

COMPLEXES CONTAINING HETERONUCLEAR METAL-METAL BONDS.
SOME RECENT ADVANCES 1980-81.

A. COMPOUNDS CONTAINING TWO DIFFERENT TRANSITION METALS
(EXCLUDING MIXED-METAL CLUSTERS)

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INTRODUCTION

In the late sixties, the predecessor volumes Annual Surveys of Organometallic Chemistry contained sections on organometallic derivatives containing two different transition metals; a total of eleven references was cited between 1964 and 1966 [1]. Recent years have witnessed an upsurge of interest in the direct interactions of different transition metals with each other; a recent article reviewing the topic of 'Mixed-metal Clusters' cited over 170 papers [2]. The present survey will be presented in two parts: an account of those compounds containing M-M' bonds, which may or may not be bridged by groups such as CO, carbenes, carbynes, ER₂ (E = P or As), SR, or hydrocarbons, and limited to those papers appearing in the calendar years 1980 and 1981, and presented hereunder; and a review of advances in the chemistry of mixed-metal clusters, which follows on directly from Gladfelter and Geoffroy's excellent survey, taking in all developments published to the end of 1981. In general, complexes containing two or more metal atoms in which there is no direct M-M' interaction will not be considered; exceptions are the interesting compounds containing M-H-M' or M-C-O-M' systems, and a brief summary of

transition metal thiometallates. The interested reader will find a complete account of the chemistry of organometallic compounds with heteronuclear metal-metal bonds in *Comprehensive Organometallic Chemistry* [3].

General advances The most important new principle applied to the synthesis of M-M' complexes was the recognition that M=C and M≡C bonds were similar to the much better known C=C and C≡C systems in that they would "complex" with suitable low-valent metal precursors to give heterometallic complexes. Although the first results of these studies were reported during 1979, the succeeding two years have seen a flood of new results from Stone and coworkers, which have been comprehensively reviewed on several occasions [4,5]. Recognition of isolobal relationships between various groups (Table 1) enabled an extensive range of designed syntheses of M-M' bonded systems to be carried out.

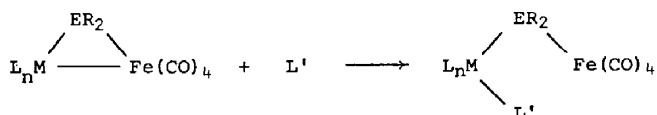
Reactions between low-valent metal complexes (initially PtL₂ fragments) with compounds containing metal-carbon multiple bonds, generally carbene or carbyne complexes, afford heterodimetal complexes with bridging alkylidene or alkylidyne ligands. These compounds, which can also be considered to be dimetallacyclopropanes or -cyclopropenes, generally have asymmetric bridging ligands. Cluster complexes can be obtained via two-step syntheses from carbyne complexes: these contain μ₃-alkylidyne ligands. Finally, extension to metal-metal multiple bonds has resulted in a range of new polynuclear heterometallic complexes. The detailed results are summarised below.

Two subsets of reports are concerned with extension of our knowledge of the range and properties of complexes available from conventional syntheses of metal-metal bonded complexes, and with the apparently inexhaustible series of ER₂-bridged complexes made by Vahrenkamp's group, which have included notable sequences and cycles containing four, five and six metal atoms. Not all have M-M' bonds, although many which do not can be induced to form them. Readers will recall the elegant series of M-M' bond-breaking and -making reactions which were applied to the

TABLE 1 *Some isolobal relationships and the addition of PtL₂ to C-C, C-M and M-M multiple bonds*

CH	CH ₂	CH ₃
M(CO) ₂ (η-C ₅ H ₅)	FeL ₄	M(CO) ₅
(M = Cr, Mo, W)		(M = Mn, Re)
Co(CO) ₃	PtL ₂	
$\begin{array}{c} \text{C} \\ \\ \text{C} \end{array} \longrightarrow \text{Pt} \equiv \begin{array}{c} \text{C} \\ \\ \text{C} \end{array} \text{Pt}$		$\begin{array}{c} \text{C} \\ \\ \text{C} \end{array} \longrightarrow \text{Pt} \equiv \begin{array}{c} \text{C} \\ \\ \text{C} \end{array} \text{Pt}$
olefin		alkyne
$\begin{array}{c} \text{C} \\ \\ \text{M} \end{array} \longrightarrow \text{Pt} \equiv \begin{array}{c} \text{C} \\ \\ \text{M} \end{array} \text{Pt}$		$\begin{array}{c} \text{C} \\ \\ \text{M} \end{array} \longrightarrow \text{Pt} \equiv \begin{array}{c} \text{C} \\ \\ \text{M} \end{array} \text{Pt}$
carbene	carbyne	
$\begin{array}{c} \text{M} \\ \\ \text{M} \end{array} \longrightarrow \text{Pt} \equiv \begin{array}{c} \text{M} \\ \\ \text{M} \end{array} \text{Pt}$		$\begin{array}{c} \text{M} \\ \\ \text{M} \end{array} \longrightarrow \text{Pt} \equiv \begin{array}{c} \text{M} \\ \\ \text{M} \end{array} \text{Pt}$

isolation and characterisation of many new complexes in the FeAsMn and FeAsCo systems [6]. Much of the work reported during the last two years has been concerned with the reactivity of the M-M' bond, and in particular its cleavage in reactions with other organometallic Lewis bases. The results demonstrate that these bonds in a variety of mixed-metal compounds of this type containing iron are essentially donor bonds from iron, the incoming ligand adding to the second metal centre.



A second area of interest has arisen from the discoveries of the role of complexes of the electron-poor transition metals, *i.e.* those in Groups IV-VI, in the oligomerisation and hydrogenation of CO, and of reactions in bimetallic systems formed by interaction of metal hydrides with acyl-metal complexes. In many of these complexes, the differences in metal electronegativities result in the formation of novel M-C-O-M' systems, rather than heterometallic bonds.

The biological implications of the Fe-Mo-S clusters probably present in nitrogenase have stimulated much work with model compounds. In addition to those containing Fe-Mo(or W)-S cubane clusters, there have been many reports of other sulphur-bridged M-M' systems. While the majority of these do not fall into the category of "classical" organo-metallic complexes, it is interesting to recall the earliest studies of metal-sulphur complexes behaving as ligands to other metals, and the discussions concerning the extent of the M-M' interactions therein. Whilst in most cases the M-M' separations are close enough for there to be some interaction, MO calculations suggest that the main bonding MO's extend over the M-S-M' bridges.

Coverage of the many studies of compounds with M-M' bonds has been divided into the following sections:

M-M' bonds which are either unsupported, or bridged by CO or

CS groups

M-M' bonds bridged by carbene or carbyne ligands

M-M' bonds bridged by ER₂ groups

M-M' bonds bridged by hydrocarbon ligands

M-M' bonds bridged by other donor ligands

Complexes containing M-H-M' systems

Heterobimetallic reduction of CO

Coordination compounds containing M-M' bonds

Transition metal thiometallate complexes

Mixed-metal molecules

Reactions which may involve direct M-M' interactions.

TABLE 2 *M-M' separations in organometallic mixed-metal systems*

M-M'	Length (Å)	Complex	Reference
Zr-Mo	3.297 (1)	$(\eta\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-}\eta^1, \eta^2\text{-CO})(\mu\text{-OCMe})\text{Mo}(\text{CO})(\eta\text{-C}_5\text{H}_5)$	[95]
Zr-Co	2.926 (1)	$(\eta\text{-C}_5\text{Me}_5)_2\text{Zr}(\mu\text{-CO})(\mu\text{-}\eta^1, \eta^2\text{-CO})\text{Co}(\eta\text{-C}_5\text{H}_5)$	[99]
V-Nb	3.725 (4)	$(\eta\text{-C}_5\text{H}_5)(\text{OC})_3\text{V}(\mu\text{-H})\text{Nb}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2$	[84]
Nb-Cr	3.453 (2)	$(\eta\text{-C}_5\text{H}_5)_2(\text{OC})\text{Nb}(\mu\text{-H})\text{Cr}(\text{CO})_5$	[84]
Nb-Fe	2.968 (1)	$(\eta\text{-C}_5\text{H}_5)_2\text{HNb}(\mu\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2$	[74]
Cr-W	2.941 (1)	$(\eta\text{-C}_6\text{Me}_6)(\text{OC})_2\text{Cr}[\mu\text{-C}(\text{tol})]\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$	[48]
Cr-Co	2.92	$(\text{OC})_3\text{Cr}(\mu\text{-}\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Co}(\eta\text{-C}_5\text{H}_5)$	[127]
Cr-Ni	2.641 (3)	$(\eta\text{-C}_5\text{H}_5)(\text{OC})_3\text{CrNi}(\text{CO})(\eta\text{-C}_5\text{H}_5)$	[128]
	2.655 (2)	$(\text{OC})_4\text{Cr}(\mu\text{-PMe}_2)_2\text{Ni}(\text{CO})_2$	[129]
Cr-Pt	2.646 (7)	$(\text{Me}_3\text{P})(\text{OC})_4\text{Cr}[\mu\text{-C}(\text{CO}_2\text{Me})\text{Ph}]\text{Pt}(\text{PMe}_3)_2$	[47]
Mo-Co	2.969 (1)	$(\text{OC})_3\text{Mo}(\mu\text{-}\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Co}(\eta\text{-C}_5\text{H}_5)$ (molecule 2)	[75]
	2.998 (1)	(molecule 1)	
Mo-Rh	2.9212 (7)	$(\text{OC})_4\text{Mo}(\mu\text{-PMe}_2)_2\text{Rh}(\eta\text{-C}_5\text{Me}_5)$	[63]
Mo-Pd	3.059 (1)	$(\eta\text{-C}_5\text{H}_5)(\text{OC})_3\text{MoPd}(\text{CH}_2\text{C}_9\text{H}_6\text{N})(\text{PMe}_2\text{Ph})$	[9]
W-Re	2.968 (2)	$(\text{OC})_4\text{W}[\mu\text{-C}(\text{PMe}_3)(\text{tol})]\text{Re}(\text{CO})_3(\text{PMe}_3)$	[55]
W-Fe	2.720 (1)	$(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{W}[\mu\text{-C}(\text{tol})\text{CMeCMe}]\text{Fe}(\text{CO})_3$	[50]
W-Co	2.552 (1)	$[(\eta\text{-C}_5\text{H}_5)(\text{OC})\text{W}(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{tol})\text{CMeCHMe}\}\text{Co}(\eta\text{-C}_5\text{Me}_5)]\text{BF}_4$	[49]
	2.664 (1)	$(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{W}[\mu\text{-C}_4(\text{CF}_3)_4]\text{Co}(\text{CO})_2$	[76]
W-Ni	2.582 (1)	$\text{Ni}[\text{W}\{\mu\text{-C}(\text{tol})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$	[52]
W-Pt	2.715 (1)	$\text{Pt}[\text{W}\{\mu\text{-C}(\text{tol})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$	[52]
	2.751 (1)	$(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{W}[\mu\text{-C}(\text{tol})]\text{Pt}(\text{PMe}_2\text{Ph})_2$	[51]
	2.795 (1)	$[(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{W}\{\mu\text{-}\eta^1, \eta^3\text{-CH}(\text{tol})\}]\text{Pt}(\text{PMe}_3)_2\text{BF}_4$	[49]
	2.825 (1)	$(\text{Me}_3\text{P})(\text{OC})_4\text{W}[\mu\text{-C}(\text{OMe})(\text{tol})]\text{Pt}(\text{PMe}_3)_2$	[44]
	2.861 (1)	$(\text{OC})_5\text{W}[\mu\text{-C}(\text{OMe})\text{Ph}]\text{Pt}(\text{PMe}_3)_2$	[43]
W-Pt	2.895 (1)	$(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{W}(\mu\text{-H})[\mu\text{-CH}(\text{tol})]\text{Pt}(\text{PMe}_3)_2$	[49]
Mn-Re	2.817 (3)	$(\eta\text{-C}_5\text{H}_5)_2(\text{OC})_2\text{Mn}(\mu\text{-PhC=C=O})\text{Re}(\text{CO})_4$	[54]
Mn-Co	2.639 (3)	$(\text{OC})_3\text{Mn}(\mu\text{-CO})(\mu\text{-Bu}^t\text{N=CHCH=NBu}^t)\text{Co}(\text{CO})_2$	[24]

Mn-Rh	2.883 (4), 2.905 (5)	(OC) ₅ MnRh [μ-CNCMe ₂ (CH ₂) ₂ CMe ₂ NC] ₄ RhMn(CO) ₅	[82]
Mn-Ni	2.613 (1)	(OC) ₅ MnNi(CO)(η-C ₅ H ₅)	[128]
Mn-Pt	2.603 (1)	(OC) ₄ Mn(μ-I)Pt(COCH ₂ CH ₂ CH ₂)(PMeBu ₂ ^t)	[46]
	2.626 (1)	(η-C ₅ H ₅)(OC)Mn[μ-C(PMe ₃)(tol)](μ-CO)Pt- [S(tol)](PMe ₃)	[56]
	2.628 (1)	(η-C ₅ H ₅)(OC) ₂ Mn[μ-C(tol)]Pt(PMe ₃) ₂	[47]
	2.641 (1)	(η-C ₅ H ₅)(OC) ₂ Mn(μ-CS)Pt(PMePh ₂) ₂	[31]
	2.645 (1)	[(η-C ₅ H ₅)(OC) ₂ Mn{μ-C(PMe ₃)(tol)}Pt- (PMe ₃) ₂][BF ₄]	[56]
	2.659 (2)	(OC) ₄ Mn[μ-C=CHCH ₂ CH ₂ O]Pt(PMe ₃) ₂ (yellow form)	[45]
	2.6909 (7)	(OC) ₄ Mn[μ-C=CHCH ₂ CH ₂ O]Pt(PMe ₃) ₂ (red form)	[45]
Fe-Co	2.456 (6)	(η-C ₅ H ₅)Fe(μ-CO) ₂ Co(η-C ₅ H ₅)(μ-AsMe ₂)Fe(CO)- (η-C ₅ H ₅)(μ-AsMe ₂)	[70]
Fe-Rh	2.623 (2)	[(OC) ₃ Fe(μ-CO)(μ-PPh ₂)Rh(μ-PPh ₂)] ₂	[73]
Fe-Au	2.519 (1)	(η-C ₃ H ₅)(OC) ₃ FeAu(PPh ₃)	[32]
Os-Ag	2.799 (1)	(Ph ₃ P) ₂ (OC)ClOs[μ-C(tol)]AgCl	[57]
Co-Ni	2.3656 (8)	(OC) ₃ Co(μ-C ₂ Ph ₂)Ni(η-C ₅ H ₅)	[80]
Co-Au	2.509 (2)	(ppn)[Au{Co(CO) ₄ }] ₂	[14]
Rh-Ir	2.636 (2)	[(dppe)Rh(μ-H) ₃ Ir(PET ₃) ₃][BPh ₄]	[86]
	2.899 (1)	(Et ₃ P) ₂ Rh(μ-H)(μ-Cl)IrH ₂ (PET ₃) ₂	[87]
Rh-Pd	2.594 (1)	(OC)Cl ₂ Rh[μ-FPh ₂ (py)] ₂ PdCl	[83]
Rh-Ag	2.651 (1), 2.636 (1)	[Ag{Rh(CO)(PPh ₃)(η-C ₅ H ₅)} ₂][PF ₆]	[36]
Ir-Pt	2.687 (2)	HIr(PET ₃) ₃ (μ-H) ₂ PtPh(PET ₃)	[88]

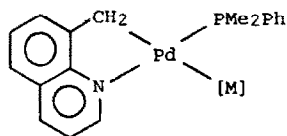
Within each section, individual studies are approximately ordered according to position in the Periodic Table. Table 2 summarises M-M' bond lengths determined by X-ray crystallography, Tables 3 and 4 summarise recent work on M(μ-S)₂M' systems, and Table 5 lists a few reactions which did not afford compounds containing M-M' bonds.

1. COMPOUNDS CONTAINING M-M' BONDS WHICH ARE EITHER UNSUPPORTED, OR BRIDGED BY CO OR CS LIGANDS

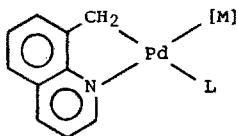
Permutation of 17e radicals $M(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ ($M = \text{Cr}, \text{Mo}, \text{or W}$), $\text{Mn}(\text{CO})_5$, $\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$, $\text{Co}(\text{CO})_4$ and $\text{Ni}(\text{CO})(\eta\text{-C}_5\text{H}_5)$ has given the seven homobinuclear and 21 heterobinuclear complexes [7]. The latter are best prepared by redistribution of the corresponding mononuclear complexes in benzene followed by recrystallisation, with chromatographic separation if necessary. Yields of between 5 and 74% were obtained for the seven new compounds (CrMn , CrFe , CrNi , MoNi , WNi , MnNi , CoNi). Extensive tabulations of spectroscopic properties are also included.

Irreversible reduction of $\text{Pt}[\text{M}]_2(\text{CNR})_2$ ($R = \text{Bu}^t$ or Cy) affords one $[\text{M}]^-$ per molecule, with $E_{1/2}$ values in the series $M = \text{Fe}(\text{CO})_3(\text{NO}) > \text{Co}(\text{CO})_4 > \text{Cr}(\text{CO})_3(\eta\text{-C}_5\text{H}_5) > \text{Mn}(\text{CO})_5 > \text{Mo}(\text{CO})_5(\eta\text{-C}_5\text{H}_5) > \text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$, and formation of a radical species $\{\text{Pt}[\text{M}](\text{L})_2\}^{\cdot}$. The radicals (of limited stability) are probably stabilised by the π -accepting isocyanide ligands; although ESR signals were obtained, these had no hyperfine structure, and further characterisation was not possible.

Complexes (1) and (2) have been obtained from the appropriate anionic metal carbonyls and the chloropalladium complexes [9]. The



(1)



(2)

$[\text{M}] = \text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$

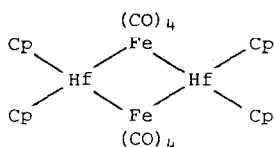
$\text{Co}(\text{CO})_4$

L	$[\text{M}]$
CO	$\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$
CO	$\text{Co}(\text{CO})_4$
py	$\text{Fe}(\text{CO})_3(\text{NO})$
py	$\text{Co}(\text{CO})_4$
4-Mepy	$\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$

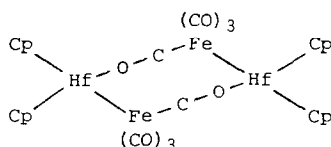
M-M' bonds in (1) are cleaved easily by chloride, suggesting that the bonds are strongly polarised (ionic), and consistent with the long

Mo-Pd bond [3.059(1)Å]. In (2), the bonds are stable, and the opposite stereochemistry is thus assigned to these complexes.

Hf-Fe Reactions between $\text{HfX}_2(\eta\text{-C}_5\text{H}_5)_2$ and $[\text{Fe}(\text{CO})_4]^{2-}$ afford dimeric (3), with $\nu(\text{Hf-Fe})$ at 184 and 138 cm^{-1} (Raman). A minor product is thought to be (4), containing an Fe-C-O-Hf linkage; the same complex is formed by dissolution of (3) in tetrahydrofuran. A $\nu(\text{CO})$ band at 1683 cm^{-1} characterises the $\mu\text{-CO}$ group [10].



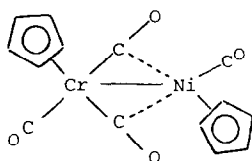
(3)



(4)

Group VI-Re The IR and Raman spectra of the carbyne complexes $(\text{OC})(\text{PhC})\text{MRe}(\text{CO})_4$ ($\text{M} = \text{Cr}, \text{Mo}$ and W ; MRePh) and of $(\text{OC})_4(\text{MeC})\text{WRe}(\text{CO})_5$ (WReMe) have been assigned [11]. The $\nu(\text{MRe})$ frequencies occur in the Raman spectra at 114vs (MoRePh), 110vs (WRePh) and 116vs cm^{-1} (WReMe), respectively. The WReMe complex is new, and was obtained from $[\text{Re}(\text{CO})_5]^-$ and *trans*-ClW(CMe)(CO)₄.

Cr-Ni The molecular geometries of $(\eta\text{-C}_5\text{H}_5)(\text{OC})_3\text{CrNi}(\text{CO})(\eta\text{-C}_5\text{H}_5)$ (5) and the isoelectronic $[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$, are determined by the intramolecular packing of ligands; regular coordination polyhedra around the metal atoms are not found, nor does the M-M' bond occupy a regular position [12]. The CrNi and Fe_2 molecules are nearly isosteric, although in the former, the $\mu\text{-CO}$ groups are highly asymmetric, with Cr-C

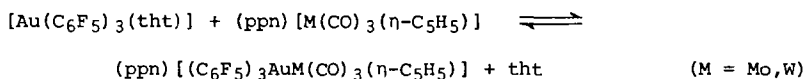


(5)

1.88(1), Ni---C 2.43(1)Å. Nevertheless, the peripheral atoms of the ligand polyhedron are virtually superimposable.

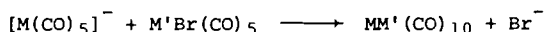
Cr-Cu UV photolysis of $\{(\eta\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{Cu}(\text{phen})\}_n$ in the presence of O_2 (CH_2Cl_2 , -70°) produces a paramagnetic species thought to be $\text{Cr}(\eta\text{-C}_5\text{H}_5)\text{-}(\text{CO})_2(\text{O}_2)$ [13].

Group VI—Au The equilibria



exist in dichloromethane; however, removal of the tetrahydrothiophene (tht) enables isolation of the Mo-Au and Mo-W complexes as cream or pale-brown solids [14]. In acetone, ionic dissociation occurs. Reaction with PPh_3 forms $\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_3)$ and the carbonylmetal anion. In contrast, the gold(I) complex $\text{Au}(\text{C}_6\text{F}_5)(\text{tht})$ affords a mixture of anionic complexes $[\text{Au}\{\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]^-$ and $[\text{Au}(\text{C}_6\text{F}_5)_2]^-$; the former were isolated as the cream $[\text{NBu}_4]^+$ salts. Reduction of $[\text{NET}_4][\text{Au}\{\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ ($\text{M} = \text{Cr}, \text{Mo}$, or W) gives an irreversible wave ($E_{1/2}$ ca -1.9 V), deposition of gold and release of $[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ [8].

Mn - Tc, Re The synthesis of mixed Group VII metal decacarbonyls by the reaction



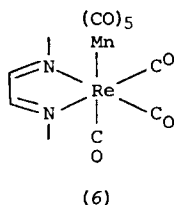
gives only 8% yields of the MnRe complex with $\text{M} = \text{Re}$, $\text{M}' = \text{Mn}$; the alternative combination ($\text{M} = \text{Mn}$, $\text{M}' = \text{Re}$) gave a 77% yield [15]. Once formed, the MnRe bond is cleaved by the more strongly nucleophilic $[\text{Re}(\text{CO})_5]^-$, but not by the Mn anion. The MnTc and TcRe complexes were prepared similarly ($\text{M} = \text{Mn}$). The IR spectra and MS ionisation energies have been measured: the heteronuclear compounds have lower IE's than either homonuclear complex.

Two kinetic studies of the reactions of $\text{MnRe}(\text{CO})_{10}$ have appeared. Substitution of CO by PPh_3 , PBu_3 or $\text{P}(\text{OPh})_3(\text{L})$ affords $(\text{OC})_5\text{MnRe}(\text{CO})_4(\text{L})$ as the main product, followed by $\text{L}(\text{CO})_4\text{MnRe}(\text{CO})_4\text{L}$; small amounts of

the Mn-isomers were also detected [16]. No ligand-exchange between Mn and Re was observed, nor were any Mn_2 or Re_2 products. The kinetic results are not consistent with the earlier conclusions that homolytic fission of the Mn-Re bond occurs [17]. Instead, a new mechanism is proposed, involving CO-dissociation from the dimer to generate an unsaturated species containing formally 16e and 18e centres as the important intermediate. Transfer of electronic unsaturation from one metal to another is a necessary feature, since CO dissociation occurs more readily from Mn, whereas L adds to Re, and is accommodated by postulating a bridging (or semi-bridging) CO group. These conclusions have been contested on the basis of halogenation (see below) and previously reported oxygenation studies [18]; however a key result that mixtures of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ do not afford $MnRe(CO)_{10}$ between 130-150° would appear to indicate that the two homonuclear carbonyls cannot both undergo substitution reactions by homolysis of the M-M bond [19].

Reactions between iodine and $MnRe(CO)_8(PPh_3)_2$ are first-order in $[MnRe]$, and involve rapid formation of an adduct with the halogen, followed by electron transfer and fission of the Mn-Re bond to give the mononuclear iodo complexes [20]. The initial site of attack is thought to be the O atoms of the CO group. Rates of reaction increase: $Mn_2 < MnRe < Re_2$.

The synthesis and properties of mixed-metal derivatives containing diazabutadiene ligands $MnRe(CO)_8(dab)$ were described in 1979 [21]. The resonance Raman spectrum of (6; $dab = pyCH=NC_6H_4Me-p$) at -170° has been assigned; $\nu(MnRe)$ could not be detected. The lowest-energy band in the electronic spectrum is assigned to a $M \rightarrow L$ charge transfer absorption; the excited state is delocalised over a CO group of the $MnRe(CO)_8$ moiety [22]. This state undergoes fast deactivation to a thermally activated ground state in which the M-M' bond is broken, allowing an explanation of the pronounced photosensitivity of this complex.

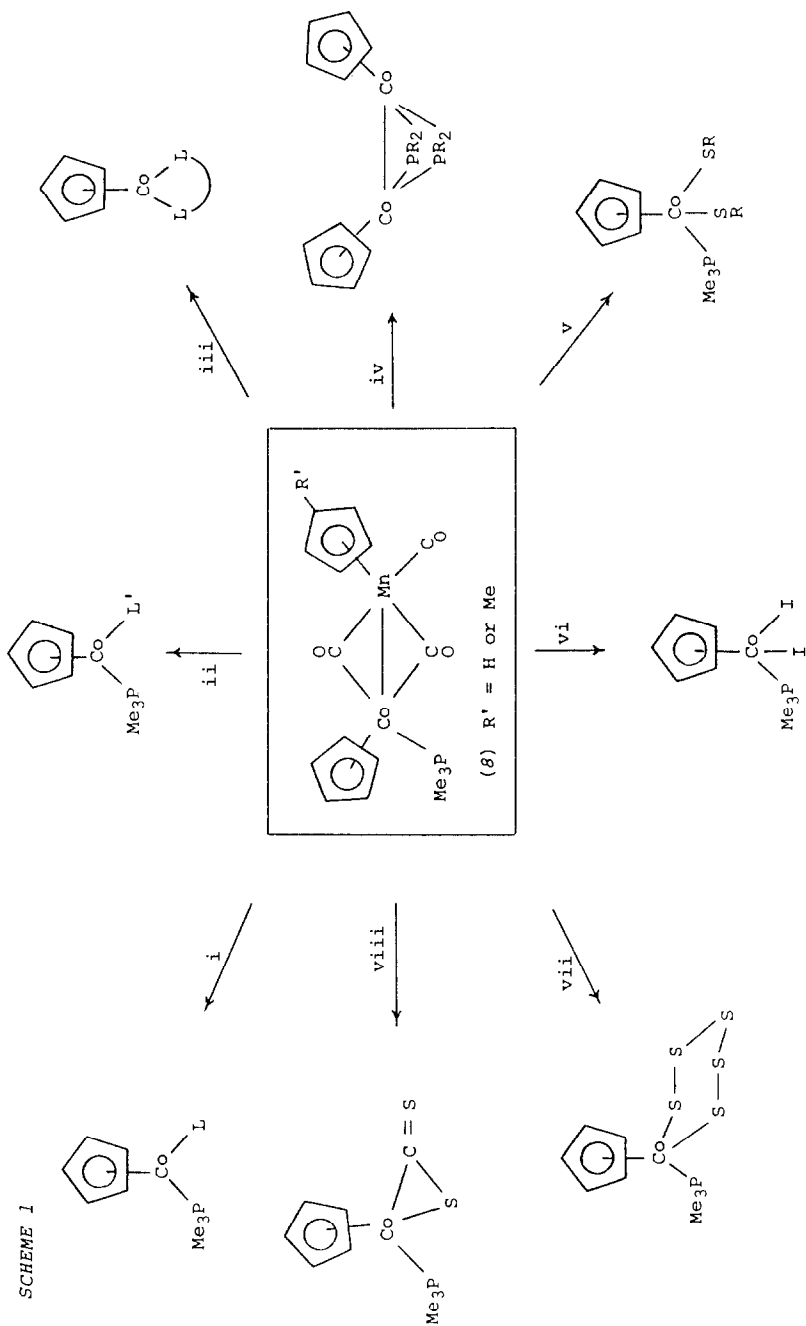


Group VII—Co A complete assignment of the $\nu(\text{CO})$ spectra of $\text{MCo}(\text{CO})_9$ ($\text{M} = \text{Mn}, \text{Tc}$ or Re), and determination of the CO force constants, was made on the basis of a free rotational model; polarisation of the $\text{M}(\delta^+) - \text{Co}(\delta^-)$ bond in the direction indicated was found to decrease: $\text{Tc} > \text{Re} > \text{Mn}$ [23].

The $\text{Mn}(\text{Re}) - \text{Co}$ complexes $\text{MCo}(\text{CO})_6(\text{dab})$ (7) [$\text{dab} = \text{RN}=\text{CHCH}=\text{NR}$ ($\text{R} = \text{Bu}^t, \text{Pr}^i, \text{Cy}, c\text{-C}_3\text{H}_5$), $\text{Pr}^i\text{N}=\text{CHCMe}=\text{NPr}^i$ or $\text{RN}=\text{CMeCMe}=\text{NR}$ ($\text{R} = c\text{-C}_3\text{H}_5$)] have been obtained from $\text{MBr}(\text{CO})_3(\text{dab})$ and $[\text{Co}(\text{CO})_4]^-$. The structure of (7; $\text{R} = \text{Bu}^t$) was determined, and reveals a semi-bridging CO group. The diimine ligand acts as a 6e donor coordinating to Co via C and N atoms, but only from N to the Mn atom: the electronic structure is described as intermediate between $\sigma^2\text{-N}, \sigma^2\text{-N}', \eta^2\text{-C}=\text{N}'$ and $\sigma^2\text{-N}, \mu^2\text{-N}', \eta^2\text{-C}=\text{N}'$ [24].

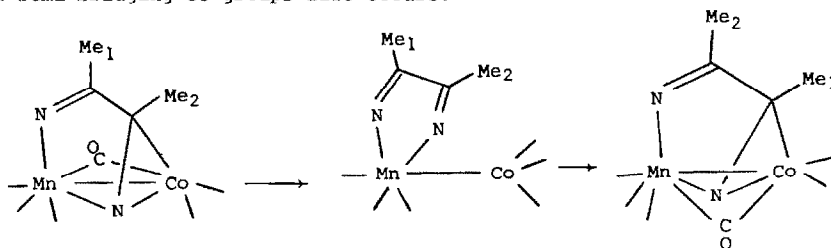
Formation of the hexacarbonyl complexes proceeds via unstable $\text{MCo}(\text{CO})_7(\text{dab})$, in which the diimine is a 4e $\sigma, \sigma\text{-N}, \text{N}'$ donor. Loss of CO is rapid at moderate temperatures, but $\text{MCo}(\text{CO})_7(\text{RN}=\text{CMeCMe}=\text{NR})$ ($\text{R} = c\text{-C}_3\text{H}_5$) are isolable as a result of the weaker $\eta^2\text{-C}=\text{N}$ interaction (compared with the $\text{HC}=\text{N}$ fragment).

Included in a number of complexes characterised by field-desorption mass spectrometry are the diazabutadiene derivatives $\text{MnCo}(\text{CO})_6(\text{RN}=\text{CHCH}=\text{NR})$ ($\text{R} = \text{Pr}^i, \text{Bu}^t, \text{Cy}, c\text{-C}_3\text{H}_5$) and $\text{ReCo}(\text{CO})_6(\text{RN}=\text{CHCH}=\text{NR})$ ($\text{R} = \text{Bu}^t, \text{Cy}$), $\text{MnCo}(\text{CO})_6(\text{RN}=\text{CHCMe}=\text{NR})$ ($\text{R} = \text{Pr}^i, c\text{-C}_3\text{H}_5$) and $\text{MCo}(\text{CO})_7(\text{RN}=\text{MeMe}=\text{NR})$ ($\text{M} = \text{Mn}, \text{Re}; \text{R} = c\text{-C}_3\text{H}_5$). The strongest ions are either $[\text{M}]^+$ or $[\text{M}-\text{CO}]^+$, especially with the heptacarbonyls, which lose CO between 20–50°. Weak dimer ions, $[2\text{M}]^+$ or $[2\text{M}-\text{CO}]^+$ are sometimes found [25]. ^1H and ^{13}C NMR studies of these complexes have revealed characteristic features associated with the bonding mode of the dab ligand [24,26]. Dynamic behav-



Reagents i L [PMe₃, PPh₃, P(OMe)₃, P(OPh)₃]; ii L' [CH₂=CHCN, *cis*- and *trans*-C₂H₂(CC₂Me)₂, maleic anhydride, C₂Ph₂]; iii L-L (dppe, nbd); iv H₂PMe₂ (R = Me), P₂Ph₄ (R = Ph); v S₂R₂ (R = Me, CH₂Ph, Ph); vi I₂; vii S₈; viii CS₂.

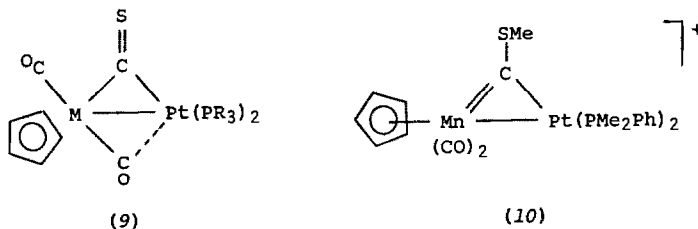
ion observed for $\text{MnCo}(\text{CO})_6(\text{RN}=\text{CMeCMe}=\text{NR})$ ($\text{R} = \text{c-C}_3\text{H}_5$) is consistent with Me exchange (coalescence temperature, -15°). Exchange of terminal and semi-bridging CO groups also occurs.



A new synthesis of (8) from $\text{Mn}(\text{CO})_2(\text{thf})(\eta\text{-C}_5\text{H}_4\text{Me})$ and $\text{Co}(\text{CO})_2(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)$ in 76% yield avoids the use of $\text{Co}(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)$ [27]. Complex (8) reacts with a wide variety of reagents with cleavage of the Co-Mn bond (Scheme 1).

Group VII—Pd,Pt Oxidative addition of $\text{BrHgMn}(\text{CO})_5$ to $\text{Pd}(\text{PPh}_3)_4$ or $\text{Pt}(\text{PPh}_3)_3$ affords $(\text{OC})_5\text{MnPd}[\text{HgMn}(\text{CO})_5]\text{Br}_2(\text{PPh}_3)_2$ and $(\text{OC})_5\text{MnPtBr}(\text{PPh}_3)_2$, respectively [30].

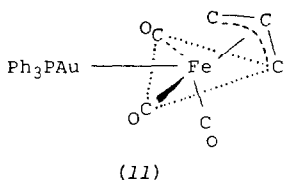
Bridging thiocarbonyl and semi-bridging CO ligands are found in $\text{M}(\mu\text{-CS})(\text{CO})_2(\text{PR}_3)_2(\eta\text{-C}_5\text{H}_5)$ ($\text{M} = \text{Mn}$ or Re , $\text{PR}_3 = \text{PMe}_2\text{Ph}$ or PMePh_2) (9) obtained from $\text{M}(\text{CO})_2(\text{CS})(\eta\text{-C}_5\text{H}_5)$ and $\text{Pt}(\eta\text{-C}_2\text{H}_4)(\text{PR}_3)_2$. Although the solid-state structure is as shown, in solution both the CO and CS ligands undergo bridge-terminal site exchange [$\Delta G^\ddagger(\text{CS}) 50 \pm 4 \text{ kJ mol}^{-1}$]; the CO group exchange is more facile than that of the CS ligand. Alkylation of the CS group occurs on reaction with $[\text{Me}_3\text{O}][\text{BF}_4]$, to give (10).



M	PR ₃
Mn	PMe ₂ Ph, PMePh ₂
Re	PMe ₂ Ph

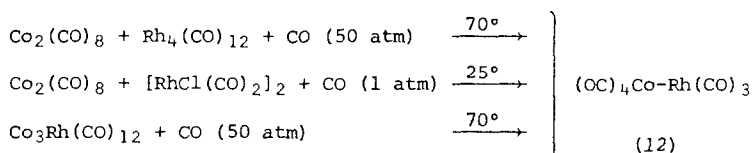
Mn-Au The compounds $\text{Au}(\text{C}_6\text{H}_5)_n(\text{tht})$ ($n = 1$ or 3) react with $[\text{Mn}(\text{CO})_5]^-$ to give $[\text{Au}[\text{Mn}(\text{CO})_5]_2]^-$ and $[(\text{C}_6\text{F}_5)_3\text{AuMn}(\text{CO})_5]^-$, respectively, isolated as cream ppt salts, which are 1:1 electrolytes in acetone [14].

Fe-Au The Fe-Au complex (11), from $\text{AuCl}(\text{PPh}_3)$ and the solution obtained from $\text{FeBr}(\text{CO})_3(\eta\text{-C}_3\text{H}_5)$ and zinc dust in Et_2O (48%), has an unusual geometry considered to consist of an $[\text{Au}(\text{PPh}_3)]^+$ moiety located on an edge between two equatorial CO groups in the trigonal bipyramidal $[\text{Fe}(\text{CO})_3(\eta\text{-C}_3\text{H}_5)]^-$ unit [32]. This contrasts with the normal pseudo-octahedral geometry found for $\text{FeBr}(\text{CO})_3(\eta\text{-C}_3\text{H}_5)$, and has been rationalised in terms of opposite polarities of the Fe-Au and Fe-Br bonds.



In solution there is only one species with a symmetrical allyl group (on the NMR timescale). The apparently semi-bridging CO ligands result from transition metal basicity and do not reflect direct interaction between the Au and CO π system; the electron density of the Au^+-Fe^- bond is located mainly on Fe in d orbitals, which are stereochemically inactive. Spectroscopic data are also consistent with a high negative charge on iron.

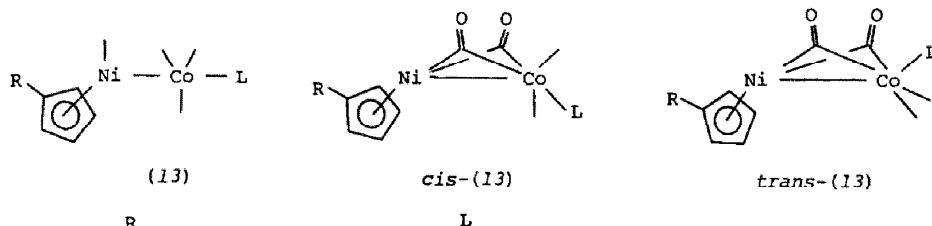
Co-Rh The Co-Rh carbonyl (12) is formed in the following reactions:



and was identified from its IR spectrum and other physical properties.

In the absence of CO, (12) forms $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$; above 100 atm CO, it is in equilibrium with $\text{CoRh}(\text{CO})_8$ (also not isolated) [33].

Co-Ni Complexes $\text{CoNi}(\text{CO})_4(\text{L})(\eta\text{-dienyl})$ (13) have been prepared from $[\text{Co}(\text{CO})_4]^-$ and $\text{NiBr}(\text{L})(\eta\text{-dienyl})$; migration of L from Ni to Co occurs. In solution, these compounds exist as an isomeric mixture of species (*cis* and *trans*) containing $\text{Ni}(\mu\text{-CO})_2\text{Co}$ moieties together with the unbridged Co-Ni isomer. The effects of solvent, temperature and changes in the various ligands were studied [34].



R	L
H	PEt_3 , PPh_3 , $\text{P}(\text{tol})_3$ $\text{P}(\text{C}_6\text{H}_4\text{F-}p)_3$ (13a), $\text{P}(\text{C}_6\text{H}_4\text{Cl-}p)_3$, $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$ $\text{PPh}(\text{o-tol})_2$, $\text{PPh}(\text{C}_6\text{H}_4\text{Cl-}p)_2$, $\text{PPh}_2(\text{o-tol})$ AsPh_3
Me	PCy_2Ph

Interconversion of isomers of (13a) is slow on the NMR timescale. The non-bridged isomer is favoured at higher temperatures, in the solvent series $\text{thf} > \text{xylene} > \text{hexane} > \text{CS}_2$, and with $\eta\text{-C}_5\text{H}_5$ rather than $\eta\text{-C}_5\text{H}_4\text{Me}$. This form is also favoured by increasing the inductive electron-withdrawing power of X in $\text{P}(\text{C}_6\text{H}_4\text{X-}p)_3$, and with smaller cone angles for L.

Co-Pd Oxidative addition of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ to $\text{Pd}(\text{dppe})_2$ afforded $(\text{dppe})\text{Pd}[\text{Co}(\text{CO})_4][\text{HgCo}(\text{CO})_4]$ [30].

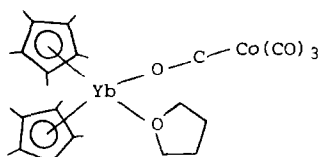
Co-Au Rapid replacement of tht in $\text{Au}(\text{C}_6\text{F}_5)_n(\text{tht})$ ($n = 1$ or 3) by $[\text{Co}(\text{CO})_4]^-$ gives cream $[\text{Au}\{\text{Co}(\text{CO})_4\}_2]^-$ or yellow $[(\text{C}_6\text{F}_5)_3\text{AuCo}(\text{CO})_4]^-$, respectively, as the ppn salts [14]. The latter reacts with PPh_3 or $\text{P}(\text{OPh})_3(\text{L})$ to give $[(\text{C}_6\text{F}_5)_3\text{AuCo}(\text{CO})_3(\text{L})]^-$. The high thermal stability of the ppn salt (14) (dec. 105°) contrasts with that of $[\text{NET}_4][\text{Au}\{\text{Co}(\text{CO})_4\}_2]$, which decomposes at -79° [35]. As expected, the Co-Au-Co unit in (14) is exactly linear, with staggered CO groups which are bent towards the Au atom.

Rh-Ag Addition of $\text{Ag}[\text{PF}_6]$ to $\text{Rh}(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ gives yellow $[\text{Ag}\{\text{Rh}(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)\}_2][\text{PF}_6]$, which contains a nearly linear trimethyl sequence (Rh-Ag-Rh , 171.0°) [36]. This complex reacts as a stable source of the reactive radical cation $[\text{Rh}(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^+$.

Pd-Pt The strong $\nu(\text{MM})$ modes in $[\text{M}_2(\text{CNMe})_6]^{2+}$ ($\text{M}_2 = \text{Pd}_2, \text{PdPt}$ and Pt_2) were found at 163, 160 and 153 cm^{-1} in the Raman spectra; only the PdPt complex exhibited a weak $\nu(\text{PdPt})$ at 161 cm^{-1} in the IR spectrum [37].

Pt-Au The interaction of $\text{Pt}(\text{PPh}_3)_3$ with $\text{AuR}(\text{PPh}_3)$ ($\text{R} = \text{Me}$ or C_6Cl_5) was reported [38] to give orange $(\text{Ph}_3\text{P})_2\text{MePtAu}(\text{PPh}_3)$ and white $(\text{Ph}_3\text{P})_2(\text{C}_6\text{Cl}_5)\text{PtAu}(\text{PPh}_3)$, respectively, although a later crystal structure study [39] shows the latter not to have a Pt-Au bond; the $\text{C}_6\text{Cl}_5\text{Au}(\text{PPh}_3)$ moiety has oxidatively added by cleavage of an *ortho*-C-Cl bond to give *trans*- $\text{PtCl}[\text{C}_6\text{Cl}_4\{\text{Au}(\text{PPh}_3)\}_2](\text{PPh}_3)_2$. Tertiary phosphines react with these complexes to displace the Au-bonded phosphine only; halogens react to give $\text{PtX}(\text{R})(\text{PPh}_3)_2$ and $\text{AuX}(\text{PPh}_3)$.

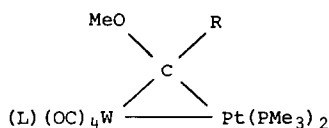
Rare-earth complexes Several complexes of rare-earth elements containing transition metals have been reported, although it would appear that in derivatives containing organometallic carbonyls or nitrosyls, the rare-earth metal acts as a Lewis acid towards the oxygen of the CO or NO group. A series of adducts of $\text{Sm}(\text{C}_5\text{H}_5)_3$ with $\text{Cr}(\text{CO})_2(\text{NO})(\eta\text{-C}_5\text{H}_5)$, $[\text{Fe}(\text{NO})(\eta\text{-C}_5\text{H}_5)]_2$, $[\text{Cr}(\text{NO})_2(\eta\text{-C}_5\text{H}_5)]_2$, $[\text{Mn}(\text{CO})(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]_2$ and $\text{Mn}_3(\text{NO})_4(\eta\text{-C}_5\text{H}_4\text{Me})_3$ has been studied spectroscopically, and the Lewis basicity of the coordinated NO was found to be: terminal NO \gg μ_2 -NO \sim μ_3 -NO [40]. A Yb-O-C-Co moiety is present in $(\eta\text{-C}_5\text{Me}_5)_2\text{YbCo}(\text{CO})_4(\text{thf})$ (15), obtained from $\text{Yb}(\text{OEt}_2)(\eta\text{-C}_5\text{Me}_5)_2$ and $\text{Co}_2(\text{CO})_8$ [41], and similar interactions may be present in $(\text{OC})_5\text{MSmCl}_2$ ($\text{M} = \text{Mn}$ or Re), isolated from reactions between $[\text{M}(\text{CO})_5]^-$ and SmCl_3 [42].



(15)

2. HETEROMETALLICS FROM CARBENE AND CARBYNE COMPLEXES

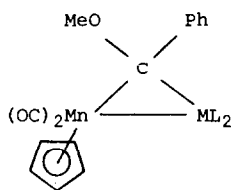
Interaction of $\text{Pt}(\text{cod})_2$ with the metal-carbon multiple bond in $\text{M}[\text{C}(\text{OMe})\text{Ph}](\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$) afforded $(\text{OC})_5\text{M}[\mu\text{-C}(\text{OMe})\text{Ph}]\text{Pt}(\text{cod})$ [43]. Similar complexes $(\text{OC})_5\text{M}[\mu\text{-C}(\text{OMe})\text{R}]\text{Pt}(\text{L})_2$ [$\text{M} = \text{Cr}, \text{Mo}, \text{R} = \text{Ph}, \text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}$; $\text{M} = \text{W}, \text{R} = \text{Me}, \text{Ph}, \text{L} = \text{PMe}_3$] were obtained from $\text{Pt}(\eta\text{-C}_2\text{H}_4)(\text{PR}_3)_2$ [prepared *in situ* from $\text{Pt}(\text{cod})_2 + \text{C}_2\text{H}_4 + \text{PR}_3$]. In (16), the asymmetrically bridging carbene is closer to Pt. Ligand substitution reactions gave $(\text{Me}_3\text{P})(\text{OC})_4\text{M}[\mu\text{-C}(\text{OMe})\text{Ph}]\text{Pt}(\text{PMe}_3)_2$ ($\text{M} = \text{Cr}, \text{W}$) and $(\text{Bu}^t\text{NC})_2(\text{OC})_3\text{Cr}[\mu\text{-C}(\text{OMe})\text{Ph}]\text{Pt}(\text{CNBu}^t)(\text{PMe}_3)$.



(16)

(a) $\text{L} = \text{CO}$
 $\text{R} = \text{Ph}$ (b) $\text{L} = \text{PMe}_3$
 $\text{R} = \text{tol}$

Pt-W	2.861(1)	2.825(1)
Pt- $\mu\text{-C}$	2.04(1)	2.03(1)
W- $\mu\text{-C}$	2.48(1)	2.37(1)



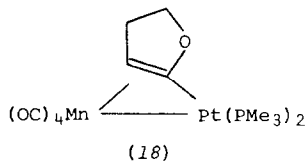
(17)

 ML_2

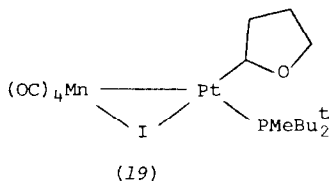
Pt(cod)
Ni(PMe ₃) ₂
Pd(PMe ₃) ₂
Pt(PMe ₃) ₂

Further examples of complexes of this type were obtained from $\text{Cr}[\text{C}(\text{OMe})(\text{C}_6\text{H}_4\text{R-p})](\text{CO})_5$ ($\text{R} = \text{Me}$ or CF_3) and $\text{Pt}(\text{cod})_2$ solutions which had been treated with C_2H_4 and 2PR_3 , or from $\text{W}[\text{C}(\text{OMe})(\text{C}_6\text{H}_4\text{R-p})](\text{CO})_5$ and $\text{Pt}(\eta\text{-C}_2\text{H}_4)(\text{L})_2$ ($\text{L} = \text{PMe}_3$ or PMe_2Ph) [44]. The complexes $(\text{OC})_5\text{W}[\mu\text{-C}(\text{OMe})\text{Me}]\text{Pt}(\text{PMe}_2\text{Ph})_2$, $(\text{OC})_5\text{Cr}[\mu\text{-COCH}_2\text{CH}_2\text{CH}_2]\text{Pt}(\text{PMe}_2\text{Ph})_2$ (16c) and $(\text{OC})_5\text{W}[\mu\text{-CPh}_2]\text{Pt}(\text{PMe}_3)_2$ (at -60°) were also described. Complex (16c) is quite unstable in solution and reverts to the original $\text{Cr}(\text{COCH}_2\text{CH}_2\text{CH}_2)(\text{CO})_5$ within minutes; its formation contrasts with the Mn system, where loss of hydrogen gives the $\text{C}=\text{CHCH}_2\text{CH}_2\text{O}$ ligand. All these compounds were stabilised by replacement of one CO on Cr or W by PMe_3 . A structural study of $(\text{Me}_3\text{P})(\text{OC})_4\text{W}[\mu\text{-C}(\text{OMe})(\text{tol})]\text{Pt}(\text{PMe}_3)_2$ (16b) shows that in comparison with (16a), there is tighter bonding in the dimetallacyclopentane ring.

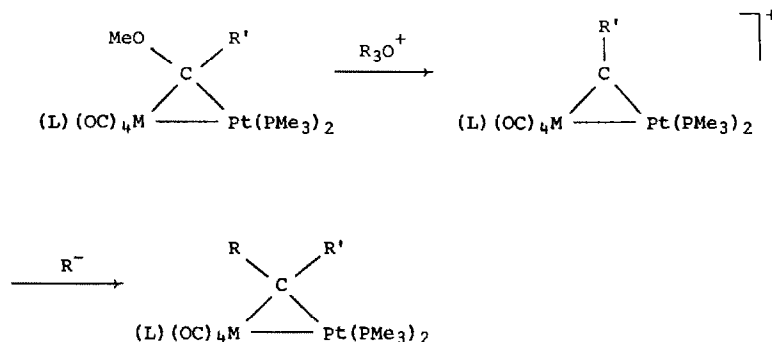
Extension of this reaction has occurred in several directions. The Mn-M complexes (17) (M = Ni, Pd, Pt) were obtained from Mn[C(OMe)Ph](CO)₂(η-C₅H₅) and Ni(cod)₂, Pd(dba)₂, or Pt(η-C₂H₄)₃ in the presence of PMe₃, or Pt(cod)₂ [45]. Substitution of the PMe₃ ligand *trans* to the μ-carbene ligand by CNBu^t occurs readily. Two forms (red and yellow) of (18), obtained from (OC)₅MnMn(CCH₂CH₂CH₂O)(CO)₄ and Pt(η-C₂H₄)(PMe₃)₂, differ in the orientation of various atom groups, and in the Mn-Pt bond lengths, which vary by 0.032Å.



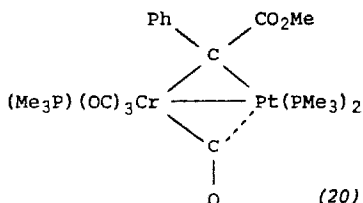
In contrast, the product (19) from MnI(COCH₂CH₂CH₂)(CO)₄ and Pt(η-C₂H₄)(PMeBu₂^t) contains the carbene ligand terminally bonded to Pt and *trans* to the μ-I ligand; the tertiary phosphine is *trans* to the Mn-Pt bond [46]. The cluster [Pt(μ-CO)(PMeBu₂^t)]₃ is also formed. Excess PMe₃ reacts with (19) to give (18) and MnI(CO)₃(PMe₃)₂; complex (18) was also produced, with MnI(CO)₄(PMe₃), in the reaction between MnI-(COCH₂CH₂CH₂)(CO)₄ and Pt(η-C₂H₄)(PMe₃)₂.



Studies of the chemistry of the dimetallacyclopentane ring in the M(μ-CRR')M' complexes were initially directed towards the synthesis of cationic μ-alkylidyne complexes, which were characterised by subsequent addition of nucleophiles such as LiC₆H₄Me-p or NaOEt [47]. However, only low yields of the anticipated products were obtained. Isolation of the intermediate salts [CrPt(μ-CPh)(CO)₄(PMe₃)₂][BF₄] and [WPt(μ-C(tol))](CO)₄(PMe₃)₃][BF₄] was followed by a study of their reactions



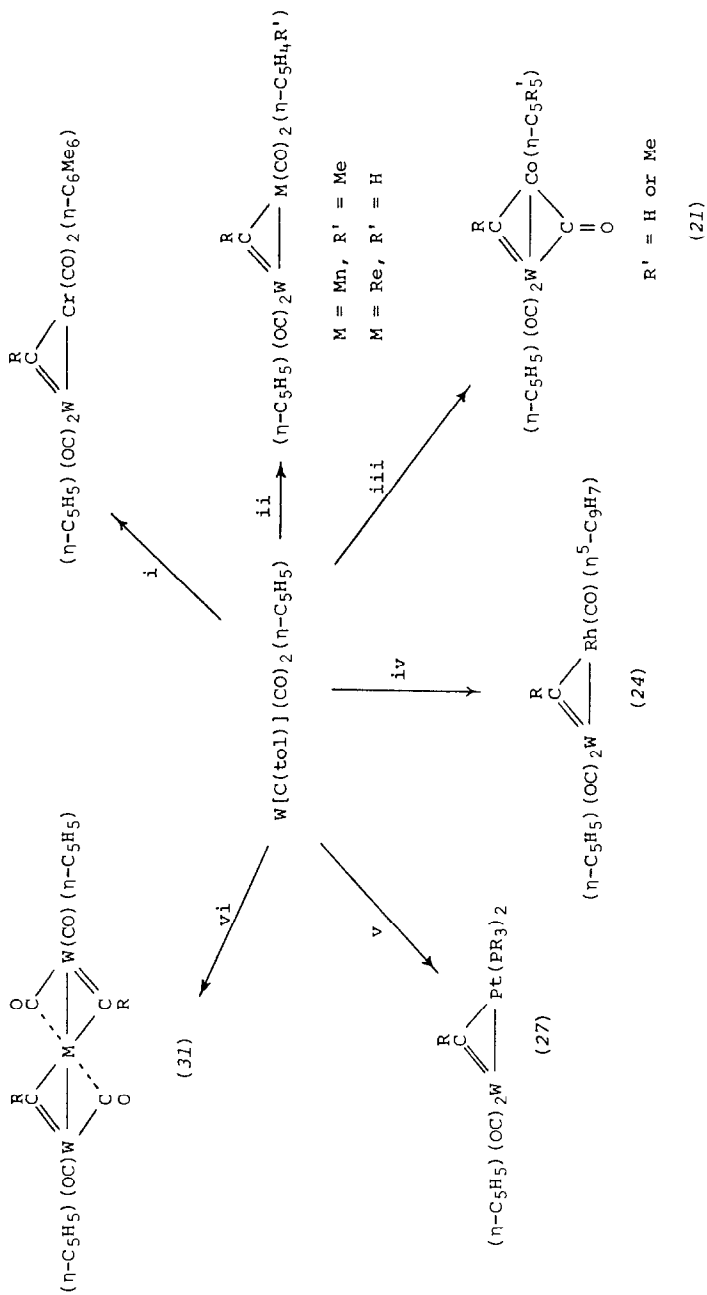
with alkoxide. This showed that a novel $\mu\text{-C}(\text{CO}_2\text{R})\text{R}'$ ligand was generated. In the Cr-Pt complex (20) studied crystallographically, this ligand asymmetrically bridges the Cr-Pt bond; there is also a semi-bridging CO group. Formation of the CO_2Me group may occur by attack of alkoxide on CO bonded to the cationic Cr or W centre, followed by migration of the ester group to the $\mu\text{-C}$. Alternatively, attack may occur on a $\mu\text{-ketene}$ moiety present in the cations, i.e. $\mu\text{-C}(\text{CO})\text{R}$, as found in the product from $[\text{M}(\text{CO})_5]^-$ and $\text{Mn}[\text{C}(\text{tol})](\text{CO})_2(\eta\text{-C}_5\text{H}_5)$.

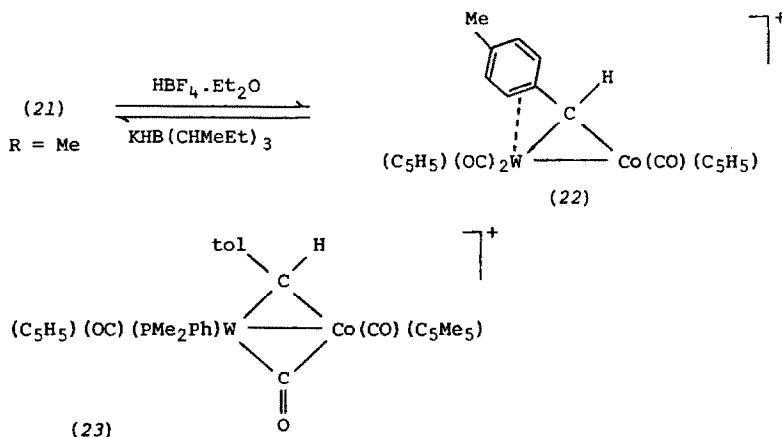


The carbyne complex $\text{W}[\text{C}(\text{tol})](\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ is a prolific source of complexes containing bridging alkylidyne ($\mu\text{-CR}$) ligands [48]. Mixed metal complexes containing W with Cr, Mn, Re, Co, Rh, Ni, Pd or Pt have been prepared (Scheme 2). The structure of the Cr-W derivative confirms the general features indicated above, and also shows the presence of a semi-bridging CO group.

Protonation of (21) with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ affords the salt (22) which contains a bridging carbene ligand with an additional interaction of one of the aryl $\text{C}=\text{C}$ double bonds with tungsten, i.e. in the η^3 mode [49].

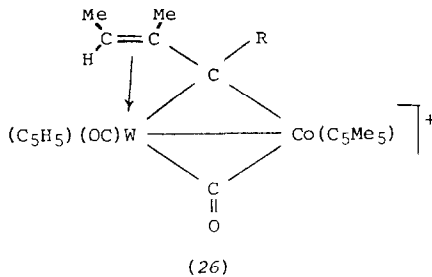
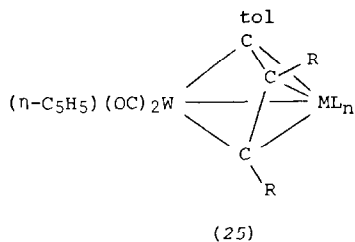
SCHEME 2





Rotation of the tolyl group about the μ -C-C bond ceases (on the NMR time scale) at -70° . The complexed aryl group is displaced from tungsten by addition of tertiary phosphines, e.g. (23), which exists as a mixture of two diastereomers which interchange rapidly at room temperature, but not at -50° .

These and related compounds react with alkynes to give heterometal complexes containing μ -C₃ units formed by addition of the alkyne to the μ -alkylidyne ligand. Thus (24) reacts with C₂Ph₂ to give (25a), and similar reactions of the W-Co complex (21, R = Me) with C₂Me₂ and C₂Ph₂ were also described [50]. The Fe-W complexes were formed from Fe₂W[μ -C(tol)](μ -CO)(CO)₈(η -C₅H₅). The structure of (25d) suggests that it might be regarded as the Fe(CO)₃ derivative of a (non-planar) tungsta-cyclobutadiene ligand, again emphasising the isolobal relationship between CH and W(CO)₂(η -C₅H₅). Two isomers of (25e) in solution correspond to the presence of C(tol)CPhCPh and CPhC(tol)CPh bridges; formation of intermediates with μ -CPh and μ -C(tol) could result in statistical scrambling of CR groups. Similarly, complex (22) reacts with C₂Me₂ to give (26), in which the bridging ligand can be considered to be a μ -vinyl-carbene. The ready formation of (26) from (22) may be contrasted with

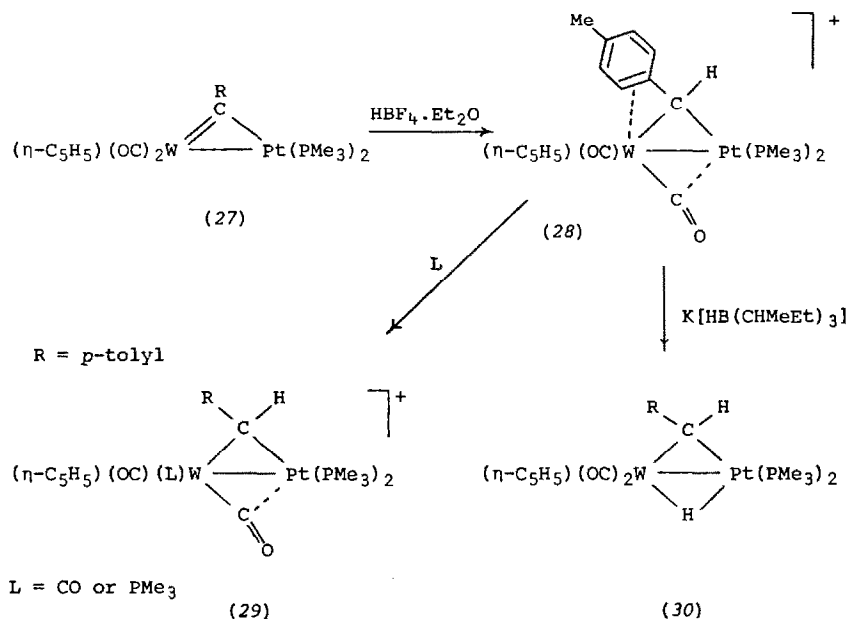


	R	ML _n
a	Ph	Rh(η-C ₉ H ₇)
b	Ph	Co(η-C ₅ Me ₅)
c	Me	Co(η-C ₅ Me ₅)
d	Me	Fe(CO) ₃
e	Ph	Fe(CO) ₃
f	CF ₃	Fe(CO) ₃
g	tol	Fe(CO) ₃

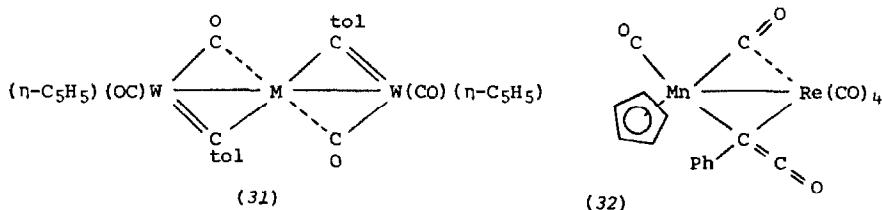
the much slower reaction of (21) with the alkyne to give (24), which affords (26) on protonation [49].

Tungsten-carbyne complexes $W[C(tol)](CO)_2(\eta-C_5H_5)$ or $WBr[C(tol)]-(CO)_4$ react with the platinum(0) complexes $Pt(\eta-C_2H_4)(PR_3)_2$ ($R_3 = Me_3, Me_2Ph$) to give $(\eta-C_5H_5)(OC)_2W[\mu-C(tol)Pt(PR_3)_2]$ (27) and $(OC)_4BrW-[\mu-C(tol)]Pt(PMe_3)_2$, respectively [51]. As with other complexes of this type, structural studies show that a dimetallacyclopropene ring is present, with multiple bond character remaining in the W-C bond.

The W-Pt complex (27) exhibits some similarity to (21) in its reactions [49]. Thus protonation affords the bridging carbene complex (28), containing a semi-bridging CO group; the tolyl group in this complex is rigid. Again, displacement of the aryl C=C double bond from tungsten occurs on addition of PMe_3 or CO to give (29); the latter adduct slowly reverts to (28) on standing. Addition of hydride gives (30), which exists in two interconverting isomers by virtue of the orientations of the C_5H_5 and H ligands relative to the $W(\mu-C)Pt$ plane.



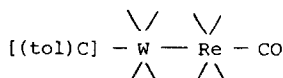
Trimetallic compounds with W-M-W sequences (M = Ni, Pd or Pt) (31) have been obtained from reactions between $\text{W}[\text{C}(\text{tol})](\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ and $\text{Ni}(\text{cod})_2$, $\text{Pd}(\eta^2\text{-C}_7\text{H}_{10})_3$ or $\text{Pt}(\eta\text{-C}_2\text{H}_4)_3$, respectively [52]. These observations further extend the analogy between the carbyne complexes and alkynes, since $\text{Pt}(\eta\text{-C}_2\text{H}_4)_3$ is known to react with alkynes to form $\text{Pt}(\eta\text{-C}_2\text{R}_2)_2$ [53]. Structural studies of the Ni and Pt compounds show the W-M-W sequence is non-linear (M = Pt, 165.5°; M = Ni, 175°) and that there is a semi-bridging CO group. In both cases, the M-W bonds are ca 0.2 Å shorter than expected for the appropriate single bonds, and may be the result of electron delocalisation within the fused dimetallacyclopropene systems.



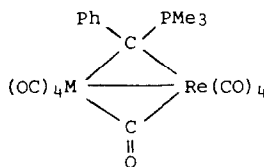
Treatment of the carbyne complex $[\text{Mn}(\text{CPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)][\text{BCl}_4]$ with $[\text{Re}(\text{CO})_5]^-$ affords the Mn-Re complex (32), in which the heteromet-

allic bond is bridged by a phenylketenyl group formed by combination of the carbyne ligand and a CO group [54].

The mixed-metal carbyne complexes $MRe(CO)_9[C(tol)]$ (33, $M = Cr, W$) react with PMe_3 to give (34), in which the tertiary phosphine has added to the carbyne ligand [55]. Excess PMe_3 and vigorous conditions result in substitution of two metal-bonded CO groups, first on Re, then on W.

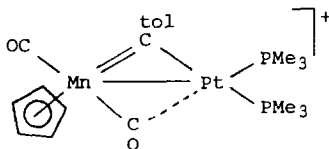


(33)



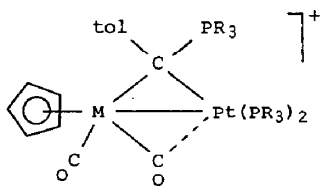
(34)

Complex (35) was obtained from $[Me_3O][BF_4]$ and $(\eta-C_5H_5)(OC)_2-$
 $Mn[\mu-C(OMe)(tol)]Pt(PMe_3)_2$; the latter was formed from $Mn[C(OMe)(tol)]-$
 $(CO)_2(\eta-C_5H_5)$ and $Pt(\eta-C_2H_4)(PMe_3)_2$, as described above. Analogous
 rhenium compounds were also made [47]. Reactions of the cationic der-
 ivatives with methoxide regenerated the neutral $\mu-C(OMe)(tol)$ complexes,
 but no compounds containing $\mu-C(CO_2Me)(tol)$ ligands were formed, thus
 contrasting with the Cr and W salts. The Mn-C distance in (35) is
 consistent with its being a double bond; there is also a semi-bridging
 CO.

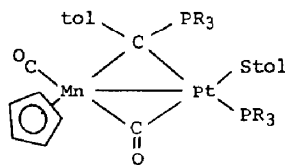


(35)

Ready formation of Mn-Pt or Re-Pt complexes (36) containing
 $\mu-C(PR_3)(tol)$ ligands occurs by addition of tertiary phosphine (PMe_3 or
 PMe_2Ph) to the salts $[MPT\{\mu-C(tol)\}(CO)_2(PR_3)_2(\eta-C_5H_5)][BF_4]$ ($M = Mn$ or
 Re ; $PR_3 = PMe_3$ or PMe_2Ph) (35) [56]. The $Mn(\mu-C)Pt$ system in (36) is



(36)



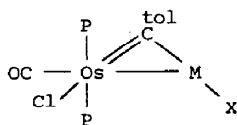
(37)

M = Mn or Re

PR₃ = PMe₃ or PMe₂Ph

significantly larger than that found in the dimetallacyclopropene precursor (35). Neutral complexes containing similar phosphonium ligands (37) were obtained from reactions between NaS(tol) and [MnPt{μ-C(tol)}-(CO)₂(PR₃)₂(η-C₅H₅)] [BF₄] (PR₃ = PMe₃ or PMe₂Ph). Formation of (37) may proceed via an intermediate containing a μ-C(SR)(tol) ligand which undergoes exchange of SR and PR₃ between carbon and platinum; such a complex was isolated from the reaction of NaS(tol) and [RePt{μ-C(tol)}-(CO)₂(PMe₂Ph)₂(η-C₅H₅)] [BF₄], which afforded RePt[μ-C(Stol)(tol)](CO)₂(PMe₂Ph)₂(η-C₅H₅).

Osmium carbyne complexes have been used as precursors to Os-M (M = Cu, Ag or Au) bonds, with Os(Ctol)Cl(CO)(PPh₃)₂ reacting with Group IB halides to form (38); the complex [Os(μ-Ctol)Ag(OCLO₃)(CO)(MeCN)(PPh₃)₂]⁺ was also prepared from AgClO₄. Reaction of HClO₄ with (38b) affords OsCl(OCLO₃)(CHtol)(CO)(PPh₃)₂ and AgCl [57].

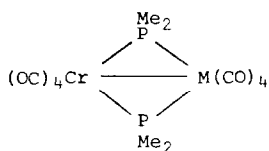


(38)

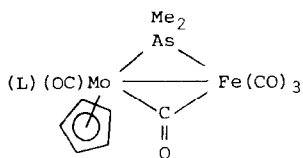
	M	X
a	Cu	I
b	Ag	Cl
c	Au	Cl

3. CHEMISTRY OF μ-ER₂ COMPLEXES

Group VI Small amounts of the Cr-Mo and Cr-W complexes (39) have been obtained by pyrolysis of bi- and tri-nuclear complexes, such as Cr[(μ-P₂Me₄)M(CO)₅]₂(CO)₄ [58].



(39)



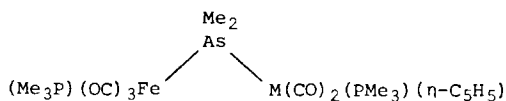
(40)

Cr-Mn Similar reactions of $\text{Cr}[(\mu\text{-P}_2\text{Me}_4)\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2(\text{CO})_4$ afforded $(\text{OC})_4\text{Cr}(\mu\text{-PMe}_2)_2\text{Mn}(\text{CO})(\eta\text{-C}_5\text{H}_5)$ [58].

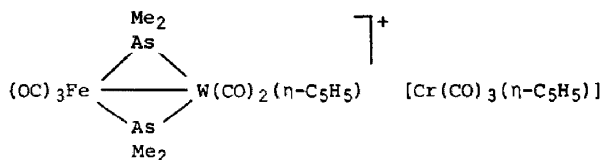
Mo,W - Fe Reaction of $\text{Fe}(\text{CO})_3(\eta^4\text{-PhCH=CHCOMe})$ with $\text{Me}_2\text{AsMo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ affords (40, L = CO); an intermediate $(\text{bza})(\text{OC})_3\text{Fe}(\mu\text{-AsMe}_2)\text{Mo}(\text{CO})_2(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)$ converts to (40, L = PMe_3) on heating [59].

Three independent fluxional processes have been revealed by variable temperature NMR studies of (40, L = CO), namely exchange of Me groups (ΔG^\ddagger 47.3 kJ mol⁻¹), exchange of CO groups on Mo (ΔG^\ddagger 47.7 kJ mol⁻¹), and exchange of CO groups between Mo and Fe (ΔG^\ddagger 59.4 kJ mol⁻¹). The same rearrangement process probably accounts for the first two exchange reactions. Rapid exchange of axial and equatorial CO groups on Fe occurs at -74°. Addition of PMe_3 to the Mo centre is a second order process [60].

The As-bridged Mo-Fe or W-Fe complexes react with organometallic arsines to give a range of products resulting from simple cleavage of the M-M' bond, substitution and rearrangement reactions [61]. In all, 26 new complexes were obtained as indicated in Scheme 3. These reactions are in accord with the presence of $\text{Fe} \rightarrow \text{M}'$ donor bonds. Subsequent reactions of complexes (41, b-d) or (42c,d,g,h) with PMe_3 resulted in displacement of the organometallic arsine and cleavage of the M-M' bond to form (44) (M = Mo and W, respectively). An unusual rearrangement



(44)

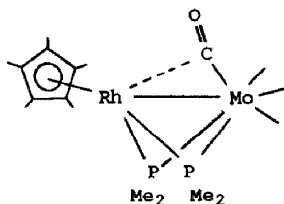


(45)

occurred in the reaction between $(\text{OC})_4\text{Fe}(\mu\text{-AsMe}_2)\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ and $\text{Me}_2\text{AsCr}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$; in the absence of solvent, complex (43) was obtained, but in benzene/hexane, the ionic complex (45) was formed.

Mo-Ru Reactions of $\text{Ru}_3(\text{CO})_{12}$ with $\text{Me}_2\text{As}[M]$ [$M = \text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$, $\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$, $\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$] afforded the monosubstituted cluster complexes $\text{Ru}_3(\text{CO})_{11}(\text{AsMe}_2[M])$; excess organometallic arsine reacted to give $\text{Ru}_3(\text{CO})_{12-n}[\text{AsMe}_2\{\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}]_n$ ($n = 2$ and 3). However, the only example of a complex with an M-M' bond was obtained from the mother liquors of the Mo reaction, which gave $(\eta\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo}(\mu\text{-AsMe}_2)\text{-Ru}(\text{CO})_4$ (2%) [62].

Mo-Rh The Mo-Rh complex (46) was obtained from the reaction between $\text{Mo}(\text{CO})_4(\text{PMe}_2\text{Li})_2$ and $[\text{RhCl}_2(\eta\text{-C}_5\text{Me}_5)]_2$; steric constraints result in a folded MoP_2Rh ring, while it also has a semi-bridging CO group [63].

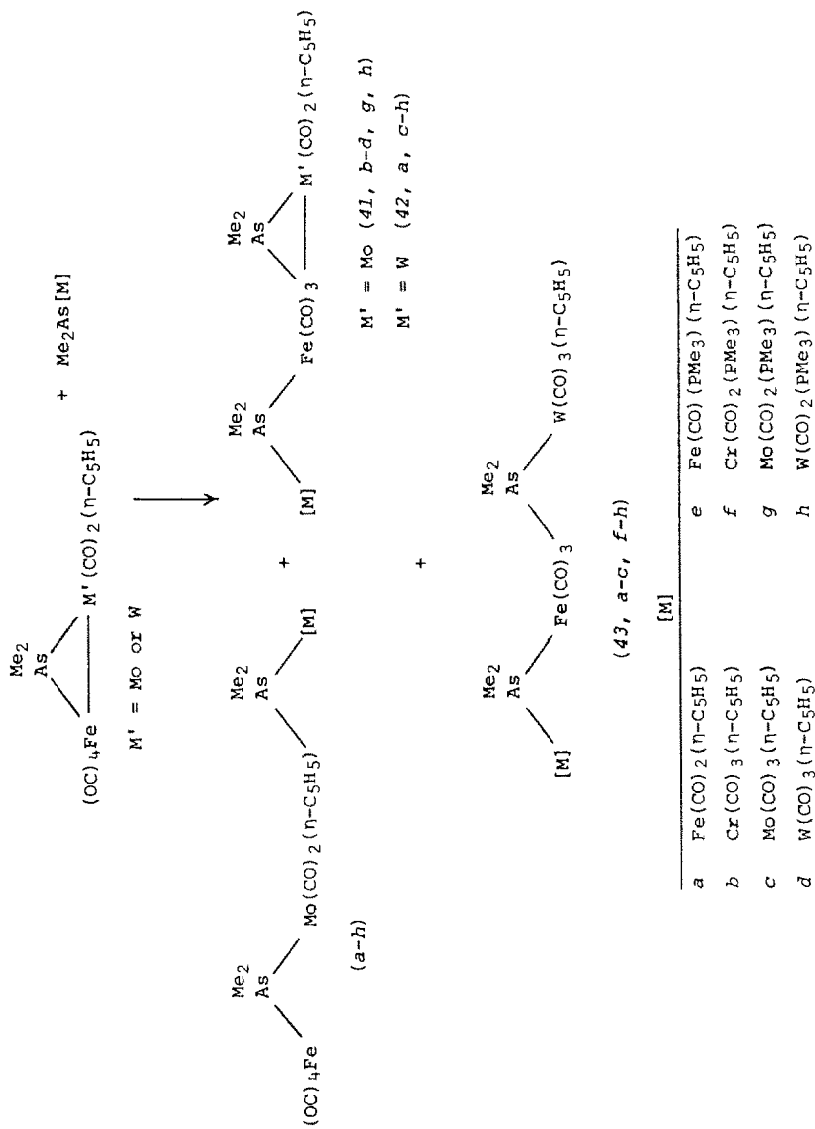


(46)

The complex is highly fluxional with only one type of CO or P-Me group.

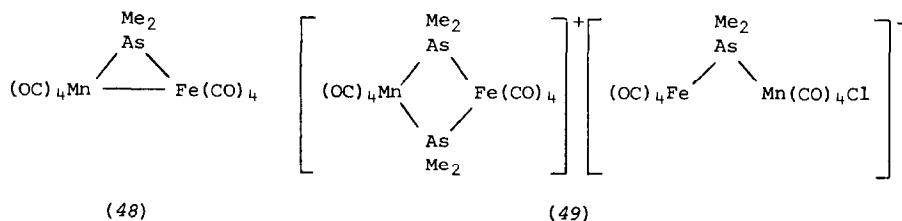
Cr-Ni The complex $(\text{OC})_4\text{Cr}(\mu\text{-PMe}_2)_2\text{Ni}(\text{CO})_2$ was reported as a minor component in the pyrolysis products from $(\text{OC})_5\text{Cr}(\mu\text{-P}_2\text{Me}_4)\text{Ni}(\text{CO})_3$ or $[\text{Cr}(\text{CO})_5(\mu\text{-P}_2\text{Me}_4)]_2\text{Ni}(\text{CO})_2$ [58].

SCHEME 3

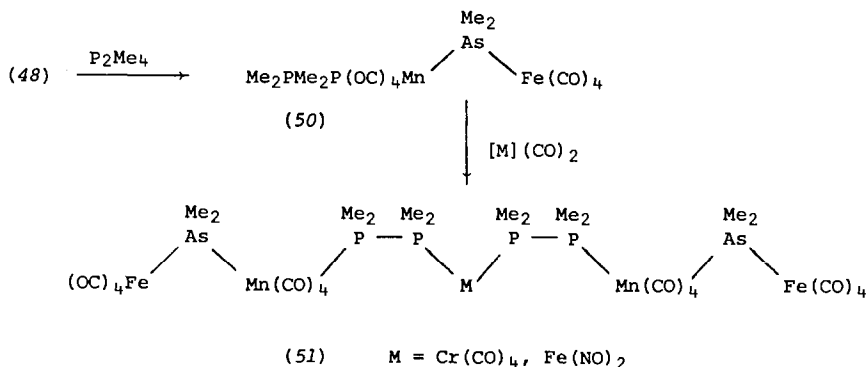


Mn-Fe The reaction of $\text{Me}_2\text{AsMn}(\text{CO})_4(\text{PMe}_3)$ with $\text{Fe}(\text{CO})_3(\eta^4\text{-PhCH=CHCOMe})$ affords $(\text{Me}_3\text{P})(\text{OC})_3\text{Mn}(\mu\text{-AsMe}_2)\text{Fe}(\text{CO})_4$ [59].

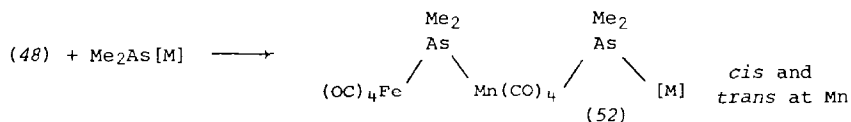
Cleavage of the Mn-Fe bond in (48) occurs with many P- and As-donor ligands, with substitution at Mn, which may be *cis* or *trans* to the Mn-As bond [64]. Thus with PClMe_2 and Me_2NEMe_2 ($\text{E} = \text{P,As}$) both isomers are formed, whereas AsClMe_2 gives only the *trans* form, together with the ionic complex (49).



Interaction of (48) with P_2Me_4 gives (50), which has been used to make complexes containing $\text{FeAsMnP}_2\text{MP}_2\text{MnAsFe}$ chains (51), by reaction with metal carbonyls [65].

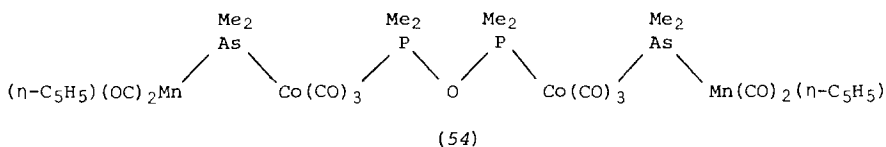
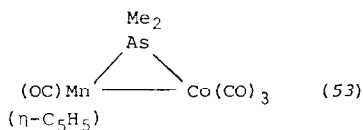


Similar reactions of Mn-Fe complexes with organometallic arsines gave trinuclear complexes with $\text{FeAsMnAsM}'$ chains, which were obtained *cis* and *trans* isomers [66,67]. The reaction with $\text{Me}_2\text{AsMn}(\text{CO})_4(\text{PMe}_3)$ afforded both *cis,cis* and *trans,trans* (at Mn) isomers of (52c).

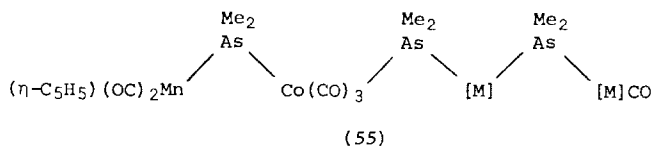


(52)	M	L or L ₂
a	Mo(CO) ₂ (L)(η-C ₅ H ₅)	CO, PMe ₃
b	W(CO) ₂ (L)(η-C ₅ H ₅)	CO, PMe ₃
c	Mn(CO) ₄ (PMe ₃)	
d	Fe(CO)(L)(η-C ₅ H ₅)	CO, PMe ₃
e	Co(CO) ₂ (L ₂)	(CO)(PMe ₃), (CO)[P(OMe) ₃], [P(OMe) ₃] ₂ , (PMe ₃)[P(OMe) ₃], (PMe ₃) ₂

Mn-Co Reaction of (53) with PClMe₂ affords the expected (η-C₅H₅)(OC)₂Mn(μ-AsMe₂)Co(CO)₃(PClMe₂), which on hydrolysis gives a tetranuclear complex with an MnAsCoPOPCoAsMn chain (54) [65].



Other tetranuclear complexes (55) were obtained by initial opening of the Mn-Co bond in (53) with norbornadiene, followed by replacement of the diene with two molecules of an organometallic arsine [68]:



M

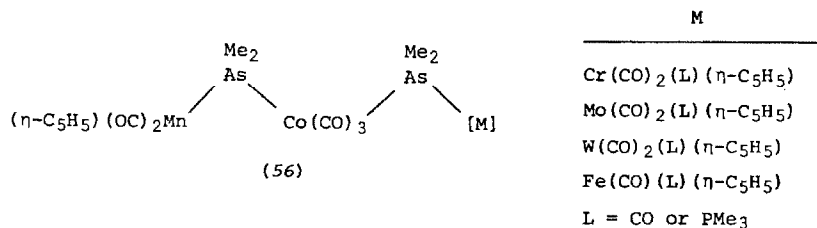
Cr(CO)₂(η-C₅H₅)

Mo(CO)₂(η-C₅H₅)

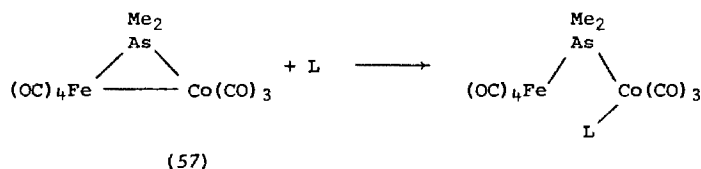
Fe(CO)(η-C₅H₅)

These reactions proceeded via a trinuclear intermediate in which the M-M' bond was reformed, and addition of the second molecule of organo-

metallic arsine occurs by the normal nucleophilic opening of this bond. Reactions of (53) with $\text{Me}_2\text{As}[\text{M}]$ give the analogous trinuclear derivatives (56) [67].



Fe-Co Recent studies of complex (57) have been concerned with nucleophilic cleavage of the Fe-Co bond by Group V donor ligands. Kinetic studies of the heterolytic Fe-Co bond cleavage reactions show

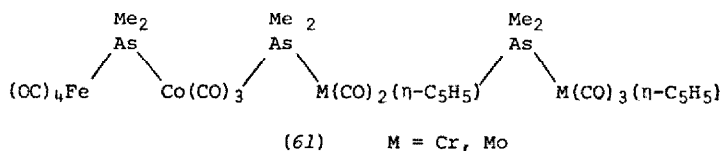


L = PCy_3 , PBu_3 , PEt_2Ph , $\text{P}(\text{OMe})_3$, $\text{P}(\text{OCH}_2)_3\text{CET}$, $\text{P}(\text{OPh})_3$, AsPh_3 , SbPh_3

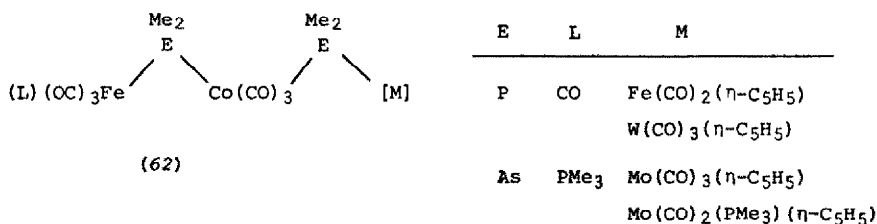
that the rates are closely first order in [L]. As the nucleophilicity of L increases, the reaction gradually changes from a concerted but largely I_d mechanism, to one which is more associative (I_a) in character, i.e. attack at Co with concerted displacement of the Fe donor atom [69].

As found with the Mn-Fe and Mn-Co complexes reactions of (57) with Me_2EX (X = Cl, NMe_2 ; E = P, As) cleave the M-M' bond, with the Group V ligand adding to cobalt [64,65]. Hydrolysis of the P-Cl bond gives tetranuclear FeAsCoPOPCoAsFe complexes. Reactions of the P_2Me_4 adduct with metal carbonyls gives compounds with FeAsCoPPCoAsFe chains.

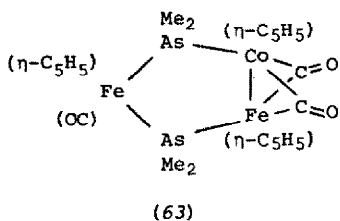
Reactions of (57) were carried out with organometallic arsines; as expected, cleavage of the Fe-Co bond resulted in substitution at cobalt to give complexes (58) [66,67]:



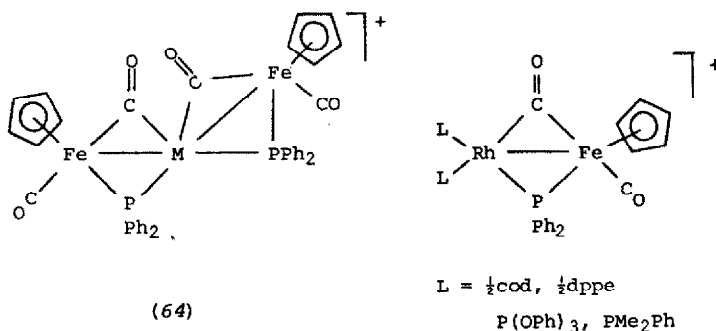
Similar reactions with $(\text{OC})_4\text{Fe}(\mu\text{-PMe}_2)\text{Co}(\text{CO})_3$ and $(\text{Me}_3\text{P})(\text{OC})_3\text{-Fe}(\mu\text{-AsMe}_2)\text{Co}(\text{CO})_3$ have afforded complexes (62) [67]:



Black-green (63) was obtained from a prolonged reaction (85°/4 d) between $\text{Me}_2\text{AsFe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ and $\text{Co}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ [70]. The five-membered ring has an envelope conformation; in the crystal structure the metal atoms in the $\text{Fe}(\mu\text{-CO})_2\text{Co}$ system cannot be distinguished.



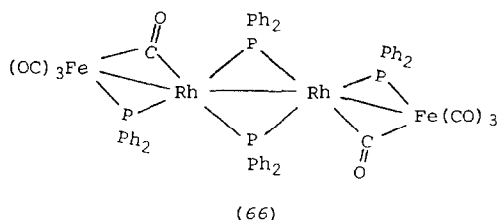
Fe-Rh, Ir Several cationic complexes containing MFEM (M = Rh or Ir) sequences (64) have been obtained from reactions between $\text{Fe}(\text{PPh}_2)(\text{CO})_2\text{-}(\eta\text{-C}_5\text{H}_4\text{R})$ (R = H or Me) and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $[\text{RhCl}(\text{cod})_2]$ or $[\text{Ir}(\text{cod})\text{-}(\text{solvent})]^+$ and subsequent transformations. A similar Fe-Rh compound



was obtained from $\text{Fe}(\text{SBU}^t)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ [70]. These cations are chiral, and earlier NMR studies have suggested racemisation processes involving solvent coordination [72]. The present paper describes rearrangement reactions with coordinating solvents (Me_2CO , MeNO_2 , MeCN , py or diglyme) which result in cleavage of the M-M' bond. Addition of $\text{P}(\text{OMe})_3$ to (64) gave a 1:1 adduct in which the phosphite is assumed to coordinate to Rh. The IrFe_2 complex reacts with H_2 reversibly, perhaps by addition to the iridium centre, but no pure complex was isolated. Several reactions are summarised in Scheme 4.

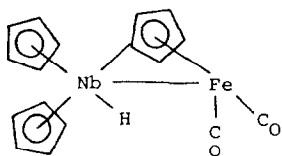
Binuclear complexes (65) could be obtained from slow addition of $\text{Fe}(\text{PPh}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ to $[\text{Rh}(\text{L})_2(\text{EtOH})_x][\text{SbF}_6]$ or $[\text{Rh}(\text{cod})(\text{L})_2][\text{SbF}_6]$.

The propene-elimination route to M-M' bonded compounds has been used to prepare red (66), containing an Fe-Rh-Rh-Fe sequence, from $\text{Fe}(\text{CO})_4(\text{PPh}_2)$ and $[\text{RhCl}(\eta\text{-C}_3\text{H}_5)_2]_2$. The metal core is bent at the Rh atoms in a transoid fashion [$\text{Fe-Rh-Rh}'$, $154.3(1)^\circ$] in the solid, although both *cisoid* and *transoid* forms are present in solution [73].



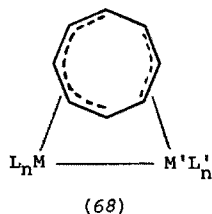
4. COMPLEXES CONTAINING M-M' BONDS BRIDGED BY HYDROCARBON LIGANDS

Nb-Fe So-called 'bent' metallocenes contain a wedge-shaped cavity normally occupied by one, two or three ligands. Reaction between



$\text{HNb}(\eta\text{-C}_5\text{H}_5)_2$ [prepared *in situ* from $\text{Nb}(\text{BH}_4)(\eta\text{-C}_5\text{H}_5)_2$ and NET_3] and $\text{FeMe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ affords red-brown $(\eta\text{-C}_5\text{H}_5)_2\text{HNb}(\overline{\mu\text{-C}_5\text{H}_4})\text{Fe}(\text{CO})_2$ (67), a further example of complexes of this type. Interestingly, the hydride ligand [Nb-H 1.67(5)Å] also appears to interact with the two CO groups to prevent them bending towards Nb [74].

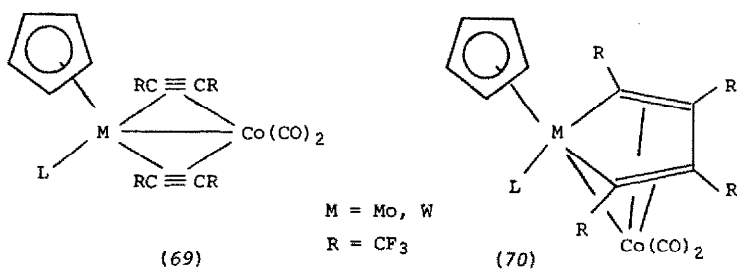
Mo-Fe Moderate yields of $\text{MoFe}(\text{CO})_6(\mu\text{-}\eta^3, \eta^5\text{-C}_8\text{H}_8)$ (68a) have been obtained from $\text{Mo}(\text{CO})_3(\text{diglyme})$ and $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_8\text{H}_8)$ [75]. As with the Mo-Co complex, the C_8 ring is fluxional.



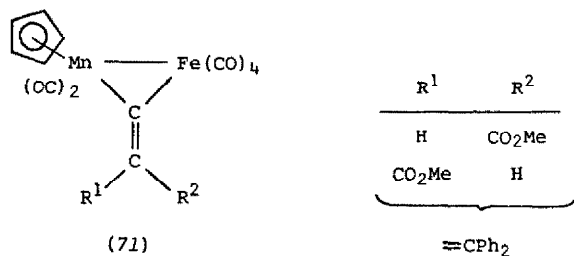
	ML_n	$\text{M}'\text{L}'_n$
a	$\text{Mo}(\text{CO})_3$	$\text{Fe}(\text{CO})_3$
b	$\text{Mo}(\text{CO})_3$	$\text{Co}(\eta\text{-C}_5\text{H}_5)$
c	$[\text{Rh}(\text{CO})_2]^+$	$\text{Fe}(\text{CO})_3$
d	$[\text{Rh}(\text{cod})]^+$	$\text{Fe}(\text{CO})_3$
e	$[\text{Rh}(\text{nbd})]^+$	$\text{Fe}(\text{CO})_3$
f	$[\text{Rh}(\text{CO})_2]^+$	$\text{Co}(\eta\text{-C}_5\text{H}_5)$
g	$[\text{Rh}(\text{cod})]^+$	$\text{Co}(\eta\text{-C}_5\text{H}_5)$
h	$[\text{Rh}(\text{nbd})]^+$	$\text{Co}(\eta\text{-C}_5\text{H}_5)$
i	$[\text{Ir}(\text{cod})]^+$	$\text{Co}(\eta\text{-C}_5\text{H}_5)$

Group VI-Co Reaction of $\text{Mo}(\text{CO})_3(\text{diglyme})$ with $\text{Co}(\eta^4\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{H}_5)$ affords dark red (68b), in which the C_8 ring is fluxional; the Mo-Co interaction is long, perhaps as a result of the steric requirements of the bridging hydrocarbon [75]. The $\text{Co} \rightarrow \text{Mo}$ donor bond required by the 18e rule also influences the Mo-CO(*trans*) bond, which is shorter than the other two bonds as a result of synergic π bonding. The CrCo and WCo complexes, obtained from similar reactions of $\text{Cr}(\text{CO})_3(\text{NCMe})_3$ and $\text{W}(\text{CO})_3(\text{dmf})_3$, respectively, are analogous.

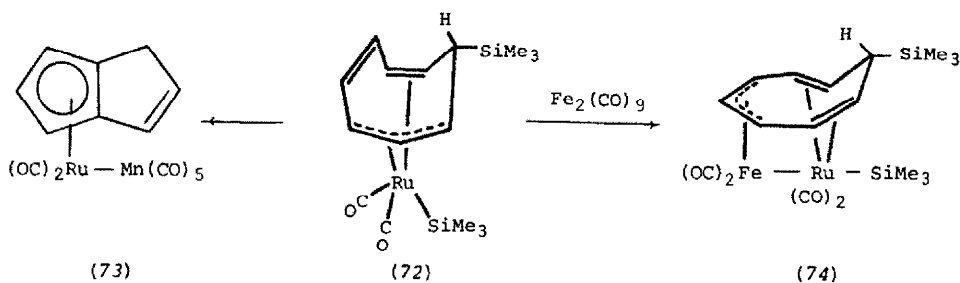
Reactions of $\text{Co}_2(\text{CO})_8$ with $\text{MCl}[\text{C}_2(\text{CF}_3)_2]_2(\eta\text{-C}_5\text{H}_5)$ afford the μ -alkyne complexes (69, $\text{L} = \text{CO}$), which are slowly converted to (70) at 30°. The latter contains a metallacyclopentadiene unit coordinated to cobalt. Complex (69, $\text{L} = \text{CO}$) reacts with PET_3 to give the bis- μ -alkyne complex (69, $\text{L} = \text{PET}_3$); metallacycle formation does not occur.



Mn-Fe Bridging vinylidene ligands are present in complexes (71) obtained from $\text{MnL}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ and $\text{Fe}_2(\text{CO})_9$ [77].



Mn-Ru The reaction between (72) and $\text{MnMe}(\text{CO})_5$ affords the dihydro-pentalenyl complex (73) by reactions involving loss of HSiMe_3 and SiMe_4 [78].

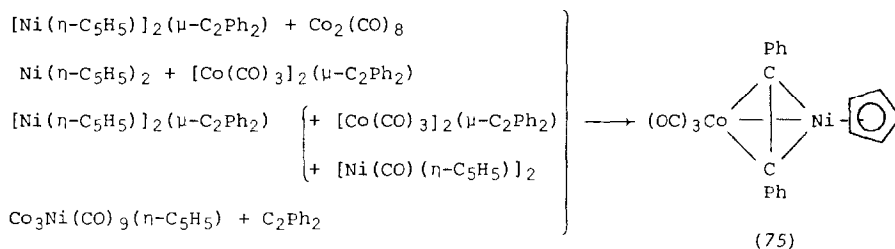


Fe-Ru The cyclooctatrienyl complex (72) reacts with $\text{Fe}_2(\text{CO})_9$, acting as a source of ' $\text{Fe}(\text{CO})_4$ ' to give the Fe-Ru derivative (74) [78]. The field desorption mass spectrum of $\text{FeRu}(\text{CO})_6(\text{Bu}^t\text{N}=\text{CHCH}=\text{NBu}^t)$ has been reported [25].

Fe-Rh Addition of $[\text{Rh}(\text{L})_2]^+$ [$\text{L} = (\text{CO})_2, \text{cod}, \text{kbd}$] to $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_8\text{H}_8)$ gives the cationic derivatives (68c-e), in which the $\mu\text{-C}_8\text{H}_8$ and olefinic ligands are fluxional [79].

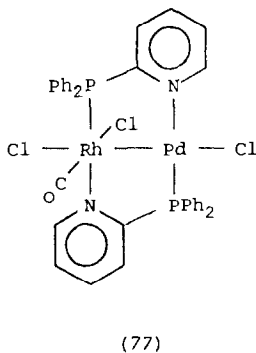
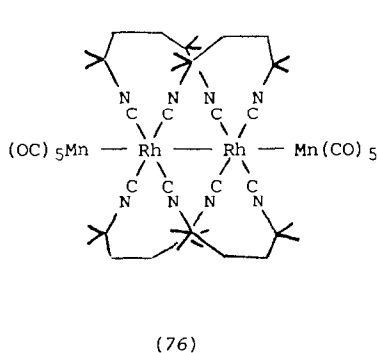
Co-Rh, Ir The mixed-metal complexes (68 *f-i*) have been obtained by reacting $\text{Co}(\eta^4\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{H}_5)$ with $[\text{Rh}(\text{L})_2]^+$ [$\text{L}_2 = (\text{CO})_2$, cod or nbd] or $[\text{Ir}(\text{cod})]^+$, respectively. The olefinic and $\mu\text{-C}_8\text{H}_8$ ligands are fluxional [75].

Co-Ni Several reactions lead to the Co-Ni complex (75); the corresponding MeC_2Ph derivative was also identified [80].



5. OTHER BRIDGING LIGANDS

Mn-Rh Irradiation of mixtures of $\text{Mn}_2(\text{CO})_{10}$ and $[\text{Rh}_2(\text{L})_4][\text{PF}_6]_2$ ($\text{L} = 2,5\text{-dimethyl-2,5-diisocyanohexane}$) gives high yields of the dark green tetranuclear complex (76) [82]. In contrast with $\{[\text{Rh}_2(\text{L})_4]_2\}^{6+}$, which is photolabile, neither the Mn-Rh nor the Rh-Rh bonds in (76) are cleaved on irradiation at 632.8 nm. This result is rationalised in terms of a simple MO treatment of the central MnRhRhMn system.



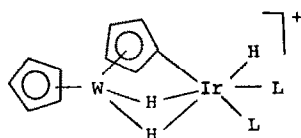
Rh-Pd Extension of the building concepts used for the construction of A-frame complexes to the use of the unsymmetrical bridging ligand

$\text{PPh}_2(\text{C}_5\text{H}_4\text{N}-2)$ has resulted in the formation of some unusual complexes, including (77). This was obtained by oxidative addition of $\text{PdCl}_2(\text{cod})$ to $\text{RhCl}(\text{CO})[\text{PPh}_2(\text{py})]_2$ [83]. The ^{31}P NMR spectrum allows unambiguous location of the metal atoms; the complex was also structurally characterized. The unprecedented oxidative addition reaction results from the closeness of the two metal atoms in any intermediate complex.

6. MIXED-METAL COMPLEXES CONTAINING $\mu\text{-H}$ LIGANDS

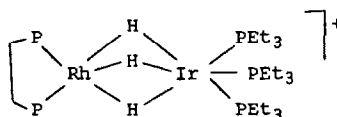
Brief references to $(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{V}(\mu\text{-H})\text{Nb}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2$ and $(\eta\text{-C}_5\text{H}_5)_2(\text{OC})\text{Nb}(\mu\text{-H})\text{Cr}(\text{CO})_5$ have been made, being obtained by irradiating mixtures of $\text{H}_3\text{Nb}(\eta\text{-C}_5\text{H}_5)_2$ with $\text{V}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)$ or $\text{Cr}(\text{CO})_6$, respectively [84].

The reactions between $\text{H}_2\text{W}(\eta\text{-C}_5\text{H}_5)_2$ and $[\text{H}_2\text{Ir}(\text{L})_2(\text{EtOH})_2]^+$ afford green (78), containing bridging H and C_5H_4 ligands [85]. The Rh-Ir complex (79) is obtained from $[\text{Rh}(\text{MeOH})_2(\text{dppe})]^+$ and *mer*- $\text{H}_3\text{Ir}(\text{PET}_3)_3$ [86]. It reacts with CO to give $[\text{fac-H}_2\text{Ir}(\text{CO})(\text{PET}_3)_3]^+$. The orange-brown complexes (80) obtained from $\text{H}_5\text{Ir}(\text{PET}_3)_2$ and $[\text{Rh}(\mu\text{-Cl})(\text{PR}_3)_2]_2$ ($\text{PR}_3 = \text{PET}_3$ or $\frac{1}{2}\text{dppe}$) have catalytic activity in alkene hydrogenation, e.g. hex-1-ene at room temperature and 5 atm H_2 [87].

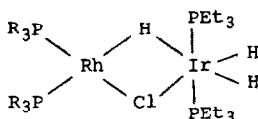


(78)

$\text{L} = \text{PET}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2$

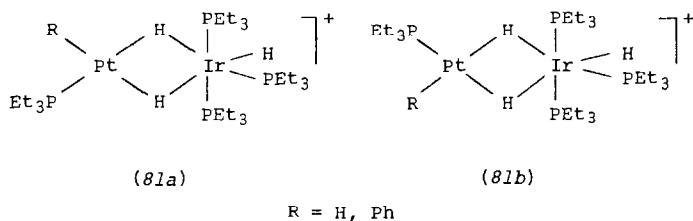


(79)



(80)

Two isomers (*cis* and *trans* at Pt) of (81) are formed in the reaction between $\text{H}_5\text{Ir}(\text{PET}_3)_2$ and $\text{trans-}[\text{PtR}(\text{MeOH})(\text{PET}_3)_2]^+$ (R = H or Ph); transfer of PET_3 to Ir occurs [88]. In all of these complexes the metal centres are bridged by H ligands. A related complex $(\eta\text{-C}_5\text{H}_5)_2\text{Mo-}$

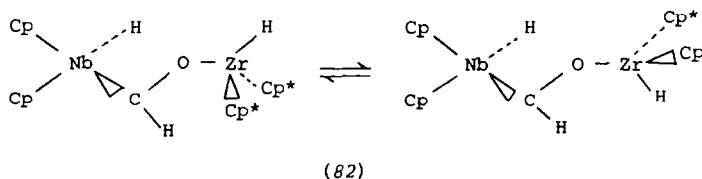


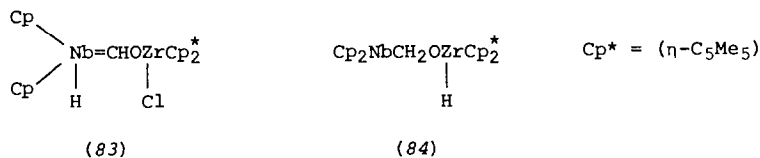
$(\mu\text{-H}_2)\text{Cu}(\mu\text{-I}_2)\text{Cu}(\mu\text{-H}_2)\text{Mo}(\eta\text{-C}_5\text{H}_5)_2$, has been described briefly [89].

7. HETEROBIMETALLIC REDUCTION OF CO

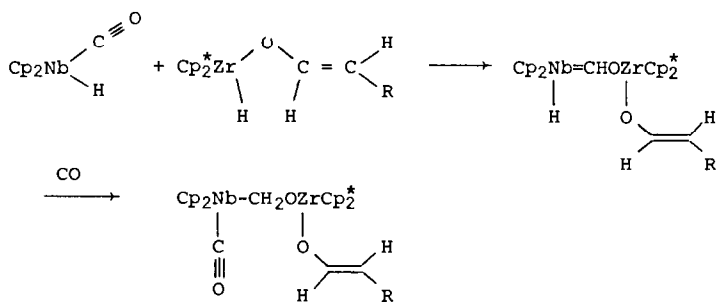
Studies of the reduction of CO by transition metal hydrides have provided a number of complexes in which two metal centres interact or cooperatively facilitate the reaction. The chemistry of CO hydrogenation with $\text{Zr}(\eta\text{-C}_5\text{Me}_5)_2$ complexes containing H and CO ligands has been reviewed [90], as has catalysis of the same reaction by Zr-Mo, Zr-W and Zr-Re systems [91].

Zr-Nb The orange zirconoxycarbene complex (82) is formed from $\text{H}_2\text{Zr}(\eta\text{-C}_5\text{Me}_5)_2$ and $\text{NbR}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2$ [R = H, Me, CH_2Ph , $\text{CH}_2\text{C}_6\text{H}_4\text{OMe-}p$, Ph or $\text{CH}_2\text{OZrH}(\eta\text{-C}_5\text{Me}_5)_2$] at -78° ; for R = H, two rotamers are present in solution [92]. Hydride transfer from Zr to coordinated CO also occurs in the reaction between $\text{HNb}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2$ and $\text{HZrCl}(\eta\text{-C}_5\text{Me}_5)_2$ which gives (83). Tautomerism of (82, R = H) to (84) occurs slowly at -80° ;

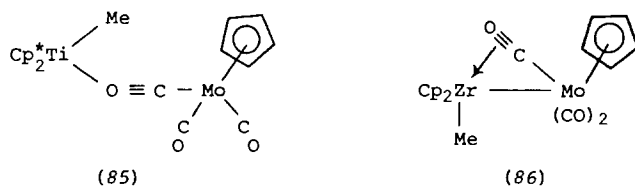




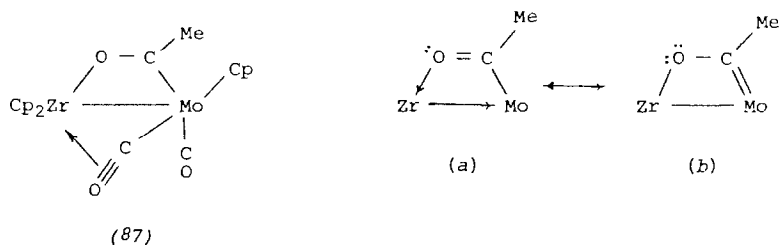
with CO, green $(\eta\text{-C}_5\text{H}_5)_2(\text{CO})\text{NbCH}_2\text{OZrH}(\eta\text{-C}_5\text{Me}_5)_2$ is formed. In the presence of H_2 or C_2Ph_2 , the alkyl-substituted carbene complexes $(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{R})\text{Nb}=\text{CHOZrH}(\eta\text{-C}_5\text{Me}_5)_2$ afford *trans*- $\text{HZr}(\text{OCH}=\text{CHR})(\eta\text{-C}_5\text{Me}_5)_2$ and $\text{H}_3\text{Nb}(\eta\text{-C}_5\text{H}_5)_2$ or $\text{HNb}(\eta\text{-C}_2\text{Ph}_2)(\eta\text{-C}_5\text{H}_5)_2$, respectively, probably by insertion of the carbene into the Nb-alkyl bond, followed by rapid $\beta\text{-H}$ elimination. The relative migratory aptitudes are $\text{H} \gg \text{Me} > \text{CH}_2\text{C}_6\text{H}_4\text{OMe-}p > \text{CH}_2\text{Ph}$. With CO, the following further reaction occurs:



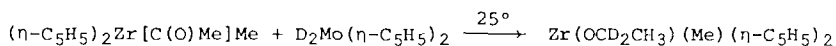
Ti,Zr-Mo,W Direct attachment of a d^0 metal to the oxygen of a terminal CO is found in the product (85) from $\text{HMo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ and $\text{TiMe}(\eta\text{-C}_5\text{Me}_5)(\eta\text{-C}_5\text{Me}_4(=\text{CH}_2))$ [93]. In (85), the $\nu(\text{CO})$ for the bridging CO appears at 1623 cm^{-1} ; MO calculations suggest the bonding to involve only the oxygen lone pair, with negligible π back-bonding to Ti. The structural characterisation of (85) led the authors to suggest a similar structure for the product from the analogous reaction with $\text{ZrMe}_2(\eta\text{-C}_5\text{H}_5)_2$, which had been assigned the $\mu\text{-}, \eta^1, \eta^2$ structure (86). This



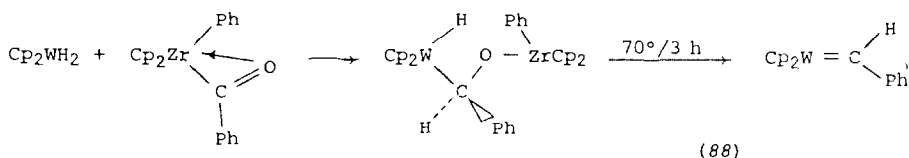
complex was first reported in 1978 [94], and a more detailed study by Norton, Caulton and coworkers includes some aspects of its chemistry [95]. ^{13}C NMR studies show the existence of a $\mu\text{-CO-CO}(t)$ exchange (ΔG^\ddagger 40.2 kJ mol $^{-1}$). Reaction of CO with (86) gives the acetyl derivative $\text{Cp}_2\text{Zr}(\eta^2\text{-Ac})\text{Mo}(\text{CO})_3\text{Cp}$, also obtained from $\text{ZrMe}(\eta^2\text{-COMe})\text{-}(\eta\text{-C}_5\text{H}_5)_2$ and $\text{HMo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$: slow loss of CO then affords (87), which was structurally characterised. The $\mu\text{-}\eta^1, \eta^2\text{-CO}$ group forms a shorter Zr-O bond [2.271(2)Å] than Zr-C [2.343(3)Å], while there is a very short Mo-C bond [1.876(3)Å] to this ligand. The $\eta^2\text{-OCMe}$ group appears intermediate between the acetyl (a) and oxycarbene (b) resonance forms, and reacts with $\text{CF}_3\text{CO}_2\text{H}$ to give EtOH, representing a stoichiometric reduction of CO to EtOH.



A second example of heterobimetallic transfer of H(D) is



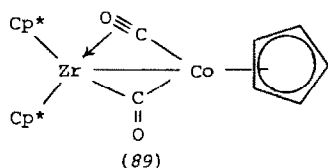
with the $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2$ fragment being either solvated, or appearing as $\text{Mo}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2$ or as $\text{Mo}_2(\text{C}_5\text{H}_4)_2(\eta\text{-C}_5\text{H}_5)_2$ [96]. With $\text{H}_2\text{W}(\eta\text{-C}_5\text{H}_5)_2$, the product is $(\eta\text{-C}_5\text{H}_5)_2\text{MeZr}(\mu\text{-OCHMe})\text{WH}(\eta\text{-C}_5\text{H}_5)_2$. The latter decomposes to $[\text{Cp}_2\text{ZrMe}]_2\text{O}$ and $\text{Cp}_2\text{W}=\text{CHMe}$, which rearranges to $\text{Cp}_2\text{W}(\eta^2\text{-C}_2\text{H}_4)$; the net result is the reduction of CO to ethylene by coupling with a Me group. The related phenyl complex, obtained similarly by the reaction:



decomposes on heating to the isolable phenylcarbene complex (88) [97,98].

Zr-Re Reactions of the acetyl(methyl)zirconium complex with $\text{HRe}(\eta\text{-C}_5\text{H}_5)_2$ give the related complex $(\eta\text{-C}_5\text{H}_5)_2\text{MeZr}(\mu\text{-OCHMe})\text{Re}(\eta\text{-C}_5\text{H}_5)$ [98].

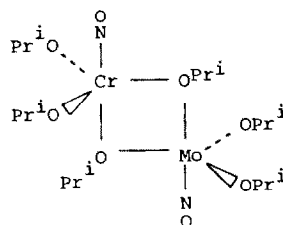
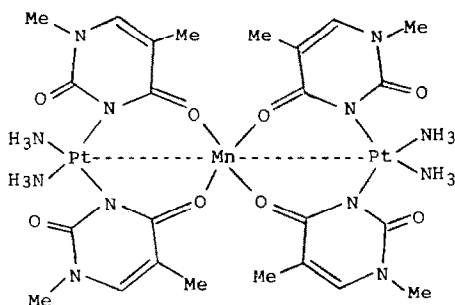
Zr-Co Interaction of $\text{H}_2\text{Zr}(\eta\text{-C}_5\text{Me}_5)_2$ or $[\text{Zr}(\text{N}_2)(\eta\text{-C}_5\text{Me}_5)_2]_2\text{N}_2$ with $\text{Co}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ affords blue-green (89); in contrast with several other metal carbonyls, a zirconoxycarbene complex is not formed. The two CO groups are bridging [$\nu(\text{CO})$ 1737, 1683 cm^{-1}], one in the $\mu\text{-}\eta^1, \eta^2$ mode [99].



Nb systems Extension of these reactions to those between $\text{H}_3\text{Nb}(\eta\text{-C}_5\text{H}_5)_2$ and several metal carbonyls in a quest for a system to convert CO to hydrocarbons was successful only with $\text{Cr}(\text{CO})_6$, which afforded ethane (10%) [100].

8. COORDINATION COMPOUNDS CONTAINING M-M' BONDS

Addition of MnCl_2 to $\text{cis-Pt}(\text{NH}_3)_2(\text{mtym})_2$ ($\text{Hmtym} = 1\text{-methyl-thymine}$) afforded (90) as a decahydrate [101]. This trinuclear cation contains square-planar Mn^{II} and Pt^{II} if the M-M' interaction is ignored; however, the Mn-Pt separation [2.704(1) Å] and the linear Pt-Mn-Pt array suggest considerable interaction between the metal centres. In the similar Pt_2Ag complex, the silver has tetrahedral coordination, with Pt-Ag 2.849(1), 2.884(1) Å, indicating weak M-M' interactions [102].



(91)

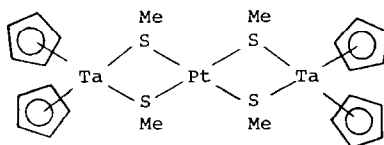
A mixture of equimolecular amounts of $\text{Cr}_2(\text{OPr}^i)_6(\text{NO})_2$ and $\text{Mo}_2(\text{OPr}^i)_6(\text{NO})_2$ exhibits ^1H NMR spectra consistent with the presence of the mixed CrMo compound (91) as well as the Cr_2 and Mo_2 species. A mass spectrum of the solid complex obtained after removal of solvent contains weak $[\text{CrMo}(\text{OPr})_6(\text{NO})_n]^+$ ($n = 1$ or 2) ions. All three complexes undergo intramolecular bridge-terminal exchange of OPr^i groups.

9. SULPHUR-BRIDGED HETEROMETALLIC SYSTEMS

Müller and coworkers have reviewed the area of transition metal thiometalates and their unique ligand properties, including the heterometallic thioanions, many of which contain the four-membered $\text{M}(\mu\text{-S})_2\text{M}'$ systems with metal-metal interactions [104]. These are of general interest, and also relevant to the special problem of the Fe-Mo-S clusters of biological interest (see Part B).

Most of the studies reported during the last two years describe compounds containing MoS_4^{2-} or WS_4^{2-} acting as ligands to other metals to form complexes of the type $\text{L}_2\text{MS}_2\text{M}'\text{S}_2$ or $\text{L}_2\text{MS}_2\text{M}'\text{S}_2\text{M}''\text{L}_2''$ (Tables 3 and 4). The structures of new MoS_4 derivatives of iron(II), copper(I) and silver(I) have been determined using resonance Raman spectroscopy, where the electronic transitions are localised in the $\text{MS}_2\text{M}'\text{S}_2\text{M}$ system [105]. In the anion $[\text{Fe}\{\overbrace{(\mu\text{-S})_2\text{Mo}(\text{S})(\text{SCH}_2\text{CH}_2\text{S})}_2\}]^{3-}$, the Mo atoms are five-coordinate with a distorted square-planar geometry [106]. The mixed Mo-Ru systems $\text{S}_2\text{Mo}(\mu\text{-S})_2\text{Ru}(\text{bipy})_2$ and $[\text{Mo}\{(\mu\text{-S})_2\text{Ru}(\text{bipy})_2\}_2]^{2+}$ can be reduced electrochemically; if methanol is present as a hydrogen source, reduced species convert acetylene to ethane and ethylene [107].

The latest example of thiolate-bridged organometallic complexes is $[\text{Pt}\{(\mu\text{-SMe})_2\text{Ta}(\eta\text{-C}_5\text{H}_5)_2\}_2][\text{PF}_6]_2$ (92), obtained from $\text{Ta}(\text{SMe})_2(\eta\text{-C}_5\text{H}_5)_2$ and $\text{PtCl}_2(\text{NCPH})_2$ [108].



(92)

TABLE 3 Recent papers describing $M(\mu-S)_2M'$ and $M[(\mu-S)_2M']_2$ systems

M-M'	Complexes	Topic*	Reference
Mo-Fe	$[S_2Mo(\mu-S)_2FeX_2]^{2-}$ (X = Cl, SPh)	a, b	[130]
	$[S_2Mo(\mu-S)_2FeCl_2]^{2-}$	b, c	[131]
Mo-Ru	$S_2Mo(\mu-S)_2Ru(bipy)_2$	a, d	[10]
Mo, W-Fe	$[S_2M(\mu-S)_2Fe(NO)_2]^{2-}$	a, b (Mo)	[132]
	$[S_2M(\mu-S)_2FeCl_2]^{2-}$	a, b	[133]
	$[S_2M(\mu-S)_2Fe(S_5)]^{2-}$	a, b	[134]
W-Fe	$S_2W(\mu-S)_2Fe(bipy)_2$ (2 polymorphs)	a, c	[135]
Mo-Fe ₂	$[Mo\{(\mu-S)_2FeCl_2\}_2]^{2-}$	a, c	[136, 137]
	$[S_2Mo(\mu-S)_2Fe(\mu-S)_2Fe(SPh)_2]^{3-}$	a, c	[138]
Mo-Ru ₂	$[Mo\{(\mu-S)_2Ru(bipy)_2\}_2]^{2+}$	a, d	[107]
Mo, W-Fe ₂	$[M\{(\mu-S)_2FeCl_2\}_2]^{2-}$	a, b (Mo)	[137]
Mo ₂ -Fe	$[(S_2Mo(\mu-S)_2)_2Fe]^{3-}$	a, b, d	[139, 140]
W ₂ -Fe	$[(S_2W(\mu-S)_2)_2Fe]^{n-}$ (n = 2, 3)	a, d	[141]
	$[(S_2W(\mu-S)_2)_2FeL_2]^{2-}$ (L = py, dmf)	a, b (dmf)	[141]
W ₂ -Co	$[(S_2W(\mu-S)_2)_2Co]^{2-}$	c, d, e	[142]
Mo, W-Ni, Pd, Pt	$[S_2M(\mu-S)_2M'(S_2CNET_2)]^{-}$	a, c	[143]
W-Pt	$O_2W(\mu-S)_2Pt(PPh_3)_2$	a	[145]
	$S_2W(\mu-S)_2PtL_2$ (L = PET ₃ , PPh ₃)	a, b	[145]
(Mo, W) ₂ -Ni, Pd, Pt	$[OSM(\mu-S)_2]_2M'^{2-}$	a, c	[143]
	$[S_2M(\mu-S)_2]_2M'^{2-}$	a, c, d	[144]
Mo-Cu	$[S_2Mo(\mu-S)_2Cu(CN)]^2$	a, b, f	[146, 147]
Mo-Cu ₂	$[Mo\{(\mu-S)_2Cu(CN)\}_2]^{2-}$	a, b	[147]
	$(Ph_3P)Cu(\mu-S)_2Mo(\mu-S)_2Cu(PPh_3)_2$	b, c	[131]

* a Synthesis; b X-ray structure; c spectra; d electrochemistry (cyclic voltammetry); e MO calculations; f ⁹⁵Mo NMR.

TABLE 4 Structural studies of $M(\mu-S)_2M'$ and $M[(\mu-S)_2M']_2$ systems

M'M'	Separation (Å)	Complex	Refer- ence	
Mo-Fe	2.718, 2.774(5)	$[NMe_4]_3 \left\{ \overbrace{[(SCH_2CH_2S)(S)Mo(\mu-S)_2]_2}^{Fe} \right\} Fe$	[106]	
	2.731(3)	$[PPh_4]_2 [S_2Mo(\mu-S)_2Fe(S_5)]$	[134]	
	2.740(1)	$[NEt_4] [ppn]_2 [(S_2Mo(\mu-S)_2)_2Fe] \cdot 2dmf$	[140]	
	2.756(1)	$[NEt_4]_2 [S_2Mo(\mu-S)_2Fe(SPh)_2]$	[130]	
	2.770, 2.781(2)	$[PPh_4]_2 [Mo\{(\mu-S)_2FeCl_2\}_2]$	[137]	
	2.775	$[NMe_3(CH_2Ph)] [PPh_4] [S_2Mo(\mu-S)_2FeCl_2]$	[131, 133]	
	2.786(1)	$[NEt_4]_2 [S_2Mo(\mu-S)_2FeCl_2]$	[130]	
	2.835(13)	$[ppn]_2 [S_2Mo(\mu-S)_2Fe(NO)_2]$	[132]	
	W-Fe	2.753(3)	$[PPh_4]_2 [S_2W(\mu-S)_2Fe(S_5)]$	[134]
		2.808	$[NMe_3(CH_2Ph)] [PPh_4] [S_2W(\mu-S)_2FeCl_2]$	[133]
2.044(1)		$[PPh_4]_2 [(S_2W(\mu-S)_2)_2Fe(dmF)_2]$	[141]	
W-Pt	2.947	$S_2W(\mu-S)_2Pt(PEt_3)_2$	[145]	
Mo-Cu	2.624	$[NPr_4]_2 [S_2Mo(\mu-S)_2Cu(CN)]$	[146]	
	2.630(1)	$[PPh_4]_2 [S_2Mo(\mu-S)_2Cu(CN)]$	[147]	
	2.630	$[NMe_4]_2 [(NC)Cu(\mu-S)_2Mo(\mu-S)_2Cu(\mu-CN)_2-catena]$	[147]	
	2.642(3) ^a 2.775(2) ^b	$(Ph_3P)Cu^a(\mu-S)_2Mo(\mu-S)_2Cu^b(PPh_3)_2 \cdot 0.8CH_2Cl_2$	[148]	

10. MIXED-METAL MOLECULES

There is increasing interest in high-dispersion multi-component metal catalys^ts, and a current view is that there is a direct interaction between the components in bimetallic clusters [109]. This view is supported by a variety of studies of bimetallic molecules which have found them to be "normal in an electronic, optical, bonding and probably chemical sense". This quotation comes from the proceedings of a Royal Society of Chemistry Faraday Symposium on 'Diatomic metals and metallic

clusters' [110]. The application of metal vapour synthetic techniques and matrix isolation studies have resulted in rapid advances in our knowledge of these reactive molecules. A significant application is to the synthesis of CrAg and CrAg₂ by cocondensation of two metals which have low miscibility; other molecules discussed include CrMo₂, Cr₂Mo, MoNb, MoAg and MnAg. Combined matrix isolation and Mössbauer studies allowed identification of FeCo, FeNi and FeCu [111]. Gingerich [112] summarised his extensive studies of stabilities of diatomic metals and metal clusters, with bond energy determinations by the Knudsen cell mass spectrometric method; a summary of many heterometallic molecules is included, with a comparison with values calculated using empirical valence bond [113] and atomic cell models [114]. Miedema described refinements to the latter model and lists calculated dissociation enthalpies for a wide range of heterodimetallic molecules [115]. Also included are calculated electronic structures for AgAu using effective core potentials [116].

Earlier applications of metal vapour syntheses have been summarised [117]. Selected reports during the last two years have included mass spectrometric studies of vapours above various rare earth-noble metal mixtures, with measurements of dissociation energies, e.g. YIr 454, YPt 470, LaPt 496 kJ mol⁻¹, calculated values (empirical valence bond model) are 451, 316 and 423 kJ mol⁻¹, respectively [118]. For YIr and YAu, $\Delta H_{f(298)}^0$ values of 638 and 483 kJ mol⁻¹ have been determined [119]. Sequential deposition of Ti and Mo in poly(methylphenylsiloxane) gives polymer-stabilised species identified by absorptions at 590 (Ti₂), 460 (TiMo) and 418 nm (Mo₂) [120]. Similar studies of NbMo showed this species has four transitions between 551-590 nm; theoretical (EH) studies suggest a bond order of 5.5, with separation 2.30Å and dissociation energy 301 kJ mol⁻¹ [121]. Codeposition of Ag with Mo, Mn or Cu in argon matrices affords AgMo, AgMn or AgCu, tentatively identified by spectroscopic studies. EH MO calculations provide satisfactory correlations between observed and calculated electronic transitions: bond

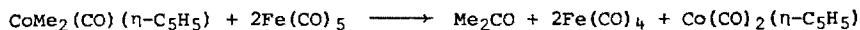
TABLE 5 Reactions that do not afford M-M' bonds

System	Reaction and product(s)	Reference
Zr, Hf-Pd, Pt	$M I_2(\eta\text{-C}_5\text{H}_5)_2 + [M'(\text{CN})_4]^{2-} \longrightarrow \text{M-N-C-M}' \text{ systems}$ <p>(M = Zr, M' = Pt; M = Hf, M' = Pd)</p>	[150]
Nb-Mn	$H_3\text{Nb}(\eta\text{-C}_5\text{H}_5)_2 + \text{Mn}_2(\text{CO})_{10} \longrightarrow [(\mu\text{-H})\{\text{Nb}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2\}_2] [\text{Mn}(\text{CO})_5]$ <p>[but not $(\eta\text{-C}_5\text{H}_5)_2(\text{OC})\text{Nb}(\mu\text{-CO})\text{Mn}(\text{CO})_4$: cf ref [152]</p>	[151]
Mn-Ni	$\text{MnCl}(\text{CO})_5, [\text{Mn}(\text{CO})_4\{\text{P}(\text{OMe})_3\}]_2 + \text{Ni}(\text{cod})_2 \longrightarrow \text{Mn}_2 \text{ species}$	[153]
Fe-Co	$\text{Fe}_2(\text{CO})_9 + \text{CoMe}_2(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5) \longrightarrow \text{Co}(\text{CO})_2(\eta\text{-C}_5\text{H}_5) + \text{Me}_2\text{CO}$	[124]
Fe-Ni	$\text{FeCl}(\text{CO})_3(\eta\text{-C}_3\text{H}_5), \text{FeCl}(\text{CO})_2(\eta\text{-C}_5\text{H}_5) + \text{Ni}(\text{cod})_2 \longrightarrow \text{Fe}_2 \text{ species}$	[153]
Ir-Pt	$\text{IrCl}_4(\text{PMe}_2\text{Ph})_2 + \text{Pt}(\eta\text{-C}_2\text{H}_4)(\text{PPh}_3)_2 \longrightarrow [(\text{Me}_2\text{PhP})_2\text{Cl}_2\text{Ir}(\mu\text{-Cl})_2\text{Pt}(\text{PPh}_3)_2] -$ <p style="text-align: center;">[IrCl₄(PMe₂Ph)₂]</p>	[154]

lengths (Å) and dissociation energies (kJ mol⁻¹) are AgMo, 3.00, 174.9; AgMn, 2.80, ~4; AgCu, 2.90, 138 [122]. Russian workers have made graphite layer compounds containing FeMo and FeW; Mössbauer and X-ray spectrometry were used to characterise these products [123].

11. REACTIONS WHICH MAY INVOLVE DIRECT M-M' INTERACTIONS

A number of reactions have been found to proceed via intermediates formed by the interaction of two metal centres, although a formal M-M' is not necessarily invoked. One such is the production of acetone (95%) in the reaction between Fe₂(CO)₉ and CoMe₂(PPh₃)(η-C₅H₅) [124]. Transfer of ligands between the two metal centres affords a number of complexes, including those with Fe-PPh₃, Fe-C₅H₅ and Co-CO links. A key reaction is postulated:



Decomposition of mixtures of Mn₂(CO)₁₀ and Co₂(CO)₈, or of MnCo(CO)₉, on alumina afforded catalysts which converted (CO + H₂) to alkanes, peaking at C₆; the manganese increases and stabilises the activity of the cobalt system [125]. Conversion rates are: Co₂ 1.36 × 10⁻³, (Mn₂ + Co₂) 4.9 × 10⁻³, MnCo 11.5 × 10⁻³ mol CO h⁻¹ (g Co)⁻¹, suggesting the increased activity stems from an Mn-Co aggregate.

Intense ions [MMn(CO)_n(C₅H₅)]⁺ (M = Fe, Mo, W; n = 2,3) in the mass spectra of (η-C₅H₅)(OC)₃MXC₅H₄Mn(CO)₃ (X = bond, CO, CH₂ or CH₂CO) suggest that it might be possible to prepare compounds such as [WMn(CO)₃(η-C₅H₅)]Cl [126].

Reactions between *trans*-MCl(CO)(PR₃)₂ (M = Rh, Ir) and rhodium(III) or platinum(IV) complexes proceed rapidly by an oxidative addition-reductive elimination sequence, involving (μ-Cl)₂ intermediates; these are inner-sphere double electron transfer processes [149].

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