equiv}CC{\equiv}CCPh_2(OH)$ gave only insoluble polymeric material. In contrast, reaction of the diynol with $IrH_2Cl(PPr^i_3)_2$ gave the hydroxydiynyl complex *trans*-$IrHCl\{C{\equiv}CC{\equiv}CPh_2(OH)\}(PPr^i_3)_2$, which on irradiation isomerized to the vinylidene *trans*-$IrCl\{{=}C{=}CHC{\equiv}CCPh_2(OH)\}(PPr^i_3)_2$.[31] The hydroxydiynyl group is not susceptible to electrophilic attack. The η^2-alkyne complex was obtained from $IrCl(coe)(PPr^i_3)_2$ and $SiMe_3C{\equiv}CC{\equiv}CCPh_2(OH)$; on heating it is transformed to $Ir\{{=}C{=}C(SiMe_3)C{\equiv}CCPh_2(OH)\}Cl(PPr^i_3)_2$. In this case, no formation of the pentatetraenylidene complex is found, even with Tf_2O in pyridine (cf., the Rh complex).

The reaction of $Ir(C_4E_4)(Cl)(PPh_3)_2$ (**132**; E = CO_2Me) with propyn-2-ol gave the vinyl–carbonyl complex $Ir(C_4E_4)(CH{=}CH_2)(CO)(PPh_3)_2$ possibly via sequential formation of the expected vinylidene and allenylidene intermediates. Addition of H_2O at C(1) gave the enol $Ir(C_4E_4)(Cl)\{C(OH){=}C{=}CH_2\}(PPh_3)_2$, from which successive loss of HCl and CO occurred to give $Ir(C_4E_4)\{C(O)CH{=}CH_2\}(PPh_3)_2$ and $Ir(C_4E_4)(CH{=}CH_2)(CO)(PPh_3)_2$ (Scheme 76).[227]

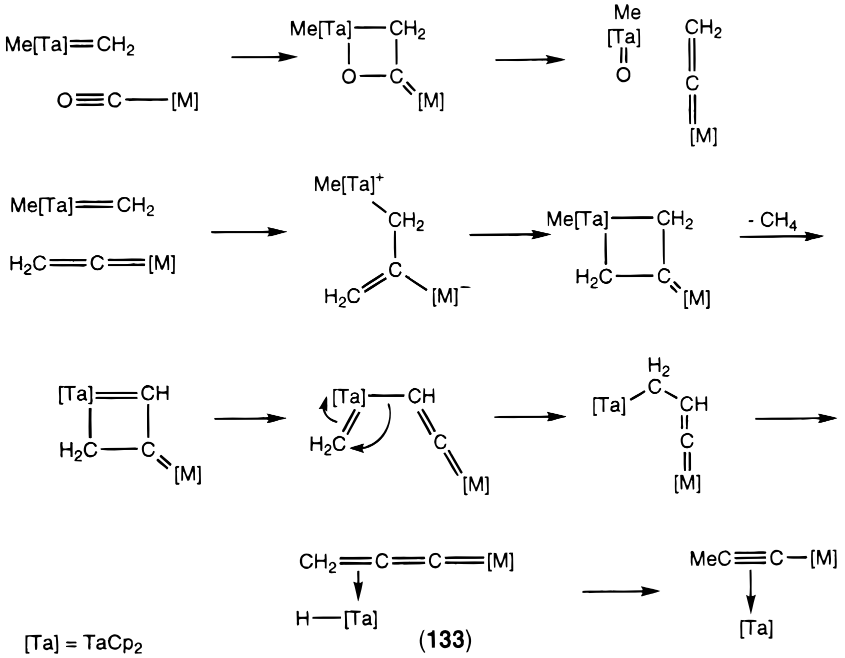
D. Platinum

Reactions of $PtHCl(PPh_3)_2$ with $HC{\equiv}CCR^1R^2(OH)$ resulted in dehydration to give $PtCl(C{\equiv}CCMe{=}CH_2)(PPh_3)_2$ (for R^1, R^2 = Me) or, if the reaction was carried out in the presence of alcohols (R^3OH), the

Scheme 76



Scheme 77



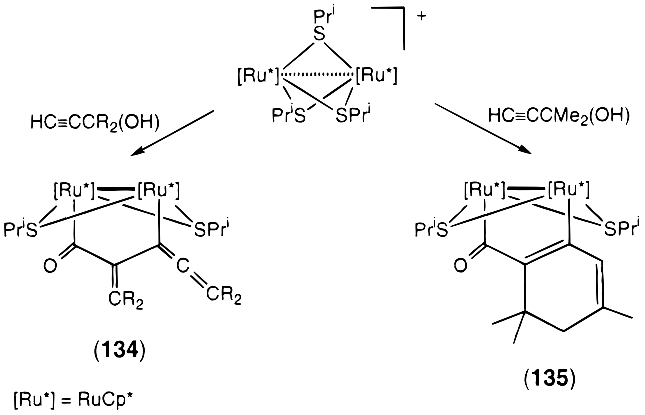
acetylides $PtCl\{C{\equiv}CCR^1R^2(OR^3)\}(PPh_3)_2$ (R^1 = Me, R^2, R^3 = Me, Et).[228]

E. Polynuclear Systems

Allenylidene intermediates have been implicated in the formation of MeC≡C ligands in reactions of $Ta(CH_2)MeCp_2$ with binuclear metal carbonyls. The reactions are driven by formation of strong Ta=O bonds, following initial cycloaddition of $Ta{=}CH_2$ to CO: both vinylidenes and allenylidenes feature in the proposed reaction scheme and labeling studies confirm that both the methyl and β-carbons are derived from the tantalum complex. It is proposed that the allenylidene (**133**) is formed by coupling of $Ta{=}CH_2$ and $M{=}C{=}CH_2$ followed by β-elimination and rearrangement (Scheme 77).[229] These reactions may have some relevance to surface-catalyzed deoxygenation of CO. Similar highly unsaturated intermediates are envisaged to account for the formation of a μ_3-C_4H_4 ligand from the reaction with $Ru_3(CO)_{12}$.

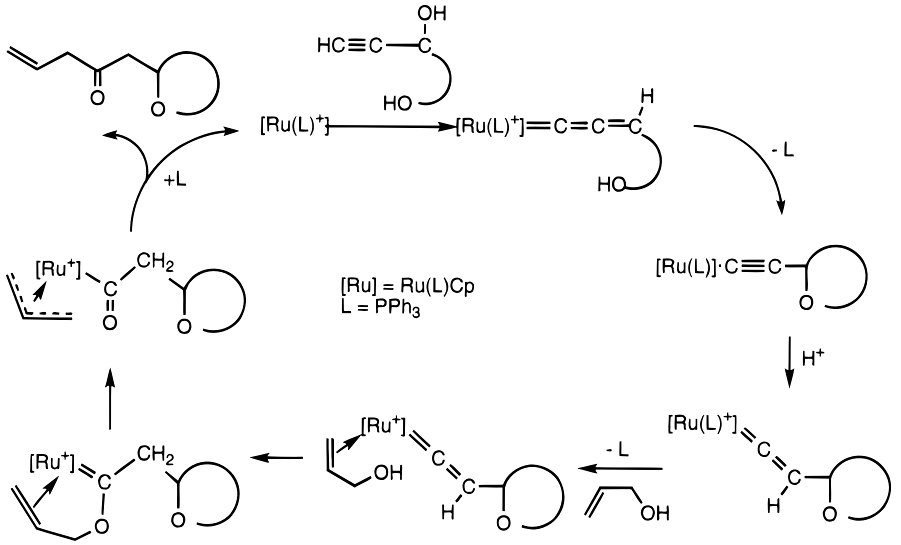
Possible intramolecular allenylidene–alkynyl or vinylvinylidene–alkynyl coupling occurred on $\{RuCp^*\}_2(\mu\text{-}SPr^i)_3$ to give μ-$C(O)C(=CR_2)C{=}C{=}CR_2$ ligands in **134** (R = Ph, tol).[69] With $HC{\equiv}CCMe_2(OH)$, intramolecular cyclization also occurred to give **135** (Scheme 78).

Scheme 78

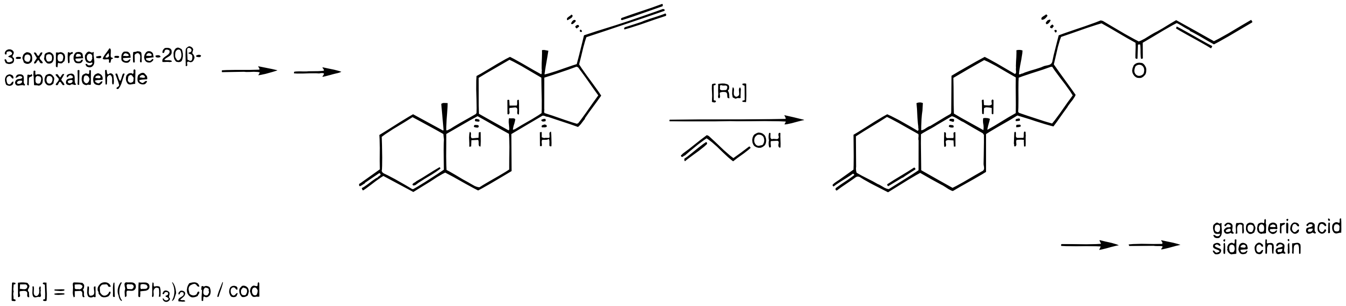


A variety of complexes has been obtained from $Ru_3(CO)_{12}$ and $HC{\equiv}CCR^1R^2(OH)$. In most cases, the

Scheme 79



Scheme 80



hydrido−alkynyl clusters $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CR^1R^2(OH)\}(CO)_9$ were formed ($R^1 = Me$, $R^2 = Et, Ph$). Dehydration (room temperature, excess CF_3CO_2H) gave $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2CR^1{=}CHR^2)(CO)_9$ ($R^1 = R^2 = Me$ and $R^1 = H$, $R^2 = Ph$, respectively).[230] The reaction between $Os_3(\mu\text{-}H)_2(CO)_{10}$ and $HC{\equiv}CCMe_2(OH)$ gave $Os_3\{\mu_3\text{-}HC_2CMe_2(OH)\}(CO)_{10}$ and $Os_3(\mu\text{-}H)\{\mu\text{-}CH{=}CHCMe_2(OH)\}(CO)_{10}$; $Os_3(CO)_{12}$ gave $Os_3(\mu\text{-}H)\{\mu_3\text{-}C_2CMe_2(OH)\}(CO)_9$. The ruthenium analogue of the latter is obtained in low yield from $Ru_3(CO)_{12}$, the main product being $Ru_2(\mu\text{-}C_4H_2R_2)(CO)_6$ isomers [$R = CMe_2(OH)$]. Complex transformations of $Os_3\{\mu_3\text{-}HC_2CMe_2(OH)\}(CO)_{10}$ occur on treatment with CF_3CO_2H in EtOH, the complexes $Os_3(\mu_3\text{-}HC_2CMe{=}CH_2)(CO)_{10}$ and $Os_3(\mu\text{-}H)(\mu_3\text{-}C_2CMe{=}CH_2)(CO)_9$ being formed by dehydration, and $Os_3\{\mu_3\text{-}HC_2CMe_2(OEt)\}(CO)_{10}$ and $Os_3(\mu\text{-}H)\{\mu_3\text{-}C_2CMe_2(OEt)\}(CO)_9$ by addition of EtOH.[231]

X. Allenylidene Complexes in Organic Synthesis

It has been suggested[25,232] that use of allenylidenes in organic synthesis requires (i) formation and reactions with nucleophiles more rapidly than vinylidenes; (ii) a lack of reactivity to allylic alcohols; (iii) the ability of the allenylidene/vinylidene (after addition of nucleophile) to participate in a catalytic cycle; and (iv) compatibility of the nucleophile with mildly acidic conditions.

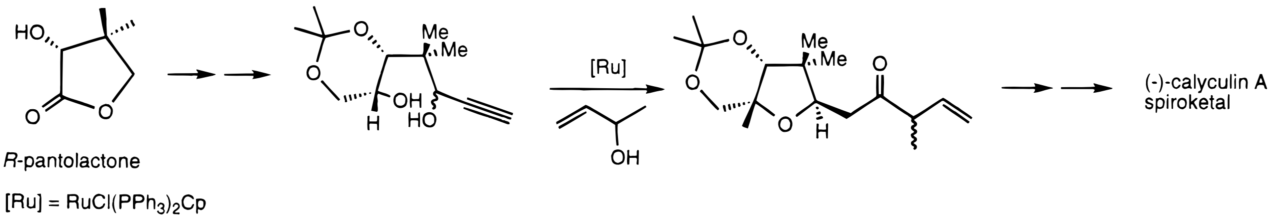
The intermediacy of allenylidene−ruthenium complexes rationalizes the synthesis of tetrahydropyranyl or furanyl ketones catalyzed by $RuCl(PPh_3)_2Cp$ (Scheme 79).[232] In one case, competition with conversion of a related vinylidene complex gives a mixture of products. The reaction has been used to create stereocenters with secondary alcohols and a third center with little selectivity. Formally, the 2-propyn-1-ol functions as a zwitterionic system $C^+{-}C^\bullet{-}C^-$. The internal nucleophile is required for reaction with the allenylidene, while in contrast, the vinylidene requires precoordination of the allylic alcohol by the olefin C=C double bond, with loss of PR_3. Ring closure precedes addition of allyl alcohol because no reaction occurs with $[Ru({=}C{=}C{=}CHBu^t)(PPh_3)_2Cp]^+$. Cyclic systems were made by making four bonds, breaking two bonds, and building in molecular complexity rapidly with reasonable atom economy.

Functionalized steroid side chains were introduced by coupling of allylic alcohols with ethynyl groups, catalyzed by $RuCl(cod)Cp/PPh_3$ in the presence of NH_4PF_6. Several derivatives of ganoderic acid (an angiotensin-converting enzyme inhibitor) were obtained (Scheme 80).[233]

The spiroketal subunit of (−)-calyculin A (a nanomolar inhibitor of two of the four major protein serine/threonine phosphatases) were similarly constructed using a cyclization and addition of an allylic alcohol catalyzed by $RuCl(PPh_3)_2Cp$ (Scheme 81).[234]

The cationic complexes $[RuCl({=}C{=}C{=}CPh_2)(PR_3)(cym)]PF_6$ ($R = Pr^i$, Cy, Ph) are efficient catalysts for ring-closing olefin metathesis, with activitites de-

Scheme 81



creasing in the order $PCy_3 > PPr^i_3 \gg PPh_3$.[235] The PCy_3 system gave good to excellent yields for ring sizes ≥ 5, including conformationally flexible dienes, with tolerance for several functional groups.

XI. Cumulenylidenes in Bimetallic Systems

Complexes containing two metal centers linked by unsaturated chains of carbon atoms have various resonance forms:

$$[M]{-}C{\equiv}C{-}[M'] \leftrightarrow [M]{=}C{=}C{=}[M'] \leftrightarrow [M]{\equiv}C{-}C{\equiv}[M']$$

$$[M]{-}C{\equiv}C{-}C{\equiv}[M] \leftrightarrow [M]{=}C{=}C{=}C{=}[M] \leftrightarrow [M]{\equiv}C{-}C{\equiv}C{-}[M]$$

$$[M]{-}C{\equiv}C{-}C{\equiv}[M'] \leftrightarrow [M]{=}C{=}C{=}C{=}[M'] \leftrightarrow [M]{\equiv}C{-}C{\equiv}C{-}[M'] \text{ etc.}$$

These complexes contain significant contributions from both allenylidene or cumulenylidene forms and the alkynylalkylidyne or diyndiyl forms.[236] A detailed consideration of the facinating chemistry and properties of these complexes is beyond the scope of this review, only a brief summary being provided below.

Structural studies of C_n complexes have been interpreted in terms of varying contributions of the allenic (cumulenic) forms. Reactions of $Re(C{\equiv}CLi)(NO)(PPh_3)Cp^*$ with metal carbonyls, followed by treatment with $[Me_3O]^+$, give $\{Re(NO)(PPh_3)Cp^*\}\{\mu\text{-}C{\equiv}C{-}C(OMe){=}\}[M]$ [M = $W(CO)_5$, $Fe(CO)_4$, $Mn(CO)_2Cp$]. The chemical shift of the Re−C is intermediate between those found for $[Re(C{\equiv}C)(NO)(PPh_3)Cp^*]^-$ and $[Re({=}C{=}CR_2)(NO)(PPh_3)Cp^*]^+$. These data combined with structural studies suggest that a contribution from the zwitterionic form $[Re^+(NO)(PPh_3)Cp^*]\{\mu\text{-}C{=}C{=}C(OMe)\}[M^-]$ is significant but not dominant.[237−239] Addition of BF_3 to the manganese derivative afforded the C_3 complex $[\{Re(NO)(PPh_3)Cp^*\}(\mu\text{-}C_3)\{Mn(CO)_2Cp\}]^+$ for which the cumulenic form of the bridging ligand dominated.

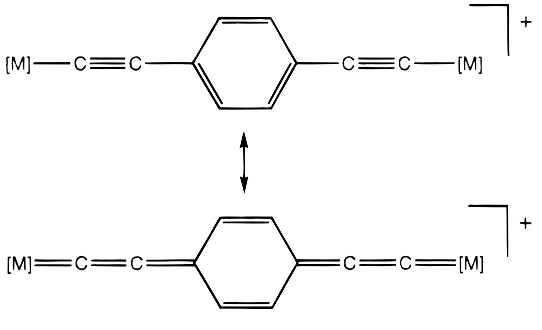
Oxidation of the diastereoisomers of $\{Re(NO)(PPh_3)Cp^*\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ with $AgPF_6$ gave air-stable deep blue (*SS*, *RR*) and (*SR*, *RS*) diastereomers of the dications $[\{Re(NO)(PPh_3)Cp^*\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)]^{2+}$.[240] Similarly, oxidation of binuclear complexes containing C_n chains capped by metal−ligand fragments affords cations whose spectra are consistent with structures containing extended multiple bond arrays:[241]

$$[Ru]{-}C{\equiv}C{-}C{\equiv}C{-}[Ru] \rightarrow\rightarrow [[Ru]{=}C{=}C{=}C{=}C{=}[Ru]]^{2+} \rightarrow\rightarrow [[Ru]{\equiv}C{-}C{\equiv}C{-}C{\equiv}[Ru]]^{4+}$$

$$[Ru] = Ru(L)(PPh_3)Cp,\ L = PMe_3,\ PPh_3 \quad (13)$$

Treatment of $Fe(C{\equiv}CH)(dppe)Cp^*$ with $[FcH]^+$ gave the bis-vinylidene, which was deprotonated to give $\{Fe(dppe)Cp^*\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$. Chemical oxidation of the latter gave mono- and dications, the latter being formulated as $[\{Fe(dppe)Cp^*\}(\mu\text{-}C_4)\{Fe(dppe)Cp^*\}]^{2+}$.[242,243] Similar results were obtained with $\{Fe(CO)_2Cp^*\}(\mu\text{-}C_4)\{Fe(dppe)Cp^*\}$.[244] Detailed physicochemical studies of the neutral and oxidized species have been reported, from which it seems that in the latter the cumulenic form of C_4 predominates in the dicarbonyl complex, while the symmetrical species retains the bis-acetylide character. A significant cumulenic contribution to the structure of $[\{Re(NO)(PPh_3)Cp^*\}(\mu\text{-}C_5)\{Mn(CO)_2(\eta\text{-}C_5Cl_5)\}]^+$ has also been proposed.[245]

One of the contributing structures for oxidized dinuclear complexes derived from 1,4-diethynylbenzene can be portrayed as the bis-allenylidene system **K** (Figure 13).[246]



(**K**)

Figure 13.

XII. Related Ligands

Many related heterocumulene ligands can be envisaged. Below are a few comments concerning some of them.

A. C_2SiH_2 Isomers

The silicon analogue of allenylidene has been made by pulsed flash pyrolysis of 2-ethynyl-1,1,1-trimethyldisilane, $HC{\equiv}CSiH_2SiMe_3$, at ∼1100 °C, condensing the products at 10 K.[247−249] The product, 1-silacyclopropenylidene, was irradiated (313 nm) to give $HC{\equiv}CSiH$. Further broad-band irradiation resulted largely in reversion to the silacyclopropenylidene, together with formation of a small amount of $:Si{=}C{=}CH_2$. The isomer $:C{=}C{=}SiH_2$ was not detected in this study. The structures and energies of 15 different isomers of C_2SiH_2 have been calculated by nonempirical theory.[248] The global minimum is 3-silacyclopropenylidene and the allenylidene analogues are found at

$$\text{1-silacyclopropenylidene (0)} < :Si{=}C{=}CH_2\ (28.5) < :C{=}C{=}SiH_2\ (233.5) < :C{=}Si{=}CH_2\ (488.3\ \text{kJ})$$

the high energies being consistent with the rare observation of Si(sp^2).[62] Three stable 1-silaallenes have been described,[250] while more reactive examples have been trapped by reactions with nucleophiles.[251]

B. C_nO

For $n = 1$ and 2, the ligands are the familiar carbonyl and ketenylidene, respectively. Free C_2O has been reported and studied theoretically.[252] Transition metal cluster complexes containing the ketenylidene ligand have been reviewed[253,254] and will not be discussed here.

C_3O has been generated by pyrolysis and identification by comparison with ab initio calculations and spectroscopically.[255−257] Metal complexes of C_3O appear to be confined to $Cr({=}C{=}C{=}C{=}O)(CO)_5$, obtained by treatment of $[CrI(CO)_5]^-$ with $AgC{\equiv}CCO_2Na$ in the presence of Ag^+. The presumed intermediate $Cr(\eta^2\text{-}AgC{\equiv}CCO_2Na)(CO)_5$ was treated with $CSCl_2$ to give $Cr(C{=}C{=}C{=}O)(CO)_5$.[100]

Mixtures of C_nO ($n = 4-9$) have been obtained from pulsed discharges through mixtures of C_3O_2 and argon. FT microwave spectra of C_nO ($n = 5, 7, 9$) show that all have singlet ground states;[258] other species have triplet ground states.[259] The molecular structure of C_5O has been determined[238] and investigated theoretically;[260] the major contributors are

$$^-C{\equiv}C{-}C{\equiv}C{-}C{\equiv}O^+ \leftrightarrow {}^-C{\equiv}C{-}C^+{=}C{=}C{=}O \leftrightarrow C{=}C{=}C{=}C{=}C{=}O$$

Free C_nO ($n = 4, 6$) molecules have been observed by ESR in Ne or Ar matrixes at 4 K as linear triplets.[261] They were formed by laser vaporization of graphite and irradiation of the C_n species with CO. INDO calculations suggest that principal spin density is in p_π orbitals on the O atom, oscillating along the C_n p_π chain, with the terminal C having the next-highest density, while ab initio calculations of the electronic configurations of C_nO ($n = 1-6$) using linear structures show alternating singlet (n = odd) and triplet states (n = even).[262] Cumulene bonding is found, but unlike the INDO calculations, the unpaired spins are p_π in character and are mainly found on C(1). The molecules C_nO ($n = 3, 5$) are more stable relative to C_n + CO or C_3O than are $n = 4, 6$.

C. C_nS

A pulsed discharge on CS_2/C_2H_2 mixtures in argon gave C_nS ($n = 3, 4, 5$).[263,264] C_3S [ν(CCC) 2046 cm^{-1}] is obtained by elimination of CS from $S{=}C{=}C{=}C{=}C{=}S$ or CO from $S{=}C{=}C{=}C{=}O$, for which several precursors have been described.[265] Similarly, irradiation of $S{=}C{=}C{=}C{=}C{=}C{=}O$ gave $S{=}C{=}C{=}C{=}C$ [ν(CCC) 1757 cm^{-1}].[266] Some of these molecules have been observed in interstellar molecular clouds.

D. 2-Azaallenylidenes

Reactions between $M(CO)_6$ (M = Cr, W) and $[N{=}CR^1R^2]^-$ [$R^1 = R^2 = C_6H_4X$-4, (X = H, Br, OMe), Bu^t, mes; R^1 = Ph, $R^2 = NMe_2$, Bu^t, Ph; $CR^1R^2 = C(C_6H_4)_2O$], followed by addition of $[Et_3O]^+$, gave $M\{{=}C(OEt)N{=}CR^1R^2\}(CO)_5$, which with BF_3 (at −100 to −60 °C) afforded deep blue $[M({=}C{=}N{=}CR^1R^2)(CO)_5]^+$. The Bu^t complexes are very labile and were not obtained pure.[267−269] The dipolar tautomers **L**−**N** (Figure 14) can be written, of which **M** is favored by comparison with the crystal structure data, in which C(1)−N is shorter than C(3)−N [1.184(7) vs 1.343(7) Å]. The Cr−C(1) bond distance is 1.895(6) Å. The ligand is essentially linear, with angles at C(1) and N 179.0(5) and 171.1(5)°, respectively.[267,268] An alternative preparation is from isocyanide complexes. Loss of Cl from $Cr(CNCCl_3)(CO)_5$ (treatment with $AlCl_3$) gave $[Cr({=}C{=}N{=}CCl_2)(CO)_5][AlCl_4]$ as a red solid.[268]

The tungsten complexes $[W({=}C{=}N{=}CR_2)(CO)_5][AlBr_4]$ [$R = C_6H_4X$-4, X = H, Br, OMe; $CR_2 = C(mes)_2$, $C(C_6H_4)_2O$], obtained from $W\{{=}C(OEt)N{=}CR_2\}(CO)_5$ and $AlBr_3$, react with thf to give 2-azaallenylidene complexes *trans*-$WBr({=}C{=}N{=}CR_2)(CO)_4$, in which the CNC moiety is substantially bent [$CNCPh_2$ 135.4(5)°].[270] The change in geometry results from the replacement of the π-acceptor CO ligand by the strong π donor, Br^-.

One-electron reduction of $[Cr\{{=}C{=}N{=}C(mes)_2\}(CO)_5][AlBr_4]$ by reaction in tetrahydrofuran gave stable paramagnetic violet $[Cr\{C{\equiv}NC^\bullet(mes)_2\}(CO)_5]$. The Cr and W complexes have E_p +0.58 and +0.66 V vs Ag/AgCl, respectively.[271] UV irradiation of $[Cr({=}C{=}N{=}CR_2)(CO)_5]^+$ [$CR_2 = CPh_2$, $C(C_6H_4)_2O$] gave $R_2C{=}CR_2$ in 34 and 29% yields, respectively. Oxidative cleavage (with Me_3NO) of the N−C bond in the latter gave xanthone. No evidence of nucleophilic attack at C(1) was obtained.

Similar reactions with $Mn(CO)_3Cp$ gave $[Mn({=}C{=}N{=}CR_2)(CO)_2Cp]^+$ [R = Ph, Bu^t; $CR_2 = C(C_6H_4)_2O$]; again the Bu^t complex was unstable.[272] The molecular structure of $[Mn({=}C{=}N{=}CPh_2)(CO)\{P(tol)_3\}Cp]BF_4$ showed short Mn=C(1) [1.792(7) Å] and C(1)=N bonds [1.184(9) Å] in an almost linear ligand. The properties of these complexes are summarized in Table 12.

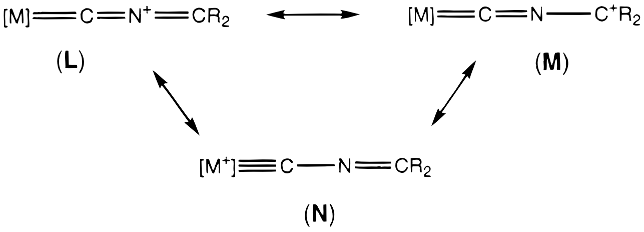


Figure 14.

Table 12. Some 2-Azaallenylidene Complexes, $[\{ML_n\}=C=N=CR^1R^2][BF_4]$

ML_n	R^1	R^2	color	yield,%	ν(CNC)	δ C(1)	δ C(3)	ref
$Cr(CO)_5$ (**a**)	$(C_6H_4)_2O$		dark blue	61	1926			267,268
$Cr(CO)_5$	Bu^t	Ph	dark blue		1865			269
$Cr(CO)_5$	Bu^t	Bu^t	red		1850			268
$Cr(CO)_5$	C_6H_4Br-4	C_6H_4Br-4	dark blue		1882			268
$Cr(CO)_5$	C_6H_4OMe-4	C_6H_4OMe-4	dark blue	76	1932			268
$Cr(CO)_5$	Cl	Cl	red		2130			268
$Cr(CO)_5$	mes	mes	dark blue		1890			268
$Cr(CO)_5$	Ph	NMe_2	orange-red	87	1937	211.2	153.9	269
$Cr(CO)_5$	Ph	Ph	dark blue		1888	200.4	166.5	267−269
$W(CO)_5$	$(C_6H_4)_2O$		dark blue		1919			268
$W(CO)_5$	Bu^t	Ph	dark blue		1857			269
$W(CO)_5$	Bu^t	Bu^t	yellow		1846			268
$W(CO)_5$	C_6H_4Br-4	C_6H_4Br-4	dark blue		1872			268
$W(CO)_5$	C_6H_4OMe-4	C_6H_4OMe-4	dark blue		1918			268
$W(CO)_5$	mes	mes	dark blue	24	1881			268
$W(CO)_5$	Ph	NMe_2	orange-red	87	1929	191.7 (WC 113)	155.3	269
$W(CO)_5$	Ph	Ph	dark blue		1880	182.3	166.1	267,269
trans-$WBr(CO)_4$	$(C_6H_4)_2O$		violet	15	1575			270
trans-$WBr(CO)_4$	C_6H_4Br-4	C_6H_4Br-4	red-black	43	1540			270
trans-$WBr(CO)_4$	C_6H_4OMe-4	C_6H_4OMe-4	deep red	45	1560	197.6	163.1	270
trans-$WBr(CO)_4$	mes	mes	deep red	36	1515	194.7	174.4	270
trans-$WBr(CO)_4$ (**b**)	Ph	Ph	deep red	67	1540	197.8	172.0	270
$Mn(CO)_2Cp$	Ph	Ph	black oil	96	1854	213	162	272
$Mn(CO)_2Cp$	$(C_6H_4)_2O$		blue-black	96	1896	n.f.	157.8	272
$Mn(CO)_2Cp$	Bu^t	Bu^t	dark green		1838			272
$Mn(CO)\{P(tol)_3\}Cp$ (**c**)	Ph	Ph	red	84	n.f.	207	151.5	272

Molecular Structures

complex	M−C(1)	C(1)−N	N−C(3)	Cr−C(1)−N	C(1)−N−C(3)	ref
a	1.895(6)	1.184(7)	1.343(7)	179.0(5)	171.1(5)	267,268
b	1.878(5)	1.275(7)	1.324(7)	169.6(5)	135.4(5)	270
c	1.792(7)	1.184(9)	1.313(9)	176.3(7)	174.4(8)	272

Reactions of the diphenyl complex with nucleophiles resulted in addition to C(3) to give isocyanide complexes:

$$[\mathrm{Mn}(=\mathrm{C}=\mathrm{N}=\mathrm{CPh}_2)(\mathrm{CO})_2\mathrm{Cp}]^+ + \mathrm{Nu} \rightarrow \mathrm{Mn}\{\mathrm{C}\equiv\mathrm{NCPh}_2(\mathrm{Nu})\}(\mathrm{CO})_2\mathrm{Cp} \quad (\mathrm{Nu} = \mathrm{OEt}_2,\ \mathrm{PMe}_3) \tag{14}$$

$$[\mathrm{Mn}(=\mathrm{C}=\mathrm{N}=\mathrm{CPh}_2)(\mathrm{CO})_2\mathrm{Cp}]^+ + \mathrm{X}^- \rightarrow [\mathrm{Mn}\{\mathrm{C}\equiv\mathrm{NCPh}_2(\mathrm{X})\}(\mathrm{CO})_2\mathrm{Cp}]^- \quad [\mathrm{X} = \mathrm{H},\ \mathrm{Me},\ \mathrm{SBu}^t,\ \mathrm{PPh}_2^-\ \mathrm{PH}(\mathrm{mes})] \tag{15}$$

The related isocyanide $Mn(CNCPh{=}CMe_2)(CO)_2Cp$ was obtained directly from $Mn(CO)_3Cp$ and $[N{=}C\text{-}Pr^iPh]^-$, followed by reaction with $SiMe_3Cl$.[257]

E. Other Heterocumulenylidenes

Many other synthetic challenges await, perhaps the most interesting being complexes containing vinylidene, allenylidene, and higher cumulenylidene ligands with electron-withdrawing substituents, such as F, CN, or CO_2Me. Undoubtedly this area will have more surprises in the future.

The introduction of other heteroatoms into the carbon chain is possible in principle, with many reactive molecules of this type having been prepared in the gas phase. To date, however, reports on their metal complexes are largely lacking. For this reason, it is appropriate only to draw the readers' attention to these systems as worthwhile targets for future synthetic efforts.

$$:\mathrm{C}=\mathrm{BR}:\mathrm{C}=\mathrm{C}=\mathrm{BR}:\mathrm{C}=\mathrm{C}=\mathrm{C}=\mathrm{BR}$$

$$:\mathrm{C}=\mathrm{B}=\mathrm{CR}_2$$

$$:\mathrm{C}=\mathrm{NR}:\mathrm{C}=\mathrm{C}=\mathrm{NR}:\mathrm{C}=\mathrm{C}=\mathrm{C}=\mathrm{NR}$$

$$:\mathrm{C}=\mathrm{PR}:\mathrm{C}=\mathrm{C}=\mathrm{PR}:\mathrm{C}=\mathrm{C}=\mathrm{C}=\mathrm{PR}$$

$$:\mathrm{C}=\mathrm{P}^+=\mathrm{CR}_2$$

XIII. Abbreviations

coe	cyclooctene
Cp	cyclopentadienyl, η^5-C_5H_5
Cp*	pentamethylcyclopentadienyl, η^5-C_5Me_5
CV	cyclic voltammogram
cym	η^6-*p*-cymene
dippe	1,2-bis(diisopropylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Fc	ferrocenyl
mes	mestityl
nbd	norbornadiene
nbe	norbornene
r.t.	room temperature
Tf	trifluoromethanesulfonyl, CF_3SO_3
tfbb	tetrafluorobenzobarrelene
tol	*p*-tolyl, C_6H_4Me-4
Tp	tris(pyrazolyl)borate, $[HB(pz)_3]^-$

XIV. Acknowledgments

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Note Added in Proof

Neutral C_nH_2 ($n = 5, 7$) species in the gas phase have been generated by charge stripping the radical anions obtained by loss of $EtO^{\bullet}$ from $[EtOCH_2(C{\equiv}C)_m]^-$ ($m = 2,3$) anions.[273,274] Binuclear complexes related to **18**, containing $Cr(CO)_3$ groups attached to the C_7 ring, have been obtained from consecutive reactions of lithiated 7-ethynylcyclohepta-1,3,5-trienes with $FeBr(CO)_2Cp$ and $Cr(CO)_3(NCEt)_3$.[275] A wide variety of ruthenium allenylidene complexes *trans*-$[RuX({=}C{=}C{=}CR^1R^2)(pp)_2]^+$ [$X = Cl$, $R^1 = Me$, $R^2 = Me$, Ph, pp = dippe; $X = Cl$, $C{\equiv}CR$ (R = H, alkyl, aryl), pp = dppe] have been made by conventional routes.[276,277] Further examples of di-, tri-, and tetrametallic cyclobutenylidene complexes were obtained from $Cr({=}C{=}CMe_2)(CO)_5$ and $Fe(C{\equiv}CC{\equiv}CR)(CO)(L)Cp$ ($R = H$, $SiMe_3$, Bu, Ph; $L = CO$, PPh_3) and subsequent coupling of the ethynyl derivative ($R = H$) with $MCl_2(PEt_3)_2$ ($M = Pd$, Pt).[278] Related diplatinum complexes were formed by intramolecular coupling of alkynyl groups in $\{Pt[\mu\text{-}\eta^1{:}\eta^2\text{-}C_2CMeEt(OH)](C_6F_5)(PPh_3)\}_2$ on treatment with HSPh.[279]

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