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Review

Metal complexes containing cumulenylidene ligands, $\{L_mM\}{=}C({=}C)_n{=}CRR'(n \geq 2)$

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Contents

Abstract

The syntheses, structures and chemistry of metal complexes containing the unsaturated carbene ligands $:C({=}C)_n{=}CRR'$ ($n \geq 2$) are reviewed.

1. Introduction

The chemistry of transition metal complexes containing highly unsaturated conjugated hydrocarbon ligands continues to be of interest, and the sub-set with carbon chains, C_n, is of potential significance in the construction of nano-devices. Metallacumulenes, with their unusual electronic structures, pose several problems with respect to their reactivity. This review provides an excellent opportunity to update part of my earlier account of the chemistry of transition metal complexes of allenylidenes and cumulenylidenes which appeared some 5 years ago [1]. Aspects of cumulenylidene chemistry have been included elsewhere [2,3]. Other articles in this volume summarise the extensive chemistry of allenylidenes that has been developed by

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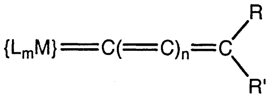
various groups during that period, so I shall confine my attention to those complexes containing ligands containing four or more carbon atoms in the chain (**1**, $n \geq 2$). A summary of the earlier work is also included.



(**1**) $n \geq 2$

The C_4 complexes have proved difficult to characterise, the first isolated example being reported in 2000 [4], although unusual dimetallic systems were described in 1999 [5]. The first example of a mononuclear C_5-ruthenium complex was described by Dixneuf and co-workers in 1994 [6], followed 2 years later by derivatives containing iridium by Werner and co-workers [7] and the Group 6 metals by Roth and Fischer [8,9]. A couple of examples of ruthenium cluster complexes containing butatrienylidenes were also known [10]. However, several groups have reported chemistry which can reasonably be interpreted as proceeding through reactive butatrienylidene intermediates, beginning with the pioneering study by Lomprey and Selegue in 1993 [11]. Not surprisingly, given the reactivity of vinylidene and allenylidene complexes, it has proved challenging to isolate and fully characterise these even more highly unsaturated derivatives, and applications to synthesis are rare to date. Theoretical calculations described below have concluded that odd-numbered carbon chains are likely to be more stable than the adjacent even-numbered chains, a result that is in accord with the experimental observations to date. Table 1 summarises the complexes reported to December 2003.

2. Syntheses

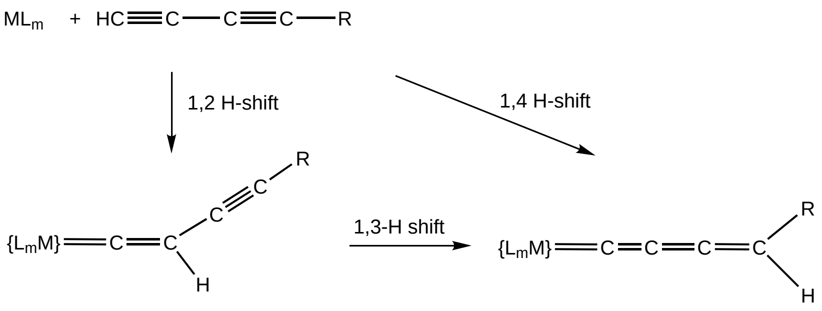
Adaptations of syntheses which are successful for vinylidenes and allenylidenes have proved to be the most fruitful approaches to complexes containing cumulenylidene ligands. Thus, reactions of terminal 1,3-diynes with several metal systems have given reactive intermediates which appear to be the desired butatrienylidene complexes (Scheme 1). Calculations have shown that there is only a small energy difference between the species $HC{\equiv}CCH{=}C{:}$ and $H_2C{=}C{=}C{=}C{:}$ [12]. So far, there has been no evidence concerning the identity of the kinetic product of protonation of metal diynyl complexes, although it has been assumed from the nature of the products that the butatrienylidene has been formed. However, the results do not preclude initial formation of the ethynylvinylidene complex which then undergoes a rapid 1,3-proton shift to form the butatrienylidene. Recently, stepwise migration of $SnPh_3$ groups has been shown to occur in reactions of $SnPh_3C{\equiv}CC{\equiv}CSnPh_3$ with a manganese complex [13] (see below). However, protonation of the 1,3,5-hexatriynyl complex $Re\{(C{\equiv}C)_3tol\}(NO)(PPh_3)Cp^*$ occurred by attack at C_β to give $[Re\{{=}C{=}CHC{\equiv}CC{\equiv}C(tol)\}(NO)(PPh_3)Cp^*]^+$ which did not rearrange further [14]. This is in accord with recent calculations on the electrophilicity of long-chain poly-ynyl complexes, which indicate that although charge alternation along the chain is evident [positive charge on C(odd), negative charge on C(even)], the magnitude of this effect is attenuated after C(4) [15].

By analogy with the well-known syntheses of allenylidene complexes from substituted propargyl alcohols, reactions of 1,3-diynols, or their derivatives, e.g., triflates, give species which undergo either spontaneous or ready dehydration to form the corresponding pentatetraenylidenes (Scheme 2) [6,16]. Longer carbon chains are present in compounds obtained from the appropriate triyne derivatives.

It may be noted that stabilisation of Group 6 derivatives occurs with electron-donating substituents, whereas the other known complexes generally have phenyl end-groups. In situ preparation of the very sensitive parent butatrienylidene complexes of Group 8 metals is used en route to the preparation of various more stable adducts. Typical ML_m end-groups are illustrated in Plate 1. These include $M(CO)_5$ (M = Cr, Mo, W; octahedral d^6), $Mn(dmpe)_2Cp$ (octahedral d^6), *trans*-$[RuCl(PP)_2]^+$ (PP = dppm, dppe, depm; octahedral d^6), $M(PP)Cp'$ [M = Fe, PP = dppe, dippe, Cp′ = Cp*; M = Ru, PP = $(PPh_3)_2$, $\{P(OMe)_3\}_2$, dppe, Cp′ = Cp; octahedral d^6] and *trans*-$MCl(PPr^{i}_{3})_2$ (M = Rh, Ir; square planar d^8).

3. Butatrienylidenes (metallapentatetraenes)

Early attempts to make butatrienylidene complexes were reported by Lomprey and Selegue [11], Bruce et al. [17],



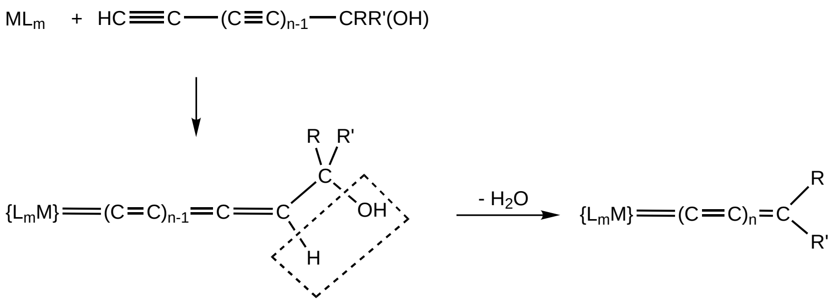
Scheme 1.

Table 1
Mononuclear cumulenylidene complexes, $\{\mathrm{L}_m\mathrm{M}\}{=}(\mathrm{C})_n{=}\mathrm{CR}^1\mathrm{R}^2$

ML_m	R^1	R^2	Colour	Yield	ν(CC)	^{13}C NMR, δ(C)	Reference
Butatrienylidenes							
Mn(dmpe)Cp	$\mathrm{SnPh_3}$	$\mathrm{SnPh_3}$	Green	80	1596, 1548	C(1) 266.5, C(2)130.6, C(3) 124.8, C(4) 140.0	[13]
Mn(dmpe)$\mathrm{Cp^{Me}}$	$\mathrm{SnPh_3}$	$\mathrm{SnPh_3}$	Green	80	1594, 1552	C(1) 267.5, C(2)131.6, C(3) 121.4, C(4) 139.9	[13]
Mn(dmpe)Cp	H	H				C(1) 281.8, C(2)158.7, C(3) 141.0, C(4) 44.4	[13]
Mn(dmpe)$\mathrm{Cp^{Me}}$	H	H				C(1) 280.8, C(2)157.9, C(3) 140.2, C(4) 44.3	[13]
Fe(dppe)$\mathrm{Cp^*}$	H	$\mathrm{Fe(CO)_2Cp^*}$	Purple	75	1952w, 1882w, 1830w	C(1) 258.7 [*J*(CP) 36], C(2) 167.4 [*J*(CH) 8.1], C(3) 128.3 [*J*(CH) 8.4], C(4) 58.4 [*J*(CH) 180.2]	[5]
Fe(dippe)$\mathrm{Cp^*}$	H	$\mathrm{Fe(CO)_2Cp^*}$	Pink	93	1945	C(1) 260.8 [*J*(CP) 34.8], C(2) 170.9 [*J*(CH) 5.7], C(3) 133.3 [*J*(CH) 6.0], C(4) 59.0 [*J*(CH) 176.6]	[5]
Fe(dppe)$\mathrm{Cp^*}$	Me	$\mathrm{Fe(CO)_2Cp^*}$	Purple	22	1942w, 1905w, 1892w	C(1) 250.5 [*J*(CP) 35], C(2) 149.8, C(3) 121.6 [*J*(CH) 7], C(4) 69.3 [*J*(CH) 18]	[5]
Fe(dippe)$\mathrm{Cp^*}$	Me	$\mathrm{Fe(CO)_2Cp^*}$	Purple	75	1946	C(1) 264.9 [*J*(CP) 36], C(2) 166.2 [*J*(CH) 6.5, *J*(CP) 2.4], C(3) 131.9 [*J*(CH) 7], C(4) 73.6 [*J*(CH) 7.8]	[5]
trans-$\mathrm{IrCl(PPr^i_3)_2}$	Ph	Ph	Orange	77	1993	C(1) 255.7 [*J*(CP) 13.7], C(2,3) 174.6, 164.1 [both *J*(CP) 3.6], C(4) 105.9 [*J*(CP) 2.5]	[4,22]
$\mathrm{IrCl(CO)(PPr^i_3)_2}$	Ph	Ph	Orange		1987		[4,22]
trans-$\mathrm{IrI(PPr^i_3)_2}$	Ph	Ph	Orange	91	1992	C(1) 215.3 [*J*(CP) 14.7], C(3) 179.1 [J(CP) 3.6], C(2) 164.4 [*J*(CP) 4.6], C(4) 109.1 [*J*(CP) 3.0]	[4,22]
trans-$\mathrm{Ir(OH)(PPr^i_3)_2}$	Ph	Ph	Green	87	1996	C(1) 227.8 [*J*(CP) 12.7], C(3) 173.2 [J(CP) 5.1], C(2) 164.0 [*J*(CP) 3.1], C(4) 103.4 [*J*(CP) 2.5]	[4,22]
trans-$\mathrm{Ir(N_3)(PPr^i_3)_2}$	Ph	Ph	Olive-green	91	1994	C(1) 233.8 [*J*(CP) 14.2], C(3) 174.1 [J(CP) 7.6], C(2) 163.8 [*J*(CP) 3.6], C(4) 105.5 [*J*(CP) 2.5]	[4,22]
trans-$\mathrm{Ir(OPh)(PPr^i_3)_2}$	Ph	Ph	Olive-green	94	1998	C(1) 229.3 [*J*(CP) 13.7], 167.7, 164.6 [both *J*(CP) 3.0], C(4) 103.7 [*J*(CP) 2.9]	[4,22]
trans-$\mathrm{IrMe(PPr^i_3)_2}$	Ph	Ph	Orange oil		1997		[4,22]
Pentatetraenylidenes							
$\mathrm{Cr(CO)_5}$	$\mathrm{NEt_2}$	$\mathrm{CMe{=}C(NMe_2)_2}$	Orange	65	2149, 2000	C(1) 175.3; C(2,3,4), =CMe 55.8, 87.3, 94.7, 102.2; C(5), $\mathrm{C(NMe_2)_2}$ 147.0, 154.0	[23]
$\mathrm{Cr(CO)_5}$	$\mathrm{NMe_2}$	$\mathrm{NMe_2}$	Orange	42	2140, 1998	C(1) 174.1; C(2,3,4) 99.5, 95.7, 49.6; C(5) 155.0	[8]
$\mathrm{W(CO)_5}$	$\mathrm{NEt_2}$	$\mathrm{CMe{=}C(NMe_2)_2}$	Yellow	61	2148, 2001	C(1) 175.2; C(2,3,4), =CMe 58.3, 87.4, 93.9, 102.5; C(5), $\mathrm{C(NMe_2)_2}$ 136.4, 146.7	[23]
$\mathrm{W(CO)_5}$	$\mathrm{NMe_2}$	$\mathrm{NMe_2}$	Orange	36	2140, 1999	C(1) 153.8 [*J*(CW) 102.6]; C(2) 94.6 [*J*(CW) 25.6]; C(3,4) 99.5, 52.1; C(5) 154.8	[8]
$\mathrm{W(CO)_5}$	$\mathrm{NEt_2}$	$\mathrm{CH{=}C(NMe_2)_2}$	Yellow	5	2161, 2145, 2003	C(1) 170.4; C(2,3,4,5) 56.0, 92.7, 93.8, 142.9, 149.8	[9]
$\mathrm{Re(NO)(PPh_3)Cp^*}$	Ar^a	Ar^a	Deep blue	79	1993m, 1902m	C(1) 256.9 [*J*(CP) 10.8], C(5) 133.8 [*J*(CP) 11.1]	[24]
$\mathrm{Re(NO)(PPh_3)Cp^*}$	Ar–Cl^b	Ar–Cl^b	Dark blue	81	1987m, 1894m		[24]
$\mathrm{Re(NO)(PPh_3)Cp^*}$	Ar–Br^c	Ar–Br^c	Deep blue	83	1991m, 1896m		[24]
trans-$\mathrm{RuCl(dppe)_2}$ [$\mathrm{BF_4}$ salt]	Ph	Ph	Deep blue	70	2024, 1918	C(1) 316.35 [*J*(CP) 14.6]; C(2) 206.7 [*J*(CP) 2.6]; C(3) 167.63 [*J*(CP) 2.3]; C(4) 160.25 [*J*(CP) 2]; C(5) 165.44	[6]

Table 1 (*Continued*)

ML$_m$	R^1	R^2	Colour	Yield	ν(CC)	^{13}C NMR, δ(C)	Reference
trans-RhCl(PPr$^i_3$)$_2$	Ph	Ph	Deep violet oil	58	1962, 1860	C(1) 205.25 [*J*(CRh) 67.4, *J*(CP) 17.8]; C(2) 246.13 [*J*(CRh) 16.5, *J*(CP) 6.4)]; C(3) 197.98 [*J*(CRh) 1.3, *J*(CP) 3.8]; C(4) 141.41 [*J*(CP) 3.5]; C(5) 156.07 [*J*(CP) 1.9]	[16]
trans-IrCl(PPr$^i_3$)$_2$	Ph	Ph	Copper-brown	80	1960, 1856	C(1) 186.70 [*J*(CP) 13.9]; C(2) 245.45 [*J*(CP) 4.0)]; C(3) 133.70 [*J*(CP) 3.3]; C(4) 209.61 [*J*(CP) 3.2]; C(5) 161.64 [*J*(CP) 1.5]	[7]

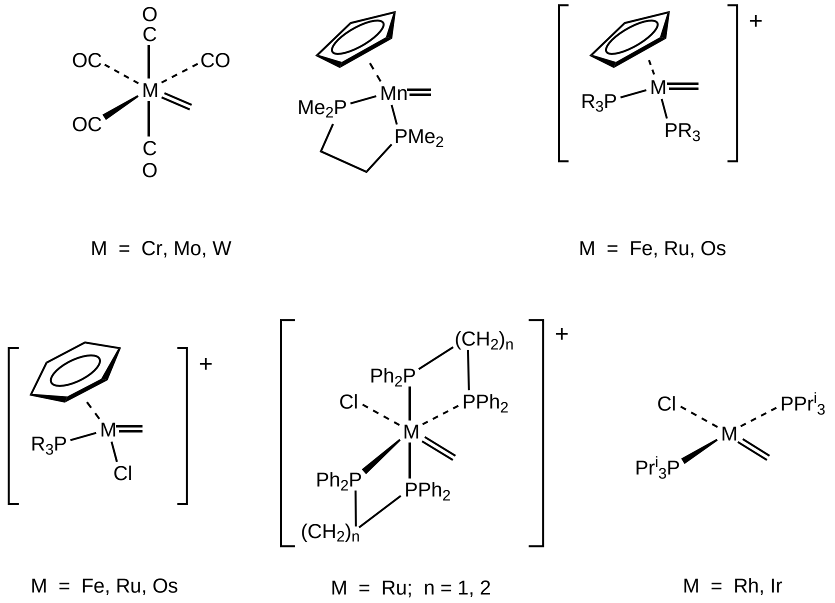


Scheme 2.

Winter and Hornung [18] and Dixneuf and co-workers [19] who partially characterised their complexes through trapping reactions with nucleophiles, or by conversion to acylvinylidene, acylalkynyl, butenynyl or allenylidene complexes.

Reactions of Mn(η^6-cycloheptatriene)Cp^R (R = H, Me) with Ph$_3$SnC≡CC≡CSnPh$_3$ in the presence of dmpe result in quantitative formation of the corresponding vinylidenes Mn{=C=C(SnPh$_3$)C≡CSnPh$_3$}(dmpe)Cp^R (**2**) (Scheme 3) [13]. The presumed intermediate η^2-alkyne complex could not be detected by NMR. Irradiation of these vinylidenes (125 W medium-pressure Hg) resulted in a 1,3-migration of the SnPh$_3$ group to give green Mn{=C=C=C=C(SnPh$_3$)$_2$}(dmpe)Cp^R (**3**) in 80% yields. Deprotection with [NBu$_4$]F (tbaf) afforded the parent butatrienylidenes Mn(=C=C=C=CH$_2$)(dmpe)Cp^R (**4**) which decompose above −5 °C, but could be characterised by NMR spectroscopy at −40 °C. All carbons of the C$_4$ chain were detected, with the Mn=C atom resonating at δ ca 280.

The reaction between Ru{C≡CC(O)Pr^i}(PPh$_3$)$_2$Cp and (CF$_3$CO)$_2$O gave Ru{C≡CC(OCOCF$_3$)=CMe$_2$}(PPh$_3$)$_2$Cp (**6**) [11], possibly being formed by interaction of the



M = Cr, Mo, W

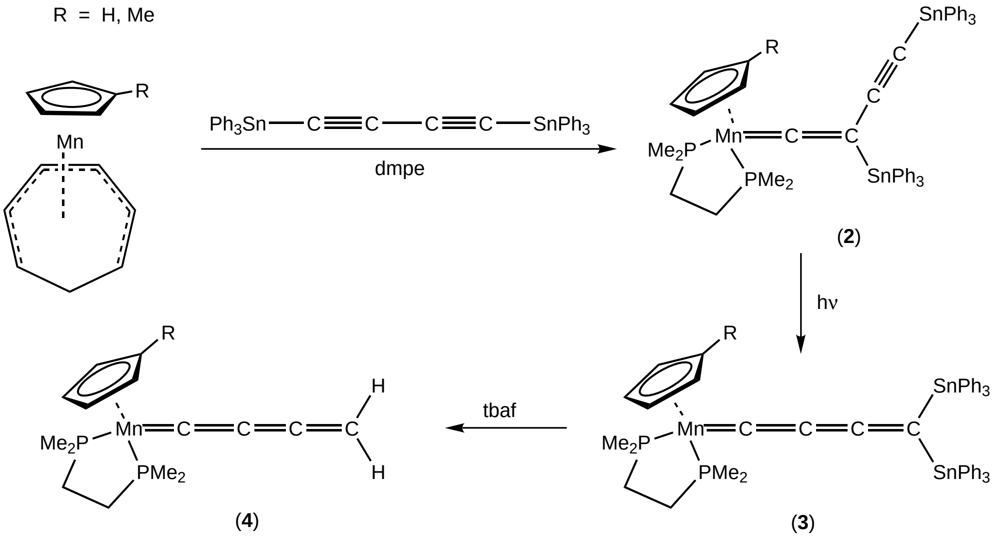
M = Fe, Ru, Os

M = Fe, Ru, Os

M = Ru; n = 1, 2

M = Rh, Ir

Plate 1.

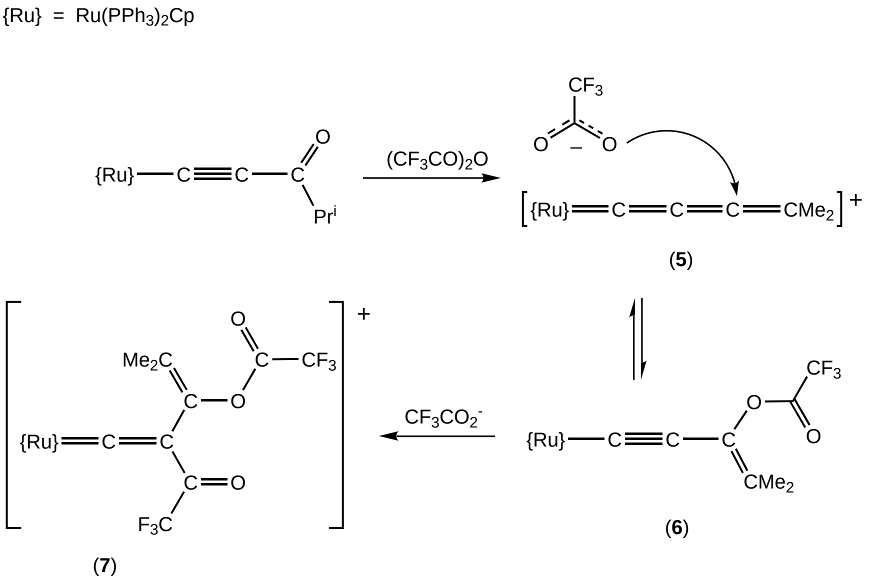


Scheme 3.

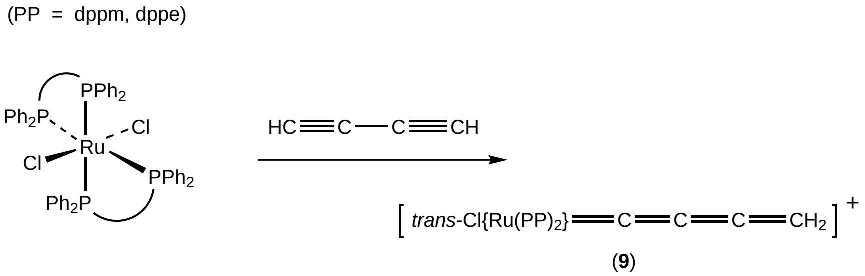
expected butatrienylidene cation $[Ru(=C=C=C=CMe_2)(PPh_3)_2Cp]^+$ (**5**) with the trifluoroacetate anion at C(3) (Scheme 4). Further reaction with a second trifluoroacetate moiety gave the vinylidene **7**.

The unsubstituted analogue $[Ru(=C=C=C=CH_2)(PPh_3)_2Cp]^+$ (**8**) is probably formed by reaction of HC≡CC≡CH with $[Ru(thf)(PPh_3)_2Cp]^+$, prepared in situ from $RuCl(PPh_3)_2Cp$ and $AgBF_4$ in thf solution [20,21]. The cation, which has not been isolated, was characterised from its subsequent chemistry (see below) and has also been obtained by protonation of $Ru(C≡CC≡CH)(PPh_3)_2Cp$. Buta-1,3-diyne (usually added <230 K) reacts with *cis*-$RuCl_2(PP)_2$ (PP = dppm, dppe) in CH_2Cl_2 in the presence of $Na[PF_6]$ to give an intense green solution assumed to contain *trans*-$[RuCl(=C=C=C=CH_2)(PP)_2]^+$ (**9**; Scheme 5), again on the basis of their subsequent reactions (see below) [18].

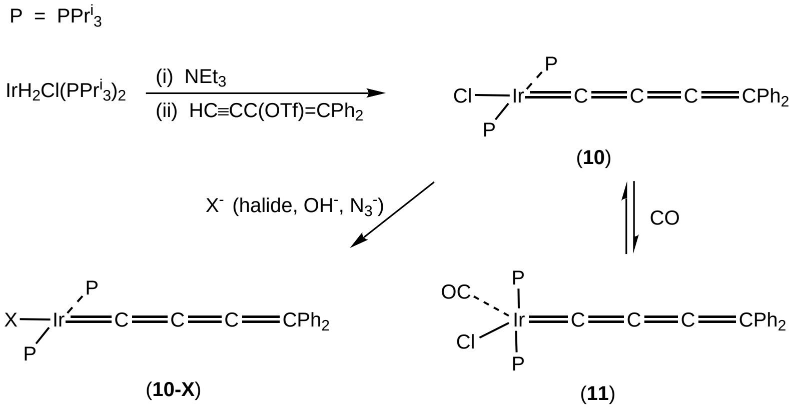
While reaction of the ethynyl ketone $HC≡CC(O)CHPh_2$ with $IrH_2Cl(PPr^i_3)_2$ gives $IrHCl\{C≡CC(O)CHPh_2\}(PPr^i_3)_2$, which readily isomerises in solution to the vinylidene $IrCl\{=C=CHC(O)CHPh_2\}(PPr^i_3)_2$, elimination of H_2O could not be achieved by treatment with either acid or base. The enol acetate $HC≡CC(OAc)=CPh_2$ gave the corresponding alkynyl–hydrido complex, which does not rearrange to the vinylidene. However, reaction of $IrH_2Cl(PPr^i_3)_2$ with enol triflate $HC≡CC(OTf)=CPh_2$ and NEt_3 at −100 °C gave *trans*-$IrCl(=C=C=C=CPh_2)(PPr^i_3)_2$ (**10**; Scheme 6) (77%) [4,22]. Five-coordinate **11** is formed in a reversible reaction with CO.



Scheme 4.



Scheme 5.

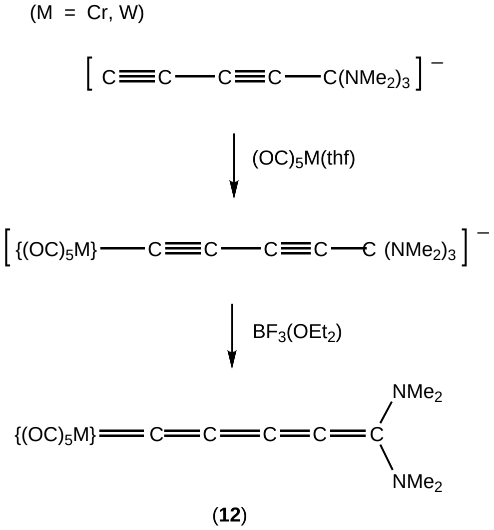


Scheme 6.

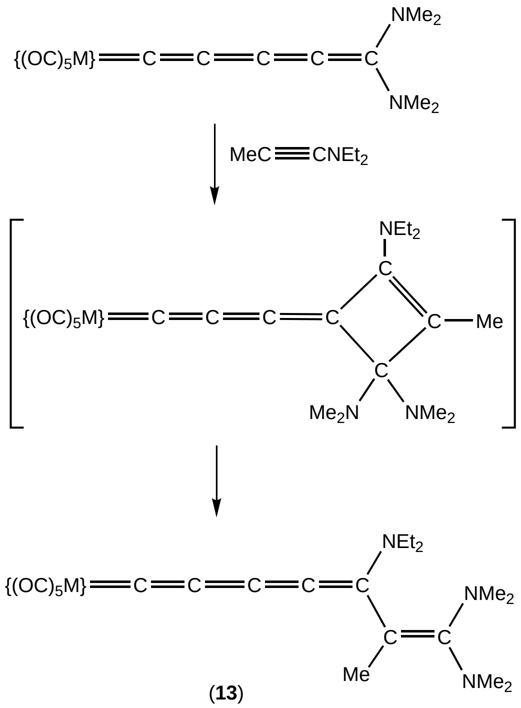
4. Pentatetraenylidenes (metallahexapentaenes)

The intermediate anionic diynyl complex obtained from M(CO)$_5$(thf) (M = Cr, W) and LiC≡CC≡CC(NMe$_2$)$_3$ reacts with BF$_3$ to give neutral M{=C=C=C=C=C(NMe$_2$)$_2$}(CO)$_5$ (**12**; Scheme 7) [8]. The reaction proceeds via anionic [M{C≡CC≡CC(NMe$_2$)$_3$}(CO)$_5$]$^-$ which with BF$_3$(OEt$_2$) affords the Cr/W complexes in 36 or 42% yields.

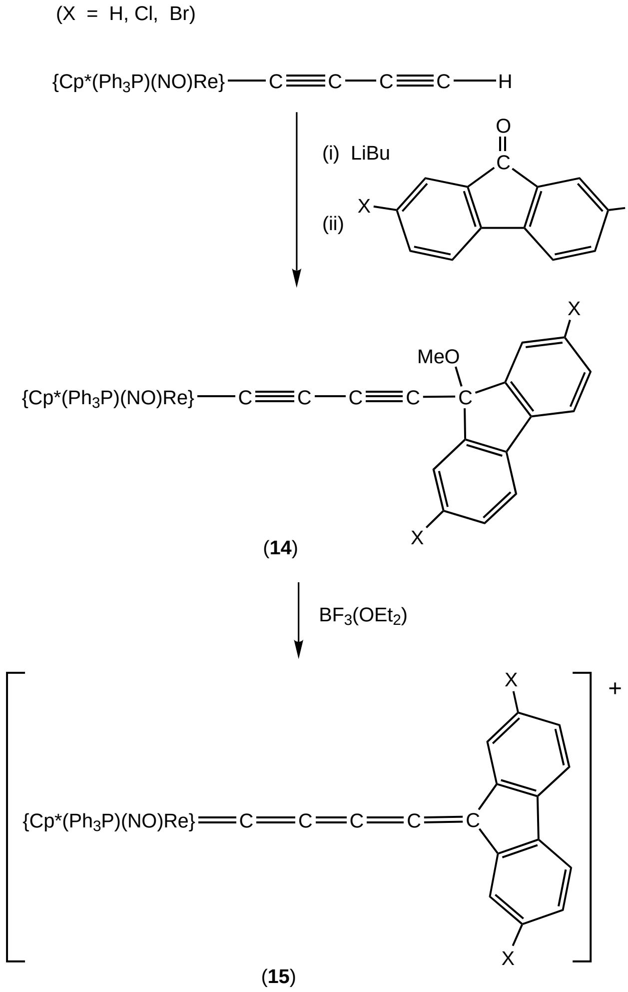
Formal insertion of the electron-rich alkyne MeC≡CNEt$_2$ into the C(4)=C(5) double bond of M{=C=C=C=C=C(NMe$_2$)$_2$}(CO)$_5$ (M = Cr, W) occurs by initial cycloaddition and subsequent ring-opening to give the air-stable heptapentaenylidenes (**13**; M = Cr, W) (Scheme 8) [23]. The major product is the *s-trans* conformer, but increasing amounts of the *s-cis* conformer appear on cooling below 280 K until at 233 K, a 1/3 mixture results.



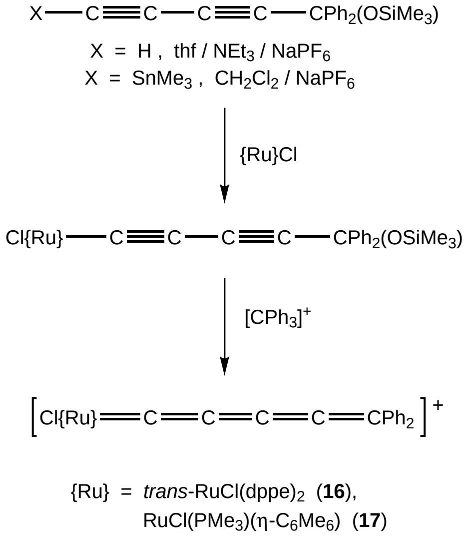
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

Lithiation (LiBu) of $Re(C\equiv CC\equiv CH)(NO)(PPh_3)Cp^*$ and reaction with fluorenone, followed by methylation, afforded the diynyl $Re\{C\equiv CC\equiv CCAr_2(OMe)\}(NO)(PPh_3)Cp^*$ (**14**; CAr_2 = 9-fluorenylidene) (Scheme 9) [24]. Analogous complexes were formed with 2,7-dihalofluorenones (X = Cl, Br). The dark blue cationic cumulenylidenes $[Re(=C=C=C=C=CAr_2)(NO)(PPh_3)Cp^*]^+$ (**15**) precipitated from reactions of the diynyls with $BF_3(OEt_2)$ at −45 °C. These complexes are reactive towards oxygen and decompose just above RT. Their IR spectra contain two $\nu(CCC)$ absorptions at 1993–1987 and 1902–1894 cm^{-1}, while the ^{13}C NMR spectrum contain down-field resonances at δ 256.9 with $J(CP)$ 10.8 Hz and 176.2, assigned to the Re–C and Ar–C carbons, respectively.

Pentatetraenylidene complexes are often obtained from reactions between 1,3-diynols and metal complexes or related chemistry. Care has to be taken, however, to ensure that solvents with little or no nucleophilic power are used, otherwise addition of solvent molecules such as alcohols, amines, etc., results in formation of substituted vinylidenes. This disadvantage has been overcome in some instances by protection of the OH group, e.g. as $OSiMe_3$, during the initial stages of the synthesis [25].

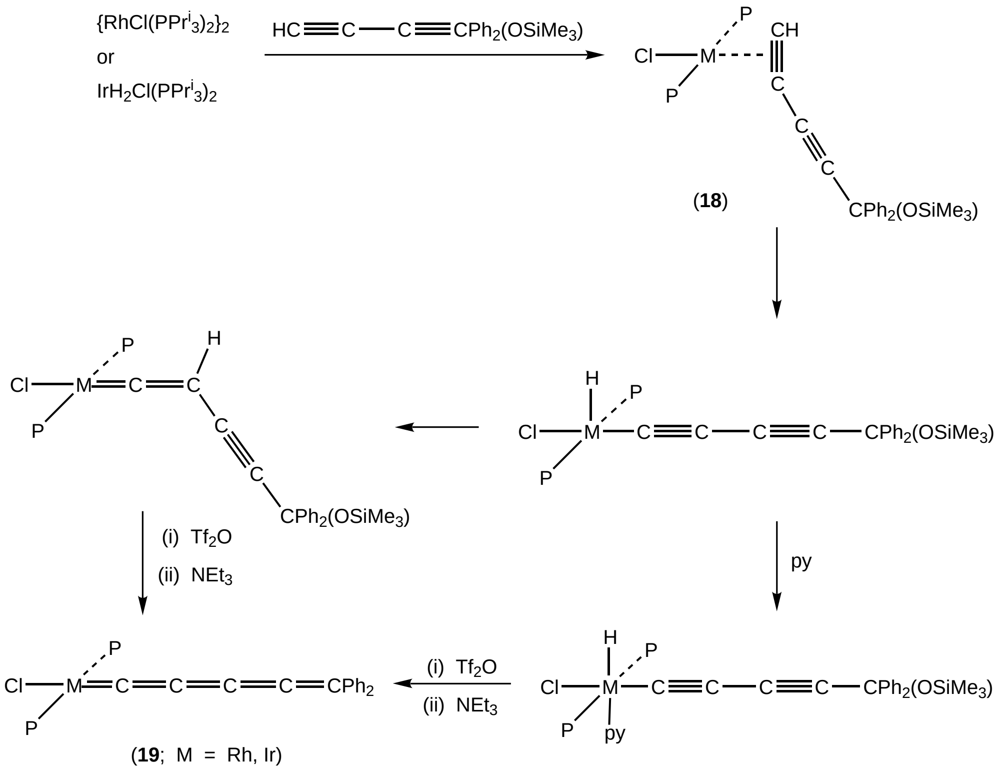
The first isolated example was deep blue *trans*-$[RuCl(=C=C=C=C=CPh_2)(dppe)_2]PF_6$ (**16**), obtained by reaction of $[CPh_3]^+$ with the diynyl complex from *cis*-$RuCl_2(dppe)_2$ and $HC\equiv CC\equiv CCPh_2(OSiMe_3)$ in the presence of both $NaPF_6$ and NEt_3 (Scheme 10) [6].

More stable complexes were obtained by using aryl groups containing electron-donating substituents, such as blue $[RuCl\{=C=C=C=C=C(C_6H_4NMe_2\text{-}4)_2\}(PMe_3)(\eta\text{-}C_6Me_6)]^+$ (**17**) which is stable in MeOH [26].

The Group 9 hydrido–diynyl complexes $RhHCl\{C\equiv CC\equiv CCPh_2(OSiMe_3)\}(PPr^i_3)_2$ and $IrCl\{C\equiv CC\equiv CCPh_2(OH)\}(PPr^i_3)_2$ have been obtained from $\{RhCl(PPr^i_3)_2\}_2$ and $HC\equiv CC\equiv CPh_2(OSiMe_3)$ or $IrCl(coe)(PPr^i_3)_2$ (coe = cyclooctene) and $HC\equiv CC\equiv CPh_2(OH)$, respectively, via intermediate η^2-alkyne derivatives **18**. Reaction of $HC\equiv CC\equiv CCPh_2(OH)$ with $IrH_2Cl(PPr^i_3)_2$ also gives the dark red hydrido(diynyl) complex. Subsequent reactions with Tf_2O and NEt_3 at low temperatures gave *trans*-$MCl(=C=C=C=C=CPh_2)(PPr^i_3)_2$ (**19**; M = Rh, Ir) (Scheme 11) [16,27]. The rhodium complex forms a deep violet viscous oil. The copper-brown solid iridium complex is strongly solvato-chromic [7], the colours of its solutions ranging from yellow through rose to violet.

5. Hexapentaenylidenes

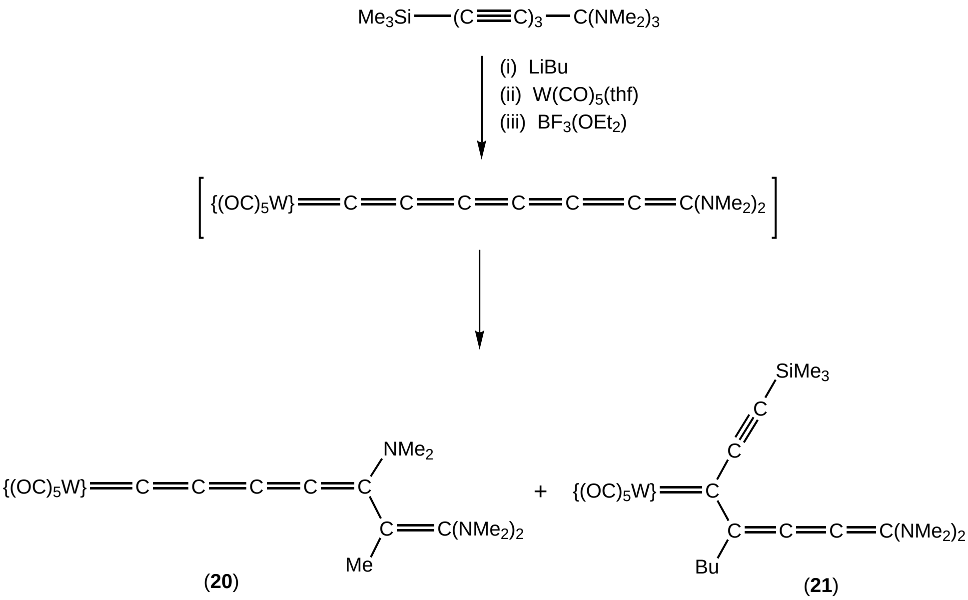
Protonation of $Re\{(C\equiv C)_3tol\}(NO)(PPh_3)Cp^*$ occurs at C(2) to give the corresponding vinylidene $[Re\{=C=CH[C\equiv CC\equiv C(tol)]\}(NO)(PPh_3)Cp^*]^+$ rather than the desired hexapentaenylidene complex [14].



Scheme 11.

6. Heptahexaenylidenes

Extension of the synthetic approach outlined above (Scheme 7) to the reaction between $SiMe_3(C{\equiv}C)_3C(NMe_2)_3$ with LiBu, followed by addition of $W(CO)_5(thf)$, gave only a mixture of $W\{=C=C=C=C=C(NMe_2)CH=C(NMe_2)_2\}(CO)_5$ (**20**) and $W\{=C(C{\equiv}CSiMe_3)CBu=C=C=C(NMe_2)_2\}(CO)_5$ (**21**), probably formed by addition of $NHMe_2$ to (undetected) $W\{=C=C=C=C=C=C=C(NMe_2)_2\}(CO)_5$ (Scheme 12) [9,23].



Scheme 12.

7. Spectroscopic properties

7.1. *Infra-red spectra*

Characteristic ν(CCC) absorptions for cumulated C=C double bonds appear in the range 1800–2100 cm^{-1} (Table 1), two bands being found for the :C=C=C=C=CR_2 complexes.

7.2. *Electronic spectra*

The intense colours of many of these complexes can be related to intervalence charge-transfer (IVCT) bands between 500–600 nm as expected from contributions from various canonical forms (see below) [23]. The tungsten cumulenylidenes show bathochromic shifts of the MLCT bands and increasing solvatochromism as the chain lengthens, e.g. $\Delta\nu$(PhMe-dmf) = 3980/3580 cm^{-1} for Cr/W [8]. Negative solvatochromism (where UV–vis λ_{max} move to shorter wavelengths as the solvent polarity increases) has been related to chain length and conformational effects. As the carbon chain lengthens, the energy of the LUMO is lowered with increasing separation of the charge centres. There is a corresponding bathochromic shift of the MLCT absorption and an increase in solvato-chromism.

7.3. ^{13}C *NMR spectra*

Table 1 also summarises the ^{13}C NMR chemical shifts for the cumulenylidene ligands, together with coupling constants if appropriate. There is a marked dependence on the nature of the ML_m fragment, with chemical shifts δ(C(1)) > δ(C(2)) > δ(C(3)) for complexes with $Fe(L_2)Cp$, $Ru(L)_2Cp$, $Ru(dppe/m)_2$ groups, δ(C(1)) > δ(C(3)) > δ(C(2)) for complexes with $M(CO)_5$, $Mn(CO)_2Cp$, RuCl(L)(η-arene) and Rh(L)Cp fragments, and δ(C(2)) > δ(C(1)) > δ(C(3)) for some $RhCl(PPr^i_3)_2$ complexes.

The characteristic pronounced low-field shift of C(1) [δ(C(1)) ~250–300 ppm], first recognised for vinylidene complexes, is also found in these spectra and has been ascribed to both diamagnetic [electron density on C(1), the most electron-deficient at lowest field] and paramagnetic effects (HOMO-LUMO gap). Some dependence on the extent of the mesomeric equilibrium has also been noted, together with influences from the terminal substituents (Ph versus NMe_2).

In NMe_2 derivatives of the Group 6 metal complexes, there is evidence for restricted rotation about the C(sp^2)–N bond, replacement by Ph resulting in a lower rotational barrier [8]. For W{=C=C=C=C=$C(NMe_2)_2$}$(CO)_5$ (**12**, M = W) two NMe_2 singlets are found, which coalesce at −83 °C ($\Delta G^{\#}_{rot}$ = 40 $\mathrm{kJ\,mol}^{-1}$), indicating that the C_5 ligand is a better π acceptor than the analogous vinylidene (non-fluxional at RT). Similarly with W{=C=C=C=C=$C(NMe_2)CH=C(NMe_2)_2$}$(CO)_5$, $\Delta G^{\#}_{rot}$ = 43, 47 (equlibration of the terminal NMe_2 groups) and 53 $\mathrm{kJ\,mol}^{-1}$ (rotation about the C_ϵ-NMe_2 bond). For R = Me, $\Delta G^{\#}$ = 64 $\mathrm{kJ\,mol}^{-1}$. Again, the results are consistent with the mesomeric equilibrium leading to a significant increase in the C–N bond order [9].

8. Non-linear optical (NLO) properties

The Group 6 complexes are very effective chromophores for NLO activity and show enhanced values for β (the first molecular hyperpolarisability) as the chain-length increases [23]. While addition of a conjugated C=C double bond only slightly enhances NLO response, an extra cumulated C=C double bond results in up to a four-fold increase in the value of β.

9. Electrochemistry

The allenylidene and pentatetraenylidene complexes containing *trans*-$RuCl(dppe)_2$ fragments undergo two 1-e reductions (CV) although the products have not yet been isolated [28]; reduction is easier for odd-numbered than for even-numbered chains. Generally, the 18-e Ru(II) configuration is preserved, with addition of the electron to the carbon chain.

CV studies showed partially reversible oxidations at $E_{1/2}$ +0.49, +1.06, +0.86 V for *trans*-RhCl{=C(=C)$_n$$Ph_2$}$(PPr^i_3)_2$ (n = 0, 1, 2, respectively) and irreversible processes at +1.23, +1.37, +1.31 V, respectively (values versus NHE). For n = 4, the first process ($E_{1/2}$ +0.90 V) is irreversible [29]. Corresponding electrochemical ligand parameters E_L [30] were determined as +0.51, +0.83, +0.71 for n = 0, 1, 2.

10. Structures

Relatively few structural details are available for complexes of this type, and the dimensions of the M–C_n chain show a pronounced dependence on the terminal substituents (Table 2). In contrast, differences in C–C distances were much less pronounced in the *trans*-$RuCl(dppe)_2$ and *trans*-$IrCl(PPr^i_3)_2$ complexes. In both types, however, the carbon chain is essentially linear, the maximum deviation at the carbon atoms being 6.5°.

The six possible resonance forms **A**–**F** (Scheme 13) have been considered for Group 6 complexes containing the :C=C=C=C=$C(NMe_2)_2$ ligand, the two ylidic ones being most important [8]. The short-long-short-long pattern of C–C bond lengths in M(=C=C=C=C=CR^1R^2)$(CO)_5$ [M = Cr, R^1 = NEt_2, R^2 = CMe=$C(NMe_2)_2$; M = W, R^1 = R^2 = NMe_2], is rationalised by a strong π interaction between the NMe_2 groups and the metal centre. Substantial contributions from tautomers **C**–**E** are indicated by the X-ray structure [C(10)–N 1.338(5) >C(8)–N 1.348(6) Å in the allenylidene], which shows that the amino N is almost planar (Σ 359.2°). There is a marked alternation in C–C bond lengths.

Similarly, the ground state of M{=C=C=C=C=$C(NMe_2)$CMe=$C(NMe_2)_2$ (**21**) is best considered as involving the

Table 2
Some bond distances (Å) and angles (°) for cumulenylidene complexes, $\{L_mM\}{=}(C)_n{=}CR^1R^2$

ML_m	R^1	R^2	M–C(1), *M–C(1)–C(2)*	C(1)–C(2), *C(1)–C(2)–C(3)*	C(2)–C(3), *C(2)–C(3)–C(4)*	C(3)–C(4), *C(3)–C(4)–C(5)*	C(4)–C(5)	Reference
Butatrienylidenes								
Mn(dppe)Cp	$SnPh_3$	$SnPh_3$	1.769(4), *173.5(4)*	1.296(5)	1.264(5), *175.5(5)*	1.316(5)		[13]
trans-IrCl(PPr^i_3)$_2$	Ph	Ph	1.816(6), *175.1(5)*	1.283(8), *178.1(6)*	1.275(8), *178.7(7)*	1.339(8)		[4,22]
Pentatetraenylidenes								
$Cr(CO)_5$	NEt_2	CMe=C(NMe_2)$_2$	2.041(6), *175.4(6)*	1.219(8), *177.1(7)*	1.379(8), *178.8(7)*	1.209(9), *180.0(10)*	1.433(8)	[23]
$W(CO)_5$	NMe_2	NMe_2	2.144(6)	1.223(9)	1.361(9)	1.192(9)	1.399(9)	[8]
trans-RuCl(dppe)$_2$ [BF_4 salt]	Ph	Ph	1.891(9), *179(1)*	1.25(1), *178(1)*	1.30(1), *179(1)*	1.24(1), *178(1)*	1.36(1)	[6]
trans-IrCl(PPr^i_3)$_2$	Ph	Ph	1.834, 1.821(5), *176.8*, *173.8(5)*	1.261, 1.278(6), *175.8*, *175.6(5)*	1.296, 1.279(6), *177.1*, *178.9(5)*	1.259, 1.249(6), *174.8*, *177.6(6)*	1.344, 1.343(6)	[7]

cumulene (**G**) but dominated by the dipolar mesomers **H**–**J** (Scheme 14) [23]. The structural determination shows strong alternation of the C–C bond lengths and short =C–N bond lengths.

In Mn{=C=C=C=C(SnPh$_3$)$_2$}(dmpe)Cp, some deviations from linearity are found in the C_4 chains [angles at C 170.6–175.5(5)°], with Mn=C [1.769(4) Å] and C=C bond lengths consistent with the cumulenic formulation [13]. However, the terminal C=C bond is longer, at 1.316(5) Å, as also found in *trans*-IrCl(=C=C=C=CPh$_2$)(PPr^i_3)$_2$ (see below).

The structure of the ruthenium complex Ru{C≡CC(OCOCF$_3$)=CMe$_2$}(PPh$_3$)$_2$Cp (**6**) is variously interpreted as the butatrienylidene "trapped" by the tfa anion, or as the product of nucleophilic addition of the anion to C(3) of the cumulene ligand [11]. Either way, the subsequent chemistry of this species is consistent with the intermediacy of the unsaturated carbene complex. The relative stability of [RuCl{=C=C=C=C=C($C_6H_4NMe_2$-4)$_2$}(PMe$_3$)(η-C_6Me_6)]$^+$ is ascribed to mesomeric contributions from three tautomeric forms involving the NMe_2 group [26].

The iridium complex *trans*-IrCl(=C=C=C=CPh$_2$)(PPr^i_3)$_2$ contains an almost linear IrC_4 chain, with an Ir=C(1) distance [1.816(1) Å] shorter than that found in the analogous allenylidene *trans*-IrF(=C=C=CPh$_2$)(PPr^i_3)$_2$ [1.853 (19) Å] or pentatetraene [1.834(5) Å]. While the internal C=C bonds are experimentally identical [1.283, 1.275(8) Å], the C(3)=C(4)Ph$_2$ separation is longer [1.339(8) Å] [4,22]. Solvent-induced spectral changes found for *trans*-IrCl(=C=C=C=C=CPh$_2$)(PPr^i_3)$_2$ indicate contributions from the zwitterionic mesomer.

11. Electronic properties

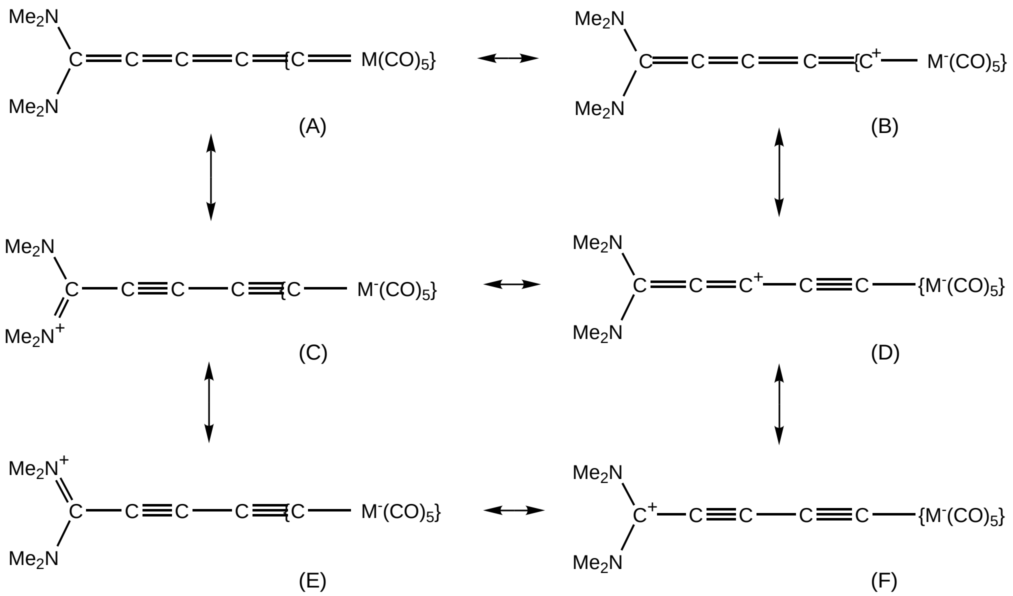
Comparison of cumulenylidene complexes shows that W(CO)$_5$ is a better π acceptor than (OC)$_5$WC$_2$ [8]. Lengthening the chain from C_3 to C_5 lowers the energy of the LUMO and increases the δ+/δ− separation. The extra C_2 unit is considered to have only a marginal effect on the bonding compared with the corresponding vinylidene.

The relative π-accepting powers of several ligands attached to *trans*-MCl(PPr^i_3)$_2$(M = Rh, Ir) centres have been probed extensively through spectroscopic and electrochemical studies [29]. Structural (M–C distances) and computational studies (below) are also consistent with the series of increasing π-acceptor ability

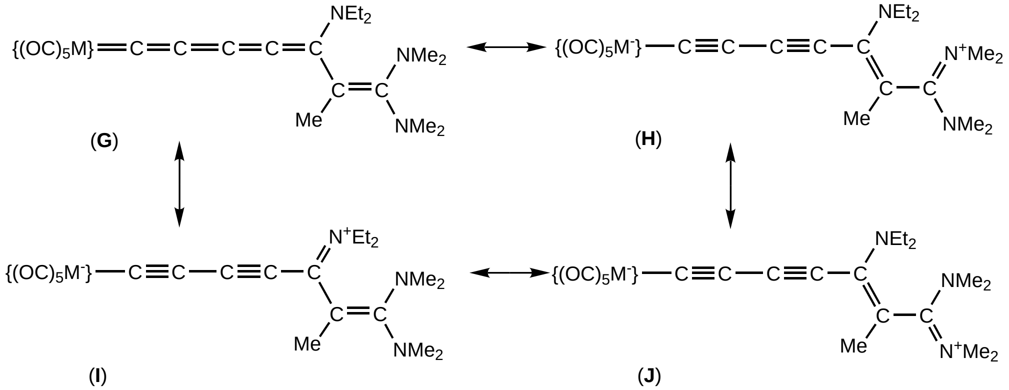
$$:CPh_2 <: C{=}C{=}CPh_2 \sim: C{=}C{=}C{=}C{=}CPh_2$$
$$<: C{=}CPh_2 < CO$$

12. Theory

The electronic structures of several metal complexes containing unsaturated carbenes have been probed using DFT



Scheme 13.



Scheme 14.

or other methods. For the series $\mathrm{Cr\{=(C=)_{n}CH_2\}(CO)_5}$ [31] and specifically for *trans*-$\mathrm{[RuCl(=C=C=C=CH_2)(PH_3)_4]^+}$ [32,33], the HOMO and LUMO are largely composed of orbitals from the metal fragments and either the occupied or unoccupied π orbitals of the C_n fragment. The former is orthogonal and the latter parallel, to the plane of the terminal $\mathrm{CH_2}$ group. Comparison of the Cr and Ru systems shows that the $\mathrm{C_4H_2}$ ligand is insensitive to the nature of the ML_m fragment. The HOMO is found mainly on the metal centre and C(2) and C(4) (ca. 39, 16 and 19% for Cr, 30, 16 and 20% for Ru), whereas the LUMO is predominantly on C(1) and C(3) (>70%), with only 13 and 17% on Cr and Ru, respectively. These results indicate that nucleophilic addition is orbitally controlled, with no selectivity between C(1) and C(3), suggesting that the experimentally observed attack at C(3) is sterically controlled.

A notable feature of the butatrienylidene–manganese complexes described above is the pronounced stability of the bis-$\mathrm{SnPh_3}$-substituted derivatives [13]. The model compounds $\mathrm{Mn(=C=C=C=CR_2)(PH_3)_2Cp}$ (R = $\mathrm{SnMe_3}$, H) have been compared using DFT calculations, which show that while the HOMOs themselves are similar for both molecules, the $\sigma(\mathrm{H–C_\delta–H})$ and $\sigma(\mathrm{Sn–C_\delta–Sn})$ orbitals differ substantially in energy. The latter makes a bonding interaction with a π-type orbital of the $\mathrm{C_4}$ chain while the $\mathrm{CH_2}$ interaction repels the π orbitals. These calculations also enabled the observed distortions in the C–C–Sn systems [angles 112.0, 122.6(3)° for R = $\mathrm{SnMe_3}$, H, respectively], to be rationalised.

The electronic structures of *trans*-$\mathrm{[RuCl(C_{n}H_2)(PH_3)_4]^+}$ (n = 1–8), which are models for several isolated complexes in the series *trans*-$\mathrm{[RuX(C_{n}R_2)(dppe)_2]^+}$ (X = Cl, CCPh; R = Me, Ph; n = 3, 5) and their 1-e reduced products, have been studied by DFT methods [32,33]. In general, the Ru–C distances increase with increasing n, being longer for odd n than for even n: the asymptotic Ru–C distance is 1.92 Å, i.e. an Ru=C double bond. Similarly, as n increases, the HOMO/LUMO gap decreases, with increasing localisation on the carbon chain. The HOMO is an anti-bonding combination of the HOMOs of the carbon chain and metal–ligand fragments. Odd *n* systems are thermodynamically more stable than those with even *n*.

13. Reactivity

Analysis of reactivity in terms of orbital control and charge distribution suggest that the former directs nucleophilic attack to C(odd), although charge control disfavours C(1), in agreement with experiment which shows nucleophilic attack to occur at C(3) and C(5). Steric protection of C(1) by bulky PR_3 ligands is also a factor. Electrophilic attack should occur at C(even) (orbital control) except for the terminal CH_2 group, but charge control disfavours the distal carbon. Experimentally, protonation is found to occur at C(2).

The structures of products obtained by addition of two electrons to these systems can be expressed by several canonical formulas, some of which involve $C(sp^2)$ or terminal $C(sp^3)$ atoms, which would be expected to result in some bending of the carbon chain in the mono-anion. Calculations gave a bent chain only for $n = 2$ only [with Ru–C(1)–C(2) 146°]. Calculated changes in bond lengths include lengthening of the Ru–C(l) bond (but decreasing with n) and shortening of some C–C bonds, especially C(1)–C(2). For the anions, ready phosphine dissociation is predicted together with short C(1)–C(2) bonds and significant bending at C(1).

Early studies using extended Hückel methods revealed the alternating electron-poor/electron-rich character of the carbons with C(1) being the most electrophilic [34,35]. Later, density functional studies have quantified this feature, showing a rapid attenuation of the effect as the chain length increases beyond four carbons. However, the electrophilicity of the inner C(1) and C(3) atoms increases with increasing chain length.

The pattern of alternating electron densities results in nucleophilic attack occurring at C(1), C(3), ... and electrophilic attack at C(2), C(4), ... (Scheme 15). The latter can occur to give carbyne complexes. Alternatively, allenyl derivatives can be formed by attack at the M–C(1) bond. The bipolar character enables cyclisation (cycloaddition) reactions to be carried out, e.g., with molecules containing an acidic H and nucleophilic centres. Experimentally, particularly in tertiary phosphine-containing complexes, significant steric protection is afforded to C(1) and C(2), so that reactions occur at the outer carbons.

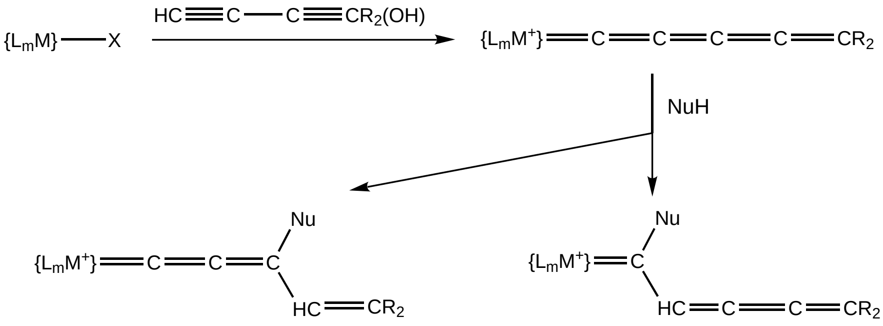
In complexes $\{L_mM\}(C{\equiv}C)_nR$, the alternation in reactivity is most pronounced if R is an electron-withdrawing group. If reactions are under charge control, C(2) is significantly more reactive than C(4), i.e. protonation of $Ru(C{\equiv}CC{\equiv}CH)(PPh_3)_2Cp$ would be expected to occur at C(2), so that the experimental observation of addition at C(4) is surprising. However, this course may be determined by the bulk of the ligands attached to Ru [the Ph groups of the PPh_3 ligands provide a degree of steric protection extending over C(1) and C(2)]. Alternatively, initial addition to C(2) may occur, followed by subsequent (fast) rearrangement. With $M(CO)_nCp$ complexes, the alternation in reactivity is attenuated, with a net decrease of 30% between analogous CO and PH_3 derivatives. The oxidatively-induced structural reorganisations to cumulenes are predicted to proceed best with C_4 chains [15].

Anionic nucleophiles (hard bases, X^-, MeO^-, Me_2N^-) generally react with the HOMO on C(1) in allenylidene complexes to give anionic intermediates which can be protonated to vinylcarbenes. Neutral molecules (soft bases, high-energy lone pairs) add to the LUMO on C(3) to give substituted alkynyl complexes. Where carbon nucleophiles are used, a variety of reaction pathways are followed which depend not only on the nucleophile but also on the ligands present on the metal centre.

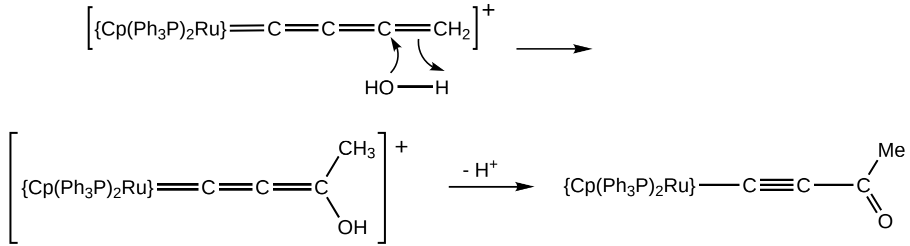
In the $RuCl(PMe_3)(\eta\text{-}C_6Me_6)$ system (ML_m in Scheme 15), both isomers have been isolated from the interaction with MeOH, further reaction with water resulting in formation of the chelate complex **47** mentioned below.

14. Butatrienylidenes

As expected, electrophiles generally react at C(2) or C(4) and nucleophiles at C(1) or C(3). Elsewhere, the utility of allenylidenes as precursors of a variety of metal-bound heterocycles by reaction with difunctional or unsaturated nucleophiles has been reported [36]. Extension to analogous reactions of butatrienylidenes, while presently somewhat limited in scope, has shown that these derivatives can also act as sources of unusual compounds. Difunctional protic

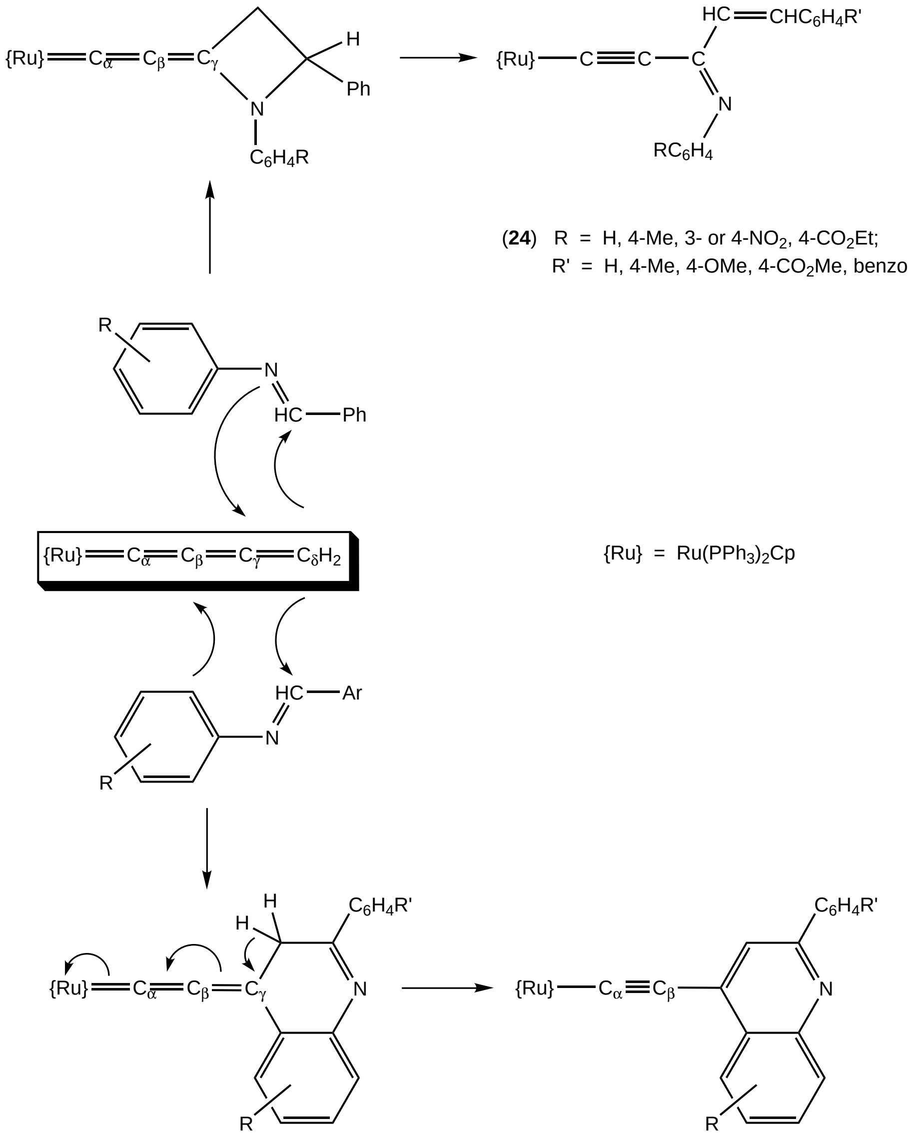


Scheme 15.



(**22**) (**23**)

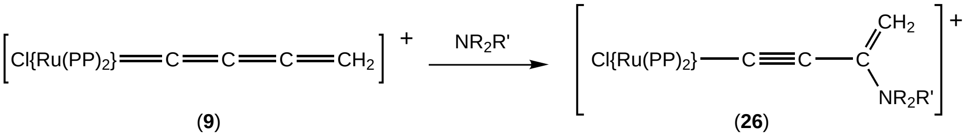
Scheme 16.



(**24**) R = H, 4-Me, 3- or 4-NO_2, 4-CO_2Et;
R' = H, 4-Me, 4-OMe, 4-CO_2Me, benzo

(**25**) R = H, 4-Me, 4-OMe, 3,5-Cl_2, benzo;
R' = H, 3- or 4-NO_2, 4-CO_2Me

Scheme 17.



Scheme 18.

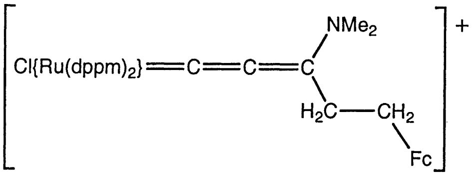
nucleophiles may cycloadd to give five-membered rings with pendant groups, often with accompanying hetero-Cope or Claisen-type [3,3]-sigmatropic rearrangements (see below).

In the initial account of the chemistry of Ru(C≡CC≡CH)$(PPh_3)_2$Cp, protonation to form the butatrienylidene cation is described, but isolation was hampered by the ready reaction of the latter with even traces of water to give Ru{C≡CC(O)Me}$(PPh_3)_2$Cp (**22**) (Scheme 16). Addition of water to C(3) and C(4) gives the hydroxy (methyl)allenylidene **23** which is then deprotonated [17].

Later studies showed that cycloaddition of aromatic imines gives two types of products, either 1-azabuta-1,3-dienes (**24**) or 4-ethynylquinolines (**25**) (Scheme 17) [37,38]. These reactions proceed either by attack of C_δ at the imine carbon, followed by bond formation between C_γ and the *ortho* carbon of the *N*-aryl group, or by cyclo-addition of C_γ=C_δ to the N=CH group, followed by ring-opening. A benzo[*h*]quinoline complex was obtained from PhCH=N(2-$C_{10}H_7$), whereas the azabutadienyl analogue was formed with PhN=CH(1-$C_{10}H_7$). Some preference for quinoline formation is evident with the more electron-rich metal centres, whereas azabutadienes are formed with ArCH=NAr (Ar = 4-RC_6H_4, R = Me, OMe).

Protonation ($HBF_4 \cdot OEt_2$) of *trans*-RuCl(C≡CC≡CSiMe_3)$(dppe)_2$ afforded the acylvinylidene *trans*-[RuCl{=C=CHC(O)Me}$(dppe)_2$]$^+$, most likely by addition of water to the intermediate butatrienylidene *trans*-[RuCl(=C=C=C=CH_2)$(dppe)_2$]$^+$ [39–41]. Reactions of *trans*-[RuCl(=C=C=C=CH_2)$(PP)_2$]$^+$ (**9**, PP = dppm, dppe) with a variety of amines occur by regioselective addition to C_γ, which is favourable both sterically and electronically. Thus, NEt_3 or benzylamines $NMe_2(CH_2Ar)$ (Ar = Ph, C_6H_4OMe-3) give the cationic alkynyl derivatives **26** (Scheme 18) [18,42]. On heating (85 °C), the latter give only intractable mixtures. Similar addition of EtSH gave *trans*-[RuCl{=C=C=CMe(SEt)}(PP)]$^+$ by H migration to the terminal =CH_2 group [43].

With $FcCH_2NMe_2$, allenylidene *trans*-[RuCl{=C=C=C$(NMe_2)CH_2CH_2Fc$}$(dppm)_2$]$^+$ (**27**) was obtained, being formed by rearrangement of first-formed *trans*-[RuCl{C≡CC(NMe_2CH_2Fc)=CH_2}$(dppm)_2$]$^+$ (also isolated as a minor product) by migration of the resonance-stabilised $FcCH_2^+$ carbonium ion [44].

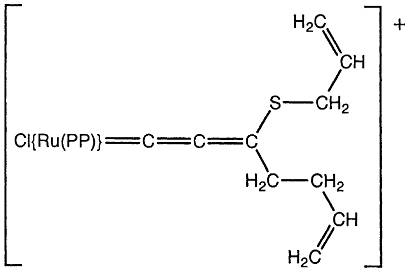


(**27**)

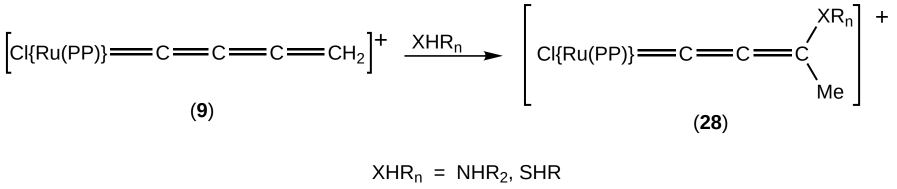
In contrast, secondary amines (NHR_2 or NHRR’) give directly *trans*-[RuCl{=C=C=CMe(NRR’)}$(PP)_2$]$^+$ (**28**), the (undetected) intermediate alkynyls *trans*-[RuCl{C≡CC(NHRR’)=CH_2}$(PP)_2$]$^+$ undergoing fast proton migration to the terminal CH_2 group (Scheme 19) [45]. A range of open chain and heterocyclic amines was used. Hindered rotation about the C(3)–N bond is found in the products, but no rearrangements analogous to the Cope rearrangement. *N*,*N*-Diethyl-2,5-Me_2-4-hydroxybenzylamine afforded *trans*-[RuCl{=C=C=CMe(NEt_2)}$(PP)_2$]$^+$ via an intermediate ammonio complex.

Allyl-substituted aprotic nucleophiles add to **9** to give vinyl cations **29** which undergo hetero-Cope (or hetero-Claisen) rearrangements to form allenylidenes **30.** The resulting cationic complexes show structures intermediate between alkynyls and the mesomeric allenylidenes, the stability of the former being enhanced by increasing donor power of the hetero-atom (Scheme 20) [32,43,46]. A range of substituents is tolerated, but intermediates **29** were only isolated with propargyl and tetrahydropyridyl amines. On heating, the former smoothly isomerised to the allenylidene, but the products from the latter were not identified.

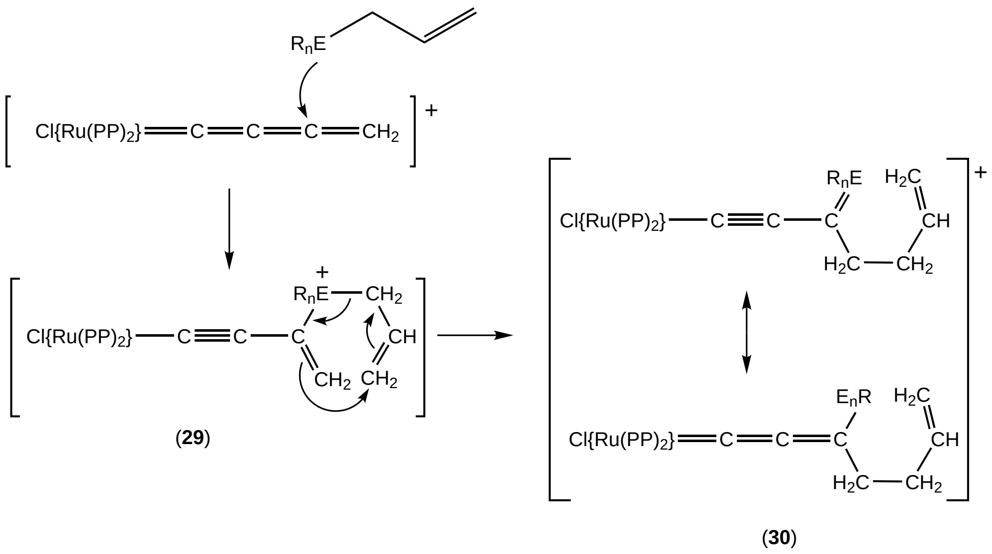
Diallyl sulfide reacts in similar fashion to give **31** [46].



(**31**)



Scheme 19.

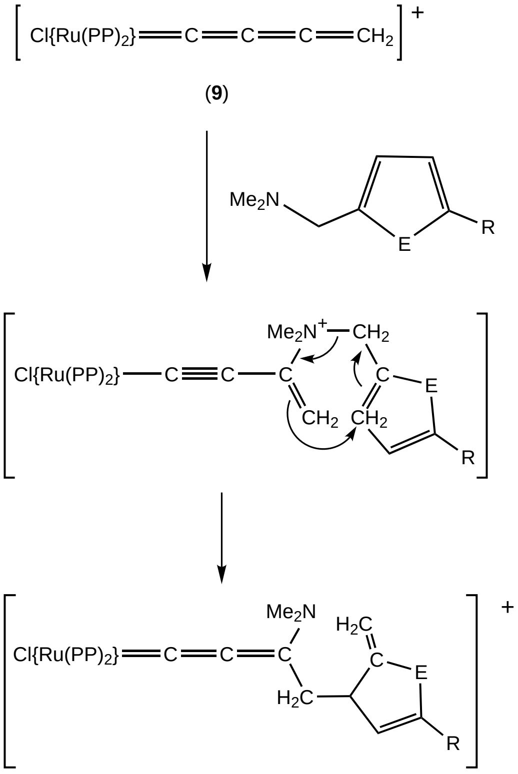


(**29**)

(**30**)

Scheme 20.

Addition of dimethylaminomethyl-substituted *O*-, *S*- and *Se*-heterocycles results in the formation of allenylidenes containing 2-methylene-2,3-dihydro heterocyclic substituents (**32**) (Scheme 21) [36]. The initial 2-ammoniobutenynyl derivative slowly transforms (days) at RT into the dimethylamino-allenylidene containing the heterocyclic substituent.



(**9**)

(**32**)

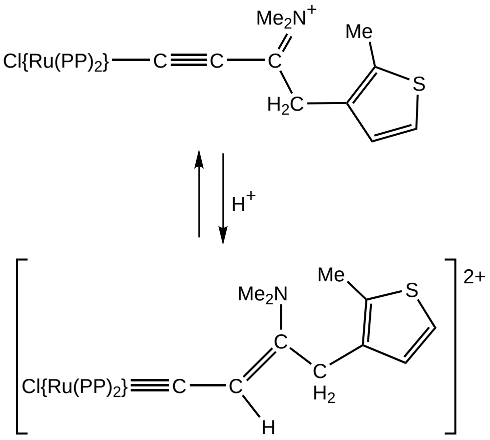
E = O, S, Se, R = H
E = O, R = CH_2OH

Scheme 21.

Examples with dihydro-furan, -thiophene and -selenophene groups were obtained.

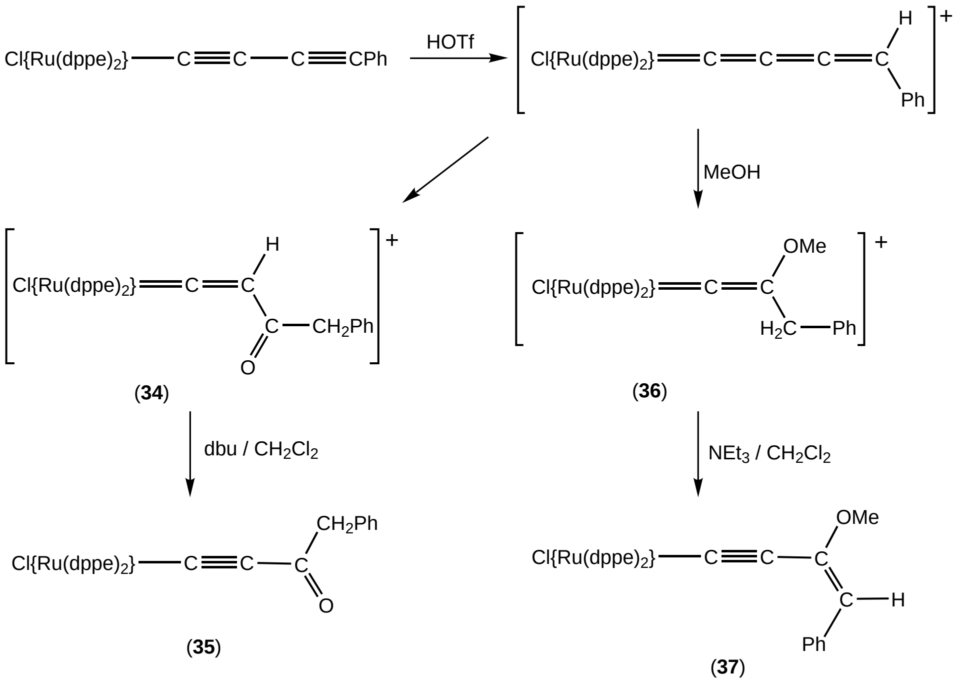
Further isomerization by 1,3-proton shift forms the corresponding furan or thiophene, a reaction which is quantitatively catalysed by strong acids ($HBF_4 \cdot Et_2O$). In the presence of an excess of HBF_4, the thiophene is protonated to a dicationic iminium-vinylidene (or aminovinylcarbene) (**33**) (Scheme 22).

Protonation of yellow *trans*-RuCl(C≡CC≡CPh)(dppe)$_2$ (HOTf in CH_2Cl_2) results in immediate formation of a bright red colour, which changes to green within seconds as the keto-vinylidene cation *trans*-[RuCl{=C=CHC(O)CH$_2$Ph}(dppe)$_2$]$^+$ (**34**) formed. This could be deprotonated to *trans*-[RuCl{C≡CC(O)CH$_2$Ph}(dppe)$_2$ (**35**) (Scheme 23) [19]. In the presence of MeOH, addition across the C(3)=C(4) double bond of the butatrienylidene afforded methoxyallenylidene (**36**), which was deprotonated to *trans*-RuCl{C≡CC(OMe)=CHPh}(dppe)$_2$ (**37**).



(**33**)

Scheme 22.



Scheme 23.

Metathetical reactions of *trans*-IrCl(=C=C=C=CPh$_2$)(PPr$^{i}_{3}$)$_2$ (**10**) with I$^-$, OH$^-$, N$_3{}^-$ (X$^-$) give deep coloured *trans*-IrX(=C=C=C=CPh$_2$)(PPr$^{i}_{3}$)$_2$, further transformation of the hydroxo complex to the phenoxide occuring with phenol in benzene solution (Scheme 24) [4,22]. In MeOH, the hydroxo complex formed the butatrienyl derivative IrH$_2$(CH=C=C=CPh$_2$)(CO)(PPr$^{i}_{3}$)$_2$ (**38**).

Methylation at the iridium centre occurs in the reaction between **10** and LiMe to give the very unstable IrMe(=C=C=C=CPh$_2$)(PPr$^{i}_{3}$)$_2$, which with CO gives *trans*-Ir{C(=CPh$_2$)C≡CMe}(CO)(PPr$^{i}_{3}$)$_2$ (**39**) by migratory insertion of the carbene into the Ir-Me bond. Similarly, insertion into the Ir–N$_3$ bond gives initially *trans*-Ir{C≡CC(N$_3$)=CPh$_2$}(CO)(PPr$^{i}_{3}$)$_2$ (**40**) which rearranges slowly in benzene to give the butatrienyl *trans*-Ir{C(N$_3$)=C=C=CPh$_2$}(CO)(PPr$^{i}_{3}$)$_2$ (**41**) [22]. The reaction with CF$_3$CO$_2$H gives the vinylvinylidene *trans*-IrCl{=C=CHC(tfa)=CPh$_2$}(PPr$^{i}_{3}$)$_2$ (**42**), i.e. addition of HX to the Cβ=Cγ bond, rather than the expected nucleophilic attack at Cα. This contrasts with Ru complexes, which add HX at the Cγ=Cδ bond. With HCl, oxidative addition to **10** occurs to give butadienyl IrCl$_2$(CH=CHCCl=CPh$_2$)(PPr$^{i}_{3}$)$_2$ (**43**), possibly via the vinylidene *trans*-IrCl(=C=CHCCl=CPh$_2$)(PPr$^{i}_{3}$)$_2$.

15. Pentatetraenylidenes

The Group 6 complexes **12** show pronounced reactivity at C$_\gamma$, such as the rapid quantitative addition of NHMe$_2$ to give M{=C=C=C(NMe$_2$)CH=C(NMe$_2$)$_2$}(CO)$_5$ (**13**) (above, Scheme 8) [8].

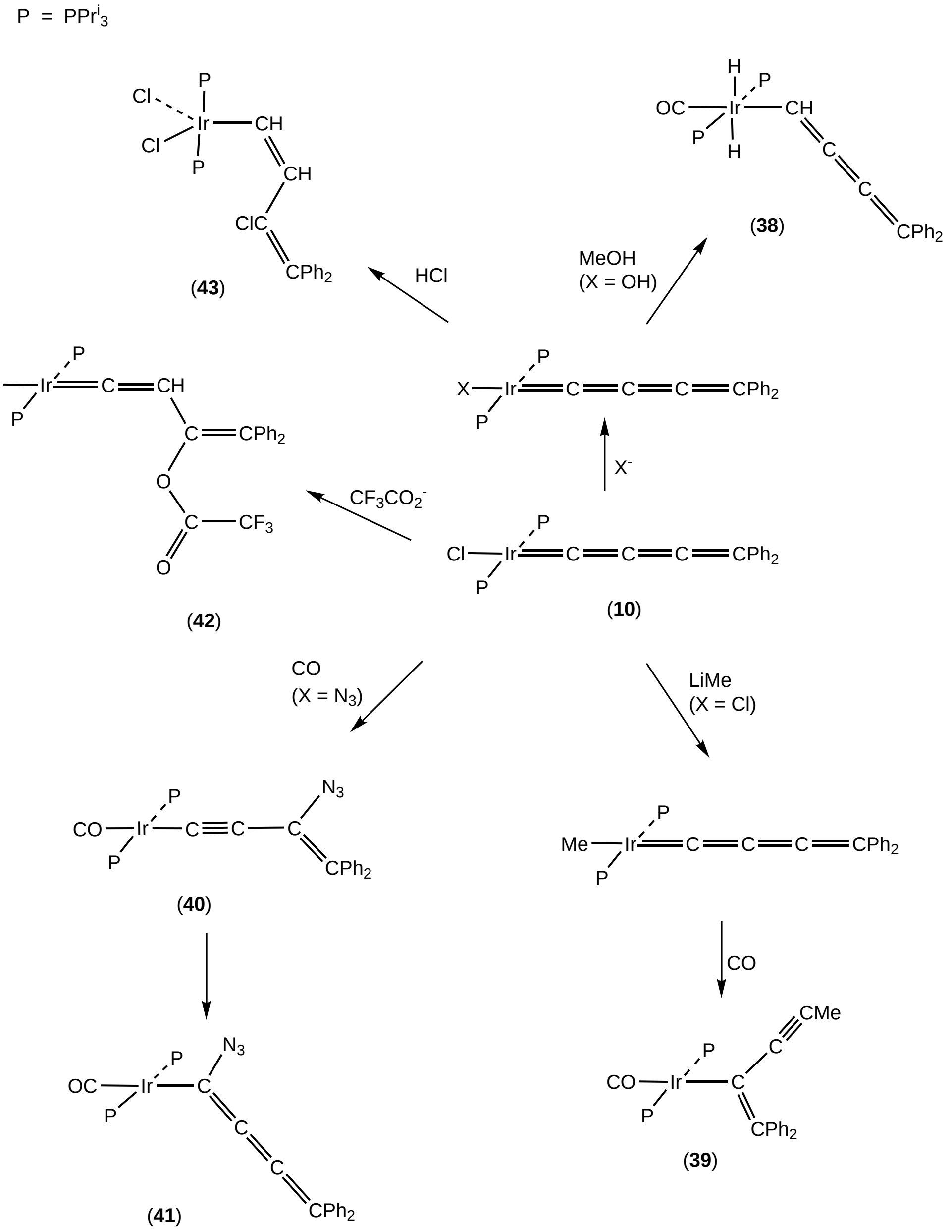
Treatment of *trans*-[RuCl(=C=C=C=C=CPh$_2$)(dppm)$_2$]$^+$ (**9**) or [RuCl(=C=C=C=C=CPh$_2$)(PMe$_3$)(η-C$_6$Me$_6$)]$^+$ (**17**) with alcohols or secondary amines in the presence of HBF$_4$ resulted in addition of the nucleophilic solvent across the C(3)=C(4) double bond to give **44**. In dichloromethane, electrophilic cyclisation of C(3) with one of the Ph groups occurred to give **45** (Scheme 25) [6,47]. The same complexes were isolated from reactions between *cis*-RuCl$_2$(dppm)$_2$ and HC≡CC≡CCPh$_2$(OSiMe$_3$), carried out in the presence of NaPF$_6$, either in MeOH or NHEt$_2$, or in dichloromethane, respectively.

The previously unknown, highly reactive cumulene 1,1-diphenylhexapentaene can be trapped as its rhodium complex (**46**) in the reaction between diazomethane and **19** (M = Rh) (Scheme 26) [16]. A 1:1 mixture of the η^2(1,2) and η^2(2,3) isomers was formed.

16. Reactions implicating cumulenlidene complexes

As mentioned above, the reactivity of cumulenylidene complexes with even weakly nucleophilic solvents often results in transformations to complexes containing substituents with less unsaturation. The reaction between FeCl(dppe)Cp* and HC≡CC≡CSiMe$_3$ in MeOH affords allenylidene [Fe{=C=C=CMe(OMe)}(dppe)Cp*]$^+$ by addition of MeOH to a presumed butatrienylidene intermediate [48].

Initial attempts to produce a pentatetraenylidene complex by the reaction between RuCl$_2$(PMe$_3$)(η-C$_6$Me$_6$) and HC≡CC≡CCPh$_2$(OH) in methanol afforded the chelate complex **47** (Scheme 27) [25,49]. Formation of this deriva-

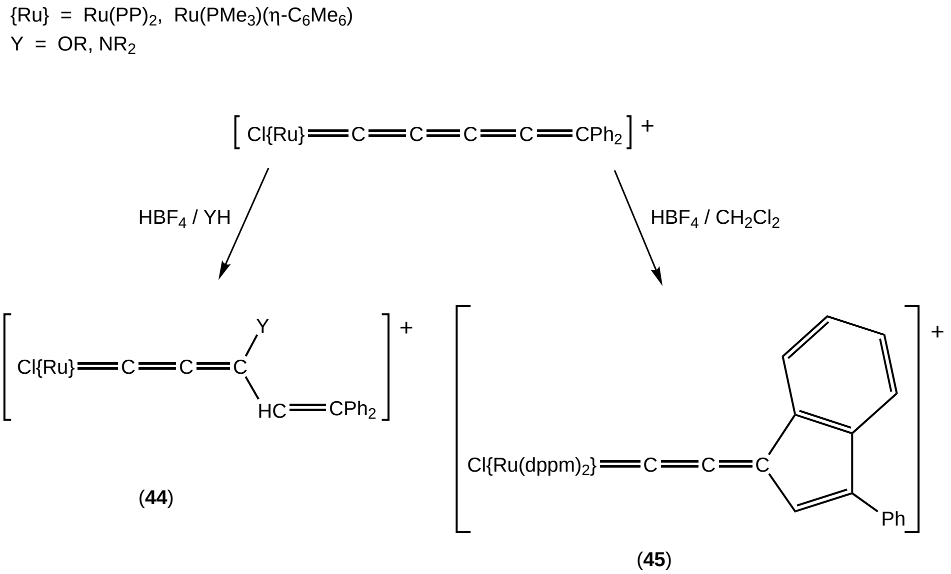


Scheme 24.

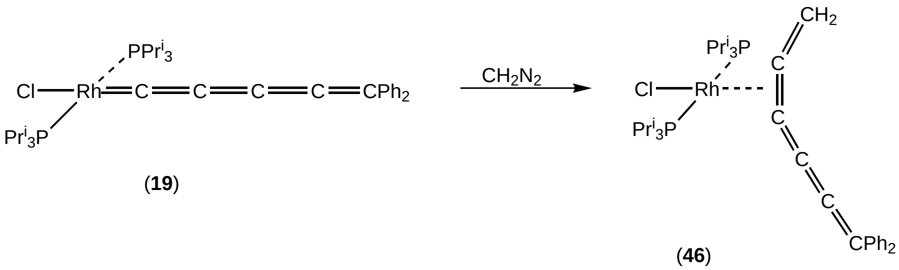
tive is considered to occur by attack of MeOH at C(1) and water at C(3), followed by ketonisation of the resulting enol.

While the reaction of $RuCl_2\{(PPh_2CH_2CH_2)_3N\}$ with $HC{\equiv}CCPh_2(OH)$ affords the expected allenylidene complex, a similar reaction with $HC{\equiv}CC{\equiv}CCPh_2(OH)$ gave an allenylidene, namely $[RuCl\{=C=C=C(OMe)CH=CPh_2\}\{(PPh_2CH_2CH_2)_3N\}]^+$, possibly formed by addition of MeOH at C(3) and C(4) of the intermediate pentatetraenylidene derivative $[RuCl(=C=C=C=C=CPh_2)\{(PPh_2CH_2CH_2)_3N\}]^+$ [50].

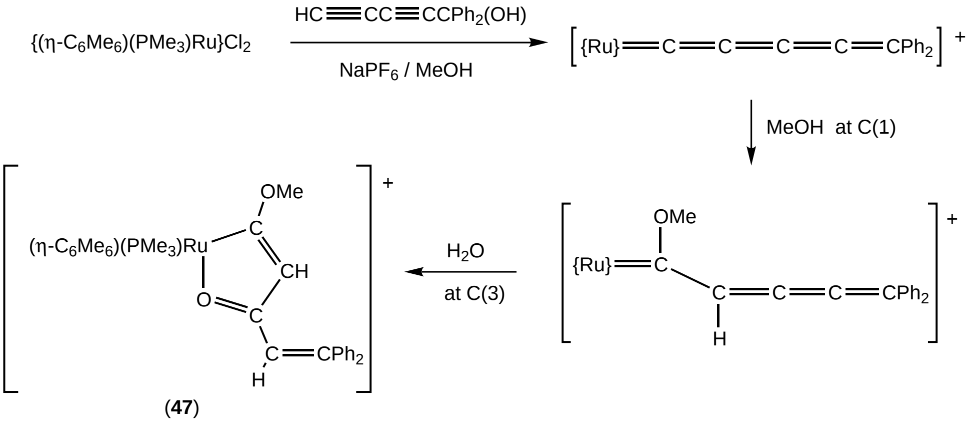
Oxidation of *trans*-$RuCl(C{\equiv}CC{\equiv}CSiMe_3)(dppe)_2$ gave a mono-cation which has a structure containing a significant contribution from the cumulenic form $[\{Ru\}=C=C=C=CSiMe_3]^+$, while the parent butadiynyl is highly reactive. Chemical oxidation ($[FeCp_2]^+$, one-half equivalent) afforded the dark purple cyclobutenylidene cation **48**, probably via a [2 + 2]-cycloaddition of the butatrienylidene with the diynyl complex [51]. A related intermediate has been postulated to add to allenylidene complexes to give binuclear complexes **49** containing a seven-carbon bridge (Scheme 28) [51]. Related chemistry has been found in the Ru(dppe)Cp* series, reactions of $Ru(C{\equiv}CC{\equiv}CSiMe_3)(dppe)Cp^*$ affording a mixture of substituted cyclobutenylidenes and ethynylvinyl-allenylidenes analogous to **48** and **49** [52].



Scheme 25.



Scheme 26.

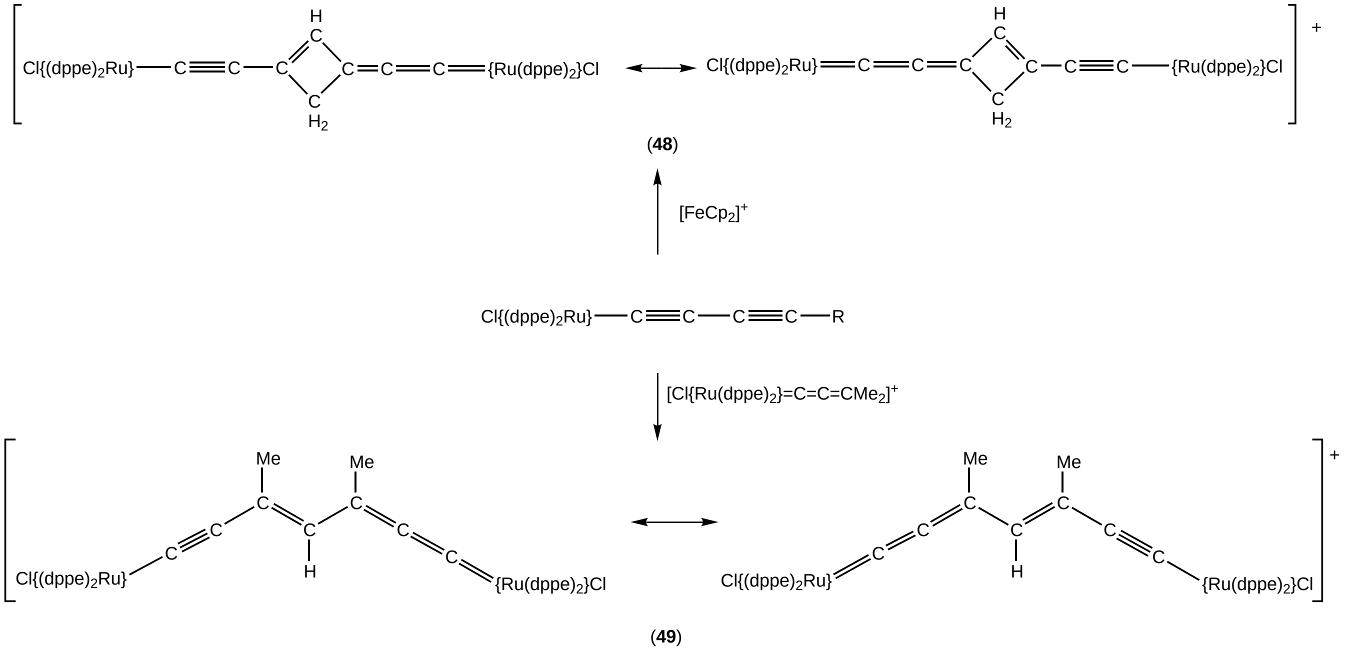


Scheme 27.

17. Binuclear butatrienylidenes

An alternative type of complex has been obtained by protonation ($HBF_4.OEt_2$) of the diyndiyl complexes {Cp*(PP)Fe}C≡CC≡C{$Fe(CO)_2Cp^*$} (**50**; PP = dppe, dippe) to give the novel butatrienylidenes [{Cp*(PP)Fe}=C=C=C=CH{$Fe(CO)_2Cp^*$}]BF_4 (**51**) containing a metal–ligand fragment at each end of the C_4 chain (Scheme 29) [5]. Deprotonation of **51** occurs with dbu to give back **50** quantitatively. The methyl-substituted complexes [{Cp*(PP)Fe}=C=C=C=CMe{$Fe(CO)_2Cp^*$}]OTf (**52**) obtained from similar reactions with methyl triflate were somewhat more stable, but all complexes are light and air-sensitive purple solids.

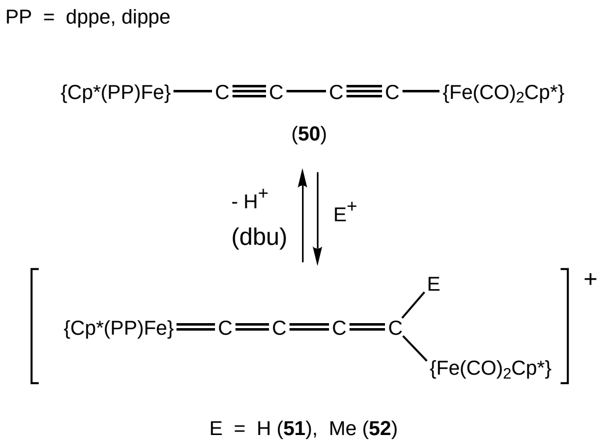
Addition of the electrophile to the carbon bearing the $Fe(CO)_2Cp^*$ group was confirmed by the ^{13}C NMR spectra, in which this carbon showed a large *J*(CH) coupling (ca. 180 Hz). The anticipated down-field shift of the other Fe-



Scheme 28.

bonded carbon to ca. δ 260 [showing J(CP) ca. 35 Hz] is also characteristic of this formulation. The IR spectra contained ν(CCC) absorptions at *ca* 1950 cm^{-1}. Similar features were found in the spectra of the methylated complexes. Further evidence is found in the Mössbauer spectra which show parameters similar to those found for $FeMe(CO)_2Cp^*$ and $[Fe\{=C=C=CMe(OMe)\}(dppe)Cp^*]^+$.

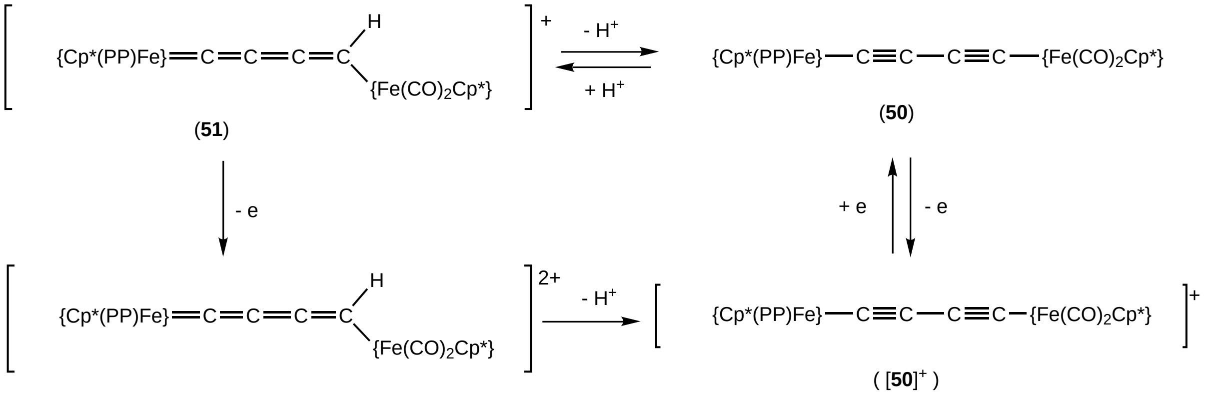
The C_4 complex contains both electron-donating and electron-withdrawing end-groups, resulting in some polarisation of the carbon chain. This is reflected in the site of addition of the electrophile. Since it is considered that the oxidised complex [**50**]$^+$ acts as a molecular wire, with electronic transmission occurring between the electron-rich and electron-poor ends of the C_4 chain, addition of the electrophile to give [**51**]$^+$ switches off the electronic exchange, a process which is reversed by deprotonation (either chemically or by further electrochemical oxidation) (Scheme 30). The redox properties of $[\{Cp^*(PP)Fe\}=C=C=C=CH\{Fe(CO)_2Cp^*\}]^+$ involve two processes at −1.13 (irrev.) and +0.40 V (rev.) (for **51-dppe**) and at −0.88 (irrev.) and +0.35 V (rev.) (for **51-dippe**) [4]. The methylated complex **52-dppe** shows a wave at −1.13 V, and reversible processes at +0.40 and +0.28 V are found for the dppe and dippe complexes, respectively. The radical dications apparently decompose into [**50**]$^+$ by loss of a proton (Scheme 28). The UV–vis spectra of $[\{Cp^*(PP)Fe\}=C=C=C=CH\{Fe(CO)_2Cp^*\}]^+$ contain an absorption at 520–550 nm which is assigned to charge transfer from an orbital on the Fe(dppe)Cp* fragment. Rapid decomposition in solution gives a new, presently unassigned, absorption between 800 and 900 nm [5].



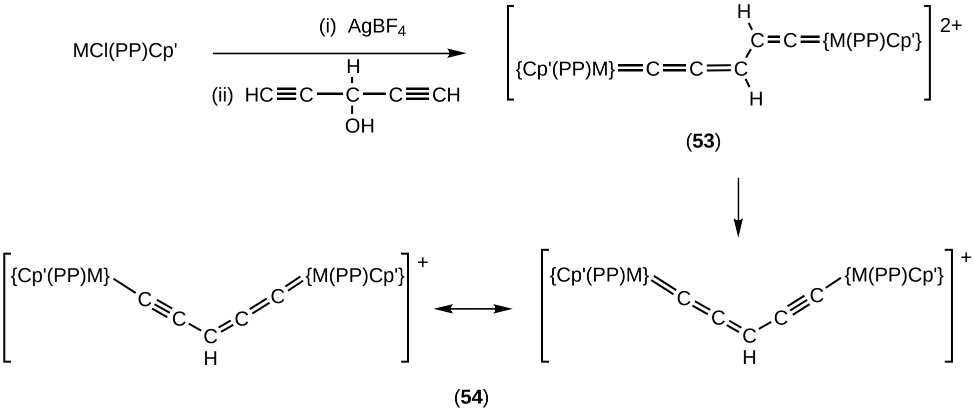
Scheme 29.

In the ruthenium series, protonation of the diyndiyl complex gives only the bis(vinylidene) from which it was originally obtained. Characterisation of the monoprotonated complex has not yet been possible. However, in the case of the mixed Fe–Ru derivative {Cp*(dppe)Fe}C≡CC≡C{Ru $(PPh_3)_2Cp$}, a purple solid is formed. NMR studies show that solutions contain two species, one of which is fluxional. More detailed studies are necessary, but one interpretation is that rapid shuttling of the proton between the Fe–C and Ru–C termini of the C_4 chain occurs [53].

Attempts to make C_5 chains with Group 8 metal–ligand end-groups by using reactions analogous to those which afford mononuclear pentatetraenylidene complexes gave instead compounds containing a C_5H ligand bridging two metal centres. Thus, spontaneous dehydration of $CH(OH)(C{\equiv}CH)_2$ in reactions with $[M(PP)Cp']^+$ [M = Fe, PP = dppe, Cp′ = Cp*; M = Ru, PP = $(PPh_3)_2$, Cp′ = Cp; PP = dppe, Cp′ = Cp*; M = Os, PP = dppe, Cp′ = Cp]



Scheme 30.



M(PP)Cp' = Fe(dppe)Cp*, Ru(PPh$_3$)$_2$Cp, Ru(dppe)Cp*, Os(dppe)Cp

Scheme 31.

gave initially [{L$_m$M}=C=C=CHCH=C={ML$_m$}]$^{2+}$ (**53**) which could be deprotonated to form [{L$_m$M}=C=C=CHC ≡C{ML$_m$}]$^+$ (**54**) on basic alumina (Scheme 31) [54–56].

18. Role of cumulenylidenes in bimetallic systems

While many examples of binuclear allenylidene derivatives have been described, we are not aware of any containing higher cumulenylidene ligands. Complexes containing carbon chains end-capped by various metal–ligand combinations continue to attract great interest [57]. Of interest in the present context are the various electronic arrangements which have been described. For even-numbered carbon chains, structures based on metal-alkynyl, -carbene or -carbyne connections can be written, examples being known for all three formulations **K**–**M** (Plate 2). For odd-numbered carbon chains, the symmetrical bis(alkynyl) formulation is not an option, at least one metal centre necessarily being attached via an M–C multiple bond. Two representations can be written, involving either alkynyl-carbyne (**N**) or bis(carbene) (**O**) arrangements. Again, examples of each have been described.

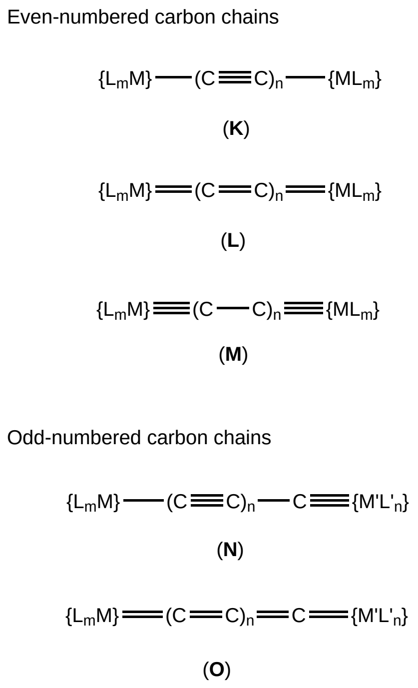
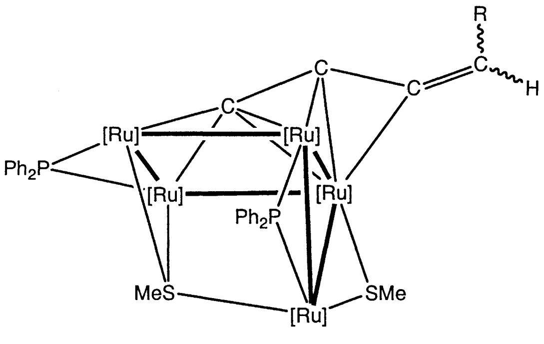
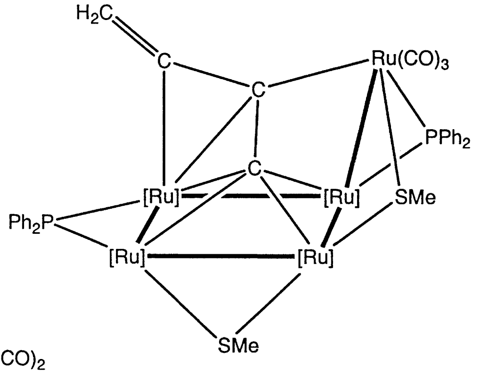


Plate 2.

Consideration of the various mesomeric forms which are then possible shows that cumulenylidene formulations are important contributors, particularly when there is the opportunity for some polarisation of heterometallic M–C_n–M′ chains. Such changes can also be achieved by redox reactions, a well-known example being the binuclear complexes containing C_4 ligands end-capped by Group 7 or Group 8 ML_m combinations, which have been shown to lose up to four electrons during electrochemical experiments. Although all five oxidation states have not yet been isolated, structural studies of the series $[\{Ru(dppe)Cp^*\}_2(\mu\text{-}C_4)]^{n+}$ ($n = 0$–2) show a continual trend towards the dimetalla-cumulene form in the dication (Scheme 32) [58].



R = $SiMe_3$ (**56**), Bu^t, H (**57**)



[Ru] = $Ru(CO)_2$

(58)

Similarly, the C_3 and C_5 complexes obtained by reactions of $Li(C{\equiv}C)_nRe(NO)(PPh_3)Cp^*$ ($n = 1$, 2) with $Mn(CO)_3(\eta\text{-}C_5X_5)$ (X = Cl, Br), followed by treatment with $[OMe_3]^+$ and BF_3, have properties (IR, structural) consistent with cumulenic formulations such as **55** for the bridging ligands [59,60]. A recent review has summarised the chemistry of these complexes in more detail than is possible here [57].

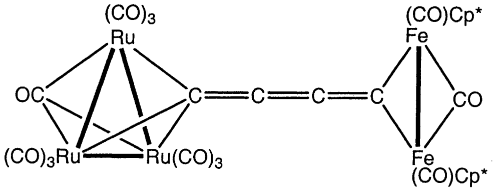
$$[(\eta\text{-}C_5Cl_5)(OC)_2Mn\}{=\!=}C({=\!=}C)_n{=\!=}C{=\!=}\{Re(NO)(PPh_3)Cp^*\}]^+$$

(55) n = 1, 2

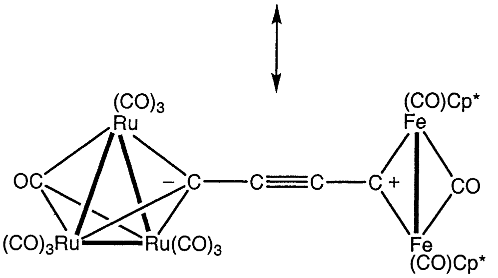
19. Cluster complexes

The chemistry of cluster complexes containing allenylidene ligands is now being developed extensively, but few examples of compounds containing longer carbon chains are known. These were obtained from reactions of $Ru_5(C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$, which contains an exposed C_2 ligand [61] with $C_2(SiMe_3)_2$. Partial proto-desilylation, isomerization to the vinylidene and addition to the C_2 fragment afforded $Ru_5\{\mu_4\text{-}CCCCH(SiMe_3)\}(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (**56**) as a mixture of two isomers. Further desilylation (KOH/MeOH) gave $Ru_5(\mu_4\text{-}CCCCH_2)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (**57**) as the first structurally characterised butatrienylidene complex. Subsequent reaction with CO gave $Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**58**). The C_4 ligand interacts with either four or five Ru atoms, respectively, in **57** and **58**, the former being electron-rich (80 cluster valence electrons) which results in an expansion of the cluster (Ru–Ru separations 2.942–3.070 Å in **57**, 2.830–2.943 Å in **58**) [10].

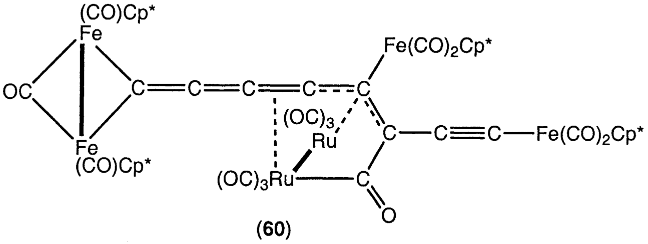
The reaction between $Ru_3(CO)_{12}$ and $\{Fe(CO)_2Cp^*\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ has given **59**, in which the carbon chain appears to be intermediate between the cumulene **59a** and the zwitterionic formulation **59b**, and **60**, for which the cumulenic structure has been determined [62]. Mixed Fe–Ru analogues have been prepared from $\{Cp^*(OC)_2Fe\}C{\equiv}CC{\equiv}C\{Ru(CO)_2Cp^*\}$.



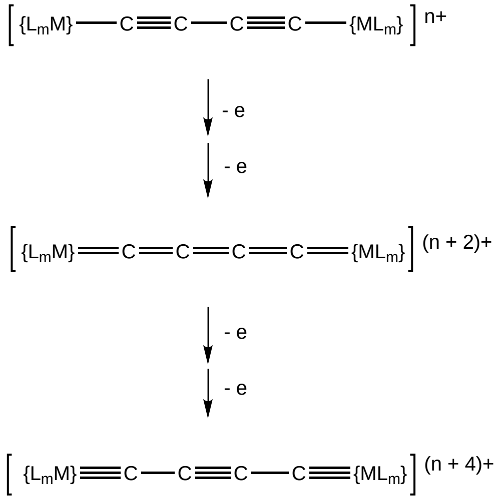
(59a)



(59b)



(60)



Scheme 32.

20. Prognosis

It is evident that isolation and characterisation of complexes containing higher cumulenylidene ligands remains a challenge. Because of the extended π systems, they are likely to have unusual electronic and non-linear optical properties. Only a limited range of end-groups, both metal-containing and organic, have so far been employed, the stabilities of some being directly linked to the presence of electron-donating substituents. The synthesis of compounds containing electron-withdrawing groups remains to be accomplished, perhaps by a "push-pull" approach, with ML_m groups with strong electron donating power being required. Recent computational studies have highlighted these problems, concluding that "higher even-numbered metallacumulenes are expected to be stabilised by the presence of π-acceptor substituents, such as NO_2, CN, COOR, $C_6H_4NO_2$, etc." [63].

Their high degree of unsaturation, which is the source of their reactivity, also makes cumulenylidene complexes of potential use in the synthesis of a wide variety of interesting molecules. In contrast to the rapidly developing chemistry of vinylidenes and allenylidenes, however, relatively few examples of the use of these complexes, even as intermediates, in other types of reactions (ligand transfer, coupling) have been reported. As reported above, several complexes are available as intermediates from relatively simple precursors, allowing the beginnings of an exploration of their reactivity. It is certain that the next decade will see a rapid development of this area, both from the point of view of novel metal complexes and in respect of their applications to the synthesis of novel organics and of new materials.

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