ORGANOMETALLIC STRUCTURES – TRANSITION METALS

ANNUAL SURVEY COVERING THE YEAR 1971

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Abbreviations

aa	*o*-allylohenyldimethylarsine
acac	acetylacetonate
an	2-methoxyphenyl
ap	*o*-allylphenyldiphenylphosphine
azb	phenylazophenyl-2*C,N'*
bipy	2,2'-bipyridyl
COD	1,5-cyclooctadiene
dam	bis(diphenylarsino)methane
dbm	dibenzoylmethanato
diaz	1,2-diazepine
dmg	dimethylglyoximato
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
DQ	duroquinone
FA	fumaric acid
Fc	ferrocenyl
ffars	1,2-bis(dimethylarsino)perfluorocyclopentene
$f_4$fars	1,2-bis(dimethylarsino)perfluorocyclobutene
$f_4$fos	1,2-bis(diphenylphosphino)perfluorocyclobutene
$f_6$fos	1,2-bis(diphenylphosphino)perfluorocyclopentene
HFA	hexafluoroacetone
ind	indenyl
Mepy	4-methylpyridine
mn	malonitrile anion
OAc	acetate
PCy_3	tricyclohexylphosphine
PPh_3	triphenylphosphine
py	pyridine
sa	*o*-styryldimethylarsine
salpn	*N,N*-bis(salicylidenimine)-1,2-propane dianion
sp	*o*-styryldiphenylphosphine
TCNE	tetracyanoethylene
THF	tetrahydrofuran
tol	tolyl
ttas	bis(*o*-dimethylarsinophenyl)methylarsine

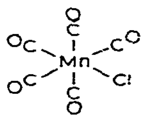
Reviews. The survey of metal–metal bonds and covalent atomic radii of transition metals in π-complexes and polynuclear carbonyls[1], briefly referred to last year, proves to be a summary of the more recent structural studies of complexes with homo- and hetero-polymetallic bonds, both within the transition metal series, and also of transition elements with metals of Groups IB–IVB, together with some attempts to correlate bond lengths.

Churchill[2] has summarised X-ray structure determinations of metal–carbon σ-bond lengths, and comments that few generalisations can yet be made; approximately 70 structural determinations are considered. A survey of crystal structures of the platinum group metal complexes has also appeared[3].

A new journal has appeared devoted to structure determinations, namely *Journal of Crystal and Molecular Structure*, together with a preliminary communication vehicle, *Crystal Structure Determinations*. Both of these publications are likely to contain structures of interest to the organometallic chemist. In addition, a listing of structures of coordination complexes appears in each issue of *Coordination Chemistry Reviews*. However, the coverage of organometallic complexes is far from complete.

Three volumes have appeared in the series *Molecular Structures and Dimensions*[4]. Volumes 1 and 2 comprise a bibliography of the period 1935–1969, dealing with general organic structures, and with complexes and organometallics, respectively. The third volume covers the period 1969–1971. Entries are arranged by chemical class, and cumulative indexes are given. At present the title of the series is somewhat misleading, since neither structures nor dimensions are detailed.

Simple metal carbonyl derivatives. During the year, the structures of several long-known metal carbonyl complexes have been determined, confirming the geometries deduced by other physical methods, and providing some structural parameters. Thus in $Mn(CO)_5Cl$ (1), the Mn–Cl bond is 2.367(4) Å[5]; in the substituted complex *cis*-$Mn(CO)_4(PPh_3)Cl$ (2), the value is 2.36 Å[6]. These values are close to estimated single bond lengths. However, the Mn–CO bond lengths *trans* to Cl (and to P) are shorter, by ~0.09 Å, than the other bonds, suggesting considerable π interaction. A preliminary result for $Mn(CO)_5Br$ quoted in ref. 5 gives an Mn–Br bond length of 2.50(1) Å.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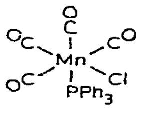
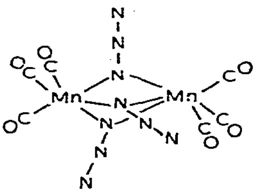

(2)

Although azide reacts with Group VI carbonyls, and with cationic carbonyls, to form isocyanate complexes, with manganese and rhenium carbonyls, complexes containing azide ligands can also be obtained. The structure of the binuclear complex $NEt_4[Mn_2(CO)_6(N_3)_3]$ (3) reveals bridging azido groups, with relatively weak metal–metal bonding[7].

The anion in N-n-$Bu_4[Rh(CO)_2Cl_2]$ (4) has the expected *cis* square planar structure, with one of the CO groups and the *trans*-Cl disordered. Here again an unusually short Rh–CO distance of 1.72(2) Å is accounted for in terms of extensive π-bonding. The same anion was also studied in the salt $[Rh(f_6fos)_2]^+[Rh(CO)_2Cl_2]^-$ (see p.337).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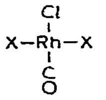
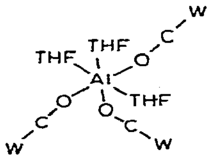

(4) X≡disordered Cl,CO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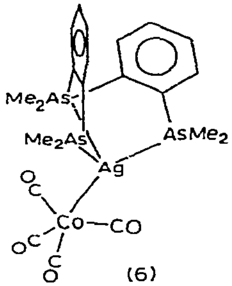
Another example of a carbonyl group bridging via both the carbon and oxygen atoms, i.e. as M–CO–M′, has been found in the product obtained from $Hg[W(CO)_3(\pi\text{-}C_5H_5)]_2$ and excess aluminium. The complex has the stoichiometry $Al[W(CO)_3(\pi\text{-}C_5H_5)]_3(THF)_3$, and an X-ray structural characterisation[9] reveals the molecular geometry as (5). Bond distances suggest rather tight bonding of the metals to each end of the CO group, with a C–O distance of 1.25(2) Å, compared with 1.16(2) Å for the normal terminal CO groups in the molecule.

Complexes containing metal–metal bonds. (a) Transition metal–main Group metal bonds. In the Group I complexes (ttas)AgCo(CO)$_4$ (6) [ttas = bis(*o*-dimethylarsinophenyl)-methylarsine] and Ph$_3$PAuCo(CO)$_4$ (7), simple metal–metal bonds are present, with the carbonyl groups bent towards the axial metal atom[10]. The larger Ag–Co bond length is attributed to the higher coordination number of the silver atom. As in previous years, a summary of metal–metal bond lengths is contained in Table 1.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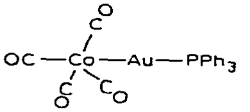
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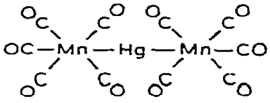
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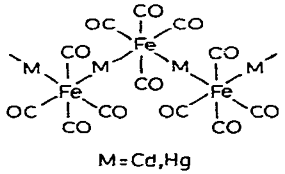

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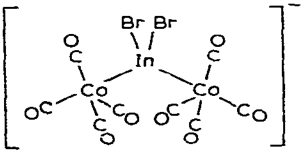
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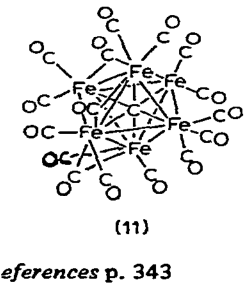
In Hg[Mn(CO)$_5$]$_2$ (8), the Mn–Hg–Mn sequence is linear; again the carbonyl groups are bent towards the mercury atom[11]. Preliminary results for MFe(CO)$_4$ (M = Cd, Hg) suggest the zig-zag chain structure (9)[12].

A reaction between InBr and Co$_2$(CO)$_8$ in the presence of NEt$_4$Cl gives the yellow complex NEt$_4$ {Br$_2$In[Co(CO)$_4$]$_2$}. In the complex anion (10), the Co–In–Co angle is 124.3(4)°, with approximate tetrahedral geometry about the indium atom.

Further structural studies of transition metal–carbon clusters have been reported. The complex anion [Fe$_6$(CO)$_{16}$C]$^{2-}$ (11) [obtained from a reaction between [Mn(CO)$_5$]$^-$ and Fe(CO)$_5$] consists of an octahedral Fe$_6$ cluster containing a central carbon atom[14]. One of the iron atoms is not bonded to a bridging carbonyl group. The cobalt–carbon clusters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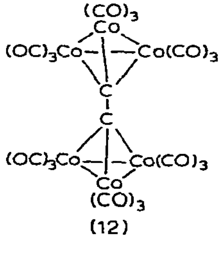
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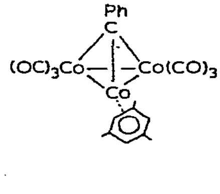
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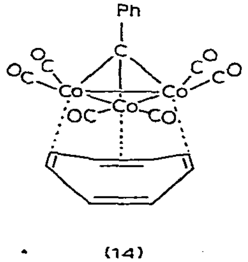
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TABLE 1

METAL–METAL BOND DISTANCES

Bond	Length (A)	Complex		Reference
Zr–Si	2.813(2)	$(\pi\text{-}C_5H_5)_2Zr(SiPh_3)Cl$		17
Nb–Nb	3.105(5)	$[(\pi\text{-}C_5H_5)(\mu\text{-}C_5H_4)NbH]_2$		157
Nb–Ni	2.77	$\{Ni[(SMe)_2Nb(\pi\text{-}C_5H_5)_2]_2\}(BF_4)_2$		230
Cr–Cr	1.975(5)	$Li_4Cr_2(C_4H_8)_4$		62
	2.650(4)	$(\pi\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2)$		159
	2.97(1)	$[(Ph_3P)_2N]_2[Cr_2(CO)_{10}]$		38
	3.406(9)	$NEt_4[Cr_2(CO)_{10}H]$	(H-bridged)	38
Mo–Mo	2.167	$Mo_2(CH_2SiMe_3)_6$		61
	2.183(2)	$Mo_2(C_3H_5)_4$		130
	2.603(2)	$[(\pi\text{-}C_5H_5)Mo(SMe)_2]_2$		33
	2.617(4)	$[(\pi\text{-}C_5H_5)Mo(SMe)_2]_2PF_6$		33
	2.62(2)	$[(\pi\text{-}C_5H_5)Mo(SCCF_3)_2]_2$		34
	2.812(av.)	$[(\pi\text{-}C_5H_5)_3Mo_3S_4]SnMe_3Cl_2$		37
	3.123(7)	$[(Ph_3P)_2N]_2[Mo_2(CO)_{10}]$		38
Mo–Mn	2.961	$(\pi\text{-}C_5H_5)(CO)Mo(\mu\text{-}C_5H_4)Mn(CO)_4$		158
Mo–Re	2.909(2)	$[(\pi\text{-}C_5H_5)MoRe_2(CO)_8](S)[SMo(CO)_3(\pi\text{-}C_5H_5)]$		35
Mo–Ni	3.064(av.)	$[(Ph_3P)_2N]_2[Mo_2Ni_3(CO)_{16}]$		41
	3.151(av.)	$[(Ph_3P)_2N]_2[Mo_2Ni_3(CO)_{16}]$		41
W–Si	2.586(5)	$W_2(CO)_8H_2(SiEt_2)_2$		18
	2.703(4)	$W_2(CO)_5H_2(SiEt_2)_2$	[W–H–Si]	18
W–W	3.183(1)	$W_2(CO)_8H_2(SiEt_2)_2$		18
W–Ni	3.057(av.)	$[(Ph_3P)_2N]_2[W_2Ni_3(CO)_{16}]$		41
	3.158(av.)	$[(Ph_3P)_2N]_2[W_2Ni_3(CO)_{16}]$		41
Mn–Mn	2.526	$(\pi\text{-}C_5H_5)_2Mn_2(NO)_3(NO_2)$		160
	2.893(4)	$NEt_4[Mn_2(CO)_6(N_3)_3]$		7
	2.971(3)	$Mn_2(CO)_8(f_4fars)$		211
Mn–Hg	2.608(2)	$Hg[Mn(CO)_5]_2$		11
Re–Re	2.957(1)	$(\pi\text{-}C_5H_5)_2Re_2(CO)_5$		164
	2.985(1)	$[(\pi\text{-}C_5H_5)MoRe_2(CO)_8](S)[SMo(CO)_3(\pi\text{-}C_5H_5)]$		35
Fe–C	1.82–1.97(4)	$(NMe_4)_2[Fe_6C(CO)_{16}]$		14
Fe–Sn	2.499(1)	$[(\pi\text{-}C_5H_5)Fe(CO)_2SnPh(OSOPh)\text{-}\mu\text{-}OH]_2$		20
	2.562(4)	$(\pi\text{-}C_5H_5)Fe(CO)(f_6fos)SnMe_3$		215
Fe–Sb	2.49(2)	$Fe(CO)_4(SbMe_3)$		207
	2.527–2.540(3)	$\{ClSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_3\}FeCl_4$		26
Fe–Fe	2.215	$(C_2\text{-}t\text{-}Bu_2)_2Fe_2(CO)_4$		137
	2.535(2)	$Fe_3(CO)_{10}(NSiMe_3)$		190
	2.539(7)	$(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$		47
	2.540(7)	$Fe_3(CO)_9(PMe_2Ph)_3$	(CO-bridged)	42
	2.544	$(Ph_2C{=}C{=}NMe)Fe_2(CO)_6$		193
	2.553–2.594(3)	$(\pi\text{-}C_5H_5)RhFe_3(CO)_{11}$		46
	2.553–2.632(10)	$(NMe_4)_2[Fe_6C(CO)_{16}]$	(CO-bridged)	14
	2.662–2.743(11)	$(NMe_4)_2[Fe_6C(CO)_{16}]$		14
	2.667(5)	$Fe_3(CO)_9(f_4fars)$	(Fe(2)–Fe(3))	213
	2.688(7)	$Fe_3(CO)_9(PMe_2Ph)_3$		42
	2.866(1)	$(C_7H_8)Fe_2(CO)_6$		138
	2.917(5)	$Fe_3(CO)_9(f_4fars)$	(Fe(1)–Fe(3))	213
	2.925(4)	$[(\pi\text{-}C_5H_5)Fe(CO)(SMe)]_2BF_4$		32
Fe–Ru	2.619–2.661	$H_2FeRu_3(CO)_{12}$	(CO-bridged)	43
	2.700	$H_2FeRu_3(CO)_{12}$		43
Fe–Rh	2.568–2.615(3)	$(\pi\text{-}C_5H_5)RhFe_3(CO)_{11}$		46
	2.570–2.598(5)	$(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$		47
Ru–Ge	2.49(1)	$[Me_2GeRu(CO)_3]_3$		21

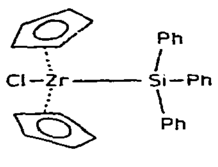
(Table continued)

TABLE 1 *(continued)*

Bond	Length (Å)	Complex		Reference
Ru–Ru	2.740(4)	$\mathrm{(C_{10}H_8)Ru_3(CO)_7}$	(CO-bridged)	50
	2.775–2.779	$\mathrm{HRu_3(CO)_9(C_{12}H_{15})}$		51
	2.777–2.816	$\mathrm{H_2FeRu_3(CO)_{12}}$		43
	2.831(3)	$\mathrm{Ru_3(CO)_{10}(f_4fars)}$		214
	2.858(6)	$\mathrm{Ru_3(CO)_{10}(f_4fars)}$	(As-bridged)	214
	2.867(5)	$\mathrm{H_2Ru_6(CO)_{18}}$		44
	2.885–2.914	$\mathrm{H_2FeRu_3(CO)_{12}}$		43
	2.926(9)	$\mathrm{[Me_2GeRu(CO)_3]_3}$		21
	2.929	$\mathrm{HRu_3(CO)_9(C_{12}H_{15})}$	(H-bridged)	51
	2.944(5)	$\mathrm{(C_{10}H_8)Ru_3(CO)_7}$		50
	2.954(3)	$\mathrm{H_2Ru_6(CO)_{18}}$	(H-bridged)	44
Os–Os	2.730(2)	$\mathrm{Os_2(CO)_6(OAc)_2}$		45
Co–In	2.652(14)	$\mathrm{NEt_4\{Br_2In[Co(CO)_4]_2\}}$		13
Co–C	1.89(2)(av.)	$\mathrm{PhCCo_3(CO)_6(C_6H_3Me_3)}$		15
	1.92(3)(av.)	$\mathrm{C_2[CCo_3(CO)_9]_2}$		16
	1.96(1)(av.)	$\mathrm{[CCo_3(CO)_9]_2}$		15
Co–Sn	2.498(1)	$\mathrm{Cl_2Sn[Co(CO)_2(C_7H_8)]_2}$		23
	2.566,2.575(3)	$\mathrm{Ph_2Sn[Co(CO)_2(C_7H_8)]_2}$		23
	2.58–2.62(1)	$\mathrm{ClSn[Co(CO)_4]_3}$		22
Co–Sb	2.614(3)(av.)	$\mathrm{Sb_4Co_4(CO)_{12}}$		28
Co–Co	2.343	$\mathrm{Co_4(CO)_8(f_4fars)_2}$		216
	2.412	$\mathrm{Co_4(CO)_8(f_4fars)_2}$		216
	2.441–2.477(5)	$\mathrm{PhCCo_3(CO)_6(C_6H_3Me_3)}$		15
	2.446	$\mathrm{Co_4(CO)_8(f_4fars)_2}$	(As-bridged)	216
	2.447–2.462(7)	$\mathrm{C_2[CCo_3(CO)_9]_2}$	-	16
	2.464–2.482	$\mathrm{Co_4(CO)_{10}(Ph_2PC{\equiv}CCF_3)_2}$		49
	2.483(4)	$\mathrm{Co_2(CO)_6(f_4fars)}$		217
	2.510(4)	$\mathrm{Co_4(CO)_8(f_4fars)_2}$		216
Co–Ag	2.66(1)	$\mathrm{(ttas)AgCo(CO)_4}$		10
Co–Au	2.50(1)	$\mathrm{(Ph_3P)AuCo(CO)_4}$		10
Rh–Rh	2.618(5)	$\mathrm{Rh_2(OAc)_2(dmg)_2(PPh_3)_2}$		262
	2.648(3)	$\mathrm{(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8}$		47
	2.717(5)(av.)	$\mathrm{N\text{-}n\text{-}Bu_4[Rh_6(CO)_{15}I]}$		48
	2.755(4)(av.)	$\mathrm{N\text{-}n\text{-}Bu_4[Rh_6(CO)_{15}I]}$		48
Ni–Ni	2.339(av.)	$\mathrm{[(Ph_3P)_2N]_2[W_2Ni_3(CO)_{16}]}$		41
	2.341(av.)	$\mathrm{[(Ph_3P)_2N]_2[Mo_2Ni_3(CO)_{16}]}$		41
Pt–Ge	2.433(2)	$\mathrm{PtPh(GePh_2OH)(PEt_3)_2}$		25
Pt–Pt	2.581	$\mathrm{Pt_2C_{20}H_{20}}$		166
Cu–Cu	2.494–2.674(5)	$\mathrm{[HCu(PPh_3)]_6}$		52
Au–Au	2.689(3)	$\mathrm{\{Au_9[P(}p\mathrm{\text{-}tol)_3]_8\}(PF_6)_3}$	(from central Au)	53
	2.729(3)	$\mathrm{\{Au_9[P(}p\mathrm{\text{-}tol)_3]_8\}(PF_6)_3}$	(from central Au)	53
	2.752–2.863(3)	$\mathrm{\{Au_9[P(}p\mathrm{\text{-}tol)_3]_8\}(PF_6)_3}$	(peripheral)	53

$\mathrm{[CCo_3(CO)_9]_2}$ (12)[15] and $\mathrm{C_2[CCo_3(CO)_9]_2}$ [16] have been studied; the latter result confirms the independent determination on a different crystalline form, containing benzene of crystallisation, reported in 1970 (see AS70; p. 61). The structures of two complexes obtained from reactions between $\mathrm{PhCCo_3(CO)_9}$ and mesitylene and cyclooctatetraene, respectively, reveal the mesitylene attached to only one cobalt in the former (13). The $\mathrm{C_8}$ ring bonds to all three cobalt atoms in $\mathrm{PhCCo_3(CO)_6(C_8H_8)}$ (14); the hydrocarbon is in the tub conformation, but tilted so that three of the four double bonds can interact with the three metal atoms.

The structure of $(\pi\text{-}C_5H_5)_2Zr(SiPh_3)Cl$ (15) reveals an unexpectedly long Zr–Si bond [2.813(2) Å], although no explanation for this can be found at present[17]. Both the silicon and zirconium are approximately tetrahedrally coordinated. The complex $W_2(CO)_8H_2(SiEt_2)_2$, obtained by irradiating a mixture of $W(CO)_6$ and SiH_2Et_2, has structure (16), containing a planar WSi_2W system[18]. This contains both W–Si and W–W bonds, the former being of unequal length. The longer bonds are presumed to be two-electron, three-centre W–H–Si bonds.



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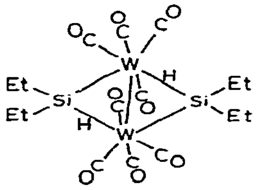

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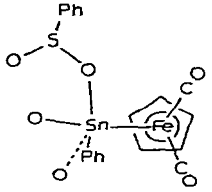
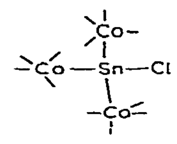


(17)

one half of the molecule shown

The complex previously formulated as $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh(OSOPh)(OH)$, and obtained from $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_3$ and SO_2, followed by ethanolysis of the product[19], has been shown to be the centrosymmetric dimer (17), with an unusual dihydroxo bridge linking two five-coordinate tin atoms[20]. The iron–tin bond length is identical to that found in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Sn(OSOPh)_2$ [AS68; p. 353]. The full details of the structure determination of $[Ru(CO)_3(GeMe_2)]_3$, obtained by pyrolysis of $Ru(CO)_4(GeMe_3)_2$, have appeared[21].



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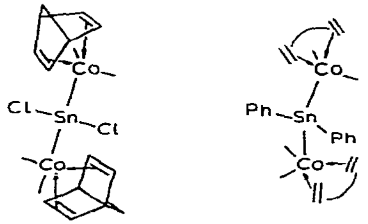


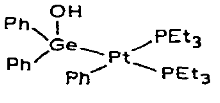
(19)

in (18) and (19) terminal carbonyl groups omitted for clarity.

The molecular structure of $ClSn[Co(CO)_4]_3$ (18) shows distorted tetrahedral geometry about the tin atom (angles CoSnCo ~114°) as a result of steric factors. The structures of $X_2Sn[Co(CO)_2(C_7H_8)]_2$ (X = Cl or C_6H_5; C_7H_8 = norbornadiene) (19), catalysts for the dimerisation of norbornadiene, show major derivations from the ideal tetrahedral geometry for the tin atom (see also AS70; p. 59)[23]. The opening of the CoSnCo angle (X = Ph, 118.3°; X = Cl, 128.3°) as the electronegativity of X increases had been predicted from IR measurements on $X_2Sn[Co(CO)_4]_2$, although this method gives larger predicted angles than found. The diene occupies one axial and one equatorial site of the trigonal bipyramidal cobalt atoms.

The compound formulated[24] as $Pt(OH)(GePh_3)(PEt_3)_2$ was shown by X-ray diffraction methods to be *cis*-$PtPh(GePh_2OH)(PEt_3)_2$ (20), establishing that an internal migration of an organic group, perhaps across the metal–metal bond, has occurred[25].

The extensive work which has been reported on complexes containing Group IVB atoms



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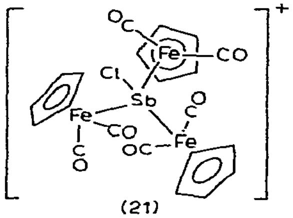
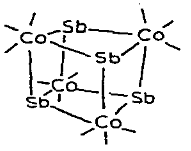


(21)

bonded to transition elements is not reflected in the neighbouring groups. Last year saw publication of accounts of the structures of the first complexes containing transition metal–antimony clusters. The reaction between $SbCl_3$ and the anion $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ affords $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_3SbCl\}FeCl_4$, obtained as the dichloromethane solvate[26]. In the complex cation (21), there is marked distortion from tetrahedral geometry about the antimony; one of the iron groups is rotated by approximately 143° about the Fe–Sb axis, and this feature destroys the pseudo-threefold symmetry of the cation. Comparisons with isoelectronic tin-containing systems underline the conclusion that d_π–d_π bonding does not appear to be an important feature of the metal–tin or –antimony bond. Similar results have been reported independently by others[27].

The tetrameric complex $Co_4(CO)_{12}Sb_4$ (22) has a cubane skeleton, joining the growing family of such molecules; this paper[28] includes a list of some seventeen complexes exhibiting this structural feature (see also AS70; p. 90). Whereas replacement of arsenic atoms in the As_4 tetrahedron by $Co(CO)_3$ groups stabilises the cluster, with antimony each triply-bridging $Co(CO)_3$ group is face-bonded, resulting in the present open structure, containing only Co-Sb bonds.



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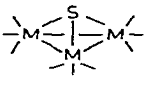


(23)

E = S, Se, Te
terminal CO groups omitted for clarity

In the cluster complex $Co_3(CO)_9S$, the unpaired electron is supposed to occupy an antibonding orbital (with respect to the cluster orbitals). Detailed comparison of the structural parameters with those of the diamagnetic $FeCo_2(CO)_9S$ cluster (23) reveals that the metal–metal bond distances decrease by 0.083 Å, whereas the metal–sulphur distances are only slightly longer [2.139(4) Å for Co_3, 2.158(4) Å for $FeCo_2$]. These results[29] provide the first structural evidence that electrons in excess of a closed-shell electronic configuration in an organometallic cluster occupy strongly antibonding metal orbitals. The determined bond distances are all equivalent [at 2.557 Å(av)], so that the crystal is disordered to the degree that each $FeCo_2$ unit is randomly distributed over three statistical orientations. These conclusions were further substantiated[30] by structure determinations of the complexes $Co_3(CO)_9Se$, $FeCo_2(CO)_9Se$ and $FeCo_2(CO)_9Te$; in the selenium complexes, the antibonding effect of the unpaired electron is less than found in the sulphur complex, as shown

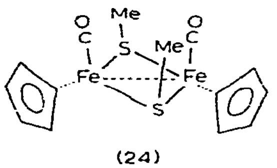
TABLE 2

AVERAGE BOND DISTANCES IN $M_3(CO)_9X$ (Å)

Complex	M–M	M–X
$Co_3(CO)_9S$	2.637(3)	2.139(4)
$Co_3(CO)_9Se$	2.616(1)	2.282(1)
$FeCo_2(CO)_9S$	2.554(3)	2.159(4)
$FeCo_2(CO)_9Se$	2.577(1)	2.285(1)
$FeCo_2(CO)_9Te$	2.598(2)	2.466(1)

by the overall decrease in Co–Co bond length in the selenium complex. The distances are summarised in Table 2. The structure of $Co_3(\pi\text{-}C_5H_5)_3S_2$ has been briefly mentioned[31].

The structures of several other cyclopentadienyl–metal–sulphur complexes have been determined. Oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)(SMe)]_2$ gives the cation (24), studied as the tetrafluoroborate[32]. The overall geometry of the cation is similar to that found previously for $[(\pi\text{-}C_5H_5)Fe(CO)(SPh)]_2$. However, the Fe–Fe bond distance decreases from 3.39 Å in the neutral dimer to 2.925(4) Å in the cation. This result is explained in terms of removal of an electron from a strongly antibonding orbital (with respect to the two iron atoms), resulting in the formation of a one-electron metal–metal bond in the cation.



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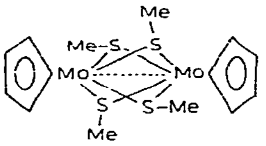
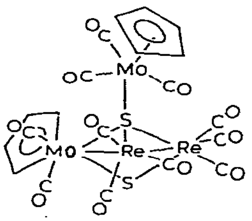


(25)

The molybdenum system $[(\pi\text{-}C_5H_5)Mo(SMe)_2]_2$, and the corresponding salt, $[(\pi\text{-}C_5H_5)Mo(SMe)_2]_2PF_6$ (25), both have the dimeric tetramercapto-bridged structure, and the metal–metal bonds in this case do not differ by more than 0.015 Å. This contrasts with the result obtained for the iron system (24), and is attributed to greater repulsion between the sulphur atoms in the neutral species[33]. In addition, the Mo–S–Mo angles (64°), presumably already strained, effectively prevent closer approach of the two metal atoms. With these steric constraints, the constancy of the bond distance need not imply that there is no change in the bond order. Reference is also made[34] to a preliminary determination of the $[(\pi\text{-}C_5H_5)Mo(SCCF_3)_2]_2$ structure, which is suggested to be similar to (25), and that the corresponding vanadium complex is isostructural.

The reaction between $[Re(CO)_4(SSnMe_3)]_2$ and $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ affords the mixed metal–sulphur complex $[Re_2Mo(\pi\text{-}C_5H_5)(CO)_8](S)[SMo(\pi\text{-}C_5H_5)(CO)_3]$ (26). The structure consists of an Re_2Mo cluster bridged by a sulphur atom on one side (as a four-electron donor), and on the other by a $SMo(\pi\text{-}C_5H_5)(CO)_3$ group. The central sulphur atom is unusual in being tetrahedrally coordinated by the four metal atoms, using all six valence electrons[35]. The only previous example is the complex $[Fe_2(CO)_6(SMe)]_2S$ [36].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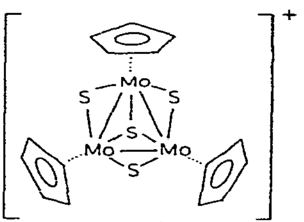
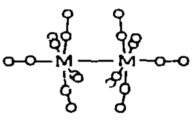

(26a)

In the complex $[(\pi\text{-}C_5H_5)_3Mo_3S_4]^+[SnMe_3Cl_2]^-$, the cation (26a) consists of a triangular Mo_3 cluster, with one triply-bridging sulphur atom, and three doubly-bridging sulphur atoms[37]. It is isostructural with $(\pi\text{-}C_5H_5)_3Mn_3(NO)_4$. The framework is a cubane-type with one $(\pi\text{-}C_5H_5)$Mo group removed. Strong electron-pair interactions are indicated by the relatively short Mo–Mo and Mo–S bond lengths.

(b) Transition metal cluster complexes. Direct comparison of two complexes differing only by the presence of a bridging hydrogen atom is possible as a result of the structure determinations of $[M_2(CO)_{10}]^{2-}$ (M = Cr or Mo) (as their $[(Ph_3P)_2N]^+$ salts) and $[Cr_2(CO)_{10}H]^{2-}$ (as the NEt_4^+ salt). Comparisons of the former with the isoelectronic $M'_2(CO)_{10}$ (M′ = Mn or Tc, respectively) are also made[38]. For isoelectronic pairs, the metal–metal bond distance is greater for the anion. ($[M_2(CO)_{10}]^{2-}$: M = Cr, 2.97(1) Å; M = Mo, 3.123(7) Å. $M_2(CO)_{10}$: M = Mn, 2.923(3) Å; M = Tc, 3.036(6) Å; M = Re, 3.04 Å.)
All four binuclear carbonyls (27) consist of two $M(CO)_5$ groups linked by a metal–metal bond, and have the staggered conformation. In contrast, the anionic hydride contains a linear Cr–H–Cr bond linking the two $Cr(CO)_5$ groups, which are eclipsed (28). The differing conformations may thus be attributed to Van der Waals interactions, and it is of interest that with $Re_2(CO)_{10}$, the eclipsed conformation is found in the vapour[39].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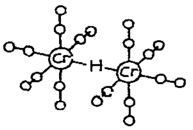
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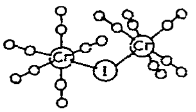
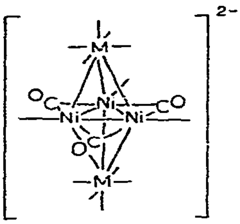

(29)

The formally related anionic carbonyl iodide $(Ph_3P)_2N[Cr_2(CO)_{10}I]$ (29) contains a bent Cr–I–Cr sequence [angle 117.9(1)°], with Cr–I distances of 2.789 Å[40].

Reactions between the dinuclear anions and $Ni(CO)_4$ have afforded a new type of cluster, the pentanuclear $[M_2Ni_3(CO)_{16}]^{2-}$ anions (M = Cr, Mo, W)[41]. These contain trigonal-bipyramidal clusters (30), consisting of a planar $Ni_3(CO)_3$ arrangement, with CO groups bridging each edge. Each $M(CO)_5$ group is symmetrically attached to the Ni_3 group using only one delocalised electron-pair bond. Disorder results in two statistical orientations of the $Ni_3(CO)_6$ fragment. The three Ni–M distances to one $M(CO)_5$ fragment are 0.1 Å shorter than to the other $M(CO)_5$ group. An MO picture allowing greater stabilisation in the anions by preferential accumulation of charge density on one side of the Ni_3 plane suggests



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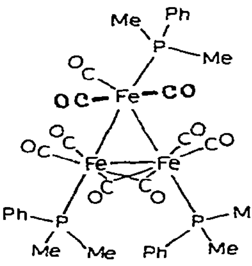

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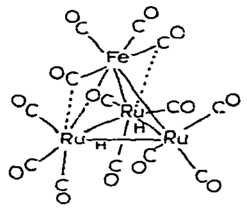
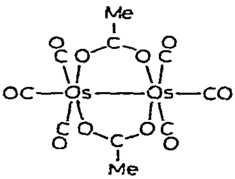


(32)

mixing of the p_y and $d_{x^2-y^2}$ orbitals, allowed by C_{3v} geometry (the asymmetry in Ni–M bond lengths deforms the M_2Ni_3 fragment from D_{3h} to C_{3v} symmetry).

The structure of $Fe_3(CO)_9(PMe_2Ph)_3$ (31) closely resembles that of $Fe_3(CO)_{12}$, with symmetric carbonyl bridges[42]. In $H_2FeRu_3(CO)_{13}$ (32) two Fe–Ru bonds are bridged asymmetrically by carbonyl groups [Fe–C, 1.68–1.86(7); Ru–C, 2.18–2.45(6) Å]; the two hydrogen atoms probably bridge Ru–Ru bonds so that the molecule as a whole has approximate mirror symmetry[43]. The full details of the structure determination of the hexanuclear hydride, $H_2Ru_6(CO)_{18}$, are now available[44]. The symmetrical enlargement of, and distortion of carbonyl groups away from two opposite faces of the octahedral Ru_6 cluster suggest the presence of mutually *trans* face-bonded hydride ligands.

The binuclear osmium complex $Os_2(CO)_6(OAc)_2$ (33) contains a single Os–Os bond, bridged by the two acetate groups in a *cisoid* conformation[45].



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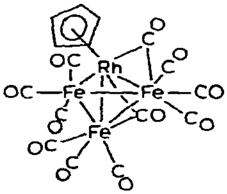

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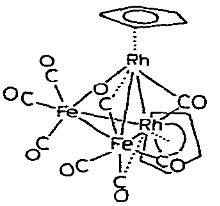
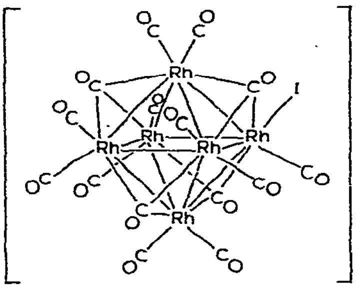


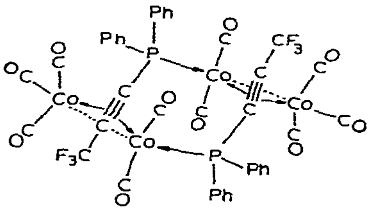
(35)

Two mixed metal clusters obtained from the reaction between $Fe_2(CO)_9$ and $(\pi\text{-}C_5H_5)Rh(CO)_2$ are $(\pi\text{-}C_5H_5)RhFe_3(CO)_{11}$ (34) and $(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$ (35). The former is a tetrahedral cluster of three $Fe(CO)_3$ groups and a $(\pi\text{-}C_5H_5)Rh$ group, with two bridging [Rh–(CO)–Fe] carbonyl groups. However, the ligands are relatively crowded, and other, probably bonding, metal–carbonyl interactions occur[46]. The Fe_2Rh_2 complex has a normal bridging carbonyl group associated with the two rhodium atoms, and two asymmetric carbonyl groups bridging iron and rhodium[47]. Ligands about the cluster are also overcrowded, as in (34). The anion $[Rh_6(CO)_{15}I]^-$ (36) consists of an octahedron of six rhodium atoms, with alternate faces triply-bridged by carbonyl groups. Five metal atoms bear two terminal carbonyls each, while the sixth has one carbonyl and the iodide ligand[48].



(36)

(c) Clusters containing organic ligands. The structure of $Co_4(CO)_{10}[Ph_2PC{\equiv}CCF_3]_2$ (37) shows the first example of a complex in which coordination is via the phosphorus and carbon–carbon triple bond[49].



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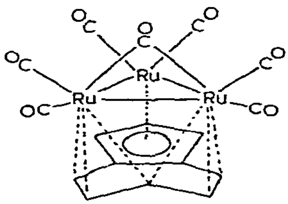
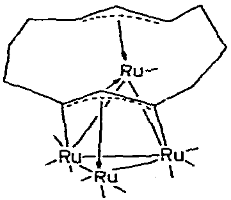


(38)

From the reaction between azulene and $Ru_3(CO)_{12}$, a trinuclear complex, $(C_{10}H_8)Ru_3(CO)_7$ (38), has been isolated[50], in addition to the tetranuclear one reported earlier (see AS69; p. 953). The azulene ligand is bonded to a triangular $Ru_3(CO)_7$ cluster, the metal atoms nearest the C_7 ring being bridged by a carbonyl group. Full details of the structure of $HRu_3(CO)_9(C_{12}H_{15})$ (39), containing a C_{12}-ring bonded to all three metal atoms, have now appeared. In last year's survey, the diagrams for this complex, and the related tetranuclear complex $Ru_4(CO)_{10}(C_{12}H_{16})$ (40), were confused; the two structures below indicate the salient features.

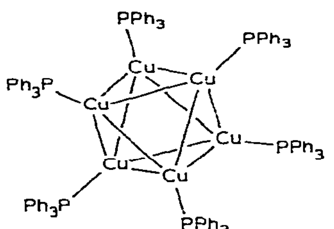
(39)



(40)

terminal CO group omitted for clarity

Although not falling within the usual definition of organometallic compounds, some clusters containing Group IB elements have been described. The copper hydride $[CuH(PPh_3)]_6$ (41), contains an octahedron of metal atoms with face-bonding hydride ligands[52]. Two phosphine-gold clusters are unusual in that they contain nine and eleven metal atoms,



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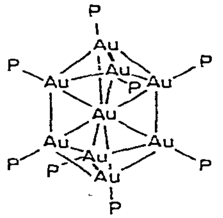

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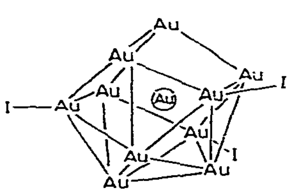
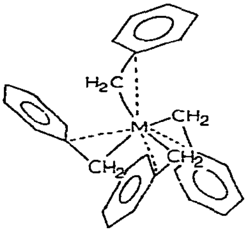


(43)

Bonds from central Au atom in (43) not shown. Phosphine ligands are attached to Au not bonded to I.

respectively; both are derived from the icosahedron as shown. The Au_9 cluster in $\{Au_9[P(p\text{-tol})_3]_8\}^{3+}$ (42) is a centred icosahedron from which an equatorial rectangle is missing[53]; the Au_{11} clusters in $[Au_{11}(PPh_3)_7]^{3+}$ [54] and in $Au_{11}[P(p\text{-}ClC_6H_4)_3]_7I_3$ (43)[55] can be similarly derived by replacing one face (three apices) by a gold atom.

Compounds containing metal–carbon σ bonds. Tetrabenzyl derivatives of the Group IV elements (44) are catalysts for the polymerisation of ethylene and α-olefins. The structures of titanium[56], zirconium[57], and hafnium[58] compounds have been determined, and compared with that of $Sn(CH_2Ph)_4$ [58]. The four benzyl groups bond to the transition metals in a distorted tetrahedral arrangement, although they are still essentially σ-bonded. In contrast, the tin compound has almost perfect tetrahedral coordination. The benzyl carbon atoms are all coplanar (within each group). The most interesting feature is an apparent M–C interaction with the β-carbon atom, probably via a π overlap of the β carbon orbitals with empty metal *d* orbitals. This feature may also explain the unusual stability of these complexes.



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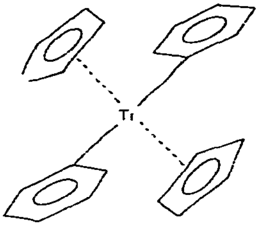

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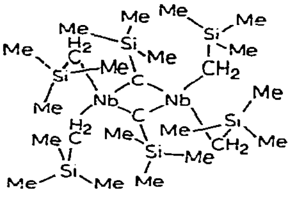
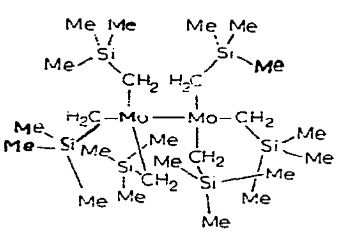


(46)

A pseudo-tetrahedral arrangement of ligands about the titanium atom was found in $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (45)[59].

The product from $NbCl_5$ and Me_3SiCH_2MgCl has the stoichiometry $Nb_2(CSiMe_3)_2(CH_2SiMe_3)_4$, with structure (46). The two metal atoms are bridged by the unusual Me_3SiC groups, with multiple Nb–C bonds; the resulting quasi-aromatic $Nb\text{–}(C)_2\text{–}Nb$ ring explains the diamagnetism, there being no metal–metal bond. The tantalum analogue is isostructural[60]. In contrast, the molybdenum compound, $Mo_2(CH_2SiMe_3)_6$, originally reported as $Mo(CH_2SiMe_3)_4$, has the staggered structure (47), with a molybdenum–molybdenum triple bond. The tungsten derivative is isostructural[61].

In $Li_4Cr_2(C_4H_8)_4$ (48), the tetramethylene groups form a CrC_4 heterocycle; two such



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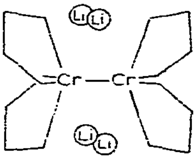

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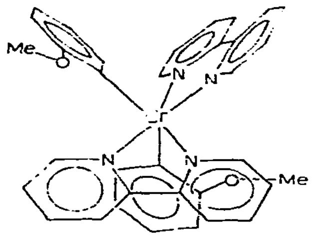

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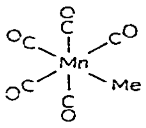


(50)

rings have a common metal atom, and are staggered with respect to the second chromium atom. The metal–metal bond is short, and there is some interaction between the four lithium atoms and the Cr–Cr quadruple bond[62]. An air- and water-stable organochromium complex can be obtained from the reaction between $CrBr_2(THF)_2$ and the 2-methoxy phenyl (an) Grignard reagent; addition of 2,2′-bipyridyl gives dark red $[Cr(an)_2(bipy)_2]I$ (49). The chromium has distorted octahedral coordination, with Cr–C bond lengths 2.10(1) Å [63].

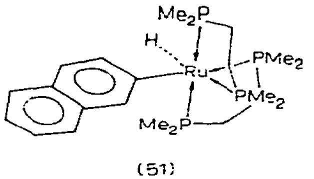
An electron diffraction determination of the structure of $MeMn(CO)_5$ (50) has been described[64].

The chemical properties of the system

$$cis\text{-}MH(C_{10}H_7)(dmpe)_2 \rightleftharpoons M(C_{10}H_8)(dmpe)_2$$

(M = Ru, Os)

suggest that the ruthenium compound behaves as the Ru^0 complex, although physical data (IR, NMR) suggest the solid is the Ru^{II} complex. Crystal structures of the ruthenium and osmium complexes confirm[65] the latter finding, and show that the hydridic hydrogen is *cis* to the σ-naphthyl group in both complexes (51).



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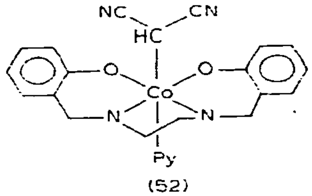
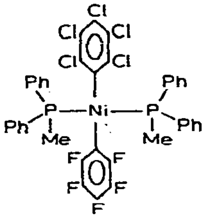


(52)

The structure of [Co(mn)(py)(salpn)] (52) [mn = $CH(CN)_2$; salpn = dianion of *N,N′*-bis(salicylideneimine)-1,2-propane] has been described briefly[66].

In *trans*-$Ni(C_6F_5)(C_6Cl_5)(PMePh_2)_2$ (53), the Ni–C_6Cl_5 bond is shorter than the Ni–C_6F_5 bond [1.905(10) vs. 1.978(10) Å]. Possible reasons for this include differences in $d_\pi - p_\pi$ metal→ligand back-bonding, in relative *trans* effects, and in Ni–C bond strengths[67]. A comparison of available data on transition metal–aryl complexes shows that within the C_6 ring, the internal angle at the metal-bonded carbon decreases from 120° (range 112–116°), while those at the *ortho*-carbons increase (122–128°).



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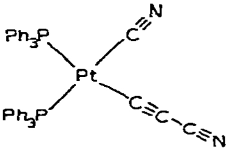
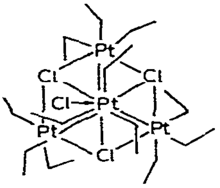


(54)

In *cis*-Pt(CN)(C≡CCN)$(PPh_3)_2$ (54), the C–C triple bond is long, whereas the C–CN bond is short [at 1.24 and 1.31(5) Å, respectively], suggesting a degree of delocalisation of the type Pt=C=C=C=N[68].

The structure of $[Et_3PtCl]_4$ (55) is another example of the cubane-type structures now becoming common. The ethyl groups are sterically restricted within the molecule[69]. A second structure determination[70] of $(\pi\text{-}C_5H_5)PtMe_3$ (56) confirms the π-complex structure; no disorder was found in the carbon atom positions. The mean Pt–C(Me) distance is 2.11 Å.



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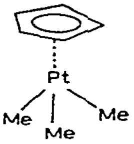
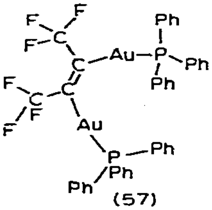


(56)

The reaction between $C_2(CF_3)_2$ and AuMe(PPh_3) affords the binuclear complex $(Ph_3PAu)_2C_2(CF_3)_2$, shown[71] to have the *cis* structure (57). It is the first ethylenic derivative in which each carbon is attached to a metal via a σ bond. The *ortho*-metallated complex $Ph_2PC_6H_4Rh(PPh_3)_2$ forms the unusual complex (58) on reaction with diphenylacetylene, containing a 5-phospha-6-rhodabenzocyclooctene heterocycle[72]. The σ,π-arrangement is also found in the bis-insertion product obtained from $(\pi\text{-}C_5H_5)Ru(PPh_3)_2H$ and $C_2(CF_3)_2$, which has structure (59), although in this case a 1,2,4-*trihapto*-butadienyl group is found[73].



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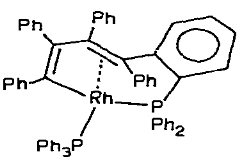
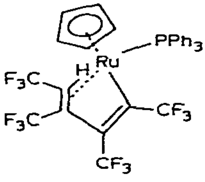
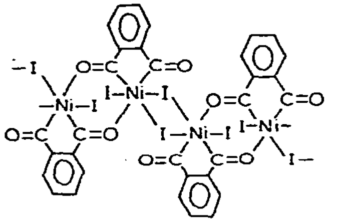


(58)



(59)

Other unusual products containing metal–carbon σ bonds include *catena*-{Ni[$C_6H_4(CO)_2$-*o*]I_2} (60), obtained from $Ni(CO)_4$ and 1,2-diiodobenzene[74], originally thought to be a benzyne complex, and three rhodium complexes. Addition of $C_2(CF_3)_2$ to Rh(acac)(COD) affords (61), containing a π-hexakis(trifluoromethyl)benzene,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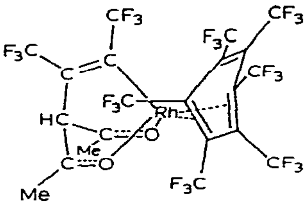
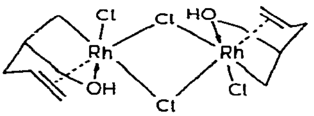

(61)

together with a σ-bonded ligand formed by 1,4 addition of the alkyne to the Rh(acac) ring[75]. With allyl alcohol, hydrated $RhCl_3$ gives (62), containing the novel tridentate $C_6H_{11}O$ ligand shown; the complex is an efficient catalyst for the cyclisation of diallyl ether to 3-methyl-4-methylenefuran[76]. With 2-methallyl alcohol, hydrated $RhCl_3$ gives yellow-brown $[RhCl_2(C_8H_{15}O_2)]_n$, which with 4-methylpyridine gives (63), containing a substituted furan σ-bonded to rhodium[77].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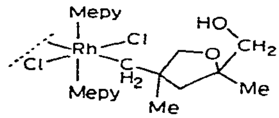
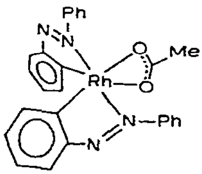

(63)

Ortho-metallated and related complexes. In recent years, the direct formation of metal–carbon σ bonds by reaction of suitable metal substrates with a variety of ligands has been noted. Among the first examples described were metallations of azobenzene (azbH) by palladium and platinum chlorides[78], and by nickelocene[79]. This coordination-directed metallation, which in the particular case of aromatic derivatives, has been termed the *ortho*-metallation reaction, has been studied in more detail by several groups. Last year the structure of a palladium–azobenzene derivative was described (AS70; p. 68), as was that of a rhodium–phosphine complex.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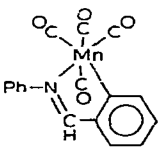
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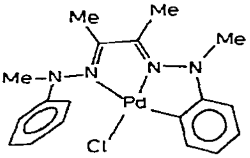
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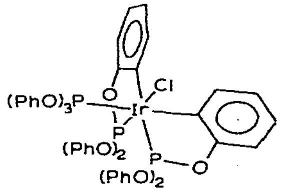
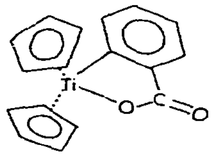

(67)

The structure of a rhodium–azobenzene complex, $(azb)_2Rh(OAc)$ (64), was the first of a complex containing a chelating phenylazophenyl group[80], and was followed later by structure determinations of a manganese–benzylideneaniline complex, $C_6H_5N{=}CHC_6H_4Mn(CO)_4$ (65)[81], and of a palladium complex (66) obtained from biacetylbis(*N*-methyl-*N*-phenyl)osazone[82]. In all cases, the complex contains a five-membered ring involving a metal–carbon σ bond. A similar feature was found in the *ortho*-metallated triphenylphosphite complex (67), obtained by controlled pyrolysis of $IrHCl_2[P(OPh)_3]_3$ in refluxing decalin[83].

Reaction of $(\pi\text{-}C_5H_5)_2TiPh_2$ with carbon dioxide affords a product (68) which also contains an *ortho*-metallated aromatic group, although its formation is considered[84] to occur via insertion of CO_2 into a Ti–C bond of the benzyne complex (68a).



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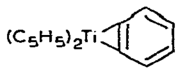
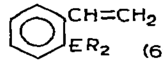
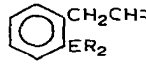


(68a)



(69a)

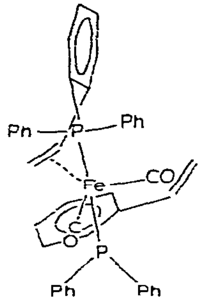
ER_2=PPh_2(sp); $AsMe_2$(sa)



(69b)

ER_2=PPh_2(ap); $AsMe_2$(aa)

Studies of the intramolecular metallation of π-bonded olefins have profited by a series of structural determinations carried out on various metal complexes obtained from the olefinic tertiary phosphines and arsines (69a and 69b; ER_2 = PPh_2 or $AsMe_2$). The reaction between sp and $M_3(CO)_{12}$ (M = Fe or Ru) give $M(CO)_3(sp)$ and $M(CO)_2(sp)_2$; the structure of the iron dicarbonyl derivative reveals that one ligand is chelated, while the second is monodentate *P*-bonded (70)[85]. Addition of HCl or HBr to complexes of the first type gives octahedral σ-bonded chelate complexes, as exemplified by the structure of the ruthenium bromo derivative (71)[86].



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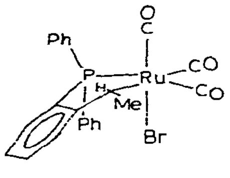
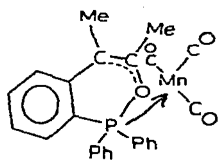


(71)

The two products obtained from the reaction between $MeMn(CO)_5$ and sp have been shown[87] to be the π-oxopropyl complex (72), and the σ-oxobutyl complex (73). The formation of the former results from acetyl attack at the vinyl α-carbon, accompanied by hydride migration; complex (73) is formed by a similar reaction at the β-carbon atom of the coordinated sp ligand.

Bromination of the linear gold(I) complexes LAuBr (L = sp or ap) gave complexes of formula $LAuBr_3$ in which the ligand itself has also been brominated with concomitant formation of a gold–carbon σ bond[88]. In the product derived from sp (74), a 5-membered ring with an envelope conformation is formed; the allylphenylphosphine reacts to give a 6-membered ring with a twist-boat conformation (75). In both cases, an exocyclic bromo-



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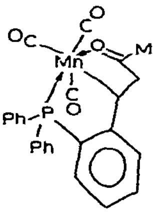
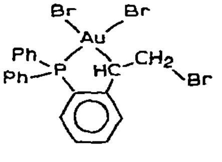


(73)



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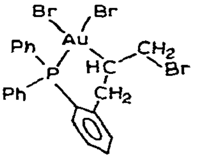

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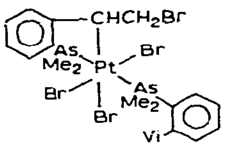

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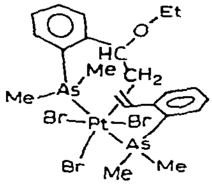
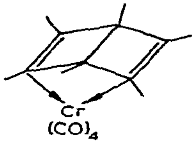


(77)

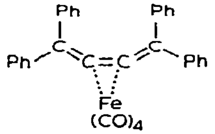


(78)

methyl group is attached to the gold-bonded carbon atom. Solvolysis of the related platinum complex (76) in ethanol gives an ethoxy derivative, which proves to contain a 6-membered chelate ring, also with the twist-boat conformation (77). An analogy with the Wagner–Meerwein rearrangements occurring in ring expansions of cycloalkanecarbinyl systems is drawn[89].

Olefin complexes. The full account of the structure of hexamethylbicyclo[2.2.0]hexa-2,5-diene–chromium tetracarbonyl (78) (see AS68; p. 359) is now published[90]. The ligand consists of two fused cyclobutene units with a dihedral angle of 113°, occupying two *cis* positions about the octahedrally coordinated metal atom.

The tetraphenylbutatriene ligand in (79) is coordinated to the iron atom via the central double bond; however, although the three double bonds are of equal length, they are longer than in the uncomplexed hydrocarbon[91]. The main effect of coordination is the bending back of the outer carbon atoms by nearly 30°.



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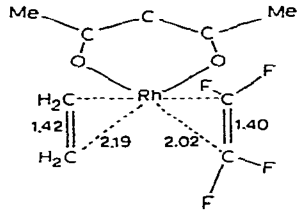

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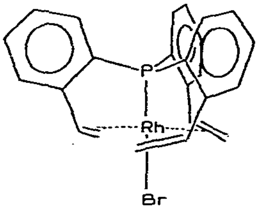
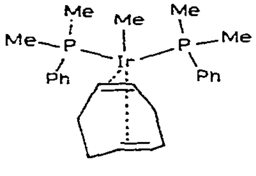


(81)

A comparison of the geometries of $Rh(acac)(C_2H_4)(C_2X_4)$ (80) (X = H or F) shows that tetrafluoroethylene is the more closely bound to rhodium, as expected from the relative π-acceptor properties of the two olefins[92]. In the tri-*o*-vinylphenylphosphine complex (81), the six olefinic carbons are nearly coplanar with the metal, which has trigonal bipyramidal coordination[93].

Full details of the duroquinone–rhodium complexes $(\pi\text{-}C_5H_5)Rh(DQ)$ [94] and (acac)Rh(DQ)[95], described last year (AS70; p. 70) have now appeared. The conformation of the duroquinone (non-planar boat) does not appear to depend on the nature of the "second" ligand attached to rhodium.

Some iridium–cyclooctadiene–tert-phosphine complexes exhibit temperature-dependent proton NMR spectra resulting from intramolecular rearrangements. The coordination of iridium in both $IrMe(C_8H_{12})(PMe_2Ph)_2$ (82) and $IrMe(C_8H_{12})(dppe)$(83) is trigonal bipyramidal[96]. The greater case of rearrangement in the latter may be related to the greater strain [cf. angles P–Ir–P in (82), 101.5(2)°, and (83), 84.9(2)°].



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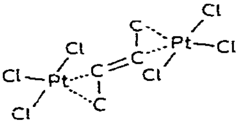
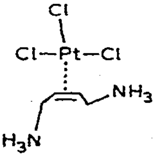


(84)

As briefly mentioned in the last survey, the structure of the prototype olefin complex, namely Zeise's salt, has been redetermined[97]. This resulted from the discovery that the true space group is $P2_1/c$, whereas in previous determinations[98], the space group $P2_1$ had been used. The resulting parameters differ little from those previously established, although there are differences in the method of linking potassium coordination polyhedra. The Pt–Cl bond lengths, *cis* and *trans* to ethylene, are 2.305(7) and 2.327(5) Å respectively; the C=C bond is 1.37(3) Å, and is symmetrically π-bonded to platinum [Pt–C, 2.13(2) Å]. In the anion of $(NMe_3Et)_2[Pt_2Cl_6(C_4H_6)]$ (84), two $PtCl_3$ groups are linked by the *trans*-buta-1,3-diene ligand[99]. The C–C bond lengths suggest that coordination involves a 1,4-addition to the diene, with the central C–C bond [1.36(3) Å] being shorter than the outer ones [1.51(3) Å]. This contrasts with the structure of $[(\pi\text{-}C_5H_5)Mn(CO)_2]_2(C_4H_6)$.

The *trans*-but-2-en-1,4-diammonium complex (85) contains both optically active cations; this paper[100] also contains a summary of the relevant structural data from ten other complexes of this type. The absolute configurations of other platinum–olefin complexes have been determined: (–)-*cis*-dichloro(*trans*-2-butene) [(*S*)-α-phenethylamine] platinum (86)[101], (+)-*cis*-dichloro[(*S*)-1-butene] [(*S*)-α-methylbenzylamine] platinum (87)[102], and *trans*-dichloro(benzylamine)[(2*R*,3*S*)-3-methyl-1-pentene] platinum (88)[103].



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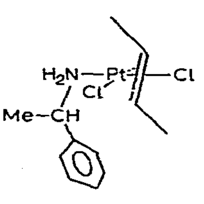

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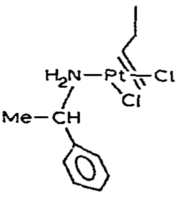

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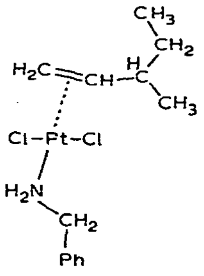
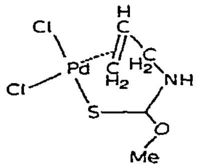


(88)

The palladium complex (89) is monomeric, and contains the *O*-methyl-*N*-allylthiocarbamate ligand chelating via the sulphur atom and the double bond[104]. The latter is short [1.30(4) Å], and indicates only a weak π-bond.

The copper(I) chloride complex of *trans*-cyclooctene of stoichiometry $Cu_2Cl_2(C_8H_{14})_3$ has the chlorine-bridged structure (90), in which the coordination of one copper atom is trigonal-planar, and the other, a distorted pyramidal-trigonal arrangement[105]. The Cu_2Cl_2 system is non-planar and asymmetric.



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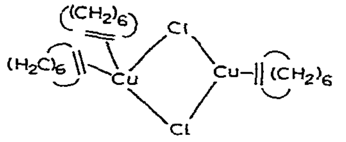
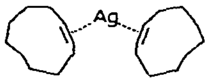


(90)

Silver has been used as the heavy atom in structure determinations of *cis*-cyclodecene (91) and 1,1,4,4-tetramethyl-*cis*-cyclodec-7-ene (92)[106], *trans*-cyclododecene (93)[107] and *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (94)[108]. Further details of the structure of the germacratriene complex have also appeared[109]. In the aromatic series, the structure of the cyclohexylbenzene complex (95) has been described[110], and in the silver complex of Antibiotic X537A, the silver is complexed to the phenyl ring in addition to five oxygen atoms[111].



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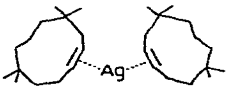

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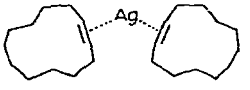


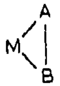
(93)

(94)

Complexes containing three-, four- and five-membered rings. Structural data for many complexes formed by oxidative-addition or -elimination reactions are summarised in Table 3. These compounds are distinguished by the presence of a three-membered ring containing the metal. Current theories about the mode of bonding between the metal and the other two atoms favour a situation in which there is considerable back-bonding into the π* orbitals of the multiple bond, resulting in an oxidation state approaching 2+ (Ni,Pd,Pt) or 3+ (Rh,Ir) for the metal, and considerable lengthening of the multiple bond. This is accompanied by a degree of rehybridisation of the atoms comprising the multiple bond, and is reflected in the structural parameters, as listed in the Table. An account of the major developments in this area was given at the 5th International Conference on Organometallic Chemistry, held in Moscow during August 1971[112].

The structures of several hydrocarbon complexes of this type have been described. A number of allene complexes have been synthesised. Full details of the structures of $Rh(acac)(C_7H_{12})_2$ and $[PtCl_2(C_7H_{12})]_2$ (C_7H_{12} = tetramethylallene) have appeared[113]. In both cases the coordinated allene is perpendicular to the coordinating plane, and behaves as a monoolefin; it is no longer linear.

TABLE 3

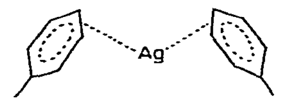
SOME STRUCTURAL DATA FOR 3-MEMBERED RINGS 

Complex $L_nM(A-B)$	Bond distances (A) M–A	M–B	A–B	Other data	Reference
(a) Tetracarbonyliron complexes					
$(CO)_4Fe(H_2C{=}CH_2)$	2.117(30)		1.46(6)		263
$[(CO)_4Fe]_2(1,5\text{-}C_8H_{12})$	2.154(5)	2.140(6)	1.400(9)		264
$(CO)_4Fe[H_2C{=}CH(CN)]$	2.09(1)	2.10(1)	1.40(2)		265
$(-)\text{-}(CO)_4Fe[(CO)_2H)HC{=}CH(CO_2H)]$	2.06(3)		1.30(4) 1.40(5)		266
$(CO)_4Fe(Ph_2C{:}C{=}C{:}CPh_2)$	2.04(1)	2.06(1)	1.35(2)	∠C=C:C 151(1)°	91
$(CO)_4Fe(C_6F_5As{=}AsC_6F_5)$	2.510(9)	2.510(9)	2.388(7)		208
(b) Acetylacetonatorhodium complexes					
$(acac)Rh(H_2C{=}CH_2)_2$	2.13(2)	2.14(2)	1.41(3)		92
$(acac)Rh(H_2C{=}CH_2)(F_2C{=}CF_2)$	2.19(1)	2.19(1)	1.42(1)	(C_2H_4)	92
	2.00(1)	2.02(1)	1.40(2)	(C_2F_4)	
$(acac)Rh(Me_2C{=}C{:}CH_2)_2$	2.06(1)	2.13(1)	1.40(1)	∠C=C:C 153(1)°	267
$(acac)Rh(Me_2C{=}C{:}CMe_2)_2$	2.027(5)	2.177(6)	1.373(8)	∠C=C:C 148(1)°	113
$[(acac)Rh(CO)]_2(H_2C{=}C{=}CH_2)$	2.06(1)	2.13(1)	1.39(1)	∠C=C:C 144.5(6)°	267
(c) Bis(tertiary-phosphine)rhodium complexes					
$(Ph_3P)_2ClRh(F_2C{=}CF_2)$	2.01(2)	2.00(2)	1.41(3)		268
$(Ph_3P)_2IRh(H_2C{=}C{:}CH_2)$	2.04(4)	2.17(4)	1.35(6)	∠C=C:C 158(4)°	269
$[(dppe)_2Rh(O{=}O)](PF_6)$	2.026(8)	2.025(9)	1.418(11)		270
(d) Bis(tertiary-phosphine)carbonyliridium complexes					
$(Ph_3P)_2(CO)HIr[(CN)HC{=}CH(CN)]$	2.110(9)		1.431(20)		271
$(Ph_3P)_2(CO)BrIr[(CN)_2C{=}C(CN)_2]$	2.148(11)		1.506(15)		272
$(Ph_3P)_2(CO)(C_6N_4H)Ir[(CN)_2C{=}C(CN)_2]$	2.176(10)	2.155(9)	1.526(12)		120
$(Ph_3P)_2(CO)ClIr(O{=}O)$	2.09(3)	2.04(3)	1.30(3)		273
$(Ph_3P)_2(CO)IIr(O{=}O)$	2.035(20)	2.082(22)	1.509(26)	CH_2Cl_2 solvate	274
$(Ph_2EtP)_2(CO)ClIr(O{=}O)$	2.036(9.5)	2.084(9.5)	1.461(14)		124
$[(dppe)_2Ir(O{=}O)](PF_6)$	1.961(18)	1.990(16)	1.625(23)		270

(Table continued)

(e) Bis(tertiary-phosphine)nickel complexes					
$(Ph_3P)_2Ni(H_2C{=}CH_2)$	2.00(2)	2.02(2)	1.46(2)		275
$(Ph_3P)_2Ni[(CF_3)_2C{=}O]$	1.89(2)	1.87(1)	1.32(2)		121
(f) Bis(isocyanide)nickel complexes					
$(t\text{-}BuNC)_2Ni[(CN)_2C{=}C(CN)_2]$	1.956(4)	1.951(4)	1.476(5)		276
$(t\text{-}BuNC)_2Ni(PhN{=}NPh)$	1.897(4)	1.897(4)	1.385(5)		126
(g) Bis(tertiary-phosphine)palladium complexes					
$(Ph_3P)_2Pd(S{=}C{:}S)$	2.00(3)	2.305(11)	1.65(3)	∠ S=C:S 140(2)°	277
(h) Bis(tertiary-phosphine)platinum complexes					
$(Ph_3P)_2Pt[(CN)HC{=}CH(CN)]$	2.05(2.4)	2.16(2.4)	1.53(3.6)		278
$(Ph_3P)_2Pt[(CN)_2C{=}C(CN)_2]$	2.12(3)	2.10(3)	1.49(5)		279
$(Ph_3P)_2Pt[Cl_2C{=}C(CN)_2]$	2.00(2)	2.10(2)	1.42(3)		119
$(Ph_3P)_2Pt(Cl_2C{=}CCl_2)$	2.02(3)	2.05(3)	1.62(3)		118
$(Ph_3P)_2Pt(H_2C{=}C{:}CH_2)$	2.03(3)	2.13(3)	1.48(5)	∠ C=C:C 142(3)°	114
$(Ph_3P)_2Pt(Me_2$ cyclopropene)	2.11(1)	2.12(1)	1.52(2)		117
$(Ph_3P)_2Pt(PhC{\equiv}CPh)$	2.06	2.01	1.32	∠ C≡C–Ph 140	280
$(Ph_3P)_2Pt$ (cyclohexyne)	2.023	2.055	1.289	∠ C≡C–C 127	115
$(Ph_3P)_2Pt$ (cycloheptyne)	2.041	2.068	1.294	∠ C≡C–C 139	116
$(Ph_3P)_2Pt[(CF_3)_2C{=}NN{:}C(CF_3)_2]$	2.02	2.11	1.44		122
$(Ph_3P)_2Pt(S{=}C{:}S)$	2.063(46)	2.328(16)	1.72(5)	∠ S=C:S 136.2(44)°	281
$(Ph_3P)_2Pt(O{=}O)$	1.90(5)	1.99(5)	1.26(5)	$CH_3C_6H_5$ solvate	282
	2.01(2)	2.01(2)	1.45(4)	$1\frac{1}{2}C_6H_6$ solvate	283
	2.006(7)		1.505(16)	$2CHCl_3$ solvate	123

The structure of $Pt(PPh_3)_2(C_3H_4)$, in contrast, shows that the allene lies in the coordination plane, and is also bent; the complex is isostructural with the carbon disulphide complexes $M(PPh_3)_2(CS_2)$ (M = Pd, Pt)[114]. Small-ring acetylenes have been stabilised by coordination to platinum. The structures of both the cyclohexyne[115] and cycloheptyne[116] complexes have been determined. The most significant differences between the two involve the ring interbond angles, the deformations at the coordinated triple bond being some 12–16° more than calculated for the free cycloalkyne. The dimethylcyclopropene complex (96) contains an intact cyclopropene ring, in contrast to reactions of cyclopropane, which forms four-membered PtC_3 rings[117]. As expected, the C=C bond is lengthened, to 1.50(2) Å.



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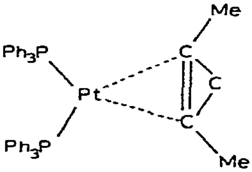
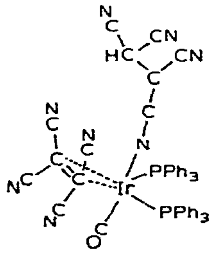


(96)

Complexes containing three-membered rings have most frequently been obtained using ligands, e.g. substituted ethylenes, containing electron-withdrawing groups, such as halogens or cyano groups. The structures of a series of these complexes, $Pt(PPh_3)_2$(olefin), containing $ClFC{=}CF_2$, $Cl_2C{=}CF_2$, $Cl_2C{=}CCl_2$, and $Cl_2C{=}C(CN)_2$ were reported during the year under review[118]. On coordination the olefin loses its planar geometry, with the substituents being bent back from the central metal atom. Comparisons with the related tetracyanoethylene complex suggest that in the chloro- and chlorofluoroolefin complexes, the Pt–C distance is shorter than those found in the former complex. This problem was examined in more detail[119] in the structure of $Pt(PPh_3)_2[Cl_2C{=}C(CN)_2]$, in which the two olefinic carbon atoms are not equidistant from the metal; the $Pt{-}CCl_2$ bond is 0.1 Å shorter than the $Pt{-}C(CN)_2$ bond. This difference is also reflected in the degree of bending of the CX_2 groups, the CCl_2 group being bent back by about twice as much as the $C(CN)_2$ group.

The structure of the product from TCNE and $IrH(CO)_2(PPh_3)_2$ was found to have the novel structure $Ir(C_6N_4H)(CO)(PPh_3)_2[(CN)_2C{=}C(CN)_2]$ (97)[120]. Formal insertion of one of the CN groups into the Ir–H bonds has given a cyano(dicyanomethyl)keteniminato group attached to the metal via an Ir–N bond. Coordination of the second TCNE molecule



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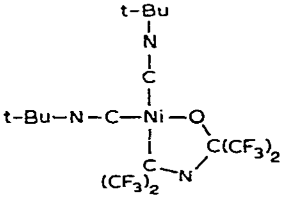

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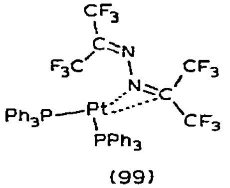

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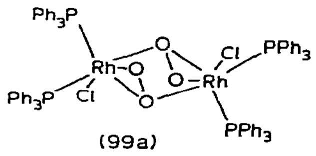


(99a)

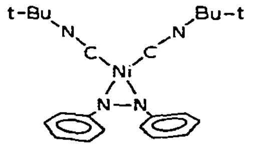
results in similar lengthening of the C=C bond, and bending of the $C(CN)_2$ groups away from the metal, to the complexes described above.

The hexafluoroacetone derivative $Ni(PPh_3)_2(HFA)$ has a structure with a sideways coordinated carbonyl group, in which the C=O bond is lengthened by 0.09 Å relative to the free ketone[121]. A ring-expansion reaction of the analogous complex $Ni(CNBu\text{-}t)_2(HFA)$ with $(CF_3)_2C{=}NH$ afforded the five-membered ring shown in (98), in which the entering imine has formally inserted into the Ni–C bond of the original complex.

A complex obtained from $Pt(PPh_3)_4$ and $(CF_3)_2CN_2$ has the structure (99), in which one of the C=N double bonds is coordinated to the platinum[122]. Rapid inversion at the coordinated nitrogen atoms occurs in solution.

The dioxygen complex $Pt(PPh_3)_2O_2$ (as the chloroform adduct) has an O–O bond length of 1.505(16) Å, compared to a value of 1.45(4) Å determined in the benzene adduct. Differences in bond lengths caused by solvate molecules have not previously been considered, and may have some bearing on discussions concerning the relative amounts of back-bonding occurring with reversible and non-reversible dioxygen adducts[123]. In $IrCl(CO)(PEtPh_2)_2(O_2)$, the bond distance is 1.461(14) Å, again emphasising that small changes in ligands cause significant changes in some bond distances[124]. In contrast to these results, the adduct $RhCl(PPh_3)_2(O_2)\cdot CH_2Cl_2$ (99a) was found to contain dimeric units, in which the dioxygen molecule is not only bonded to the rhodium in the usual manner [O–O, 1.44(2) Å], but also acts as a bridging ligand to the second metal atom[125].

A novel example of an unsaturated molecule π-bonded to nickel via two non-carbon atoms is found in the azobenzene complex $Ni(CNBu\text{-}t)_2(PhN{=}NPh)$, which has structure (100). As with most complexes of this type, the N=N bond is significantly longer than in the free ligand [1.385(5) vs. 1.17, 1.23 Å][126].



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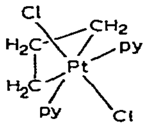

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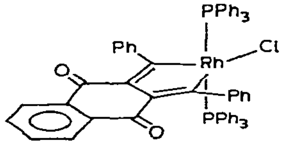

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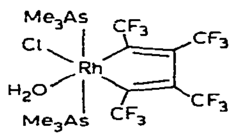


(103)

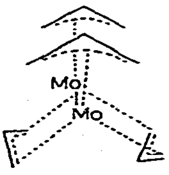
The reaction between cyclopropane and chloroplatinic acid gives $[PtCl_2(C_3H_6)]_n$; subsequent addition of pyridine affords $[PtCl_2(py)_2(C_3H_6)]$ (101), in which the platinum has inserted into the C_3-ring[127]. Detailed discussion of the bond lengths in the C_3Pt ring was not possible because of limited diffraction data.

The reaction between $RhCl(PPh_3)_3$ and 1,2-bis(phenylpropynoyl)benzene gave the metallocyclopentadiene derivative (102), thought to be formed via a similar insertion reaction[128]. Decarbonylation of $RhCl(CO)(AsMe_3)_2[C_4(CF_3)_4]$ in moist benzene affords (103), also containing a substituted metallocyclopentadiene ring[129]. This complex is notable for the presence of a coordinated water molecule. As in $RhCl(SbPh_3)_2C_4(CF_3)_4$ (AS70; p. 92), the RhC_4 ring is essentially planar.

Complexes containing acyclic 3-, 4-, and 5-electron donors. The structure of $Mo_2(C_3H_5)_4$ (104) reveals a strong quadruple metal–metal bond, with two symmetrically-bridging allyl groups[130]. It is very similar to that of the chromium complex (AS69; p. 964).

The rhodium(III)–allyl complex (105) is obtained from Rh(dbm)$(C_2H_4)_2$ and allene; the four allene molecules have oligomerised to form a 2,5-bis(π-allyl)hexa-1,5-diene ligand[131].

Palladium–allyl complexes whose structures have been determined include the β-(3-chloro-1-propen-2-yl)allyl derivative (106)[132], and the cyclohexanone oxime complex (107)[133]. In the latter, the oxime is coordinated to one palladium via the nitrogen atom. A chlorine forms a Cl$\cdots$H–O hydrogen bond with the oxime hydroxyl group. The norbornene-π-methallylpalladium insertion product, studied as the acetate (108), contains the 2-methylallyl-3-norbornyl ligand bonded via the allyl double bond, and a Pd–C σ bond from the norbornene residue[134].



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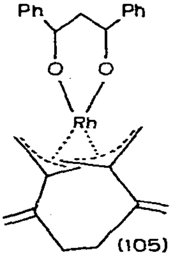

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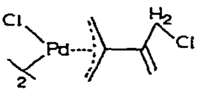

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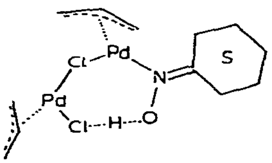
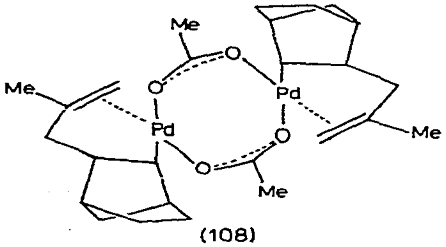


(107)

A complete account of the structure of the enyl–diene–cobalt complex, Co$(C_8H_{13})(C_8H_{12})$ has appeared[135] (AS69; p. 961).

The reaction between $Fe_2(CO)_9$ and an equimolar mixture of 1- and 2-bromomethylnaphthalene affords the substituted trimethylene–methane complex (109). Coordination to iron results in loss of aromaticity of the ring and consequent bond localisation[136].



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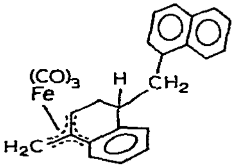

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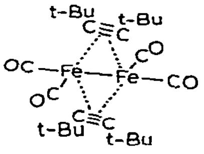
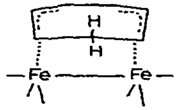


(110)

The unusual complex (110), obtained from $Fe_3(CO)_{12}$ and $C_2Bu\text{-}t_2$, has a very short Fe–Fe bond, apparently of bond-order two[137]. The two acetylene ligands both bridge this bond. The C≡C triple bonds are lengthened to 1.283 Å, and the t-butyl groups are bent back by some 37°.

Cycloheptatriene–$Fe_2(CO)_6$ has structure (111) in the crystal, and the proton NMR spectrum suggests this structure is preserved in solution[138]. The complex is stereochemically rigid, and the differences between (111) and formally similar C_8-ring complexes, which exhibit fluxional behaviour, are discussed.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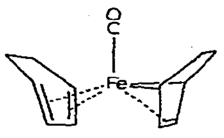
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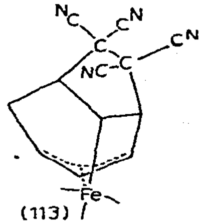
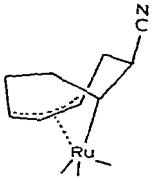

(113)

The preparation of bis(diene)iron carbonyl complexes in three laboratories was followed quickly by a structural determination of $Fe(CO)(C_6H_8)_2$ (112). This complex is chiral, and the two C_6-rings differ in conformation. This feature may be a result of the predominance of 2π-bonding in one ring and $\pi,2\sigma$-bonding in the other[139]. Addition of tetracyanoethylene to cycloheptatriene–$Fe(CO)_3$ occurs 1,3 to give (113), in which the bicyclic C_9 ligand is attached in a 2,3,4,6-*tetrahapto* fashion, with the TCNE fragment *exo* to the $Fe(CO)_3$ group[140]. A complex with a related 1,2,3,6-*tetrahapto*-C_8-ring (114) is obtained from $Ru(CO)_3(C_8H_{12})$ and trityl cation, followed by reaction with cyanide[141].

The structure of the acetylated azepine complex (115), obtained directly from the parent complex, confirms the spectroscopic assignment of structure[142]. In particular, substitution has occurred in the non-complexed part of the ring. The 1,2-diazepine complex (116) similarly contains the $Fe(CO)_3$ group bonded to the four carbon atoms adjacent to the NCO_2R group; the outer two carbon atoms have some sp^3 character[143].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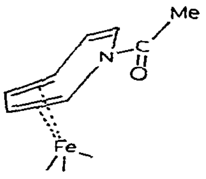
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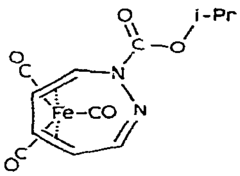
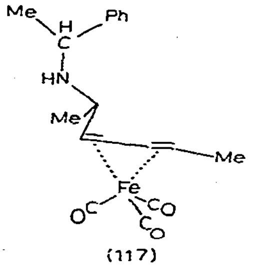

(116)

The absolute configuration of one of the two diastereoisomeric products (117) obtained from *S*-α-methylbenzylamine and the 1,5-dimethylpentadienyl-$Fe(CO)_3$ cation, determined by X-ray diffraction methods, proves conclusively that *exo* attack has occurred[144].

A full account of the structure of 3-[π-(2-cyclohexadienyl)]-σ-propenoyl–$Fe(CO)_2$ is available (see AS70; p. 77); this reveals that the iron atom has moved out of the pseudo-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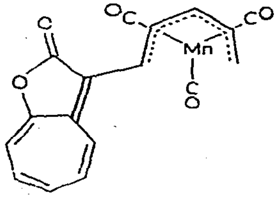
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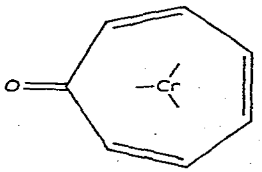
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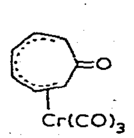
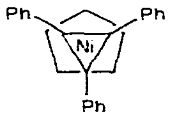

(119 a)

mirror plane of the cyclohexadienyl ligand[145]. Considerable strain results from the formation of the Fe—C σ bond to the side chain.

The reaction between tropone and $Mn_2(CO)_{10}$ affords the π-pentadienyl complex (118). The formation of this unusual oxaazulene derivative may involve ring opening of one tropone molecule followed by condensation with a second molecule, and subsequent rearrangements[146].

The tropone ring in its $Cr(CO)_3$ complex (119) is non-planar, although the distortion is not as much as that found in cycloheptatriene complexes; the carbonyl group is bent away from the metal, as shown[147]. The bond lengths show some alternation, but it is suggested that the complex is best represented as (119a).

Cyclic conjugated systems. (a) C_3 and C_4 hydrocarbons. The structures of two cyclopropenylnickel complexes have been reported. In the mixed sandwich $(\pi\text{-}C_3Ph_3)Ni(\pi\text{-}C_5H_5)$ (120), the rings are parallel, with the phenyl groups bent away from the metal and twisted out of the C_3-ring plane[148]. The C_3-rings in (120), and in $[(\pi\text{-}C_3Ph_3)NiCl(py)_2]$ (121) (as its pyridine solvate)[149], are respectively 1.779 and 1.759 Å from the nickel atom; in both cases true π-complexes are formed.



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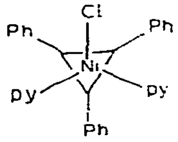

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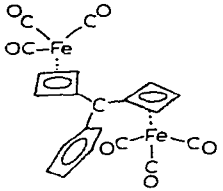
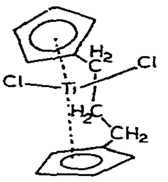


(122)

The α-cyclobutadienyl—$Fe(CO)_3$ carbonium ion (122) can be isolated as the BF_4 salt, and the preliminary account[150] of the structure indicates that the two C_4-rings are closely coplanar with the exocyclic carbon and attached three carbon atoms, while the C_6-ring is twisted by 43°. This suggests that the stabilisation of this ion arises from the organometallic group, although the metal atom does not enter into any significant direct interaction with the exocyclic carbon atom.

(b) Cyclopentadienyl complexes. In the cyclopentadienyl series, the structures of both $M(C_5H_5)_4$ ($M = Ti$ or Zr) molecules are described. The former complex contains two *pentahapto* and two *monohapto* C_5-rings, resulting in a 16-electron configuration for titanium. The proton NMR spectrum has been interpreted in terms of h^5–h^1-cyclopentadienyl ring exchange, and the determined structure supports this conclusion[151]. The zirconium complex is reported to contain three *pentahapto* and one *monohapto* C_5-rings, resulting in a 20-electron configuration for zirconium[152]. Unfortunately, partial decomposition of the crystal in the X-ray beam prevents a detailed analysis of variations in C—C and Zr—C bond lengths, and in the previous account, Cotton and coworkers[151] suggest that $Zr(C_5H_5)_4$ contains one h^1-C_5H_5 ring, one h^5-C_5H_5 ring, and two of the severely tilted rings [as found in $(C_5H_5)_3MoNO$] which act as four-electron donors.

The zirconium halides $(\pi\text{-}C_5H_5)_2ZrX_2$ have been studied by X-ray ($X = F$ or I)[153] or electron diffraction ($X = Cl$)[154] methods, and have a distorted tetrahedral coordination about the metal. The Zr–X bond lengths are: F, 1.98(1); Cl, 2.309(5); I, 2.832(2) Å, with X–Zr–X angles of: F, 96.2(3); Cl, 104(2); I, 96.2(1)°. The strange discrepancy in the Cl–Zr–Cl angle is not explicable at this time. The structure of the titanium analogue has not been determined in the crystalline state, although that of the trimethylene-bridged complex (123) shows a Cl–Ti–Cl angle of 93.69(5)°, with long Ti–Cl bonds of 2.368(4) Å.



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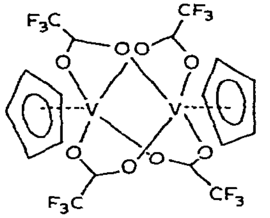

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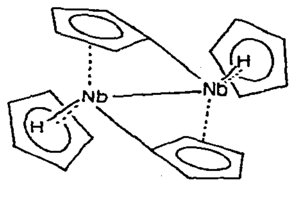
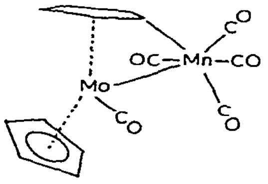


(125)

There is no metal–metal bond in $[(\pi\text{-}C_5H_5)V(CF_3CO_2)_2]_2$ (124), the two metal atoms being bridged by the four trifluoroacetate groups. The low magnetic moment probably results from exchange interaction via the carboxylate ligands[156].

The dicyclopentadienyl niobium ("niobocene") complex has the unusual structure (125)[157]. Essentially the molecule is a dimeric niobium hydride, with bridging C_5H_4 groups, and terminal hydride and cyclopentadienyl groups. A similar type of bridging C_5H_4 group was found in $(\pi\text{-}C_5H_5)(CO)Mo\text{-}\mu\text{-}C_5H_4Mn(CO)_4$ (126), obtained from the reaction between $(\pi\text{-}C_5H_5)_2MoH_2$ and $MeMn(CO)_5$ [158]. In both cases, the M–C bond to the C_5H_4 group is bent out of the C_5-ring plane. Evidence is also presented for the presence of similar groups in the analogous tungsten complex, in $(\pi\text{-}C_5H_5)(H)Re(C_5H_4)Mn(CO)_4$, in "titanocene" and "tantalocene", and in the polymerisation catalyst $[(\pi\text{-}C_5H_5)Ti(C_5H_4)AlEt_2]_2$ [157].



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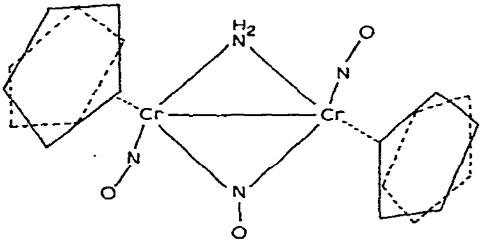
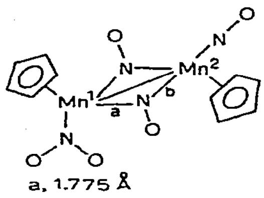


(127)

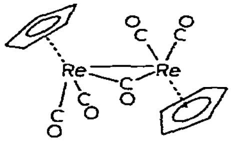
In the crystal, the molecule of $(\pi\text{-}C_5H_5)(NO)Cr(NO)(NH_2)Cr(NO)(\pi\text{-}C_5H_5)$ (127) achieves mirror symmetry by disorder in the two bridging groups; the two C_5-rings each occupy two alternative orientations[159]. The manganese nitrosyl $(\pi\text{-}C_5H_5)_2Mn_2(NO)_3(NO_2)$ (128) is notable for the highly unsymmetrical bridging nitrosyl groups shown, indicative of donation of two electrons by each group to Mn^1, but only one each to Mn^2. A structure for $(C_5H_5)_3Mn_2(NO)_3$ is suggested[160].

Several structure determinations of phosphine-substituted cyclopentadienylmolybdenum



(128)

carbonyl derivatives include those of (π-C_5H_5)$Mo(CO)_2(PR_3)I$ (R = n-Bu[161] or Ph[162]), (π-C_5H_5)$Mo(CO)(PPh_3)_2NCO$[163], and (π-C_5H_5)Mo(CO)(dppe)Cl[162]. The dicarbonyls have *cis* (R = n-Bu) and *trans* (R = Ph) geometries for the carbonyl groups. In the isocyanate, formed in a photolytic reaction between (π-C_5H_5)$Mo(CO)_2(NO)$ and PPh_3, the two phosphines are mutually *trans*, although the proton NMR spectrum shows that the bulk sample is a 1/2 mixture of both isomers. The structure of the dppe complex has been independently determined (AS70; p. 80).



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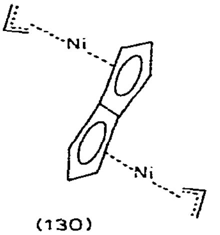


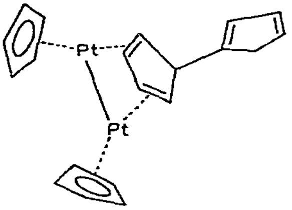
(130)

Irradiation of (π-C_5H_5)$Re(CO)_3$ affords yellow (π-C_5H_5)$_2Re_2(CO)_5$ (129), containing a single bridging carbonyl group supporting the metal–metal bond[164]. A somewhat similar structure had previously been suggested for $Os_2(CO)_9$.

The binuclear allylnickel dihydropentalenylene complex (130) has the two nickel atoms *trans* to each other[165]. Green, diamagnetic $Pt_2C_{20}H_{20}$ (from $PtCl_2$ and NaC_5H_5) has the unusual structure (131), where two (π-C_5H_5)Pt groups are bridged via olefinic bonds in one of the C_5-rings of a 5-cyclopentadienylcyclopentadiene unit[166].

Uranium is bonded symmetrically to each C_5-ring in $UCl(ind)_3$ (132) and has tetrahedral coordination[167]; the structure is similar to that of $UCl(C_5H_5)_3$.

(c) C_6 systems. Black $UAl_3Cl_{12}(C_6H_6)$ is obtained from UCl_4, $AlCl_3$ and aluminium in benzene, and has structure (133), in which the C_6-ring interacts symmetrically with the metal atom[168]



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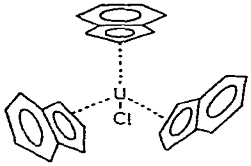
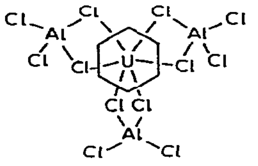


(132)

Chromium tricarbonyl complexes of the large-ring hydrocarbons [14] annulene and *anti*-1,6:8,13-bismethano[14] annulene have been studied. The former undergoes a ring closure reaction, the resulting ligand being *trans*-6*a*,12*a*-dihydrooctalene; two $Cr(CO)_3$ groups are bonded in *trans* positions in (134)[169]. The bridged annulene does not rearrange, and the structure (135) reveals that unusually only five carbon atoms (of the end ring containing two double bonds) are attached to the metal[170].



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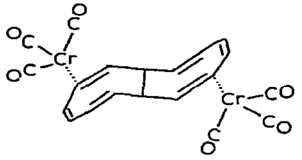

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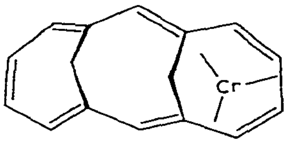
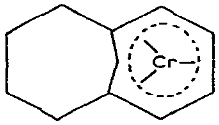


(135)

In the $Cr(CO)_3$ complex of bicyclo[4.4.1]undeca-1,3,5-triene (136), the metal is attached to a 6π homoaromatic ring, with the C^1-C^6 separation 1.72(2) Å [171], comparable to that suggested for an analogous tricyclo[4.3.1.0^{1,6}]deca-2,4-diene complex (AS70; p. 82). In the complex with trimethylcyclohepta[*b*] thiophene (137), the metal is clearly attached to the C_7 ring by six of the carbon atoms, C^8 being bent up out of the ring plane[172].



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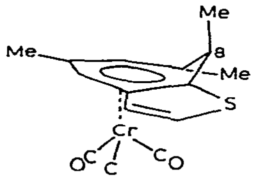
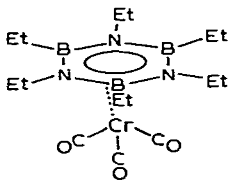


(137)

The hexaethylborazine complex (138) contains a B_3N_3-ring, the overall geometry corresponding to that of $(\pi\text{-}C_6H_6)Cr(CO)_3$. The nitrogen atoms are staggered with respect to the CO groups. Differing Cr–B and Cr–N bond lengths (corresponding to the difference between the respective covalent radii) lead to a puckered ring and chair conformation[173].

In $Ru(\pi\text{-}C_6Me_6)_2$ (139), one ring is planar, and forms a normal π-arene–metal bond. The second ring is bent about an axis passing through *para* carbon atoms, being attached to ruthenium via a 4π,C_4 unit. Conjugation in this ring is disturbed, and the non-coordinated double bond is localised[174].



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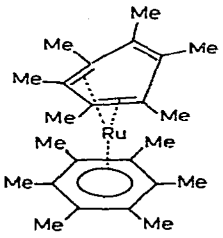
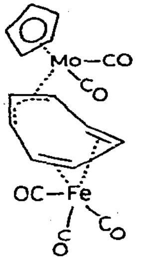


(139)

(d) C_7 and C_8 hydrocarbons. The complex $C_7H_7[(\pi\text{-}C_5H_5)Mo(CO)_2][Fe(CO)_3]$ (140) is the only reported example of a fluxional compound containing two separate metals. The structure of this complex, and of the related molybdenum complex (141) have been reported[175]. In the latter, the $(\pi\text{-}C_5H_5)Mo(CO)_2$ group is attached to a three-carbon unit of the C_7-ring, while in (140), the $Fe(CO)_3$ is attached on the other side of the ring to the remaining four carbons.



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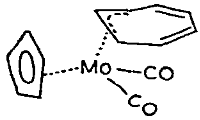

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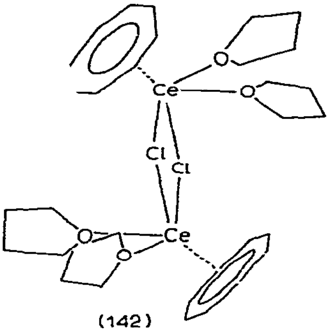
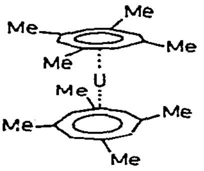


(142)

The cerium–cyclooctatetraenyl complex $[Ce(C_8H_8)(THF)_2Cl]_2$ is a chlorine-bridged dimer (142). The C_8 rings in all these complexes are planar, and should be considered to be examples of the $10\pi\,(C_8H_8)^{2-}$ system[176]. The uranium complex of 1,3,5,7-tetramethylcyclooctatetraene has a unit cell in which two types of molecule are present; in one the methyl groups are eclipsed, while the second has them staggered (143)[177]. The titanium derivative $(\pi\text{-}C_5H_5)Ti(\pi\text{-}C_8H_8)$ (144) has the expected C_5–C_8 sandwich structure[178]



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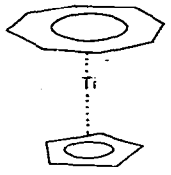

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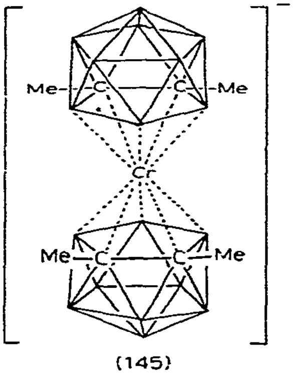

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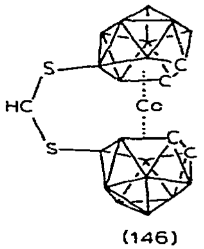
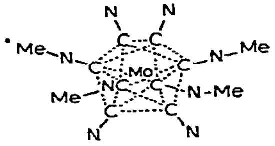


(146)

Complexes containing boron ligands. The structure of the anion in $Cs[Cr(B_9C_2H_9Me_2)_2]$ (145) consists of two icosahedra sharing a common apex, the chromium atom. The latter is bonded to two B_3C_2 faces, the two methyl groups on each face being as remote as possible from each other. Complete details of the structure of $Co[(B_9C_2H_{10})_2S_2CH]$ (146), from CS_2 and $K[Co(B_9C_2H_{11})_2]$, have been published; the two boron ligands are linked by a delocalised $[S\text{—}C\text{—}S]^+$ unit.

Isonitrile derivatives. The coordination of the eight carbon atoms about molybdenum in $Mo(CNMe)_4(CN)_4$ (147) is triangular dodecahedral. The tungsten complex is isomorphous.

The structures of *cis*-$PtCl_2(CNEt)(PEt_2Ph)$ (148) and *cis*-$PtCl_2(CNPh)_2$ (149), of some interest as being precursors of carbene complexes, have been determined. Both are square-planar platinum(II) complexes. The Pt–C bond distances indicate that the π-acceptor strength decreases: CO > RNC > carbene, although the *trans* influences of RNC and CO are comparable.



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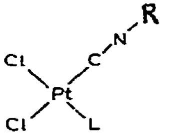
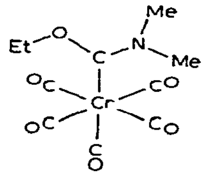


148; L = PEt_2Ph; R = Et
149; L = CNPh; R = Ph

Carbene, nitrene and related complexes. A complexed carbene containing two heteroatoms is present in $Cr(CO)_5C(OEt)NEt_2$ (150); only the *trans* configuration is present in the solid state[183]. Reaction of $[PtCl_2(PEt_3)]_2$ with an electron-rich olefin has given complex (151) in which the carbene is *trans* to phosphine; the carbene *trans* effect is estimated as about equal to that of a tertiary phosphine[184].



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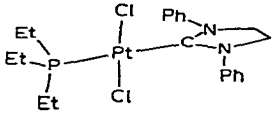

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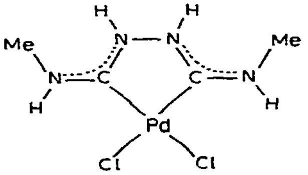
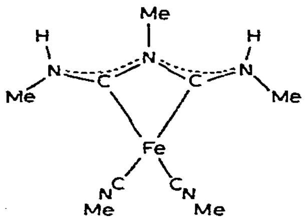


(152)

Addition of hydrazine to $PdCl_2(MeNC)_2$ afforded the chelate complex (152)[185], and the similar reaction between $MeNH_2$ and $[Fe(MeNC)_6]^{2+}$ produced the four-membered chelate ring shown in (153)[186]. In both complexes, coordination involves trigonal carbon atoms, although structures with delocalised N–C–N units are preferred over the carbene description. Similarly, in the platinum–pyridinium propylide complexes (154) and (155), first reported in 1966[187], the ylide formulation, rather than the isomeric carbene, is favoured on the basis of the stereochemistries of the metal-bonded carbon atoms, both tetrahedral[188].



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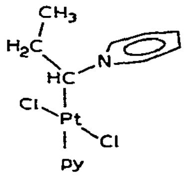

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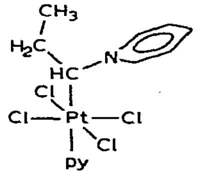
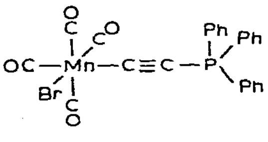


(155)

The reaction between $Mn(CO)_5Br$ and $C(PPh_3)_2$ produces the unusual complex (156), containing a phosphonium acetylide ligand[189].

Trimethylsilylnitrene has been stabilised in $Fe_3(CO)_{10}NSiMe_3$ (157), obtained from $Fe_3(CO)_{12}$ and Me_3SiN_3; the coordination about the triply-bridging nitrogen atom approximates to tetrahedral[190].



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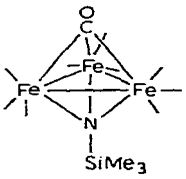
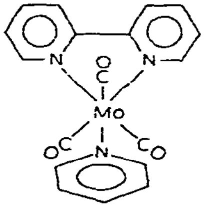


(157)

Complexes containing Group V donor ligands. (a) Nitrogen-containing ligands. The complex $[Mo(CO)_3(py)(bipy)]$ (158) has mutually *cis* carbonyl groups, in agreement with the structure deduced from IR measurements. However, there is some distortion from ideal octahedral geometry[191]. The reaction between 3-chloro-2-methylnitrobenzene and $Fe(CO)_5$ affords the complex $\{Fe(CO)_3[C_6H_3Cl(Me)NO]\}_2$, which has structure (159). The nitroso groups bridge the iron atoms unsymmetrically, with a planar Fe_2N_2 ring[192]. No metal–metal bond is present. The azabutadiene complex $(Ph_2C{=}C{=}NMe)Fe_2(CO)_6$ has a new type of C_2N unit bridging the two iron atoms (160)[193], reminiscent of the thioketocarbene complex reported last year (AS70; p. 90).



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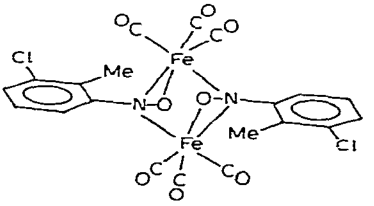

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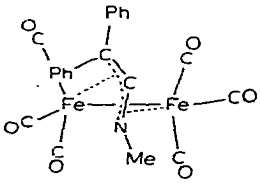
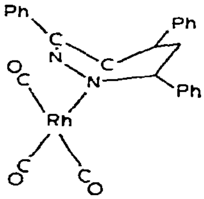


(160)

The rhodium complex $RhCl(CO)_2(diaz)$ (161), obtained from the reaction between $[Rh(CO)_2Cl]_2$ and 3,5,7-triphenyl-4H-1,2-diazepine, contains the unchanged ligand bonded to rhodium by only one nitrogen atom[194]. Bond distances in the tetrazene–iridium complex (162) favour the iridium(III) formulation shown; the four nitrogen atoms are coplanar[195].



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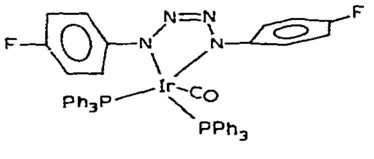
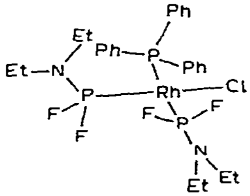


(162)

(b) Phosphorus, arsenic and antimony ligands. The structures of $Cr(CO)_2(PH_3)_4$ [196] and of *cis*-$FeI_2(CO)_2(PH_3)_2$ [197] have been reported. In the former, there are two Cr–P distances, a lengthening being found in the bond *trans* to CO [2.338(4) vs. 2.282(4) Å], and is taken as a further indication of the π-acidity of PH_3 (see AS69; p. 984). The trifluorophosphine derivative, $Mo(CO)_5(PF_3)$, has been studied by electron-diffraction methods[198]. The Mo–P bond length is some 0.08–0.13 Å shorter than found for other phosphine complexes. Trifluorophosphine appears to be a better π-acceptor than CO, the equatorial CO groups being bent away from the PF_3 group [P–Mo–C, 92(2)°]. An independent electron-diffraction investigation[199] of the $Ni(PF_3)_4$ structure (AS70; p. 89) has given values of bond distances and angles in good agreement with those reported earlier. Some differences are noted in the parameters involving rotation-sensitive distances. The structure of $RhCl(PF_2NEt_2)_2(PPh_3)$ (163) has also been reported[200].



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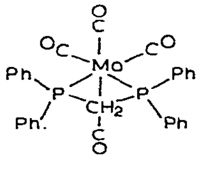


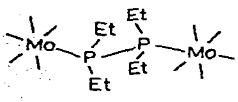
(164)

The tetracarbonyl $Mo(CO)_4[(PPh_2)_2CH_2]$ (164) shows significant shortening of the Mo–CO bonds *trans* to phosphorus [1.93(1) vs. 2.04(2) Å][201]. Two complexes obtained from P_2Et_4 and molybdenum hexacarbonyl are the binuclear $Et_4P_2[Mo(CO)_5]_2$ (165)[202], with a zig-zag Mo–P–P–Mo chain, and the phosphorus-bridged $[Et_2PMo(CO)_4]_2$ (166)[203].

The formally electron-deficient complexes obtained by halogenation of Group VI carbonyls, followed by addition of phosphine or arsine, have been shown to be monomeric. The molybdenum derivative, $MoBr_2(CO)_2(PPh_3)_2$ (167), is non-octahedral; this feature is related to the paramagnetism of the complexes[204]. Easy addition of carbon monoxide results in formation of the tricarbonyls, which are disordered and have a three-fold axis. Complexes with the chelating ligand $CH_2(AsPh_2)_2$(dam) also behave as CO-carriers:

$$M(CO)_3(dam)_2X_2 \ (168) \rightleftharpoons M(CO)_2(dam)_2X_2 \ (169) + CO \quad (M = Mo \text{ or } W)$$

Both complexes are seven-coordinate, the arsenic ligands being monodentate in (168), with one chelating in (169). In other respects the configurations of the two complexes are similar[205].



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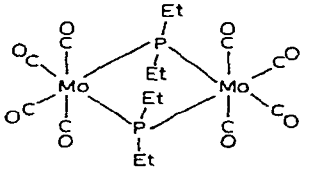

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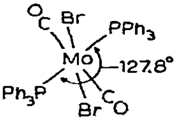

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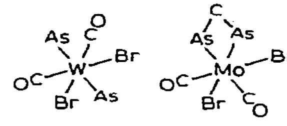
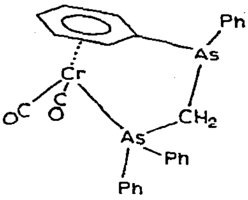


Both viewed down CO vector (omitted from diagram) to the metal atom

(168) (169)

With chromium carbonyl, this ligand forms the unusual complex (170), in which one of the phenyl groups is π-bonded to the metal[206].

Trimethyl-arsine and -stibine complexes of iron carbonyl, $Fe(CO)_4(EMe_3)$ (E = As, Sb) have the expected trigonal bipyramidal structure[207]. The equatorial CO groups are bent towards the ligand by about 2°.



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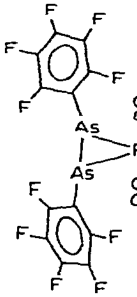

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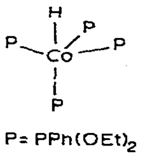

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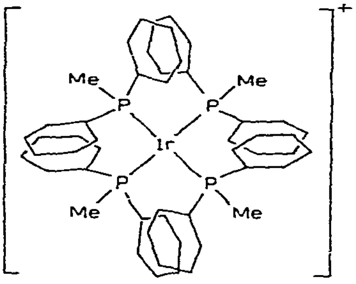
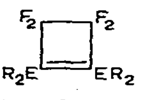


(173)

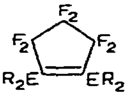
The first example of a complex containing the arsenobenzene ligand has been obtained from $Fe(CO)_5$ and $[AsC_6F_5]_4$ [208]. The resulting complex has structure (171). The ligand may be considered to bond via an As–As multiple bond formally similar to that in the azobenzene complex (100) (see p. 325). The As–As bond length [at 2.388(7) Å] is shorter than that in $(AsPh)_6$ [2.456(5) Å], and longer than the double bond in $As_2Co_2(CO)_5(PPh_3)$ [2.273(3) Å].

Other examples of complexes containing P-donor ligands whose structures are of interest include the fluxional hydride $HCo[PPh(OEt)_2]_4$ (172)[209], and the cation $[Ir(PMePh_2)_4]^+$ (173), in which approach by additional ligands such as carbon monoxide or oxygen is severely hindered[210] (cf. the ready formation of an oxygen adduct by $[Ir(dppe)_2]^+$).

(c) Fluorocarbon phosphine and arsine ligands. Structural determinations of several complexes obtained from the fluorocarbon derivatives prepared from perfluorocyclobutene and perfluorocyclopentene, namely $f_4$fos (174), $f_6$fos (175), $f_4$fars (176) and ffars (177) have been reported, together with some complexes of the related ligands derived from fluorinated ethylenes, (178), (179) and (180).



(174) ER_2=PPh_2
(176) ER_2=$AsMe_2$

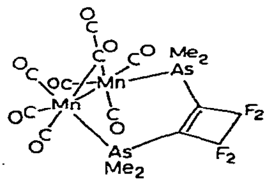


(175) ER_2=PPh_2
(177) ER_2=$AsMe_2$

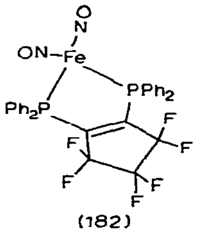
(178) $Me_2P\cdot CFH\cdot CF_2\cdot PMe_2$
(179) $Me_2As\cdot CFH\cdot CF_2\cdot AsMe_2$
(180) $Me_2As\cdot CF(CF_3)\cdot CF_2\cdot AsMe_2$

Manganese and rhenium carbonyls react with $f_4$fos and $f_4$fars to give the binuclear complexes $LM_2(CO)_8$; a structure determination[211] of the manganese–$f_4$fars complex (181) revealed the ligand-bridged metal–metal bonded structure shown. Ready cleavage of the metal–metal bond occurs with iodine, to give ($f_4$fars) $[Mn(CO)_4I]_2$. A preliminary report of the structure (R = 15.3%) shows no Mn–Mn bond, with rotation of the Me_2As groups resulting in the $Mn(CO)_4I$ groups being on opposite sides of the C_4 ring.

Distorted tetrahedral coordination about the iron atom is found in $(f_6fos)Fe(NO)_2$ (182); the P–Fe–P angle is smaller than tetrahedral (86.8°). The nitrosyl groups are linear. Bond distances indicate a considerable degree of metal-to-ligand back donation via the NO π^* orbitals[212]. Reaction of $f_4$fars with $Fe_3(CO)_{12}$ gives a trinuclear complex (183) in which the cluster has rearranged, and an $AsMe_2$ group has been cleaved from the ligand[213]. Three $Fe(CO)_3$ groups and the $AsMe_2$ group are linked in a distorted square-planar arrangement, and are held together via Fe–C σ bond, a C=C bond, and an arsenic σ donor bond to the three metal atoms. In the reaction of this ligand with $Ru_3(CO)_{12}$, the complex $(f_4fars)Ru_3(CO)_{10}$ (184) is formed, retaining the triangular Ru_3 cluster, and with the ligand bridging two metal atoms[214]. In the complex $(\pi\text{-}C_5H_5)Fe(CO)(f_6fos)SnMe_3$ (185), the ligand is monodentate[215]; the Fe–Sn bond is about 0.03 Å longer than that in $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_3$.



(181)



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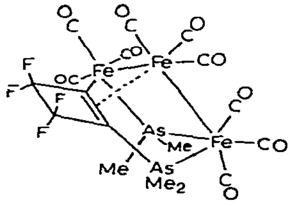

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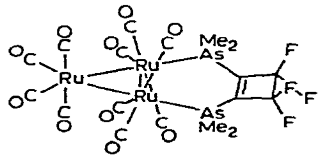

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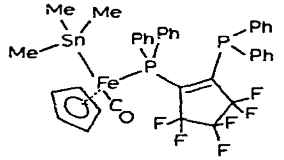
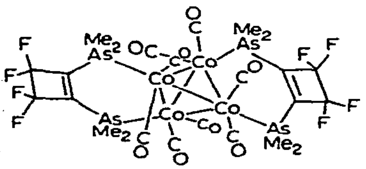


(185)

Disproportionation of the cluster in $CF_3CCo_3(CO)_9$ occurs on reaction with $f_4$fars, giving a tetranuclear complex, $Co_4(CO)_8(f_4fars)$ (186)[216]. The four metal atoms form a tetrahedral cluster, each $f_4$fars ligand bridging two cobalt atoms. All carbonyl groups are terminal, in contrast to $Co_4(CO)_{12}$, which contains three bridging CO groups. Weak interactions of the carbon atoms of some CO groups with adjacent metal atoms are present. The full details of the structure determination of $(f_4fars)Co_2(CO)_6$ are available[217] and include a summary of other determinations of Co–Co bond lengths.

The reaction between $f_6$fos and $[Rh(CO)_2Cl]_2$ affords the salt $[Rh(f_6fos)_2]^+[Rh(CO)_2Cl_2\text{-}cis]^-$, the cation having structure (187). Both the fluorocarbon and RhP_2C_2 rings are puckered, with square-planar coordination about the rhodium atom[218].



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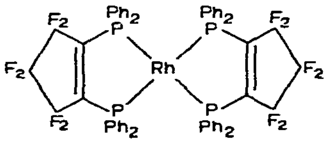
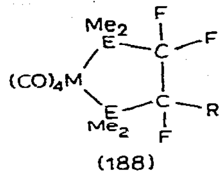


(187)

Initial results of structural studies of complexes of the type $(Me_2E\text{-}CFR\text{-}CF_2EMe_2)M(CO)_4$ (188) (M = Cr, Mo; E = P, As; R = H, CF_3) which suggested considerable contributions from the canonical form (188a), have now been modified.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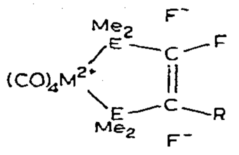
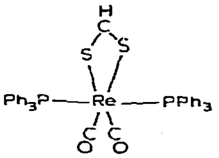

(188a)

The conclusions were drawn from unusually longer CF bond distances, and comparisons with related structures indicate that the crystal contains a disordered arrangement of molecules with normal geometries and dimensions. The structural studies involve the following molecules: $Me_2As{-}CF(CF_3){-}CF_2AsMe_2Mo(CO)_4$ [219,220], $Me_2AsCFH{-}CF_2AsMe_2Mo(CO)_4$ [219,221], $Me_2PCFH{-}CF_2PMe_2Mo(CO)_4$ [219], and $Me_2AsCFHCF_2AsMe_2Cr(CO)_4$ [219].

Ligands containing sulphur. The reaction between CS_2 and $ReH(CO)_2(PPh_3)_3$ affords a dithioformato complex, shown to have structure (189), in which the two phosphine groups are *trans*[222]. The dithiobenzoate, $Re(S_2CPh)(CO)_4$ (189a) has a related structure; the rhenium has distorted octahedral coordination[223]. As expected the Re–CO bonds *trans* to the sulphur atoms are lengthened, by about 0.06 Å. The chelate complex, $(\pi\text{-}C_5H_5)_2Mo(S_2C_6H_4)$, exists in two conformations in the crystal, with a staggered or eclipsed arrangement of the C_5 rings. The benzene-1,2-dithiolate group completes a distorted tetrahedral coordination about the metal atom. A small (9°) bending of the chelate group out of the MoS_2 plane was found[224].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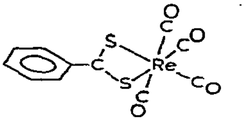
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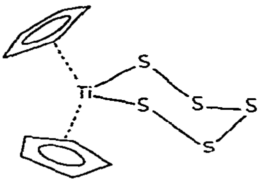
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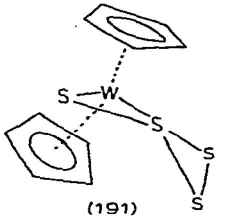
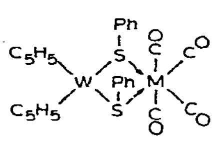

(191)

The reaction between $(\pi\text{-}C_5H_5)_2TiCl_2$ and polysulphide ion gives $(\pi\text{-}C_5H_5)_2TiS_5$, with structure (190). The main feature is a six-membered TiS_5 ring having a chair configuration[225]. The related tungsten complex $(\pi\text{-}C_5H_5)_2WS_4$ (191) contains a non-planar WS_4 ring which is symmetric with respect to the two C_5 rings[226]. Some evidence for $d_\pi{-}d_\pi$ back bonding from tungsten to the terminal sulphur atoms was obtained.

Mercapto-bridged complexes. Sulphur-bridged binuclear transition metal complexes, particularly the Mo–S–Fe system, are important in biological systems e.g. nitrogenase. The structures of several examples of this type of complex have been reported[227]. Most contain a planar $M{-}(S)_2{-}M^1$ ring, although the dimensions vary. In the complexes

$(\pi\text{-}C_5H_5)_2W(SPh)_2M(CO)_4$ (192) (M = Cr, Mo, W), the metal–metal distances are all ca. 4.0 Å, with M–S–M^1 angles > 90°. The complex $(\pi\text{-}C_5H_5)_2Ti(SMe)_2Mo(CO)_4$ (193) in contrast, has a Ti–Mo separation of 3.32 Å, with the angle at sulphur 82.8°. Spectroscopic properties also indicate a metal–metal interaction in this complex[227,228]. The two methyl groups lie on the same side of the Mo–S_2–Ti plane. An example of a complex more closely approaching the nitrogenase system is $(\pi\text{-}C_5H_5)_2Mo(SBu\text{-}n)_2FeCl_2$ (194), and the important difference from the complexes already discussed is the bent Mo–S_2–Fe fragment; the inclination of the MoS_2 and FeS_2 planes is 148° [229]. The Mo–Fe separation is 3.66 Å. In $[(\pi\text{-}C_5H_5)_2Nb(SMe)_2Ni(SMe)_2Nb(\pi\text{-}C_5H_5)]^{2+}$ (195), the nickel is tetrahedrally coordinated; within the Nb–$(S)_2$–Ni ring there is substantial metal–metal bonding. Formally, the nickel can be considered to be zerovalent, unusually stabilised by sulphur ligands and a Ni→Nb two-electron donor bond[230].



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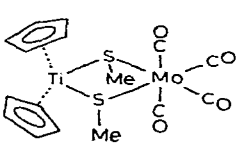

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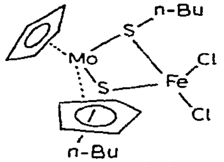

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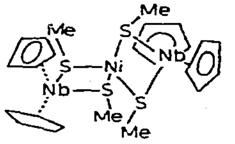
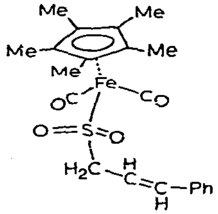


(195)

Complexes containing sulphur–oxygen ligands. Sulphur dioxide insertion products are of some current interest; the structure of the product from SO_2 and the σ-phenylallyl complex $(\pi\text{-}C_5Me_5)Fe(CO)_2CH_2CH{=}CHPh$ is (196), showing that no rearrangement of the allyl fragment has occurred. The ligand is *S*-bonded[231]. With $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C{\equiv}CMe$, the adduct (197) contains a sultine ring system, probably formed by rearrangement of an initial product from reaction of SO_2 with the acetylenic group[232]. The structure of $(\pi\text{-}C_5H_5)Fe(CO)_2SO_2C_6F_5$ (198), reveals[233] the expected *S*-bonded ligand, with some double bond character, as also found in (196).



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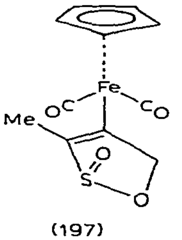

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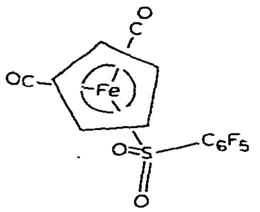
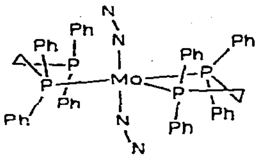
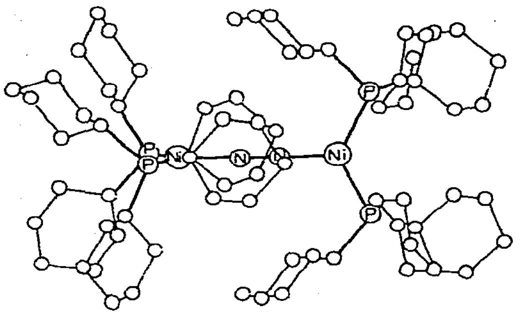


(198)

Dinitrogen complexes. The similarities and differences between CO and N_2 as ligands in transition metal complexes are sufficient to justify inclusion of structures of complexes containing dinitrogen as a ligand in this survey. The rhenium complex $ReCl(N_2)(PMe_2Ph)_4$ is of interest for several reasons: (i) there is a carbonyl analogue; (ii) it has a low ν(NN), at 1922 cm^{-1}; (iii) it reacts with $MoCl_4$-etherate to form a complex probably containing the Re–N–N–Mo sequence. The complex is octahedral, with *trans* Cl and N_2 ligands, with partial disorder between these two groups[234].



(199)



(200)

The molybdenum complex $Mo(N_2)_2(dppe)_2$ (199) has mutually *trans* dinitrogen ligands, with Mo–N–N angles of 171.8(1.1)° [235].

A complex containing a bridging dinitrogen ligand has been obtained from nickel acetylacetonate and $AlMe_3$ in the presence of PCy_3 and nitrogen. The structure of $[(Cy_3P)_2Ni]_2N_2$ (200) reveals a linear Ni–N–N–Ni system, with the dinitrogen bridge enclosed in a cage formed by four cyclohexyl groups[236].

For convenience, a reference list of structures of dinitrogen complexes is given in Table 4.

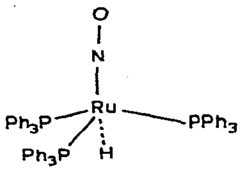
TABLE 4

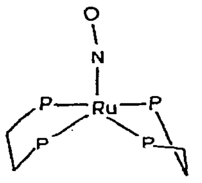
STRUCTURAL STUDIES ON DINITROGEN COMPLEXES

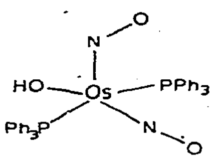
Complex	Bond distances (Å)		Angle (°)	Reference
	M–N	N–N	M–N–N	
$CoH(N_2)(PPh_3)_3, Et_2O$	1.80	1.16	175	284
$CoH(N_2)(PPh_3)_3$ [a]	1.829(12)	1.123(13)	178(1)	285
	1.784(13)	1.101(12)	178(2)	
$[Ru(N_2)(NH_3)_5](BF_4)_2$	2.10(4)	~1.03	–	286
$[Ru(N_2)(NH_3)_5]Cl_2$	2.10(1)	1.12(8)	~180	287
$[Ru(N_2)(N_3)(en)_2]PF_6$	1.894(9)	1.106(11)	179.3(9)	288
$Re(N_2)Cl(PMe_2Ph)_4$	1.966(21)	1.055(30)	177(1)	234
$Mo(N_2)_2(diphos)_2$	2.01(1)	1.10(2)	171.8(1.1)	235
$\{N_2[Ru(NH_3)_5]_2\}(PF_6)_4$	1.928(6)	1.124(15)	178.3(5)	289
$N_2[Ni(PCy_3)_2]_2$	1.77; 1.79	1.12	178.2	236

[a] Two independent molecules.

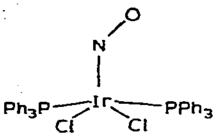
Nitrosyl complexes. Although not strictly organometallic, many nitrosyl complexes show features which have relevance to the bonding of more conventional ligands to metals. Consequently, reports on the structures of these compounds are considered here. Most contain NO bonded to a metal–phosphine complex. Within the last few years, it has become apparent that two different types of metal–nitrosyl group, namely a linear M–N–O arrangement, and the so-called bent M–N–O group, can be recognised. In the latter, the angle at nitrogen is generally of the order of 120°, and the NO group is considered as a one electron donor (NO^-), whereas in the linear M–N–O group, NO acts as a three-electron donor (NO^+). This point is discussed in detail by others[237].

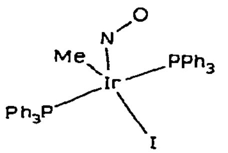

(201)

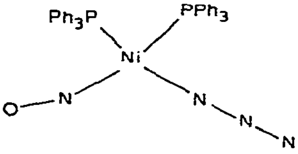

(202)

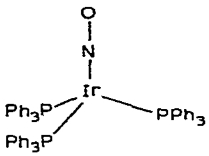

(203)

Linear M–N–O coordination was found in $Ru(NO)H(PPh_3)_3$ (201) and $[Ru(NO)(diphos)_2]^+$ (202)[238], in contrast to both types found in $[Os(OH)(NO)_2(PPh_3)_2]^+$ (203)[239], and in $[Ru(NO)_2Cl(PPh_3)_2]^+$[240]. The latter two complexes are coordinatively unsaturated d^6 systems. In the iridium complex $[IrH(NO)(PPh_3)_3]^+$, isoelectronic with (201), the Ir–N–O is linear, and this is best formulated as an Ir^I complex[241]. The bent Ir–N–O groups in $IrCl_2(NO)(PPh_3)_2$ (205)[242] and $IrIMe(NO)(PPh_3)_2$ (206)[243] similarly indicate that these may be considered as iridium(III) complexes.

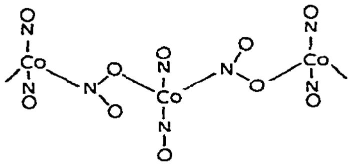

(205)

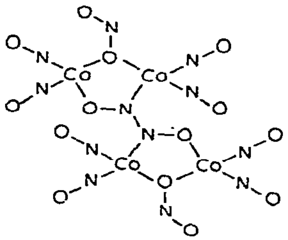

(206)

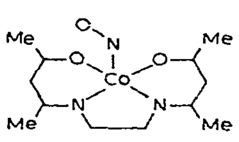

(207)


(208)

In the pseudo-tetrahedral $Ni(N_3)(NO)(PPh_3)_2$ (207), the Ni–N–O angle is 152°; in four-coordinate complexes, this angle appears to be strongly dependent on the nature of the ligands and the coordination geometry[244]. Particularly, the equilibrium Ni–N–O angle will depend on mutual interaction of $d \rightarrow \pi^*$ bonding, and d electron-ligand repulsions. The structure of $Ir(NO)(PPh_3)_3$ (208) is discussed in terms of unbalanced packing of chiral molecules; the Ir–N–O group is linear[245].


(210)


(211)

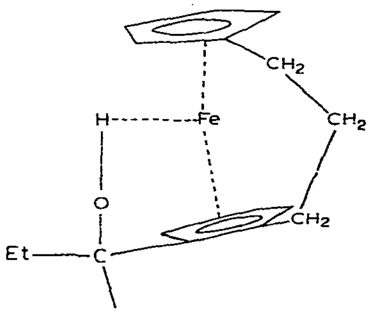

(212)

Other examples of nitrosyl complexes, all containing cobalt, whose structures have been reported, include $[Co(NO)_2Cl]_2$[246], $Co(NO)_2NO_2$ (210)[247], $Co_4(NO)_8(NO_2)_2(N_2O_2)$ (211), containing bridging nitrite groups, and a quadridentate hyponitrite ligand[248], the compound $[Co(NO)(NH_3)_5]Cl_2$[249], and the Schiff-base complex (212)[250].

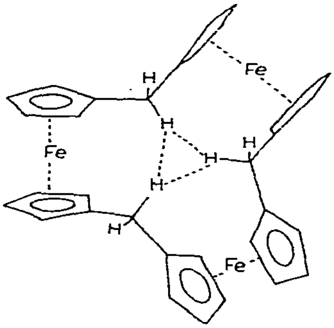
Ferrocene derivatives. The structure of *trans*-β-ferrocenylacrylonitrile reveals no unusual features which might cause the substantial differences from the *cis* isomer observed in some physical properties (e.g. proton NMR spectra). The acrylonitrile group is almost coplanar with the cyclopentadienyl ring; the crystal contains molecules of only one optical isomer (configuration not established)[251]. The C_5 rings have a conformation intermediate between eclipsed and staggered (angle 20°) (referred to eclipsed (0°) and staggered (36°)).

The structure of $[FcCH_2NHMe_2{}^+]_2ZnCl_4{}^{2-}$ dihydrate, an intermediate in the $ZnCl_2$-catalysed self-condensation of *N,N*-dimethylaminomethylferrocene, consists of ionic layers with the nitrogen side chains projecting into the layers[252]. Extensive hydrogen bonding is found with N–H· · · ·Cl, N–H· · · ·O and O–H· · · ·Cl systems. The C_5 rings are nearly eclipsed (7°). Reaction of $FcCH_2NMe_3{}^+I^-$ with formamide affords the *N*-formylaminomethyl derivative; two distinct molecules are linked by two different N–H· · · ·O bonds in an alternating head-to-tail manner[253]. The relative conformations of the nearly eclipsed rings in the two molecules are −7.8° and +4.2°; in the side chains, the four heavy atoms are nearly coplanar.

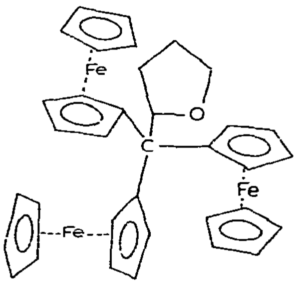
The reaction between PhMgBr and racemic 2-propionyl-1,1′-trimethyleneferrocene shows some stereospecificity, affording two diastereoisomeric alcohols. Both contain ν(OH) bands suggesting interaction of the hydroxyl function with the metal atom. The isomer obtained in highest yield has m.p. 122°, and structure (214), with the two C_5 rings deviating from coplanarity by 9°, was determined[254].



(214)



(215)



(216)

Ferrocene derivatives containing more than one metallocene nucleus have been described by several workers. The structure of [1.1.1]ferrocenophane (215), obtained from $FeCl_2$ and the dianion from dicyclopentadienylmethane, confirms the proposed structure[255]. The actual geometry is a hybrid of several idealised conformational structures of a large ring formed by the three linked ferrocenyl nuclei. It appears that an important factor controlling the molecular conformation of $[1^n]$ferrocenophanes is the minimisation of intramolecular nonbonded hydrogen contacts. A trinuclear ferrocene derivative of formula $Fc_3C(C_4H_7O)$ has structure (216). In the two independent molecules in the unit cell, the relative conformations of the two C_5 rings range from 1.8 to 27.4° [256].

The structure of 1,1′-dimethylferricinium triiodide shows that the rings are almost eclipsed (2.2°), as are the two methyl groups. Consequently, there is some steric interaction between the two methyl groups, reflected in a ring tilt of 6.6°. The inter-ring distance (3.39 Å) is longer than in ferrocene (3.32 Å)[257].

Miscellaneous. Preliminary details (e.g. unit all dimensions, space groups, etc.) have been reported for the following compounds: $Fe(CO)(C_4H_6)_2$ [258], *cis*-$RuCl_2(CO)_2(AsEtPh_2)_2$ [259], $[Co(C_5H_5)_2]_2MCl_4$ (M = Zn, Co)[260], and $[Ir(OMe)(C_8H_{12})]_2$ [261].

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ERRATA

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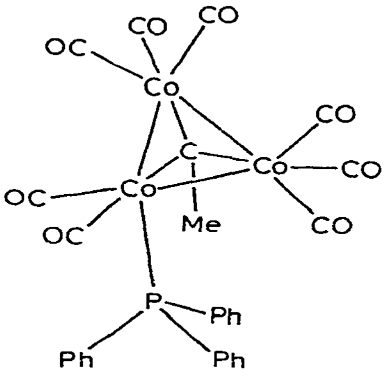
Page 61, structure (20) should read:



(20)

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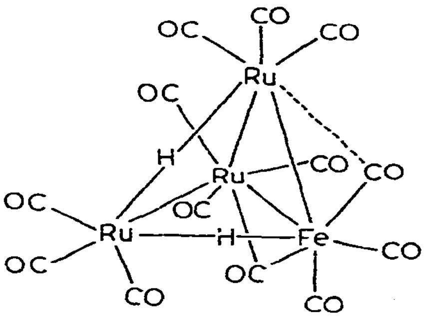

(25)