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COORDINATION CHEMISTRY OF METAL ALKYNYL COMPOUNDS

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CONTENTS

ABBREVIATIONS

t-bu	tertiary butyl
cp	cyclopentadienyl
cy	cyclohexyl
dma	dimethylacetylenedicarboxylate
dpe	1,2-bis(diphenylphosphino)ethane
et	ethyl
me	methyl
pc	divalent anion of phthalocyanine
ph	phenyl

phen	1,10-phenanthroline
i-pr	isopropyl
pyr	pyridine
tcne	tetracyanoethylene
THF	tetrahydrofuran

A. INTRODUCTION

In 1953 the first experiments for the preparation of alkynyl complexes ("complex acetylides") started from the simple idea that monovalent anions of alk-1-ynes $[RC{\equiv}C|]^-$ (R = H, alkyl, aryl) should exhibit complexing properties similar to those of the isoelectronic cyanide ion $[|C{\equiv}N|]^-$ [1]. The validity of this assumption has been generally confirmed by the isolation of *d*-metal complexes $[M(C{\equiv}CR)_z]^{(z-n)-}$ (n = oxidation number of M) the stoichiometry and magnetism thereof being generally analogous to those of the corresponding cyanides [2,3]. Since 1959 an increasing number of uncharged alkynyl complexes of *d*- and *f*-metals have been prepared and structurally characterised by dipole measurements, vibrational and NMR spectroscopy. Moreover, the structures of a growing number of complex acetylides have been determined by X-ray diffraction investigations. In 1972 and during the following years the interesting alkynyl compounds of *d*-metal clusters were discovered and structurally characterised. Quite recently, particular attention has focused on the structural chemistry and reactivity of polynuclear metal carbonyls containing bridging alkynyl ligands.

B. IONIC COMPLEX ACETYLIDES

The majority of this class of compounds consists of the anionic complex acetylides, whereas only a few cationic and zwitterionic complexes are known at present.

(i) Anionic complexes of metals

Anionic complexes of metals in common oxidation states

The anionic acetylides of the *d*-metals and of the group IB and IIB metals (Table 1) are the most reactive of all alkynyl complexes so far isolated. The strong basic character of the alkynyl ions as well as the anionic nature of the complex ions causes an extreme sensitivity of these compounds to protolysis. Many of the solid substances, being mostly insoluble in the usual organic solvents, explode on impact unless their central atoms possess filled or half-filled *d*-orbitals. Because of these properties the structures proposed for the complex anions rest entirely on the magnetic and IR data of the solids.

TABLE 1

Electron configurations d^n and magnetic moments μ_{eff} of "common-valent" metals in anionic complex acetylides

Complex	d^n	μ_{eff} (B.M.)
$K_3[Cr(C_2H)_6]$ [4]	3	3.9
$K_3[Mn(C_2H)_6]$ [5]	4	
$M_2[Mn(C_2R)_4]$ ($M=K$; $R=H$, me [5,6], o-$C_6H_4C_2H$ [7] $M=Ba/2$; $R=ph$ [5,6])	5	5.9
$K_3[Fe(C_2H)_6]$ [8]	5	
$K_4[Fe(C_2R)_6]$ ($R=H$, me, ph [8], cy [9])	6	0
$Na_3[Co(C_2R)_6]$ ($R=H$, me [10])		
$Na_4[Co(C_2me)_6]$ [10], $[Pph_4]_3Na[Co(C_2R)_6]$ ($R=H$, ph) [11]	7	1.8–2.4
$K_4[Co(C_2cy)_6]\cdot 2\ NH_3$ [9]		2.8–3.3
$K_2[Ni(C_2R)_4]$ ($R=H$, me, ph [12,13], $CH_2CR'_2CN$ [15])	8	0
$Li_2[Ni(C_2ph)_4]\cdot 4$ THF [14]		
$K_2[Pd(C_2R)_4]$ ($R=H$, ph [16], $CH_2CR'_2CN$ [15])		
$K_2[Pt(C_2R)_4]$ ($R=H$, me, ph [17], $CH_2CR'_2CN$ [15])		
$K_2[Cu(C_2R)_3]$, $K[Cu(C_2R)_2]$ ($R=H$, me, ph) [18]	10	0
$K_3[Cu(o$-$C_6H_4(C\equiv C)_2)_2]$ [19]		
$K_2[Zn(C_2H)_4]$ [20]		
$K[Ag(C_2R)_2]$ ($R=H$, me, ph) [21]		
$Ba[Cd(C_2R)_4]$ ($R=H$, ph) [22]		
$K[Au(C_2R)_2]$ ($R=H$, me, ph) [23]		
$[ph_4P]_2[RC_2Au{-}C\equiv C{-}AuC_2R]$ ($R=H$, me, ph) [24]		
$Ba[Hg(C_2R)_4]$ ($R=H$, ph) [25]		

Excepting the high-spin complex acetylides of manganese(II) and the low-spin compounds of the type $[Co(C_2R)_6]^{4-}$, these being different from the low-spin cyano complexes $[Mn(CN)_6]^{4-}$, $[Co(CN)_5]^{3-}$ and $[Co_2(CN)_{10}]^{6-}$ respectively [26], all the anionic alkynyl complexes correspond to the complex cyanides in respect of stoichiometry, colour and magnetism. (A similar analogy is observed between the dinuclear gold(I) complexes $[Pph_4]_2[RC_2Au{-}C\equiv C{-}AuC_2R]$ and $[Pph_4]_2[NCAu{-}C\equiv C{-}AuCN]$ [24]. The vibrational spectra of these compounds support the assumption that their anions are linear, containing end-on bridged $C\equiv C$

groups. Similar bridges exist presumably in the infinite chains $-Ag-C\equiv C-Ag-C\equiv C-$ of the polymeric $[KC\equiv CAg]_n$ [21], being comparable with the linear chains $-Ag-C\equiv N-Ag-C\equiv N-$ of the polymeric $[AgCN]_n$ [27].) The preparation of anionic acetylides of the d^9-metal copper(II) failed because of the redox reaction (1) [18]

$$2[RC\equiv C]^- + 2\,Cu^{2+} \rightarrow 2\,Cu^+ + RC\equiv C-C\equiv CR \qquad (1)$$

In the same way the redox reaction (2) is an obstacle to the preparation of alkynylpentacyanoferrates(III) [28]

$$2[RC\equiv C]^- + [Fe(CN)_5NO_2]^{3-} \rightarrow [Fe(CN)_5NO_2]^{4-} + RC\equiv C-C\equiv CR \qquad (2)$$

Nevertheless it was possible to isolate a series of mixed anionic complex acetylides such as the low-spin compounds *cis*-$Na_2[Co(C_2H)_4(Pet_3)_2]$, *trans*-$Na_2[Co(C_2H)_4(Pph_3)_2]$, *trans*-$Na_2[Co(C_2ph)_4(Pet_3)_2]$, *trans*-$[Pph_4]Na[Co(C_2ph)_4(Pph_3)_2]$ [29], $K_2[Co(C_2cy)_4(NH_3)_2]$ [9], the diamagnetic complexes *trans*-$Ba[Pd(C_2R)_2(CN)_2]$ ($R = H, ph$) [30] and *trans*-$K_{2n}[Pt(C_2R)_4(dpe)]_n$ ($R = H, me, ph$) [31]. The geometry of the anions $[Co(C_2R)_4(PR')_2]^{2-}$ is obviously determined by the spatial requirements of R and R′, and the polymeric nature of $[Pt(C_2R)_4(dpe)]_n^{2n-}$ appears to be caused by dpe bridges. The IR spectra of the presumably planar anions $[Pd(C_2R)_2(CN)_2]^{2-}$ accord better with a *trans*-structure than with a *cis*-arrangement of the ligands as formerly postulated.

The cyano ligands of the "nitroprusside" ion can also be partially substituted by phenylacetylide ligands. However, the reaction products $[Pph_4]_2[Fe(C_2ph)(CN)_4NO]$ and $[Pph_4]_2[Fe(C_2ph)_3(CN)_2NO]$ are thermally too unstable for structural characterization [32] and less stable than the diamagnetic *trans*-$K_4[Fe(C_2cy)_2(CN)_4]$ [9].

In more recent years it has been shown that the phthalocyanines of some *d*-metals add one or two phenylacetylide ligands to form the deeply coloured anionic complexes $Li[M(C_2ph)_2(pc)] \cdot n$ THF ($M^{III} = Cr, Co$; $n = 5, 4$), $Li[Mn(C_2ph)(pc)] \cdot 4.5$ THF, $Li_2[Fe(C_2ph)_2(pc)] \cdot 7$ THF, $Li_2[Co(C_2ph)(pc)]_2 \cdot 8$ THF and $Na[Zn(C_2ph)(pc)] \cdot 5$ THF [33]. Apart from the cobalt(II) compound, the complexes of all the other metals behave magnetically in a manner quite similar to the corresponding complexes of Table 1. However, the cobalt(II) complex is diamagnetic and is therefore believed to be dimeric by Co–Co interaction.

Recently the first complex acetylides of tervalent *f*-metals have been reported as air- and moisture sensitive compounds of the type $LiM(C_2R)_4(THF)_x$ ($M = Eu, Er, Yb, Lu$; $R = bu, t\text{-}bu$; $x = 0\text{–}1$) [34]. As far as alkynyl complexes of main group metals are concerned, only some thallium(III) compounds of the type $[Pph_4][Tl(C_2R)_4]$ ($R = me, ph$) are known at present [35]. These weak electrolytes are easily protolysed and are non-explosive.

Anionic complexes of metals in low oxidation states

For the stabilisation of low oxidation states of the central *d*-metal atoms, alkynyl anions are just as efficient ligands as the cyanide ion. This is shown in the preparation of alkynyl and cyano complexes containing formally zerovalent nickel, palladium and platinum respectively (Table 2). These diamagnetic compounds are obtained by the reduction of the metalates(II) $[M(C_2R)_4]^{2-}$ and $[M(CN)_4]^{2-}$ respectively (M = Ni, Pd, Pt) with alkali metals in liquid ammonia. The same method yielded the tris(phenylethynyl)cuprate(0) $Ba_3[Cu(C_2ph)_3]_2$ whose diamagnetism is interpreted by dimerisation of the anions via Cu–Cu bonds [39]. All these complexes are extremely sensitive to any traces of oxygen and water and are partially pyrophoric. Consequently the proposed structures of the anions are entirely based on the IR data of the solids. In contrast to the well-known $K_4[Ni_2(CN)_6]$ [40] anionic complex acetylides of the d^9-metal nickel(I) are still unknown. The existence of the formerly postulated "$K_6[Ni_2(C_2R)_8]$" has not been confirmed [41,42]. Finally, some tris(alkynyl)tricarbonylmetalates(0) belong to this category of complexes. The diamagnetic compounds $K_3[M(CO)_3(C_2R)_3]$ (R = H, me, ph; M = Cr [43], Mo, W [44]) are easily protolysed and are partially pyrophoric. The coordination geometry of their anions is still obscure.

Surveying the properties of the anionic complex acetylides, one finds that the course of their protolysis seems to depend on the electron configuration of the central metal atom. The action of acids on the complexes of the high-spin d^5-metal manganese(II) and on the d^{10}-metals of the group IB and IIB quantitatively liberates the alkynes RC≡CH, whereas the protolysis of all the other complexes additionally yields unidentified organic products by

TABLE 2

Probable geometries of the anions in alkynyl and cyano complexes of "zerovalent" d^{10}-metals

Complex	Coordination geometry
$K_4[Ni(C_2H)_4]$ [12] $K_4[Ni(CN)_4]$ [36]	Tetrahedral
$K_2[Pd(C_2R)_2]$ (R = H, me, ph) [16,30] $M_2[Pd(CN)_2]$ (M = K, Pph_4) [37]	Linear
$K_2Pt(C_2R)_2$ (R = H, me, ph)	Symmetry lower than $D_{\infty h}$
$[ph_4P]_2[Pt(CN)_2]$ [38]	Linear

side-reactions. The protolytic decomposition of the "zerovalent" d^{10}-metal compounds produces mixtures of the corresponding alkynes and their hydrogenated products $RCH{=}CH_2$, RC_2H_5 besides tar-like substances. The fact that the 18-electron rule strictly holds neither for complex acetylides nor for complex cyanides emphasizes the coordinative similarities between both.

(ii) Cationic alkynyl complexes

Some years ago several diamagnetic cationic complexes of platinum(II) and palladium(II) were described, such as *trans*-$[L(Pet_3)_2M{-}C{\equiv}CC_6H_4C{\equiv}C{-}M(Pet_3)_2L](ClO_4)_2$ (M = Pt; L = CO, pyr, Pet_3 [45]. M = Pd; L = pyr, Pet_3 [46]) and the alkynyl–carbene complexes *trans*-$[Pt(C_2R)(C(CH_2R)OR')(Pme_2ph)_2]^+PF_6^-$ (R = H, me, ph; R′ = me, et, pr, i-pr) [69]. The hydrophobic and non-explosive perchlorates are air-stable and soluble in polar organic solvents as strong electrolytes. The two metal atoms in the complex cations are bridged by a linear divalent anion of the 1,4-diethynylbenzene, and the *trans*-planar environment of both central metals has been demonstrated by the vibrational spectra and the NMR data (^1H, ^{31}P) of the complexes.

(iii) Zwitterionic alkynyl complexes

Some zwitterionic alkynyl compounds have been known for eight years past, and these may be considered as connecting links between the ionic and the uncharged alkynyl complexes. The first of this class was the dinuclear complex $[ReCu(C_2C_6F_5)_2(CO)_3(Pph_3)_2]$ [47], and a single crystal X-ray study has shown that the compound consists of ion-pairs $[[CuPph_3]^+[Re(C_2C_6F_5)_2(CO)_3(Pph_3)]^-]$. These are held together by alkynyl bridges. The formation of such bridges in the coordination polymers $[CuC_2R]_\infty$ via dative bonds of the type $\mathrm{Cu}\underset{\underset{\mathrm{Cu}}{\downarrow}}{\mathrm{C{\equiv}C}}\mathrm{R}$ has been previously postulated [53]. In this way the cationic copper(I) has approximate trigonal planar coordination, and the anionic rhenium(I) possesses a distorted octahedral coordination environment. (A comparable molecular structure in the trinuclear complex $[RhAg_2(C_2C_6F_5)_5(Pph_3)_3]$ built up by the ions $[[AgPph_3^+]_2[Rh(C_2C_6F_5)_5(Pph_3)]^{2-}]$ [48] has been demonstrated crystallographically. Each tetrahedrally coordinated silver atom is attached to the pseudooctahedral complex anion side-on by π linkages from three C≡C groups [49].) Similar zwitterionic aggregates are assumed in other complexes such as $[[CuPph_3]^+[Ru(C_2C_6H_4R{-}p)_2(h^5{-}cp)]^-]_n$ (R = me, F; $n = 1, 2$) [50], $[[CuPph_3]^+[Ir(C_2C_6F_5)_4(Pph_3)_2]^-]$ [51] and $[[AgPph_3]^+[M(C_2C_6F_5)_4(Pph_3)_2]^-]$ (M = Rh, Ir) [52]. Again cations of the type $[MPh_3]^+$

(M = Cu, Ag) and complex acetylide anions are believed to be held together by dative side-on π-bonds of MC≡CR moieties (M = Ru, Rh, Ir) to the cationic metals. This major feature is experimentally supported by the IR and NMR (^{1}H, ^{19}F) spectra of the compounds.

It has to be noted here that the polynuclear compounds $[CuC_2ph(Pme_3)]_4$ [54] and $[AgC_2ph(Pme_3)]_\infty$ [55] may also be regarded in some respects as zwitterionic complexes of the type $[[M(Pme_3)]^+[M(C_2ph)_2]^-]_n$ (M = Cu, Ag). The structures of these and the bridging function of the MC≡CR units will be discussed in more detail in Sections E and G.

C. UNCHARGED LOW-MOLECULAR WEIGHT ALKYNYL COMPLEXES

All the compounds belonging to this extensive class contain additional auxiliary ligands such as tertiary phosphines, arsines, stibines, CO, cyclopentadienyl and monovalent anionic ligands. These mostly diamagnetic and non-explosive coordination compounds are considerably less reactive than the anionic complex acetylides. Soluble in organic solvents, they are structurally well characterized by dipole measurements, IR, Raman and NMR spectroscopy. Their central atoms are predominantly four-coordinate but some octahedral complexes and a few presumably five-coordinate compounds have also been described.

(i) Four-coordinate compounds

This category of complexes involves many *trans*- or *cis*-planar monomeric compounds of group VIII metals as well as some pseudo-tetrahedral complexes of group IIB metals. Planar compounds of the types $[M(C{\equiv}CR)_2(L)_2]$, $[M(C{\equiv}CR)(X)(L)_2]$ and $[M(C{\equiv}CR)(CO)(PR'_3)_2]$ are formed principally by spin-paired d^8-metals whereby a *trans*-arrangement of the ligands occurs more frequently, of course, than the *cis*-arrangement.

Trans-planar complexes $[M(C_2R)_2(L)_2]$, $[MC_2R(X)(L)_2]$ *(M = Ni, Pd, Pt) and* $[MC_2R(CO)(PR'_3)_2]$ *(M = Ir, Rh)*

Complexes of the first type summarized in Table 3 exhibit a great variety of R (H, alkyl, aryl, alk-1-enyl, alk-1-ynyl, halogenated groups) and L (PR'_3, AsR'_3, SbR'_3). Most of these compounds as well as the *trans*-planar derivatives of 1,4-diethynylbenzene *trans*-$HC_2C_6H_4C_2Pt(L)_2[C_2C_6H_4C_2Pt(L)_2]_n C_2C_6H_4C_2H$ (n = 1, 2 [65], ≫ 2 [45]) are air-stable except that they contain terminal ethynyl groups as in the butadiynyl complex $[Pd(C{\equiv}C{-}C{\equiv}CH)_2(Pbu_3)_2]$ which can be dehydrogenated by oxygen. The radicals formed thereby may couple to straight-line oligomers such as *trans*-$HC_2{-}C_2Pd(L)_2[C_2{-}C_2Pd(L)_2]_nC_2{-}C_2H$ (L = Pbu_3, n = 9–10) [65]. The complexes

TABLE 3

Planar complexes of the type *trans*-$[M(C_2R)_2(L)_2]$

M	L	R
Ni	Pet_3	H, me, ph [56], CF_3 [57], CH_2F, $CH{=}CH_2$, C_2H, C_2ph [58]
	Pph_2et, $Pphet_2$	ph [56]
	Pph_3	ph [56], o-$C_6H_4C_2H$, p-$C_6H_4C_2H$ [59]
	Ppr_3	ph [56]
	Pbu_3	o-$C_6H_4C_2H$, p-$C_6H_4C_2H$ [59]
Pd	Pme_3	ph, $CH{=}CH_2$ [58]
	Pet_3	H, me [61], CH_2OH [62], CH_2F, C_2H, C_2ph [58], ph, p-$C_6H_4NO_2$ [60] o-$C_6H_4C_2H$, p-$C_6H_4C_2H$ [63]
	Pph_3	ph [58]
Pt	Pme_3	$CH{=}CH_2$, ph [58]
	Pet_3	H, me, ph [64,65], CF_3 [57], $CH{=}CH_2$, C_2H, C_2ph [58]
	Pbu_3	H, $CH{=}CH_2$, C_2H, ph, p-$C_6H_4C_2H$ [65]
	Pme_2ph	CF_3 [68], H, me, ph [69]
	Pph_3	ph [58], C_6F_5, p-C_6H_4F [66], CH_2OH, CH_2Nme_2, $(CH_2)_6C_2H$ [67], $Cme{=}CH_2$ [83]
	$Asme_3$	CF_3 [68], me, ph [69]
	$Aset_3$	ph [64]
	$Sbet_3$	ph, C_2ph [58]

trans-[$M(C_2R)_2(L)_2$] react with anhydrous acids HX in a different way. Treated with gaseous hydrogen chloride in polar solvents the phenylethynyl complexes of nickel and platinum form mono-substituted chloro complexes according to eqn. (3)

$$[M(C_2ph)_2(L)_2] + HCl \rightarrow \textit{trans}\text{-}[MC_2ph(Cl)(L)_2] + phC_2H \qquad (3)$$

$$(M = Ni;\ L = Pet_3, Pet_2ph\ [56].\ M = Pt,\ L = Pph_3\ [70])$$

Only one alkynyl ligand is cleaved off even if an excess of HCl is applied. Other platinum complexes react analogous to eqn. (3) only if an excess of HCl is avoided [69]. In more recent years the chemistry within the coordination sphere of *trans*-[$Pt(C_2R)_2(L)_2$] ($R = H$, me, CF_3, ph; $L = Pme_2ph$, $Asme_3$) in relation to many protic and aprotic reactants has been extensively studied. A detailed investigation of the overall reaction (3) with $M = Pt$, $R = H$, $L = Pme_2ph$ in perdeuterated organic solvents by means of IR and ^1H NMR spectroscopy has demonstrated the intermediate formation of the α-chlorovinyl complexes *trans*-[$PtC_2H(CCl{=}CH_2)(L)_2$], *trans*-[$Pt(CCl{=}CH_2)_2(L)_2$] and *trans*-[$PtCl(CCl{=}CH_2)(L)_2$] [71]. The latter compound and some of its analogues can be smoothly prepared by the addition of two equivalents of HCl to the corresponding alkynyl complexes in benzene or toluene according to

$$[Pt(C_2R)_2(L)_2] + 2\ HCl \rightarrow \textit{trans}\text{-}[Pt(CCl{=}CHR)_2(L)_2] \qquad (4)$$

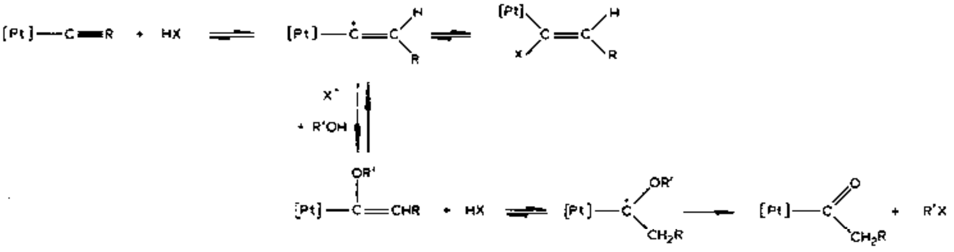
$$(L = Pet_3,\ R = CF_3\ [57].\ L = Pme_2ph;\ R = H,\ CF_3\ [69])$$

The addition of a third equivalent of HCl leads to the formation of *trans*-[$PtCl(CCl{=}CHR)(L)_2$] which is slowly converted in aqueous acetone to the acyl complex *trans*-[$PtCl(C(O)R)(L)_2$] ($R =$ me, et; $L = Pme_2ph$) [69]. The reaction of one equivalent HPF_6 or $HSbF_6$ in alcoholic solvents R′OH with *trans*-[$Pt(C_2R)_2(L)_2$] affords cationic alkynylalkoxycarbene complexes in good yields according to eqn. (5) [69]

$$[Pt(C_2R)_2(L)_2] + HX + R'OH \rightarrow \textit{trans}\text{-}[PtC_2R(C(CH_2R)OR')(L)_2]X \qquad (5)$$

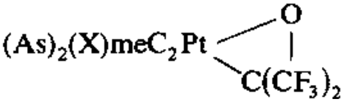
$$(L = Pme_2ph, Asme_3;\ R = H, me, ph;\ R' = me, et, pr, i\text{-}pr;\ X = PF_6, SbF_6)$$

Based on the results of IR, ^1H NMR and isotopic labelling studies of reaction (5) the general scheme (1) has been proposed. The platinum-stabilized vinyl carbonium ion $Pt{-}\overset{+}{C}{=}CHR$ formed by the protonation of a PtC_2R moiety is believed to be an essential intermediate which accounts for the formation of the vinylic and alkoxycarbene compounds involved in the overall reactions (4) and (5) [69,71]. The complexes *trans*-[$Pt(C_2R)_2(P)_2$] and *trans*-[$Pt(C_2R)_2(As)_2$] ($R = H$, me; $P = Pme_2ph$; $As = Asme_3$) react also with aprotic substrates and it has been shown that platinum(II) activates the



X = Cl, PF_6, SbF_6 ; [Pt] = *trans*-$PtX'(L)_2$ (X' = C_2R, Cl)

Scheme 1

σ-bonded alkynyl ligand towards addition reactions of different types [72]. The propynyl compounds react with one equivalent of hexafluoroacetone under the formation of five- or six-coordinated π complexes of the type  $(As)_2(X)meC_2Pt\begin{smallmatrix}\diagup O\\ \mid\\ \diagdown C(CF_3)_2\end{smallmatrix}$ (X = C_2me, Cl) whereas the ethynyl complexes insert $(CF_3)_2CO$ into both H–C≡ bonds forming *trans*-[Pt(C≡C–C(OH)$(CF_3)_2)_2(P)_2$]. Tetracyanoethylene, however, is inserted into one Pt–C≡ bond, yielding *trans*-[PtC≡CH(C(CN)$_2$C(CN)$_2$C≡CH)(P)$_2$] and trifluoroacetylchloride is added to the C≡C bonds whereby a bisvinyl complex e.g. *trans*-[Pt(CCl=CmeC(O)CF$_3$)$_2$(As)$_2$] is formed. Finally, iodine compounds of the type I–X (X = I, Br, CN, me, CF_3) are oxidatively added to the central Pt with the formation of platinum(IV) complexes *trans*-[Pt($C_2R)_2(L)_2$(I)(X)] (R = H, me, CF_3; L = Pme$_2$ph, Asme$_3$). The relative ease of oxidative addition follows the orders I–X (X = I, Br, CN) > CF_3I > meI, R = me > H > CF_3 and L = Asme$_3$ > Pme$_2$ph. The ν(C≡C) stretching frequencies of the platinum(IV) complexes are always greater (30–60 cm^{-1}) than those of the platinum(II) parent compounds. This is considered to be indicative of the relative degree of Pt to C≡Cπ* back-bonding, Pt(II) > Pt(IV) [72].

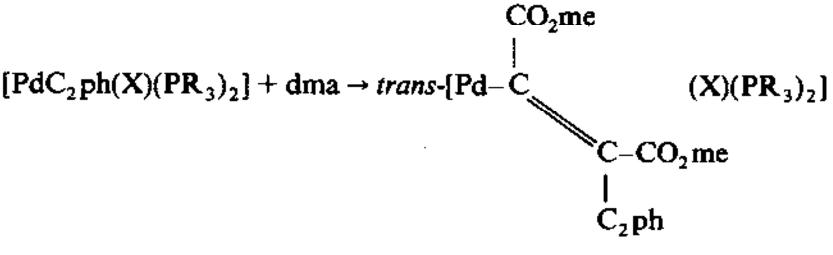
The complexes *trans*-[MC$_2$R(X)(L)$_2$] of Table 4 as well as the dinuclear complex derivatives of 1,4-diethynylbenzene *trans*-[(Pet$_3$)$_2$(X)M–C≡CC$_6$H$_4$C≡C–M(X)(Pet$_3$)$_2$] (M = Pd; X = Cl, Br, I, NCS [46]. M = Pt; X = Cl, Br, I, H, NCS [45]) contain halogens, pseudohalogens or organic ligands as substituting groups X. The chemical behaviour of these substances is rather similar to that of the unsubstituted complexes. The platinum complexes add anhydrous HCl in CH_2Cl_2 and form the α-chloropropenyl compounds *trans*-[Pt(CCl=CHR)$_2$(L)$_2$] (R = me, ph; Pme$_2$ph, Asme$_3$ [69]) which exist as a mixture of *cis*- and *trans*-isomers relating to the C=C double bond. The reactions with HPF_6 in an alcohol R'OH yield the cationic alkoxycarbene compounds  *trans*-$[Pt\text{–}C\begin{smallmatrix}\diagup OR'\\ \diagdown CH_2R\end{smallmatrix}(Cl)(L)_2]^+$ (R = H, me, ph;

TABLE 4

Planar complexes of the type *trans*-$MC_2R(X)(L)_2$

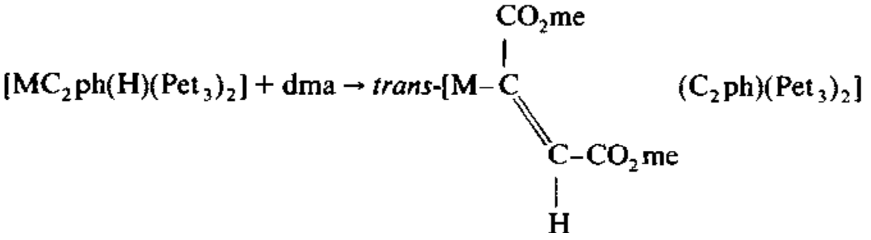
M	L	X	R
Ni	Pet_3	I	CF_3 [57]
	Pet_2ph	Cl	ph [56]
	Pme_2ph	C_6Cl_5	H, me, et, CH_2OH, CH_2CH_2OH, ph, *p*-C_6H_4Ome [185]
		Mesityl, $CCl{=}CCl_2$ $C_6H_3(Ome\text{-}o)_2$	H, me, ph, *p*-C_6H_4Ome [186]
Pd	Pet_3	Cl, Br	ph [72]
		Cl, Br, I, CN, NCS	*o*-$C_6H_4C_2H$ [74]
	Pbu_3	Cl, Br, I	ph [72]
Pt	Pet_3	H, Cl	ph [74]
		H	ph [74], C_6F_5 [66]
		p-C_6H_4F, *m*-C_6H_4F	ph [75]
	Pme_2ph	Cl, me	CF_3 [68]
		Cl	H, me, ph [69]
	Pet_2ph	Cl	ph [76]
	Pph_3	Cl [70], Br, I [77] $Snme_3$, $Snet_3$ [87]	ph
	$Asme_3$	Cl	me, ph [69]
	$Asme_2ph$	Cl	ph [69]

R' = me, et, pr, i-pr; L = Pme_2ph) [69]. Analogous reactions of $HClO_4$ in $R'OH$ with *trans*-$[NiC_2H(C_6Cl_5)(Pme_2ph)_2]$ lead to the formation of the alkoxycarbene complexes *trans*-$[Ni{-}C\begin{smallmatrix}\diagup OR'\\ \diagdown me\end{smallmatrix}(C_6Cl_5)(Pme_2ph)_2]ClO_4$ (R' = me, t-bu) [185]. Again, all these reactions may be interpreted by Scheme 1. Some of the complexes *trans*-$[MC_2ph(X)(PR_3)_2]$ (M = Pd, Pt) are able to insert dimethylacetylenedicarboxylate. The course of these reactions depends on the nature of X as it is shown by eqns. (6) and (7)



$$[PdC_2ph(X)(PR_3)_2] + \text{dma} \rightarrow trans\text{-}[Pd{-}\underset{\substack{\Vert\\ C-CO_2me\\ |\\ C_2ph}}{\overset{\substack{CO_2me\\ |}}{C}}(X)(PR_3)_2] \tag{6}$$

(X = Cl, Br, I; R = et, bu [73])



$$[MC_2ph(H)(Pet_3)_2] + dma \rightarrow trans\text{-}[M{-}\overset{\displaystyle CO_2me}{C}{=}\underset{\displaystyle H}{C}{-}CO_2me\;(C_2ph)(Pet_3)_2] \qquad (7)$$

$(M = Pd, Pt$ [79]$)$

Planar alkynyl hydrido complexes of the type $NiC_2R(H)(PR'_3)_2$ have been proposed as active intermediates for both the linear and cyclic polymerisation of alk-1-ynes catalysed by $Ni(CO)_2(PR'_3)_2$ [189].

The *trans*-planar coordination geometry of most of the complexes summarized in Tables 3 and 4 has been evidenced by the vibrational and NMR spectra of the dissolved compounds. Additionally, analogous structures of some solid complexes such as *trans*-$[Ni(C_2ph)(Pet_3)_2]$ [80,81], *trans*-$[Ni(C_2C_6H_4C_2H\text{-}o)_2(Pbu_3)_2]$ [82], *trans*-$[Pt(C_2C(me){=}CH_2)_2(Pph_3)_2]$ [83], *trans*-$[Pt(C_2ph)_2(Cl)(Pet_2ph)_2]$ [77], *trans*-$[Pd(C_2C_6H_4C_2H\text{-}o)(NCS)(Pet_3)_2]$ [84] and *trans*-$[(SCN)(Pet_3)_2Pt{-}C_2C_6H_4C_2{-}Pt(Pet_3)_2(NCS)]$ [85] have been demonstrated by X-ray analysis (Table 9).

Over the last decade some *trans*-planar Vaska-type complexes of iridium(I) and rhodium(I) such as $[IrC_2R(CO)(Pph_3)_2]$ (R = me, et, bu, t-bu, cy, $COHme_2$, $C_6H_{10}OH$ [86], ph [87,97]), $[IrC_2ph(CO)(Pphme_2)_2]$ [88], $[RhC_2R(CO)(Pph_3)_2]$ (R = me, et [86], ph [88], o-$C_6H_4C_2H$, p-$C_6H_4C_2H$ [89]) and $[RhC_2R(CO)(PR'_3)_2]$ (R = o-$C_6H_4C_2H$, p-$C_6H_4C_2H$; R′ = p-C_6H_4F [89]) have been prepared. None of these has been investigated crystallographically but the *trans*-planar structure of all these compounds has been demonstrated by IR and NMR spectroscopy. The complexes are converted by HCl quantitatively into the parent compound *trans*-$[MCl(CO)(Pph_3)_2]$ with displacement of the alkynyl ligands and under subsequent oxidative addition of further HCl to $[IrH(Cl)_2(CO)(Pph_3)_2]$. The compounds *trans*-$[IrC_2R(CO)(Pph_3)_2]$ undergo a wide range of addition reactions with neutral ligands L such as Pph_3, CO, SO_2, O_2, $(NC)_2C{=}C(CN)_2$, $(CF_3)FC{=}CF(CF_3)$, $F_2C{=}CF{-}CF{=}CF_2$, $F_3CC{\equiv}CCF_3$ and dma forming adducts of the type $[IrC_2R(L)(CO)(Pph_3)_2]$ (R = me, et, bu, t-bu [86]; R = ph, L = O_2 [87,99]. The addition of O_2 is irreversible in all these cases due to the “soft” nature of the alkynyl ligands. Corresponding addition reactions of *trans*-$[RhC_2R(CO)(Pph_3)_2]$ occur much less frequently. The adducts $[RhC_2R(L)(CO)(Pph_3)_2]$ (R = me, et; L = Pph_3, CO, SO_2, $C_2(CN)_4$) [86] have been obtained so far. The structure and bonding of these adducts will be discussed in Section C (ii).

Cis-planar complexes $[M(C_2R)_2(L)_2]$ *and* $[MC_2R(X)(L)_2]$ *(M = Pd, Pt)*

The *cis*-complexes are thermodynamically less stable than the corresponding *trans*-compounds and nickel complexes of these types are still unknown. Recently a few *cis*-complexes of palladium such as *cis*-$[Pd(C_2R)_2(dpe)]$ (R = H, me, ph) and *cis*-$[Pd(C_2C_6H_4C_2H\text{-}o)(Cl)(dpe)]$ have been isolated [16]. *Cis*-$[Pd(C_2R)_2(dpe)]$ as well as the analogous platinum compounds *cis*-$[Pt(C_2R)_2(dpe)]$ (R = H, me, ph) [31] react quantitatively with aqueous solutions of KCN according to eqn. (8)

$$cis\text{-}[M(C_2R)_2(dpe)] + 4\,CN^- \rightarrow [M(CN)_4]^{2-} + dpe + 2\,RC_2H \qquad (8)$$

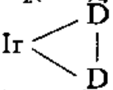
(M = Pd, Pt; R = H, me)

The anionic complexes $K_2[Pd(C_2R)_4]$ and $K_{2n}[Pt(C_2R)_4(dpe)]_n$ are formed with KC_2R. Further, several *cis*-complexes of platinum with monodentate phosphines such as $[Pt(C_2R)_2(Pet_3)_2]$ (R = H, CH=CH$_2$, ph) [65], $[Pt(C_2R)_2(Pbu_3)_2]$ (R = H, C_2H, ph) [65] and $[Pt(C_2R)_2(Pph_3)_2]$ (R = ph [70], CF_3, C_2F_5 [90]) have been prepared. The *cis*-structure of all these compounds is confirmed from IR, Raman and NMR data. Moreover, the structure of *cis*-$[PtC_2CN(CN)(Pph_3)_2]$ formed by isomerisation of $Pt(Pph_3)_2(NC{-}C{\equiv}C{-}CN)$ has been established by X-ray studies [91]. Recently the four-coordinate complexes $[M(C_2cy)_2(Pph_3)_2]$ (M = Fe, Co) have been reported. The diamagnetic Fe(II) complex and the low-spin Co(II) compound are believed to be planar [9].

Pseudo-tetrahedral complexes

It was not until few years ago that X-ray diffraction measurements of the mercury alkynyl complexes $[Hg(C_2R)_2(phen)]$ (R = ph [92], CH_2Cl [93]) showed that the Hg atoms are coordinated by two carbon and two nitrogen atoms forming an extremely distorted tetrahedron. Similar structures may be assumed for analogous complexes with R = me, CH_2Br, ph [94] and for $[phHgC_2R(phen)]$ (R = H, me, CH_2Cl, ph) [95]. A pseudo-tetrahedral arrangement of the ligands seems likely in the complex non-electrolytes $[Zn(C_2R)_2(NH_3)_2]$ (R = H, ph) [96] as well as in the dinuclear beryllium compounds $[(L)RC_2Be(\mu\text{-}C_2R)_2BeC_2R(L)]$ (R = me, t-bu; L = Nme_3, THF) [187]. Recently the black diamagnetic $NiC_2ph(NO)(Pph_3)_2$ has been described [97] and its IR-active $\nu(NO)$ stretching frequency (1742 cm^{-1}) is similar to that of the corresponding diamagnetic cyano complex $NiCN(NO)(Pph_3)_2$ (1760 cm^{-1}) [98]. The latter compound is said to have a pseudo-tetrahedral structure.

(ii) Five- and six-coordinate complexes

The first example of a five-coordinate alkynyl complex was the diamagnetic dark red $[Ni(C_2ph)_2(Pphet_2)_3]$ [56], the structure of which is still unknown. A similar cyano complex $[Ni(CN)_2(Pphme_2)_3]$ exhibits a distorted trigonal bipyramidal structure with the phosphine ligands in the equatorial plane [100]. The adducts $[MC_2R(L)(CO)(Pph_3)_2]$ (M = Ir, Rh), mentioned in Section C (i), also represent five-coordinate compounds provided that L is a monodentate ligand such as CO, Pph_3 and SO_2. The structures of these complexes should be comparable to those of the trigonal bipyramidal adducts $[IrCl(CO)_2(Pph_3)_2] \cdot C_6H_6$ (with the phosphines at the apices) [101] and $[RhH(CO)(Pph_3)_3]$ (with the phosphines in the basal plane) [102] and to those of the tetragonal pyramidal adducts $[MCl(SO_2)(CO)(Pph_3)_2]$ (M = Ir [103], Rh [104]) wherein the sulphur atom is placed at the apex and the *trans*-phosphines in the basal plane. The structures of the adducts $[Ir(C_2R)(O_2)(CO)(Pph_3)]$ should resemble those of the complexes $[IrX(O_2)(CO)(Pph_3)]$ (X = Cl [105], I [106]) wherein the oxygen atoms of the O_2-ligand are equidistant from the iridium atom placed in the coordination plane together with CO and X. The tetracyanoethylene complexes of the type $[MC_2R((NC)_2C{=}C(CN)_2)(CO)(Pph_3)_2]$ (M = Ir, Rh) presumably have structures comparable to that of $[IrBr((NC)_2C{=}C(CN)_2)(CO)(Pph_3)_2]$ [107]. The structure of the latter complex differs from those of the compounds $[IrX(O_2)(CO)(Pph_3)_2]$ (X = Cl, I) insofar as the *cis*-phosphine ligands are placed in the basal coordination plane with X and CO above and below this plane. The O–O distance as well as the C–C distance of the added ligands are markedly longer than those of the uncomplexed molecules O_2 and $(NC)_2C{=}C(CN)_2$. Thus, these adducts may be considered either as five-coordinate trigonal bipyramidal Ir(I) complexes with side-on π-bound O_2 and $C_2(CN)_4$ ligands or as pseudo-octahedral Ir(III) complexes containing  moieties (D = O, C). The bonding in the three-membered ring has been described by a three-centre MO scheme assuming C_{2v} symmetry for each centre [107].

The coordination number six is undoubtedly realized in the platinum(IV) compounds *trans*-$[Pt(C_2R)_2(L)_2(I)(X)]$ (described in Section C (i)) as well as in the diamagnetic d^6-metal complexes $[IrC_2R(X)(Y)(CO)(Pph_3)_2]$ (R = bu; X = me, Y = I, X + Y = SO_4 [86]; X = Cl, Y = H, R = CO_2et [108]; R = ph, X = Cl, Y = HgC_2ph [108]), $[Ir(C_2ph)_2(Snme_3)(CO)(Pph_3)_2]$ [88], *trans*-$[Pt(C_2R)_2(H)_2(Pph_3)_2]$ (R = 1-hydroxycyclohexyl) [109], $[ReC_2R(CO)_5]$ (R = ph, C_6F_5) [57], *trans*-$[ReC_2C_6F_5(CO)_3(Pph_3)_2]$ [50] and *trans*-$[CoC_2R(salen)(H_2O)]$ (R = ph, p-C_6H_4me) [110].

Finally, the pseudo-octahedral low-spin Co(II) complexes *trans*-$[Co(C_2R)_2(dpe)_2]$ (R = H, ph) [29] and the IVB-metal complexes *trans*-$[M(pc)(C_2R)_2]$ (R = H, me, t-bu, ph; M = Si, Ge, Sn) [111] have been described.

D. ALKYNYL COMPOUNDS OF METAL–CYCLOPENTADIENYL SYSTEMS

The complexes of this category may be roughly subdivided as follows: (i) Complexes of the type $[(\eta^5\text{-cp})_2M(C_2R)_2]$ formed by the group IVA metals and by vanadium(IV); (ii) complexes of the type $[(\eta^5\text{-cp})_2MC_2R]_n$ formed by group IIIA, predominantly 4*f*-metals, and by uranium(IV); (iii) monocyclopentadienyl complexes of the metallocene-forming metals Mo, Fe, Ni, Ru and Os which contain one alkynyl ligand besides phosphines and/or CO ligands.

(i) Compounds of group IVA metals

The monomeric air-stable complexes of Table 5 as well as some methylcyclopentadienyl derivatives $[(\eta^5\text{-me}C_5H_4)_2M(C_2R)_2]$ (R = ph, cy, n-C_6H_{13} etc.; M = Ti [114], Zr [116]) are structurally well characterised by IR and ^1H NMR data. The vanadium(IV) complex exhibits the paramagnetism of one unpaired electron. The M–C_2ph bonds of these compounds are cleaved by HCl with the formation of cp_2MCl_2 and phC_2H.

Some years ago the methylcyclopentadienyl compound $[(\eta^5\text{-me}C_5H_4)_2\text{-}TiC_2ph]_2$ was prepared by different methods and characterised by X-ray studies [190]. In this molecule two titanium atoms are bridged by a *trans*-1,4-diphenylbutadiene ligand formed via oxidative coupling of two primary phenylethynyl groups. The unsubstituted compound $[(\eta^5\text{-cp})_2\text{-}TiC_2ph]_2$ [113] probably has the same structure whereas $[(\eta^5\text{-cp})_2VC_2ph]$ [113] seems to be a real alkynyl complex of vanadium(III).

TABLE 5

Complexes of the type $[(\eta^5\text{-cp})_2M(C_2R)_2]$

M	R
Ti	CF_3 [57], ph [112] [113] [114], cy, n-C_6H_{13}, CH_2Cph_2H, CH_2Cph_2CN [114]
Zr	ph [115] [116], CH_2Cph_2H, CH_2Cph_2CN, cy, n-C_6H_{13} [116]
Hf	ph [115]
V	ph [113]

(ii) Compounds of group IIIA metals

Complexes of the type cp_2MC_2ph are formed by Sc [117] and the lanthanides Gd, Ho, Er, Yb [118,119]. The alkynyl and cyclopentadienyl ligands are readily protolyzed by water and in this respect these complexes behave similarly to the ionic cyclopentadienides. However, the IR and electronic spectra of the lanthanide complexes are indicative of the existence of polarized π-bonded cp groups and σ-bonded phenylethynyl ligands. This has been confirmed quite recently by the paramagnetically shifted ^1H NMR spectra of the more soluble ytterbium complexes $(\eta^5\text{-cp})_2YbC_2R$ (R = bu, cy, n-C_6H_{13}) [120]. These complexes as well as $(\eta^5\text{-cp})Ho(C_2ph)_2$ [119] are obviously associated in the solid state, presumably by means of alkynyl bridges. The virtual molecular weights correspond to the formulae $[cp_2ScC_2ph]_2$ in THF [117] and $[(\eta^5\text{-cp})_2YbC_2R]_{2.5-3}$ (R = bu, n-C_6H_{13}) in benzene [120]. The magnetic moments of the solid lanthanide complexes at room temperature correspond well with the values theoretically predicted for the tripositive oxidation states of these metals. However, in marked contrast to the magnetic behaviour of the lanthanide chlorides cp_2LnCl and $cpLnCl_2 \cdot 3$ THF, the magnetic moments decrease with falling temperature and this fact has been connected with a more covalent character of the σ-bonds $Ln-C_2ph$ [119].

The only actinide compounds of this category so far known are the uranium(IV) complexes $(\eta^5\text{-cp})_3UC_2R$ (R = H [121], ph [122]). The room temperature moment of the solid $(\eta^5\text{-cp})_3UC_2ph$ ($\mu_{eff} = 2.88$ BM) is consistent with a spin-free $5f^2$ electronic configuration for the metal. The occurrence of π-bonded cp ligands and of a polarized σ-bond $U-C_2R$ is experimentally supported by the IR and ^1H NMR spectra and could be confirmed by a crystal structure determination of $[(\eta^5\text{-cp})_3UC_2ph]$ [123]. The uranium atom of the discrete molecule is pseudo-tetrahedrally coordinated with the centroids of the cp rings and with an almost linear η^1-phenylethynyl ligand. Any participation of 5*f*-orbitals in the bonding is doubtful.

(iii) Monocyclopentadienyl compounds of metallocene-forming metals

Most of these monomeric diamagnetic complexes belong to the type $[\eta^5\text{-cpMC}_2R(L)(L')]$ and are formed by the iron group metals Fe, Ru and Os (Table 6). The iron complexes $[\eta^5\text{-cpFeC}_2R(CO)_2]$ react with copper(I) halides in acetone or THF yielding the dimeric adducts $[\eta^5\text{-cpFeC}_2R(CO)_2(CuX)]_2$ (R = ph, me; X = Cl; R = ph, X = Br) [125]. The analogous complexes $[\eta^5\text{-cpFeC}_2R(CO)_2(CuCl)]_2$ (R = C_6F_5, *p*-C_6H_4me, *p*-C_6H_4F) are obtained by the reaction of $[\eta^5\text{-cpFeCl(CO)}_2]$ with the corresponding copper(I) acetylides $[CuC_2R]_n$ in THF [125]. A similar reaction of

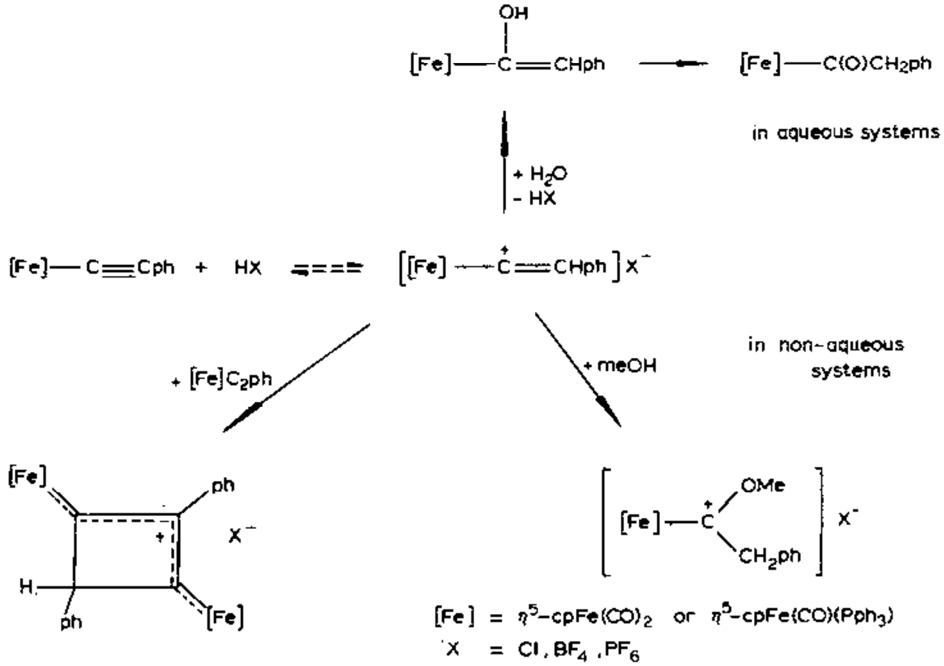
TABLE 6

Complexes of the type $[\eta^5\text{-cpMC}_2\text{R(L)(L}')]$

M	R	L	L′	Ref.
Fe	CF_3, ph, C_6F_5	CO	CO	57
	bu	CO	CO	124
	me	CO	CO	125, 127
	H	CO	CO	132
	bu, ph	CO	Pph_3	124
	H, me	dpe/2	dpe/2	133
Ru	ph, C_6F_5, p-C_6H_4F	Pph_3	Pph_3	50
	me, pr, CO_2me			126
	ph	dpm/2	dpm/2	126
	ph	dpe/2	dpe/2	
Os	ph	Pph_3	Pph_3	126

the ruthenium complex $[\eta^5\text{-cpRuCl(Pph}_3)_2]$ with $[\text{CuC}_2\text{R}]_n$ affords the adducts $[\eta^5\text{-cpRuC}_2\text{R(Pph}_3)_2\text{(CuCl)}]$ (R = ph, me, p-C_6H_4F) and $[\eta^5\text{-cpRuC}_2\text{ph(Pph}_3)_2\text{(CuCl)}]_{>1}$ [50]. X-ray studies of the monomeric $[\eta^5\text{-cpRuC}_2\text{ph(Pph}_3)_2\text{(CuCl)}]\cdot\text{me}_2\text{CO}$ [128] and of the dimeric $[\eta^5\text{-cpFeC}_2\text{ph(CO)}_2\text{(CuCl)}]_2$ [129] have shown that the copper atoms of the CuCl ligands in both complexes are symmetrically π-bonded to the triple bond system of the MC≡Cph moieties. The iron complex is dimerised by chloro bridges of the planar ring $\rightarrow\mathrm{Cu}\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}\mathrm{Cu}\leftarrow$. In this way the iron complex reveals trigonal copper(I) whereas the monomeric ruthenium compound contains linear two-coordinate copper(I).

Dilute aqueous acids convert the compounds $[\eta^5\text{-cpFeC}_2\text{R(CO)}_2]$ to the acyl complexes $[\eta^5\text{-cpFe–C(O)CH}_2\text{R(CO)}_2]$ (R = me [127], ph [125]) by an acid-catalyzed addition of water while concentrated aqueous HCl forms $[\eta^5\text{-cpFeCl(CO)}_2]$ [124]. The complex $[\eta^5\text{-cpFeC}_2\text{ph(CO)(Pph}_3)]$ similarly reacts with dilute aqueous HBF_4 yielding the corresponding acyl compound [130]. The formation of acyl complexes has been explained by the intermediate existence of a vinylidene cation $[\mathrm{Fe}]\overset{+}{\mathrm{C}}{=}\mathrm{CHR}$ (Scheme 2) which may be alternatively named a metal-stabilized vinyl carbonium ion. This hypothesis has been strongly supported by the isolation of the unstable pink $[[\text{Fe}]\text{–C=CHph}]\text{BF}_4$ from non-aqueous solvents which is readily converted by methanol to the stable alkoxycarbene complex $[[\text{Fe}]\text{–C(Ome)CH}_2\text{ph}]\text{BF}_4$



Scheme 2

($[Fe] = \eta^5$-cpFe(CO)(Pph$_3$)) [130]. In the absence of the nucleophilic methanol the vinylidene complex cation reacts with a second molecule of the alkynyl compound and forms a 1,3-dimetallo-stabilized cyclobutenium salt [130] as shown in Scheme 2. It has been demonstrated quite recently that vinylidene cations are stabilized by chelating dpe ligands and crystalline vinylidene complexes have been prepared from non-aqueous solvents by the acid–base reaction

$$[Fe]C{\equiv}CR + HX \rightleftharpoons [[Fe]{=}C{=}CHR]^+X^- \tag{9}$$

$$\left([Fe] = \eta^5\text{-cpFe(dpe)};\ R = H, \text{me};\ X = PF_6, SO_3F\right)$$

Thereby the first unsubstituted vinylidene complex [η^5-cpFe$=$C$=$CH$_2$(dpe)]PF$_6$ was obtained [133].

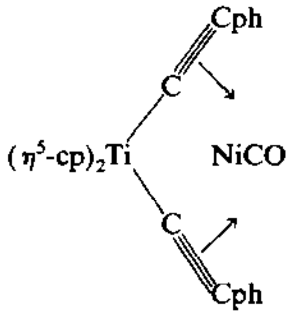
Finally, [η^5-cpFeC$_2$ph(CO)(L)] (L = CO, Pph$_3$) also reacts with neutral electrophiles such as tcne and $(CF_3)_2CO$ whereby a (2 + 2) cycloaddition to the alkynyl ligand occurs. (The ruthenium and osmium complexes of Table 6 are also readily protonated at the C^β atoms of the MC≡CR moieties by HPF$_6$ or HBF$_4$. The resulting vinylidene complexes [η^5-cpM$=$C$=$CHR(Pph$_3$)$_2$]$^+$ (M = Ru, Os) are much more stable than the corresponding iron compounds and the reverse deprotonation of these reforms the alkynyl compounds in high yield [126].) In addition to the compounds of Table 6, the air-stable monomeric complexes [η^5-cpMC_2R(CO)$_3$] (M = Cr, Mo, W; R = bu, ph) [124,134] and [η^5-cpNiC_2R(Pph$_3$)] (R = H, ph [131], C_2H, *o*- and *p*-$C_6H_4C_2H$ [132]) have been prepared. Those nickel complexes which contain terminal ethynyl groups (R = H, C_2H) can be oxidatively coupled according to eqn. (10) [132]

$$2[\mathrm{Ni}]-(\mathrm{C{\equiv}C})_n-\mathrm{H} \xrightarrow[\mathrm{me_2N(CH_2)_2Nme_2}]{\mathrm{O_2,\ CuCl}} [\mathrm{Ni}]-(\mathrm{C{\equiv}C{-}C{\equiv}C})_n-[\mathrm{Ni}] \qquad (10)$$

$\left([\mathrm{Ni}] = \eta^5\text{-cpNi(Pph}_3)_2,\ n = 1 \text{ or } 2\right)$

The electronic spectra of these products exhibit a bathochromic shift of the absorption bands (250–700 nm) with the increase of the conjugated acetylenic linkages.

[η^5-cpNiC_2ph(Pph$_3$)] as well as [η^5-cpFeC_2ph(CO)$_2$] react with the dinuclear metal carbonyls $Fe_2(CO)_9$ and $Co_2(CO)_8$ with the formation of trinuclear metal clusters such as [(η^5-cp)$_2$Ni$_2$Fe(CO)$_3$(C_4ph$_2$)], [η^5-cpFe$_3$(CO)$_7$(C_2ph)] and [η^5-cpFeCo$_2$(CO)$_6$(C_2ph)] (Section F), whereas the reaction between [(η^5-cp)$_2$Ti(C_2ph)$_2$] and Ni(CO)$_4$ affords the side-on bridged compound [136]



E. POLYNUCLEAR COMPLEXES OF THE TYPES [MC≡CR]$_x$ AND [M(C≡CR)$_2$]$_x$

Complexes of this category are formed by the group IB and IIB metals. The long-known acetylides of copper, silver and gold [MC_2R]$_x$ (R = alkyl, aryl) as well as the recently described corresponding complexes of silver and gold with R = CH_2Cme$_2$CN and CH_2Cph$_2$CN [137] are believed to be polymeric on account of their insolubility in all solvents. The more soluble 3,3,3-trifluoropropynyl compounds [MC_2CF_3]$_x$ (M = Cu, Ag) [138] seem to be less associated and the molecular weights of the 3,3,3-trimethylpropynyl compounds of copper and gold in boiling benzene correspond to the formulae [CuC_2t-bu]$_8$ [139] and [AuC_2t-bu]$_4$ [140]. A rigid proof of the polymeric nature of these compounds, however, is available in only the solid $[CuC_2ph]_\infty$. This coordination polymer contains infinite zigzag chains of copper atoms at bond distances from each other [141]. Each copper atom is surrounded in an approximately trigonal arrangement by the terminal carbon atoms of two C_2ph groups (σ-bonds) and symmetrically by two ethynyl carbon atoms of a third C_2ph ligand (side-on π-bond).

All the coordination polymers $[CuC_2R]_x$ so far investigated are depolymerized by addition of tertiary phosphines. The 1:1 adducts thus formed correspond cryoscopically to the formulae $[CuC_2R(PR'_3)]_2$ (R = t-bu, R' = me; R = ph, R' = me, et; R = C_2ph, R' = pr) in nitrobenzene [139]. A few higher coordinated adducts e.g. $[CuC_2\text{t-bu}(Pme_3)_2]$, $[CuC_2ph(Pet_3)_3]$ have been described which seem to be monomeric in benzene and nitrobenzene respectively [139]. Suspensions of $[CuC_2ph(NH_3)]_x$ [18] or $[CuC_2me]_x$ in liquid ammonia form soluble adducts with carbonmonoxide, which are too unstable to be isolated [142].

Though phenylethynyl(trimethylphosphine) copper is dimeric in nitrobenzene, X-ray studies have shown that it consists of discrete tetrameric molecules in the crystalline state [54]. The molecule $[CuC_2ph(Pme_3)]_4$ contains a four-membered zigzag chain $(me_3P)_2Cu(1)–Cu(2)\ldots Cu(3)–Cu(4)(Pme_3)_2$ with the phosphine ligands at the ends. The distances (Cu(1)–Cu(2)) = (Cu(3)–Cu(4)) = 245 (±0.3) pm are less than the separation in the metal (255.6 pm) suggesting some bonding between the outer and the inner copper atoms. The distance Cu(2)...Cu(3) (269.3 ± 0.6 pm) is markedly longer and the whole molecule can be described by a zwitterionic structure $[[(me_3P)_2Cu]^+[CuC_2ph)_2]^-]_2$. Alkynyl bridges connect the cations of the pseudo-tetrahedrally coordinated Cu(1) and Cu(4) with the non-linear anions of Cu(2) and Cu(3) and hold together the whole tetramer, which is almost planar. An alternative description of the bonding will be discussed in Section G (ii).

The phenylethynyl(trimethylphosphine) silver, dimeric in boiling benzene [139], has been shown to be polymeric in the crystalline state [55]. The macromolecule $[AgC_2ph(Pme_3)]_\infty$ contains an infinite almost straight chain of silver atoms with Ag–Ag distances of 303.3 pm being somewhat longer than in the metal (288.9 pm). Again, the structure may be considered as built up by $[Ag(Pme_3)]^+$ cations and nearly linear anionic units $[phC_2AgC_2ph]^-$ held together by alkynyl bridges. In this way the cationic silver atoms are pseudo-tetrahedrally coordinated by two phosphine ligands and side-on by two ethynyl groups. The corresponding triethylphosphine complex $[AgC_2ph(Pet_3)]_n$ is associated with $n = 2$ in nitrobenzene and $n = 2.6–2.7$ in benzene [53].

The polymeric $[AuC_2ph]_x$ forms many adducts of the type $[AuC_2ph(L)]$ with L = PR_3 (R = et, ph, O–ph), $Aset_3$, $Sbet_3$, RNC (R = bu, o-C_6H_4et,

p-C_6H_4me), NH_3, primary and secondary amines, pyr; all but the amine complexes are monomeric in benzene [140]. The relative donor character of various ligands L towards phenylethynyl gold has been established by a series of displacement reactions and follows the order $Pet_3 > P(O\text{-}ph)_3 > p$-$meC_6H_4NC > Aset_3 > Sbet_3 > NH_3 > RNH_2 > R_2NH > R_3N$ [140]. The dipole moments of the monomeric complexes [AuX(Pet_3)] in benzene show that the electronegativities of X arise in the order me < ph < C_2ph < Cl [143] and there is no reason to doubt that the gold(I) atoms have the coordination number two in all monomeric compounds with a linear arrangement L–Au–C_2ph. This has been confirmed by X-ray analysis of the crystalline isopropylamine (phenylethynyl)gold which consists of individual molecules [AuC_2ph(i-prNH_2)] with an almost linear arrangement N–Au–C≡C–ph [144]. The Au–Au distances (372.2 and 327.4 pm) are much greater than in the metal (288.4 pm) and the lattice seems to be held together by hydrogen bonding between the NH_2 group of one monomer and the ethynyl group of another. Analogous structures of the n-pentylamine and n-octylamine complexes are inferred by comparison of their unit-cell dimensions with those of the [AuC_2ph(i-prNH_2)] [144].

The solid phenylethynyl compounds $M(C_2ph)_2$ (M = Zn [96], Cd [22]), insoluble in non-donor solvents, also seem to be polymeric and the octynyls of these metals $M(C_2C_6H_{13})_2$ are associated even in hot benzene [145]. Further, associated structures of the deeply coloured phenylacetylides of divalent ytterbium [146] and nickel [147] are likely. The paramagnetism of the latter compound is consistent with a polymeric structure $[NiNi(C_2ph)_4]_x$ which contains alternating spin-free and spin-paired nickel(II) atoms.

F. ALKYNYL COMPLEXES OF *d*-METAL CLUSTERS

Metal to metal bonds occur not only in some group IB metal acetylides mentioned in the foregoing section but also in a series of group VIIIB metal acetylides which have been prepared and structurally characterised during the past ten years. Bridging alkynyl groups beside other ligands (e.g. PR_3, CO, aryl groups) are attached in these compounds to homonuclear or heteronuclear metal clusters as shown in Fig. 1. The Vaska-type complexes *trans*-[MCl(CO)(PR_3)$_2$] (M = Ir, Rh) react with the polymeric acetylides $[MC_2ar]_x$ (M = Cu, Ag) in refluxing organic solvents whereby the deeply coloured cluster acetylides $[M_2Cu_4(C_2ar)_8(Pph_2R)_2]$ (M = Ir, Rh; ar = ph, C_6F_5, p-C_6H_4F, p-C_6H_4me; R = ph, me) [51] and $[M_2Ag_4(C_2ar)_8(Pph_3)_2]$ (M = Rh, Ir; ar = ph, C_6F_5) [48,52] are formed. X-ray studies of the compound $Ir_2Cu_4(C_2ph)_8(Pph_3)_2$ [148] have shown that the six metal atoms form a slightly irregular octahedron in which the iridium atoms are in mutually *trans* positions. Each iridium atom is σ-bonded to one phosphine ligand and to four phenylethynyl ligands; each copper atom is attached by asymmetric π-interactions to two $C{\equiv}C$ moieties, one above and one below the equatorial plane. Presumably, the other compounds of this type have broadly similar structures and it is of interest in this connection that the $[Rh_2Ag_4]^{8+}$ core is isoelectronic with the octahedral rhodium cluster found in $[Rh_6(CO)_{16}]$ [149]. Ir_2Cu_4 clusters seem also to be preserved in the compounds $[Ir_2Cu_4(C_2ar)_8(Pph_3)_2(Fe(CO)_4)_2]$ (ar = ph, p-C_6H_4me) which have been obtained by reaction of $Fe_2(CO)_9$ with $[Ir_2Cu_4(C_2ar)_8(Pph_3)_2]$ [51]. The IR and ^1H NMR data of these compounds suggest the presence of $Fe(CO)_4$ moieties side-on π-bonded to $C{\equiv}C$ groups.

Homonuclear Cu_6 clusters are realised in the complexes $[Cu_6(C_2R)_2(ar)_4]$ (R = ph, p-C_6H_4me, 2,4-xylyl, mesityl; ar = p-$C_6H_4Nme_2$) which are available by the reaction of $[Cu(ar)]_x$ with $[CuC_2R]_x$ as well as by some other methods [150]. X-ray studies have shown that the center of the molecule $[Cu_6(C_2H_6H_4me\text{-}p)_2(C_6H_4Nme_2\text{-}p)_4]$ consists of a slightly distorted octahedron Cu_6 [151]. Two opposite edges of the equatorial Cu_4 plane are symmetrically η^1-bridged by linear p-tolylethynyl ligands and four triangular faces of the octahedron are spanned by p-dimethylaminophenyl groups bridging a Cu_{eq}–Cu_{ap} edge via carbon and bonding to a third Cu_{eq} atom by nitrogen coordination. Due to this structure the thermal decomposition of these compounds affords the asymmetric cross-coupling products ar$C{\equiv}C$R in almost quantitative yield [152]. The existence of a triangular Fe_3 cluster has been demonstrated by X-ray diffraction data of the complex $[\pi$-$cpFe_3(C_2ph)(CO)_7]$ [153]. In this molecule one CO ligand asymmetrically bridges the shortened π-cpFe–$Fe(CO)_3$-edge whereas the alkynyl ligand forms a μ_3–η^2 bridge between the three iron atoms of the isosceles triangle by one σ- and two side-on π-bonds. Similar structures without CO bridges, however, are believed to be realised in the complexes $[\pi$-$cpFe_2Ru(C_2ph)(CO)_6(Pph_3)]$ [50] and $[\pi$-$cpFeCo_2(C_2ph)(CO)_6(Pphme_2)]$ [136]. An equilateral triangle Ru_3 has been found by neutron-diffraction studies of the complex $[HRu_3(C_2t\text{-}bu)(CO)_9]$ [154]. Therein the alkynyl ligand is coordinated to the Ru_3 cluster via a μ_3–η^2 bridge and the hydridic atom, deriving from the acidic hydrogen of the reactant t-bu$C{\equiv}CH$ [155], forms a symmetrical bridge $\underset{\mathrm{H}}{\mathrm{Ru{-}Ru}}$ out of the cluster plane. This structure is preserved also in the substitution product $[Ru_3(\mu_2\text{-}H)(\mu_3\text{–}\eta^2\text{-}C_2t\text{-}bu)(CO)_8(Pph_2Oet)]$ as shown by X-ray data [155]. The osmium analogues $[HOs_3(C_2R)(CO)_9]$ (R = H, me) [156] probably possess similar structures.

Over the last decade novel reactions between tertiary alkynylphosphines and bi- or trinuclear carbonyls of the iron group metals have been discovered by Carty and coworkers. A CO ligand is thereby initially displaced from $Fe_2(CO)_9$ and $M_3(CO)_{12}$ (M = Ru, Os respectively) by the phosphorus atom

TABLE 7

Multinuclear carbonyls of iron group metals containing alkynyl- and phosphido bridges

	Complex[a]	Geometry of metal framework	Ref.
1a	$Fe_2(CO)_6(P)(\mu_2-\eta^2-C_2ph)$	M–M	158
1b	$Fe_2(CO)_5(Pph_3)(P)(\mu_2-\eta^2-C_2ph)\cdot C_6H_{12}$	M–M	159
2a	$Ru_2(CO)_6(P)(\mu_2-\eta^2-C_2t\text{-}bu)$	M–M	
2b	$Ru_2(CO)_5(Pph_2C_2i\text{-}pr)(\mu_2-\eta^2-C_2i\text{-}pr)$	M–M	156
3a	$Ru_3(CO)_9(P)(\mu_3-\eta^2-C_2i\text{-}pr)$	Opened isosceles triangle M_3	160
3b	$Os_3(CO)_9(P)(\mu_3-\eta^2-C_2i\text{-}pr)$	with two M–M bonds	
4	$Ru_3(CO)_6(\mu_2\text{-}CO)_2(P)(\mu_3-\eta^2-C_2t\text{-}bu)\cdot 0.5\ C_6H_6$	Closed isosceles triangle Ru_3	
5	$Ru_3(CO)_6(Pph_2C_2t\text{-}bu)(P)(\mu_2-\eta^1-C_2t\text{-}bu)(\mu_2-\eta^2-C_2t\text{-}bu)\cdot C_6H_5me$	All three Ru–Ru distances of the triangle are different	161
6	$Ru_4(CO)_7(Pph_2C_2t\text{-}bu)(\mu_2\text{-}CO)(P)(\mu_2-\eta^1-C_2t\text{-}bu)(\mu_2-\eta^2-C_2t\text{-}bu)$	Shallow "butterfly" structure	156
7	$Ru_4(CO)_{13}(P)(\mu_2-\eta^2-C_2t\text{-}bu)$	containing five Ru–Ru bonds	
8	$Ru_5(CO)_{13}(P)(\mu_4-\eta^2-C_2ph)$	Tetragonal pyramid	162

[a] $P=\mu_2\text{-}Pph_2$.

of $ph_2PC{\equiv}CR$, and subsequently the $P{-}C_{sp}$ bond of the substitution product is split under appropriate experimental conditions with formation of phosphido and acetylide bridges. A series of homonuclear cluster compounds containing μ-phosphido and μ-alkynyl ligands have been prepared by this method. They are summarised in Table 7 insofar as they have been structurally characterised by X-ray data.

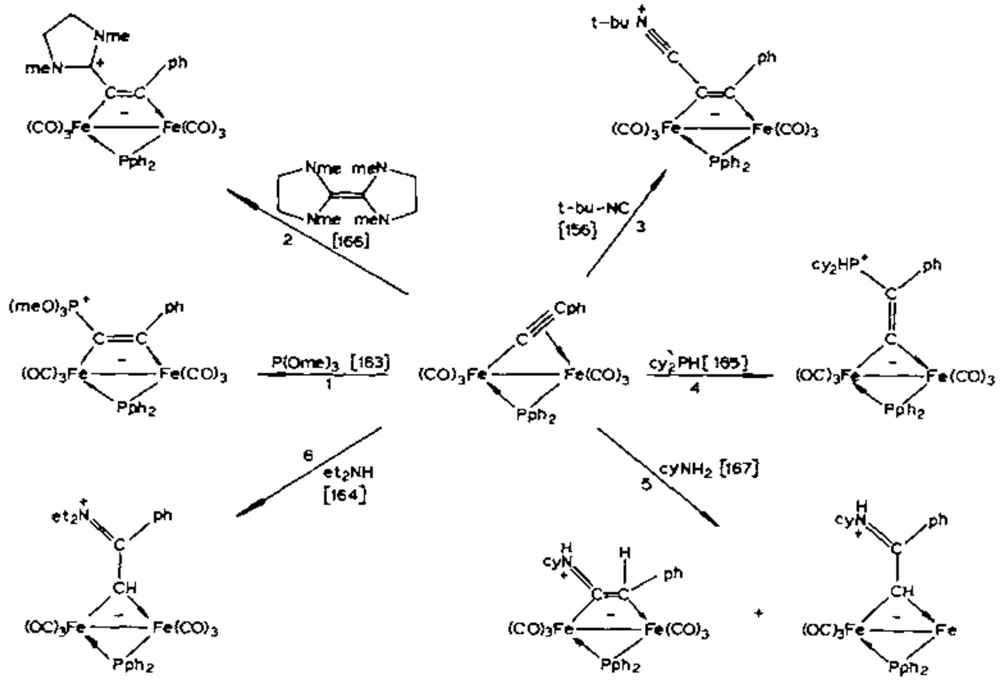
The complex **8** exhibits a novel alkynyl bridge, wherein all the four ruthenium atoms of the pyramidal base are bridged by one symmetrical η^1-three-centre bond and two unsymmetrical η^2–π bonds of the C_2ph ligand. Another interesting finding is the reversible addition reaction (11)

$$[Ru_3(CO)_8(Pph_2)(C_2\text{i-pr})] + CO \rightleftharpoons [Ru_3(CO)_9(Pph_2)(C_2\text{i-pr})] \tag{11}$$

One Ru–Ru bond of the triangular cluster in the type **4** complex is thereby split and the opened cluster of complex **3a** is formed. Such reversible M–M bond fissions are believed to be key processes in homogeneous cluster catalysis [160].

The μ_2–η^2-bound alkynyl ligand of the complex **1a** is easily attacked at the acetylenic carbon atoms by nucleophiles such as amines, phosphines, phosphites, isonitriles and carbenes as shown by reactions 1–6 of Scheme 3. X-ray studies of the adducts thereby formed have demonstrated their zwitterionic structures, with the negative charges probably delocalised into the binuclear cores. Amines, phosphines and isonitriles are also added not only to the triple bonds of the μ_2–η^2-alkynyl bridges of $[Ru_2(CO)_6(Pph_2)(C_2ph)]$ [156] and $[HOs_3(CO)_{10}(C_2ph)]$ [168] but also to those of the μ_3–η^2-alkynyl bridges of $[Os_3(CO)_9(Pph_2)(C_2ph)]$ and $[HRu_3(CO)_9(C_2ph)]$ [156]. The course of these reactions resembles that of reactions 3, 4 and 5, respectively, of Scheme 3.

Quite recently Carty and coworkers have synthesised and structurally characterised several new cluster compounds of ruthenium in which the organic ligand fragment is derived from a multi-site bound acetylide group. Hydrogenation of $[Ru_3(CO)_8(\mu_3\text{–}\eta^2\text{-}C_2R)(\mu_2\text{-}Pph_2)]$ (R = t-bu, i-pr) generates the coordinatively unsaturated cluster $[Ru_3(CO)_9(\mu_2\text{-}Pph_2)(\mu_2\text{–}H)]$ in which a P–phenyl linkage interacts with an electron deficient ruthenium atom. Further hydrogenation leads to the phosphinidene cluster $[Ru_3(CO)_9(\mu_3\text{-}Pph)(\mu_2\text{-}H)_2]$ [191]. The opened cluster acetylide $[Ru_3(CO)_9(\mu_2\text{-}Pph_2)(\mu_3\text{–}\eta^2\text{-}C_2\text{i-pr})]$ can be isomerised to the vinylidene complex $Ru_3(CO)_9[C{=}C(CHme_2)(Pph_2)]$ [192] and the pentanuclear compound **8** (Table 7) adds CO with formation of $[Ru_5(CO)_{14}(\mu_2\text{-}Pph_2)(\mu_4\text{–}\eta^2\text{-}C_2ph)$ [193].



Scheme 3

G. STRUCTURE AND BONDING

The linear arrangement of the C≡C–C groups of many alkynes has been demonstrated by diffraction investigations or by microwave spectroscopy while the linearity of the "free" ions R–C≡C|$^-$ in the salt-like alkali acetylides has been crystallographically established so far for the propynylides MC≡C–CH_3 (M = Na, K) only [169]. The ν(C≡C) stretching frequencies of the alkali acetylides depend heavily on the polarity of the M–C bonds as is illustrated in Table 8. The almost undisturbed anion of the cesium salt exhibits the lowest value whereas the *o*-$C_6H_4(C{\equiv}C{-}Si(me)_3)_2$ containing strong Si–C≡ σ-bonds shows the highest ν(C≡C) frequency. A similar enhancement of the ν(C≡C) values by a decrease of the ionic character of the $\overset{(+)}{M} - \overset{(-)}{C}\equiv$ interaction is observed in other acetylides of alkali and alkaline earth metals such as MC≡CR (R = H, me, ph [172], *p*-$C_6H_4C_2M$ [173,174], cy [175]) and M(C≡Cph)$_2$ (M = Ca, Sr, Ba) [176]. These findings have been interpreted as inferring that the highest occupied molecular orbital of RC≡C|$^-$, populated by the "lone"-pair electrons, has some antibonding character with respect to the C≡C bond. Consequently the force-constant

TABLE 8

IR-active $\nu(C\equiv C)$ frequencies (cm^{-1}) of some solid metal derivatives of 1,2-diethynylbenzene $o\text{-}C_6H_4(C\equiv CM)_2$

M [172]	$\nu(C\equiv C)$	M [171]	$\nu(C\equiv C)$
Cs	1992	H	2105
Rb	1996	$Pb(me)_3$	2120
K	1998	$Sn(me)_3$	2135
Na	2012	$Ge(me)_3$	2155
Li	2032	$Si(me)_3$	2158

$f_{C\equiv C}$ and hence the $\nu(C\equiv C)$ values must be enhanced by the gradual formation of a σ-bond $\overset{(+)}{M} - \overset{(-)}{C} \equiv$ parallel with increasing electronegativities of M^+ [170].

(i) Alkynyl groups as terminal ligands

This type of alkynyl ligand, bound to a transition or non-transition metal by a σ-bond $M\text{–}C_{sp}$ has been established by X-ray studies of the following twelve complexes summarised in Table 9: **1**, $o\text{-}C_6H_4(C_2Sn(me)_3)_2$; **2**, $Hg(C_2ph)_2(phen)$; **3**, $Hg(C_2CH_2Cl)_2(phen)$; **4**, *trans*-$Pd(C_2C_6H_4C_2H\text{-}o)(NCS)(Pet_3)_2$; **5**, *trans*-$Pt(C_2C(me)=CH_2)_2(Pph_3)_2$; **6**, *trans*-$PtC_2ph(Cl)(Pphet_2)_2$; **7**, *cis*-$PtC_2CN(CN)(Pph_3)_2$; **8**, *trans*-$(et_3P)_2SCN\text{–}Pt\text{–}C_2C_6H_4C_2\text{–}Pt\text{–}NCS(Pet_3)_2$; **9**, *trans*-$Ni(C_2ph)_2(Pet_3)_2$; **10**, *trans*-$Ni(C_2C_6H_4C_2H\text{-}o)_2(Pbu_3)_2$; **11**, $AuC_2ph(i\text{-}prNH_2)$; **12**, $(\pi\text{-}cp)_3UC_2ph$. The bond angles listed therein demonstrate the practically linear arrangements of the $C\equiv C\text{–}C$ groups as well as those of the $M\text{–}C\equiv C$ groups. Only the $Pt\text{–}C\equiv C$ fragment of complex **6** exhibits a greater departure from linearity, presumably caused by steric factors. There is no reason to doubt that linear $M\text{–}C\equiv C\text{–}R$ groups are also present in the other complexes described in sections B, C and D. Only the Mn–C interactions in the high-spin anions $[Mn(C_2R)_2]^{2-}$ (R = H, me, ph) and $[Mn(C_2\text{–}R\text{–}C_2)_2]^{2-}$ ($R = 1,2\text{-}C_6H_4$) are considered to be mainly ionic [6,7]. However, the fact that the vast majority of the 3*d*-metal alkynyl compounds are low-spin complexes indicates the strong-field nature of the terminal alkynyl ligands which appear to be placed in the spectrochemical series near the strong-field cyano ligand. The MC distances of compounds **1**–**6** lie in the ranges which may be expected for a single-bond $M\text{–}C_{sp}$. The $Pt\text{–}C_{sp}$ distances in **7** and **8**, however, are shorter than expected and this result has been attributed to some double-bond

TABLE 9

Angles (°) and lengths (pm) of the M–C≡C–C moieties in the low molecular metal alkynyl compounds **1–12**

Compound [a]	Angle		Distance			Ref.
	MCC	C≡CC	M–C	C≡C	C–C≡	
1	178 ±1	178 ±1	209 ±1	122 ±2	142 ±2	177
2	173 ±0.4	176 ±1	205 ±1	118 ±1	141 ±2	92
3	177 ±1	177 ±4	208 ±4	112 ±8	145 ±8	93
4	176 ±1	174 ±1	195.2±0.7	120 ±1	146 ±1	84
5	177.4±0.5	176.5±0.7	202.4±0.6	118 ±1	144 ±1	83
6	162 ±3	174 ±2	198 ±2	118 ±3	144 ±3	77
7	172.2±2.9	173.7±3.7	196 ±3	124 ±5	131 ±5	91
8	173 ±2	178 ±2	192.1±1.2	122 ±2	145 ±3	85
9	177.3±1.1	176.9±1.3	187.9±1.1	121.8±1.4	146.4±1.5	80
	176.5±1.5	176.5±1.5	187 ±1	118 ±2	146 ±2	81
10	175.9±1.4	178.2±1.6	185.9±1.7	121.8±2.4	146.9±2.4	82
11	174.2±1.8	178.6±2.1	193.5±1.9	121 ±2.8	147.9±2.8	143
12	175 ±2		233 ±2	125 ±2		123

[a] See text.

character of these bonds caused by back-donation of the type $d \rightarrow \pi^*$. Due to the extremely short distance C–C≡ in **7**, the structure of this complex has been illustrated by the canonical forms $Pt{-}C{\equiv}C{-}C{\equiv}N| \leftrightarrow Pt{=}C{=}C{=}C{=}N$ with a marked contribution of the latter. In turn, the interatomic distances of 3-dimethylamino-3-phenylallenylidenepentacarbonyl–chromium exhibit an essential contribution of the canonical form $(OC)_5^-\,Cr{-}C{\equiv}C{-}C(ph){=}\overset{+}{N}me_2$ at least in the crystal lattice [178]. Recently a Ni–C_{sp^3} bond length of 197.3 ± 0.6 pm has been found in the *cis*-planar nickel(II) complex [Ni–et(N(R)=CH(R′))(dipyr)] (R = B(et)$_3$, R′ = t-bu, dipyr = 2,2-dipyridine) [179] corresponding to a covalent single-bond radius of 120.3(6) pm for planar four-coordinated Ni(II) (radius of C_{sp^3} = 77 pm). Starting from this value and using a C_{sp}-radius of 69 pm, Ni–C_{sp} distances of 189.3(6) pm should be expected in complexes **9** and **10**. Actually, the observed NiC distances in **9** agree with this prediction whereas the NiC distances of complex **10** are somewhat less. This shortening may be accounted for either by some double-bond character of the NiC bond via back-donation or by a partial ionic character according to $\overset{(+)}{Ni} - \overset{(-)}{C_{sp}}$. However, there is little doubt about the π-acceptor properties of alkynyl ligands in the unsubstituted anionic complex acetylides of "zerovalent" *d*-metals. The large accumulation of electron density on the low-valent metal atoms may be diminished by partial electron transfer from suitably oriented filled *d*-orbitals into vacant anti-bonding π^*-orbitals of the alkynyl ligands. Such a transfer must reduce the bond order of the C≡C system which is reflected by a decrease of the ν(C≡C) frequencies. Indeed, the ν(C≡C) values of the phenylethynylmetallates(0) of palladium and platinum are markedly less than those of the corresponding metal(II) complexes (Table 10).

In the tris(phenylethynyl)tricarbonylmetallates(0) of chromium and molybdenum, however, the powerful π-acidic CO ligands predominantly accept electron density via back-bonding and the unusually high ν(C≡C)

TABLE 10

IR-active ν(C≡C) frequencies (cm^{-1}) of some solid phenylethynyl complexes of "zerovalent" *d*-metals

Complex	Frequency (cm^{-1})	Complex	Frequency (cm^{-1})
$K_2[Pd(C_2ph)_2]$	2024	$K_2[Pd(C_2ph)_4]$	2083 [16]
$K_2[Pt(C_2ph)_2]$	2028, 1894	$K_2[Pt(C_2ph)_4]$	2096 [17]
$K_3[Cr(CO)_3(C_2ph)_3]$	2176 [43]	$K_3[Mo(CO)_3(C_2ph)_3]$	2190 [44]

frequencies of these complexes reveal almost undisturbed C≡C triple-bonds and consequently the existence of mainly covalent $M\text{-}C_2ph$ single-bonds.

(ii) Alkynyl groups as bridging ligands

A survey of the results so far obtained by X-ray-, electron- or neutron diffraction studies reveals that bridging alkynyl ligands can coordinate to metals in the ways shown in Fig. 1.

Symmetrical (μ_2–η^1)-bridge (i)

A linear alkynyl ligand acts as one-electron donor which forms a three-centre electron deficient bond with two metal atoms. The M–C distances are not significantly different and the C≡C vector is approximately perpendicular to the M–M vector. This form of bridge is realised in the beryllium complex $[meBe(\mu\text{-}C_2me)Nme_3]_2$ [180], in the copper cluster $[Cu_6(C_2C_6H_4me\text{-}p)_2R_4]$ [151] and in compounds **5** and **6** of the Table 7 where one C_2t-bu ligand in each connects two atoms of the cluster Ru_3 and Ru_4 respectively. Apart from the beryllium complex the M–M distances suggest strong metal to metal bonds.

(μ_2–η^2)-bridge (ii)

A bent alkynyl ligand σ-bonded to M^1 acts as three-electron donor by the utilization of two π-electrons of the C≡C group which are donated into a

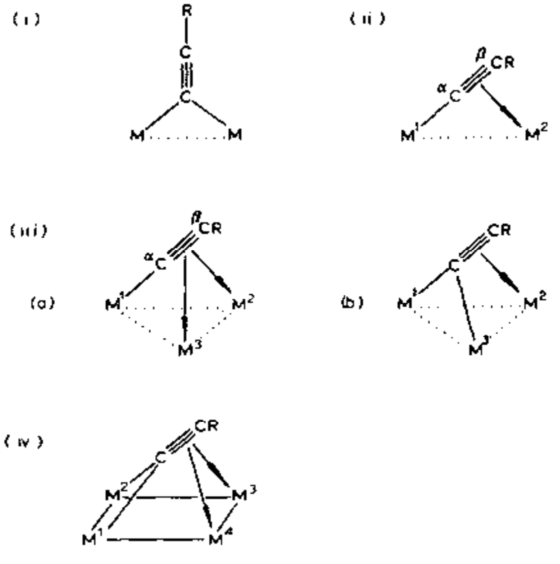


Fig. 1. Modes of coordination of bridging alkynyl groups.

suitably orientated empty orbital of M^2. This more or less strong side-on π-bond can be symmetrical (distances $M^2–C^\alpha = M^2–C^\beta$) or unsymmetrical ($M^2–C^\alpha < M^2–C^\beta$). The symmetrical type has been observed so far in the complexes $[\pi\text{-cpFe(CO)}_2(C_2\text{ph})(\text{CuCl})]_2$ [129] and $[\pi\text{-cpRu(Pph}_3)_2(C_2\text{ph})(\text{CuCl})]$ [128] ($M^2 = \text{Cu}$) which exhibit non-bonding $M^1–M^2$ distances.

Unsymmetrical side-on bonds occur in the compounds $[\text{ph}_2\text{Al}(\mu\text{-}C_2\text{ph})]_2$ [181], $[\text{me}_2\text{Al}(\mu\text{-}C_2\text{me})]_2$ [182], $[\text{ReCu}(C_2C_6F_5)_2(\text{CO})_3(\text{Pph}_3)_2]$ [47] ($M^2 = \text{Cu}$), $[\pi\text{-cpW(CO)}_3(\mu\text{-}C_2\text{ph})\text{W}(\pi\text{-cp})(\text{CO})(\text{HC}_2\text{ph})]\text{BF}_4$ [188], with non-bonding $M^1–M^2$ distances as well as in the cluster compounds **1a**–**2b** [156,158,159], **5** [161], **6**, **7** [156] (Table 7) and in $[\text{Cu}_4\text{Ir}_2(C_2\text{ph})_8(\text{Pph}_3)_2]$ ($M^2 = \text{Cu}$) [148]. The ionic units $[\text{Ag(Pme}_3)_2]^+$ $[\text{phC}_2\text{AgC}_2\text{ph}]^-$ of the polymer $[\text{AgC}_2\text{ph(Pme}_3)]_\infty$ are likewise held together by unsymmetrical weak (μ_2–η^2)-bridges [55].

(μ_3–η^2)-bridges (iii)

In type (a) the bent alkynyl ligand σ-bonded to M^1 acts as a five-electron donor by the utilization of both orthogonal sets of acetylenic $p\pi$-bonds for bridging. Symmetrical side-on bonds ($M^2–C^\alpha = M^2–C^\beta$ and $M^3–C^\alpha = M^3–C^\beta$) have been found so far in the trinuclear complex $\pi\text{-cpFe}_3(C_2\text{ph})(\text{CO})_7$ [153] only. Unsymmetrical dative π-bonds ($M^2–C^\alpha \neq M^2–C^\beta$ and $M^3–C^\alpha \neq M^3–C^\beta$) are realised in the cluster compounds **3a**, **3b** and **4** of the Table 7 as well as in $\text{HRu}_3(C_2\text{t-bu})(\text{CO})_9$ [154] and in the zwitterionic non-cluster complex $[\text{RhAg}_2(C_2C_6F_5)_5(\text{Pph}_3)_3]$ ($M^2 = M^3 = \text{Ag}$) [49]. It should be noted here that a "dative π-bond" is actually a σ-bond with respect to its rotational symmetry.

In type (b) a bent alkynyl ligand forms a symmetrical (μ_2–η^1)-bridge between M^1 and M^3 and a symmetrical π-bond side-on to M^2. This type may be recognized in $[\text{CuC}_2\text{ph(Pme}_3)]_4$ [54] wherein M^1 and M^2 represent anionic copper atoms and M^3 stands for a cationic Cu atom being additionally bound to M^1. In view of the interatomic distances, however, the structure of the tetramer can also be described by type (a) bridges. This observation demonstrates that (a) and (b) are not always distinct but they merge into one another.

(μ_4–η^2)-bridge (iv)

This type of bridge has been found for the first time quite recently in the pentanuclear cluster compound $\text{Ru}_5(C_2\text{ph})(\mu_2\text{-Pph}_2)(\text{CO})_{13}$ [162]. In this the basal atoms of the pyramidal Ru_5 cluster are bridged by a bent C_2ph ligand which forms as five-electron donor a symmetrical (μ_2–η^1)-bridge between M^1 and M^2 and two almost symmetrical dative π-bonds to M^3 and M^4 respectively.

The η^2-bridging metal acetylide groups MC≡CR (Fig. 1, (ii)–(iv)) which form one or two dative side-on π-bonds to metal atoms markedly deviate from linearity adopting a *trans*- or *cis*-bent configuration. The lowering of the C≡C bond order caused by the η^2-interactions is shown by the lengthening of the C≡C distances observed in all η^2-bridged cluster acetylides so far investigated. For the complexes of Table 7 it has been shown that the distances of the formal triple bonds as well as the bend-back angles of the η^2-bridging MC≡CR groups are increased in the order $\mu_2 < \mu_3 < \mu_4$ [156]. The elongations of the C≡C distances of the zwitterionically associated acetylides such as $ReCu(C_2C_6F_5)_2(CO)_3(Pph_3)_2$, $RhAg_2(C_2C_6F_5)_5(Pph_3)_3$, $[CuC_2ph(Pme_3)]_4$ and $[AgC_2ph(Pme_3)]_\infty$ are slight if present at all. However, it should be noted that the correlation between bond length and bond order is not linear [183] and a small lengthening of a C≡C bond can still indicate a marked decrease of its bond order. This reduction of the bond order should be reflected by a decrease of the ν(C≡C) frequency. In fact, the ν(C≡C) values of $[CuC_2ph]_\infty$ (1933 cm^{-1}), which is polymerised by strong η^2-bridges, are lower than those of the partly depolymerised $[CuC_2ph(Pme_3)]_4$ (2045, 2019 cm^{-1}) [54], and the ν(C≡C) wavenumbers of the η^2-bridged [π-cpRuC$_2$ph(Pph$_3$)$_2$(CuCl)] (1979, 1934 cm^{-1}) are less than those of the unbridged [π-cpRuC$_2$ph(Pph$_3$)$_2$] (2076 cm^{-1}) [50]. However, the bond order and stretching frequencies of bridging MC≡CR groups will be influenced to an unknown extent by any kind of back-bonding from populated *d*-orbitals of the η^1- and/or η^2-bound metal atom into vacant π^*-orbitals of the C≡C system. Any conclusions drawn from ν(C≡C) values therefore have to be applied with caution.

Summarising the coordinative behaviour of alkynyl ligands, it can be recognised that the terminal alkynyl groups of complex acetylides resemble the CN ligand, whereas alkynyl groups are comparable with CO ligands in view of their bridging properties [184].

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NOTE ADDED IN PROOF

Recently some high-molecular alkynyl complexes have been described wherein planar four-coordinate metal(II) atoms of the nickel group or six-coordinate Si(IV) atoms are linked by linear –C≡C–R–C≡C– ligands. The yellow complexes –[–Ni(Pbu$_3$)$_2$C≡C–R–C≡C–]$_n$– (R = p-C_6H_4, *trans*-Ni(Pbu$_3$)$_2$(C≡C)$_2$, *trans*-Pt(Pbu$_3$)$_2$(C≡C)$_2$ and *trans*-Pt(Pbu$_3$)$_2$ (C≡CC$_6$H$_4$C

$\equiv$C-p$)_2$ have been prepared by ligand exchange reactions of *trans*-[Ni(Pbu$_3)_2$(C$_2$H$)_2$] with the α,ω-dialkynes HC$_2$–R–C$_2$H [194]. The green one-dimensional conductors $-[-$Si(pc)C$\equiv$C$-]_n-$ and $-[-$Si(pc)C$\equiv$CR$-]_n-$ (R = C$\equiv$C, p-C$_6$H$_4$C$\equiv$C) are formed by the reaction of Si(pc)X$_2$ (X = C$_2$H, Cl) with appropriate Grignard reagents [195,196]. These macro-molecules are air-stable and much less reactive than the anionic polymers K$_{2n}$[M(C$\equiv$CC$_6$H$_4$C$\equiv$C-p$)_2]_n$ (M = Ni, Pd) which have been isolated quite recently [197].

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