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SELECTIVE METAL–LIGAND INTERACTIONS IN HETEROMETALLIC TRANSITION METAL CLUSTERS

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CONTENTS

A. AIMS OF THE REVIEW

This article is not a comprehensive review, but rather a *choice* of examples of *selective* metal–ligand interactions in *transition metal clusters*. A few particularly significant bimetallic derivatives will also be considered; others

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have already been extensively discussed in the literature.

From the great variety of available candidates only the most common ligands found on clusters have been taken into account. However, in some instances, emphasis has been given to promising new developments rather than to the bulk of well-known and hence repetitive examples. It is always very difficult to choose from many examples, and some general criteria must be followed; we considered that those listed below (not in order of importance) would correctly fulfil the purpose of this work.

A limited number of well-known ligands was chosen; these are generally used as "assembling ligands" (or cluster stabilizing ligands). Some of these are "flexible ligands" allowing the study of reversible metal–metal bond formation and the resulting reactivity of other cluster-bound ligands. Metal–ligand interactions relevant to "model" studies on metal-surface chemistry are reported.

Examples conducive to rationalization of the *selective* metal–ligand interactions are particularly discussed. These could offer some help for rational heterometallic cluster syntheses and provide a deeper insight into cluster structures, reactivity and isomerism.

The increased interest in heterometallic cluster chemistry [1] has led, in the last few years, to the synthesis of many complexes with ligands bridging or capping [2] two or more transition metal atoms. The large number of structures which are known allows a better assessment of the possible selective metal–ligand interactions.

Interest in these is due to the following. Knowledge of the preferred metal–ligand interactions can help preparative chemists in planning new rational syntheses or improving reactions already known. An obvious problem for chemists interested in metal–metal bond synthesis is to find appropriate reactions and suitable precursors. Generally, two main approaches are followed, namely: M–M′ bond formation between mononuclear fragments or nuclearity increase from bi- or poly-metallic systems with or without the help of "assembling ligands" (via pyrolysis, redox condensation, photochemistry).

The homo- and hetero-metallic clusters have been discussed as useful models for the coordination of small molecules on metal centres [3], and hence for surface chemistry of metals and alloys. Spectroscopic studies of surfaces frequently show preference of the ligands for one of the possible chemisorption sites, and sometimes ligand migration to the preferred site.

Quite recently, important breakthroughs in the knowledge of metal cluster structures have been achieved. Cotton's studies [4] on semi-bridging carbonyls, Wade's [5] and Mingos's [6] work on the skeletal electron count rules (SEC rules) and the development of the isolobal analogy [7] all represent fundamental steps forward in this field of chemistry.

A discussion of the relationship between the metal–metal distances and the nature of the bridging ligands in bimetallic complexes has been published [8]. This work is an attempt to show the potential of correct "handling" of selective metal–ligand interactions in clusters. We provide a number of Tables; the reader will be referred, as much as possible, to the original literature, covered generally until the end of 1983. Also, since "one drawing is worth ten thousand words" [9], we shall make extensive use of schemes and diagrams.

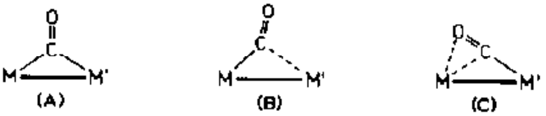
The bridging ligands considered in transition metal clusters will be: H, CO and CS, carbynes, acetylides, alkynes (and derived ligands), isonitriles, sulfur, SR, and PPh_2. Only a few bimetallic examples will be considered, as these have been extensively reviewed by Roberts and Geoffroy [10].

We will mainly take into account the solid state structures of the complexes because of the easier availability of these and of the resulting accurate determination of bonding distances and angles. However, some isomerism and fluxionality (IR and NMR studies) problems will also be considered, as well as some ligand exchange reactions. Solid state and solution data will be compared (when available) and discussed. In some instances (e.g. for the CO ligand) the effects of lattice interactions in the solid state can be important [11].

B. CARBONYL AND THIOCARBONYL LIGANDS

The CO ligand, as well as CS, is found either terminally bound, or bridging two, three or four metal centres. A variety of bonding modes is possible; we will try to show that this depends—at least in part—on the nature of the metals. We shall limit ourselves to some examples and invite the reader to consult a recent general review on bridging carbonyl systems [11].

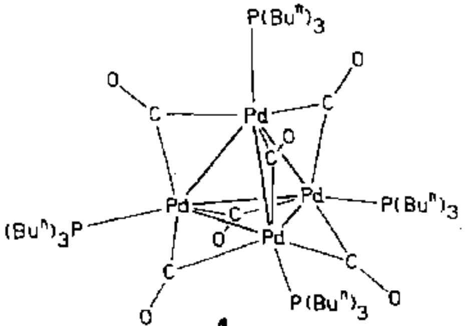
Three different bonding modes can be found for the carbonyl ligand when bridging two metals:



Scheme 1

Bonding modes (A) and (B) occur commonly in homo- and hetero-metallic bi- and poly-nuclear complexes. Several recent examples have been reported of the rarer bonding mode (C) especially in heterometallic complexes.

Bonding mode (A) is usually found in homometallic compounds when the metals are in similar electronic situations. This is therefore out of the scope of this work. Nevertheless, two examples are worthy of mention because of the rarity of carbonyl bridges in palladium bimetallic and cluster systems. The clusters $Pd_4(\mu\text{-CO})_6(PBu^n_3)_4$ (**1**) and $Pd_{10}(\mu_3\text{-CO})_4(\mu\text{-CO})_8(PBu^n_3)_6$ [12] contain either doubly- or triply-bridging CO's (mostly symmetric) which probably contribute to the stabilization of the molecule. The structure of (**1**) is shown below.



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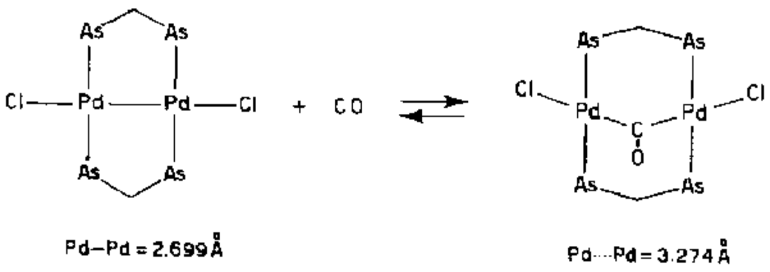
The second example concerns the reversible Pd–Pd bond formation in the bimetallic complex $Pd_2Cl_2(diars)_2$ [13], shown in Scheme 2.



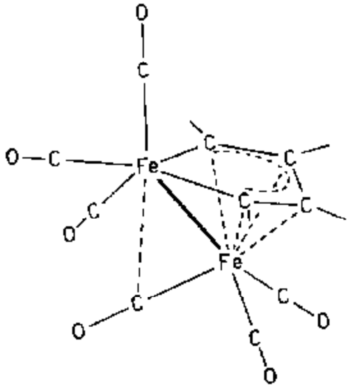
Scheme 2

(i) Bonding mode (B)

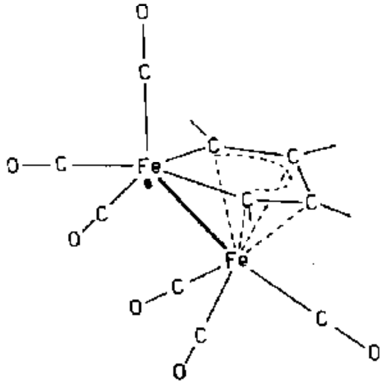
Bonding mode (B) is worthy of discussion for both homo- and heterometallic compounds.

Homometallic examples include the well-known binuclear "non-sawhorse" $Fe_2(CO)_6(RC_2R')_2$ derivatives (complexes **2a**). The two iron atoms have different coordination environments; the asymmetry in the CO bridge (or better "semibridge" [4]) is indicated by the following features: (a) M–C, M′–C bond distances, and M–C/M′–C ratio [11]. (b) M–C–O angles. (c) IR stretching frequencies for the CO's. (d) ^{13}C NMR spectra when available.

Comparable data for selected homo- and hetero-metallic binuclear compounds are reported in Tables 1 and 2.



2a



2b

In complexes of type **2a** a considerable difference exists between the environments of the two iron atoms; the semi-bridging CO's apparently "balance" this difference, acting as stabilizing ligands [4]. However, the closely-related "sawhorse" structures (**2b**) do not contain CO bridges [25], even though in this case crystal lattice effects could play a role, as we are dealing with solid-state structures [11]. This illustrates the care which should be exercised when discussing asymmetric CO bridges, particularly in hetero-metallic compounds. Only isosubstituted complexes with related structures should be compared.

Homobimetallic complexes in which the metal centres have different oxidation or coordination numbers are good candidates for presenting

TABLE 1

"Semi-bridging" CO's in selected homobimetallic complexes

Complex	M–M distance (Å)	M–C distance M′–C distance (Å)	M′–C/M–C ratio	∠M–C–O (°)	Ref.
$Fe_2(CO)_6[C_2(OH)Me]_2$	2.493	1.736 2.484	1.43	168	14
$Fe_2(CO)_6(C_2Ph_2)$	2.520(3)	1.727(13) 2.472(13)	1.43	164.8(11)	15
$Fe_2(CO)_6(C_4H_4)$	2.515(1)	1.779(7) 2.508(4)	1.41	167.3(7)	16
$Fe_2(CO)_6(C_{12}H_{16})$	2.462(3)	1.753(21) 2.321(19)	1.32	161.9(28)	17
$Fe_2(CO)_7(bipy)$	2.611	1.80 2.37	1.32	160.5	4

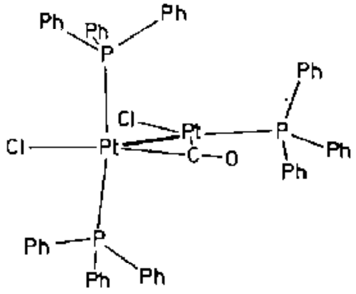
TABLE 2

"Semi-bridging" CO's in selected heterobimetallic complexes

Complex	M–M′ distance (Å)	M–C M′–C distances (Å)	M′–C/M–C ratio	C–O distance (Å)	∠M–C–O ∠M′–C–O (°)	ν_{CO}(cm^{-1}) [a] ^{13}C(CO) NMR (ppm)	Ref.
Cp(CO)Mn(μ-CO)$_2$Rh(CO)(η^5-C$_5$Me$_5$) (**4**)	2.703(2)	1.866(7) 2.172(7)	1.16	1.178(9)	153.0(6) 123.3(5)	1983, 1935, 1818, 1807 252.2, 227.6, 188.3	18
Cp(CO)Cr(μ-CO)$_2$Ni(CO)Cp (**5**)	2.641(3)	1.866(7) 2.172(7)	1.29	–	168(1)	1910, 1890	19
(CO)$_3$Co(μ-CO)PdPy($\overline{\mathrm{C\,N}}$) (**6**)	2.604(1)	1.768(9) 2.330(9)	1.32	1.141(12)	166.1(5)	2022, 1942, 1883	20
(CO)$_2$Co(μ-CO)$_2$Rh(CO)(PEt$_3$)$_2$ (**7**)	2.676(1)	1.774(7) 2.555(8)	1.44		169.4(2)	1990, 1963, 1953 1920, 1888	21
		1.769(7) 2.466(6)	1.39		170.0 (5)	210.3, 180.9	
Cp(CO)Mo(μ-CO)$_2$PtH(PPh$_3$)$_2$ (**8**)	2.839(1)	1.97(1) 2.61(1)	1.32	1.16(2)	169(1)	1916, 1828, 1797	22
		1.95(1) 2.51(1)	1.29	1.15(1)	168(1)		
Cp(CO)Re(μ-CO)$_2$Mo(Cp)$_2$ (**9**)	2.959(1)	1.993(10) 2.267(14)	1.14	1.171(15)	144.4(10) 127.8(8)	1876, 1789 1724, 1678	23
		1.981(13) 2.337(14)	1.18	1.201(18)	147.2(11) 126.7(9)		
(η^6-C$_6$Me$_6$)(CO)Cr(μ-CO)-(μ-CC$_6$H$_4$Me-4)W(CO)$_2$Cp (**10**)	2.941(1)	1.840(6) 2.69(1)	1.46	1.17(1)	163(1)	1921, 1861, 1837 249, 245, 237, 222	24

[a] Frequencies and chemical shifts are given for all CO ligands.

asymmetric or semi-bridging carbonyls. One example is the Pt^{I} binuclear complex $Pt_2Cl_2(\mu\text{-}CO)(PPh_3)_3$ (**3**) in which the Pt(1)–C and Pt(2)–C distances are 1.88(3) and 2.10(3) Å, respectively [26].



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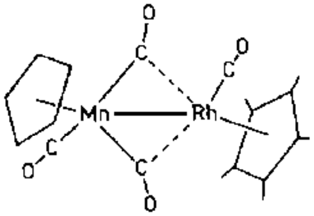
An interesting example of a binuclear (18 + 16) electron complex containing unsymmetrical μ-CS ligands is $Cp(PMe_3)Co(\mu\text{-}CS)_2CoCp$ [27].

Heterobimetallic examples are $Cp(CO)Mn(\mu\text{-}CO)_2Rh(CO)(\eta^5\text{-}C_5Me_5)$ (**4**) [18], $Cp(CO)Cr(\mu\text{-}CO)_2Ni(CO)Cp$ (**5**) [19], $(CO)_3Co(\mu\text{-}CO)PdPy(\overline{C\;N})$ ($\overline{C\;N}$: Ph–C(Me)=N–NHPh) (**6**) [20], $(CO)_2Co(\mu\text{-}CO)_2Rh(CO)(PEt_3)_2$ (**7**) [21], $Cp(CO)Mo(\mu\text{-}CO)_2PtH(PPh_3)_2$ (**8**) [22], $Cp(CO)Re(\mu\text{-}CO)_2Mo(Cp)_2$ (**9**) [23] and $(\eta^6\text{-}C_6Me_6)(CO)Cr(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}4)W(CO)_2Cp$ (**10**) [24], shown below:



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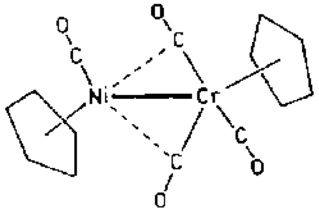

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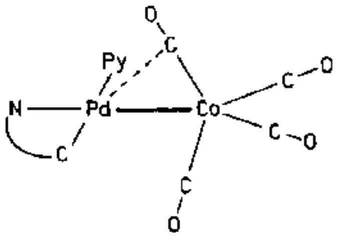

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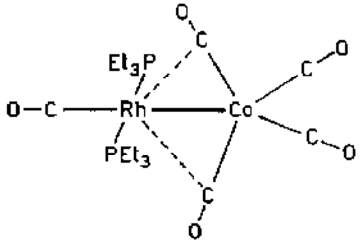

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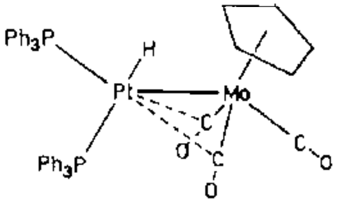
$Cp = \eta\text{-}C_5H_5$;

Multiple bonds, e.g., C≡O, M≡M, aromatic rings are generally not depicted in diagrams.



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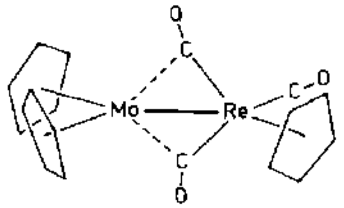

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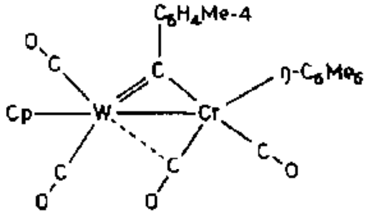

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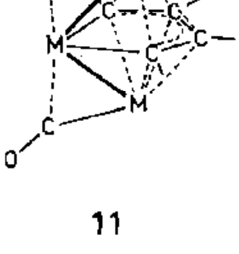
Complex **5** was described as being formed by two 17-electron fragments with very little polarity in the M–M′ bond: for this reason weakly semi-bridging CO's are found and the Cr–CO parameters for both terminal and semi-bridging CO's are very close (Table 2). This complex is isoelectronic and virtually isosteric with $(Cp)_2Fe_2(CO)_4$ [19].

It is well known that within any transition metal triad bridging CO's are more frequently found for the lighter metals (e.g., in the order Fe > Ru > Os). In complexes **4–10** the shorter bond of the bridging CO's involves the metal belonging to the "lower" group (with the exception of **9**), that is in the group order VI, VII, VIII, and within the VIII group metals the order is Fe, Co, Ni.

This behaviour results from the electronic situation at the metals, and represents a good example of selective interaction for (B) type CO's.

Examples of bonding mode (B) in open and closed homotrimetallic clusters are also worthy of mention. In the open clusters, e.g. $Fe_3(CO)_8(C_2Ph_2)_2$ [28], $Ru_3(CO)_8(C_{12}H_{18})$ [29] and $Ru_3(CO)_8(HC_2Bu^t)_3$ [30] (complexes **11**), the asymmetry of the bridging CO's is relatively low and



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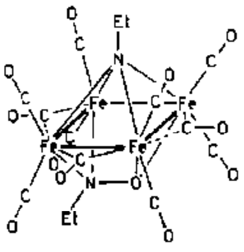
is due to the different coordination of the central vs. the two terminal metal atoms. The main feature of these derivatives is the considerable "rigidity" of the $M_3(\mu\text{-}CO)_2$ frame, found even in heterometallic complexes (see section K).

Examples of closed clusters containing (B) bonded CO's are $Fe_3(CO)_8(C_4H_8S)_2$ [31], $Fe_3(CO)_8(HC_2Me)_3$ [32] and $Fe_3(CO)_7(HC_2Et)_4$ [33]. In these complexes also the asymmetry of the CO ligand always depends on the Effective Atomic Number (EAN) situation and on the coordination around each metal centre.

Sometimes long metal–carbon (carbonyl) distances are found, and the assignment of the bridging nature of the CO's is based mainly on the M–C–O angles and on the ν(CO) stretching frequencies. These two parameters display a close relationship, as shown in Table 3, where structural and spectroscopic data are given for bridging CO's in clusters.

When the M–C–O angles open towards linearity an increase in the ν(CO) frequency (increase in the C–O bond order) is observed.

Noteworthy are some nearly square-planar tetrametallic complexes sucb as $Fe_4(CO)_{11}(NEt)(ONEt)$ (**12**) [37], $Fe_4(CO)_{11}(HC_2Et)_2$ (**13**) [38], $Fe_4(CO)_{11}[P(\text{-}p\text{-tolyl})]_2$ [46], $Fe_2Co_2(CO)_{11}(E)_2$ (E = S, PPh) (**14**) [47,48] characterized by bridging and semi-bridging CO's. Their presence is not expected as similarly substituted metals are present. Interestingly, these complexes are electronically unsaturated (62 electrons) and some of them easily add another ligand (CO, PPh_3) losing the bridging character of the carbonyls [48].



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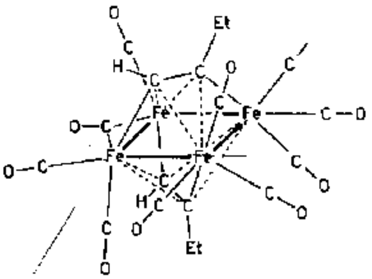

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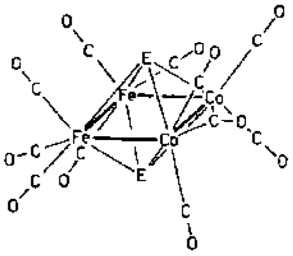

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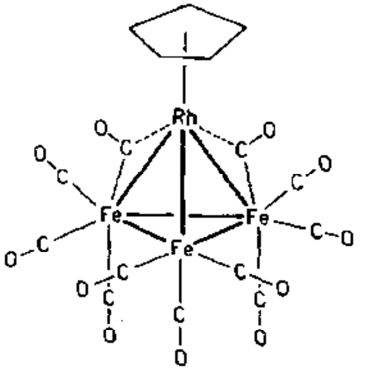
Heterometallic examples of bonding mode (B) have been found in $CpRhFe_3(CO)_{11}$ (**15**) [49], $(Cp)_2Rh_2Fe_2(CO)_8$ (**16**) [50], $CpWPt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2$ (**17**) [51] and in $Co_2Pt_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2$ [52]:

TABLE 3

Relationship between the CO bridge symmetry, M–C–O angles, and ν_{CO} in selected examples of homo- and hetero-metallic clusters

Complex	M–M′ (Å)	M–C, M′–C (Å)	$\left(\frac{M'-C}{M-C}\right)$ Ratio	C–O (Å)	∠M–C–O (°)	ν_{CO} (cm^{-1})	Ref.
(a) Symmetric CO bridges							
$Fe_3(CO)_9(PMe_2Ph)_3$	2.540(7)	1.97(2)–1.97(2)	1.0		141(2)–138(2)	1745, 1792	34
		2.02(3)–2.04(3)			142(2)–139(2)		
$Fe_3(CO)_8(HC_2Me_2)_4$	2.525(3)	1.875(4)–2.031(4)	1.07	1.169(5)	143.5(3)–136.0(3)	1818, 1865	35
	2.515(3)	1.884(5)–2.004(4)	1.08	1.171(5)	141.2(3)–138.3(3)		
$Fe_3(CO)_{11}(PPh_3)$ isomer A	2.568(8)	1.90(4)–1.99(4)	1.05	1.21(4)	139(3)–139(3)	1825	36
		1.86(4)–2.04(4)	1.10	1.21(4)	144(4)–132(3)		
isomer B	2.558(9)	1.86(4)–2.07(4)	1.11	1.25(4)	144(3)–135(3)		
		1.85(5)–2.04(5)	1.10	1.22(4)	142(4)–136(4)		
$Fe_4(CO)_{11}(NEt)(ONEt)$ (**12**)	2.552(3)	1.91(1)–1.95(1)	1.02	1.18(2)	139.5(11)		37
$Fe_4(CO)_{11}(HC_2Et)_2$ (**13**)	2.515(5)	1.963(13)–1.976(14)	1.01	1.144(19)	142.3(10)–138.3(9)	1855	38
$Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$	2.710(1)	2.01(1)–2.08(1)	1.03	1.19(2)	139(1)–137(1)	1825, 1861	39
	2.695(1)	2.02(1)–2.10(1)	1.04	1.19(2)	139(1)–139(1)		
(b) Slightly asymmetric CO ligands							
$Fe_3(CO)_{12}$	2.558(1)	1.96(4)–2.11(4)	1.08	1.12(5)	143(3)–140(3)	1830, 1875	40
		1.93(2)–2.21(3)	1.15	1.14(2)	152(3)–132(2)		
$Fe_3(CO)_8(C_2Ph_2)_2$	2.428(3)	1.842(19)–1.991(19)	1.08	1.194(22)	143.8(15)–137.7(15)	1858, 1869	28
"black isomer"	2.435(3)	1.771(21)–1.988(21)	1.12	1.238(25)	148.2(17)–131.2(16)		

$Ru_3(CO)_8(HC_2Bu^t)_3$	2.669(1)	1.98(1)–2.14(1)	1.08		1.17(2)	144(1)–135(1)	1859, 1878	30
	2.661(2)	2.01(1)–2.12(1)	1.05		1.16(2)	143(1)–137(1)		
$Ru_3(CO)_8(C_{12}H_{18})$	2.681(1)	1.990(7)–2.153(8)	1.08		1.16(1)	144.3(6)–135.8(5)	1860, 1880	29
	2.645(2)	1.992(7)–2.148(8)	1.08		1.14(1)	143.8(7)–136.8(7)		
$(Cp)NiRu_3(CO)_8(C_6H_9)$	2.693(3)	1.994(21)–2.173(21)	1.09		1.133(25)	146.0(17)–133.5(6)	1833, 1854	41
	2.708(3)	1.987(21)–2.280(19)	1.15		1.141(25)	147.8(16)–133.8(16)		
$(Cp)_2Ni_2Ru_3(CO)_8(C_2Ph_2)$	2.724(2)	1.99(1)–2.14(1)	1.07		1.15(1)	143.8(8)–133.5(8)	1835, 1865	42
	2.735(3)	2.02(1)–2.13(1)	1.05		1.15(1)	142.0(9)–135.4(9)		
$(Cp)NiCoFe(CO)_5(PPh_3)$ (C_2Ph_2)	2.467(4)	1.74(2)–2.07(2)	1.19		1.19(3)	148(1)	1827	43
(c) Very asymmetric CO bridges								
$(Cp)Fe_3(CO)_7$ (C_2Ph)	2.524(1)	1.788(5)–2.273(6)	1.27		1.155(6)	157.6(6)–126.3(5)		44
$Fe_3(CO)_7(HC_2Et)_4$	2.631(4)	1.758(10)–2.413(11)	1.37		1.160(12)	160.6(10)–123.0(8)	1853, 1865	33
$Fe_3(CO)_8(HC_2Me)_3$	2.542(3)	1.812(5)–2.489(5)	1.37		1.148(6)	164.1(4), 125.2(4)	1870	32
$Fe_3(CO)_8(C_4H_8S)_2$	2.645(2)	1.76(1)–2.55(1)	1.45		1.16(1)	167.4(7)–119.4(6)	1903	31
$Fe_4(CO)_{11}(NEt)(ONEt)$	2.485(3)	1.83(2)–2.47(2)	1.35		1.16(2)	163.3(14)		37
	2.488(3)	1.78(2)–2.44(2)	1.38		1.17(2)	165.2(13)		
$Fe_4(CO)_{11}(HC_2Et)_2$	2.608(4)	1.780(11)–2.586	1.46		1.155(13)	169.0(11)		38
	2.633(4)	1.789(13)–2.705	1.51		1.138(16)	169.3(15)		
$Ru_5(CO)_{16}(PPh_2)(\mu_5\text{-}P)$		1.948(9)–2.578(9)	1.32			159.8(3)		45
		1.987(9)–2.487(9)	1.25			155.5(3)		



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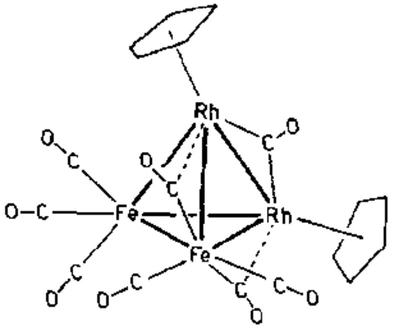

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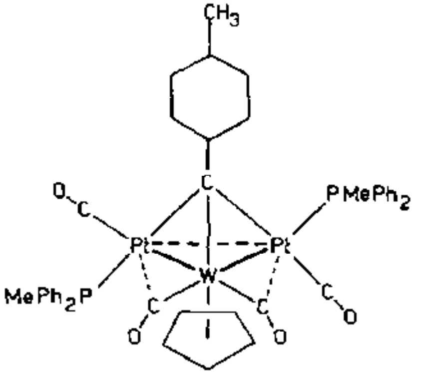
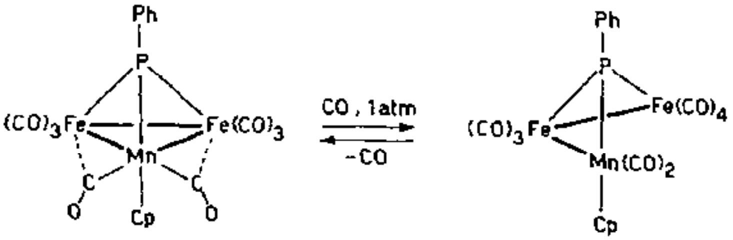


17

In all these derivatives the CO asymmetry is consistent with that observed in the heterobimetallic ones; the shorter bonds are formed with the less electron-rich metal. Synthetic methods for **17** and its derivatives are discussed in section D.

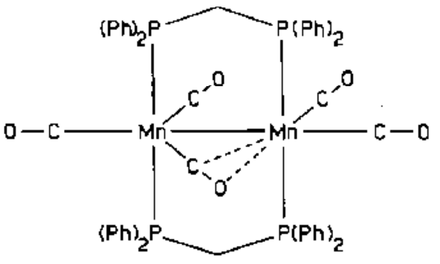
The CO-induced, reversible opening of the trinuclear cluster CpMnFe$_2$ (μ_3-PPh)(CO)$_8$ [53] was also shown to involve semi-bridging CO's; this reaction is represented in Scheme 3.



Scheme 3

(ii) Bonding mode (C)

This bonding mode is becoming more frequently found, especially in bimetallic derivatives, although it is difficult to predict when homometallic complexes will present this feature [54]. In complexes $Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2$ (**18**) [55] and $(Cp)_2Mo_2(CO)_4$ (**19**) [56], shown below, the formally four-electron donor CO [56] is linearly bridging metals of the same nature showing the same coordination environment.



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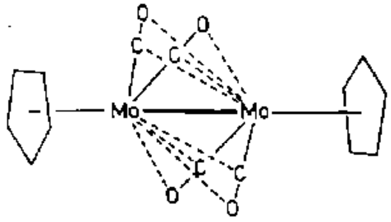
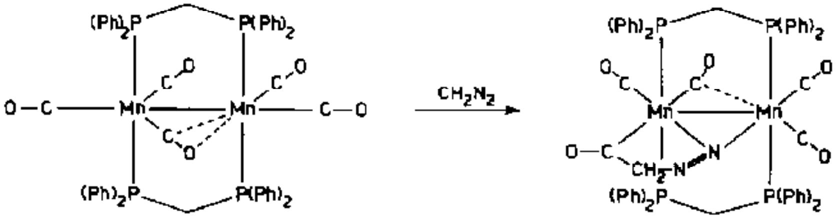


19

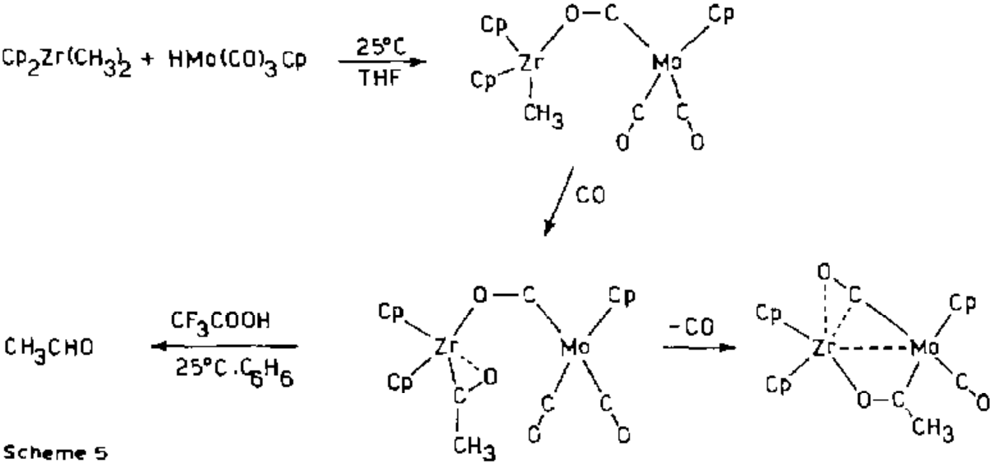
However, recent LCAO–MO–SCF ab-initio calculations on the $Mn_2(CO)_5(PH_3)_4$ model system indicate that the bonding of the semi-bridging carbonyl ligand is best accounted for by a three-center two-electron attractive interaction between the π^* orbital of the semi-bridging ligand and an occupied, in-phase combination of the metal *d* orbitals of appropriate symmetry [57]. The linear geometry of the Mn–C–O unit and the rather large Mn–Mn bond length are rationalized on the basis of the maximization of this interaction, and the η^2-CO ligand, having an electronic structure quite similar to that of the μ-CO ligand in the isoelectronic $[(Cp)Fe(\mu\text{-}CO)(CO)]_2$ system, should not be considered as a four-electron donating ligand [57]. Similarly, the view of CO ligands as four-electron donors in **19** has been recently challenged [58]. Obviously, further investigations are needed in this interesting area.

Mode (C) probably represents an efficient way of activating the CO bond towards dissociation rather than towards nucleophilic attack at the carbon atom. However, reaction with CH_2N_2 appears to occur at this carbon [59] (Scheme 4).



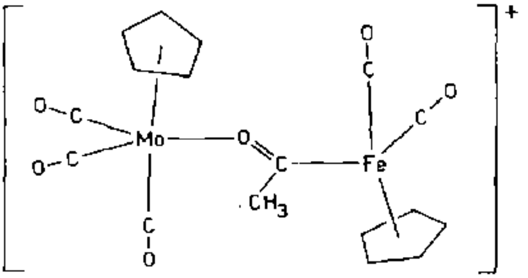
Scheme 4

Another example of CO reactivity has been reported; methyl migration to the CO leads to a bridging acetyl group [60], as shown in Scheme 5.



Scheme 5

Related to the acetyl bonding mode in the previous compound is the situation found in the cation $[(Cp)(CO)_2Fe(\mu\text{-}COCH_3)Mo(CO)_3Cp)]^+$ (**20**), where the bridging acetyl is C-bonded to the iron and O-bonded to the molybdenum [61]:



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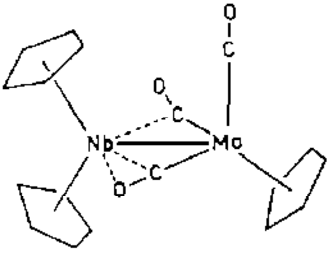
Further heterobimetallic examples of interaction of the carbonyl oxygen with the less electron-rich metal are $(Cp)_2NbMo(CO)_3Cp$ (**21**) [62] $(Cp)_2W_2Mo(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_6$ (**22**) [63] and $(Cp)_3WTi(CO)_2(\mu\text{-}CC_6H_4Me\text{-}4)$ [64].



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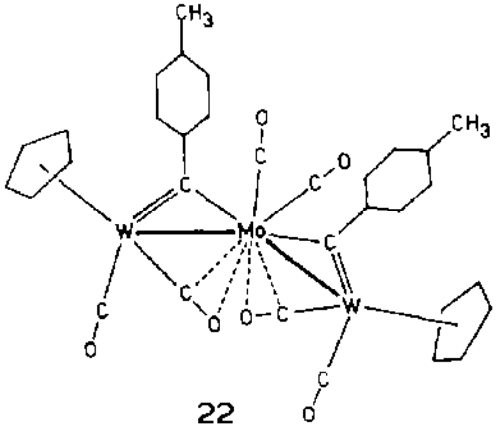

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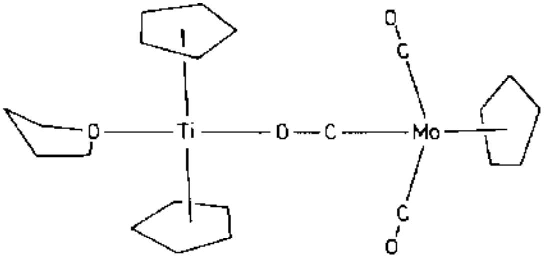
An extreme case worth mentioning is when the bimetallic structure is no longer achieved through metal–metal bonding, but through a μ, η^2 bridging carbonyl, as in $(Cp)_2Ti(THF)OCMo(CO)_2Cp$ (**23**) [65a]. (The first reported such example was $[V(THF)_4][V(CO)_6]_2$ [65b].)



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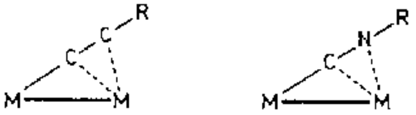
This can be explained by the presence of a "hard" $(Cp)_2Ti^+$ center, forming an acid–base pair with the "harder" oxygen site of the carbonyl ligand [65a].

Bonding mode (C) can be compared with the behaviour of bridging acetylides and isonitriles on two metal centres (section C). Indeed, similarities have been found in the coordination of the acetylides and CO to several metal centers in clusters, these two ligands being isoelectronic [39,66].



Scheme 6

Indeed, the reactivity at carbon in (C) bound CO's finds its counterpart in the reactivity at C_α in the acetylides [66,67].

In Table 4 the bonding characteristics of some (C) bound CO's are reported; noteworthy are the CO distances, generally shorter than for mode (B).

Another example of CO's apparently bound in mode (C) is found in the anion $[Zn\{Fe(CO)_4\}_2]^{2-}$ (**24**) [68], containing a non-transition metal. In this instance, however, the structural features have been interpreted as due to steric rather than to electronic reasons. A discussion of the behaviour of carbonyl ligands in other zinc-containing complexes is given in ref. 68.

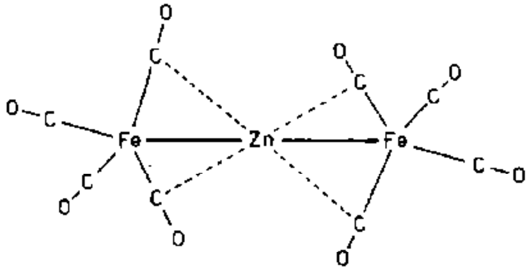


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TABLE 4

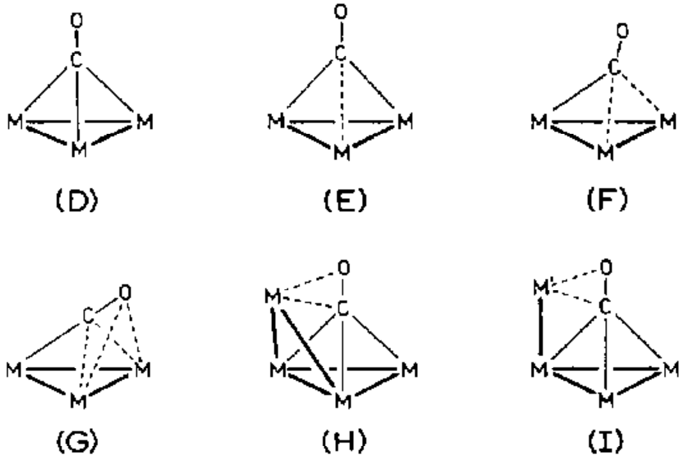
Structural and spectroscopic parameters for some (C) bonded carbonyls

Complex	M–C, M′–C (Å)	M′–O (Å)	∠M–C–O (°)	C–O (Å)	ν_{CO} (cm^{-1})	Ref.
$Mn_2(CO)_5(dppm)_2$ **(18)**	1.93(3)–2.01(3)	2.29(2)	173(3)	1.10(4)	1645	55
$(Cp)_2Mo_2(CO)_4$ **(19)**	2.13(5) [a]–2.56(5) [a]	–	175.9(12) [a]	1.16(2) [a]	1850, 1900	56
$(Cp)_2NbMo(CO)_3(Cp)$ **(21)**	1.94(1)–2.22(1)	2.26(1)	176.8	1.22(1)	1757	62
$(Cp)_2W_2Mo(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_6$ **(22)**	1.918(15)–2.355(12)	–	170.3(12)	1.19(2)	–	63
	1.923(10)–2.348(14)	–	169.7(10)	1.20(1)	–	
$[Zn(Fe(CO_4)_2]^{2-}$ **(24)**	1.729(5)–2.502(5)	–	177.7(7)	1.172(6)	–	68

[a] Average values.

(iii) CO (CS) bridges on three or four "heterometals".

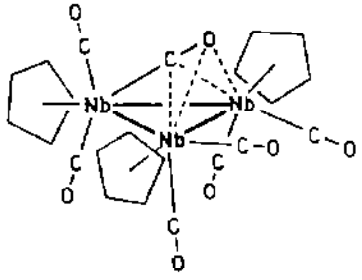
For trimetallic clusters, as well as for the triangular faces of polyhedral structures, Scheme 7 shows the bonding situations which have been found for CO.



Scheme 7

The bonding interactions (H) and (I) have been found only recently in tetrametallic clusters. Bonding modes (D), (H) and (I) are also known for CS.

The symmetrical mode (D) is out of the scope of this review but bonding modes (E), (F) and (G) are of interest; for the last, only one example has been reported, $(Cp)_3Nb_3(CO)_7$ (**25**) [69].



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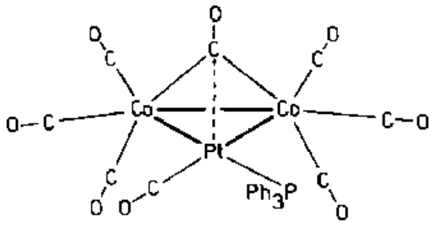
To our knowledge, no heterometallic transition metal cluster showing this feature has been reported. Mode (G) can be compared with the well-known μ_3, η^2 bonding of the acetylides on three metals (section C).

Bonding mode (E), however, is well documented in several complexes. Selected heterometallic examples are: $PtCo_2(CO)_8(PPh_3)$ (**26**) [70], $[(C_5Me_5)_2Rh_2Pt(\mu\text{-}H)(CO)_3(PPh_3)]^+$ (**27**) [71], $(Cp)_2Ni_2Fe_2(CO)_7$ (**28**) [72] and $(C_5Me_5)_4Rh_4Pt(CO)_4$ (**29**, orthorhombic modification) [73]. It is noteworthy that, in complex **28**, no evident reason for a triply-bridging CO can be found; a double bridge would better satisfy the EAN count for both iron and nickel.



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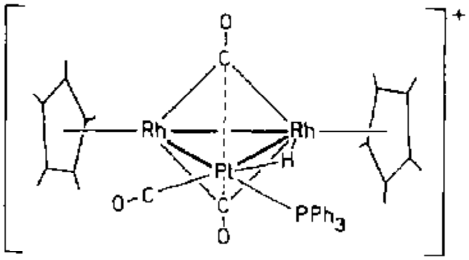

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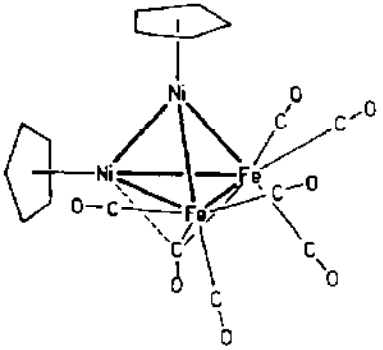

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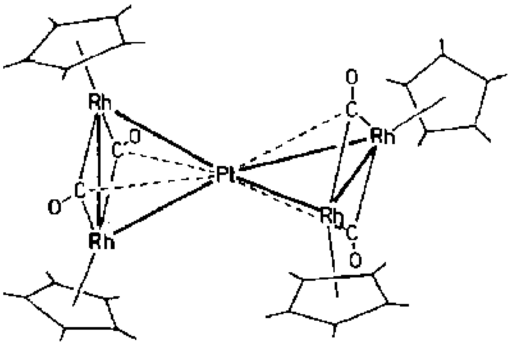

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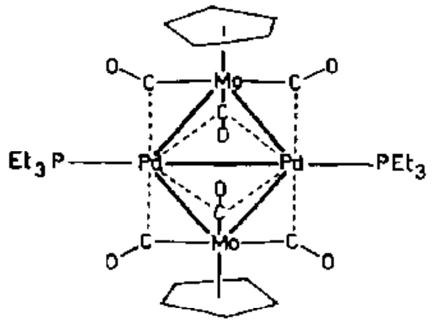
Examples of bonding mode (F) are the planar $(Cp)_2M_2M'_2(CO)_6(PR_3)_2$ clusters (M = Cr, Mo, W; M′ = Pd, Pt) (**30**, for M′ = Pd) [74,75]. Also, in view of their relatively rare occurrence it is worth mentioning the semi-triply bridging CO's on a MFe_2 open face in $(Cp)_2M_2Fe_2(CO)_6S_2$ (M = Cr, Mo) (**31**, for M = Mo) [76,77].



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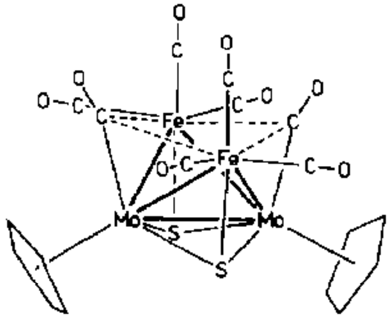

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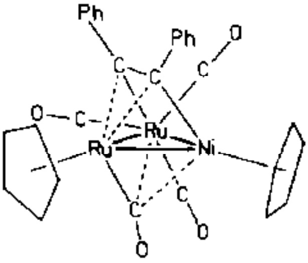
Some bonding characteristics (compared with those of some homometallic derivatives) are given in Table 5.

Like the doubly-bridging carbonyls (see above), relationships between the asymmetry of the bridge and the IR stretching frequencies of the triply-bridging CO's can be obtained. For the homometallic examples (also reported in Table 5) the asymmetry is due, as already discussed, to the different coordination environments of the metals.

Isomers which differ by the bonding mode (B) or (F) of one carbonyl ligand have been isolated in the solid state or characterized in solution, such as $(Cp)_2NiRu_2(CO)_4(C_2Ph_2)$ (**32a** and **32b**) [80] and $Fe_3(CO)_{10}S$(**85**) [147].



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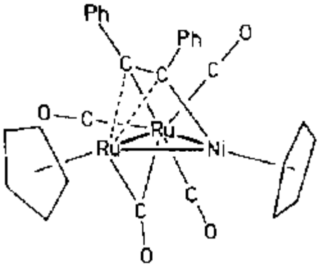
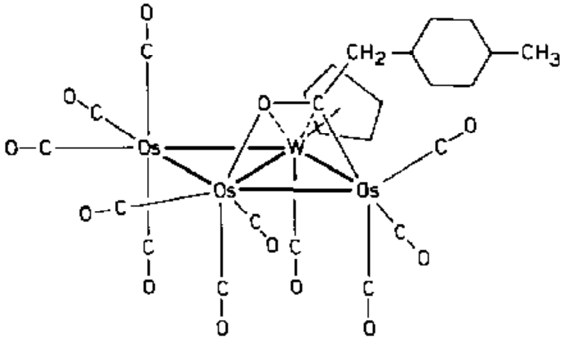


32b

Finally, a CO-derived acyl group has been found coordinated to a triangular face of the cluster in $CpWOs_3(CO)_{11}[C(O)CH_2C_6H_4Me\text{-}4]$ (**33**) [82]; originally the CO was a terminal or more probably a bridging ligand:



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The (semi)triply-bridging mode of CO and CO-derived ligands is relevant to the study of the interactions between small molecules and metal surfaces [75,82].

Bonding modes (H) and (I) are still uncommon. Mode (H) has been found only for the homometallic $[HFe_4(CO)_{13}]^-$ anion (**34**) [83] and a comparable bonding mode of CS has been reported in $Os_4(CO)_{12}(CS)S$ (**35**) [84], represented below:

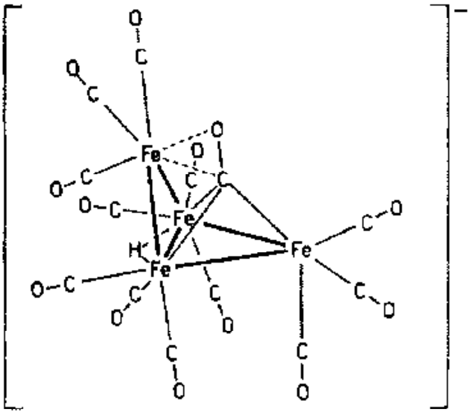
TABLE 5

Structural and spectroscopic parameters for selected examples of triply-bridging CO ligands

Complex	M–C, M′–C	C–O	∠M–C–M (°)	∠M–C–O (°)	ν_{CO} (cm^{-1})	^{13}C NMR (ppm)	Ref.
Bonding mode G				i			
$(Cp)_3Nb_3(CO)_6(\mu_3,\eta^2\text{-}CO)$ **(25)**	1.966(12) 2.226(18), 2.278(14)	1.303(14)	85.0(4), 98.5(7) 102.7(6)	169.6(11)	1850, 1838 1330	247	69
Bonding modes E, F							
Homometallic derivatives							
$Fe_3(CO)_7(HC_2Et)_4$	1.765(13) 2.552(11), 2.590(11)	1.174(16)	69.8(4), 69.4(4) 61.5(3)	164.0(9) 123.5(8), 123.5(8)	–	–	33
$(Cp)_3Rh_3(\mu_3\text{-}CO)(C_2Ph_2)$	1.958(8), 2.052(9) 2.208(8)	1.188(9)	78.4(3), 76.5(3) 82.9(3)	136.3(7), 132.9(6) 127.2(7)	1675		78
Heterometallic derivatives							
$(Cp)_2Cr_2Fe_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6$	1.86(1) 2.53(1), 2.53(1)	1.18(2)	76.4(4), 76.4(4) 93.9(5)	156(1) 118(1), 118(1)	1765	–	76
$(Cp)_2Mo_2Fe_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2\text{-}(CO)_6$ **(31)**	1.90(4) 2.62(3), 2.64(3)	– –	 –	159(3) 119(2), 116(2)	1791	–	77
$(Cp)_2Ni_2Fe_2(\mu_3\text{-}CO)(CO)_6$ **(28)**	1.961(10), 1.981(11) 2.110(10)	1.181(13)	79.9(4) 72.6(4), 72.1(3)	139.2(9), 139.5(9) 126.2(8)	1722	–	72
$(Cp)_2Ni_2Fe_2(\mu_3\text{-}CO)(CO)_5\text{-}(C_5H_6)$ **(38)**	1.755(11) 2.184(13), 2.352(10)	1.172(13)	73.6(4), 69.2(3) 61.9(3)	160.9(10) 124.4(10), 123.6(9)	1785	267 or 287.3	79
$(Cp)_2NiRu_2(\mu_3\text{-}CO)(CO)_3\text{-}(C_2Ph_2)$ **(32)**	1.909(7) 2.249(7), 2.307(7)	1.192(8)	–	147.8(5) 129.6(5), 124.4(5)	1610, 1640 1780 [a]	–	80

$PtCo_2(\mu_3\text{-}CO)(CO)_7(PPh_3)$ **(26)**	1.882(10), 1.932(10) 2.570(10)				1768		70
$(C_5Me_5)_2Rh_2Pt(CO)_3(PPh_3)$	1.988(13), 2.005(15) 2.56(2)	1.19(2)	68.8(5), 71.4(5) 83.0(5)	137.9(12), 137.3(11) 126.8(11)	1791		81
	2.00(2), 2.013(15) 2.476(13)	1.18(2)	70.5(4), 73.1(4) 82.6(6)	138.1(11), 137.1(11) 125.1(12)			
$[(C_5Me_5)_2Rh_2Pt(H)\text{-}(CO)_3(PPh_3)]^+$ **(27)**	1.977(11), 2.044(11) 2.760(11)	1.169(14)	67.3(3), 69.6(3) 83.1(4)	141.7(9), 134.7(9) 124.9(8)	1773, 1769	235.5	71
	1.989(11), 2.026(11) 2.733(11)	1.174(14)	67.8(3), 70.4(3) 83.2(4)	140.6(9), 135.8(9) 122.9(8)			
$(C_5Me_5)_4Rh_2Pt(CO)_4$ [b] **(29)**	1.94(2), 2.03(2) 2.55(2)	1.19(2)	82(1), 69(1)	140(1), 136(1) 127(1)	1706, 1716 1756, 1776	241.5	73
	1.92(2), 1.92(2) 2.56(2)	1.25(2)	86(1), 71(1)	136(1), 125(1)			
	1.94(2), 1.94(2) 2.52(2)	1.19(2)	85(1), 70(1)	137(1), 126(1)			
$(Cp)_2Cr_2Pd_2(\mu_3\text{-}CO)_2\text{-}(CO)_4(PEt_3)_2$	1.84(1) 2.37(1), 2.34(1)	1.17(1)	80.2(3)	165.7(7) 114.7(6)	1773		75
	1.92(1) 2.34(1), 2.26(1)	1.17(1)	81.3(3), 80.5(3) 68.0(2)	156.6(5) 118.1(8), 117.7(6)			
$(Cp)_2Mo_2Pd_2(\mu_3\text{-}CO)_2\text{-}(CO)_4(PEt_3)_2$ **(30)**	2.04(1) 2.31(1), 2.38(1)	1.17(1)	80.9(2), 80.3(2) 66.7(1)	156.2(4) 119.0(4), 118.3(5)	1772		75

[a] Other isomer with doubly-bridging CO. [b] Orthorhombic modification.



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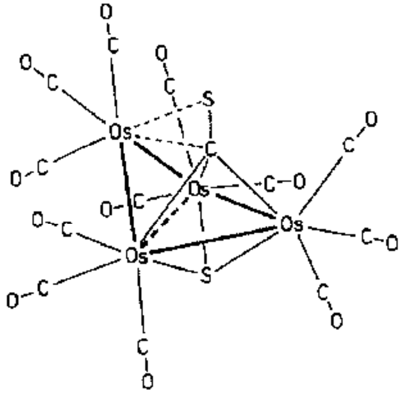
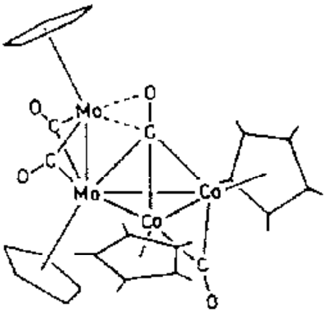


35

Several homo- and hetero-metallic butterfly clusters with C(carbide), N(nitride), or μ_4, η^2-bound CH, COMe, COOMe, C=CHR (vinylidene) ligands are known [85]. These are considered good examples for the activation and reduction of small molecules.

Only one example of mode (I) is known, $(C_5Me_5)_2Co_2(Cp)_2Mo_2(CO)_4$ (**36**) [86], clearly showing the ability of the CO ligand to keep together the Co_2 and Mo_2 fragments (as illustrated also by the preparative method). Bonding mode (I) is also found for CS in $Fe_4(CO)_{12}(CS)S$ (**37**) [87], whose structure is considerably different from that of **35**.



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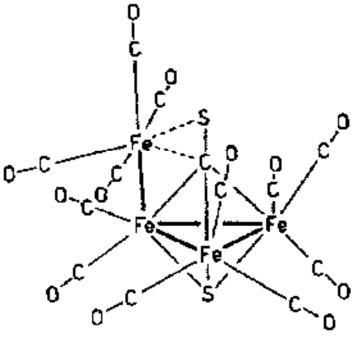
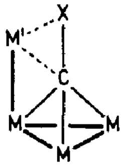


37

Related structures have also been found in the isopropenylalkyne-substituted heterometallic complexes $(Cp)_2Ni_2Fe_2(CO)_6(C_5H_6)$ (**38**) [79] and $(Cp)_2Ni_2Ru_2(CO)_6(C_5H_6)$ (**39**) [88] both being "out of the plane, spiked triangular" clusters.

TABLE 6

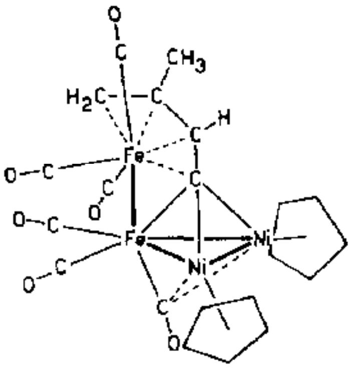
Structural parameters in some selected "spiked-triangular" clusters



Scheme 8

Complex	M–M in the cluster	M–M′ in the "spike"	∠M–M–M′	M–C (Å)	M′–C (Å)	∠M–C–M	C–X (Å)	Ref.
$(C_5Me_5)_2Co_2(Cp)_2Mo_2(CO)_4$ (**36**)	2.709(1) [b] 2.404(1) [c]	2.574(1) [d]		2.281(3) [e] 1.869(2) [f]	2.404(3)		1.283(3) (X = O)	86
$Fe_4(CO)_{12}(CS)S$ (**37**)	2.564(2) [g]	2.710(2)	110.8(1) 109.4(1)	1.971(5) [g]	2.706(6)	78.6(2) 82.9(2) 81.9(2)	1.695(5) (X = S)	87
$(Cp)_2Ni_2Fe_2(CO)_6(C_5H_6)$ (**38**)	2.384(3) [h] 2.384(2) [h] 2.337(3) [i]	2.755(3) [j]	100.1(1) 93.7(1)	1.905(8) [k] 1.868(8) [l] 1.913(7) [l]	2.266(8) [k]	76.3(3) 77.3(3) 78.4(3)	1.410(12) (X = C)	79
$(Cp)_2Ni_2Ru_2(CO)_6(C_5H_6)$ [a] (**39**)	2.515(6) [a] 2.495(5) [m] 2.368(5) [i]	2.960(5) [n]	91.4(1) 94.7(1)	2.06(2) [o] 1.83(3) [l] 1.85(3) [l]	2.46(3) [o]	79(1) 80(1) 80(1)	1.45(4) (X = C)	88

[a] Average values for two independent molecules. [b] Mo–Co. [c] Co–Co. [d] Mo–Mo. [e] Mo–C. [f] Co–C. [g] Fe–Fe or Fe–C. Average values. [h] Fe–Ni. [i] Ni–Ni. [j] Fe–Fe. [k] Fe–C. [l] Ni–C. [m] Ru–Ni. [n] Ru–Ru. [o] Ru–C.



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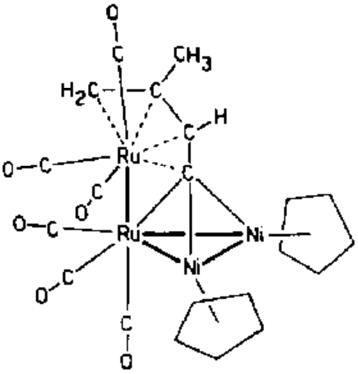


39

A type (F) triply-bridging CO is observed in **38** but not in **39**. Moreover, a square planar isomer of **38** is known [79]. Further aspects of such cluster cores will be considered in section **K**.

Structural parameters for **36–39** are reported in Table 6.

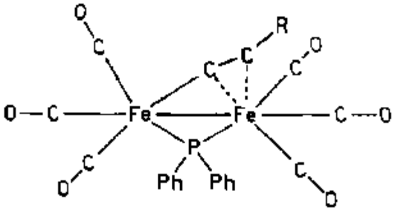
C. ACETYLIDES AND ISONITRILES

The bonding of the acetylide ligand to two or three metal atoms (bonding modes (J) and (K) respectively) is comparable with that of CO (bonding modes (C) and (G) respectively).

(J) (K)

Scheme 9

Examples of (J) bonding mode include bimetallic complexes $M_2(CO)_6(\mu\text{-}C_2R)(\mu\text{-}PPh_2)$ (M = Fe (**40**) or Ru) [67] and $Pt_2[P(C_6H_{11})_3]_2(\mu\text{-}C_2Ph)_2(\mu\text{-}SiMe_2)$ (**41**) [89], and the homometallic clusters $Ru_3(CO)_6(Ph_2PC_2Bu^t)$



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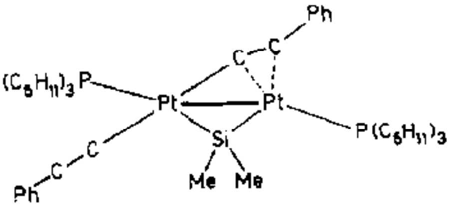

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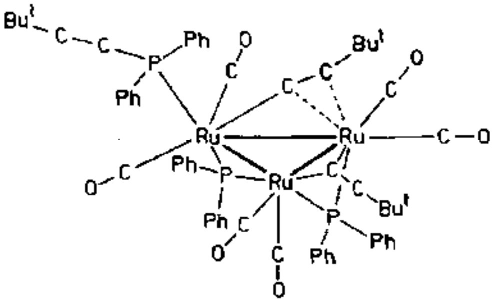
$(\mu,\eta^1\text{-}C_2Bu^t)(\mu,\eta^2\text{-}C_2Bu^t)(\mu\text{-}PPh_2)_2$ (**42**) [90] and $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu,\eta^2\text{-}C_2Bu^t)$ (**43**) [91].



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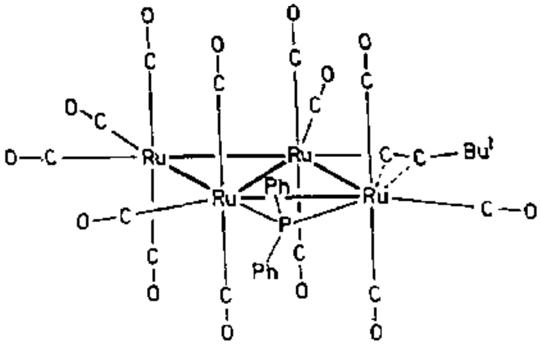

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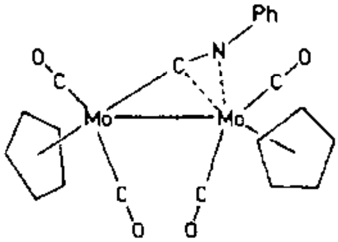
One example of an isonitrile bonded to two metals in a similar way has been found in $(Cp)_2Mo_2(CO)_4(\mu,\eta^2\text{-}CNPh)$ (**44**) [92].



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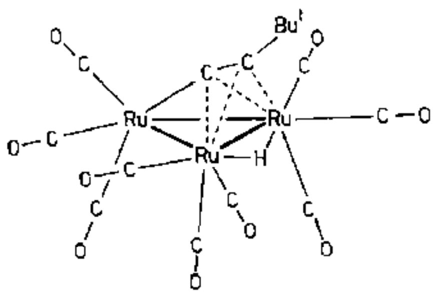
The bonding mode (K) has been frequently found in homo- and heterometallic clusters; homometallic examples are $M_3(\mu\text{-}H)(CO)_9(\mu_3,\eta^2\text{-}C_2Bu^t)$, M = Ru (**45**) or Os [93], $Ph_3PAuRu_3(CO)_9(\mu_3,\eta^2\text{-}C_2Bu^t)$ (**46**) [94], $M_3(\mu\text{-}PPh_2)(CO)_9(\mu_3,\eta^2\text{-}C_2Pr^i)$, M = Ru (47) or Os [95], and

$(Cp)Fe_3(CO)_7(\mu_3,\eta^2\text{-}C_2Ph)$ (**48**) [44], which are represented below.



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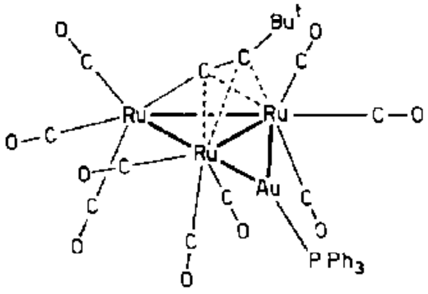

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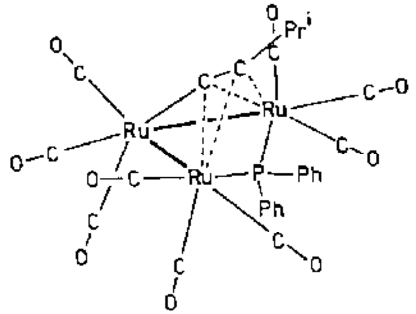

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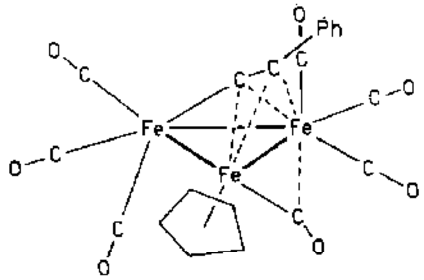
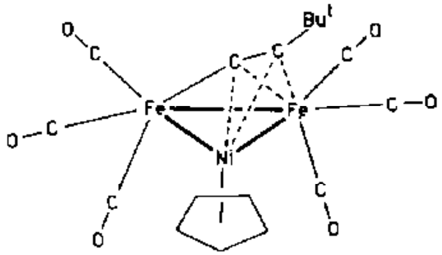


48

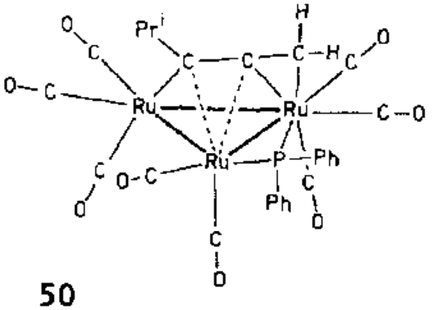
Heterometallic examples are: $(Cp)NiFe_2(CO)_6(\mu_3,\eta^2\text{-}C_2Bu^t)$ (**49**) [96] with a π bond involving nickel, and $(Cp)WFe_2(CO)_8(\mu_3,\eta^2\text{-}C_2C_6H_4Me\text{-}4)$ [97].



49

Very rich chemistry has been found for the acetylide α-carbon both in bimetallic complexes [67] and on homometallic clusters [98,99]. As observed for the (C) bonded CO bridges, the (K) bonded acetylides can also react with CH_2N_2 to give addition at C_α first and then at C_β with hydrogen transfer. The complexes obtained in these reactions are $Ru_3(\mu\text{-}PPh_2)(CO)_8(CH_2C_2Pr^i)$ (**50**) and $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7(CHC_2Pr^iCH_2)$

(**51**) [100].



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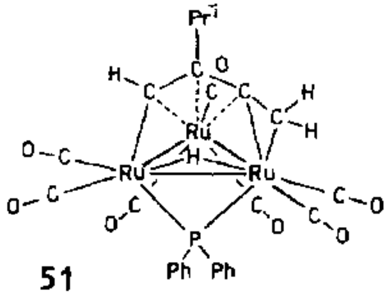

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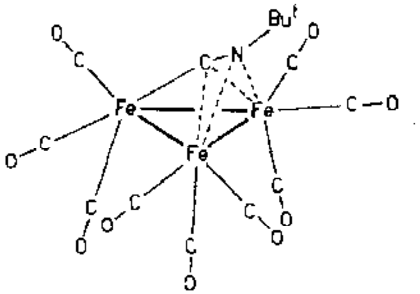
Cluster reactivity has also been observed for **45** and **47** (reversible M–M bond formation [101], isolobal substitution of $AuPPh_3$ for H [94]); in these reactions the acetylide is found unaltered and probably has the effect of increasing the stability of the cluster.

Comparable nitrile coordination on iron clusters has been reported by Andrews and Kaesz [102].

Recently a six-electron donor isonitrile has been found on an iron cluster, $Fe_3(CO)_9(CNBu^t)$ (**52**) [103]. This situation can be compared with that of the bridging carbonyl ligand in **25** [69].



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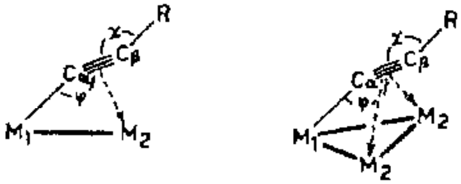
Structural features for some complexes having acetylides with bonding modes (J) and (K) are collected in Table 7.



Scheme 10

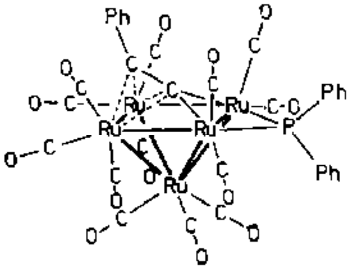
TABLE 7

Comparison of the bonding parameters for μ, η^2 and μ_3, η^2 bound acetylides (see Scheme 10)

Complex	Ligand coordination	M_1–M_2 (Å)	M_1–C(α) (Å)	M_2–C(α) (Å) M_2–C(β)	C–C (Å)	ψ (°)	χ(°)	Ref.
$Fe_2(CO)_6(\mu\text{-}PPh_2)(C_2Bu^t)$	μ, η^2	2.5959(5)	–	–	1.223(4)	162.4(1)	161.1(1)	104
$Fe_2(CO)_4(Bu^tNC)_2(\mu\text{-}PPh_2)(C_2Bu^t)$	μ, η^2	2.5946(7)	–	–	1.225(5)	161(1)	161.3(1)	104
$Ru_2(CO)_6(\mu\text{-}PPh_2)(C_2Bu^t)$	μ, η^2	2.7523(3)	–	–	1.218(4)	158.9(1)	158.5(2)	104
$Ru_3(CO)_6(PPh_2C_2Bu^t)(PPh_2)_2$- $(\mu\text{-}C_2Bu^t)(\mu,\eta^2\text{-}C_2Bu^t)$ (**42**)	μ, η^2	3.139(1)	2.046(9)	2.323(8) 2.422(9)	1.24(3)	169.8	159.8	90
$Ru_4(CO)_{13}(\mu\text{-}PPh_2)(C_2Bu^t)$ (**43**)	μ, η^2	3.157(1)	2.044(8)	2.285(8) 2.509(8)	1.199(12)	173.5(4)	159.9(5)	91
$Ru_4(CO)_8(\mu\text{-}PPh_2)_2(PPh_2C_2Bu^t)$- $(\mu,\eta^2\text{-}C_2Bu^t)(\mu_3,\eta^2\text{-}C_2Bu^t)$	μ, η^2	–	2.041(7)	2.292(11) 2.620(7)	1.228(1)	173.5(3)	163.3(4)	91
	μ_3, η^2	–	1.961(7)	–	1.315(9)	160.8(2)	138.3(1)	
$HRu_3(CO)_9(C_2Bu^t)$ (**45**)	μ_3, η^2	–	1.947(3)	2.207(3), 2.214(3) 2.268(3), 2.271(3)	1.315(3)	153.7(2)	141.0(2)	93
$Ru_3(CO)_9(\mu\text{-}PPh_2)(C_2Pr^i)$	μ_3, η^2	–	1.96(1)	–	1.284(8)	154.0(2)	145.2(3)	95
$Ru_3(CO)_8(\mu\text{-}PPh_2)(C_2Pr^i)$	μ_3, η^2	–	2.05(1)	–	1.24(1)	–	–	95
$Os_3(CO)_9(\mu\text{-}PPh_2)(C_2Pr^i)$	μ_3, η^2	–	–	–	1.28(1)	153.6(3)	142.0(8)	104
$[Ru_3(CO)_9(C_2Bu^t)]^-$	μ_3, η^2	2.790(3) 2.800(3)	1.95(2)	2.18(2), 2.16(2) 2.24(2), 2.24(2)	1.27(3)	156(1)	141(2)	105
$Ph_3PAuRu_3(CO)_9(C_2Bu^t)$(**46**)	μ_3, η^2	2.786(2) 2.800(1)	1.95(1)	2.19(1), 2.22(1) 2.21(1), 2.27(1)	1.29(2)	152(1)	139(1)	94
$(Cp)Fe_3(CO)_7(C_2Ph)$ (**48**)	μ_3, η^2	2.524(1) 2.632(1)	1.829(6)	2.006(5), 2.040(4) 2.031(5), 2.081(5)	1.299(9)	152.9(4)	144.7(5)	44
$(Cp)NiFe_2(CO)_6(C_2Bu^t)$ (**49**)	μ_3, η^2	2.610(3) 2.564(3) [a]	1.813(10)	1.929(10) [b], 2.010(10) 2.034(10) [b], 2.060(10)	1.284(14)	155.8(9)	142.8(9)	96

[a] Fe–Ni bonds. [b] Ni–C bonds.

Homo- and hetero-metallic examples of acetylides bonded to four or five metals are also well known: $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4,\ \eta^2\text{-}C_2Ph)$ (**53**) [106,107], $Ru_5(CO)_{14}(\mu\text{-}PPh_2)(\mu_5,\eta^2\text{-}C_2Ph)$ (**54**) [107], $NiRu_4(CO)_9(\mu\text{-}PPh_2)_2(\mu_4,\eta^2\text{-}C_2Pr^i)_2$ (**55**) [108]; $(Cp)FeRuCo_2(CO)_{10}(\mu_4,\eta^2\text{-}C_2Ph)$ [109] and $(Cp)_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}C_2Ph)$ (**56**) [110].



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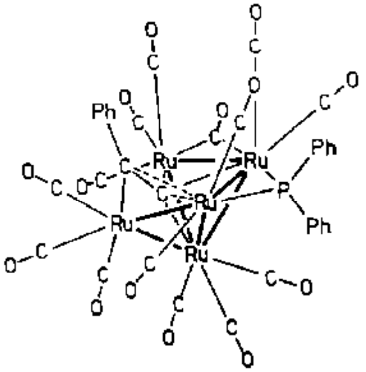

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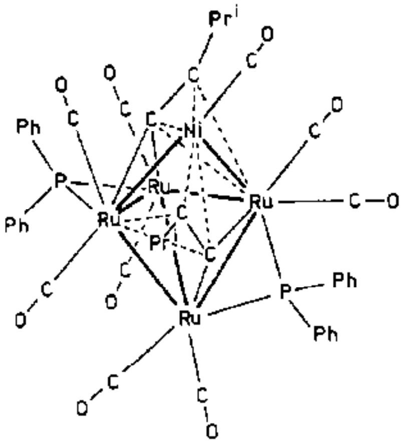

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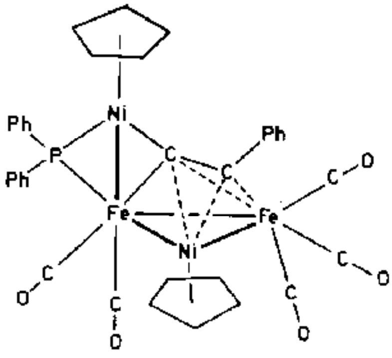


56

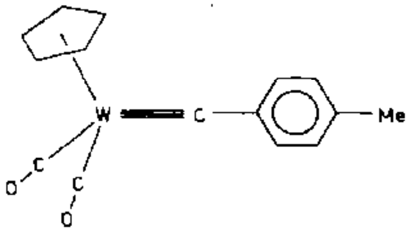
Interestingly, cluster **54** is obtained reversibly from cluster **53** in the presence of CO, a key role of the acetylide being prevention of demolition of the cluster.

D. METAL CARBYNE, VINYLIDENE AND ALKENYLIDENE LIGANDS

As there is an isolobal relationship [7] between the C≡C and M≡C triple bonds, the metal carbynes [111] can be considered to be ligands comparable to the alkynes. On this basis one of the most interesting and rational synthetic ways for obtaining heterometallic clusters has recently been developed by Stone and coworkers [112].

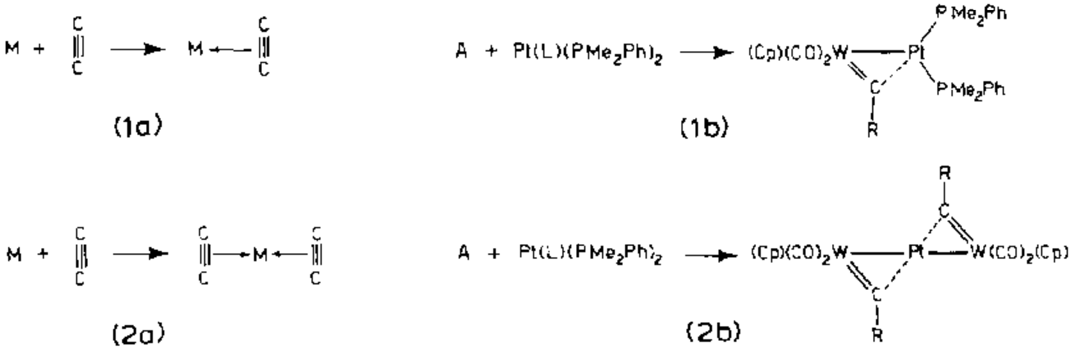
Obviously, the M≡C triple bonds show electronic distribution and polarity different to both symmetrically and unsymmetrically substituted C≡C triple bonds; hence, selective interaction with an heterometal M′ can occur, depending on the nature of M and of M′.

One of the most extensively used metal carbynes is Fischer's (Cp)(CO)$_2$W≡C–C_6H_4Me-4 (complex **A**) [113].



(A)

The reactivity of the complex **A** towards metals is comparable with that of alkynes:

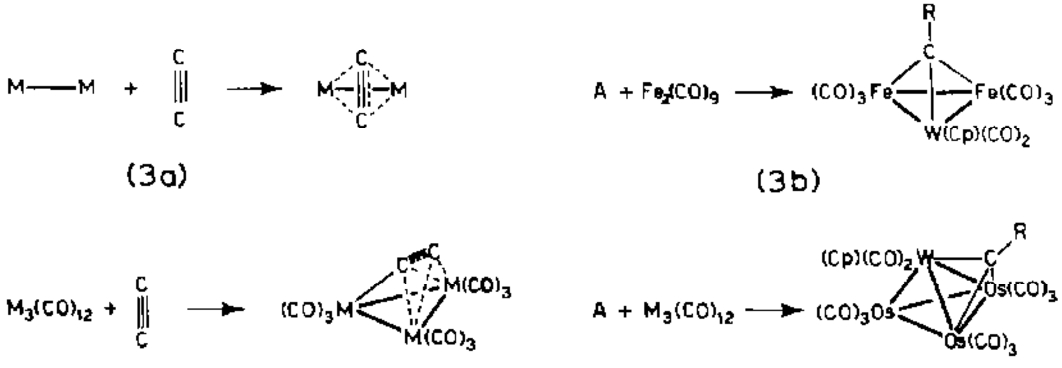


(1a) (1b)

(2a) (2b)

Scheme 12

In the presence of pre-formed M′–M′ bonds, the following reactions have been observed:

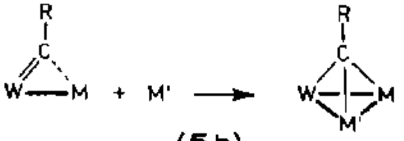


(3a) (3b)

(4a) (4b)

Scheme 13

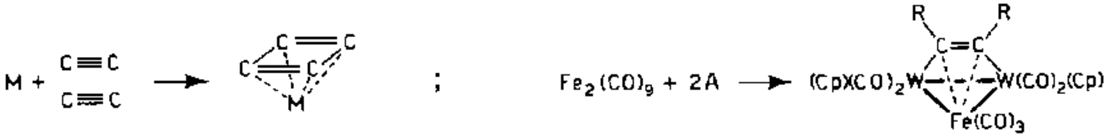
The bridging carbyne complexes resulting from reactions (1b) and (2b) show, as expected, nucleophilic reactivity at C_α as found for coordinated CO and acetylides, and can further lead to complexes containing three different transition metals:



(5b)

Scheme 14

Finally, another reaction can be found, corresponding to the "coupling" of alkynes, as in the following example:

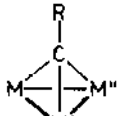


(6a) (6b)

Scheme 15

For the above reasons, the metal carbynes have been shown to be very useful "assembling ligands" for the selective formation of heterometallic complexes.

Several of the above complexes have cluster cores with three different metals. Similar cluster frames can also be obtained by metal exchange reactions [114]. In general, these metal–carbon arrangements are characterized by a nearly symmetrical bonding of the "apical" carbon (bonding mode L) despite the difference in the nature and substitution of the metals, and in contrast with bonding modes (E) and (F) observed for CO.



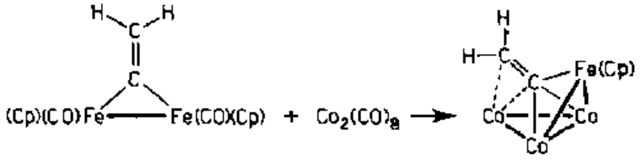
(L)

Scheme 16

The μ_3-CR ligands on heterometallic bent chains may contribute to their stabilization, as in $(Cp)_3Pt_2W_3(\mu\text{-}CR)_2(\mu_3\text{-}CR)(CO)_6$ and $(Cp)_2Pt_3W_2(\mu_3\text{-}CR)_2(CO)_4(cod)_2$ ($R = C_6H_4Me\text{-}4$) [115].

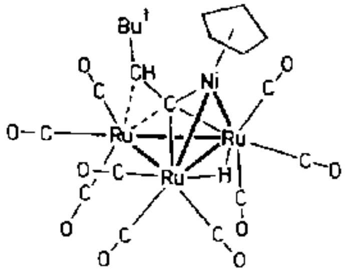
In the context of the carbyne ligands, it is interesting to note that in $Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_9(PPh_3)_2$ [116] the capping μ_3-COMe spans the Ru_3 face somewhat asymmetrically (Ru–C distances in the range 2.064(13)–2.103(13) Å), whereas in $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CMe)(CO)_9$ the carbyne ligand is more symmetrically bound (Ru–C distances in the range 2.078(12)–2.086(10) Å) [117]. This reflects the electronic symmetry at the Ru centres in the latter case. Other examples of asymmetric bonding for the μ_3-COMe ligand have been reported [118].

Alkenylidene ligands bridging two metals can also behave as assembling ligands in the formation of heterometallic complexes [119]:



Scheme 17

Complexes comparable with (Cp)FeCo$_3$(CO)$_7$(μ-CO)$_2$(μ_4, η^2-C=CH$_2$) (Scheme 17) are the heterometallic (Cp)NiM$_3$(μ-H)(CO)$_9$ (μ_4,η^2-C=CHBu^t) (M = Ru (**57**); M = Os) [120] and the homometallic Ru$_4$(CO)$_{10}$(μ-PPh$_2$)(μ-OR)(μ_4,η^2-C=CHPr^i) (M = Ru, R = H (**58**)) [121].



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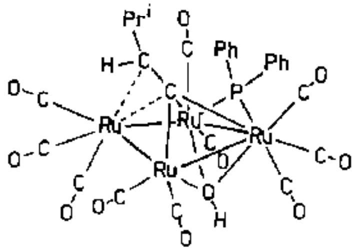

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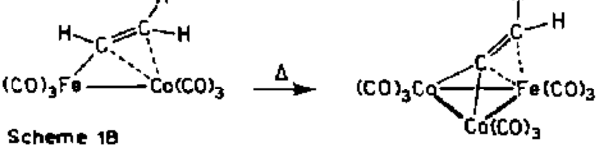
The bonding of the vinylidene ligands in the above clusters is closely comparable to that of mode (H) for carbonyls.

The transformation of a vinyl ligand into a bridging vinylidene can accompany cluster formation [122]:



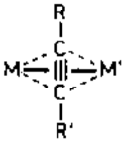
Scheme 18

The bonding interactions described in this section and elsewhere [66] are particularly relevant to the development of organic transformations at di- and poly-metal centres [123].

E. ALKYNE LIGANDS

Considerable variety in the bonding interactions of alkynes with two or more metal centres has been found; these ligands have been extensively studied, mainly for this reason [66].

We do not consider here the "classical" bonding mode (M), found either in homo- or in hetero-bimetallic complexes and only rarely in clusters [124].



(M)

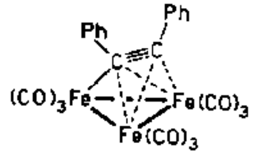
Scheme 19

In trimetallic clusters, the bonding modes (N) and (O) are most frequently found.

(N) (O)

Scheme 20

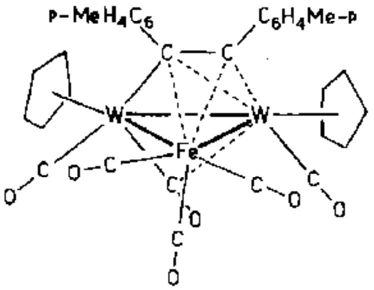
Bonding mode (N) (μ_3,η^2-$\perp$) can be described as addition of a metal on a face of the "tetrahedral" arrangement (M); it is comparable with the bonding mode (G) for CO and (K) for the acetylides and has been found in particular for iron, e.g. in $Fe_3(CO)_9(C_2Ph_2)$ (**59**) [125].



59

However, this bonding mode is rare for Ru or Os; in such clusters mainly (K) bound acetylides are found, with C_α not bearing substituents.

Few heterometallic examples for this type of structure are known; among these are $(Cp)_2W_2Fe(CO)_6[C_2(C_6H_4Me\text{-}4)_2]$ (**60**) [113], and $(Cp)_2W_2Fe(CO)_5(O)[C_2(C_6H_4Me\text{-}4)_2]$ [126]



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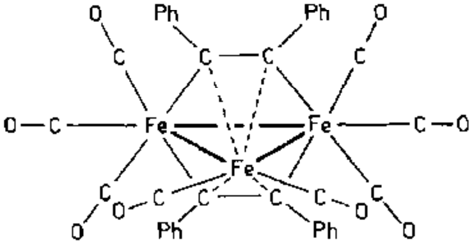
On the contrary, bonding mode (O) (μ_3,η^2-||) is one of the most commonly found either in homo- or hetero-metallic complexes; it can be easily rationalized by using the SEC rules [5] and is one of the best examples of selective σ–π bonding.

The homometallic "violet isomer" of $Fe_3(CO)_8(C_2Ph_2)_2$ (**61**) [28] deserves attention. This is, indeed, a rare example of two alkynes coordinated to the same cluster and not interacting with each other.



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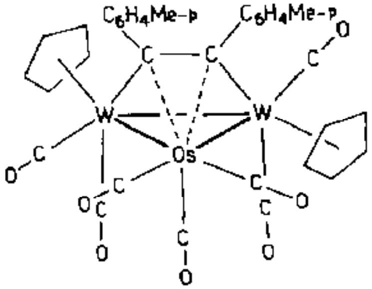
Of particular interest is the considerable variety of heterometallic structures observed; those of $(Cp)_2W_2Os(CO)_7[C_2(C_6H_4Me\text{-}4)_2]$ (**62**) [113,127], $(Cp)NiFeCo(CO)_5(PPh_3)(C_2Ph_2)$ (**63**) [43], $FeCo_2(CO)_9(C_2Et_2)$ (**64**) [128], $RuCo_2(CO)_9(C_2Ph_2)$ (**65**) [129], $(Cp)_2Ni_2M(CO)_3(C_2Ph_2)$ (M = Fe, Ru; **66** with M = Fe) [130], $(Cp)_2Ru_2Ni(CO)_4(C_2Ph_2)$ (**32a**) [80] $[(Cp)NiFe_2(CO)_6(C_2Ph_2)]^-$ (**67**) [131], $(Cp)NiFeCo(CO)_6[C_2Ph(COOPr^i)]$ (**68**) [132], $(Cp)_2NiMoFe(CO)_5[C_2Ph(COOPr^i)]$ (**69**) [132], $(Cp)_2W_2Fe(CO)_6[C_2(C_6H_4Me\text{-}4)_2]$ (**70**) [113, 127], $Os_3(CO)_9(CH_2)(C_2Ph_2)$ (**71**) [133], $OsPt_2(CO)_5(PPh_3)_2(C_2Me_2)$ (**72**) [134] are shown below.



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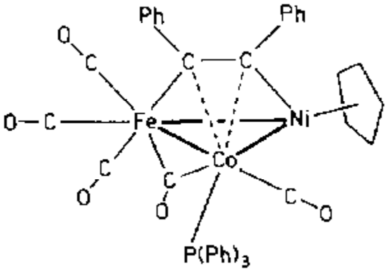

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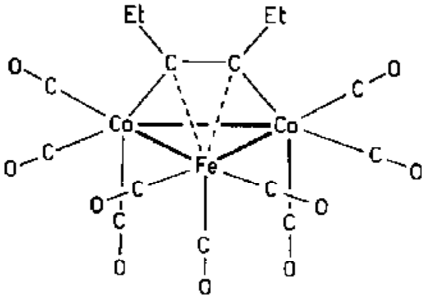

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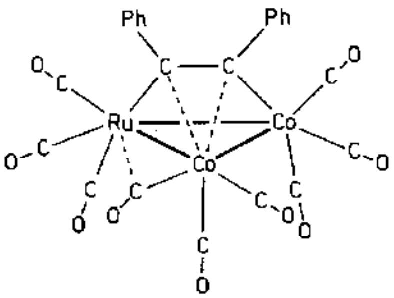

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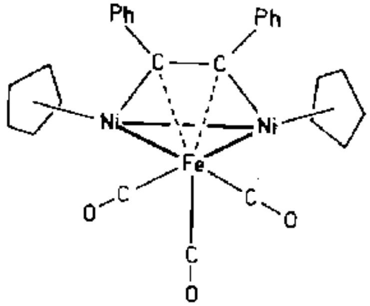

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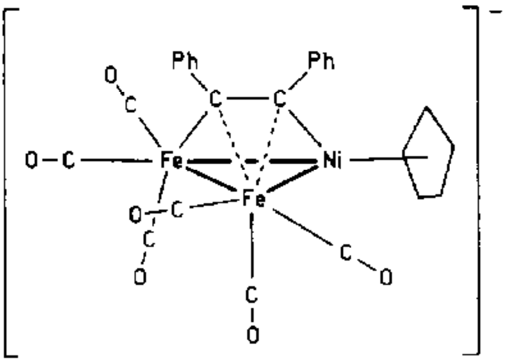

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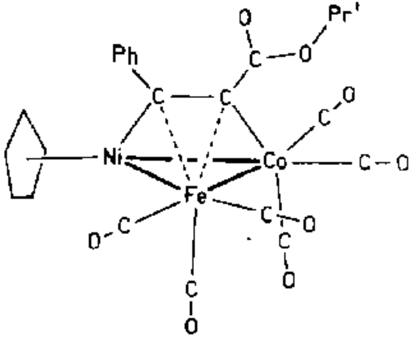

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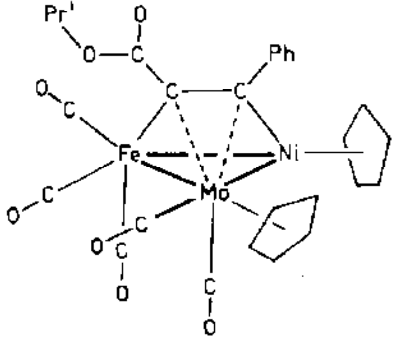

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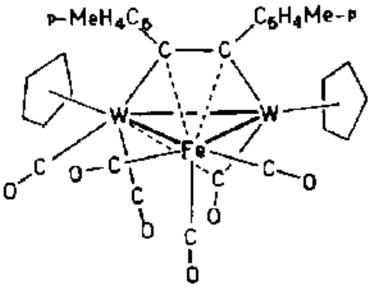

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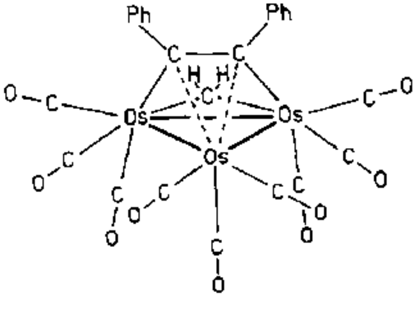

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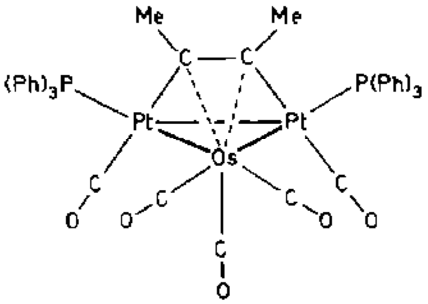


72

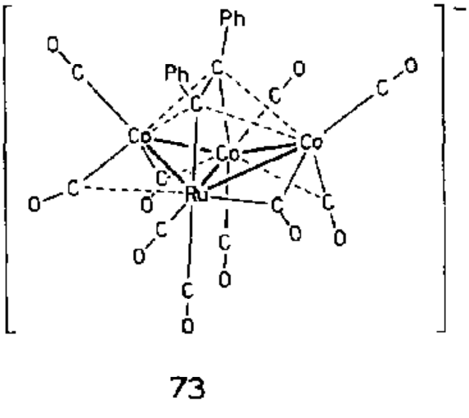
A number of complexes show the same trend, in that the π bond is directed towards the less electron-rich metal:

$\mathrm{Mo} > \mathrm{Fe} > \mathrm{Co} > \mathrm{Ni}$

$(d^6)(d^8)(d^9)(d^{10})$

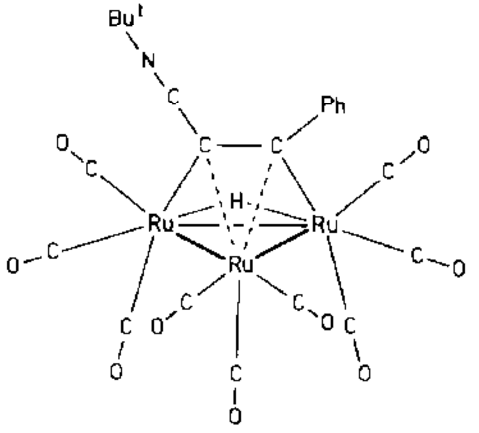
This may allow predictions for the synthesis of new heterometallic derivatives.

The behaviour of **62** may be due to its synthetic origin; in **63** a semi-bridging CO accounts for the electronic situations of the metals. The related complexes **64** and **65** differ by the orientation of the alkyne towards the Co–Co bond. This could be related to the synthetic origin of **65**, resulting from the proton-induced fragmentation of $[\mathrm{RuCo_3(CO)_{10}}(\mu_4,\ \eta^2\text{-}\mathrm{C_2Ph_2})]^-$ (**73**) in which the alkyne is parallel to the Co-Ru hinge bond of the butterfly [129]. Because of the better π back-bonding capacity of Ru compared to Co, such an arrangement could be preferred since hinge atoms are particularly involved in back-bonding to the alkyne in such butterfly structures [135]. On the other hand, wing-tip atoms accept electron donation from the alkyne. On going from **73** to **65** the alkyne seems to retain the "memory" of its orientation.



73

Bonding mode (O) can also be found as a consequence of the nucleophilic reactivity of (K) type acetylide complexes discussed above, as in $HRu_3(CO)_9(PhC_2CNBu^t)$ (**74**) and in $Os_3(CO)_9(PPh_2)$-$[PhC_2C(NHBu^t)(NHBu^n)]$ (**75**) [99] where the π bond is towards the metal not H bridged and not P bridged, respectively.



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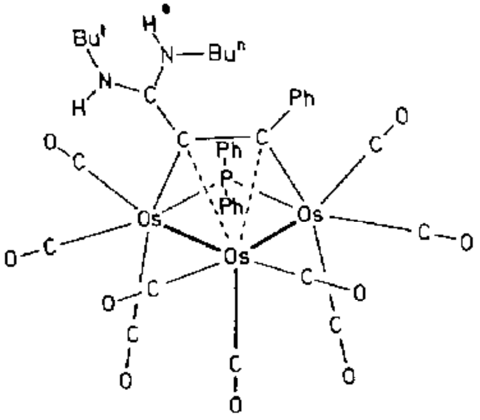

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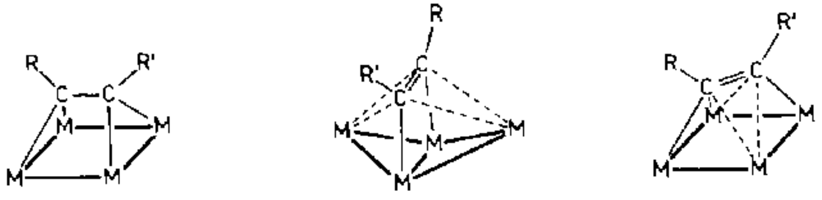
When the alkynes interact with four metals, the bonding modes (P), (Q) and (R) shown in Scheme 21 are found. A detailed discussion of these can be found elsewhere [66,85]. Bonding mode (P) has been found only for one homometallic example [136], bonding modes (Q) and (R), in particular the former, are more frequent either in homometallic or in heterometallic clusters, such as $FeRu_3(CO)_{12}(C_2Ph_2)$ [137].

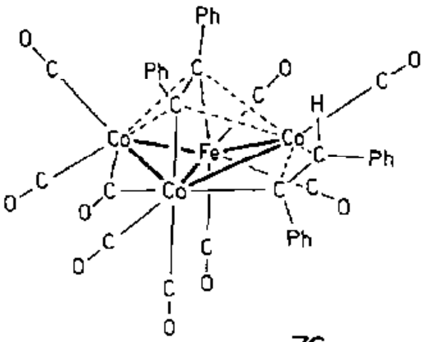


(P) (Q) (R)

Scheme 21

$FeCo_3(CO)_9[PhC_2(H)Ph](C_2Ph_2)$ (**76**) [138], $[RuCo_3(CO)_{10}(C_2Ph_2)]^-$ (**73**) [129] and $RuCo_3(CO)_9(PPh_2)(HC_2Bu^t)$ (**77**) [139], are all characterized by MCo_3 cores and bridging CO's; for the reasons discussed above M (Fe or Ru) is always in the cluster hinge.

Another heterometallic cluster $Ru_2Co_2(CO)_{13}$ (**78**) [140] provides an example of "hetero site" reactivity under very mild conditions, which gives



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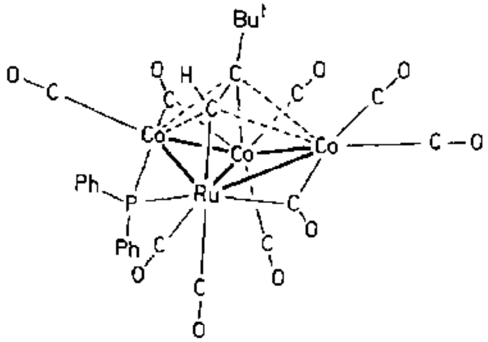
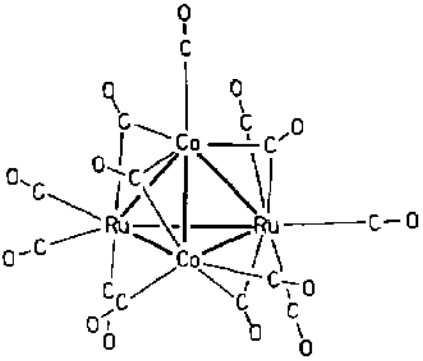


77

metal-specific reactions. Hydrogen reacts at the ruthenium atoms, giving $H_2Ru_2Co_2(CO)_{12}$ (**79**), whereas alkynes insert into the Co–Co bond forming the butterfly complex $Ru_2Co_2(CO)_{11}(C_2R_2)$ (**80** with R = Ph) [140].

An increasing number of examples is known for the bonding mode (R); homometallic examples are $M_4(CO)_{11}(RC_2R')_2$ (M = Fe, R = H, R′ = Et,



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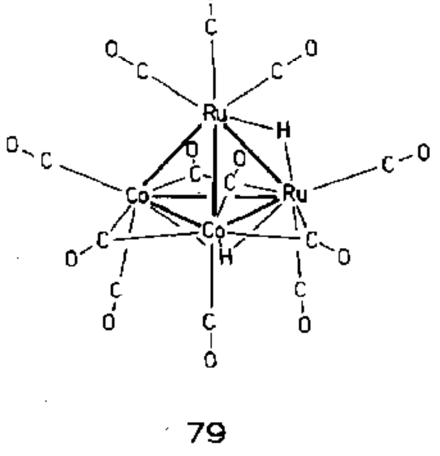

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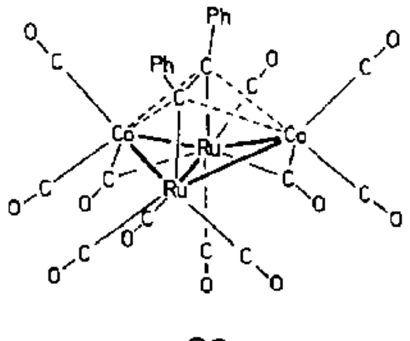
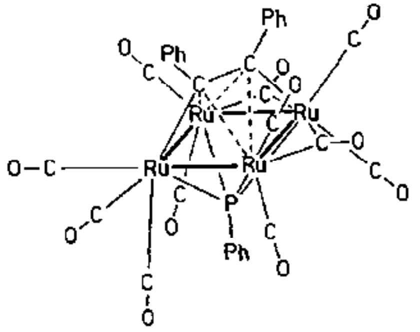


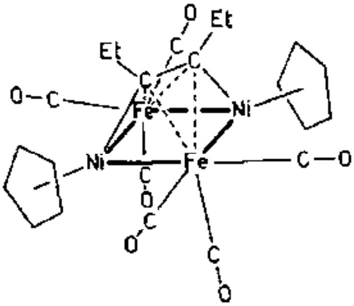
80

complex **13** [38]; M = Ru, R = Me, R′ = Ph [142]) and $Ru_4(CO)_{11}(\mu_4$-$PPh)(\mu_4,\eta^2$-$C_2Ph_2)$ (**81**) [143]. Complexes $M_4(CO)_{11}(RC_2R')_2$ are 4 M–M quasiplanar 62 e^- structures with two non-interacting alkynes on the same cluster. When considering the phosphorus atom as a framework constituent, **81** is a square pyramidal cluster.



81

Heterometallic examples are $(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (**82**) [72] and $(Cp)_2Ni_2Ru_3(CO)_8(C_2Ph_2)$ (**83**) [42].



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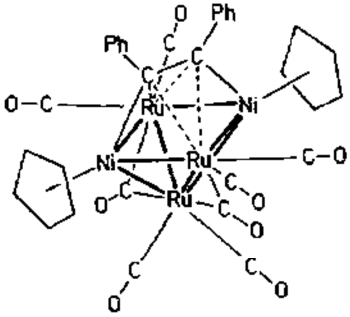


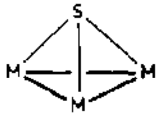
83

In these clusters nickel is σ-bonded to the alkyne; these derivatives are obtained from $(Cp)_2Ni_2(RC_2R')$ probably via cleavage of the Ni–Ni bond [42]. However, the alkyne apparently keeps the nickel atoms together, thus allowing the formation of the hetero-tetrametallic or -pentametallic derivatives.

F. SULFUR AS A BRIDGING LIGAND

A large number of sulfur-containing clusters is known [144,145]. Here we will consider only a few examples, those showing greatest similarities with the CO, acetylide, μ_3-CR and alkyne chemistry.

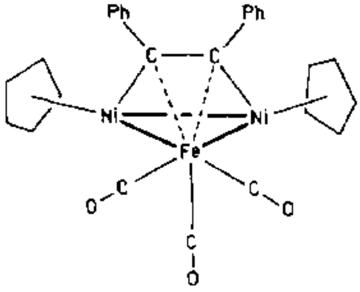
Indeed one of the best known bonding modes for sulfur is (S), formally similar to the bonding modes (D), (E) and (F) for CO and to the (L) mode of the apical CR group.



(S)

Scheme 22

However, when considering the electron donor properties of the sulfur atom, closer similarities can be found between the (S) bonding mode for sulfur and the (μ_3,η^2-||) bonding of the alkynes (bonding mode O). An example is provided by $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (**66**) [130] and $(Cp)_2Ni_2Fe(CO)_3S$ (**84**) [146]



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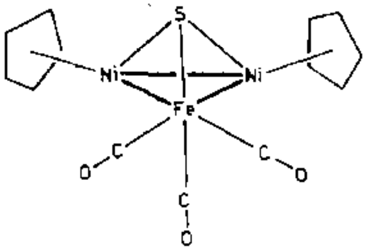
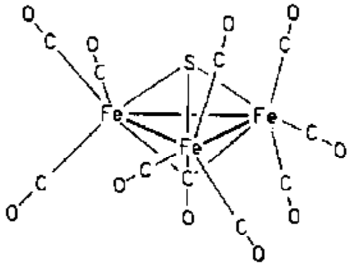


84

The complexes $(Cp)_2Ru_2Ni(CO)_4(C_2Ph_2)$ (**32**) and $Fe_3(CO)_{10}S$ (**85**) [147] are also comparable; they both show a μ_3- to μ_2-CO isomerism in solution.



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Important structural parameters for complexes with triply-bridging S atoms are collected in Table 8. Noteworthy are the shallow M–S–M′ apical

TABLE 8

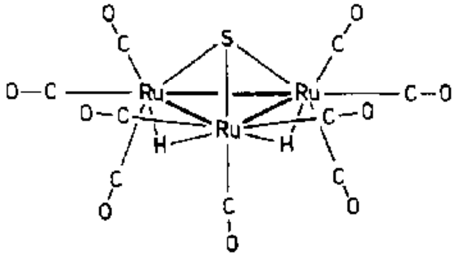
Selected structural parameters for sulfur cluster derivatives

	M–M or	M–M′ (Å)	M–S or	M′–S (Å)	M–S–M or	M–S–M′ (°)	Ref.
$(Cp)_2Cr_2Fe_2(\mu_3\text{-}CO)_2(CO)_6(\mu_3\text{-}S)_2$	Fe–Cr	2.762(3) [a]	Fe–S	2.160(5) [a]	Cr–S–Cr	77.0(1) [a]	76
	Cr–Cr	2.775(4) [a]	Cr–S	2.230(4) [a]	Fe–S–Cr	78.0(1) [a]	
$(Cp)_2Mo_2Fe_2(\mu_3\text{-}CO)_2(CO)_6(\mu_3\text{-}S)_2$ "butterfly" (**31**)	Fe–Mo	2.818(5)	Mo–S	2.335(9)	Fe–S–Mo	77.4(7)	77
		2.815(5)		2.327(9)		77.5(3)	
	Mo–Mo	2.846(5)	Fe–S	2.165(8)	Mo–S–Mo	75.3(3)	
$(Cp)_2Mo_2Fe_2(\mu\text{-}CO)_2(CO)_6(\mu_3\text{-}S)_2$ "lozenge" (**88**)	Fe–Mo	2.776(1)	Mo–S	2.344(1)	Fe–S–Mo	75.00(5)	149
		2.805(1)		2.381(1)		75.14(5)	
	Mo–Mo	2.821(1)	Fe–S	2.213(2)	Mo–S–Mo	73.30(4)	
$(Cp)_2Ni_2Fe(CO)_3(\mu_3\text{-}S)$ (**84**)	Ni–Fe	2.427(4)	Ni–S	2.109(5)	Ni–S–Fe	69.3(2)	146
		2.419(4)		2.114(5)		69.0(2)	
	Ni–Ni	2.404(9)	Fe–S	2.158(5)	Ni–S–Ni	69.4(1)	
$FeCo_2(CO)_9(\mu_3\text{-}S)$	Fe–Co Co–Co	2.254(3) [b]	Fe–S Co–S	2.158(4) [b]	Fe–S–Co Co–S–Co	72.5(2) [b]	148
$Fe_3(CO)_{10}(\mu_3\text{-}S)$ (**85**)	Fe–Fe	2.61(1) [c]	Fe–S	2.21(1) [c]	–		147

[a] Average values in two independent complexes. [b] Average values because of disorder. [c] Average values.

angles (about 70° against about 80° for apical CO and CR). These assembling ligands should therefore lead to different distances and reactivities of the metal–metal bonds they span. The sulfur may be found (S) coordinated either on closed or open clusters as in $H_2Ru_3(CO)_9S$ (**86**) and $H_2Ru_3(CO)_8(SnCl_3)ClS$ (**87**) [150].

An iron cluster with bridging sulfur and SO has also been reported [151].



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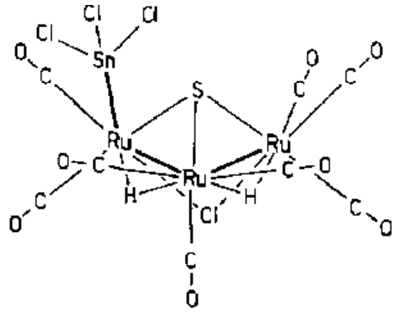

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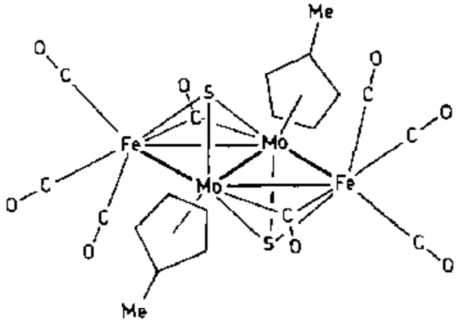
Heterometallic examples of μ_3-S bridges have been found in $(Cp)_4Cr_2Ni_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)$ [152] and $(Cp)_2M_2Fe_2(CO)_6(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2$ (M = Cr, Mo (**31**)) [76,77], both showing a butterfly arrangement of the metals, with sulfur atoms capping the wings. Another example is that of $(C_5H_4Me)_2Mo_2Fe_2(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}S)_2$ (**88**) [149], showing a planar triangulated metal atom arrangement, which is isomeric with the complex **31** (with C_5H_4Me replacing Cp).



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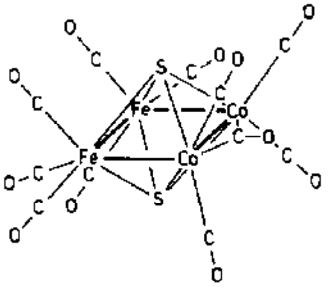
The fact that **31** and **88** are formed by the same reaction exemplifies the possible occurrence of stable isomers of comparable energy (see also section K).

Another example of considerable interest is $(Cp)_2FeCoMoW(\mu_3\text{-}S)(\mu\text{-}AsMe_2)(CO)_7$, the first cluster obtained containing four different metals

[114]. The presence of the μ_3-ligand stabilizing the FeCoMo ensemble of the precursor allowed this synthesis.

Finally, as the alkynes frequently do, sulfur can also bridge four metal atoms in a μ_4 fashion, as in the square planar $Fe_2Co_2(CO)_{11}(\mu_4\text{-}S)_2$ (**89**) [153].



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G. THIOLATE LIGANDS

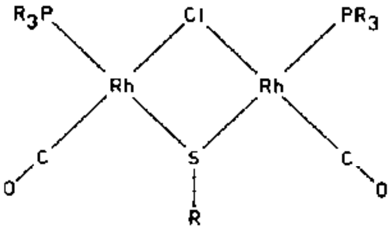
From the various ligands used for their bridging properties and available for "promoting" metal–metal bonding, we have chosen two groups frequently found in clusters and considered to represent good examples of *flexible* and usually *inert* bridges; these are the thiolate (SR) [154] and μ-phosphido bridges (discussed in section H).

These ligands can keep together two metal centres with or without the presence of metal–metal bonds, and hence could allow the reversible cleavage of the M–M and M–M′ bonds. This property is fundamental for organometallic reactions and is relevant to the development of cluster-catalyzed reactions.

This behaviour is due to the geometrical flexibility of the ligands, and, for the thiolate, also to its electronic flexibility as it can contribute a different number of electrons in different bonding situations.

For iridium derivatives many Ir(μ-SR)Ir situations have been described [155,156].

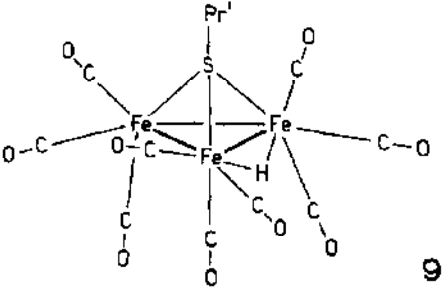
Rhodium complexes having one chlorine and one sulfur bridge of the type shown below have now been structurally characterized [157].



Scheme 23

Oxidative addition of one mole of CH_3I to $Rh_2(\mu\text{-}SBu^t)_2(CO)_2(PMe_2Ph)_2$ allowed the isolation of a Rh^I–Rh^{III} complex [158] and related phosphite complexes showed catalytic activity in the hydrogenation of olefins [159].

The remaining sulfur lone pair can be used for coordinating other metals and indeed μ_3-SR groups are known, as for example in $HFe_3(CO)_9(\mu_3\text{-}SPr^i)$ (**90**) [160] and related complexes [141].



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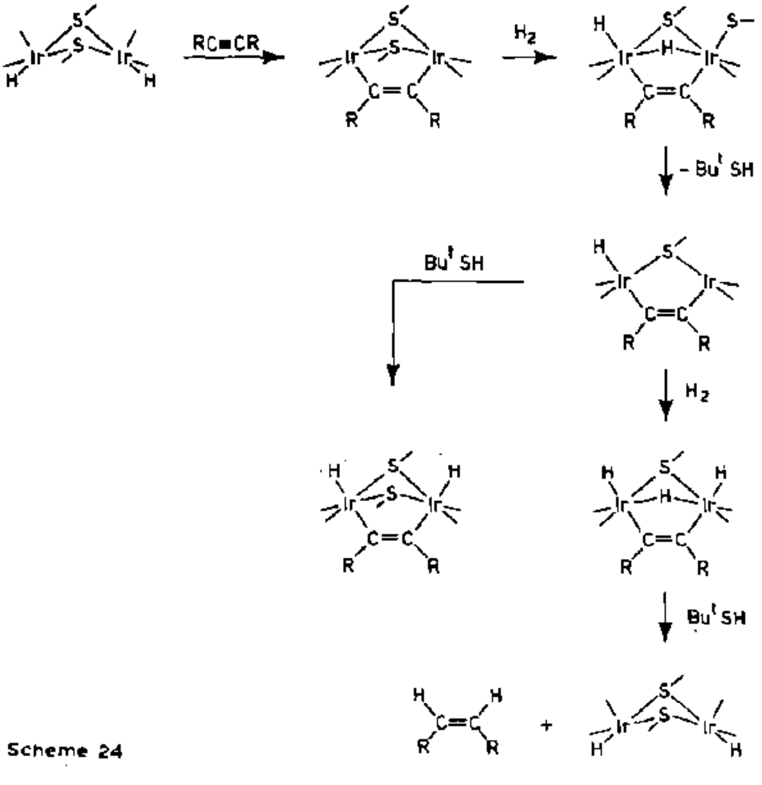
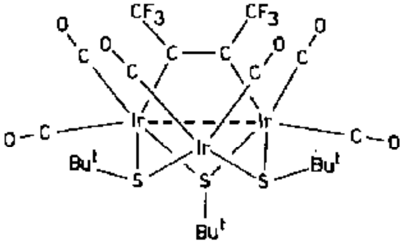
Stepwise rational cluster syntheses can therefore be envisaged.

Many homo-bimetallic thiolato-bridged complexes are known and their chemistry well investigated. The synchronous addition of dihydrogen and acetylene to dimetallic complexes d_8–d_8 (Rh_2, Ir_2) or d_7–d_7 (Fe_2) has been the subject of a recent theoretical study [161]. In the iridium derivatives, insertion of alkyne and of hydrogen between the metals takes place with reversible elimination of one bridging-SR group; the following sequence of steps converts alkynes into alkenes [214]:



Scheme 24

The presence of SR bridges can also favor reactivity at two metal centres [162], leading to metal–metal bond formation. Complexes $Ir_3(\mu\text{-}SBu^t)_3(\mu\text{-}C_4F_6)(CO)_6$ (**91**) [163] and $Ir_3(\mu\text{-}SBu^t)_3(\mu\text{-}CO)(CO)_4(PMe_3)_2$ (**92**) [164] display "crown-like" structures:



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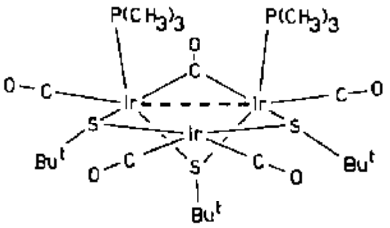

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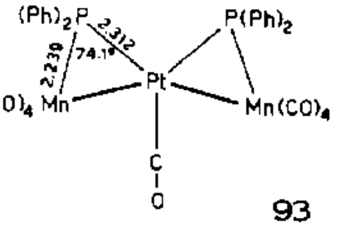
H. THE PHOSPHIDO LIGANDS

These ligands, which are usually considered inert (although recent reports emphasize that this is not always true, particularly under catalytic conditions [165]) are widespread in polymetallic systems. Interesting studies on the synthesis and reactivity of hetero-metallic phosphido-bridged complexes can be found in refs. 104 and 166.

The phosphido ligand is in most cases symmetrically bound to the metals, although asymmetry may be found when the metals are different. This can be shown, for example, in the following complexes which furthermore illustrate the great flexibility of the μ-PPh_2 group: $(OC)_4Mn(\mu\text{-}PPh_2)Pt(CO)(\mu\text{-}PPh_2)Mn(CO)_4$ (**93**), $(OC)_4Mn(\mu\text{-}PPh_2)PtH(\mu\text{-}PPh_2)_2Mn(CO)_4$ (**94**) and $(OC)_4Mn(\mu\text{-}PPh_2)Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)Mn(CO)_4$ (**95**) [167].

The formal 3 e^- donor, neutral μ-PPh_2 group may give rise to a wide variety of M–P–M angles as shown in Table 9. The relationship between the flexibility of this ligand and the ^{31}P NMR data is discussed in ref. 104.

The structure of $M_3(\mu_3\text{-}C_6H_4)(\mu\text{-}PPh_2)_2(CO)_7$ (M = Ru, (**96**), Os) shows the presence of an asymmetrically bridged CO, μ_3, η^2-bonded benzyne and PPh_2 groups. For this ligand the asymmetry has been related either to the presence of M–P (donor) and M–P (phosphido) bonds, or to the difference in the groups *trans* to phosphorus [172].



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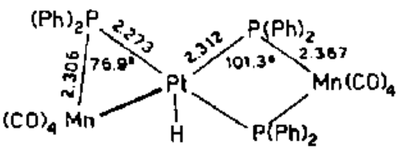

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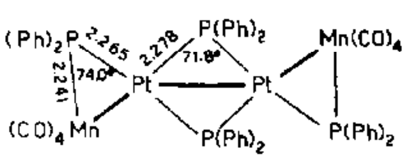
TABLE 9

Correlations between the ^{31}P NMR data and the M–P–M angles in selected examples of μ-PPh_2 bound clusters

Complex	$\delta(^{31}P)$ [a] (μ-PPh_2)	∠M–P–M (°)	Ref.
Homobimetallic complexes			
$Fe_2(CO)_6(PPh_2)(C_2Bu^t)$	148.3	71.7	104
$Fe_2(CO)_6(PPh_2)L$ [b]	123.0–198.5	69.8–75.6	104
$Fe_2(CO)_5(PPh_2)(\mu\text{-}C(O)Me)(PPh_2Me)$	166.7–187.8	74.1(1)	170
$Ru_2(CO)_6(PPh_2)(C_2Bu^t)$	123.9	72.0	104
trans-$Ru_2(CO)_5(PPh_2)(C_2Pr^i)(PPh_2C_2Pr^i)$	127.0	73.4	104
Heterobimetallic complexes			
$(Cp)MnFe(CO)_5(\mu\text{-}H)(PPh_2)$	176.7	–	169
$(Cp)MnFe(CO)_5(PPh_2)(\mu\text{-}C(O)Me)$	106.4	106.4(1) [c]	169
		107.1(1)	
$FeIr(CO)_5(PPh_2)(PPh_3)_2$	114.1	81.62(7)	168
$RuCo(CO)_6(PPh_3)(PPh_2)$	170.3	75.5(1)	171a
$RuCo(CO)_5(PPh_3)_2(PPh_2)$	167.5	74.6(1)	171b
$WOs(CO)_6(PPh_2)(PPh_2Me)[\mu\text{-}PPh_2CH(OMe)]$	79.1	76.14(8)	165
Homometallic clusters			
$Ru_3(CO)_9(PPh_2)(C_2Pr^i)$ [d]	−51.8	92.8	95
$Ru_3(CO)_8(PPh_2)(C_2Pr^i)$	113.3	74.4	95
$Ru_3(CO)_6(PPh_2)_2(C_2Bu^t)_2(PPh_2C_2Bu^t)$	152.5	79.9	90
	121.8	75.9	
$Os_3(CO)_9(PPh_2)(C_2Pr^i)$ [d]	−65.4	93.2	95
Heterometallic clusters			
$RuCo_2(CO)_8(PPh_2)$	180.4	73.9(1)	171a
$RuCo_3(CO)_9(PPh_2)(HC_2Bu^t)$	222.0	69.84(3)	139
$Mn_2Pt(CO)_9(PPh_2)_2$	161	74.31(9)	167
		73.97(12)	
$Mn_2Pt(CO)_8(H)(PPh_2)_3$	124	76.87(15)	167
	−84 [d]	101.26(15)	
	−102 [d]	101.30(15)	
$Mn_2Pt_2(CO)_8(PPh_2)_4$	162	74.1(1)	167
	273	71.8(1)	
		73.9(1)	

[a] In ppm, downfield positive with respect to H_3PO_4. [b] L = Cl, CHC(NEt$_2$)Ph, CHC(NHCy)Ph, CC(Cy$_2$Ph)Ph, C_2Ph, C(NHCy)(CH)Ph, C(CNMe(CH$_2$)$_2$NMe)CPh, C(CNBu^t)CPh, CH$_2$C(Ph)NMe, minimum and maximum value. [c] Two independent molecules. [d] No M–M bond supported by the μ-PPh_2 bridge.



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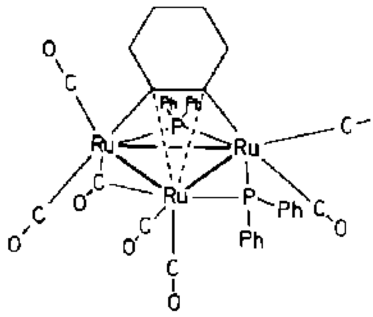

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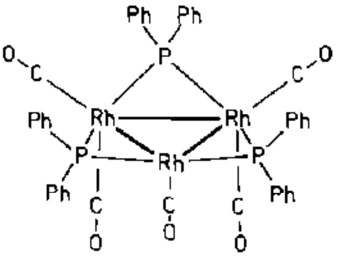
The versatility of this kind of ligand is also illustrated by the possibility of being either in or out of the plane of the metals; an example is given by $Rh_3(\mu\text{-}PPh_2)_3(CO)_5$ (**97**) [173], in which both arrangements are present.



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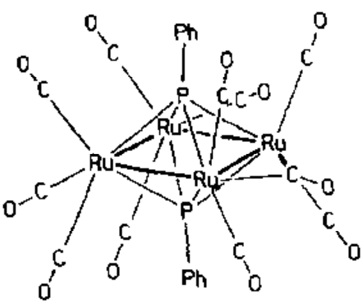
Finally, the possible ortho-metallation of the phenyl rings should also be taken into account and new complexes may result. In particular the unsaturated $HRu_3(CO)_9(PPh_2)$ can be obtained, which is active in the homogeneous hydrogenation of alkynes [67,174]. In the presence of hydrogen the phenyl group can give benzene and leave a μ_3-PPh group on the cluster. Related reactions have also been observed with the $Ph_2PCH_2PPh_2$ ligand, the degradation of which can lead to a μ_3-PPh bridge [175]. Such bridges are frequently found (e.g. refs. 47, 215); angles at P are in the range 77–79° and ^{31}P values span 274–330 ppm (downfield positive with respect to H_3PO_4).

"Strong" cluster frames are generally obtained when these ligands are present; the same happens for the now quite widespread μ_4-PR clusters, such as $Ru_4(CO)_{11}(\mu_4\text{-}PPh)_2$ (**98**) [176] and $Ru_5(CO)_{15}(\mu_4\text{-}PPh)$ (**99**) [177], in which angles of about 90° at phosphorus are found. Related complexes based on square-planar arrangements of metals have already been discussed in section B (complexes **14**).



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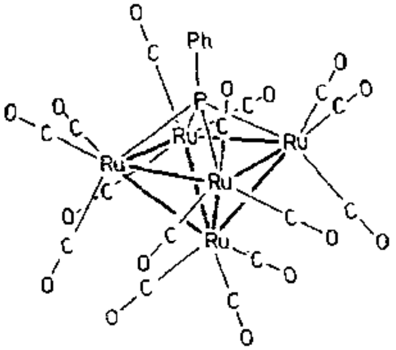

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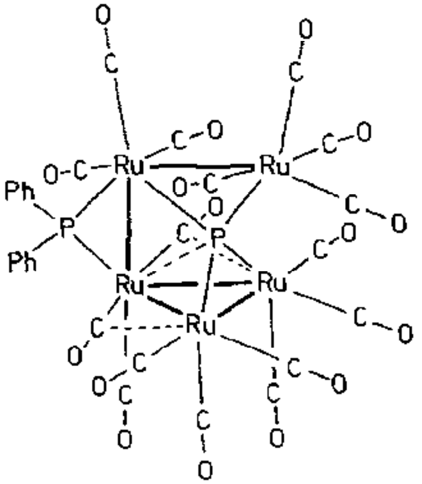
An unusual μ_5-P interaction has been reported in the complex $Ru_5(CO)_{16}(\mu\text{-}PPh_2)(\mu_5\text{-}P)$ (**100**) [45]. The phosphorus atom bonded to five metals seems to be a very effective assembling ligand for this open arrangement of metals.



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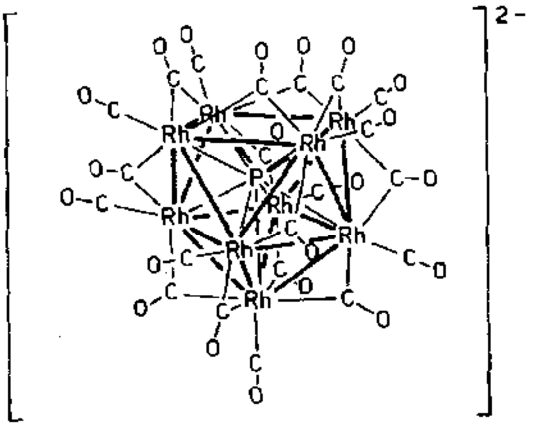
Finally another example of "naked" phosphorus coordinated to many metal atoms is found in the anionic cluster $[Rh_9P(CO)_{21}]^{2-}$ (**101**) [178], in which the P atom is asymmetrically encapsulated in a cubic antiprismatic cavity.



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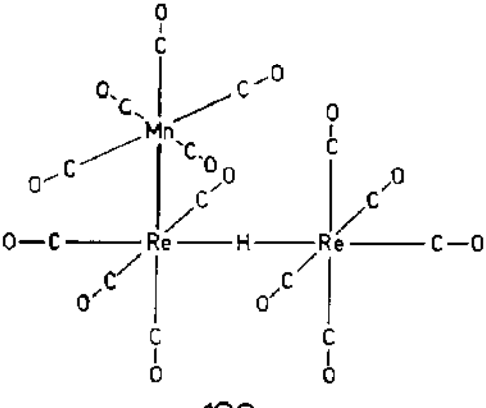
I. THE BRIDGING HYDRIDE LIGAND

Last in this ordering, but not least in importance, is the hydride ligand. Its occurrence as an assembling ligand is rarer than that of the molecules or atoms discussed above. Examples of this behaviour are $HRe_2Mn(CO)_{14}$ (**102**) [179], as well as $[(Cp)_2(H)W(\mu\text{-}H)Pt(Ph)(PEt_3)_2]^+$ (**103**) and $[(Cp)_2W(\mu\text{-}H)_2Pt(Ph)(PEt_3)]^+$ (**104**) [180], the W–Pt interaction being considerably stronger in the dihydride than in the related monohydride bridged species. (In these examples the hydrogen atoms could not be located in the X-ray analyses, and have been placed in the positions proposed by the authors.)



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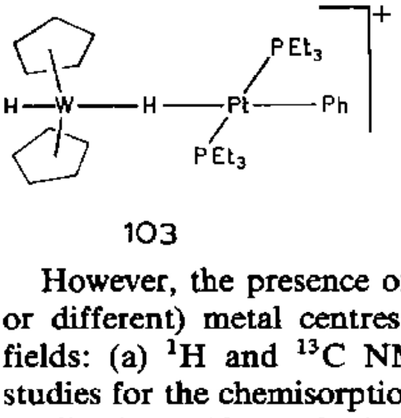

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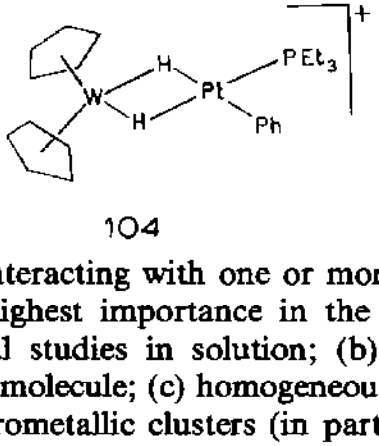

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However, the presence of hydrides interacting with one or more (similar or different) metal centres is of the highest importance in the following fields: (a) ^1H and ^{13}C NMR fluxional studies in solution; (b) "model" studies for the chemisorption of the H_2 molecule; (c) homogeneous catalytic applications; (d) synthesis of new heterometallic clusters (in particular the gold-containing clusters, obtained via isolobal substitution of Au(L) for H [181]).

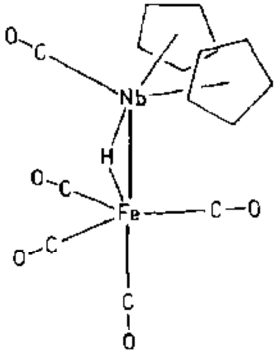
Unfortunately, the X-ray location of this ligand is difficult and relatively few neutron diffraction studies are available because of the cost, limited access and difficulty in obtaining crystal specimens suitable for this technique.

Recent review articles on hydride complexes of the transition metals

[182,183] and on crystallographic studies of transition metal hydride complexes [184] have been published and provide an excellent coverage of the field.

From the literature available, it appears that μ-H is a commonly found bonding mode. Three main structural features should be considered: the dihedral angle between the cluster plane and the M–H–M plane; the M–H distances (when available); and the M–H–M bond angle, which can be indicative of the overlap type between the metals and hydrogen orbitals. These features have recently been discussed and can be consulted in the literature [94,181–184]. Few examples of asymmetric hydride bridges are available; however there are sound indications that this ligand is sensitive to several effects.

In **74** [99] (section E) an asymmetric bridge (Ru–H = 1.67(5) and 1.75(5) Å) has been found, perhaps due to the different substitution of the two Ru atoms. In $(Cp)_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$ (**105**) [185] the asymmetrical bridge (Nb–H = 1.91(3) and Fe–H = 1.61(3)) involves two different metal centers (even though in **27** [71] the bridge involving Rh and Pt is nearly symmetrical, Rh–H = 1.747(1) and Pt–H = 1.750(1) Å).



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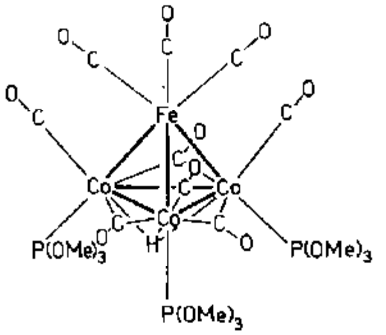
Heterobimetallic complexes are good candidates for studying the preferential bonding mode of the H ligand, bridging as in the previous cases, or terminal as in $(Cp)(CO)_3MoPtH(PPh_3)_2$ (**8**) [22]. These situations are relevant to the study of hydrogen transfer from one center to a neighbouring center and have implications in homogeneous catalysis.

Also, in complexes **86** and **87** [150] the hydride bridge seems sensitive to the cluster structural changes (from closed to open) and ligand substitution. The structural parameters are: in **86** (closed cluster) Ru–H 1.67–1.59(5) and 1.69–1.75(5) Å, in **87** (open cluster) Ru–H 1.64–1.81(6) and 1.77–1.76(6) Å (the Ru–H–Ru angles are 124(3) and 114(3)° in **86** and 118(3) and 112(3)° in **87**).

Triply-bridging μ_3-H examples have also been reported, among which are $HFeCo_3(CO)_9[P(OMe)_3]_3$ (**106**) [186] and $HRu_4(CO)_{10}(PPh_2)(HC_2Pr^i)$ (**107**) [143]. In **106** (whose structure has been determined by both X-ray and neutron diffraction methods) the hydrogen atom nearly symmetrically bridges the three cobalt atoms (Co–H = 1.728(3), 1.731(1) and 1.742(3) Å) in a position 0.978(3) Å out of the plane of the three Co atoms on the side opposite to the iron atom. In contrast in **107** the hydrogen asymmetrically bridges a wing of the Ru_4 butterfly (Ru–H = 1.63, 1.91 and 2.04 Å)



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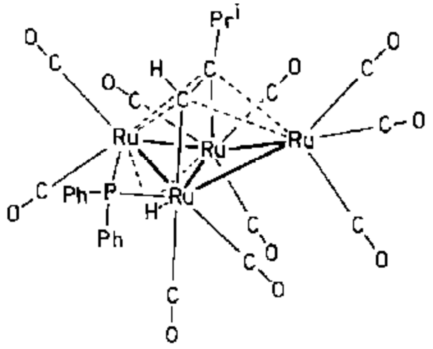

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For soluble complexes ^1H NMR is a very useful technique allowing, in particular, the study of dynamic processes. Furthermore, when the H ligand(s) is (are) bonded to a metal center possessing a nuclear spin, very useful information can be gained with the determination of the corresponding coupling constants.

Extension of the NMR analyses to the solid state, looking at H, P, CO and carbide resonances, would be of great importance and would better link homogeneous cluster chemistry and surface chemistry.

J. EXAMPLES OF SPECTROSCOPIC STUDIES RELEVANT TO THE CLUSTER-SURFACE ANALOGY

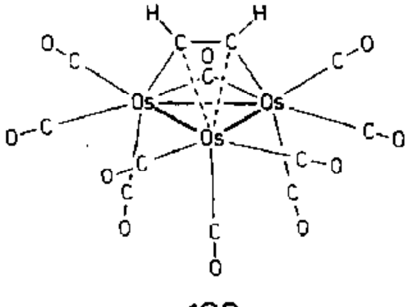
Carbonyl and hydride ligands in clusters can easily be investigated by spectroscopy in solution; these ligands have also been studied but with greater technical problems, when chemisorbed on surfaces. With the data available a comparison between the molecular and surface science results is difficult and limited to a few examples only [3].

Thus, the IR, ^1H and ^{13}C NMR fluxionality studies or the ^{31}P data in solution are only indicative of what could happen on metal surfaces (e.g., chemisorption, splitting, isomerization, migration, and oligomerization of ligands).

Recently, studies on low-temperature matrix-isolated species [188] and on species chemisorbed on well-defined metal crystal faces [189] have been performed. With the help of ^{12}CO and ^{13}CO vibrational coupling, identification of different adsorption sites in the incommensurate compression structure of chemisorbed CO on Cu(111) [216] has been achieved recently.

On the other hand, C–C stretching vibrations for surface-bound organic molecules have frequently been reported and assigned [190], whereas little has been published for the same cluster-bound molecules [191]. Infrared and Raman spectroscopic studies of some acetylenic compounds adsorbed on zinc oxide have shown that acetylide and propargylic species are formed, resulting from dissociative chemisorption [192]. Related $[R\text{–}CH_2C{\equiv}C]^-$, $[R\text{–}CH{=}C{=}CH]^-$ and $[R\text{–}C{\equiv}C{=}CH_2]^-$ fragments have also been found in clusters.

The IR and Raman spectra of the acetylenic ligand in $Os_3(CO)_9(\mu\text{-}CO)(\mu_3,\eta^2\text{-}C_2H_2)$ (**108**) have been analyzed and close analogies with electron energy loss spectra obtained from acetylene chemisorbed on Pt(111) and Pd(111) crystal faces confirm that the adsorbed species have the same hydrocarbon structure as the cluster-bound ligand (values of frequencies are given) [193].



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Detailed infrared and Raman studies of $HOs_3(CH{=}CH_2)(CO)_{10}$ and $H_2Os_3(C{=}CH_2)(CO)_9$ have aimed at defining the fingerprint patterns of the coordinated hydrocarbon ligands. The olefinic groups are characterized by ν(CH) bands above 2980 cm^{-1} and a strong $\gamma(CH_2)$ band between 800–1000 cm^{-1} whereas the low-wavenumber ν(C=C) modes between 1310 and 1480 cm^{-1} are only explicable in terms of π and σ bonding [194]. Related studies have appeared [195].

^{13}C NMR shift range studies of C_1 and C_2 cluster-bound hydrocarbon fragments and assignment of the vibrational frequencies of the C_2H_n moieties point to the rearrangement of acetylene to a μ_3, η^2-vinylidene on Ni(111) and Fe(110) surfaces [196].

A "cluster-centered" acetylene–vinylidene rearrangement has recently been described by Bernhardt and Vahrenkamp [197].

Recent spectroscopic studies on the bridging methylene ligand in the metal cluster complexes $Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}$ and $Os_3(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_{10}$ have assigned the frequencies at ca. 2940 and 1430 cm^{-1} to the symmetric C–H stretch and CH_2 deformation modes, respectively [191]. These are very close to the values reported for the same species postulated on W(110) [198].

Studies of hydrocarbons chemisorbed on metal surfaces have implicated methylidyne radicals. An EELS study of C_2H_2 adsorbed on a Ni(111) crystal surface provided evidence for an unsymmetrically bridging CH fragment [199], whereas a symmetrically bridging CMe unit has been proposed for ethylene chemisorbed on Pt(111) [200]. Studies by e.g. Churchill et al. [201], suggest that the bonding mode adopted by such a CX fragment on the surface may be dependent upon the metal, the substituent on the methylidyne, and the other molecules on the surface. Further study of metal clusters should provide both model compounds for spectroscopic comparison with surface species and information about the factors influencing the bonding.

Solid state IR studies on single crystals of $Co_3(CO)_9CR$, M≡C–R and M≡C–NR_2 complexes have been reported. Spectroscopic parameters of interest for carbyne complexes are: ν(M≡C) vibrations at ca. 1350 cm^{-1} (ca. 1150 cm^{-1} for amino-carbyne), force constants of 6.0–7.50 mdyn $Å^{-1}$ and bond orders of 2.1 for M≡C [202].

Spectroscopic studies on surfaces have also shown that, upon chemisorption, easy modification of ligands can occur, giving new species (e.g., transformation of CO to formyl, COOH and other functional groups; of acetylene into vinylidene or methylene fragments [198]).

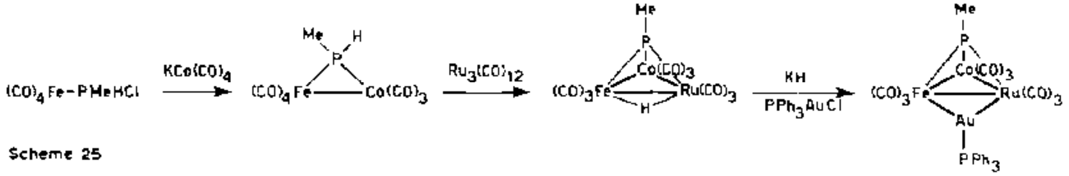
Related ligand modifications may happen on clusters, as a consequence of the selective interaction between metals and ligands; a profound modification of the reactivity of the organic molecule may result. Formation of new chemical bonds between the metals and the ligand-derived fragments will be the driving force for this modification. Recently, C–O or C≡C bond scissions have been observed on WOS_3 clusters [218].

To our knowledge no solution or solid state spectroscopic data on organic ligands bound to heterometallic clusters have yet allowed a comparison to be made with the properties of the same ligands on the corresponding alloys.

K. SOME COMMENTS ON THE SEC RULES AND ON THE ISOLOBAL ANALOGY. METAL CLUSTER CORE ISOMERISM

Recent theoretical approaches to rationalize the structures of clusters have been very useful for attempting their "planned syntheses".

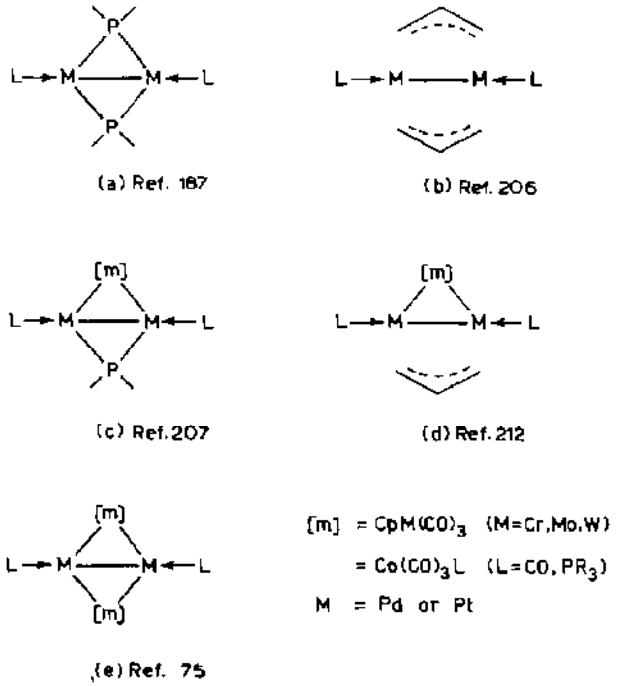
The skeletal pairs approach of Wade [5] and Mingos [6] and the isolobal analogy [7] allow, at least formally, the "substitution" of building blocks while maintaining the same overall geometry. This permits rationalization of the structural results and the correlation of apparently very different structures. The recent work of Stone and coworkers (Section D) [112] is based on this approach and represents a further step in the rational synthesis of clusters, originally developed by Vahrenkamp and coworkers, via the condensation of metal fragments "assisted" by ligands (see refs. 19, 114, 140, 153) as in the examples below [203].



Scheme 25

"Addition" reactions leading to stepwise synthesis of homometallic osmium based clusters have also been recently reported [204].

In recent studies, metal carbonyl fragments have been considered to be bridging "ligands" in a series of clusters emphasizing the similarities between the structures in Scheme 26. In each of these molecules, the bridging

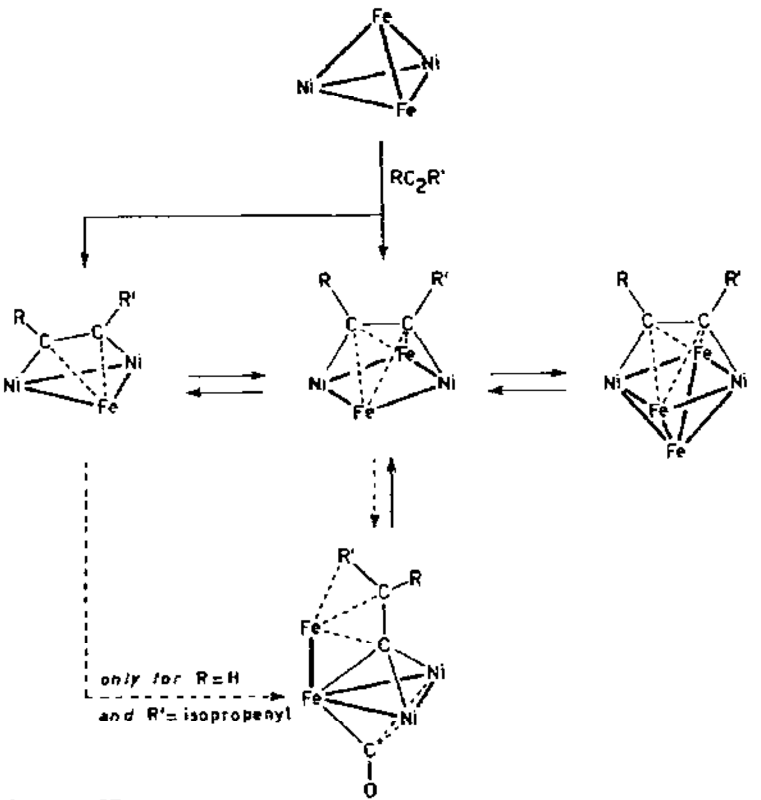


(a) Ref. 187
(b) Ref. 206
(c) Ref. 207
(d) Ref. 212
(e) Ref. 75

Scheme 26

fragment i.e. PPh_2, allyl, metal carbonyl, behaves formally as a neutral three electron donor ligand bridging the linear L → M–M ← L unit.

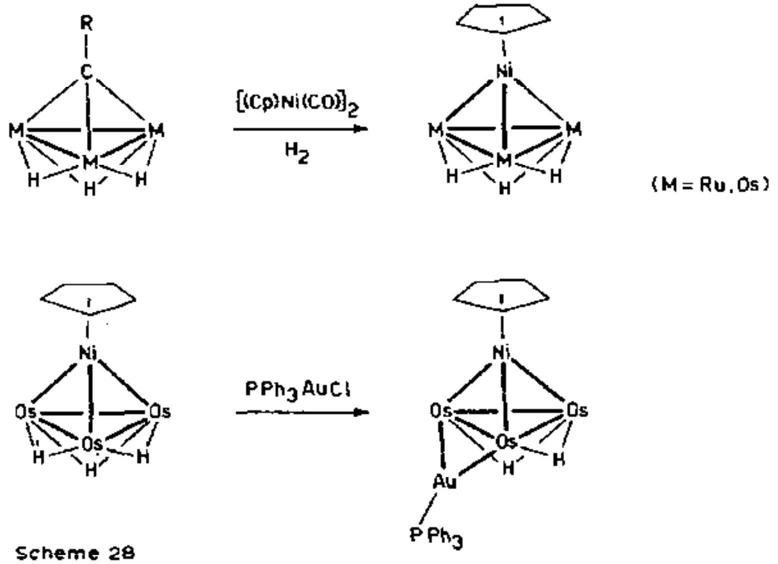
Finally, frame expansion and contraction reactions of alkyne-substituted clusters also occur during the synthesis of new clusters [205] and may



Scheme 27

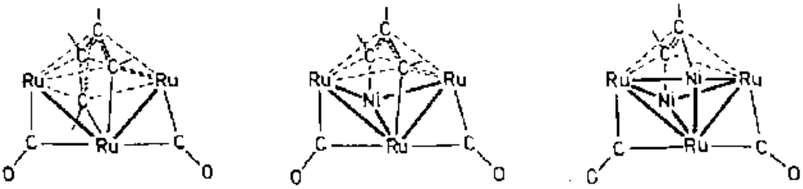
account for the observed "cluster frame" isomerism (Scheme 27).

"Isolobal substitution" reactions leading to new clusters are in considerable expansion, two examples being [181,213]:



Scheme 28

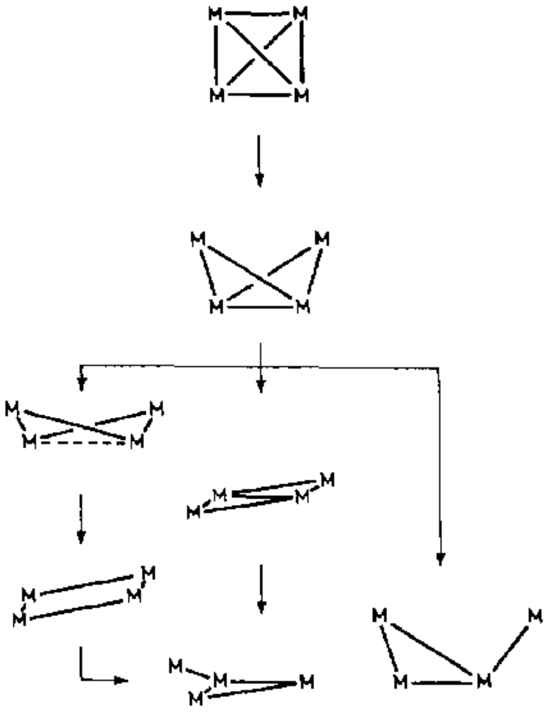
Finally, the structures of different clusters (all containing alkynes or alkyne-derived ligands, but a different number of metals) can be rationalized in terms of the isolobal analogy (scheme 29) [42]. However, the preparation of these clusters does not result from a retrosynthetic pathway.



Scheme 29

Examples of cluster core isomerism have been reported for heterometallic clusters; "metal isomerism" is found in $FeRu_3(CO)_{12}(RC_2R')$ clusters [137] where iron is on a wingtip or, alternatively, in a hinge position. In the related $[RuCo_3(CO)_{10}(C_2Ph_2)]^-$ cluster (**73**), the Ru atom is found only in the hinge position [129], probably because of its better π back-bonding ability towards the alkyne. Protonation of this cluster results in $RuCo_2(CO)_9(C_2Ph_2)$ (**65**) [129] in which the alkyne is parallel to the RuCo bond as in the precursor, whereas in the related $FeCo_2(CO)_9C_2Et_2$ (**64**) it has been found parallel to the Co–Co bond [128].

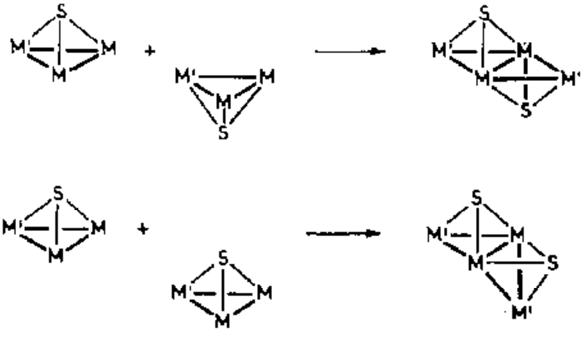
It is generally accepted that the tetrahedral, butterfly, lozenge, square planar, and "spiked triangular" ("in plane" or "out of plane") clusters are correlated as shown below, by successive addition of two electrons:



Scheme 30

However, one situation of particular interest concerns the occurrence of the same metal atoms and the same (or almost the same) ligands in different structural types corresponding to the same formula.

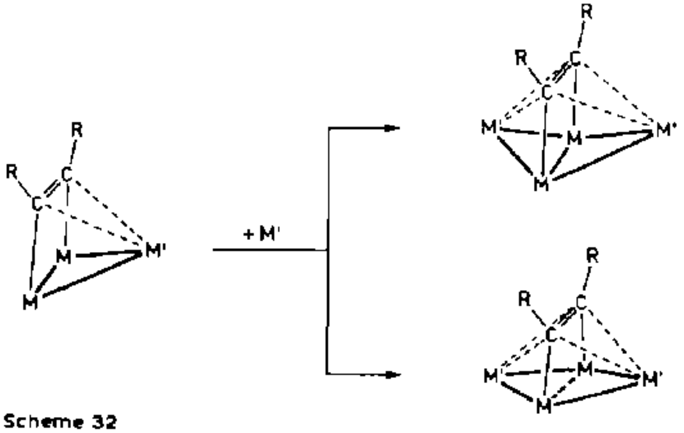
This has been rarely encountered and the first heterometallic examples are the $(Cp)_2Mo_2Fe_2(CO)_8S_2$ clusters (**31** and **88**). Thus the butterfly [77] and planar [149] isomers may formally be constructed by combining the Mo_2FeS fragments in the two following ways:



Scheme 31

Indeed, these two isomeric structures have been rationalized by considering the sulfur atoms as skeletal atoms [217].

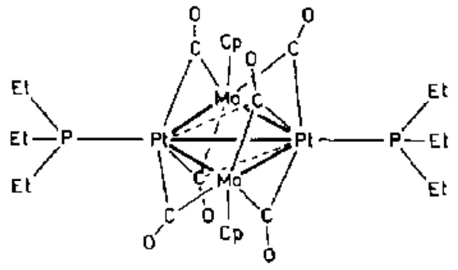
Mass spectrometry studies [208] seem to indicate that the following scheme could be observed:



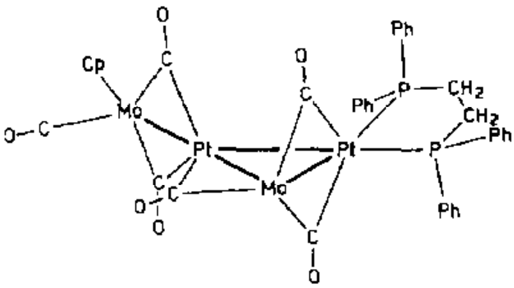
Scheme 32

Finally, as discussed previously (page 273, scheme 27) square-planar and "spiked-triangular" isomers have been observed for alkyne clusters of identical composition. The selective interaction of the ligand with the metals is particularly obvious here [79].

Tetrametallic Pt_2Mo_2 cores of lozenge (5 M–M bonds) and spiked-triangular (4 M–M bonds) structures have been found in $Pt_2Mo_2(Cp)_2(CO)_6(PEt_3)_2$ (**109**) [74b] and $Pt_2Mo_2(Cp)_2(CO)_6(dppe)$ (**110**) [209], respectively. Although the phosphine ligands are not the same, these



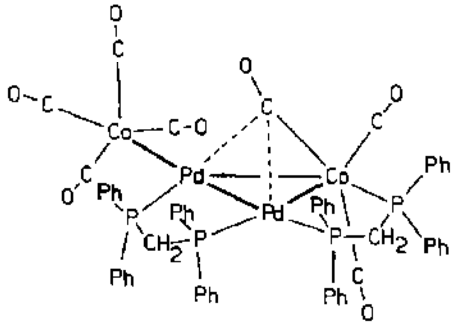
109



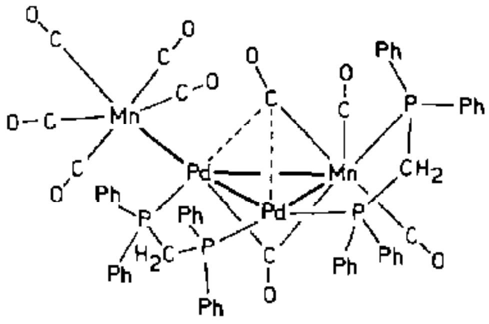
110

two clusters are obviously related and have the same electron count. This allows one to easily identify the importance of the steric changes when going from two monodentate phosphines to a bidentate one.

The presence of bidentate ligands also seems to favour a "spiked-triangular" structure in $Pd_2Co_2(CO)_7(dppm)_2$ (**111**) [209] and $Pd_2Mn_2(CO)_9(dppm)_2$ (**112**) [210] complexes, both showing an asymmetrical triply-bridging CO.



111



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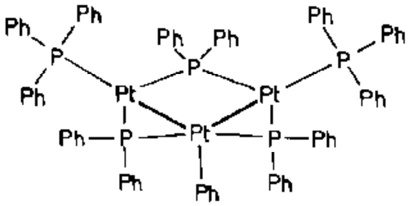
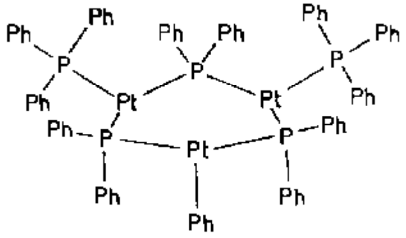
The possibility of observing structures based on the same type and number of metals, but with different numbers of metal–metal bonds, is of high catalytic relevance since it implies a significant change in the coordination spheres of the metals without affecting the electron count of the complex.

The ability of bridging ligands to allow reversible metal–metal bond breaking has already been discussed (sections G and H). A new example of isomerism has been found, the two complexes having the same formula $Pt_3(PPh_2)_3(PPh_3)_2(Ph)$ (**113** and **114**). One consists of an "open" (2 M–M bonds) triangular cluster [187a,b] and the other of a triangular arrangement of metals with three long Pt–Pt separations [187b]. These show the same type of terminal and bridging ligands and, obviously, the same overall electron count but with differing electron densities at the metals.

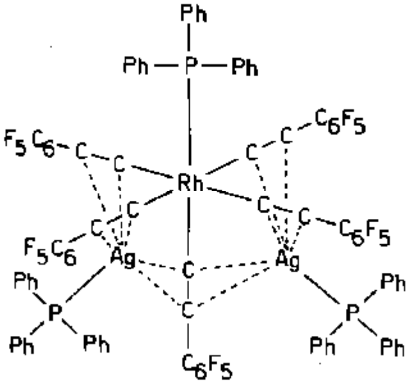


113



114

Because of the similar electron count between Pt–Pt and Ag–Rh units it is interesting at this point to remember the structure of the $RhAg_2(PPh_3)_3(C_2C_6F_5)_5$ (**115**) complex where the acetylides act as assembling ligands [211]. The presence of metal centres with different electronic and coordination environments, with potentially vacant coordination sites, in ligand-stabilized structures is of obvious interest for homogeneous catalytic applications.



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