COMPLEXES CONTAINING HETERONUCLEAR METAL-METAL BONDS. SOME RECENT ADVANCES 1982-83

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

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INTRODUCTION

This survey of progress in the synthesis and chemistry of mixed-metal complexes follows on from the account covering the period 1980-81.* As in that article, coverage of compounds containing M-M' bonds has been divided into the following sections:

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* M.I. Bruce, *J. Organomet. Chem.*, 242 (1983) 147.

ABBREVIATIONS

cod	1,5-cyclooctadiene
dba	dibenzylideneacetone
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dtpe	1,2-bis(di-*p*-tolylphosphino)ethane
nbd	norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)
pdma	phenylene-1,2-bis(dimethylarsine) (diars)
phen	1,10-phenanthroline
ppn	bis(triphenylphosphine)iminium
py	2-pyridyl (in 2-diphenylphosphinopyridine)
thf	tetrahydrofuran
tol	*p*-tolyl

General developments

Continuing studies on the use of $W[C(tol)](CO)_2(\eta\text{-}C_5H_5)$ [1] as a source of tungsten-containing heterometallic complexes have been summarised [2], and later developments appear in Section 2. A photochemical approach to the generation of coordinatively unsaturated fragments which

TABLE 1 *Some isolobal relationships* [a]

CH_3	CH_3^+/CH_2	CH_2^+/CH	CH^+
$Mn(CO)_5$	$Cr(CO)_5$	$Re(CO)_4$	$Fe(CO)_3$
$Co(CO)_4$	$Fe(CO)_4$	$Co(CO)_3$	
$HPt(PR_3)_2$	$Pt(PR_3)_2$		$Pt(PR_3)$
$Au(PR_3)$			
$Mo(CO)_3(\eta\text{-}C_5H_5)$	$Mn(CO)_2(\eta\text{-}C_5H_5)$	$W(CO)_2(\eta\text{-}C_5H_5)$	
$Fe(CO)_2(\eta\text{-}C_5H_5)$	$Rh(CO)(\eta\text{-}C_5H_5)$	$Fe(CO)(\eta\text{-}C_5H_5)$	
$Ni(CO)(\eta\text{-}C_5H_5)$			
$Zn(\eta\text{-}C_5H_5)$	$Cu(\eta\text{-}C_5H_5)$	$Ni(\eta\text{-}C_5H_5)$	$Rh(\eta\text{-}C_5H_5)$
	BH_3	BH_2	BH

[a] For a fuller account in the context of the chemistry of homo- and heterometallic compounds, see ref. [6].

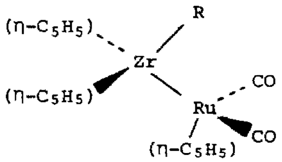
will add to metal-carbon (and metal-metal) multiple bonds has been used [3,4]. Further extensions of the isolobal approach have continued to appear, including the application of the reagent $Cu(C_5Me_5)$ [5]. A summary of much of this work has appeared [6]. Table 1 lists some of the commoner isolobal equivalents.

An unusual extension of the isolobal analogy between CH^+ and $Fe(CO)_3$ was applied to the conceptual replacement of a ring CH group in cobalticinium or rhodicinium cations. The resulting "metalla-metallocenes" could be envisaged as novel aromatic species. The synthesis of several examples of these complexes was reported by two groups [79,80] (Section 4), and much new chemistry centred on these systems may be anticipated.

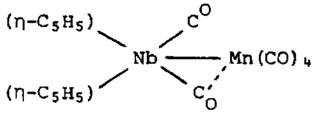
The use of bridging ligands to bring two metal atoms within bonding (or interacting) distance has been the most conspicuous new development. Favoured ligands are 2-(diphenylphosphino)pyridine, $Ph_2P(py)$, used mainly by Balch, and bis(diphenylphosphino)methane (dppm), whose monodentate complexes have been elegantly converted to a variety of $M(\mu\text{-dppm})_2M'$ systems by Shaw (Section 5).

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

Zr-Ru Reactions between $[Ru(CO)_2(\eta\text{-}C_5H_5)]^-$ and $ZrCl(R)(\eta\text{-}C_5H_5)_2$ (R = Cl, Me, OBu^t) afforded the Zr-Ru complexes (1); the last two can also be prepared from the chloro complex and LiMe or $KOBu^t$, respectively [7]. The iron analogues were obtained from similar reactions employing $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$. The preference for sterically less demanding carbonylmetallates to form M-M' bonds with Lewis acids resulted in the



(1)



(2)

formation of complexes such as (1), rather than the μ-CO derivatives obtained previously with $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$.

V,Nb-Mn The unusually reactive $V(CO)_5(NO)$, obtained from $[V(CO)_6]^-$ and $[NO][BF_4]$, afforded orange-yellow $[AsPh_4][(ON)(OC)_4VMn(CO)_5]$ with $[AsPh_4]$-$[Mn(CO)_5]$; the structure of the anion is analogous to those of $[Cr_2(CO)_{10}]^{2-}$ and $[CrMn(CO)_{10}]^-$ [8].

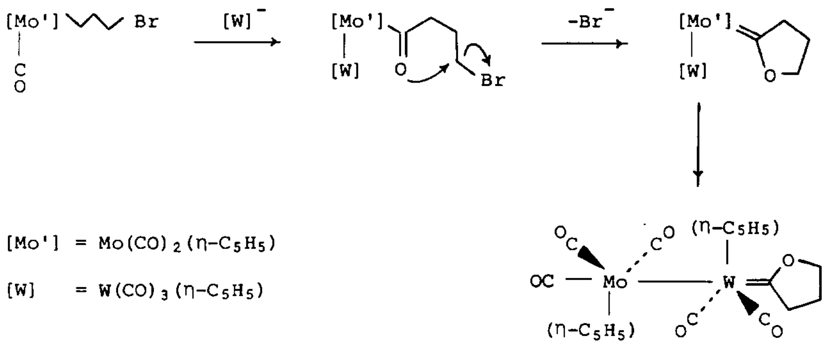
In the presence of NEt_3, $Mn_2(CO)_{10}$ and $Nb(BH_4)(\eta\text{-}C_5H_5)_2$ reacted in refluxing toluene to give dark-red (2) [9,10].

Group V-Co Binuclear complexes containing V-Co bonds were formed in reactions between VCp'_2 ($Cp' = C_5H_4Bu^t$, $C_5H_4CO_2Me$, C_5Me_5 or C_5Me_4Et) and $Co_2(CO)_8$ [11]. With vanadocene, the first-formed $(\eta\text{-}C_5H_5)_2VCo(CO)_4$ reacted with excess $Co_2(CO)_8$ to give the salt $[V(CO)_2(\eta\text{-}C_5H_5)_2][Co(CO)_4]$, together with $(\eta\text{-}C_5H_5)_2VOCCo_3(CO)_9$; the related binuclear $C_5H_4Bu^t$ and $C_5H_4CO_2Me$ derivatives could not be isolated, only $Co_4(CO)_{12}$ being recovered from the latter reaction. The peralkylated derivatives are more stable, the VCo complexes being obtained in 70% yield; they reacted with $Co_2(CO)_8$ to give the corresponding $[V(CO)_2Cp'_2][Co(CO)_4]$ salts and $Co_4(CO)_{12}$.

Similar complexes were isolated from reactions between $H_3MCp'_2$ or $HM(CO)Cp'_2$ (M = Nb or Ta, $Cp' = C_5H_4Bu^t$) and $Co_2(CO)_8$; the compounds $Cp'_2M(CO)Co(CO)_4$ reacted with excess $Co_2(CO)_8$ to give $Cp'_2(OC)MOCCo_3(CO)_9$ [12].

V-Au The $Au(PPh_3)$ group caps an octahedral face of the $V(CO)_6$ moiety in $V\{Au(PPh_3)\}(CO)_6$ [13].

Mo-W The reaction between $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ and $Mo\{(CH_2)_3Br\}(CO)_3$-$(\eta\text{-}C_5H_5)$ afforded the heterodimetallic cyclic carbene complex (3), which is formed by the carbonylmetallate-induced alkyl migration to CO, followed by displacement of Br^- by the acyl oxygen, and carbene transfer from Mo to W [14]:



$[Mo'] = Mo(CO)_2(\eta\text{-}C_5H_5)$

$[W] = W(CO)_3(\eta\text{-}C_5H_5)$

(3)

Although metathesis does not occur between $Cr_2(CO)_4(\eta\text{-}C_5H_5)_2$ and $Mo_2(CO)_4(\eta\text{-}C_5H_5)_2$, heating $[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$ and $[W(CO)_3(\eta\text{-}C_5H_5)]_2$ together in refluxing diglyme afforded a mixture of $MoW(CO)_6(\eta\text{-}C_5H_5)_2$, $MoW(CO)_4(\eta\text{-}C_5H_5)$, and the homodinuclear complexes, which could be separated by column chromatography [15]. The Mo_2, MoW and W_2 tetracarbonyl complexes were in equilibrium at the reaction temperature, being obtained in *ca* 1:2:1 ratio. In solution, the MoW complex was fluxional (CO site exchange via μ-CO intermediates, E_a 43.5 kJ mol^{-1}), the low-temperature limiting ^{13}C NMR spectrum being observed at -50°C.

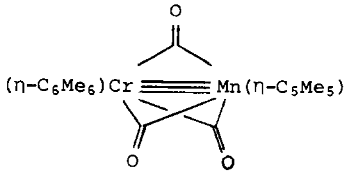
The reaction of $[Mo(\eta^2\text{-}C_8H_{14})(NO)_2(\eta\text{-}C_5H_5)]^+$ with $HW(NO)_2(\eta\text{-}C_5H_5)$ afforded dark green $[HMoW(NO)_4(\eta\text{-}C_5H_5)_2][BF_4]$; in CD_3NO_2 solution the homo- and heteronuclear cations were in equilibrium [16].

Group VI-Mn ^{17}O NMR spectra of $[MMn(CO)_{10}]^-$ (M = Cr, Mo, W) as their $[NEt_4]^+$ salts gave separate resonances for CO ligands bonded to the two metal atoms: chemical shifts (δ) in p.p.m. are

M	$M(CO)_5$	$Mn(CO)_5$
Cr	375	398
Mo	368	400
W	358	393

Resonances of axial and equatorial CO ligands were not resolved [17].

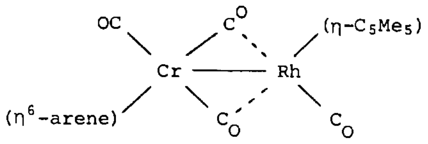
Photolysis of a mixture of $Mn(CO)_3(\eta\text{-}C_5Me_5)$ and $Cr(CO)_3(\eta\text{-}C_6Me_6)$ in thf afforded deep-green (4), containing a Cr≡Mn triple bond [3].

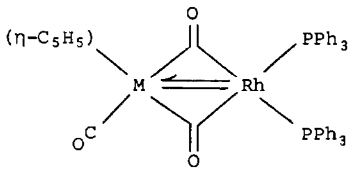


(4)

W-Co The reaction between $Na[Co(CO)_4]$ and *trans*-$ClW(CPh)(CO)_4$ afforded $(OC)_4CoW(CPh)(CO)_4$ as yellow-orange crystals [18].

Group VI-Rh Irradiation (UV) of mixtures of $Cr(CO)_3(\eta\text{-arene})$ and $Rh(CO)_2(\eta\text{-}C_5Me_5)$ has given the CrRh complexes (5); an η^5-indenyl-Rh complex was also prepared from $Cr(CO)_2(thf)(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)$ and $Rh(CO)_2\text{-}(\eta^5\text{-}C_9H_7)$ [19]. An X-ray study of (5a) showed the C_5 and C_6 rings to be *trans*; two CO groups semi-bridge the Cr-Rh bond.





(5)	arene
a	C_6H_6
b	$C_6H_3Me_3\text{-}1,3,5$
c	C_6Me_6

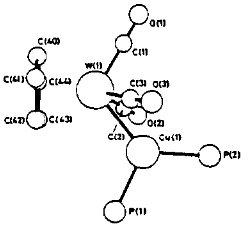
(6)	M
a	Mo
b	W

Reactions between $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Mo or W) and $RhCl(PPh_3)_3$ gave the black M-Rh complexes (6); the Mo-Rh bond in (6a), which is bridged by two CO ligands, was considered to be a double bond involving a dative link from Rh, as shown [20]. Photolysis of (6a) in the presence of nitrosodurene (L) afforded paramagnetic $[Mo(CO)_n(L)(\eta\text{-}C_5H_5)]^{\bullet}$; (6a) also catalysed addition of H_2 to cyclohexene, although less effectively than $RhCl(PPh_3)_3$.

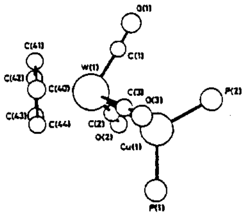
Mo-Pt Orange $(\eta\text{-}C_5H_5)(OC)_3MoPtH(PPh_3)_2$ was obtained from $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ and *trans*-$HPtCl(PPh_3)_2$; it showed dynamic behaviour in solution [21].

Group VI-Cu Oxygenation of the complex $(\eta\text{-}C_5H_5)(OC)_3CrCu(phen)$ in CH_2Cl_2 gave an ESR-active species formulated as $Cr(O_2)(CO)_n(\eta\text{-}C_5H_5)$ [22].

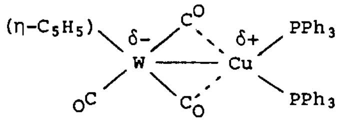
Mo,W-Cu,Ag Salt-elimination reactions between $[CuCl(PPh_3)]_4$ and $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Mo or W) afforded $CuM(CO)_3(PPh_3)(\eta\text{-}C_5H_5)$, which for M = W, exists in two isomeric forms, yellow (7a) and red-orange (7b). The major differences lie in the shorter W-Cu and shorter Cu...O separations in the latter, features which were rationalised in terms of changes in heteropolarity of the M-M' bond and resulting reduction in electron deficiency at the Cu atom (7c). In solution, only one form (which is non-rigid) of each complex was found [23].



(7a)



(7b)



(7c)

Stable adducts $[Ag\{M(CO)_4(L_2)\}_2]^+$ were isolated as BF_4^- or PF_6^- salts by simple addition of AgX (X = BF_4, PF_6) to $M(CO)_4(L_2)$ (M = Mo, L_2 =

dppm, dppe; M = W, L_2 = dppe), and are seven-coordinate complexes containing Ag-M bonds [24].

Mn-Re Further studies of the scrambling reaction

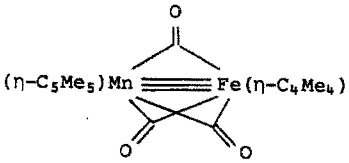
$$Mn_2(CO)_{10} + Re_2(CO)_{10} \rightleftharpoons 2MnRe(CO)_{10}$$

have appeared. In contrast with the photochemical reaction, no detectable amounts of $MnRe(CO)_{10}$ were formed from equimolar amounts of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ held at 130°C for 92 h, although slow conversion to the heterometallic carbonyl occurred at 140°C [25]. Both this reaction, and the reverse, which proceeded slowly at 130°C under N_2, were inhibited by added CO. At higher temperatures (170-190°C), however, a clean reaction proceeded to a stable equilibrium mixture via two paths [26]. One involved prior aggregation to tetranuclear $Mn_2Re_2(CO)_{20}$ which lost CO stepwise to give quasi-tetrahedral cluster intermediates containing Mn-Re and Mn(μ-CO)Re bonds. This was followed by CO insertion, either directly or after redistribution of M-M and M(μ-CO)M bonds in the cluster, to give an $Mn_2Re_2(CO)_{20}$ species containing two Mn-Re bonds, which fragmented to give product. The second, minor, pathway proceeded via loss of CO prior to aggregation. Kinetic studies suggested that scrambling occurred via $Mn_2Re_2(CO)_{16}$. Equilibrium constants measured for the scrambling reaction gave values of $\Delta H^{\emptyset}$, 34.4 ± 1.3 kJ mol^{-1} and $\Delta S^{\emptyset}$, 80.3 ± 2.5 J K^{-1} mol^{-1} [27].

Pulse radiolysis of $MnRe(CO)_{10}$ has been used to generate the $Re(CO)_5$ radical, together with a longer-lived species which was not further characterised [28]. The manganese apparently formed $[Mn(CO)_5]^-$. Neutron irradiation of $MnRe(CO)_{10}$ gave total yields of 25, 32 and 36%, respectively, for ^{56}Mn, ^{186}Re and ^{188}Re, which were found as $M_2(CO)_{10}$, $M(CO)_5$ and $M(CO)_4$ (M = Mn or Re), as well as $MnRe(CO)_{10}$. The yield of $M(CO)_5$, but not of $M(CO)_4$, was markedly reduced by thermal treatment after irradiation [29].

The heterobinuclear formyl complex Li[MnRe(CO)$_9$(CHO)] was obtained from Li[HBEt$_3$] and MnRe(CO)$_{10}$; it was a weaker hydride donor, e.g. to PhCHO, Fe(CO)$_5$, than the homonuclear Mn$_2$ and Re$_2$ complexes. Thermal decomposition gave MnRe(CO)$_{10}$, together with Li[M(CO)$_5$] (M = Mn, Re) [30].

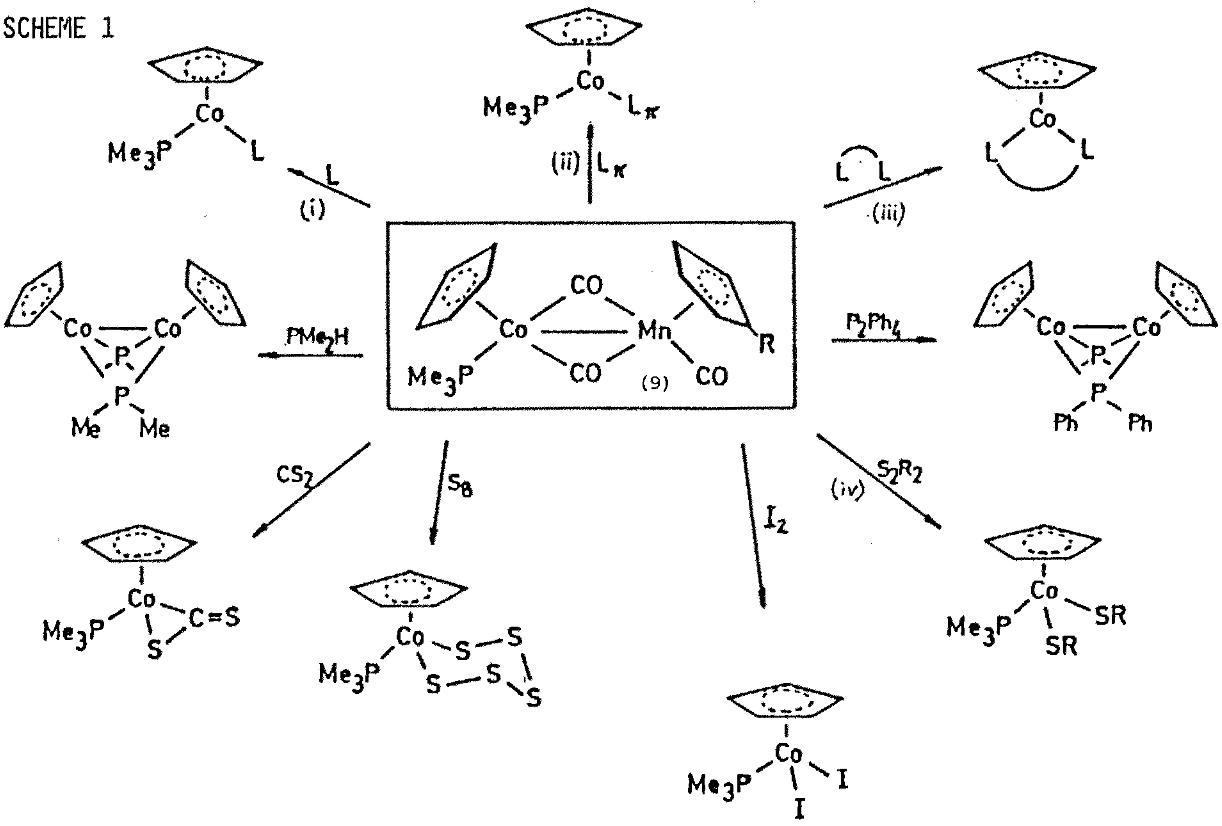
Mn-Fe UV irradiation of a mixture of Mn(CO)$_3$(η-C$_5$Me$_5$) and Fe(CO)$_3$-(η-C$_4$Me$_4$) in thf afforded brown-black (8), containing an Mn≡Fe triple bond [3].



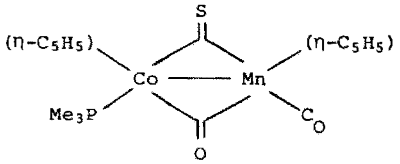
(8)

Mn-Co Reactions of MnCo(μ-CO)$_2$(CO)(PMe$_3$)(η-C$_5$H$_5$)(η-C$_5$H$_4$R) (9; R = H or Me) [from Co(L)(PMe$_3$)(η-C$_5$H$_5$) (L = CO or PMe$_3$) and Mn(thf)(CO)$_2$(η-C$_5$H$_4$R)] are summarised in Scheme 1 [31,32]. They proceed by cleavage of the Mn-Co bond and displacement of the Mn(CO)$_3$(η-C$_5$H$_4$R) "ligand" from the coordinatively unsaturated Co(PMe$_3$)(η-C$_5$H$_5$) fragment, which then reacts with a range of nucleophiles and electrophiles. The (η-C$_5$Me$_5$)Co analogue has also been described [33]. Reaction of (9) with Co(η^2-SCS)(PMe$_3$)(η-C$_5$H$_5$) afforded the cluster complex Co$_3$(μ$_3$-CS)(μ$_3$-S)(η-C$_5$H$_5$)$_3$. Complex (10), the CS analogue of (9), was obtained from Co(CS)(PMe$_3$)(η-C$_5$H$_5$) and Mn(thf)(CO)$_2$(η-C$_5$H$_5$); if two equivalents of the Mn complex were used, (11) was obtained quantitatively. Addition of PMe$_3$ to (11) gave (10) and Mn(CO)$_2$(PMe$_3$)(η-C$_5$H$_5$) [34]. Alkylation of (10) with CF$_3$SO$_3$Me afforded the μ-thiocarbyne complex (12).

SCHEME 1



Reagents: (i) L = PMe_3, PPh_3, $P(OMe)_3$, $P(OPh)_3$; (ii) L_π = $CH_2{=}CHCN$, *cis-* and *trans*-$CH(CO_2Me){=}CH(CO_2Me)$, maleic anhydride, C_2Ph_2; (iii) LL = dppe, nbd; (iv) R = Me, CH_2Ph, Ph.



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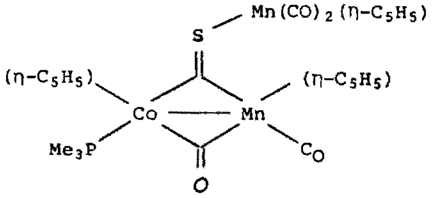
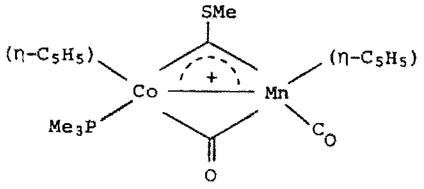
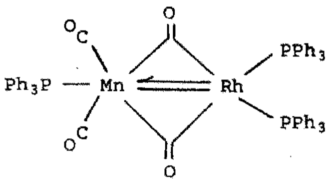


(11)



(12)

Mn-Rh Treatment of $RhCl(PPh_3)_3$ with $[Mn(CO)_5]^-$ afforded (13) in a reaction involving loss of NaCl and transfer of PPh_3 from Rh to Mn [20]. As with the Mo and W analogues, there is a dative Rh → Mn bond. Irradiation (UV) with nitrosodurene (L) gave $[Mn(CO)_n(PPh_3)(L)]^{\bullet}$, and with O_2, $[Mn(CO)_n(PPh_3)(O_2)]^{\bullet}$, both identified by ESR.



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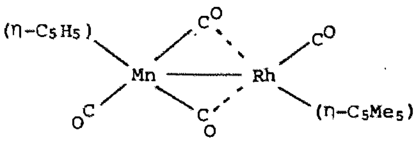
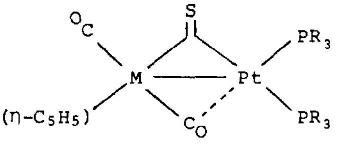


(14)

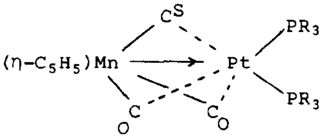
The yellow-brown complex (14), in which the Mn-Rh bond is semi-bridged by two CO ligands, was prepared from $Mn(thf)(CO_2)(\eta\text{-}C_5H_5)$ and

$Rh(CO)_2(\eta\text{-}C_5Me_5)$ [35].

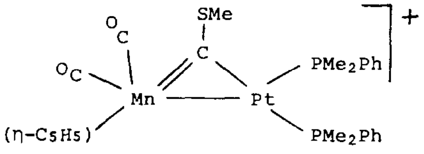
Mn,Re-Pt Addition of $M(CO)_2(CS)(\eta\text{-}C_5H_5)$ (M = Mn or Re) to $Pt(\eta\text{-}C_2H_4)(PR_3)_2$ gave complexes (15); the X-ray study of (15a) showed the presence of μ-CS and semi-bridging CO ligands [36]. In solution, site exchange for CO and PR_3 ligands was observed, possibly via rotation of the $Pt(PR_3)_2$ moiety within a pocket of semi-bridging CO and CS ligands attached to M (15d). Alkylation of (15b) with $[Me_3O][BF_4]$ gave (16), containing a μ-thiocarbyne ligand, which undergoes CO, but not PR_3, site exchange.



(15)	M	PR_3
a	Mn	$PMePh_2$
b	Mn	PMe_2Ph
c	Re	PMe_2Ph

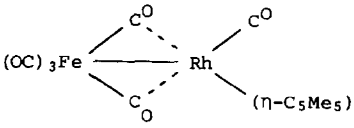


(15d)



(16)

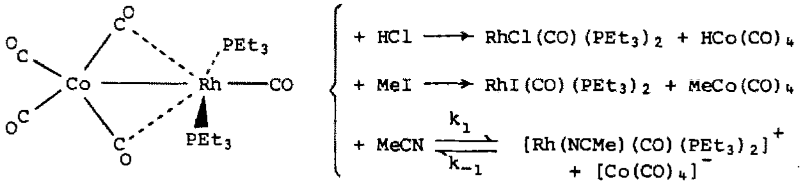
Fe-Rh The reaction between $Fe_2(CO)_9$ and $Rh(CO)_2(\eta\text{-}C_5Me_5)$ afforded (17), together with an Fe_2Rh cluster (see Part B). Purple (17) is isoelectronic with (14), and probably has a similar structure [35].



(17)

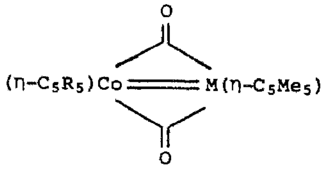
Os-Au   The electron-rich complexes Os(CNR)(PMe_3)(η-C_6H_6) (R = Me, tol) acted as bases towards AuCl(PPh_3), affording [Os{Au(PPh_3)}(CNR)(PMe_3)(η-C_6H_6)]Cl [37].

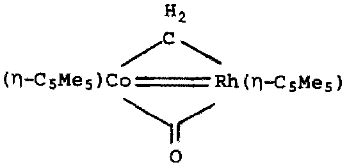
Co-Rh,Ir   The complex CoRh$(CO)_5(PEt_3)_2$ (18) underwent reversible heterolytic cleavage of the Co-Rh bond in weakly coordinating solvents. Orange-red (18) was formed from K[Co$(CO)_4$] and RhCl(CO)$(PEt_3)_2$; the axial CO groups on Co point towards the Rh atom [38]. Reactions of (18) indicated a dipolar Co-Rh bond, the reaction with MeCN being fast (rate constants $k_1 = 1.7 \times 10^4$, $k_{-1} = 5.1 \times 10^6$ M^{-1} s^{-1}, at 20°C in MeCN/thf).



(18)

Reactions between Co(η-C_2H_4)$_2$(η-C_5R_5) and M$(CO)_2$(η-C_5Me_5) afforded the black complexes (19a-c; M = Rh, R = Me [3,39]; M = Ir, R = H, Me [3]). Quantitative addition of CH_2 (from CH_2N_2 at -78°C) occurred; the Co-Rh complex lost CO when heated in toluene to give (20) [39]. Addition of a second equivalent of Co(η-C_2H_4)$_2$(η-C_5H_5) to (19b) gave a Co_2Ir cluster (see Part B).





(19)	R	M
a	Me	Rh
b	H	Ir
c	Me	Ir

(20)

Ir-Pd The reaction between $Ir(CO_2Me)(CO)_2(PPh_3)_2$ and *cis*-$PdCl_2(NCPh)_2$ was reported to give $(Ph_3P)_2Ir(CO)_2PdCl_2$, which reacted with H_2 and CO to give Pd and an iridium phosphine-carbonyl complex [40].

Rh,Ir-Group IB The mixed-metal complexes $(Ph_3P)Ir(CO)_3Cu(PPh_3)$ and $(Ph_3P)_2Rh(CO)_2Au(PPh_3)$ were prepared from $[Ir(CO)_3(PPh_3)]^-$ and $CuCl(PPh_3)$, and from $(Rh(CO)_2(PPh_3)_2]^-$ and $AuCl(PPh_3)$, respectively [41]. The Rh-Au complex reacted with CO_2, but no pure product was obtained; the Ir-Cu compound decomposed under these conditions.

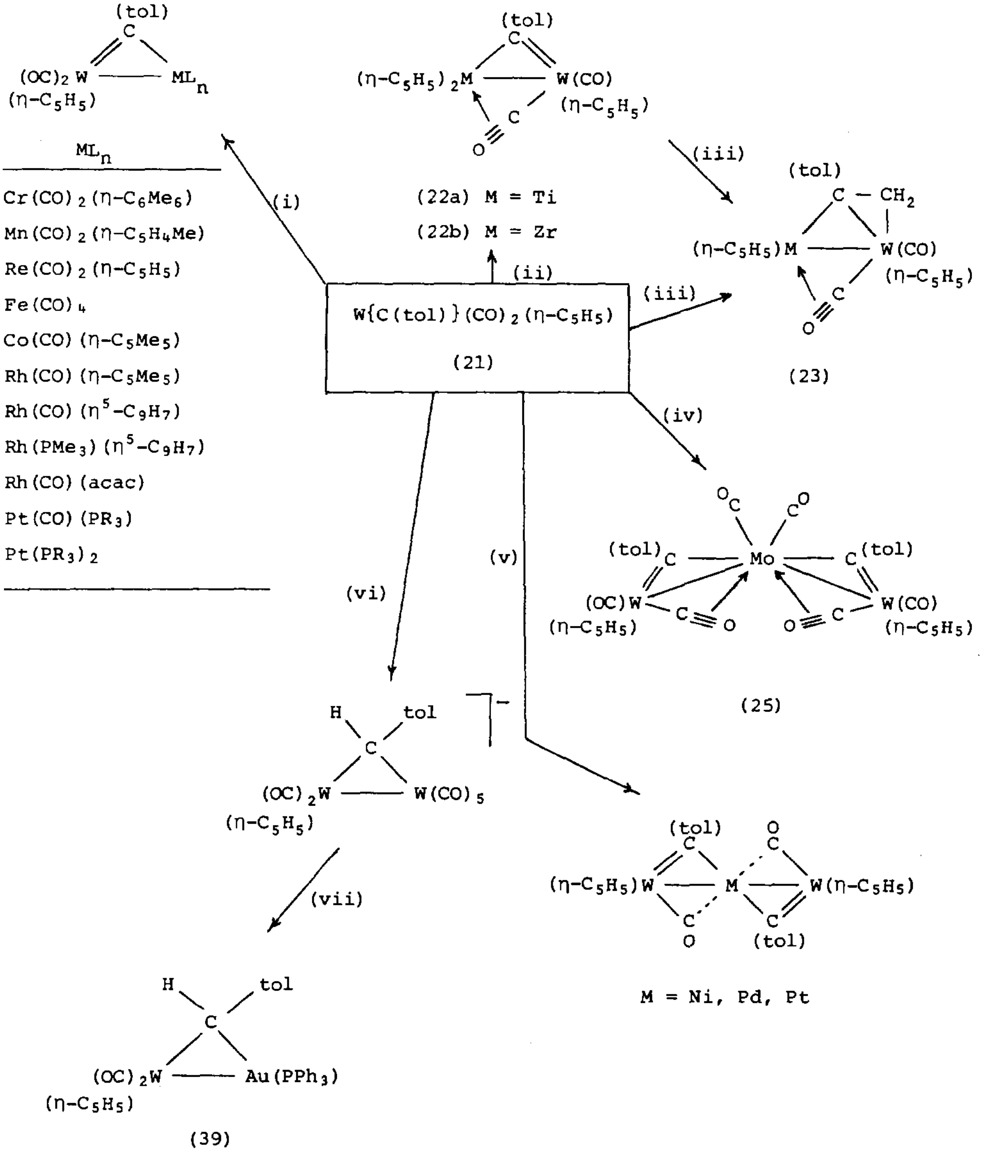
The reaction between $Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)$ and $AgPF_6$ afforded $Ag[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]_2$, which acted as a stabilised source of the 17e species $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ [42]. For example, with NO, a mixture of Ag metal, $Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)$ and $[Rh(NO)(PPh_3)(\eta\text{-}C_5H_5)][PF_6]$ was obtained.

2. HETEROMETALLICS FROM CARBENE, CARBYNE OR VINYLIDENE COMPLEXES

Complexes derived from $W[C(tol)](CO)_2(\eta\text{-}C_5H_5)$ *and related complexes*

This tungsten complex (21) continues to be a prolific source of heterometallic complexes, both binuclear (Scheme 2) and polynuclear (see Part B) [1]. The chemistry of many of these is now being developed, a notable example being that associated with the W-Pt derivatives described below. The general approach to the synthesis of mixed-metal complexes has been the reactions of (21) with various sources of low-valent metal fragments which can bond to the $W\equiv C$ triple bond in (21); some of these have been generated photochemically [4]. In these and related complexes the geometry of the bridging CO group serves as an indicator of the relative electron densities at the two metal atoms: in the TiW (22) and WPt complexes (30), for example, the CO group is either actually or incipiently η^2-bonding to Ti or Pt, whereas in the WCo or WRh complexes,

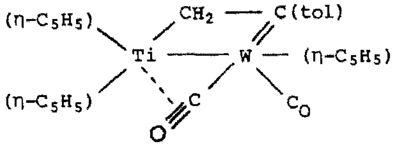
SCHEME 2



Reagents: (i) Various: see ref. [2,4]; (ii) $M(CO)_2(\eta\text{-}C_5H_5)_2$; (iii) Tebbe's reagent $[(\eta\text{-}C_5H_5)_2\overline{Ti(ClAlMe_2CH_2)}]$; (iv) *fac*-$Mo(CO)_3(NCMe)_3$; (v) $Ni(cod)_2$ (M = Ni); $Pd(\eta^2\text{-}C_7H_{10})_3$ (M = Pd); $Pt(\eta\text{-}C_2H_4)_3$ (M = Pt); (vi) $[HW(CO)_5]^-$; (vii) $AuCl(PPh_3)$.

the semi-bridging CO is transferring charge from Rh to W. In the CrW derivative, the μ-CO ligand is terminally bonded to Cr, suggesting that it is the tungsten centre which is the more electron-rich.

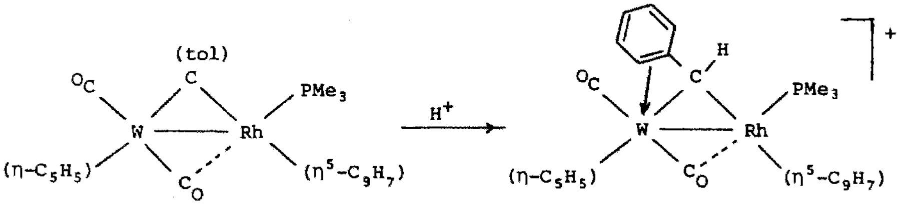
Formation of Ti,Zr-W heterometallic complexes (22) occurred on heating M(CO)$_2$(η-C$_5$H$_5$)$_2$ with W[C(tol)](CO)$_2$(η-C$_5$H$_5$); both complexes are thermally quite stable [43]. The X-ray study confirmed the presence of an μ-η^1,η^2-CO ligand suggested by IR ν(CO) bands at 1638 and 1578 cm^{-1} for the Ti and Zr compounds, respectively. Complex (23) was obtained from (22a) and Tebbe's titanium-methylene complex $\overline{\text{Ti(ClAlMe}_2\text{CH}_2}$)(η-C$_5H_5$)$_2$, although (22a) did not react with CH$_2$N$_2$ [44]. Tebbe's reagent also reacted with (21) to give (23), probably via an intermediate such as (24).



(24)

Purple (25) was formed on refluxing Mo(CO)$_3$(NCMe)$_3$ with (21), and contains a bent W-Mo-W sequence supported by bridging carbyne and CO groups [45]. Stepwise displacement of W[C(tol)](CO)$_2$(η-C$_5$H$_5$) units occurred on reaction with CO; the intermediate MoW complex is very unstable.

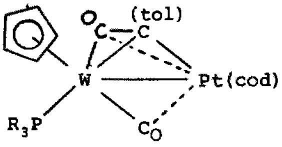
Addition of unsaturated metal-ligand fragments to the ketenyl complex W{η^2-OC=C(tol)}(CO)(PR$_3$)(η-C$_5$H$_5$) has given several heterometallic complexes [46]. With Rh(η-C$_2$H$_4$)$_2$(η^5-C$_9$H$_7$), complex (26) was formed, in which the W-Rh bond is bridged by μ-carbyne and semi-bridging CO ligands. The former ligand is attached asymmetrically, consistent



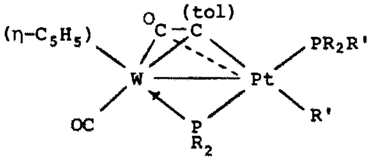
(26) (27)

with the presence of a dimetallacyclopropene system. Complex (26) is also formed from RhW[μ-C(tol)](CO)$_3$(η-C$_5$H$_5$)(η^5-C$_9$H$_7$) and PMe$_3$, a reaction which proceeds via displacement of W[C(tol)](CO)$_2$(η-C$_5$H$_5$) and formation of Rh(CO)(PMe$_3$)(η^5-C$_9$H$_7$), followed by combination of these two complexes. Protonation of (26) gave (27).

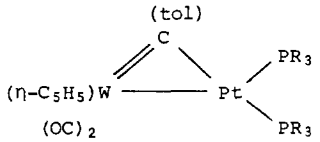
The ketenyl complex W[η^2-OC=C(tol)](CO)(PMe$_3$)(η-C$_5$H$_5$) reacted with Pt(cod)$_2$ to give (28a), in which the ketenyl-W moiety is coordinated to a Pt(cod) fragment. A similar complex was obtained containing PMe$_2$(CH$_2$Ph) as the tertiary phosphine. However, when the PMe$_2$Ph complex was used, a mixture of (28c) and (29a) was obtained; with the PMePh$_2$ complex, only (29b) was formed, while with the PPh$_3$ complex, the μ-carbyne derivative (30a) formed [46].



(28)	PR$_3$
a	PMe$_3$
b	PMe$_2$(CH$_2$Ph)
c	PMe$_2$Ph

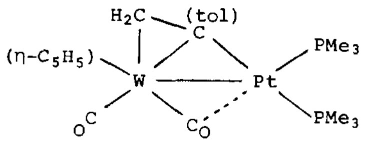


(29)	R	R'
a	Me	Ph
b	Ph	Me

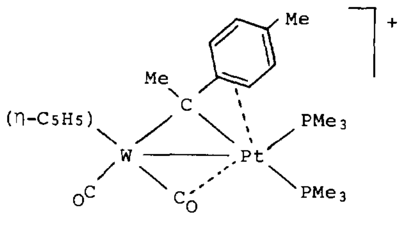


(30)	PR_3
a	PPh_3
b	PMe_3

Complex (30b) reacted with Tebbe's reagent to give yellow (31), which could also be obtained by deprotonation of (32); addition of $HBF_4 \cdot OEt_2$ to (31) reversed the reaction [44]. In turn, (32) was formed by alkylation of (30b) with $[OMe_3][BF_4]$; (30b) does not react with CH_2N_2.



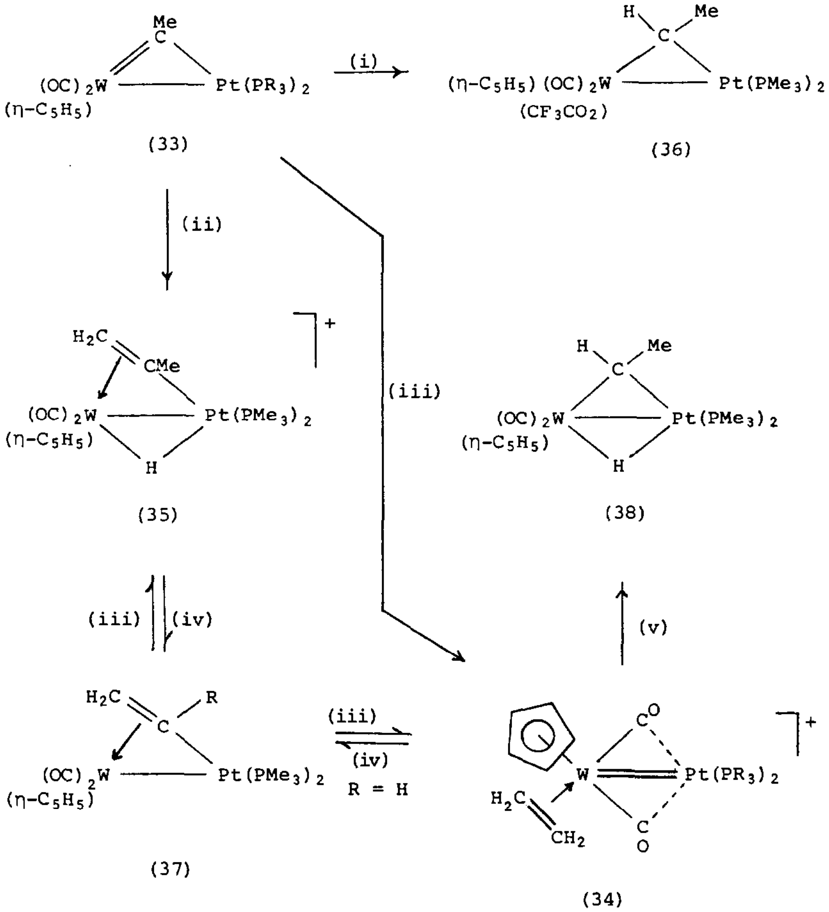
(31)



(32)

Scheme 3 shows the reactions of a CMe group bridging two different metal centres which occur on protonation or methylation [47]. Formation of the η-C_2H_4 complex (34), containing two semi-bridging CO ligands, occurs on protonation of (33). Methylation (CF_3SO_3Me) afforded cationic (35), containing a μ-vinyl ligand, while addition of CF_3CO_2H gave the μ-CHMe complex (36). Deprotonation of (34) or (35) affords neutral μ-vinyl complexes (37), addition of $HBF_4 \cdot Et_2O$ reversing these reactions. The hydrido-μ-carbene derivative (38) was obtained as a mixture of diastereomers from (34) and $NaBH_4$. Deuterium-labelling studies suggested that this transformation proceeds via attack on the η-C_2H_4 ligand to give the ethyl complex, which rapidly scrambles via β-elimination/(W-H + C_2H_4) addition sequences.

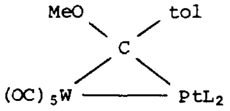
SCHEME 3



Reagents: (i) CF_3CO_2H; (ii) CF_3SO_3Me in CH_2Cl_2; (iii) $HBF_4.Et_2O$; (iv) $K[BHBu^s_3]$ in thf (R = Me); (v) $NaBH_4$; (vi) PMe_3.

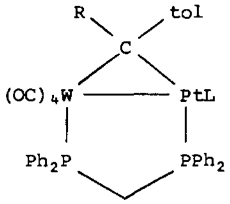
The anion $[(\eta\text{-}C_5H_5)(OC)_2\overline{W[\mu\text{-}CH(tol)]W}(CO)_5]^-$ (from $W[C(tol)](CO)_2(\eta\text{-}C_5H_5)$ and $[HW(CO)_5]^-$) reacted with $AuCl(PPh_3)$ to give the W-Au complex (39), in which the isolobal replacement $W(CO)_5 \leftarrow\!\!o\!\!\rightarrow Au(PPh_3)^+$ has occurred [45].

Complexes obtained from $W[C(OMe)R](CO)_5$ (R = Me or tol) Complex (40a) was formed by reaction of $W[C(OMe)(tol)](CO)_5$ with $Pt(cod)_2$; the cod ligand was readily displaced by $2PMe_3$, dppe or pdma to give (40b-d).



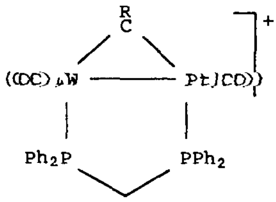
(40)	L_2
a	cod
b	$(PMe_3)_2$
c	dppe
d	pdma
e	dppm

However, with CO, the products were $W(CO)_6$ and $Pt_3[\mu\text{-}C(OMe)(tol)]_3(CO)_3$, the latter being obtained as a mixture of isomers; this reaction, and the complex mixture obtained from the reaction with $CNBu^t$ [containing $W(CO)_4(CNBu^t)_2$ and $Pt_3[\mu\text{-}C(OMe)(tol)]_x(CNBu^t)_y(CO)_z$], show that cleavage of the W-Pt bond occurs readily with π-acceptor ligands [48]. The

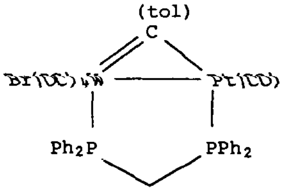


(41)	R	L
a	MeO	CO
b	MeO	η^1-dppm
c	Me	CO
d	H	CO
e	C_2Bu^t	CO
f	S(tol)	CO
g	C_5H_5	CO

analogous reaction with dppm afforded complexes (41a and b), formed via (40e) which readily isomerised to (41a), together with the homonuclear cluster $Pt_3[\mu\text{-}C(OMe)(tol)]_3(CO)_3$ [49]. Protonation of (41a) gave the cationic μ-carbyne complex (42), which afforded the neutral bromo derivative (43) on treatment with $[NEt_4]Br$; (43) was also obtained from (41a) and BBr_3, although in lower yield. Other reactions of (42) with nucleophiles (OMe^-, Me^-, H^-, $[C_2Bu^t]^-$ or $[S(tol)]^-$) gave complexes (41a,c-f), respectively; with $Mg(C_5H_5)_2$, the first-formed product was (41g), although only (44) could be isolated.



(42) R = tol
(48) R = Me



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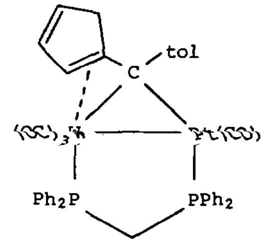
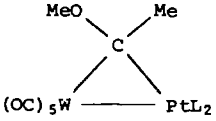
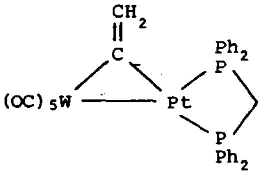


(44)

There are some interesting differences in the reactivities of the C(OMe)Me and C(OMe)(tol) complexes. Reaction of $W[C(OMe)Me](CO)_5$ with $Pt(cod)_2$ afforded (45a) which reacted with dppm to give (45b); unlike (40c) this complex was relatively stable, although if it was chromatographed on basic alumina, loss of MeOH afforded (46) [50]. Isomerisation

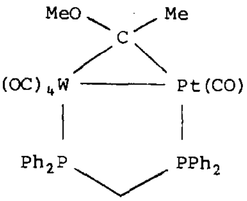


(45)	L_2
a	cod
b	dppm



(46)

of (45b) to the μ-dppm complex (47) occurred slowly (15 h in toluene), and was accompanied by formation of the (μ-dppm)(η^1-dppm) complex analogous to (41b). Protonation of (47) gave (48), which reacted with methoxide with the expected regeneration of (47), together with formation of (49), which could also be obtained by treatment of (48) with $K[HBBu^s_3]$.



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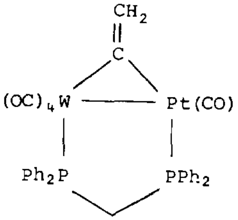
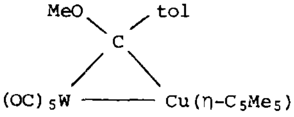


(49)

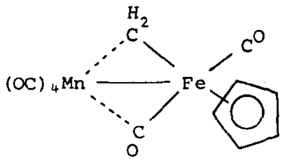
The reaction between $W[C(OMe)(tol)](CO)_5$ and $Cu(C_5Me_5)$ afforded (50), in which the $Cu(C_5Me_5)$ group behaves as an isolobal replacement for $Pt(PMe_3)_2$, and eventually, CH_2 [5].



(50)

Other heterobimetallics containing μ-carbene ligands Both crystalline forms of (51) are disordered, with each bridging site being occupied statistically by (0.5 CH_2 + 0.5CO) [51].

Addition of $[Co(CO)_4]^-$ to $[Fe\{C(SMe)_2\}(NCMe)(CO)(\eta\text{-}C_5H_5)]^+$ afforded (52), which could be oxidised (I_2, Br_2, CPh_3^+, $C_7H_7{}^+$, FcH^+; two equivalents) to $[Fe\{C(SMe)_2\}(CO)_2(\eta\text{-}C_5H_5)]^+$ (52).



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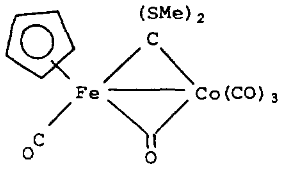
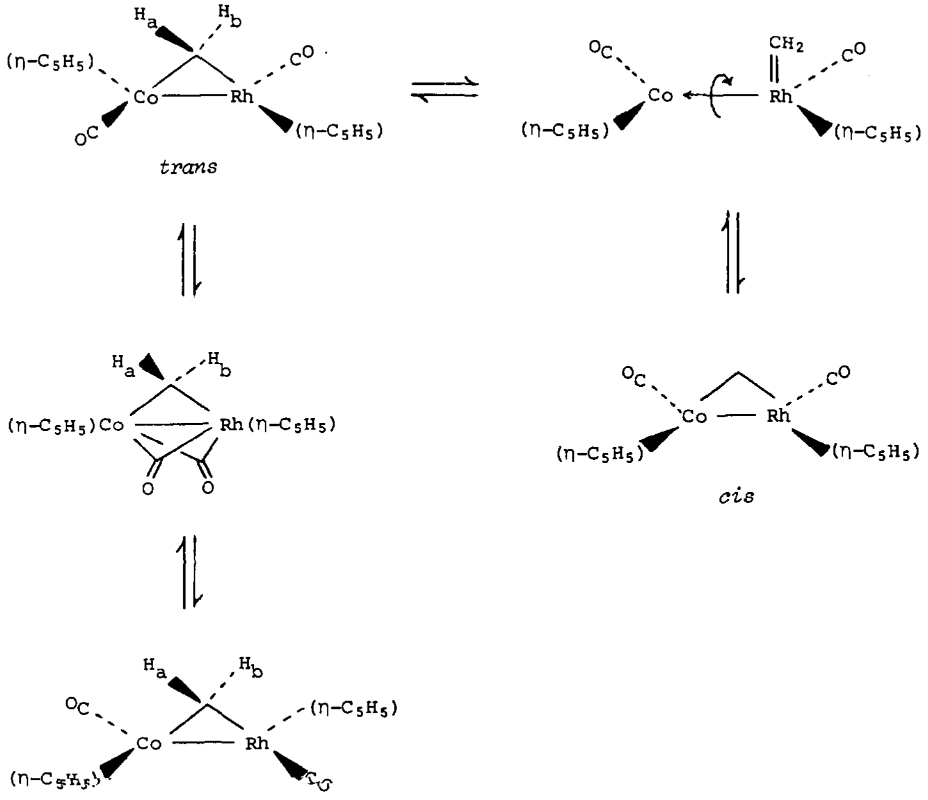


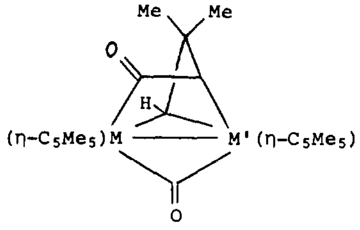
(52)

A mixture of (53) and the analogous Co_2 and Rh_2 complexes was obtained after heating $Rh(CO)_2(\eta\text{-}C_5H_5)$ with $Co_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)$ in benzene {53}. In solution (53) exists as a mixture of *cis* and *trans* isommers, which interconvert by cleavage of a Co-C bond, and rotation about the Co-Rh bond ($\Delta G^{\ddagger}_{c\rightarrow t}$ 71.1, $\Delta G^{\ddagger}_{t\rightarrow c}$ 76.2 kJ mol^{-1}). A second dynamic process is interconversion of the two enantiomers of *trans*-(53), which is thought to proceed via μ-CO intermediates ($\Delta G^{\ddagger}$ 54.4 kJ mol^{-1}).



(53)

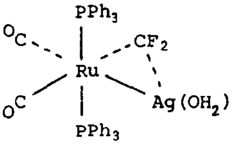
The reaction of 3,3-dimethylcyclopropene with $CoRh(\mu-CO)_2(\eta-C_5Me_5)_2$ afforded (54); the CoRh complex had a higher reactivity than either homodimetallic analogue [54]. The unusual bridging ligand contains a μ-carbene centre, and is believed to be formed by CO-insertion into one of the four metal-C bonds of a dicarbene intermediate formed by addition of the cyclopropene across the Co=Rh double bond.



M,M' = Co, Rh

(54)

The difluorocarbene complex $Ru(CF_2)(CO)_2(PPh_3)_2$ reacted with $Ag[SbF_6]$ to give (55), and with $[NEt_4][AuI_2]$ to give (56) [55]. The methylene complex $Os(CH_2)Cl(NO)(PPh_3)_2$ reacted with the latter reagent to give (57); formation of a similar adduct with $AuCl(PPh_3)$ is readily reversible, and even in (57), the Au-Os and Au-C interactions are weak [56].



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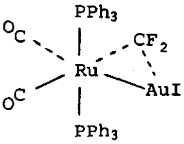

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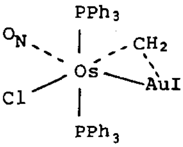
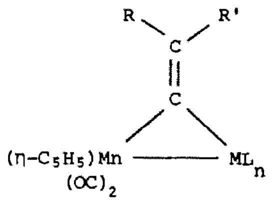
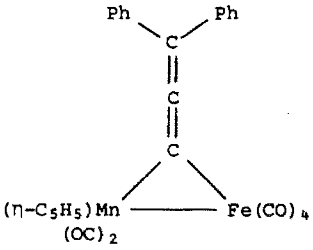


(57)

Heterometallic complexes containing μ-vinylidene ligands Two isomers of the heteronuclear complex (58) were obtained from reactions between $Fe_2(CO)_9$ and either $Mn(C{=}CHCO_2Me)(CO)_2(\eta\text{-}C_5H_5)$ or $Mn(\eta^2\text{-}HC{\equiv}CCO_2Me)\text{-}(CO)_2(h\text{-}C_5H_5)$; although there is a twist of *ca* 7° about the C=C double bond, the MnFeC system is stable towards isomerisation. The μ-allenylidene derivative (59) was similarly obtained from $Fe_2(CO)_9$ and $Mn(C{=}C{=}CPh_2)(CO)_2(\eta\text{-}C_5H_5)$ [57].



(58)	ML_n	R	R'
a	$Fe(CO)_4$	H	CO_2Me
b	$Fe(CO)_4$	CO_2Me	H
c	$Pt[P(OEt)_3]_2$	H, Ph	

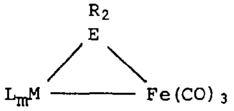


(59)

The vinylidene-bridged Mn-Pt complex (58c) was obtained from the reaction between $Mn(C{=}CHPh)(CO)_2(\eta\text{-}C_5H_5)$ and $Pt[P(OEt)_3]_4$, together with $Mn[\eta^2\text{-}CHPh{=}CHP(O)(OEt)_2](CO)_2(\eta\text{-}C_5H_5)$ [58].

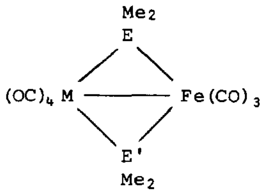
3. CHEMISTRY OF COMPLEXES CONTAINING $\mu\text{-}ER_2$ (E = P, As) OR $\mu\text{-}SR$ (E = S, Se) GROUPS

Complexes (60) have been considered as possible hydrogenation catalysts for CO or alkenes [59]. The Mo and Mn compounds added CO with M-M' bond cleavage; under hydrogen, the complexes decomposed with relative stabilities Mo > Mn > Co. No formation of MeOH or CH_4 was found when any of the compounds was heated with CO/H_2 mixtures. However, their solutions catalysed the isomerisation 1-octene → *cis*- and *trans*-2-octene, and the conversion of 1-octene to n-octane under H_2, suggesting the formation of hydrido-metal species.

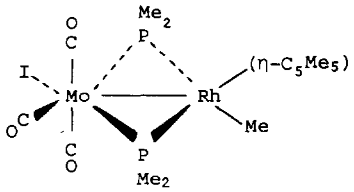


(60)	ML_n
a	$Mo(CO)_2(\eta\text{-}C_5H_5)$
b	$Mn(CO)_4$
c	$Co(CO)_3$

Group VI-Fe Heterodinuclear complexes (61) containing Cr, Mo or W-Fe bonds were obtained from $M(CO)_4(EMe_2X)_2$ (M = Cr, Mo or W; E = P or As; X = H, Li or Cl) and $FeY_2(CO)_4$ (Y = K or I). A comprehensive discussion of their electronic spectra and redox properties was included [60].



(61)	M	E	E'
	Cr	P	P
	Mo	P	P
	W	P	P
	Cr	P	As
	Cr	As	As
	Mo	As	As
	W	As	As



(62)

Mo-Rh Oxidative addition of MeI to $(\eta\text{-}C_5Me_5)Rh(\mu\text{-}PMe_2)_2Mo(CO)_4$ occurred regiospecifically to give $(\eta\text{-}C_5Me_5)MeRh(\mu\text{-}PMe_2)_2MoI(CO)_3$ (62).

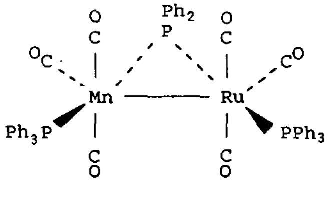
Structural and NMR parameters support the formal oxidative scheme:

$$Rh^{II} — Mo^{I} \xrightarrow{MeI} MeRh^{III} — Mo^{II}I$$

although some contribution from an Rh^{IV} - Mo^{I} structure is evidenced by IR data. In polar solvents, facile reversible dissociation of iodide was observed [61].

W-Ir The hydrido complex (63; Scheme 4) is formed from $Li[W(CO)_4(PHPh_2)(PPh_2)]$ and *trans*-$IrCl(CO)(PPh_3)_2$, and was considered to have a polar W^{0} - Ir^{III} bond [62]. No addition of H_2 to the Ir centre occurred. However, treatment with LiR (R = Me, Ph) afforded directly the stable acyl hydride complexes (64); subsequent methylation of (64) gave the stable carbene hydride complexes (65). Neither (64) nor (65) showed any evidence of hydride migration to the acyl or carbene carbon. Protonation of (64b) afforded the hydroxycarbene complex (66), which decomposed >25°C to PhCHO and (63). The reaction between (63) and $K[HBBu^{s}_3]$ gave the dihydride (67) rather than a formyl complex.

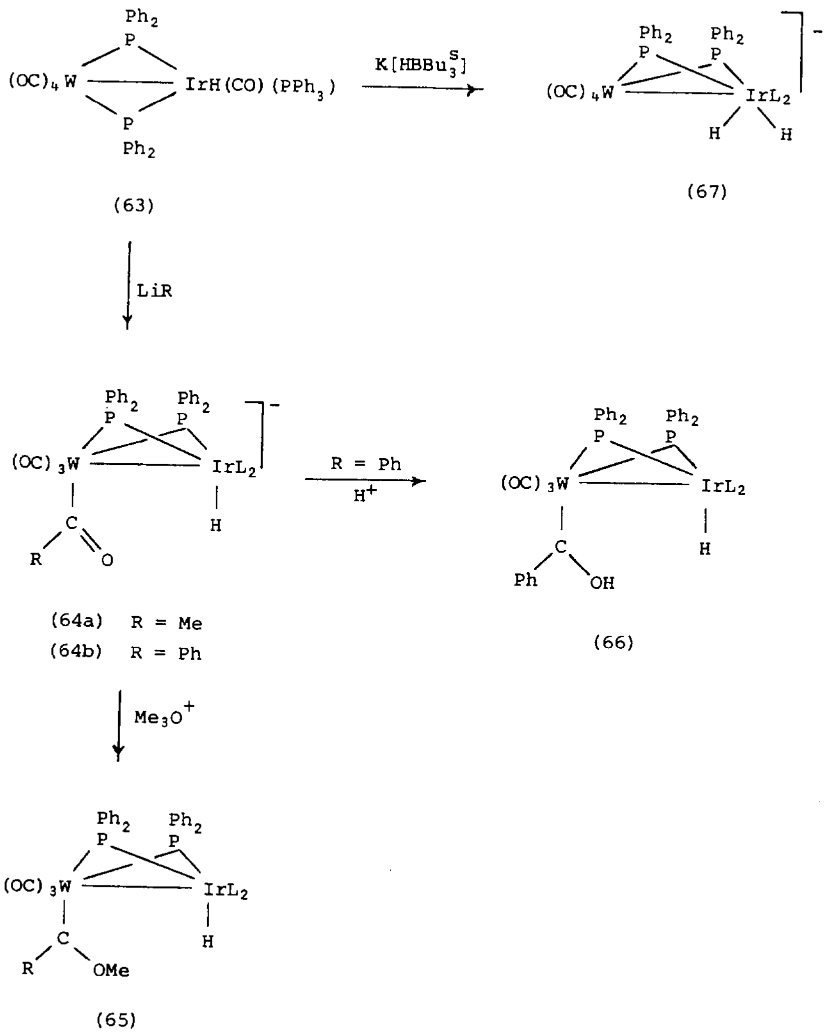
Mn-Fe,Ru The reaction between $Fe(CO)_4(HPMeCl)$ amd $[Mn(CO)_5]^-$ afforded $MnFe(\mu\text{-}PHMe)(CO)_8$ [63]. Complex (68) was obtained from the reaction of $[Mn(CO)_5]^-$ with $RuCl_2(PPh_3)_3$, together with $Ru(CO)_3(PPh_3)_2$; the reaction probably proceeds via a hydrido complex which eliminates C_6H_6 [64].



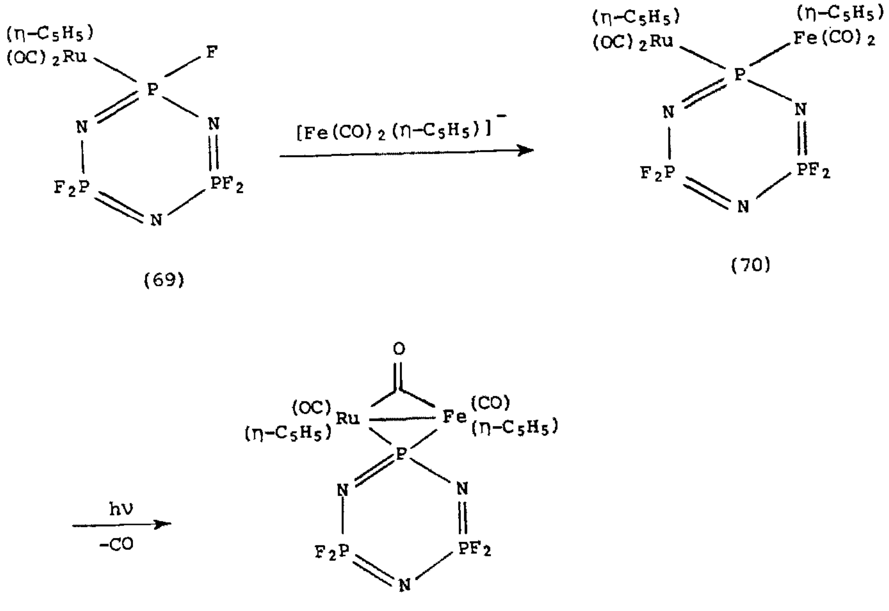
(68)

Fe-Ru Reaction of the cyclotriphosphazene $(NPF_2)_3$ with one equivalent of $[Ru(CO)_2(\eta\text{-}C_5H_5)]^-$ afforded (69; Scheme 5), which in turn reacted with $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ to give the disubstituted derivative (70); photolytic

SCHEME 4



SCHEME 5



(69)

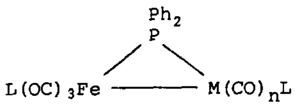
(70)

(71)

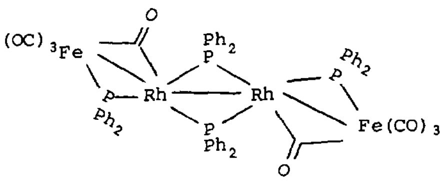
decarbonylation gave the phosphazene-bridged heterometallic complex (71) [65]. The mixed Fe-Ru derivative (70) was not obtained by the reverse reaction, only the long-sought $FeRu(CO)_4(\eta\text{-}C_5H_5)_2$ being formed instead. This complex, which can also be prepared from $FeI(CO)_2(\eta\text{-}C_5H_5)$ and $[Ru(CO)_2(\eta\text{-}C_5H_5)]^-$, disproportionated to the homonuclear Fe_2 and Ru_2 species on heating.

Fe-Co,Rh,Ir Reactions between $[Co(CO)_4]^-$ and $Fe(CO)_4(PMeRCl)$ (R = H or NMe_2) afforded $FeCo(\mu\text{-}PRMe)(CO)_7$; the μ-PHR' (R = Me or Bu^t) complexes exchanged H for Br on treatment with CBr_4 [63]. Nucleophilic attack on $FeCo(\mu\text{-}AsMe_2)(CO)_7$ by $M(SAsMe_2)(CO)_3(PMe_3)_2$ (M = Mn or Re) afforded the open trinuclear complexes $(Me_3P)_2(OC)_3M(\mu\text{-}SAsMe_2)Co(CO)_3(\mu\text{-}AsMe_2)Fe(CO)_4$ [66].

Reactions between $Li[Fe(CO)_4(PPh_2)]$ and *trans*-$MCl(CO)(PR)_3)_2$ (M = Rh, R = Et, Ph; M = Ir, R = Ph) afforded the complexes (72) [67,68]. A small amount of $FeIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)$ was also isolated from the appro-prioate reaction. The long Fe-Ir separation in (72c) suggests a weak donor-acceptor type interaction. In (72a), the Fe-bonded L is *trans* to the PPh_2 group, while the Rh-bonded L is *trans* to the Fe-Rh bond, whereas in (72c), both ligands L are *trans* to the PPh_2 group. The FeRh complexes, containing 16e Rh centres, reversibly added CO, while (72c) lost CO on heating or irradiation. The latter complex also added CO with cleavage of the Fe-Ir bond.



(72)	M	L	n
a	Rh	PEt_3	1
b	Rh	PPh_3	1
c	Ir	PPh_3	2
d	Ir	PPh_3	1

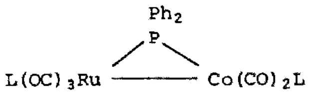


(73)

Addition of H_2 occurred similarly to (72c), whereas (72d) added $2H_2$, one to each metal centre, with loss of CO and retention of the Fe-Ir bond. Complex (72d) also gave an HCl adduct, which on heating (162°C, refluxing mesitylene) gave $Fe(CO)_3(PPh_3)_2$, *trans*-$IrCl(CO)(PPh_3)_2$ and $[Ir(\mu\text{-}PPh_2)(CO)(PPh_3)]_2$.

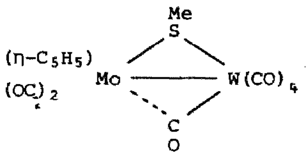
The straight-chain tetranuclear complex $Fe_2Rh_2(\mu\text{-}PPh_2)_4(CO)_8$ (73) was obtained from the reaction of $Fe(CO)_4(PHPh_2)$ with $[RhCl(\eta\text{-}C_5H_5)]_2$ in the presence of CO. In solution, NMR data suggest the presence of a *cis*-bent isomer [69].

Ru-Co Reactions between $Co_2(CO)_8$ and $RuCl_2(PPh_2X)(\eta^6\text{-}p\text{-cymene})$ (X = H or Cl) afforded $RuCo(\mu\text{-}PPh_2)(CO)_7$ (74a), together with a small yield of $RuCo(\mu\text{-}PPh_2)(CO)_4(\eta^6\text{-}p\text{-cymene})$ (for X = H) [70]. Complex (74b) was obtained from a reaction between $HRuCl(CO)(PPh_3)_3$ and $[Co(CO)_4]^-$, by coupling of the hydride with a Ph group of a PPh_3 ligand [71]. Addition of HCl to (74b) gave a mixture of $HRuCo(\mu\text{-}PPh_2)(Cl)(CO)_4(PPh_3)_2$ isomers, one of which contained a hydrido-bridged Ru-Co bond. With CO, successive replacement of the PPh_3 ligands gave $RuCo(\mu\text{-}PPh_2)(CO)_{7-n}(PPh_3)_n$ (n = 1,0). The markedly shorter Ru-Co bond compared with that found in the Fe-Ir complex (72c) was ascribed to the stronger tendency for Co to have an 18e configuration, thus avoiding the steric interaction of the two PPh_3 ligands in (72c).



(74a) L = CO

(74b) L = PPh_3

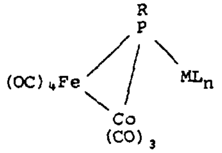


(75)

Group VI The thiolato bridged complexes MM'(μ-SR)(CO)$_8$(η-C_5H_5) (M,M' = Cr, Mo, W; R = Me or Ph) have been obtained from mixtures of M(CO)$_6$ and M(SR)(CO)$_3$(η-C_5H_5) after photolysis [72]. On heating, MM'-bonded complex (75) formed by loss of CO; photolysis under CO reversed this reaction. In (75), the semi-bridging CO allows distribution of electron density over the MM' system. On heating (75) with excess SMe$_2$, green (η-C_5H_5)(OC)-Mo(μ-SMe)$_3$W(CO)$_3$ was obtained.

Other complexes containing M-M' bonds bridged by Main Group elements

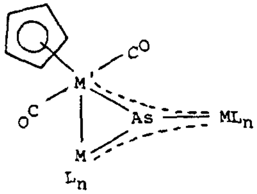
Introduction of a third metal carbonyl residue by interaction of carbonylmetallates with FeCo(μ-PRX)(CO)$_7$ (R = Me, X = Cl or Br; R = Bu^t, X = Br) gave (76a,b) [63].



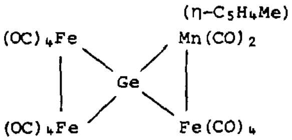
R = Me,Bu^t

(76a) ML$_n$ = Mn(CO)$_5$

(76b) ML$_n$ = Fe(CO)$_2$(η-C_5H_5)



(77)	M'	ML$_n$
a	Mo	Mn(CO)$_2$(η-C_5H_4Me)
b	Mo	Cr(CO)$_5$
c	W	Cr(CO)$_5$



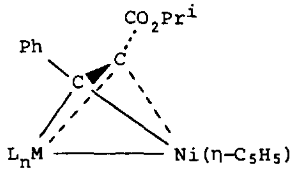
(78)

The unusual complexes (77) containing trigonal-planar As atoms bridging three metal atoms were obtained by reactions of ClAs[ML$_n$]$_2$ [ML$_n$ = Cr(CO)$_5$, Mn(CO)$_2$(η^5-C_5H_4Me)] with [M'(CO)$_3$(η-C_5H_5)]$^-$ (M' = Mo, W) [73]. M-M' bond formation with loss of CO accompanies the usual salt elimination reaction; the short M-As and M'-As distances (2.23-2.50Å) indicate considerable back-bonding from the metal atoms to As to compensate for its electron deficiency.

The red $GeMnFe_3$ complex (78) was obtained from the reaction between $Ge[Mn(CO)_2(\eta-C_5H_4Me)]_2$ and $Fe_2(CO)_9$, together with the related $GeFe_4$ derivative [74].

4. COMPLEXES CONTAINING M–M′ BONDS BRIDGED BY HYDROCARBON LIGANDS

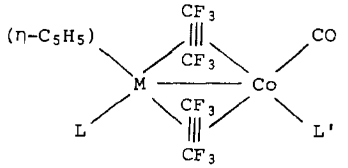
Alkynes The alkyne-bridged heterometallic systems (79) have been obtained from mixtures of the alkyne, $Co_2(CO)_8$, and $[Mo(CO)_3(\eta-C_5H_5)]_2$ or $Ni(\eta-C_5H_5)_2$ [75]. Such complexes are chiral if the two alkyne substituents differ; the rate of racemisation of these complexes could be measured by using CO_2Pr^i (diastereotopic Me groups) as one substituent. NMR studies showed that a facile racemisation process occurred which was rationalised on the basis of interconversion of *nido* clusters with an empty site (≡ tetrahedral MM'CC' cluster).



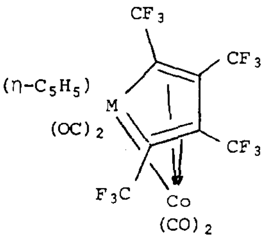
	ML_n
(79a)	$Mo(CO)_2(\eta-C_5H_5)$
(79b)	Co CO)$_3$

The synthesis and spectroscopic characterisation of the μ-alkyne complexes $[CoFe(\mu-R_2CC{\equiv}CR')(CO)_6$ and $[CoFe(\mu-R_2CC{\equiv}CCR_2OH)(CO)_5(PPh_3)]$ have been reported [76].

Reactions between $Co_2(CO)_8$ and $MCl[\eta-C_2(CF_3)_2]_2(\eta-C_5H_5)$ (M = Mo, W) afforded the bis(μ-alkyne) complexes (80a,b), which react with CO to give the metallacyclopentadiene complexes (81) by addition of CO to M. In contrast, CO-substitution reactions with PEt_3 gave (80c) and (80d) [77].

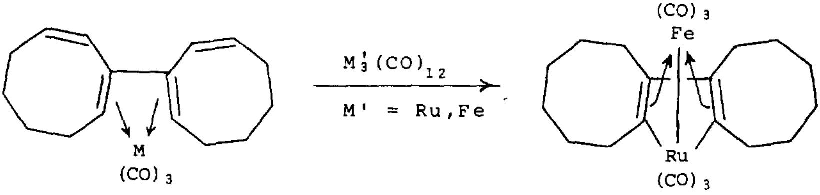


(80)	M	L	L'
a	Mo	CO	CO
b	W	CO	CO
c	Mo	PEt₃	CO
d	W	PEt₃	PEt₃



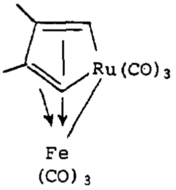
(81) M = Mo,W

Metallacyclopentadiene complexes Bi-2,7-cyclooctadienyl reacted with $M_3(CO)_{12}$ (M = Fe, Ru) to give (82), which reacted with the second $M_3(CO)_{12}$ to give (83) [78]. A mechanism involving formation of an intermediate metallacyclopentene, with hydrogen transfer, was proposed. In the presence of excess ligand, hydrogen was transferred to the free hydrocarbon. This latter reaction was used to prepare (84) from $Fe_3(CO)_{12}$, $Ru(CO)_3(\eta^4\text{-}CH_2\text{=}CMeCMe\text{=}CH_2)$ and the free diene as H-acceptor.



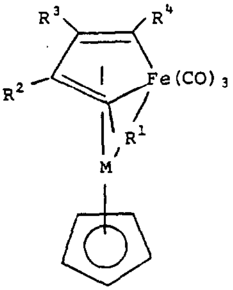
(82) M = Fe,Ru

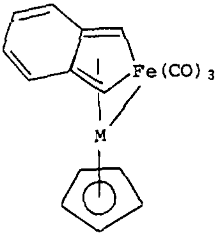
(83)



(84)

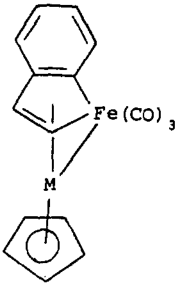
Two groups reported the synthesis of novel "metallametallocenes" (85), either by insertion of $M(CO)_2(\eta\text{-}C_5H_5)$ (M = Co, Rh) into η^4-cyclobutadiene-iron complexes [79], or from reactions between $Fe_2(CO)_9$ and cobaltacyclopentadienes [80]. Complexes (85a,b) were obtained from reactions between $Fe(CO)_3(\eta\text{-}C_4H_4)$ and $M(CO)_2(\eta\text{-}C_5H_5)$ (M = Co, Rh); similar Fe-Co derivatives were obtained from acylcyclobutadiene-$Fe(CO)_3$ complexes, the 2- and 3-substituted complexes being formed in ratios of 1:3 (acetyl) or 1:2:8 (benzoyl). Insertion of the $M(\eta\text{-}C_5H_5)$ fragment into (benzocyclobutadiene)$Fe(CO)_3$ afforded (86a,b). Ferrametallocenes (85) were also obtained in high yield from (87) and $M(CO)_2(\eta\text{-}C_5H_5)$, and also from the *sym*- and *unsym*-(benzoferrole)$Fe(CO)_3$ complexes, which also gave (86a,b), respectively. Both complexes (85a,b) are readily reduced [$E_{\frac{1}{2}}$ -1.39 (85a), -1.76 V (85b)], but are still sufficiently electron-rich to undergo Friedel-Crafts acylation reactions, substitution occurring at the carbon adjacent to Fe in the ferrole ring. Diacetylation of the Fe-Co complex (85a) was observed to give the 2,5-diacetyl derivative, *i.e.* substitution on both carbons adjacent to Fe. Complexes (85a,c-i) were obtained from reactions between $Fe_2(CO)_9$ and $\overline{\mathrm{Co(CR^1{:}CR^2CR^3{:}C}}\mathrm{R^4)(PPh_3)}$-$(\eta\text{-}C_5H_5)$ [80]. The stability of the observed metallametallocene structure over a possible alternative (88) was examined theoretically: (85) is the more stable by *ca* 17 kJ mol^{-1}, as a result of a better overlap of the d_{xy} orbital of the $Fe(CO)_3$ fragment with the diene.



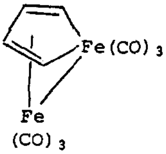


(sym)
(86a)

(85)	M	R^1	R^2	R^3	R^4
a	Co	H	H	H	H
b	Rh	H	H	H	H
c	Co	Ph	H	H	H
d	Co	Ph	H	Ph	H
e	Co	Ph	Ph	Ph	Ph
f	Co	Me	Me	Me	Me
g	Co	Ph	Ph	CO_2Me	CO_2Me
h	Co	Ph	CO_2Me	CO_2Me	Ph
i	Co	Ph	CO_2Me	Ph	CO_2Me



(unsym)
(86b)



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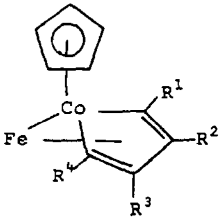

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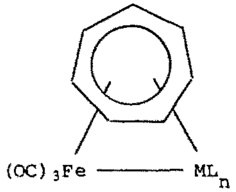
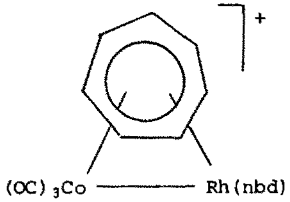


(89)

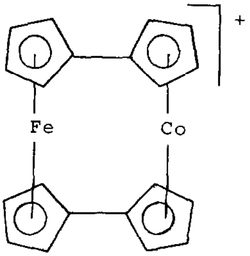


(90)

	ML_n		ML_n
a	Rh(C_6H_8)	f	Pd(C_4H_7)
b	Rh(nbd)	g	Rh$(CO)_2$
c	Rh(cod)	h	Rh$[P(OMe)_3]_2$
d	Ir(cod)	i	Rh$[P(OPh)_3]_2$
e	Pd(C_3H_5)		

Cyclic C_7 and C_8 polyolefins A series of M(μ-cycloheptatrienyl)M' complexes (89) has been obtained from reactions of Li[Fe$(CO)_3$(η^3-C_7H_7)] with suitable precursors. In this way, complexes (89a-d) were prepared from $[RhCl(diene)]_2$ (diene = 1,3-C_6H_8, nbd, cod) and $[IrCl(cod)]_2$, and (89e,f) from $[PdCl(all)]_2$ (all = η^3-C_3H_5,η^3-C_4H_7) [81]. Exchange of diene for CO or phosphites gave (89g-i). In contrast, addition of PPh_3 to (89e,f) afforded only Pd$(PPh_3)_4$. The Fe-Rh and Fe-Ir complexes are fluxional, the low temperature limiting spectrum of (89d) being obtained at -10°C. A related cationic Co-Rh complex (90) was prepared from Co$(CO)_3$(η^3-C_7H_7) and "[Rh(nbd)][BF_4]", while complexes containing Fe-Rh bonds bridged by cyclooctatetraene had been isolated earlier from reactions between Fe$(CO)_4$(η^4-C_8H_8) and $[Rh(diene)(L)_2]^+$. Structural and ^{103}Rh NMR studies [82] supported a structure with an η^3 interaction of the ring with the Fe$(CO)_3$ moiety, and η^4 or η^5 interactions with the RhL_2 fragments in the neutral and cationic complexes, respectively.

Other complexes The mixed Fe-Co bis(fulvalene) complex (91) was obtained by reacting a mixture of $FeCl_2(thf)_2$ and $CoCl_2(thf)_2$ with the fulvalene dianion (from NaC_5H_5 and I_2 at -60°C, followed by addition of LiBu); the chloride and PF_6^- salts were isolated. Cyclic voltammetry showed two waves ($\Delta E_{\frac{1}{2}}$ 1.64 V), and the observed paramagnetism [μ_{eff} 1.03 BM (77 K), 2.37 BM (295 K)] suggested a valence averaging process occurs; however, there is no Fe-Co bond present.



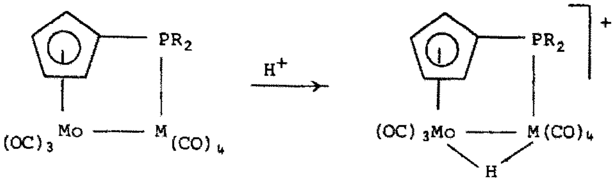
(91)

Bimetallic sulphur complexes of unknown structure, containing NiPd, NiPt or PdPt combinations, have been obtained from propene-elimination reactions between $[M(SH)(\eta\text{-}C_3H_5)]_2$ and $M'(\eta\text{-}C_3H_5)_2$ (M,M' = NiPd or Pt) [84].

5. COMPLEXES CONTAINING OTHER BRIDGING LIGANDS

Ligands containing hydrocarbon and Main Group donor sets

Halide exchange between $[M(\mu\text{-}Br)(CO)_4]_2$ (M = Mn, Re) and $Li[Mo(CO)_3(\eta\text{-}C_5H_4PR_2)]$ (R = Ph, tol) afforded the heteronuclear complexes (92) as yellow or orange solids. No addition of the H_2 to these complexes was found before decomposition set in [85]. Protonation of (92b,c) with CF_3SO_3H gave cationic complexes (93) in which the hydrogen bridges the Mo-M bond; the reaction was reversed on addition of NEt_3 or $Li[HBEt_3]$ [86].

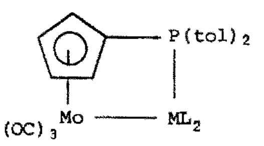


(92)	M	R
a	Mn	Ph
b	Mn	tol
c	Re	tol

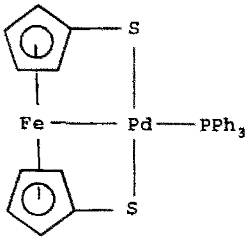
(93)

A series of Mo-Rh and Mo-Ir complexes (94) have been prepared by reactions of $Mo(CO)_3[\eta^5-C_5H_4P(tol)_2Li]$ with suitable chlorine-containing precursors [87]. Exchange of CO in (94b) for PMe_3 or $P(tol)_3$ was observed in the rhodium complexes; none reacted with H_2 to give metal hydrides.

The Mo-Ir complex (94e), obtained from $IrCl(CO)_2(tol)]$, also exchanged CO for PMe_3 or PPh_3, and all complexes afforded dihydride derivatives by ready oxidative addition of H_2 to the Ir centre. None of these compounds were effective catalysts for the hydrogenation of CO or cyclohexene.



(94)	M	L$_2$
a	Rh	dtpe
b	Rh	$(CO)_2$
c	Rh	$(PMe_3)_2$
d	Rh	$[P(tol)_3]_2$
e	Ir	$(CO)_2$
f	Ir	$(PMe_3)_2$
g	Ir	$(PPh_3)_2$



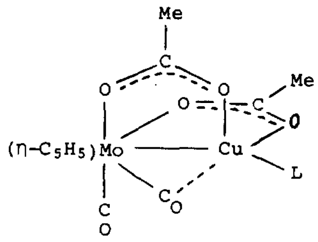
(95)

Addition of LiBu to Ti(η-C_5H_5)(η-C_7H_7), followed by reaction with $PClPh_2$, affords Ti(η-C_5H_5)(η-$C_7H_6PPh_2$), which was used to make bimetallic complexes by displacement of CO from $Mo(CO)_6$, $Fe(CO)_5$ or $Ni(CO)_4$. However, none of these complexes contain heterometallic bonds [88].

The unusual complex (95) was obtained from 1,2,3-trithia[3]-ferrocenophane and $Pd(PPh_3)_4$, and contains a weak dative Fe → Pd bond; a weak bond is also suggested by the C_5 ring tilt angle (19.6°) [89].

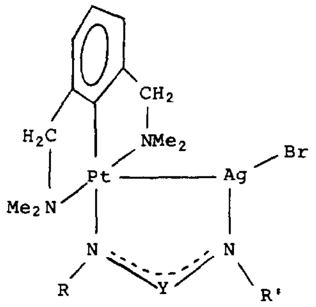
Anionic bridging ligands

Acetate-bridged Mo-Cu bonds are present in the complexes (96) obtained from $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ and $Cu_2(OAc)_4(L)_2$; similar W-Cu compounds are mentioned [90].



L = NC_5H_4R-4 (R = H, Me, Bu^t)

(96)

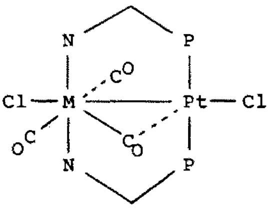


(97)	Y	R	R'
a	CH	tol	Me
b	CH	tol	Et
c	CH	tol	Pr^i
d	CH	tol	tol
e	N	tol	Me
f	N	tol	Et
g	N	tol	Pr^i

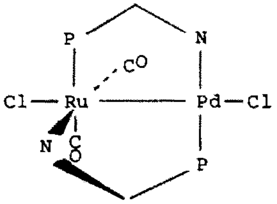
Binuclear complexes (97) containing μ-formamidino or μ-triazenido ligands were formed by reactions of AgL with $PtBr[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$; two isomers (R,R' interchanged) were obtained if unsymmetrical ligands are used, the relative proportions of which depend on steric and electronic properties of the substituents R'. For R' = Me, the illustrated isomer predominates; for R' = Et or Pr^i, the N(R') group is bonded to Pt [91]. The *trans*-N,N coordination of the Pt and resulting increased electron density enhances the stability of the Pt → Ag donor bond. Attempts to obtain isostructural and isoelectronic carbonylato complexes were unsuccessful. The INEPT NMR technique was applied to the ^{109}Ag NMR spectra of the formamidino complexes, and confirmed the presence of two isomers except in the (tol)NCHN(tol) complex. A direct Pt-Ag interaction was indicated by the first measurements of J (^{109}Ag-^{195}Pt) (*ca* 170 Hz) [92].

2-(Diphenylphosphino)pyridine (Ph_2Ppy) complexes

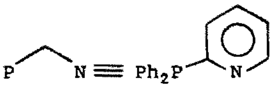
Complexes (98) containing Mo,W-Pt bonds were obtained from reactions between $Mo(CO)_4(nbd)$ [or $W(CO)_3(NCMe)_3$] and $PtCl(Ph_2Ppy)_2$; alternatively the Mo complex was formed from $Mo(CO)_4(P\text{-}Ph_2Ppy)_2$ and $PtCl_2(cod)$ [93]. In this case, the Ph_2Ppy ligand facilitates oxidative addition of the Mo or W halide to Pt; the thermodynamic head-to-head (*HH*) isomer is the only one isolated or detected.



M = Mo, W
(98)

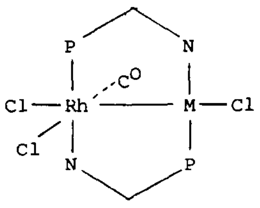


(99)



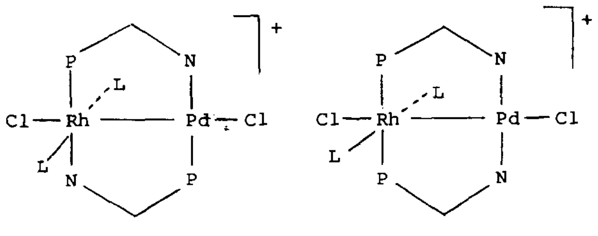
Reactions between $PdCl_2(cod)$ and $Ru(CO)_3(Ph_2Ppy)_2$ were complex, affording $RuCl_2(CO)_2(Ph_2Ppy)_n$ (n =1,2), $Pd_2Cl_2(Ph_2Ppy)_2$, and two isomers of the heterometallic complex $RuPdCl_2(CO)_2(Ph_2Ppy)_2$. The latter were more conveniently prepared from $RuCl_2(CO)_2(Ph_2Ppy)_2$ and $Pd_2(dba)_3$. The two isomers were interconverted on heating, and an X-ray structure of one of them showed it to have structure (99); the structure of the second isomer has not been determined unequivocally [94].

The same Rh-Pd complex (100) was obtained from reactions of $RhCl(CO)(Ph_2Ppy)_2$ with $PdCl_2(cod)$, and of $PdCl_2(Ph_2Ppy)_2$ with $[RhCl(CO)_2]_2$, and contains the bridging ligands in the head-to-tail (*HT*) arrangement. During these reactions, the Rh centre is oxidised [95]. ^{31}P NMR studies indicate that these reactions are complex, with at least one fluxional species (perhaps undergoing exchange of Cl and CO on Rh) being detected. A similar cationic complex (101) was prepared from $[Rh(CNMe)_2(Ph_2Ppy)_2]^+$ and $PdCl_2(cod)$, or from $[Rh(CNMe)_4]^+$ and $PdCl_2(Ph_2Ppy)_2$. The reaction between $[Rh(CNMe)_2(Ph_2Ppy)_2]^+$ and $PdCl_2(NCPh)_2$ afforded an isomeric cation in which both tertiary phosphine ligands are *P*-bonded to Rh. Conversion of the *HH* isomer of (101) to the thermodynamically more stable *HT* isomer occurs on heating: ^{31}P NMR studies show that the isomerisation is accompanied by formation of several other products.



(100) M = Pd

(102) M = Pt

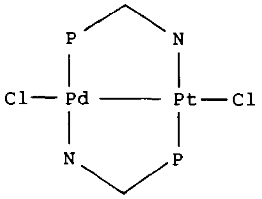


HT

HH

(101)

The ionic complex $[PtCl(PPh_2py)_2][RhCl_2(CO)_2]$ was obtained from reactions between $[RhCl(CO)_2]_2$ and *cis*-$PtCl_2(PPh_2py)_2$; on heating, it lost CO to form (102). The latter oxidatively added Cl_2 at the Pt atom to give $RhPt(\mu\text{-}PPh_2py)_2(CO)Cl_5$. The bromo analogues of both complexes were also prepared [96].

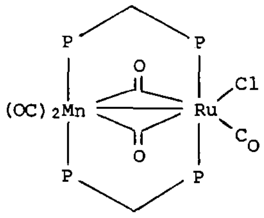


(103)

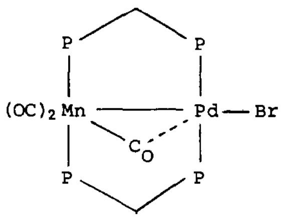
Reaction of $Pd_2(dba)_3$ with $PtCl_2(Ph_2Ppy)_2$ afforded $PdPtCl_2(\mu\text{-}Ph_2Ppy)_2$ (103) as the *HT* isomer. The analogous iodide, obtained similarly, exists as the *HH* isomer, with both bridging ligands P-bonded to Pt [97]. On heating in $CHCl_3$, isomerisation to the *HT* isomer occurs without any disproportionation to Pd_2 or Pt_2 complexes. The origin of the different isomers is kinetic, with the iodo complex reacting via the small amount of *trans* isomer present, whereas the *cis*-dichloro complex reacts via a different route to form the stable *HT* isomer.

Bis(diphenylphosphino)methane (dppm) complexes

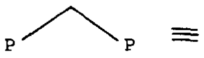
The reaction between *cis*-$RuCl_2(dppm)_2$ and $[Mn(CO)_5]^-$ gave red (104), together with an ionic derivative which is similar to the yellow, air-sensitive $[Ru_2(\mu\text{-}Cl)_3(PMe_3)_6][Mn(CO)_5]$ obtained from $RuCl_2(PMe_3)_4$ in an analogous reaction [64].



(104)



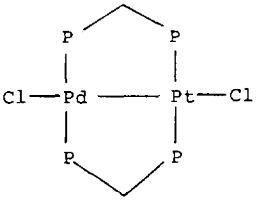
(105)



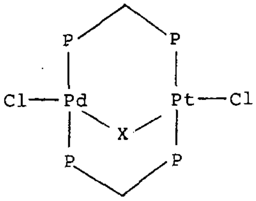
$Ph_2PCH_2PPh_2$
(dppm)

Reaction of $Pd_2(dppm)_3$ with $MnBr(CO)_5$ afforded (105); these and similar complexes were also obtained in higher yield by adding an intimate mixture of $Pd(dba)_2$, $MnX(CO)_5$ (X = Cl, Br, I) and dppm to refluxing toluene [98]. One CO ligand is semi-bridging, and the Mn---Pd separation is rather large. Metathetical exchange of halogen gave analogous azido, NCO and NCS derivatives, while addition of $SnCl_2$ gave the purple $SnCl_3$ complex. Complex (105) could be oxidised (Br_2, PhN_2^+) to $[MnPd(\mu\text{-dppm})_2(Br)(CO)_3]^+$, and in acetonitrile, addition of $AgBF_4$ afforded purple $[MnPd(\mu\text{-dppm})_2(NCMe)(CO)_3]^+$. Some catalytic activity in CO/H_2 and CO_2/H_2 reactions was noted.

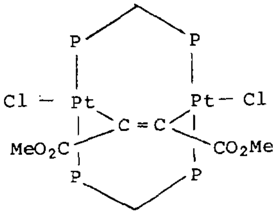
Remarkably, the mixed Pd-Pt complex (106) was obtained analytically pure in 83-92% yields from reactions between $PtCl_2(NCBu^t)_2$ and the red solution obtained from $Pd(PPh_3)_4$ and dppm [99]. Complex (106) does not disproportionate to the homobinuclear complexes, nor is (106) formed from mixtures of the Pd_2 and Pt_2 complexes; consequently this unusual reaction is the result of kinetic factors.



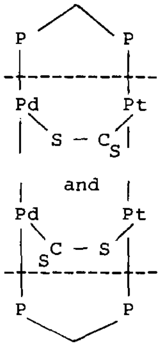
(106)



(107)	X
a	CO
b	SO_2



(108)



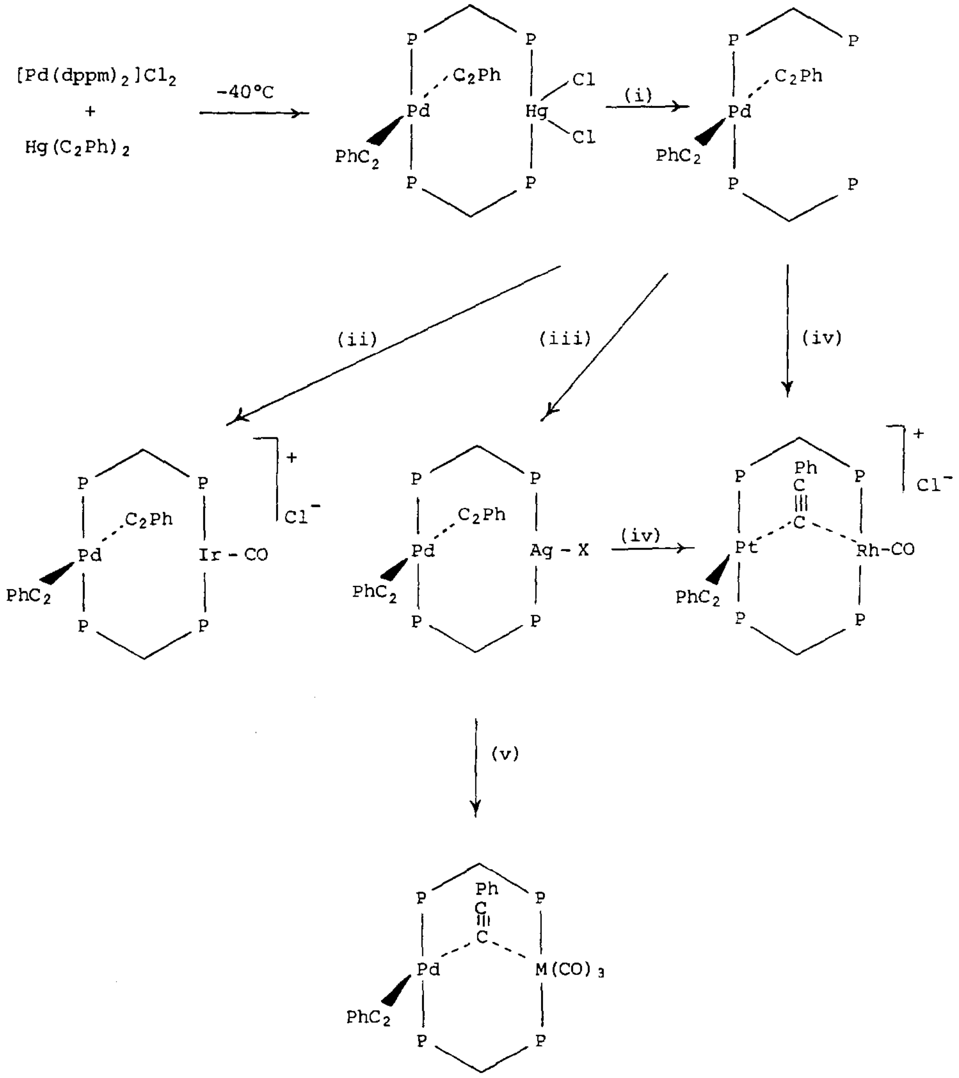
(109)

Ready exchange of Cl for Br, I or SCN occurred and complete Cl/I scrambling took place if 0.5 mole equivalent of NaI in acetone was used. As found for other μ-dppm complexes, small molecules readily inserted into the Pd-Pt bond, complexes (107)-(109) being obtained with CO, SO_2, CS_2 and $C_2(CO_2Me)_2$, respectively. Flushing a solution of (107a) with N_2 displaced the SO_2 (as found for the Pd_2 analogue, but not with the Pt_2 complex); addition of CO or CS_2 was also reversible, with SO_2 catalysing the reversible uptake of CO. The CS_2 complex was obtained as a mixture of isomers.

A large number of heterometallic complexes has been obtained by Shaw and coworkers who utilised the complexes $MR_2(\eta^1\text{-dppm})_2$ as chelating ligands to other metal-ligand systems. The rationale of the synthetic method has been to use a group R which has a strongly *trans* activating effect (such as acetylide, cyanide or alkyl), so that the tendency for the dppm ligand to chelate is reduced. Not all of the resulting complexes require the presence of an M-M' bond to satisfy the 18e rule, although it is likely that some interaction occurs as a result of the relatively short intermetallic distances resulting from the bite of the two bridging ligands. The scope of this chemistry, as reported in the two years under review, is illustrated in Schemes 6-10; it is evident that there is much more interesting and novel chemistry to be found in these systems.

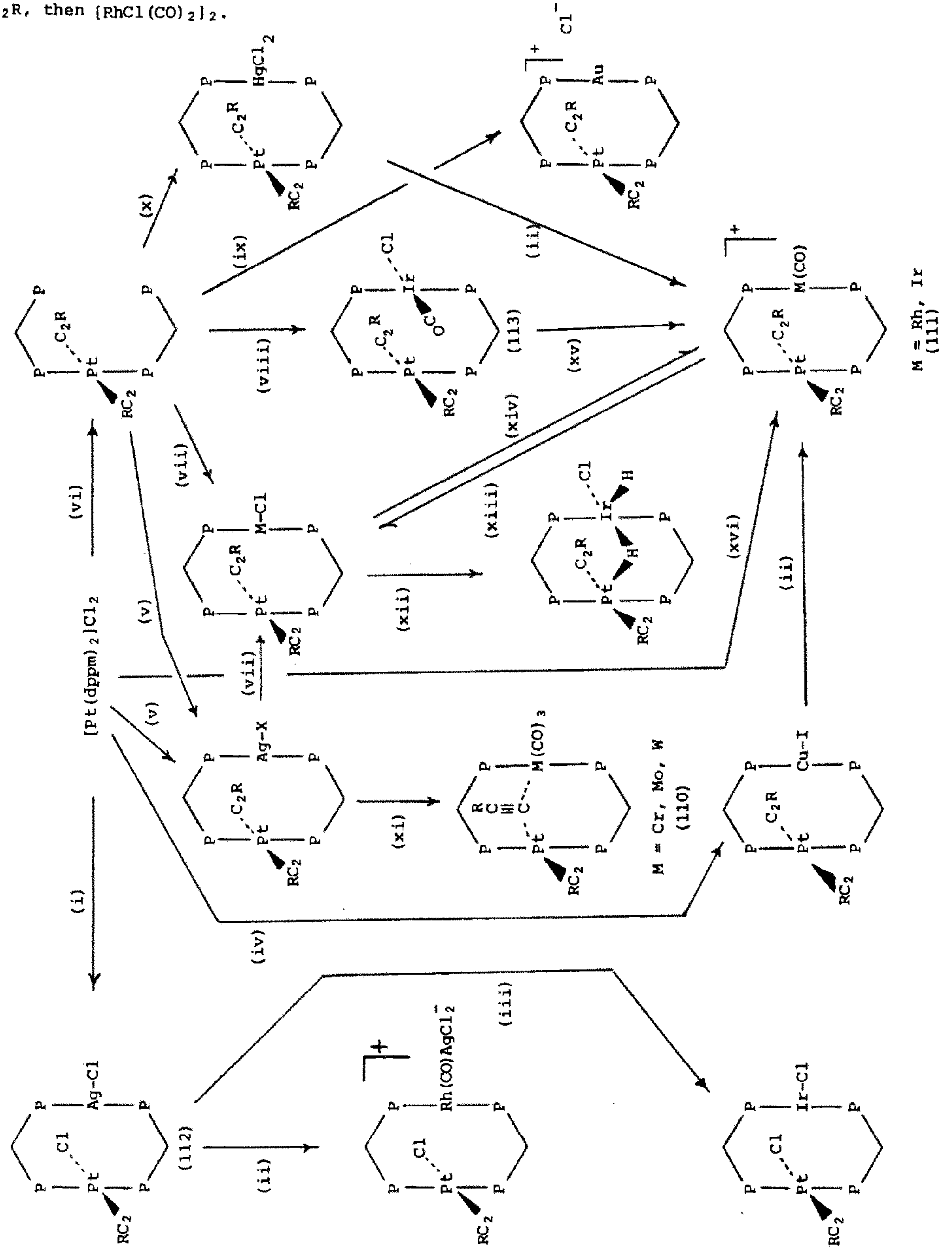
Thus the species $[M(dppm)_2]X_2$ (M = Pd, Pt; X = Cl, I) were readily converted to the corresponding *trans*-$M(C_2R_2)(\eta^1\text{-dppm})_2$, which interacted with *fac*-$W(CO)_3(NCMe)_3$, $[RhCl(CO)_2]_2$, $[M'Cl(C_8H_{14})]_2$ (M' = Rh or Ir), $IrCl(CO)(PPh_3)_2$, $AgNO_3$ or $AuCl(PPh_3)$ to give the mixed-metal complexes shown in Schemes 6 and 7 [100,101]. The Pt-Ag complex was also obtained directly from $[Pt(dppm)_2]X_2$ and a mixture of HC_2Ph and AgOAc; well-resolved NMR spectra were obtained at -50°C which allowed measurement of *J* $(^{31}P\text{-}^{107}Ag)$ and *J* $(^{31}P\text{-}^{109}Ag)$ (364 and 422 Hz, respectively, for

SCHEME 6



Reagents: (i) Na_2S; (ii) $[IrCl(C_8H_{14})]_2$, then CO; (iii) $[AgCl(PPh_3)]_4$ (X = Cl), $[AgI(PPh_3)]_4$ (X = I); (iv) $[RhCl(CO)_2]_2$; (v) $Mo(CO)_3(cht)$ (M = Mo), *fac*-$W(CO)_3(NCMe)_3$ (M = W).

SCHEME 7 R = Me, Ph, *p*-tol (but not all combinations) *Reagents:* (i) $AgOAc/HC_2R$ (1:1); (ii) $[RhCl(CO)_2]_2$; (iii) $[IrCl(C_8H_{14})]_2$; (iv) NaI, then $LiCu(C_2R)_2$; (v) $AgOAc/HC_2R$ (1:2) (X = Cl); $AgNO_3$, then NaI (X = I); (vi) LiC_2Ph; (vii) $[MCl(C_8H_{14})]_2$ (Rh, Ir); (viii) $IrCl(CO)(PPh_3)_2$; (ix) $AuCl(PPh_3)$; (x) $Hg(OAc)_2/HC_2R$; (xi) $Cr(CO)_4(nbd)$ (M = Cr); $Mo(CO)_4(nbd)$ or $Mo(CO)_3(cht)$ (M = Mo); *fac*-$W(CO)_3(NCMe)_3$ (M = W); (xii) H_2; (xiii) refluxing toluene, −CO; (xiv) CO; (xv) X^- (BF_4^-, PF_6^-, etc.); (xvi) one-pot synthesis from $Hg(OAc)_2$ + HC_2R, then $[RhCl(CO)_2]_2$.



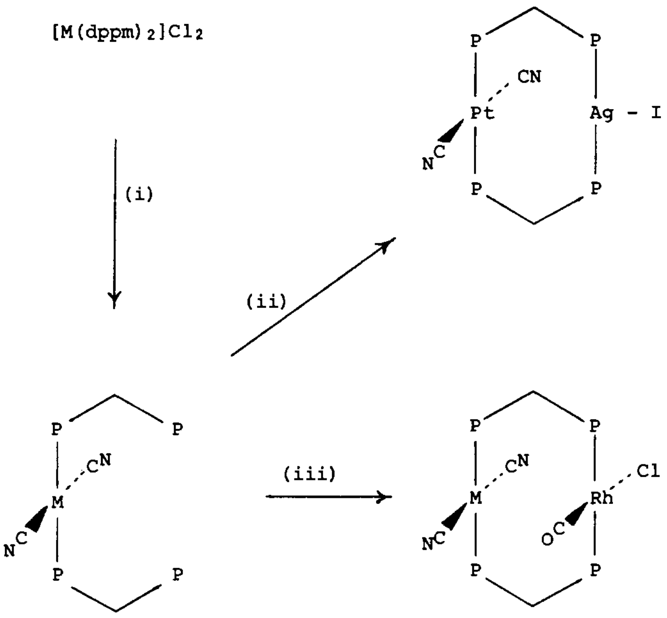
X = I) [102]. The palladium derivatives were obtained from reactions between $[Pd(dppm)_2]Cl_2$ [from $PdCl_2(dppm)$ and dppm] and $Hg(C_2R)_2$; addition of Na_2S afforded HgS and *trans*-$Pd(C_2Ph)_2(\eta^1\text{-dppm})_2$, which could then be reacted with the Rh, Ir or Ag precursors [103]. In both the Pd and Pt series, the silver and mercury derivatives were also used in transmetallation reactions to give better preparations of complexes containing the Group VI metals, Rh or Ir [103,104]. Structural studies revealed that the acetylide group is semi-bridging the two metal atoms in (110, M = W). A one-pot synthesis of the Pt-Rh complex (111, M = Rh) in 71% yield was carried out by adding $Hg(OAc)_2$ and HC_2Ph to $[Pt(dppm)_2]Cl$, followed by $[RhCl(CO)_2]_2$. Adjusting the stoichiometry allowed preparation of the chloro-acetylide Pt-Ag derivative (112), which was converted to the corresponding Pt-Rh and Pt-Ir complexes by reactions with $[RhCl(CO)_2]_2$ or $[IrCl(C_8H_{14})_2]_2$, respectively [105]. Preliminary experiments showed that facile reactions of (113) with non-coordinating anions afforded cationic complexes which added with small molecules such as H_2, CO, allene, butadiene or phenylacetylene to give in each case a single Pt-Ir product [100].

Cyanide stabilises η^1-dppm complexes in the same way as acetylide, preventing chelation, and allowing the synthesis of fluxional *trans*-$M(CN)_2(\eta^1\text{-dppm})_2$ (114; M = Pd, Pt), which have been used as key intermediates in the synthesis of heterometallic Pt-Ag, Pd-Rh or Pt-Rh complexes (Scheme 8) [106].

Complexes in which the two metals are kept further apart were obtained by addition of suitable precursors to *cis*-$PtR_2(\eta^1\text{-dppm})_2$ [107]. These complexes were obtained from *cis*-$PtCl_2(dppm)$ and the appropriate organo-lithium or Grignard reagent, followed by addition of free dppm, when the equilibrium

$$cis\text{-}PtR_2(dppm) + dppm \rightleftharpoons cis\text{-}PtR_2(\eta^1\text{-dppm})_2$$

SCHEME 8



(114)

Reagents: (i) NaCN/EtOH (M = Pd, Pt); (ii) $AgNO_3$, then NaI (M = Pt); (iii) $[RhCl(CO)_2]_2$ (M = Pd, Pt).

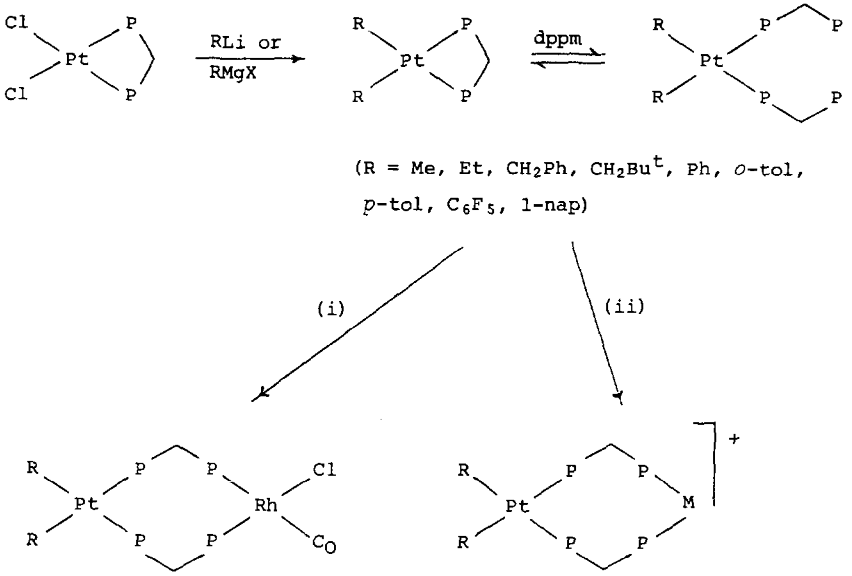
is set up. Scheme 9 summarises the heterometallic complexes obtained. Several isomers of the Rh-Pt complex (115) exist in solution, some as a result of restricted rotation of the naphthyl groups, a situation also obtaining for the homometallic Pt_2 complex containing *p*-tolyl ligands, for which *syn* and *anti* isomers were identified by NMR studies.

Extension of this chemistry to dppm complexes of rhodium and iridium has been described (Scheme 10) [108]. The Ir-Group IB complexes (116) were obtained from the coordinatively-saturated precursor $[Ir(CO)(dppm)_2]Cl$ and CuC_2Ph or $AgOAc/HC_2R$ (R = Me, Ph, tol). Complex (116b) readily gave the cationic derivative (117a) with $NaBPh_4$; either complex reacted with hydrogen to form the silver hydride (118), and the analogous copper hydride derivative was obtained from (116a). The Ir-Au complex (117b) was obtained directly from $[Ir(CO)(dppm)_2]^+$ and AuC_2Ph. Reactions of the iridium precursor with $[MCl(PPh_3)]_4$ afforded (119), which underwent transmetallation reactions with $[RhCl(CO)_2]_2$ to give two Ir-Rh complexes (120) and (121) which are related by CO loss or addition; they were also formed from $[Ir(CO)(dppm)_2]^+$ and $[RhCl(CO)_2]_2$. Some related reactions of $[Rh(CO)(dppm)_2]^+$ were also described. Some of the Group IB complexes showed broadened ^{31}P NMR spectra as a result of rapid phosphine exchange at Cu or Ag.

6. MIXED-METAL COMPLEXES CONTAINING μ-H LIGANDS

The structures of many complexes containing bridging hydride ligands is such that the μ-H ligand occupies a position common to the coordination geometries of both metal atoms; the metal hydride can be considered to be acting as a 2e-donor. Consequently many of the complexes described in this Section can be obtained by addition of a metal hydride species to a coordinatively-unsaturated metal complex. A feature

SCHEME 9

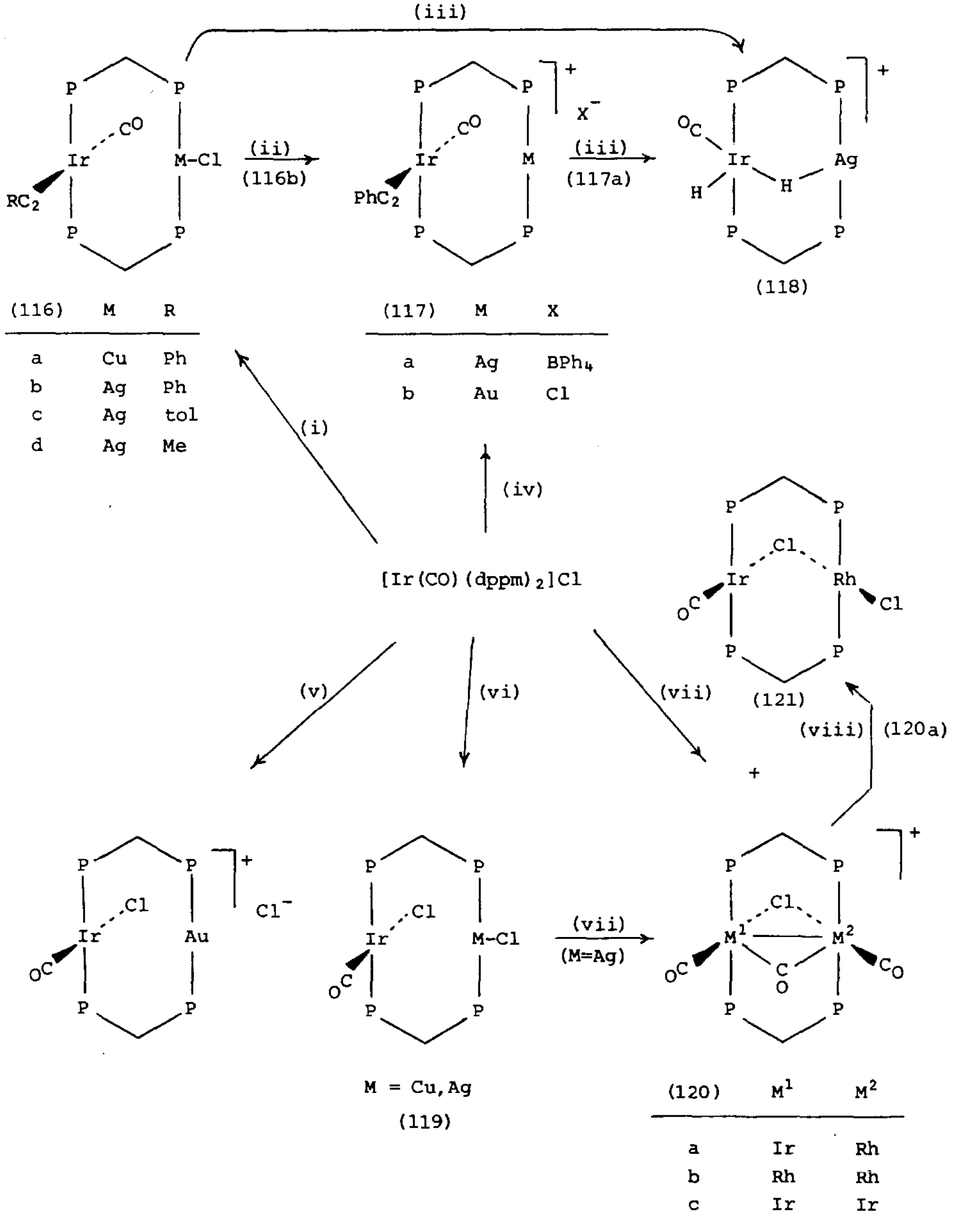


(R = Me, Et, CH_2Ph, CH_2Bu^t, Ph, *o*-tol, *p*-tol, C_6F_5, 1-nap)

(115)

Reagents: (i) $[RhCl(CO)_2]_2$ (R = 1-nap); (ii) $AgI(PPh_3)$ (M = Ag, R = Me), $AuCl(PPh_3)$ (M = Au, R = Me)

SCHEME 10



(116)	M	R
a	Cu	Ph
b	Ag	Ph
c	Ag	tol
d	Ag	Me

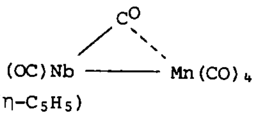
(117)	M	X
a	Ag	BPh$_4$
b	Au	Cl

(120)	M^1	M^2
a	Ir	Rh
b	Rh	Rh
c	Ir	Ir

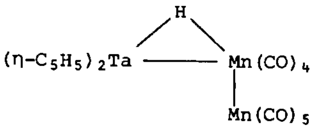
Reagents: (i) CuC$_2$R, or AgOAc/HC$_2$R; (ii) [BPh$_4$]$^-$; (iii) H$_2$; (iv) AuC$_2$Ph; (v) AuCl(PPh$_3$); (vi) [MCl(PPh$_3$)]$_4$ (M = Cu, Ag); (vii) [RhCl(CO)$_2$]$_2$; (viii) CO of these studies has been the preparation of stable complexes containing silver- or gold-hydride moieties.

Addition of $M(CO)_5(thf)$ to a mixture of $Nb(BH_4)(\eta-C_5H_5)_2$ and NEt_3 gave red brown *cis*-$M(CO)_4[(\mu-H)Nb(\eta-C_5H_5)_2]_2$; the X-ray structure of the Mo complex showed two Mo(μ-H)Nb moieties which are too long for any direct Nb-Mo interaction [10]. Reactions between $HTa(CO)(\eta-C_5H_5)_2$ and $M(thf)(CO)_5$ gave $(\eta-C_5H_5)_2(OC)Ta(\mu-H)M(CO)_5$ (M = Cr, Mo or W) [109].

The reaction between $H_3Nb(\eta-C_5H_5)_2$ and $Mn_2(CO)_{10}$ was first described in 1981 as giving $[(\mu-H)\{Nb(CO)(\eta-C_5H_5)_2\}][Mn(CO)_5]$ [110]. Further examination by other groups has shown that this reaction proceeds to give small amounts of $HMn(CO)_5$, and via $HNb(CO)(\eta-C_5H_5)_2$ and a second, unidentified complex, to what may be the $NbMn_2$ analogue of (123) [111]. Other products from this complex are (122) and $[(\mu-H)\{Nb(CO)(\eta-C_5H_5)_2\}_2]$-$[Mn(CO)_5]$. Irradiation of a mixture of $H_3Ta(\eta-C_5H_5)_2$ and $Mn_2(CO)_{10}$ afforded the trinuclear complex (123) [111], which is isoelectronic with the long-known $HRe_2Mn(CO)_{14}$. The reaction between $HTa(CO)(\eta-C_5H_5)_2$ and $Mn(thf)(CO)_2(\eta-C_5H_5)$ afforded $(\eta-C_5H_5)_2(OC)Ta(\mu-H)Mn(CO)_2(\eta-C_5H_5)$ [109].



(122)



(123)

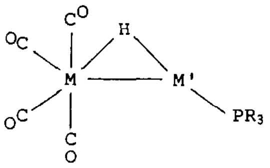
A reaction between $Ni(CO)_4$ and $Nb(BH_4)(\eta-C_5H_5)$ afforded dark red $Ni(CO)_3[(\mu-H)Nb(CO)(\eta-C_5H_5)_2]$, in which the Nb---Ni separation is considered to be practically non-bonding [10]. In complexes of this type, direct bonding of the Nb lone pair appears to be prevented by steric interactions between CO ligands on the different metals.

A reaction between $Cr(CO)_5(thf)$ and $[ppn][HW(CO)_4\{P(OMe)_3\}]$

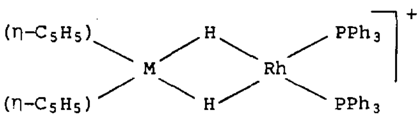
afforded [ppn][$(OC)_5Cr(\mu$-$H)W(CO)_4\{P(OMe)_3\}$] [112], whose IR ν(CO) spectrum was similar to that of the crystallographically-characterised [NEt_4]-[$(OC)_5Mo(\mu$-$H)Mo(CO)_4(PPh_3)$], in which the tertiary phosphine is *trans* to CO.

Treatment of $AgI(PMe_3)$ or $AuCl(PPh_3)$ with $[HM(CO)_5]^-$ (M = Cr or W) or $[HMo_2(CO)_{10}]^-$ in the presence of $TlPF_6$ afforded (124a-e); an X-ray study of the CrAu complex shows a bent Cr(μ-H)Au as expected for a 3-centre interaction [113].

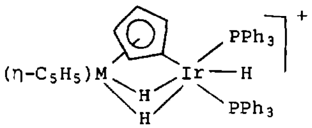
The hydrides $H_2M(\eta$-$C_5H_5)_2$ (M = Mo, W) have been used to prepare many mixed-metal hydrido complexes. Thus, reactions with $[H_2M'(OCMe_2)_2$-$(PPh_3)_2][PF_6]$ (M' = Rh, Ir) have given the cationic complexes (125) and (126), respectively, the latter being formed via $[(\eta$-$C_5H_5)_2M(\mu$-$H)_2IrH_2$-$(PPh_3)_2]^+$ [114]. Ready cleavage of (125) by ligands such as pyridine affords $[Rh(py)_2(PPh_3)_2]^+$ and $H_2M(\eta$-$C_5H_5)_2$, and dilute aqueous HCl affords



(124)	M	M'	R
a	Cr	Ag	Me
b	W	Ag	Me
c	Cr	Au	Ph
d	Mo	Au	Ph
e	Mo	Au	Ph

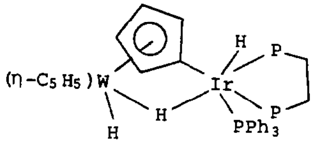


(125) M = Mo,W



(126) M = Mo,W

$[RhCl(PPh_3)_2]_2$ and $[H_3W(\eta\text{-}C_5H_5)_2]^+$; rapid H-D exchange of the C_5H_5-protons occurs in $(CD_3)_2CO/D_2O$ mixtures. The green iridium complexes (126) are fluxional (exchange of all three H involving other ligands as well). Addition of ligands such as pyridine, MeCN or NH_3 gave purple solids which lose the ligand in vacuum; these materials are probably adducts formed by cleavage of one of the M-H-Ir bridges. With dppe, the resulting complex (127) was stable and characterised by an X-ray structure.



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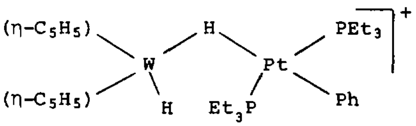

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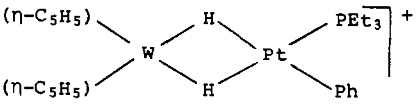
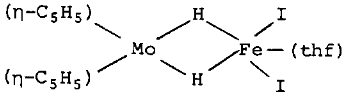


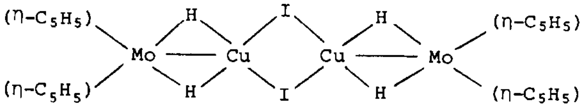
(129)

The reaction between $H_2W(\eta\text{-}C_5H_5)_2$ and *trans*-$[PtPh(OCMe_2)(PEt_3)_2]^+$ afforded (128), which on addition of a second equivalent of the platinum cation, eliminated PEt_3 to form (129) [115]. Comparison of the W-Pt distances in the two complexes emphasises the weaker interaction in the former. In (128), the terminal and bridging H atoms undergo rapid exchange.

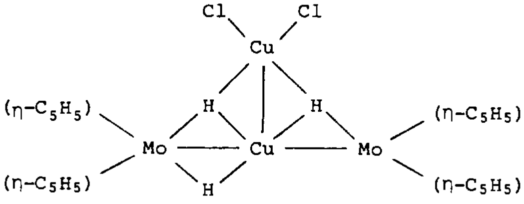
Reactions between $H_2M(\eta\text{-}C_5H_5)_2$ and metallic halides in acetonitrile solution have given a wide range of binuclear derivatives of general formula $(\eta\text{-}C_5H_5)_2M(\mu\text{-}H)_2M'X_n$ (M = Mo, W, $M'X_n$ = $FeCl_2$, FeI_2, $CoCl_2$, CoI_2, CuCl, CuI; M = Mo, $M'X_n$ = $FeBr_2$, $FeCl_3$, $CoBr_2$, AgCl) which were thought to have H-bridged structures [116,117]. X-ray studies of three of these complexes have shown them to be (130) [118], (131) [119] and (132) [120].



(130)



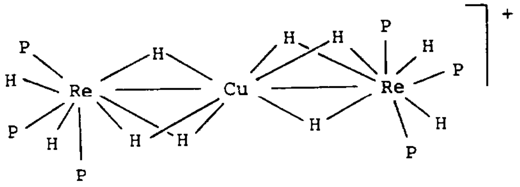
(131)



(132)

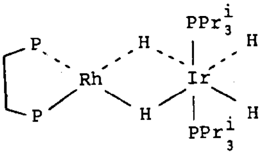
While the large Mo---Fe separation in (130) [2.854(2)Å] probably precludes any significant bonding interaction, the copper atoms are closer to the molybdenums in (131) and (132), and form $\overline{\mathrm{Mo}(\mu\text{-H})_2\mathrm{Cu}}$ bonding units. In (132), the central copper has unusual planar *seven*-coordination (4H, 2Mo, Cu).

Addition of $[\mathrm{Cu(NCMe)_4}][\mathrm{PF_6}]$ to $\mathrm{H_5Re(PMe_2Ph)_3}$ gave the unusual complex cation $[\mathrm{Cu\{(\mu\text{-}H)_3ReH_2(PMe_2Ph)_3\}_2}]^+$ (133) in which the copper is coordinated to six hydride ligands and could be considered to be *eight*-coordinate [121].

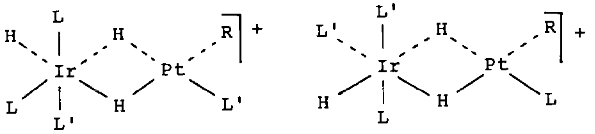


(133) P = PMe_2Ph

Addition of an equimolar amount of $H_5Ir(PPr^i_3)_2$ to a solution of $[Rh(MeOH)_2(dppe)]^+$ in the presence of $NEtPr^i_2$ afforded complex (134); the $Rh(\mu\text{-}H)_2Ir$ separation is shorter than that found in a related $Rh(\mu\text{-}H)(\mu\text{-}Cl)Ir$ complex, but longer than in an $Rh(\mu\text{-}H)_3Ir$ system [122]. Similarly, the bimetallic hydrido-bridged cations (135a-c) have been prepared



(134)

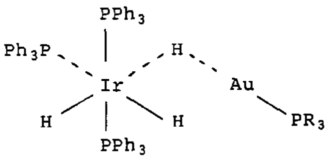


(A) (B)

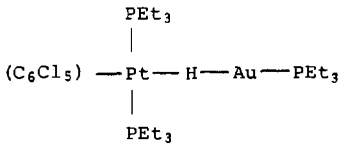
(135)	R	L	L'	A/B
a	H	PEt_3	PEt_3	1/2
b	Ph	PEt_3	PEt_3	1/1
c	H	PEt_3	PPr^i_3	100/0
d	Et	PEt_3	PEt_3	1/99

from reactions between *trans*-$[PtR(MeOH)L_2]^+$ and H_5IrL_2; transfer of PR_3 from Pt to Ir occurred during the reaction, and in some cases, extensive phosphine scrambling took place [123]. In solution, both isomeric forms of cations (135a) and (135b) were present; isomerisation occurs via bridge-cleavage of the H-Pt bond. Complex (135d) was obtained by the reaction of (135a) with C_2H_4; with hydrogen it formed ethane and $[(Et_3P)_2H_2Ir(\mu\text{-}H)_2Pt(PEt_3)_2]^+$. Reaction of CO with (135a) afforded $[H_2Ir(CO)(PEt_3)_3]^+$ and Pt_4 and Pt_5 clusters.

Addition of $[Au(thf)(PR_3)]^+$ to solutions of *mer*-$H_3Ir(PPh_3)_3$ gave the binuclear gold hydride cations (136), and a similar reaction with *trans*-$HPt(C_6Cl_5)(PEt_3)_2$ afforded the related Pt(μ-H)Au complex (137) [124].



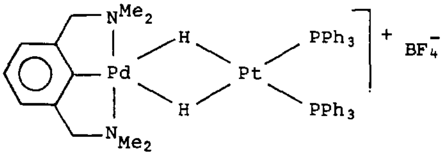
(136) R = Et,Ph



$$(C_6Cl_5)-\underset{\displaystyle PEt_3}{\overset{\displaystyle PEt_3}{\overset{|}{\underset{|}{Pt}}}}-H-Au-PEt_3$$

(137)

Complex (138) was obtained by reaction of $[Pd(OH_2)\{C_6H_3-(CH_2NMe_2)_2-2,2'\}]^+$ with a hydride species generated from $Pt(cod)_2$, $2PPh_3$ and hydrogen [125].

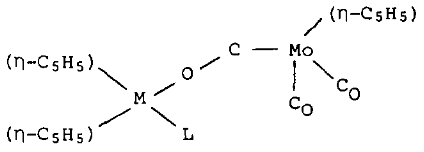


(138)

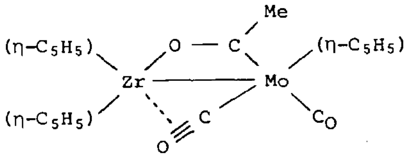
Reactions of $H_2MCp'_2$ (M = Mo, W; Cp' = η-C_5H_5, η-$C_5H_4Bu^t$) with $Fe_2(CO)_9$ or $Co_2(CO)_8$ afforded only the ionic complexes $[HM(CO)(Cp')_2]$-$[M'L_n]$ [$M'L_n$ = $HFe_3(CO)_{11}$, $Co(CO)_4$] [126], while among the multitude of products obtained from reactions between $Mn_2(CO)_{10}$ and $HMo(CO)_2(PPh_3)$(η-C_5H_5) or $HFe(CO)(PPh_3)$(η-C_5H_5) were the heterometallic complexes $MoMn(CO)_8$(η-C_5H_5) and $MnFe(CO)_7$(η-C_5H_5) [127]. The latter reactions have radical character, and the nature of the products indicates the intermediacy of 17e species, which exhibit little selectivity in their recombination reactions.

7. HETEROBIMETALLIC REACTIONS OF CO, AND RELATED CHEMISTRY

The paramagnetic complex (139a) obtained from $Ti(CO)_2(\eta\text{-}C_5H_5)_2$ and $[Mo(CO)_2(\eta\text{-}C_5H_5)]_2$ in thf contains a Ti(OC)Mo system, giving rise to a ν(CO) band at 1650 cm^{-1} [128].



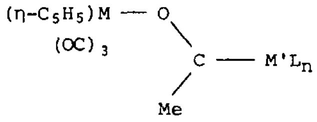
(139)	M	L
a	Ti	thf
b	Zr	Me
c	Zr	η^2-O=CMe



(140)

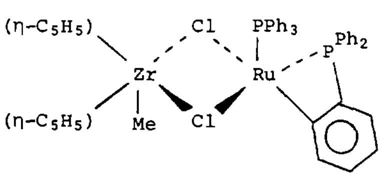
Elimination of CH_4 from a mixture of $ZrMe_2(\eta\text{-}C_5H_5)_2$ and $HMo(CO)_3(\eta\text{-}C_5H_5)$ gave unstable (139b); under CO, this was converted to (139c), which was better obtained directly from $ZrMe(\eta^2\text{-}O{=}CMe)(\eta\text{-}C_5H_5)_2$ and $HMo(CO)_3(\eta\text{-}C_5H_5)$ [129]. In polar solvents, such as MeCN, ionisation of (139c) to $[Zr(OCMe)(NCMe)(\eta\text{-}C_5H_5)_2]^+$ and $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ occurred, while in non-coordinating solvents the solid-state structure was generally preserved. Some concentration-dependent changes in the chemical shift of the *Me*CO group were found. There is no Zr-Mo bond in either of the two conformers of (139c) in the crystal. Loss of CO (1-2 days, toluene) gave an isomer of (139b), shown to have structure (140) with a Zr-Mo bond; addition of CO (50 bar) reformed (139c). The reaction between $H_2Zr(\eta\text{-}C_5H_5)_2$ and $W(CO)(\eta\text{-}C_5H_5)_2$ afforded the μ-formyl complex $(\eta\text{-}C_5H_5)_2HZr(\mu\text{-}OCH)W(\eta\text{-}C_5H_5)_2$ [130].

Several groups have studied the reactions that occur between the reactive cations $[M(CO)_3(\eta\text{-}C_5H_5)]^+$ (M = Mo or W) and metal alkyls or acyls. Homo- or hetero-bimetallic μ-acyl complexes were obtained: whereas the Mo_2 complex contains a Mo-Mo bond bridged by the acyl group, the heterometallic derivatives have an M(μ-OCR)M' sequence (141), as was shown by an X-ray study of (141b). With $Co(CO)_2(\eta\text{-}C_5H_5)$, the first-formed adduct decomposed in $(CD_3)_2CO$ to give $[Mo\{OC(CD_3)_2\}(CO)_3(\eta\text{-}C_5H_5)]^+$; a redox reaction occurred between $[Mo(CO)_3(\eta\text{-}C_5H_5)]^+$ and $Co(\eta\text{-}C_5H_5)_2$ to give $[Co(\eta\text{-}C_5H_5)_2][Mo(CO)_3(\eta\text{-}C_5H_5)]$ [132].



(141)	M	M'Ln	Reference
a	Mo	$Mn(CO)_4(PPh_3)$	[131]
b	Mo	$Fe(CO)_2(\eta\text{-}C_5H_5)$	[131-133]
c	Mo	$Fe(CO)(PPh_3)(\eta\text{-}C_5H_5)$	[133]
d	W	$Fe(CO)_2(\eta\text{-}C_5H_5)$	[133]

There is no Zr-Ru bond in the μ-CH_2 complex (142), which is formed via the halogen-bridged cyclometallated compound (143) by irradiating mixtures of $ZrClMe(\eta\text{-}C_5H_5)$ and $RuCl_2(PPh_3)_3$ [134].



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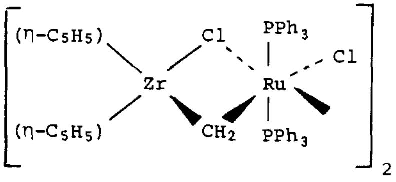
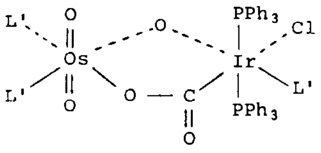
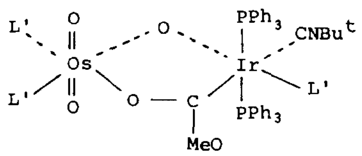


(143)

Oxidation of coordinated CO to CO_2 occurred in the reaction between Vaska's complex and OsO_4, which gave (144) in the presence of 4-t-butylpyridine; addition of Bu^tNC and CF_3SO_3Me afforded the crystallographically characterised (145) [135].





L' = $NC_5H_4Bu^t$-4

(144)

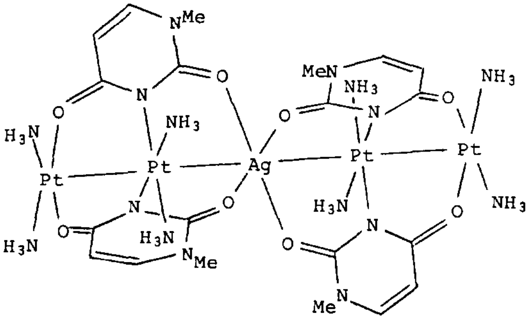
(145)

8. COORDINATION COMPLEXES CONTAINING HETEROMETALLIC BONDS

The heterotrinuclear complex $Mn[Pt(NH_3)_2(1\text{-}MeT)_2]_2Cl_2$ (1-MeT = 1-methylthymine), described in the last report (p. 189), was found to have a large zero-field splitting for the Mn(II) atom; the axial Pt(II) groups produce a much larger tetragonal distortion than found for MnO_4I_2 ligand sets [136].

Reactions between *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2$ (1-MeU = 1-methyluracil) and $CuSO_4$ afforded bi- and tri-nuclear complexes *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2\text{-}Cu(OH_2)_2]SO_4$ and *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(1\text{-}MeU)_2Pt(NH_3)_2]SO_4$; $Cu(NO_3)_2$ afforded only the nitrate salt of the latter cation. In the former, the Pt and Cu are bridged by the 1-methyluracilato ligand, with a Pt-Cu distance of 2.765(3)A; both metals have square planar coordination. This paper discusses the possibility of the formation of long heteronuclear Pt_xM_y metal chains [137].

Deep yellow crystals of (146) were obtained from a solution of *cis*-$[Pt_2(NH_3)_4(1\text{-}MeU)_2][NO_3]_2$ and $AgNO_3$; on standing in water, or heating, (146) is rapidly converted to a crystalline "platinum blue". The cations of (146) are stacks of Pt_4 units linked by the Ag, which is coordinated by four O from the 1-methyluracil ligands [138].



(146)

9. MISCELLANEOUS STUDIES OF HETEROMETALLIC SYSTEMS

Reactions of V(η-PhMe)$_2$ with Cr atoms, or of Cr(η-PhMe)$_2$ with V atoms, in methylcyclohexane at 140-160K gave binuclear MM'(PhMe)$_2$ (MM' = VCr, V$_2$ and Cr$_2$), by direct addition of V or Cr to the metal centre. Similar reactions occur between metals and Ph groups in poly(methylphenylsiloxane) [139].

Rare gas matrix isolation studies of codeposited Fe and Cr vapours allowed the identification of FeCr by Mössbauer spectroscopy at 4.2K. Other heterometallic species present included Fe$_2$Cr, Fe$_2$Cr$_2$, FeCr$_2$ and FeCr$_3$, together with Fe$_n$Cr$_m$ (n,m >2). SCF-X$_\alpha$-scattered wave MO calculations on FeCr indicated ferromagnetic coupling between the metal atoms [140].

Although iron atoms (vapour) react with toluene solutions of Mn$_2$(CO)$_{10}$ to give only Fe(PhMe)$_2$, which decomposed to colloidal metal with chemisorbed CO above 243K, the reaction between preformed Fe(PhMe)$_2$ and Mn$_2$(CO)$_{10}$ in thf at 150K resulted in an electron transfer cleavage of the Mn-Mn bond to give [Mn(CO)$_5$]$^-$, which then reacted with Fe(PhMe)$_2$ to give MnFe complexes. In the presence of CO, [MnFe(CO)$_9$]$^-$ and [Fe$_2$Mn(CO)$_{12}$]$^-$ could be isolated [141].

10. STRUCTURAL STUDIES

Table 2 summarises the many X-ray structural studies of compounds containing actual or suspected M-M' interactions.

TABLE 2 *M-M' separations in heterometallic complexes*

M-M'	Length (Å)	Complex	Reference
Ti-W	2.977(4)	$(\eta\text{-C}_5\text{H}_5)_2\overline{\text{Ti}(\mu\text{-CO})[\mu\text{-C(tol)}]\text{W}}(\text{CO})(\eta\text{-C}_5\text{H}_5)$	[43]
	3.082(2)	$(\eta\text{-C}_5\text{H}_5)_2\overline{\text{Ti}(\mu\text{-}\eta^1,\eta^2\text{-CO})[\mu\text{-}\eta^1,\eta^2\text{-C(tol)CH}_2]\text{W}}(\text{CO})(\eta\text{-C}_5\text{H}_5)$	[44]
Zr-Mo	3.297(1)	$(\eta\text{-C}_5\text{H}_5)_2\overline{\text{Zr}(\mu\text{-OC})(\mu\text{-OCMe})\text{Mo}}(\text{CO})(\eta\text{-C}_5\text{H}_5)$	[129]
Zr-Ru	2.910(1)	$(\eta\text{-C}_5\text{H}_5)_2(\text{Bu}^t\text{O})\text{ZrRu}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$	[7]
V-Au	2.690(3)	$(\text{OC})_6\text{VAu}(\text{PPh}_3)$	[13]
Nb-Mo	3.565(2), 3.579(2)	$[(\eta\text{-C}_5\text{H}_5)_2(\text{OC})\text{Nb}(\mu\text{-H})]_2\text{Mo}(\text{CO})_4$	[10]
Nb-Mn	3.176(1)	$(\eta\text{-C}_5\text{H}_5)_2(\text{OC})\overline{\text{Nb}(\mu\text{-CO})\text{Mn}}(\text{CO})_4$	[9,10]
Nb-Ni	3.218(1)	$(\eta\text{-C}_5\text{H}_5)_2(\text{OC})\text{Nb}(\mu\text{-H})\text{Ni}(\text{CO})_3$	[10]
Ta-Mn	3.441(1)	$(\eta\text{-C}_5\text{H}_5)_2(\text{OC})\text{Ta}(\mu\text{-H})\text{Mn}(\text{CO})_4\text{Mn}(\text{CO})_5$	[111]
Cr-Mo	3.131(1)	$(\text{OC})_5\overline{\text{Cr}\{\mu\text{-As}[\text{Cr}(\text{CO})_5]\}\text{Mo}}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$	[73]
Cr-W	2.941(1)	$(\eta\text{-C}_6\text{Me}_6)(\text{OC})\overline{\text{Cr}(\mu\text{-CO})[\mu\text{-C(tol)}]\text{W}}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$	[4]
	3.128(2)	$(\text{OC})_5\overline{\text{Cr}\{\mu\text{-As}[\text{Cr}(\text{CO})_5]\}\text{W}}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$	[73]
Cr-Rh	2.757(2)	$(\eta\text{-C}_6\text{H}_6)(\text{OC})\overline{\text{Cr}(\mu\text{-CO})_2\text{Rh}}(\text{CO})(\eta\text{-C}_5\text{Me}_5)$	[19]
Cr-Au	2.770(2)	$(\text{OC})_5\overline{\text{Cr}(\mu\text{-H})\text{Au}}(\text{PPh}_3)$	[113]
Mo-W	2.938(1)	$(\text{OC})_2\text{Mo}[\overline{(\mu\text{-CO})\{\mu\text{-C(tol)}\}\text{W}}(\text{CO})(\eta\text{-C}_5\text{H}_5)]_2$	[45]
	3.131(1)	$(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\overline{\text{Mo}(\mu\text{-SMe})\text{W}}(\text{CO})_5$	[72]

	3.239(4)	$(\eta-C_5H_5)(OC)_3MoW(CO)_2[C(CH_2)_3O](\eta-C_5H_5)$	[14]
Mo-Mn	3.054(1)	$(OC)_3Mo(\mu-\eta^5,\underline{P}-C_5H_4PPh_2)Mn(CO)_4$	[85]
	3.070(1)	$(\eta-C_5H_5)(OC)_2Mo\{\mu-As[Mn(CO)_2(\eta-C_5H_4Me)]\}Mn(CO)_2(\eta-C_5H_4Me)$	[73]
Mo-Fe	2.854(2)	$(\eta-C_5H_5)_2Mo(\mu-H)_2FeI_2(thf)$	[118]
Mo-Rh	2.588(1)	$(\eta-C_5H_5)(OC)Mo(\mu-CO)_2Rh(PPh_3)_2$	[20]
	2.957(1)	$(OC)_3IMo(\mu-PMe_2)_2RhMe(\eta-C_5Me_5)$	[61]
Mo-Pt	2.839(1)	$(\eta-C_5H_5)(OC)_3MoPtH(PPh_3)_2$	[21]
	2.845(1)	$(OC)_2ClMo(\mu-CO)(\mu-PPh_2py)_2PtCl$	[93]
Mo-Cu	2.644(1), 2.661(1)	$[(\eta-C_5H_5)_2Mo(\mu-H)_2]_2Cu(CuCl)_2$	[120]
	2.729(-)	$[(\eta-C_5H_5)_2Mo(\mu-H)_2Cu(\mu-I)]_2$	[119]
W-Co	2.758(1)	$(\eta-C_5H_5)(OC)W(\mu-CO)[\mu-C(tol)]Co(CO)(\eta-C_5Me_5)$	[4]
	2.940(2)	$(OC)_4(PhC)WCo(CO)_4$	[18]
W-Rh	2.721(1)	$[(\eta-C_5H_5)_2W(\mu-H)_2Rh(PPh_3)_2][PF_6]$	[114]
	2.796(1)	$(\eta-C_5H_5)(OC)W(\mu-CO)[\mu-C(tol)]Rh(PMe_3)(\eta^5-C_9H_7)$	[46]
W-Ir	2.8764(4)	$(OC)_4W(\mu-PPh_2)_2IrH(CO)(PPh_3)$	[62]
	3.077(1)	$[(\eta-C_5H_5)HW(\mu-H)(\mu-\eta^1,\eta^5-C_5H_4)IrH(PPh_3)(dppe)][PF_6]$	[114]
W-Pt	2.602(1)	$[(\eta-C_5H_5)(\eta-C_2H_4)W(\mu-CO)_2Pt(PEt_3)_2][BF_4]$	[47]
	2.663(1)	$[(\eta-C_5H_5)_2W(\mu-H)_2PtPh(PEt_3)][BPh_4]$	[115]
	2.728(1)	$(\eta-C_5H_5)(Me_3P)W(\mu-CO)[\mu-OCC(tol)]Pt(cod)$	[46)

	2.774(1)	$(OC)_5W(\mu\text{-}C{=}CH_2)Pt(dppm)$		[50]
	2.818(3)	$(OC)_4W(\mu\text{-}dppm)[\mu\text{-}C(OMe)(tol)]Pt(CO)$		[49]
	2.820(1)	$(\eta\text{-}C_5H_5)(OC)W(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}C(tol)CH_2]Pt(PMe_3)_2$		[44]
	3.037(1)	$(OC)_3W(\mu\text{-}dppm)_2[\mu\text{-}C_2(tol)]Pt[C_2(tol)]$		[105]
	3.501(1)	$[(\eta\text{-}C_5H_5)_2HW(\mu\text{-}H)PtPh(PEt_3)_2][BPh_4]$		[115]
W-Cu	2.721(1)	$(\eta\text{-}C_5H_5)(OC)_3WCu(PPh_3)_2$	(7a)	[23]
	2.771(1)	$(\eta\text{-}C_5H_5)(OC)W(\mu\text{-}CO)_2Cu(PPh_3)_2$	(7b)	[23]
W-Au	2.729(1)	$(\eta\text{-}C_5H_5)(OC)_2W[\mu\text{-}CH(tol)]Au(PPh_3)$		[45]
Mn-Fe	2.615^a	$(OC)_4Mn(\mu\text{-}CH_2)(\mu\text{-}CO)Fe(CO)(\eta\text{-}C_5H_5)$		[51]
	2.703(4)	$(\eta\text{-}C_5H_5)(OC)_2Mn[\mu\text{-}C{=}CH(CO_2Me)]Fe(CO)_4$	(isomer a)	[57]
	2.865(1)	$[(\eta\text{-}C_5H_4Me)(OC)_2MnFe(CO)_4]Ge[Fe_2(CO)_8]$		[74]
Mn-Rh	2.703(2)	$(\eta\text{-}C_5H_5)(OC)Mn(\mu\text{-}CO)_2Rh(CO)(\eta\text{-}C_5Me_5)$		[35]
Mn-Pd	2.810(2)	$(OC)_2Mn(\mu\text{-}CO)(\mu\text{-}dppm)_2PdBr$		[99]
Mn-Pt	2.641(1)	$(\eta\text{-}C_5H_5)(OC)_2Mn(\mu\text{-}CS)Pt(PMePh_2)_2$		[36]
Re-Cu	2.607(2)	$[Cu\{(\mu\text{-}H)_3Re(PMePh_2)_3\}_2][PF_6]$		[121]
Fe-Ru	2.630(2)	$(OC)_3Fe(\mu\text{-}C_{16}H_{22})Ru(CO)_3$		[78]
	2.698(1)	$(\eta\text{-}C_5H_5)(OC)Fe(\mu\text{-}CO)(\mu\text{-}PNPF_2NPF_2N)Ru(CO)(\eta\text{-}C_5H_5)$		[65]
Fe-Co	2.482(1)	$[(OC)_3FeC_8H_6]Co(\eta\text{-}C_5H_5)$		[79]
Fe-Rh	2.557(2)	$[(OC)_3FeC_4H_4]Rh(\eta\text{-}C_5H_5)$		[79]

	2.623(2)	$(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)Rh(\mu\text{-}PPh_2)_2Rh(\mu\text{-}CO)(\mu\text{-}PPh_2)_2Fe(CO)_3$	[69]
Fe-Ir	2.960(2)	$(Ph_3P)(OC)_3Fe(\mu\text{-}PPh_2)Ir(CO)_2(PPh_3)$	[67,68]
Ru-Co	2.750(1)	$(Ph_3P)(OC)_3Ru(\mu\text{-}PPh_2)Co(CO)_2(PPh_3)$	[71]
Ru-Pd	2.660(1)	$(OC)_2ClRu(\mu\text{-}PPh_2py)_2PdCl$	[94]
Os-Au	2.838(1)	$(Ph_3P)_2(ON)ClOs(\mu\text{-}CH_2)AuI$	[56]
Co-Rh	2.404(3)	$(\eta\text{-}C_5Me_5)Co(\mu\text{-}CO)_2Rh(\eta\text{-}C_5Me_5)$	[39]
	2.676(1)	$(OC)_4CoRh(CO)(PEt_3)_2$	[38]
Rh-Ir	2.662(1)	$(dppe)Rh(\mu\text{-}H)_2IrH_2(PPr^i_3)_2$	[122]
Rh-Pd	2.594(1)	$(OC)Cl_2Rh(\mu\text{-}PPh_2py)_2PdCl$	[95]
Rh-Ag	2.651(1)	$[(\eta\text{-}C_5H_5)(Ph_3P)(OC)Rh]_2Ag$	[42]
Ir-Pt	2.682(1)	$[(Et_3P)_3HIr(\mu\text{-}H)_2PtEt(PEt_3)][BPh_4]$	[142]
	2.690(1)	$[(Et_3P)_3HIr(\mu\text{-}H)_2PtPh(PEt_3)][BPh_4]$	[142]
Ir-Cu	2.832(1)	$(OC)(PhC_2)Ir(\mu\text{-}dppm)_2CuCl$	[109]
Ir-Au	2.765(1)	$(Ph_3P)_3H_2Ir(\mu\text{-}H)Au(PEt_3)$	[124]
Pt-Cu	2.765(3)	$[\underline{cis}\text{-}(H_3N)_2Pt(\mu\text{-}1\text{-}MeU)_2Cu(OH_2)_2][SO_4]$	[137]
Pt-Ag	2.787(1)	$[Pt_4Ag(NH_3)_8(1\text{-}MeU)_4][NO_3]_5$	[138]
	3.146(3)	$(PhC_2)_2Pt(\mu\text{-}dppm)_2AgI$	[102]

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[a] Average of two forms

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