STRUCTURES OF ORGANO-TRANSITION METAL COMPLEXES

ANNUAL SURVEY COVERING THE YEAR 1973 (PART 1)

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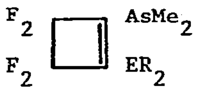
Abbreviations

acac	acetylacetonate	
bipy	2,2'-bipyridyl	
bzac	benzoylacetonate	
cod	cycloocta-1,5-diene	
Cy	cyclohexyl	
dba	dibenzylideneacetone	
dbm	dibenzoylmethanate	
DCP	dicyclopentadiene	
diglyme	$(MeOCH_2CH_2)_2O$	
dppe	$Ph_2PCH_2CH_2PPh_2$	
dppp	$Ph_2P(CH_2)_3PPh_2$	
f_4asp	$ER_2 = PPh_2$	in 
f_4fars	$ER_2 = AsMe_2$	
ind	indenyl	
nbd	norbornadiene	
py	pyridine	
pz	pyrazolyl	
sp	o-$CH_2=CHC_6H_4PPh_2$	
terpy	2,2',2''-terpyridyl	

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tol	tolyl
TPP	tetraphenylporphin
triphos	$MeC(CH_2PPh_2)_3$
VA	vinyl alcohol

Introduction

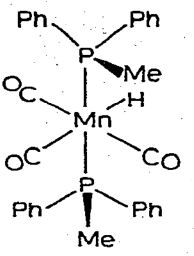
This review of structures of organo-transition metal complexes determined by X-ray, neutron, or electron diffraction methods follows the pattern of last year's survey, and is presented in two parts. The continued rapid growth in this area (undoubtedly caused by the general increase in availability of suitable automated four-circle diffractometers and associated computing facilities) is shown by the number of structures reported below, which approaches 170.

Simple metal carbonyl derivatives

In $HMn(CO)_3(PMePh_2)_2$ (1), the two phosphine ligands are trans.[1] In the planar $Mn(CO)_3$ portion, the trans CO groups are bent towards the hydrogen atom [angle C-Mn-C, 153°], so that the MnC_3P_2 fragment forms a distorted trigonal bipyramid. The geometry of the $[HFe(CO)_4]^-$ anion (2) has been determined[2] in its $(Ph_3P)_2N^+$ salt, and is a distorted trigonal bipyramid, the three equatorial CO groups being bent towards the axial hydrogen. The Fe-H distance is 1.57(12)Å. The geometry of the isoelectronic $HCo(CO)_4$ is probably similar.

The reaction between $Re_2(CO)_{10}$ and ReF_6 in anhydrous HF has afforded two complexes, $Re(CO)_5F.ReF_5$ (3) and $[Re(CO)_6]^+[Re_2F_{11}]^-$.[3] In the former, the two octahedrally-coordinated rhenium atoms are linked by a bent fluorine bridge. Discrete $[Re(CO)_6]^+$ and $[Re_2F_{11}]^-$ ions are presen in the second complex; in the cation, mean distances are: Re-C, 2.01(4); C-O, 1.13(3)Å.

Sulphur dicyanide reacts with Vaska's complex with cleavage of an S-C bond, to give $IrCl(CN)(NCS)(CO)(PPh_3)_2$, containing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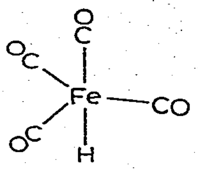
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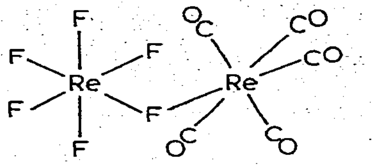
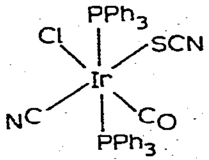

(3)

S-bonded thiocyanate; on recrystallisation, isomerisation to the N-bonded isomer (4) occurs.[4] The CO group is disordered with trans Cl, and CN with the NC of the thiocyanate group.

Complexes containing metal-metal bonds (a) To Main Group elements

In (terpy)Cd[Mn(CO)$_5$]$_2$ (5), both the trigonal bipyramidal (Cd) and octahedral (Mn) environments of the metals are considerably distorted.[5] The two Cd-Mn bond lengths differ [2.760(4), 2.799(5)Å] probably due to packing forces; the angle Mn-Cd-Mn is 132.4(2)°.

The suggested trigonal planar structure for In[Co(CO)$_4$]$_3$ (6) is confirmed by the structure determination.[6] The In-Co bond length [2.594(3)Å] does not suggest any d_π-p_π bonding interaction, although the bond is shorter than the sum of the single-bond covalent radii. Comparisons of the covalent radii of metals indicate that these vary considerably (0.07-0.23Å) with substituent. Some interaction of the empty In p_z orbital and filled in-plane equatorial carbonyl-C p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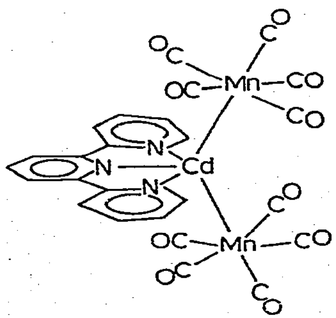
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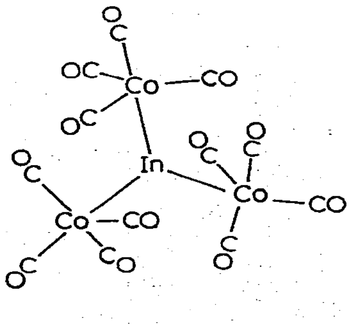
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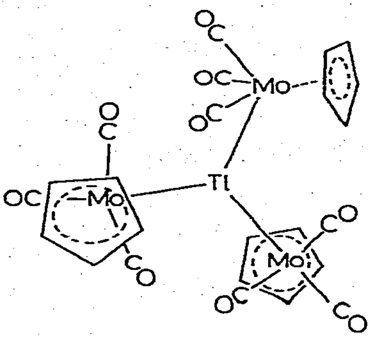
orbitals is suggested. An average Tl-Mo bond length of 2.965Å is found[7] in $Tl[Mo(CO)_3(C_5H_5)]_3$, (7), although individual values differ significantly [range, 2.938(2)-3.001(3)Å]. No other metal-metal interactions were found.

The reaction between $(C_5H_5)_2TiCl_2$ and $KSiH_3$ affords $[(C_5H_5)_2Ti(SiH_2)]_2$ (8), in which the two titanium atoms are bridged by two SiH_2 groups, with Ti-Si bonds lengths of 2.159(13)Å.[8]



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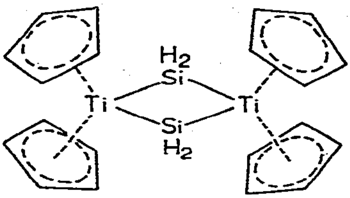
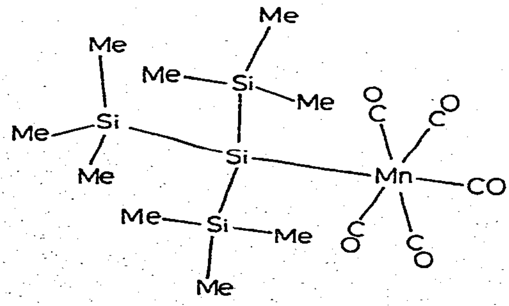


(8)

The structure of $(Me_3Si)_3SiMn(CO)_5$ (9) shows no unexpected features; the Si-Mn bond length [2.564(6)Å] suggests that any electronic effects resulting from (d-d)π bonding are outweighed, or at least balanced, by the necessity to minimise steric repulsions between $SiMe_3$ and CO groups[9]. Such interactions also lead to lengthening of the Si-Si bonds [2.374(5) vs. 2.352(3)Å in $Si(SiMe_3)_4$].



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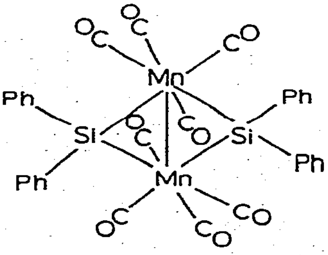
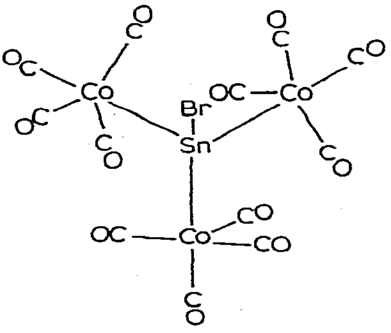


(10)

The complexes $Mn_2(CO)_8(SiPh_2)_2$ (10) contains a planar Mn_2Si_2 rhombus in which the formation of a strong Mn-Mn bond is evidenced both by the acute Mn-Si-Mn angles [73.4(1)°] and the short Mn-Mn distance of 2.871(2)Å.[10]

The structure of $BrSn[Co(CO)_4]_3$ (11) confirms the absence of any Co-Co bonds; the relative bulk of the $Co(CO)_4$ groups results in a reduction in symmetry to C_3, minimising interactions between CO groups.[11] The complex $[(Me_2Sn)Co(C_5H_5)(CO)]_2$ (12) contains a Co_2Sn_2 rings, with angles at cobalt and tin of 78 and 102°, respectively.[12] By comparison with the related complex $[Me_2SnFe(CO)_3]_2$, in which the Fe-Sn bond length is 2.64Å, there must be considerable π-character (multiple bonding) in the cobalt-tin complex, in which the Co-Sn bond length is 2.54(2)Å.



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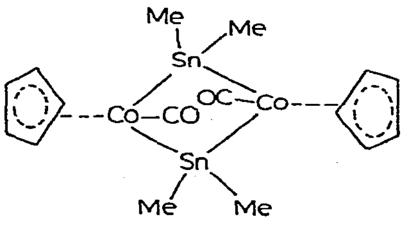
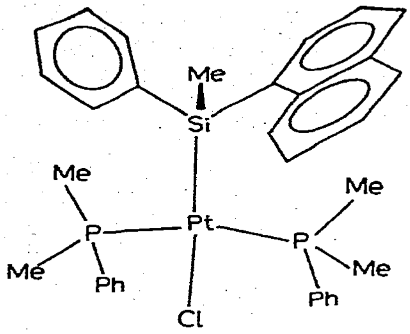


(12)

The optically active complex $(+)\text{-}PtCl[SiMe(1\text{-}C_{10}H_7)Ph](PMe_2Ph)_2$ has structure (13) with absolute configuration (S), corresponding to that of the $(R)(+)\text{-}Me(1\text{-}C_{10}H_7)PhSiH$ from which it was obtained.[13] Oxidative addition of Pb_2Ph_6 to $Pt(PPh_3)_4$ affords $Pt(PbPh_3)_2(PPh_3)_2$, which in dichloromethane slowly decomposes to cis-$PtPh(PbPh_3)(PPh_3)_2$ (14). This complex can also be obtained directly from LiPh and $Pt(PbPh_3)_2(PPh_3)_2$. The cis configuration is found by an X-ray study, which reveals Pt-Ph and Pt-Pb bond lengths of 2.055(3) and 2.698(9)Å, respectively.[14]

The new cluster complex $As_2[Fe(CO)_3]_3$ (15), obtained from AsF_3 and $Fe(CO)_5$ at 120°, exists in the crystal in two orientations (each with one-half occupancy), distributed randomly. Basically, the structure consists of a triangular $Fe_3(CO)_9$ cluster, with the two arsenic atoms acting as triply-bridging ligands, lying above and below the Fe_3 plane.



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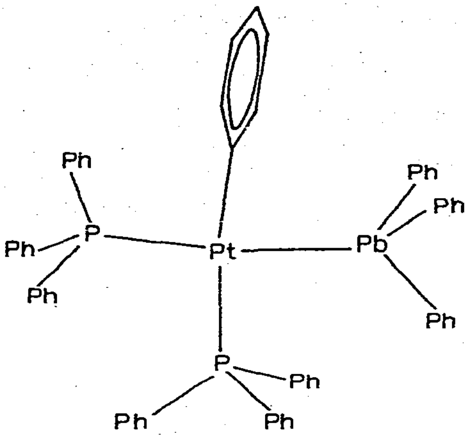

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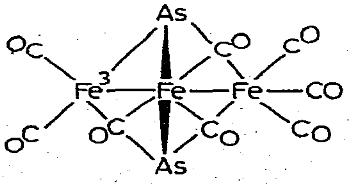
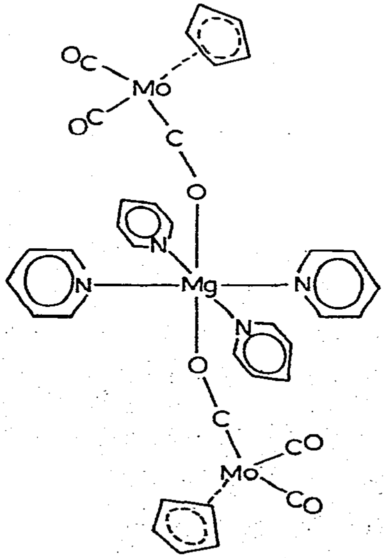


one CO hidden by Fe^3

(15)



(16)

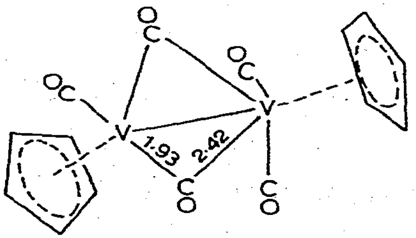
Metal exchange between magnesium and Hg$[(C_5H_5)Mo(CO)_3]_2$ in THF, followed by recrystallisation of the product from pyridine, afforded $[(\underline{h}^5\text{-}C_5H_5)Mo(CO)_3]_2Mg(py)_4$ (16). In this complex, the magnesium is O-bonded to the Mo-CO groups,[16] the first example to a Main Group metal other than aluminium.

(b) To Transition Metals

The structure of $(C_5H_5)_2V_2(CO)_5$ (17) reveals a $(C_5H_5)V(CO)$ moiety attached to a $(C_5H_5)V(CO)_2$ group via a metal-metal bond and two highly asymmetric bridging CO groups [V-CO, 1.94(1); V'-CO, 2.42(1)Å]. However, two points are not clear at present; (a) the order of the V-V bond, and (b) the precise nature of.the bridging CO group.[17]

The new nitrosyl-carbonyl hydride $HW_2(CO)_9(NO)$ (18) staggered equatorial WL_4 groups; the hydride probably bridges the long W-W bond; and intersection of the two axial W-CO bonds gives a W-H-W angle of 159°.[18] A single hydrogen atom also bridges the two metal atoms in $HReCr(CO)_{10}$ (19). The Re-Cr distance is 3.435(1)Å, and although not directly located, the hydrogen is considered to be colinear with the metal atoms.[19]

The reaction between diphenylacetylene and $(C_5H_5)Ni(CO)(PPh_2)Fe(CO)_3$ results in replacement of the bridging CO group, and insertion into the Ni-P bond to give the unusual complex (20).[20]



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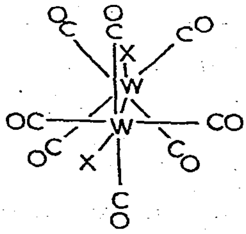
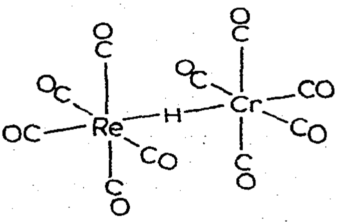


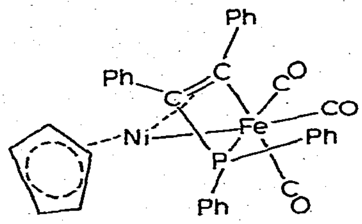
(18)

X = CO or NO
H lies between W atoms



(19)

The full details of the structure of dichloromethane-solvated $[Rh(CO)(PPh_3)_2]_2$ have been given.[21] The complex is characterised by the presence of a Rh-Rh bond [2.630(1)Å], bridging CO groups which may interact with the solvent via a C-O---H-$CHCl_2$ hydrogen bond, and an unusual five-coordination geometry for the metal atoms. The homogeneous hydrogenation catalyst $[(C_5Me_5)RhCl]_2HCl$ (21) contains bridging hydrogen and chlorine atoms, both of which were refined.[22] The RhHClRh unit is planar, with the Rh-H-Rh linkage best described as a three-centre, two-electron bond. The Rh-Rh distance of 2.9064(10)Å suggests some metal-metal interaction, which is supported by the Rh-Cl-Rh angle of 73.20(6)°. The Rh-H bond length is 1.849(47)Å.



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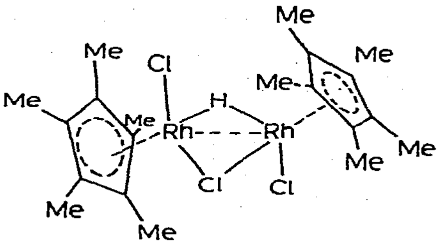
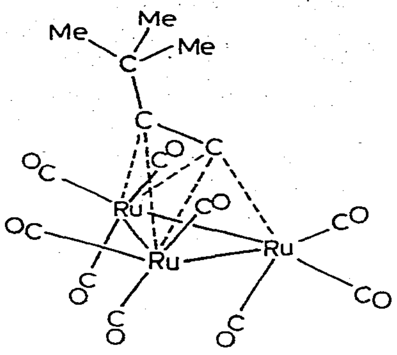


(21)

(c) Cluster complexes

A complex $Ru_3(CO)_9(Bu^tC_2H)$, obtained from the acetylene and $Ru_3(CO)_{12}$, has structure (22), in which the acetylene interacts with two metal atoms with a μ-type bond, and with the third by a σ-type bond.[23] Full details of the structure determination of (azulene)$Ru_3(CO)_7$ (23) have been given.[24] The bicyclic hydrocarbon is attached to one metal atom via an essentially symmetric π-cyclopentadienyl group, and via a delocalised bond between the remaining five carbons in the C_7 ring and the other two metal atoms. An analogous situation has been described in bis(pentadienyl)dinickel.[25]

Preliminary crystallographic data, including the dimensions of the central cluster, have been given for $H_2Os(CCH_2)(CO)_9$ (24), derived from a reaction between $Os_3(CO)_{12}$ and ethylene.[26]



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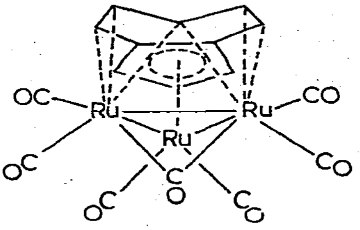

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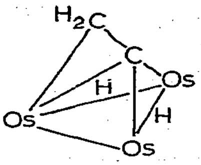
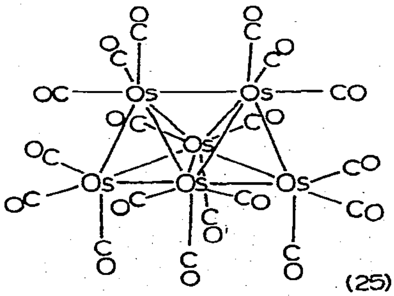


(24)

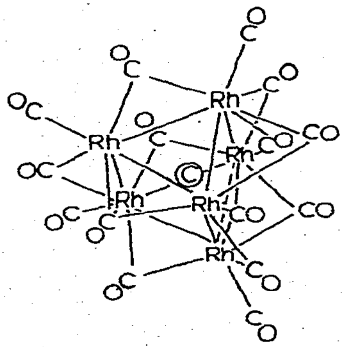
Interestingly, the complex is asymmetric; the two metal-hydrogen atoms are different (n.m.r.), and the two vinylidene protons exchange.

Of the many unusual condensation products obtained by pyrolysis of $Os_3(CO)_{12}$,[27] the structure of $Os_6(CO)_{18}$ (25) has now been reported.[28] The central metal cluster is based on an Os_4 tetrahedron, two faces of which are capped by the other metal atoms. The various Os-Os bond lengths [range 2.732-2.836(1)Å] reflect the coordination number and formal oxidation state of the metal atoms. A brief comparison of MO with polyhedron skeletal electron pair theories is made, and predictions of structures of $Os_7(CO)_{22}$ and $Os_8(CO)_{23}$ are made, and substantiated in the former case.



(25)

A trigonal prismatic metal cluster has been found[29] in the new carbido complex $[NMe_3(CH_2Ph)]_2[Rh_6C(CO)_{15}]$ (26). Each edge of the prism is bridged by a CO group, each metal atom also having one terminal CO group. The carbide carbon is at the centre of the prism. The Rh–Rh bonds are of two types, within the basal triangles [2.776(3)Å], and between them [2.817(2)Å]. The prismatic geometry results from the impossibility of accommodating the 90 outer valence electrons in an octahedral cluster (maximum 86), and an interpretation of the structure in terms of the polyhedral skeletal electron-pair theory is given.



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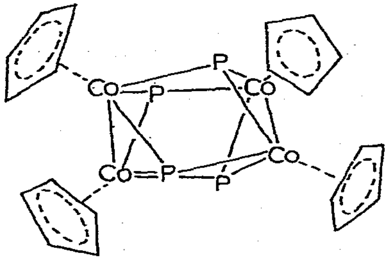


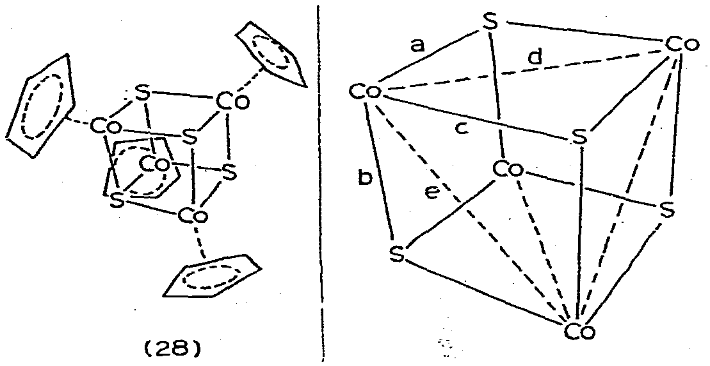
(27)

The direct reaction between phosphorus and $(C_5H_5)Co(CO)_2$ afforded a low yield of $[Co_4(C_5H_5)_4P_4]$ (27), in which a tetragonally-distorted Co_4P_4 cube is found. The distortion results from there being two types of Co–Co distances: two at 2.504(2)Å, corresponding to a two-electron bonding interaction, and four at 3.630(av)Å, which are non-bonding. Comparisons are made with the isoelectronic $[Fe_4(C_5H_5)_4S_4]$ cluster, and the sulphur-cobalt analogue $[Co_4(C_5H_5)_4S_4]$. In the latter, which does not have any net metal-metal interaction (see below), the electron differences are reflected in chemical equivalent Co–Co distances and cubic T_d geometry found in the latter, together with long S–S contacts [compared with relatively short P–P contacts found in (27)].

Comparison of the geometries of the clusters $[Co_4(C_5H_5)_4S_4]$ and its monocation (28) gave information about the antibonding character of the unpaired electron. The neutral cluster does not contain any Co-Co electron pair bonds, and the Co_4S_4 core has cubic T_d symmetry, with Co-Co distances of 3.295(av)Å. The cation is tetragonally distorted (idealised D_{2d}) with two long (non-bonding) Co-Co distances of 3.330(5)Å, and four shorter ones of 3.172(5)Å. On the basis of a metal cluster MO model, the observed distortion and shortening reflects an increase in individual Co-Co bond order from 0 to 0.125, with a total limiting Co-Co valence bond order of 0.5.

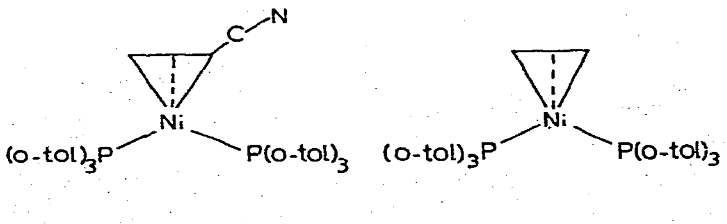
Olefin complexes

A comparison has been made between the structures of nickel-olefin complexes $LNi[P(O\text{-}\underline{o}\text{-tol})_3]_2$ (29) (L = CH_2:CHCN and C_2H_4)[32]. In the former, the acrylonitrile is more strongly bonded to



(28)

	Neutral	Cation
a	2.230(2)	2.221(7)
b	2.230(2)	2.215(5)
c	2:232(2)	2.217(7)
d	3.315(2)	3.330(5)
e	3.236(1)	3.172(5)



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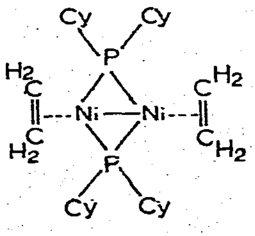


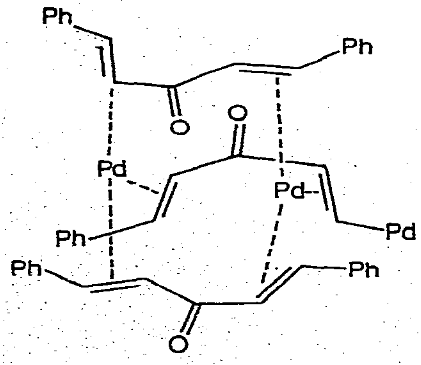
(30)

nickel than is ethylene, and in addition the geometry is altered to maximise the interaction of the CN group with the Ni-olefin bond. This is thought to be an electronic effect resulting from the stabilisation of the olefin π^* orbital by the CN group, and is consistent with the σ-π (Dewar-Chatt-Duncanson) idea of metal-olefin bonding. A similar effect is found in the complex $(CH_2{=}CHCN)Fe(CO)_4$. A comparison of C=C bond distances in 24 olefin-metal complexes (of Ni^o, Pt^o, PtII, RhI, IrI and Fe^o) is also given.

The complex $[Ni(PCy_2)(C_2H_4)]_2$ (30) contains a nickel-nickel bond [2.388(1)Å] bridged by the two phosphido groups; the two olefins are coplanar with the central Ni_2P_2 group.[33] The angle at phosphorus is 67.6°.

The composition of dibenzylideneacetone (dba) complexes of palladium(0) depends on solvent, and when isolated from dichloromethane or chloroform, the composition is $Pd_2(dba)_3$.solvent.[34] The CH_2Cl_2 adduct has structure (31). Each palladium is trigonally coordinated to three double bonds in bridging dba ligands; one of the ligands has the symmetric syn,syn conformation, while the other two are in the syn, trans form.

Vinyl alcohol(VA) can be stabilised (with respect to conversion to acetaldehyde) by complexing to metals. The structure of



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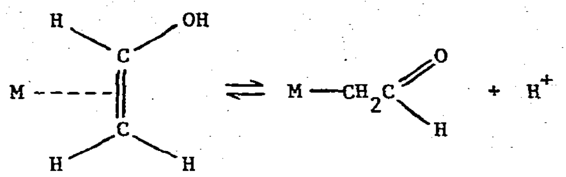
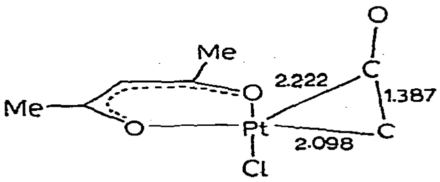
[PtCl(acac)(VA)] (32) contains the alcohol bonded in a manner intermediate between a π-olefinic and σ-aldehyde, consistent with NMR evidence of a rapid solution equilibrium:



and explained by a bonding model (32a) intermediate between the 2 extremes.[35] Structural data for twelve olefin-platinum(II) π-complexes are compared.



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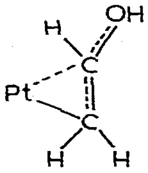

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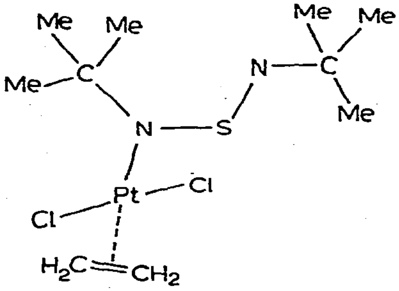


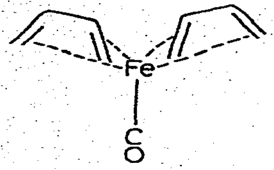
(33)

The reaction between $[PtCl_2(C_2H_4)]_2$ and di-t-butylsulphurdiimine affords a complex (33) containing N-bonded sulphurdiimine, trans to the ethylene.[36]

Diene complexes

Bond distances and angles in $Fe(CO)(C_4H_6)_2$ (34) are similar to those in the related cyclohexa-1,3-diene complex[37]; the two diene units are planar but not parallel.[38] The structure of $IrCl(C_4H_6)_2$ (35)[39] is not significantly different from the rhodium analogue.[40] Some Ir-Cl distances in other (unpublished) structures [trans-$IrCl(C_2H_4)_2(py)$, $IrCl(C_2H_4)_4$] are also given.

The absolute configuration of the dissymetric olefin endo-dicyclopentadiene (endo-DCP) has been determined via the molecular



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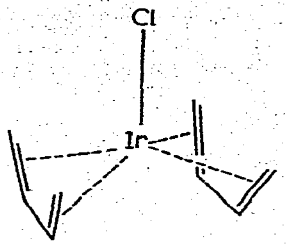

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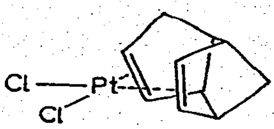

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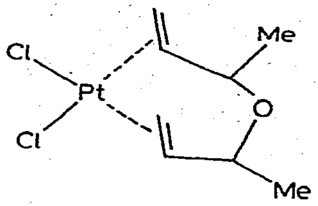


(37)

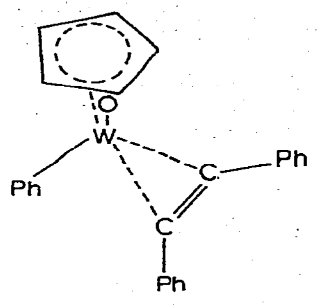
structure of (+)-$[PtCl_2($<u>endo</u>$-DCP)]$ (36).[41] A product from the reaction between crotyl alcohol and K_2PtCl_4 is the ether complex <u>cis</u>-$PtCl_2[(CH_2{=}CHCHMe)_2O]$ (37). The ether is coordinated as a diolefin; during its formation, isomerisation of the original crotyl group occurs.[42]

<u>Acetylene derivatives</u>

The photochemical reaction between C_2Ph_2 and $(C_5H_5)W(CO)_3Ph$ affords the carbonyl-free $WOPh(C_5H_5)(C_2Ph_2)$ (38), containing a π-bonded acetylene.[43] The formal electron deficiency of this molecule is reflected in W-Ph, W-C_2Ph_2 and W-O bonds shorter than normally found.

The unprecedented formation of a π-cyclopentadienyl ligand from diphenylacetylene is found in the reaction of the latter with $Pd(OAc)_2$ in methanol; also formed is $PhC(OMe)_3$.[44] The metal-containing product, formed quantitatively, is $Ph_2C_2[Pd(C_5Ph_5)]_2$ (39), which is structurally analogous to the long-known nickel complex, $Ph_2C_2[Ni(C_5H_5)]_2$.

The complex anion in $K[PtCl_3\{Et_2C(OH)C{\equiv}CC(OH)Et_2\}]$ has the expected square planar structure (40).[45] The $C{\equiv}C$ bond length is 1.18(3)Å, i.e. not significantly lower than an uncoordinated acetylene, although the angles of the acetylenic carbons, $C{\equiv}C{-}C$, average 160°.



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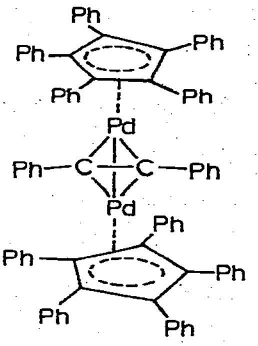

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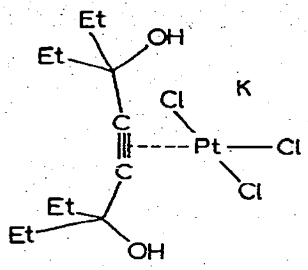
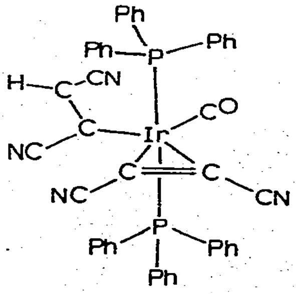


(40)

The location of the hydroxyl groups makes it unlikely that any significant stabilisation of complexes of hydroxyacetylenes is achieved via hydrogen bonding, although oxygen-potassium interaction may be important in this respect.

Complexes derived from electron-deficient olefins and acetylenes

The structure of Ir[C(CN)=CH(CN)](CO)[$C_2(CN)_2$]$(PPh_3)_2$ (41) has been determined.[46] Of interest are the bond lengths of the central C-C portions of the $C_2(CN)_2$ and C(CN)=CH(CN) moieties, which are equal [1.29(2)Å]. Both cyanocarbon fragments lie in the trigonal plane. As expected, the dicyanoacetylene ligand is no longer linear, with the average angle C≡C-CN 139.5(13)°. This interesting paper concludes with an extensive discussion of the bonding of vinyl and acetylene groups to metals.



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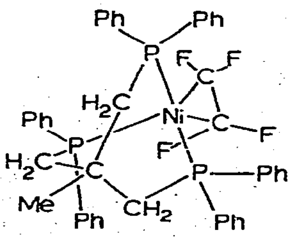
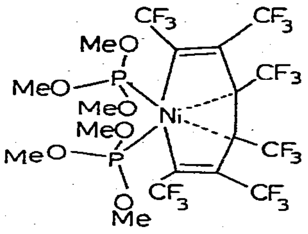


(42)

The complex $Ni(C_2F_4)$(triphos) (42) does not react with excess C_2F_4 to give a five-membered ring complex; the structure determination reveals that there is no vacant coordination site, all three phosphorus atoms being coordinated to the metal.[47] The bonding of the C_2F_4 ligand is similar to those found previously, but in the olefin, each CF_2 plane has been bent back by 42°. A nickel derivative of $C_2(CF_3)_2$ has been shown[48] to contain the seven-membered C_6Ni ring, in which there is a significant cross-ring π-interaction between the metal and the double bond (43). The structure may be compared with that of $\overline{Rh(C_2Ph_2)_2C_6H_4PPh_2}(PPh_3)$.

The product from hexafluorobut-2-yne and $Pt(PEt_3)_3$ contains a $C_6(CF_3)_6$ molecule bonded to platinum via only one double bond (44); the metal is sited underneath the ring plane. In solution, the molecule exhibits fluxional behaviour.[48]



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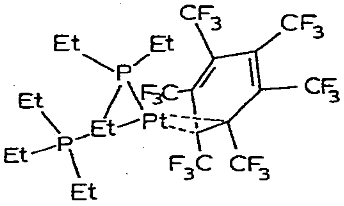

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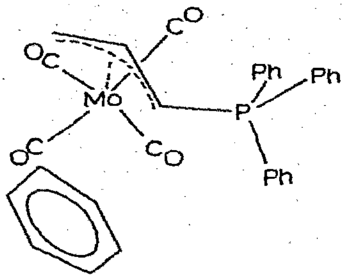
Complexes containing allylic groups, and other extended acyclic π-systems

An X-ray study[50] of $Mo(CO)_4(Ph_3P{:}C_3H_4)(C_6H_6)$ [obtained from $Mo(CO)_6$ and $Ph_3P{:}CHCH{:}CH_2$] revealed that the crystals are a clathrate of benzene and complex (45). The phosphorane is coordinated via the allylic group, resulting in a zwitter-ionic complex which may be represented as in (45a) [cf. the organophosphonium acetylide complex, $Ph_3PC_2Mn(CO)_4Br$[51]].



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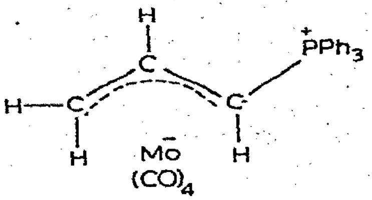

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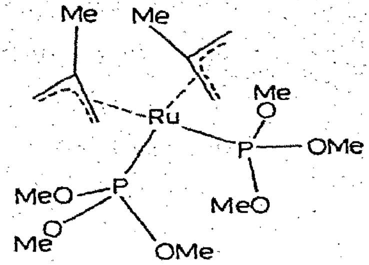

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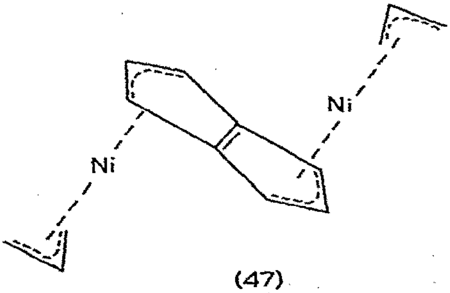
The complex $Ru(C_4H_7)_2[P(OMe)_3]_2$ (46) (monoclinic form) has a similar structure[52] to that of $Ru(C_3H_5)_2(PPh_3)_2$ reported last year.[53] The bonding of the 2-methallyl groups is asymmetric, with Ru-C distances of 2.38(2) (trans to P) and 2.18(2)Å (trans to C). The methyl group is bent out of the allyl plane by 12° away from the metal atom, in contrast to other methallyl complexes studied. Crystal data for an orthorhombic form are given.

(Dihydropentalenylene)dilithium and $[(C_3H_5)NiCl]_2$ afford the binuclear complex (47), in which the two $Ni(C_3H_5)$ units have a transoid configuration.[54] They are closest to the non-bridged carbons of the bicyclic ligand, which is nearly planar.



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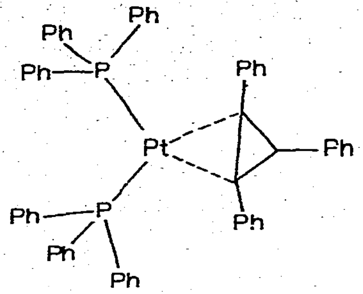
Complexes containing cyclic C_3 and C_4 systems

Addition of $C_3Ph_3^+PF_6^-$ to $Pt(C_2H_4)(PPh_3)_2$ affords the new cyclopropenyl complex $[Pt(C_3Ph_3)(PPh_3)_2]PF_6$ (48), containing a localised cyclopropenyl ring asymmetrically bonded to the metal.[55] Two Pt–C distances are 2.09(1)Å, while the third is 2.48(1)Å, suggesting that the complex is best described as involving bonding from a localised double-bond in the C_3 ring.

In $(\pi\text{-}C_5H_5)Rh(\pi\text{-}C_4Ph_4)$ (49), the phenyl groups are twisted



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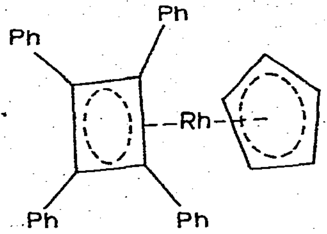
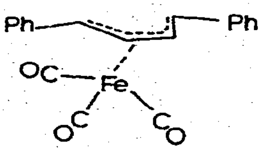


(49)

relative to the C_4 ring, and bent away from the metal atom.[56] The plans of the C_4 and C_5 rings are intersect at an angle of 2.4°.

Iron carbonyl derivatives of unsaturated hydrocarbons

The structure of the unsolvated 1,4-diphenylbutadiene (L) complex (50) has been determined.[57] The first-formed of the two complexes obtained from 1,4-diphenylbutadiene and $Fe_2(CO)_9$ has been shown to be the "solvated" complex $L.Fe(CO)_3.\frac{1}{2}L$.[58] Comparisons between the two structures show few differences. The $Fe(CO)_3$ derivative of 1-carbethoxy-1H-diazepine has structure (51), in which the iron is bonded to the C_4 diene unit of the ring.[59]



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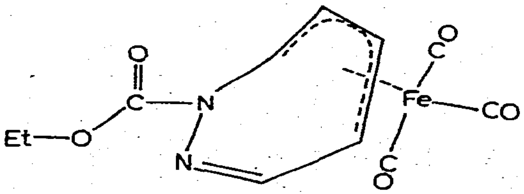

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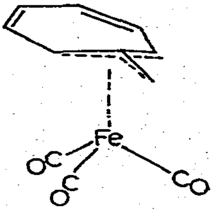

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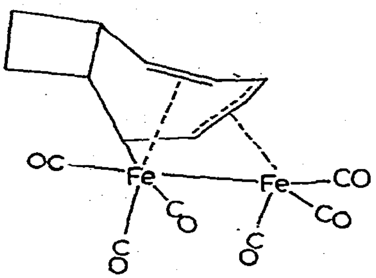
The 1,6,7,8-$\underline{h}^4$ isomer of (heptafulvene)Fe(CO)$_3$ (52) confirms the proposed structure as a trimethylenemethane derivative.[60]

The fluxional molecule $C_{10}H_{12}Fe_2(CO)_6$ ($C_{10}H_{12}$ = <u>cis</u>-bicyclo[6.2.0]deca-2,4,6-triene) has structure (53), in which one iron atom is attached to three adjacent carbons, and to the second metal atom, which is bonded to the other carbons not involved in the C_4 ring.[61] The structure is similar to those of $(C_8H_8)Ru_2(CO)_6$ and $(C_8H_{10})Fe_2(CO)_6$. An interesting communication[62] reports the outline structures of four more complexes, out of a total of eight, isolated from reactions between $Fe_2(CO)_9$ and this hydrocarbon (54-57). Some of these were completely identified directly by X-ray crystallographic methods, without recourse to spectroscopic methods; in the case of fluxional molecules, or of the more complex structures encountered here, conventional spectroscopic data would be unlikely to reveal the actual structures. It is reported that "the working time, total elapsed time, and direct cost are all as good or better than they would be in a classical approach".



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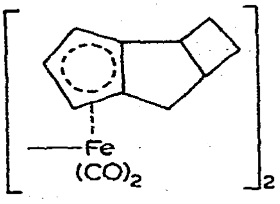

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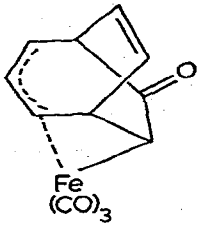

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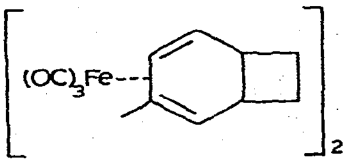

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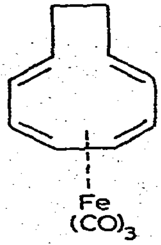

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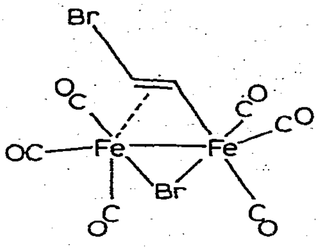
Irradiation of $(1,2\text{-}C_2H_2Br_2)Fe(CO)_4$ in solution afforded the binuclear complex $C_2H_2Br_2Fe_2(CO)_6$, shown to have structure (58).[63] The two $Fe(CO)_3$ moieties are linked by a metal-metal bond (2.525Å) bridged by bromine, and a π-bromovinyl group, although the bonding of the latter suggests formation of a 1-ferra-π-allyl system.



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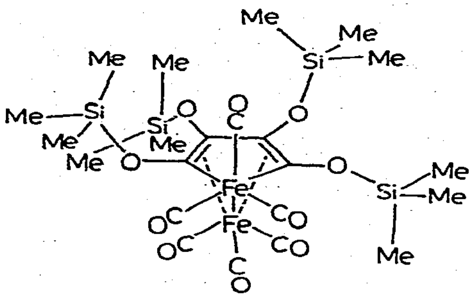
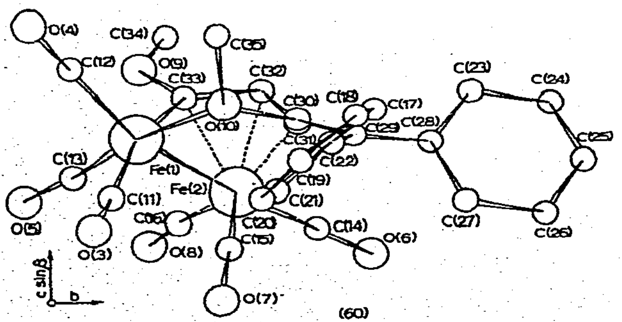


(59)

The interaction of Me_3SiI with $Na_2Fe(CO)_4$ has given a complex initially formulated as $[(Me_3Si)_2Fe(CO)_4]_2$, but shown to be the ferrole complex $C_4(OSiMe_3)_4Fe_2(CO)_6$ (59) by an X-ray study.[64] The structural features are similar to those found earlier in $C_4(OH)_2Me_2Fe_2(CO)_6$.[65] One of the products obtained from this ferrole complex and diphenyldiazomethane has structure (60),[66] analogous to the product from chloramine T and the ferrole. The diagrams (Figures 1 and 3) in this paper actually relate to the isomeric product also isolated from the reaction, and described in a previous paper (J.C.S.Dalton, 1972, 2169). Dr. Jeffreys has kindly supplied the correct diagram, which is given here.

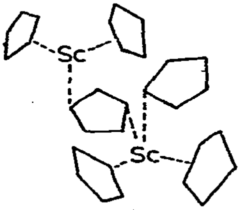


(60)

Cyclopentadienyl complexes

In $Sc(C_5H_5)_3$ (61), each metal atom is coordinated to two $\underline{h}^5$-C_5H_5 groups, and to two others via essentially $\underline{h}^1$-C_5H_5 groups, resulting in a polymeric arrangement containing both bridging and terminal C_5 units.[67] The presence of the former is taken as an indication of some degree of covalency in the appropriate Sc–C bonds. Some comparison with the structure of $Sm(C_5H_5)_3$ is made.[68] In tri-indenylsamarium (62),[69] the metal is symmetrically bonded to the C_5 portions of the ligands, with the angles between the normals approaching 120°. The electron-rich C_1 position of the indenyl group is not preferentially bonded in this (unsolvated) complex, as has been suggested for $Sm(ind)_3(OC_4H_8)$.[70]

The structure of $UCl(C_5H_4CH_2Ph)_3$ (63) (the substituent was chosen to secure a well-ordered crystal, with minimum electronic perturbation of the C_5 group) reveals approximate tetrahedral coordination of uranium.[71] The C_5 ligands are symmetrically bonded; individual carbon positions in the previously studied $UCl(C_5H_5)_3$ were



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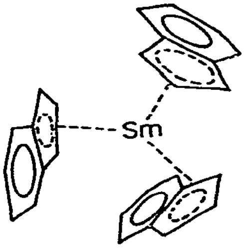

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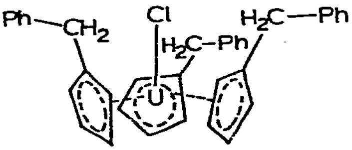

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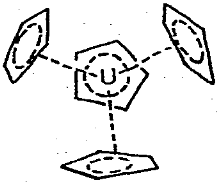
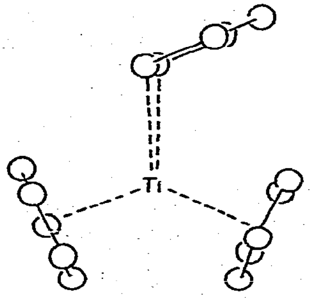


(64)

not refined.[72] Tetracyclopentadienyluranium (64) has a tetrahedrally coordinated uranium atom bonded to four $\underline{h}^5$-cyclopentadienyl groups.[73]

Paramagnetic tris(cyclopentadienyl)titanium (65) has two pentahapto-cyclopentadienyl groups bonded to the metal, as found in many bent $(\underline{h}^5\text{-}C_5H_5)_2TiX_2$ systems; the third C_5 ring is attached by two adjacent carbons, although it is suggested that this ligand acts as a three-electron donor, with the titanium adopting a 17-electron configuration. An M.O. picture is presented.[74] The structure of $TiCl_2(1,3\text{-}Ph_2C_5H_3)_2$ (66) shows no unusual features, although the phenylcyclopentadienyl moieties are not planar.[75] The neutron diffraction study[76] of $[C_5H_4(CH_2)_3C_5H_4]TiCl_2$ (67) reveals a slight displacement of the ring hydrogens towards the metal atom [cf. the similar effect found with the methyl groups in $U(C_8H_4Me_4)_2$]. Other



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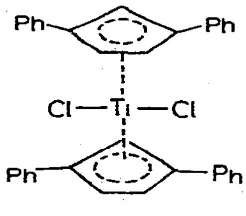

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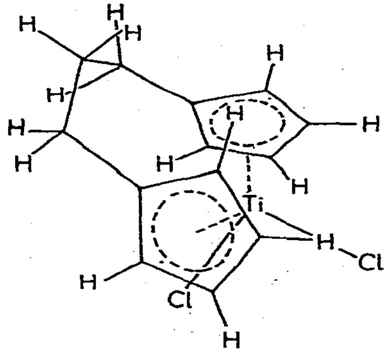

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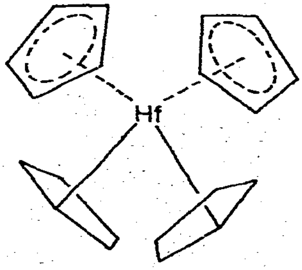
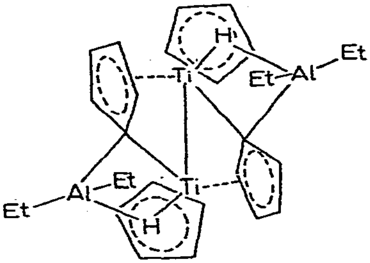


(68)

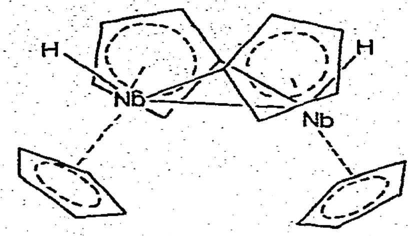
features, with the exception ofthe expectedly larger ring C-C distances, are in agreement with the earlier X-ray study.[77] Tetracyclopentadienylhafnium contains two h̲^{5}-C_5H_5 and two h̲^{1}-C_5H_5 ligands (68),[78] and is thus similar to the analogous titanium complex.

The olefin polymerisation catalyst formulated[79] as $[(C_5H_5)_2TiAlEt_2]_2$ has been shown[80] to be the hydride complex $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$ (69), another member of the bridging cyclopentadienyl complexes also found in $(C_5H_5)(CO)Mo(C_5H_4)Mn(CO)_4$ [81] and $[(C_5H_5)(C_5H_4)NbH]_2$,[82] the so-called niobocene dimer. This is actually a hydride complex containing a h̲^{5}-cyclopentadienyl group also attached to the other metal atom (70). Other features of the niobium complex include Nb-H [1.70(3)Å] and Nb-Nb [3.105(6)Å] bonds. Comparisons with 21 selected complexes containing $(C_5H_5)_2M$ groups, particularly with respect to the angle C_5H_5-M-C_5H_5, are made.



(69)

In the hydride $(C_5H_5)_2Nb(CO)H$ (71), the C_5-ring dihedral angle is 37°, and the rings are essentially "eclipsed".[83] The Nb-H distance was assumed to be 1.5Å. The complex $[(\pi-C_5H_5)V(C_4H_3OCO_2)_2]_2$ (72) is dimeric via bridging carboxylate groups, as previously found in the trifluoroacetate, with a V---V separation of 3.625Å.[84]



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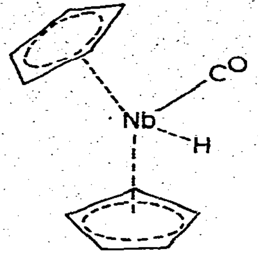

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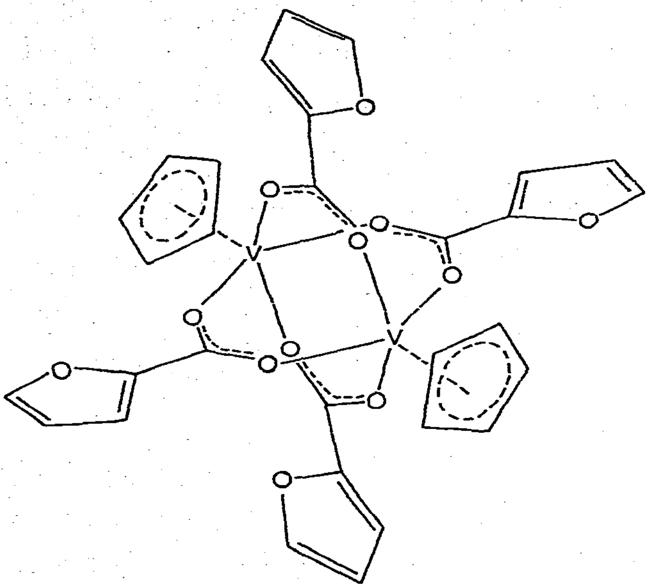


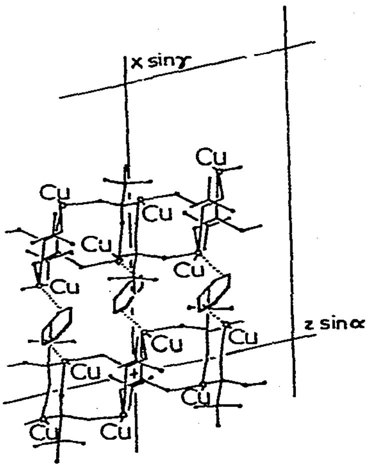
Complexes containing cyclic C_6, C_7 and C_8 systems

In the complex $C_6H_6CuSO_3CF_3$ (73), two copper atoms are π-bonded to each ring; the $CuSO_3CF_3$ forms infinite chains, cross-linked by the arene molecules.[85]

In $(C_5H_5)Ti(C_7H_7)$, the carbons of the planar C_5 and C_7 rings are respectively 2.32 and 2.19Å from the metal atom; the latter is unusually short.[86] The full details of the structure of $[(C_7H_7)Mo(CO)_3]BF_4$ (74) have appeared[87]; the molecule has a conventional piano-stool configuration, with a planar C_7 ring attached to an $Mo(CO)_3$

moiety. A comparison of Mo-CO distances in some 15 complexes shows that only that in $Mo(CO)_6$ is longer than those found in (74).

Further details of $\underline{h}^8$-cyclooctatetraene derivatives have appeared. The ion-pair salt K(diglyme)$[Ce(C_8H_8)_2]$ has structure (75), in which the cation is coordinated on one side by the ether, and on the other by one of the $C_8H_8{}^{2-}$ rings.[88] The latter are planar, and attached to the cerium atom so that the molecular symmetry of the anion is D_{8d} (staggered rings). Full crystallographic and structural data for $U(C_8H_4Me_4)_2$ are now available.[89] In both independent molecules, the uranium is bonded to planar $C_8H_4Me_4{}^{2-}$ rings. The two molecules differ in the relation of the methyl group, one being staggered, the other eclipsed; the methyl groups are bent towards the metal atom, for which phenomenon two hypotheses are proposed.



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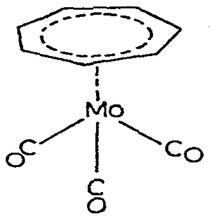

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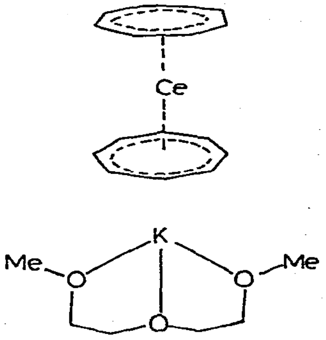
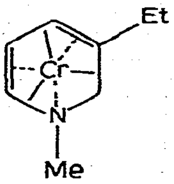


(75)

Complexes containing π-complexed heterocycles

The mixture of 1,2- and 1,6-dihydropyridines obtained by $NaBH_4$ reduction of N-methyl-3-ethylpyridinium iodide reacts with $Cr(CO)_3(MeCN)_3$ to give the isomeric complexes (76) and (77) as stable examples of dihydropyridines.[90] Bond lengths are intermediate between those expected for alkene and aromatic systems, and the chromium interacts with two double bonds and the nitrogen lone pair with a distorted octahedral coordination.

The $Mn(CO)_5$ derivative of Ph_4C_4As readily loses CO on heating or irradiation to give the tricarbonyl.[91] This has structure (78), and contains a new example of a π-bonded heteroaromatic system; incorporation of the relatively large arsenic atom into the planar heterocycle causes large angular distortions e.g. CAsC, 84.9(4)°, and CCC average 114°.



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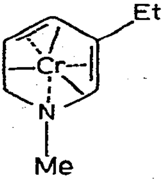

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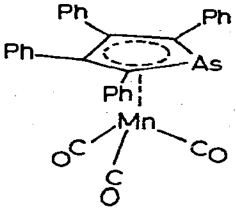
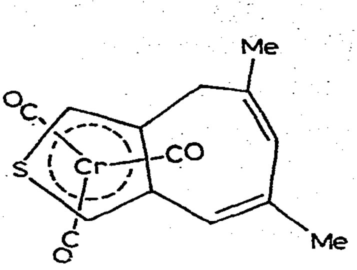


(78)

The structureof a cyclohepta[c]thiophene complex (79) containing a $Cr(CO)_3$ moiety attached to the thiophene ring has been described.[92] In contrast with the free ligand, the tropilidene ring has the boat conformation. Details of the structures of the two complexes (80 and 81) obtained from a cyclohepta[b]thiophene have been given.[93] In both cases, the $Cr(CO)_3$ group is attached to the C_7 ring, the bond distances indicating two different conformations, and suggesting $\underline{h}^6$-attachments in these complexes. During the reaction isomerisation of the ligand (by hydrogen migration) occurs, and the structures of these complexes help the interpretation of the mechanism of the reaction.



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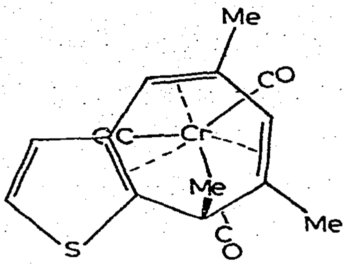

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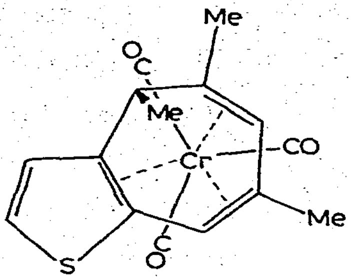
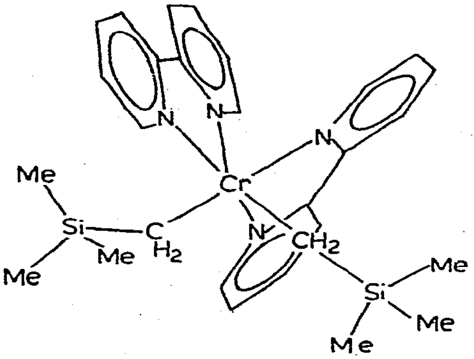


(81)

Complexes containing metal–carbon σ bonds (a) Simple alkyls and aryls

The structure of $[Cr(CH_2SiMe_3)_2(bipy)_2]I$ (82) has been compared with those of related aryls.[94] The Cr–C(sp^3) bond length [2.107(9)Å] is not significantly different from the Cr–C(sp^2) bonds found in the aryls. The structure of $[CrPh_2(bipy)_2]I$ (83) is similar to that of the analogous 2-methoxyphenyl derivative, with a Cr–C bond length of 2.087(4)Å.[95]



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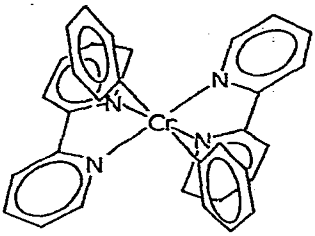

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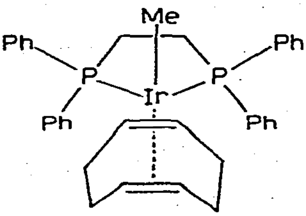
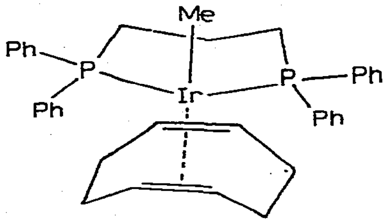


(84)

The stereochemically non-rigid complex IrMe(C_8H_{12})(dppe) (84) has a distorted trigonal-bipyramidal coordination about the metal, with the methyl group occupying an axial position.[96] The structure is compared with that of IrMe(C_8H_{12})(PMe_2Ph)$_2$, reported in 1972.[97] The observed differences correlate with differences in the rates of stereoisomeric interconversion, and with the proposed Berry pseudorotation mechanism for this process.[98] Comparison can also be made with IrMe(C_8H_{12})(dppp) (85).[99] In these three complexes, the P-Ir-P angles are 101.5(2) (PMe_2Ph), 93.4(1) (dppp) and 84.9(2)° (dppe), which correlate directly with the rates of the stereoisomeric interconversions (cf. values for free energies of activation, ΔG , which are 16.3, 13.4 and <9.2 kcal mol^{-1}, respectively).



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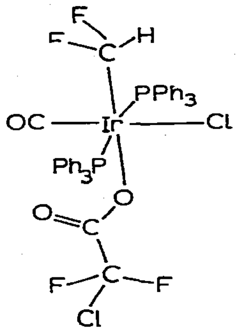

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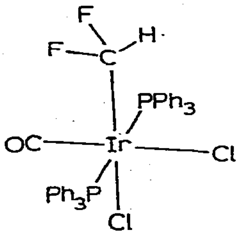
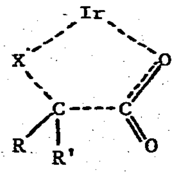
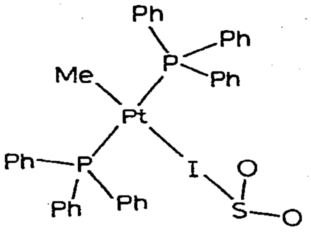


(87)

The reaction between sodium chlorodifluoroacetate and Vaska's complex affords initially the complex IrCl($OCOCF_2Cl$)(CHF_2)(CO)(PPh_3)$_2$ (86), while prolonged reaction gives $IrCl_2$(CHF_2)(CO)(PPh_3)$_2$ (87).[100] In the latter, the chloride trans to the CHF_2 group originates from the trihaloacetate, perhaps via the cyclic transition state



The full account[101] of the structure of trans-PtMe$(PPh_3)_2ISO_2$ (88) contains a comparison of this adduct with similar adducts of SO_2 with amines, e.g. $Me_3N.SO_2$, and other metal complexes, such as Vaska's complex. Indeed, reaction between IrI(CO)$(PPh_3)_2$ and SO_2 affords the bis-adduct Ir(CO)$(PPh_3)_2ISO_2(SO_2)$.



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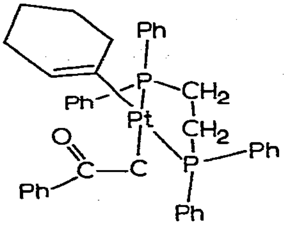


(89)

The complex $Pt(C_6H_9)(CH_2COPh)(dppe)$ (89), obtained from the reaction between Pt(cyclohexyne)(dppe) and acetophenone, contains a relatively long Pt-CH_2COPh bond [2.175(10)Å].[102] This and other structural data suggest that this bond has some ionic character, with a contribution from the form

$$Pt^{+}{-}{-}{-}{-}CH_2{=}{=}{=}{=}CPh{=}{=}{=}{=}O^{-}$$

The bond angle at the appropriate carbon atom does not indicate any rehybridisation, however.

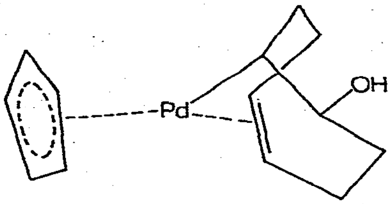
(b) Complexes formed by nucleophilic attack on coordinated olefines

The structure of a palladium hydroxycyclooctenyl complex (90) has been reported.[103] The C_8 ligand is boat-shaped, and as expected, is bonded via σ and π bonds. The absolute configuration of one diastereoisomeric form of complex (91) ([α] −42.3; c 1.2, $CHCl_3$) has been determined from the X-ray structure,[104] and the absolute configurations can be assigned to the two chiral centres, as shown.

Addition of diethylamine to olefin-platinum complexes affords a zwitter-ionic complex.[105] The product from $NHEt_2$ and trans-$[PtCl_2(C_2H_4)(NHEt_2)]$ has structure (92). The particular conformation probably results from the formation of an N-H---Cl hydrogen bond as shown, which may stabilise the complex. The two amines differ: the coordinated $NHEt_2$ has the all-trans conformation, while the $NH_2Et_2^+$ group is gauche.

(c) Products obtained by so-called "insertion" reactions

The reaction between hexafluoroacetone and $(\pi-C_5H_5)Ru(PPh_3)_2-[\sigma-C_2(CO_2Me)_2H]$ gives a 1:1 adduct (93), containing as novel features (a) the C_5 ring attached to a $C(CF_3)_2OH$ moiety, and (b) intramolecular hydrogen bond to an ester carbonyl group.[106] The structure of the product of insertion of norbornadiene into the Pd-C bond in $[(C_4H_7)PdCl]_2$ (derivatised as the acetate) (94) has been further refined.[107] This confirms the asymmetry of the π-vinyl coordination (probably as a result of substituent effects on the π^* orbital), and a



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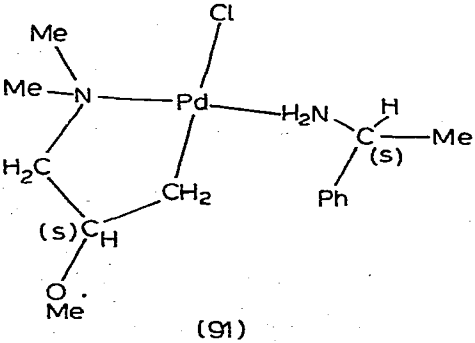

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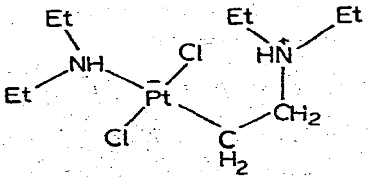

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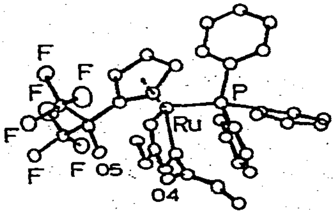

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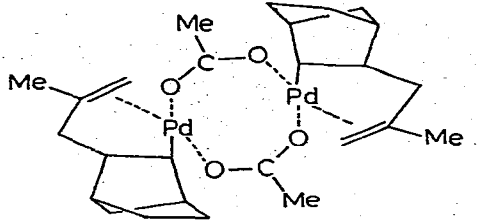

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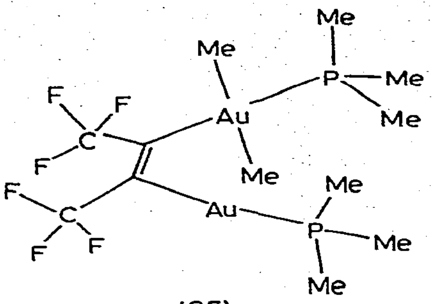


(95)

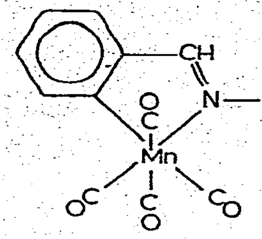
demonstration of the higher trans influence of the σ-bonded carbon relative to the π-vinyl group. Hexafluorobut-2-yne reacts with MeAuL (L = tertiary phosphine) to give intermediates, $(MeAuL)_2C_4F_6$, which break down to give either cis-$LAuC(CF_3):C(CF_3)Me$ (the insertion product), or cis-$LAuC(CF_3):C(CF_3)AuL$ (with elimination of ethane). The intermediate ($L = PMe_3$) has structure (95), and contains Au(I) and Au(III), and a reaction mechanism is proposed.[108]

(b) Complexes containing internally-metallated ligands

The structures of two ortho-metallated complexes containing manganese, derived from benzylideneaniline and N,N-dimethylbenzylamine, have been described. In the former, $PhN{=}CHC_6H_4Mn(CO)_4$ (96), a planar five-membered chelate ring is formed, with equal Mn-C and Mn-N distances.[109] In the second complex, $Me_2NCH_2C_6H_4Mn(CO)_4$ (97), the chelate ring is now puckered, resulting from the presence of saturated N and C atoms.[110] Trends in Mn-CO distances in both complexes are discussed, the shortest being trans to nitrogen.

One product from the reaction between p-$FC_6H_4N_2BF_4$ and Vaska's complex is the ortho-metallated aryl diimide derivative (98).[111] Dimensions within the five-membered C_2N_2Ir ring are similar to those reported for related complexes.

Rapid intramolecular hydride addition at the free vinyl group in $HMn(CO)_4(sp)$ affords two isomeric complexes, one of which is $(MeCHC_6H_4PPh_2)Mn(CO)_4$ (99). The complex contains a small amount of the



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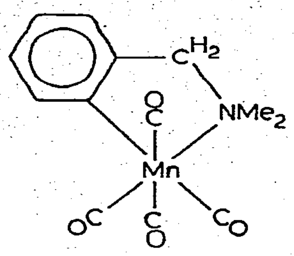

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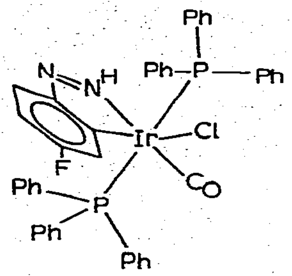
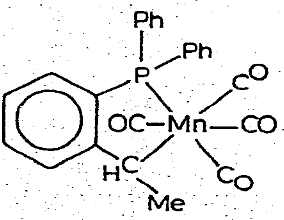


(98)

second isomer (anti-Markownikoff addition) which probably gives rise to about 20 symmetry forbidden reflections.[112]

One of the many products obtained from the reaction between $\text{Ph}_2\text{PC}_6\text{H}_4\text{Mn(CO)}_4$ and cis-$\text{MeMn(CO)}_4\text{(PPh}_3\text{)}$ (refluxing toluene, 2 hr) is the unusual tricyclic complex (100), in which the metallated phosphine phenyl group in the initial complex has undergone CO-insertion, and a second metallation has occurred, with the donor atom in this case being the carbonyl oxygen.[113]

Three iridium complexes containing internally metallated phosphines have been studied[114]: $\overline{\text{IrC}_6\text{H}_4\text{P}}\text{Ph}_2\text{(PPh}_3\text{)(C}_2\text{H}_4\text{)}$, $\overline{\text{IrC}_6\text{H}_4\text{P}}\text{Ph}_2\text{(PPh}_3\text{)(CO)}$ and $\overline{\text{IrCHMeCH}_2\text{P}}\text{Pr}^i_2\text{(PPr}^i_3\text{)(C}_2\text{H}_4\text{)}$. The coordination about iridium is similar in all three complexes and is shown in (101); metallation of the i-propyl group occurs at the β carbon atom. The structures of three isomeric complexes containing metallated PBu^t(o-tol)$_2$ ligands have been determined[115]; one (102) contains the



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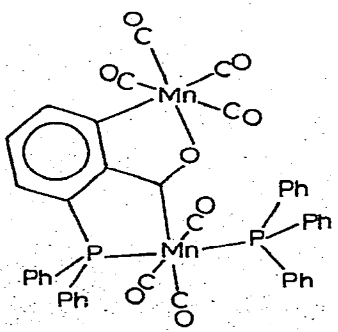

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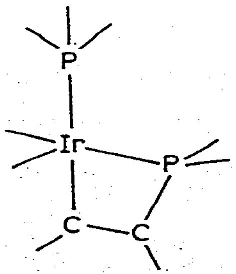

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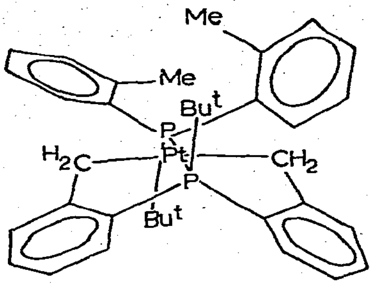

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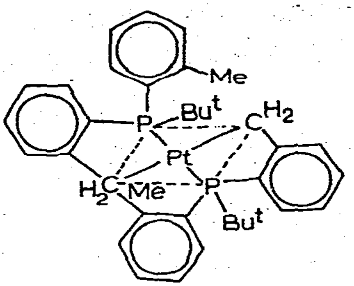

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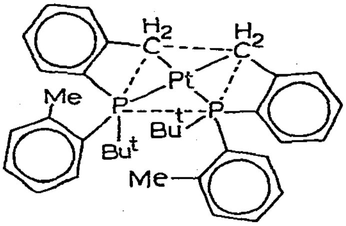
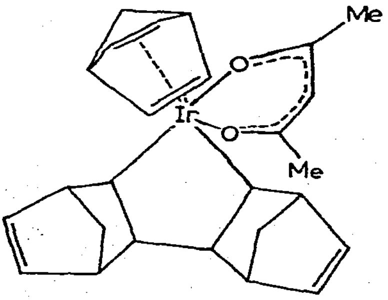


(104)

first example of a dimetallated tridentate ligand. On heating isomerisation to the bis-monometallated complex occurs, formed as cis and trans isomers (103, 104).

(e) Metallocyclic derivatives

The structure of Ir(acac)(nbd)$_3$ (105) [derived from [IrCl(cod)]$_2$ and norbornadiene] reveals that two of the hydrocarbons have combined with the iridium to form a metallocycle.^{116} This complex



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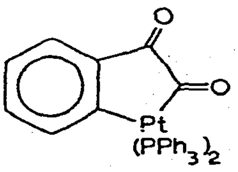


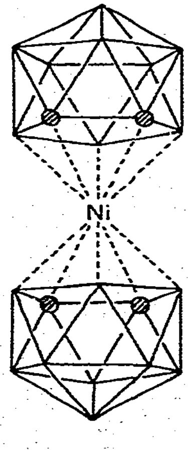
(106)

is considered to be an intermediate in the metal-promoted [2+2] cyclo-dimerisation of norbornadiene to the exo-trans-exo dimer, which can be isolated by refluxing $Ir(nbd)_3Cl$ with excess PPh_3.

Two conformers of a platina-cyclopentenedione (106) have been obtained from $Pt(PPh_3)_4$ and 1,2-benzocyclobutadienequinone, via an unsymmetrical opening of the four-membered ring.[117] The two isomers (deep red and deep blue in colour) are interconvertible; the former is the more stable. The major structural difference lies in the twist angles of the two CO groups about the connecting C-C bond.

Metallocarboranes and related polyhedral borane derivatives

The structure of $NMe_4[Ni(B_9C_2H_{11})_2]$ (107) reveals a symmetrical sandwich-type anion, and completes the series of Ni^{II}, Ni^{III} and Ni^{IV} structures.[118] Bond distances (Ni-B and Ni-C) suggest that it is the latter which accommodate electronic differences between the three complexes. However, intercage non-bonded interactions are also important in determining the stereochemistry of this type of complex. A full account of the structure determination of the asymmetric metallocarborane complex $NEt_4[(B_9C_2H_{11})Co(B_8C_2H_{10}py)]$ has been given.[119] The metal atom



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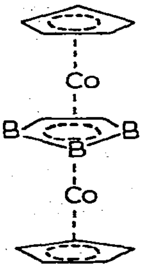
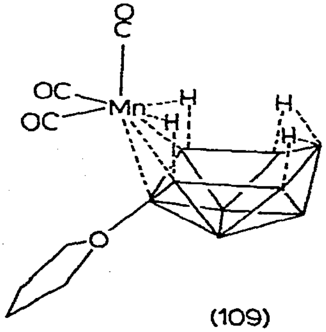


(108)

is sandwiched between the mutually staggered carborane anions; the B_8C_2 ion is linked to cobalt via an open CB_3 face.

Crystallographic verification of the existence of "triple-decker" sandwich compounds has been obtained in the case of $(C_5H_5)Co[3\text{-}Me\text{-}(1,7)\text{-}2,3\text{-}C_2B_3H_4]Co(C_5H_5)$ (108).[120] The rings are all planar, but not parallel; relative to the C_2B_3 plane, the C_5 rings are tipped by 4.6 and 5.5°. One C_5 ring eclipses the C_2B_3 group, while the other is staggered.

A product from reactions between $Mn(CO)_5Br$ and $B_9H_{14}^-$ in tetrahydrofuran[121] is $Mn(CO)_3[B_9H_{12}(OC_4H_8)]$ (109). In this complex, the B_9 cage acts as a tridentate five-electron donor to the metal, by a single Mn-B bond [2.196(6)Å], and two three-centre two-electron Mn-H-B bonds. The zwitterion $Mn(CO)_3[B_9H_{12}\{O(CH_2)_4NEt_3\}]$ (110) is formed from $Mn(CO)_3[B_9H_{12}(OC_4H_8)]$ by a complex rearrangement, involving cleavage of the THF group, and a shift of the bond to oxygen from B(2) to B(10).[122]



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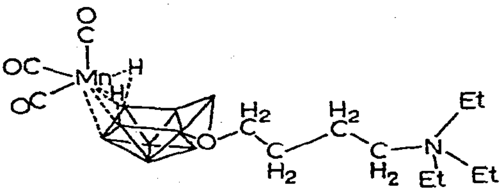

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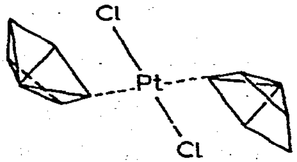
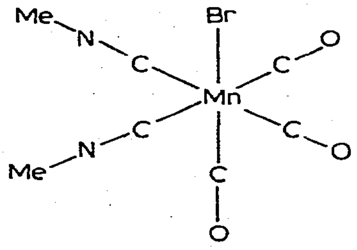


(111)

The structure of trans-$PtCl_2(B_6H_{10})_2$ (111), obtained from Zeise's salt and B_6H_{10}, and determined at -170°, reveals that the two boron ligands are coordinated via the centres of the B(4)-B(5) vectors, which are lengthened from 1.6Å (in free B_6H_{10}) to 1.82(5)Å, a value typical of triangulated polyhedral boranes.[123]

Complexes containing donor-atom ligands (a) Carbon (isocyanides, carbenes and related ligands)

The complex $MnBr(CO)_3(CNMe)_2$ (112) is nearly octahedral, and bond length data, coupled with MO calculations, indicate that back-bonding to the isocyanide ligands occurs even when CO, a much stronger π-acceptor ligand, is present.[124] Several structural studies, summarised in this paper, indicate that M-CNMe (methyl isocyanide) distances are close to expected M-CN (cyanide) distances.



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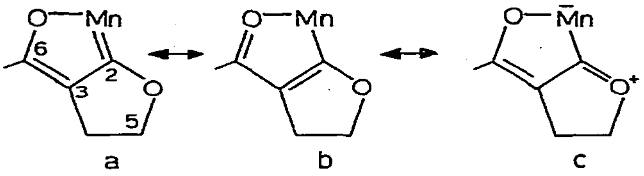

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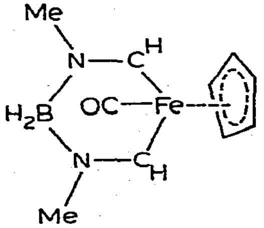
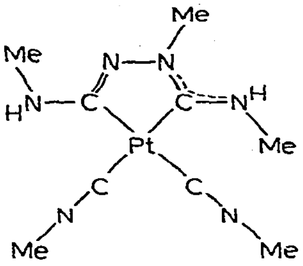


(114)

The acetyldihydrofuranyl complex (113) has a structure in which the C(2)-C(3) and C(3)-C(6) bonds have nearly the same length.[125] This and other features have been explained in terms of the resonance structures (113a-c); in particular, the short C(2)-O bond, and the near planarity of the MnC(5)OC(2)C(3) system support form (113c) (carbonyl groups omitted).

The FeC_2N_2B ring in $(\pi\text{-}C_5H_5)Fe(CO)[(CHNMe)_2BH_2]$ (114), formed by addition of borohydride to the cationic isocyanide complex, has a boat conformation; a planar ring is precluded by the geometrical requirements of the constituent atoms.[126]

Reaction of methylhydrazine with $[Pt(CNMe)_4]^{2+}$ results in the formation of a chelate ligand by addition of the hydrazine to two isocyanide molecules, as in (115). In this complex one nitrogen has lost a proton; addition of HCl results in protonation of this nitrogen atom. The complex ligand can be regarded as a chelating dicarbene moiety.[127] Addition of EtSH to the $[Pt(CNMe)_4]^{2+}$ cation affords the



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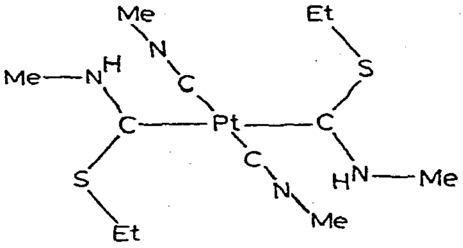

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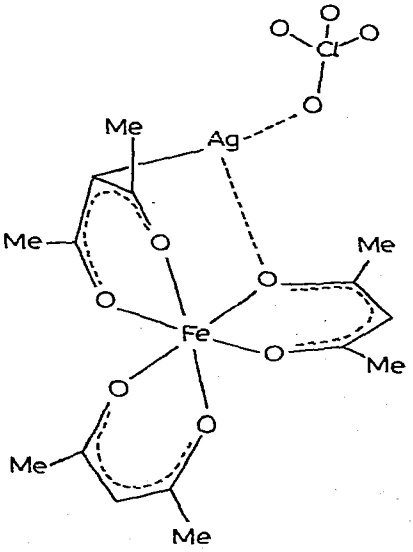


(117)

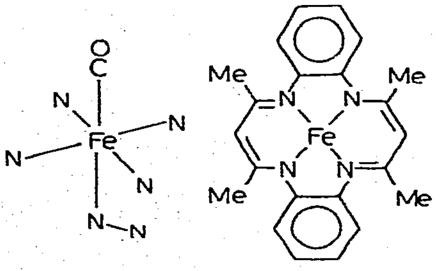
methylamino(thioethoxy)carbene complex (116). Comparison of structural parameters for a number of related platinum complexes supports the idea that carbenes are strongly σ-bonding ligands with a trans influence similar to that of tertiary phosphines.[128]

Adducts are formed between silver salts and metal acetvlacetonates, and the structure of $Fe(acac)_3.AgClO_4$ (117), with an Ag-CH(acac) bond of 2.32Å, indicates an interaction of Ag^+ with the electron pair on the methylene carbon.[129] A similar feature is found in $Ag_3(NO_3)_2Ni(acac)_3$.[130]

(b) Nitrogen

The monocarbonyl (118) has been obtained from the reaction of the free macrocyclic ligand with iron(II) in the presence of CO.[131] In this complex the iron atom has a similar environment to that in CO adducts of heme proteins.

The system $Ru_3(CO)_{12}$-tetraphenylporphine (TPP) has been reexamined.[132] Initially, the lability of the Ru^{II} complexes formed



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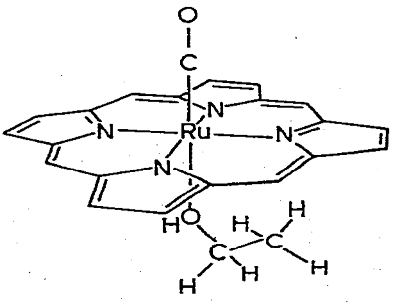
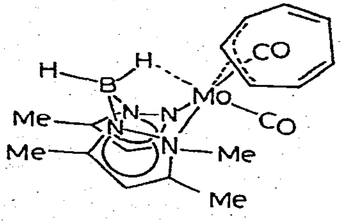


Phenyl groups omitted

(119)



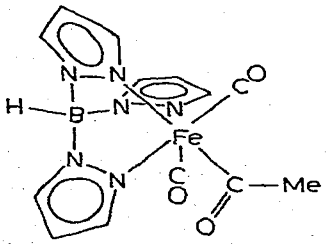
(120)

was interpreted on the basis of a ready association of ligands with the five-coordinate monocarbonyl Ru(CO)(TPP)(EtOH)(I). More recently [see AS72/1: *J.Organometal.Chem.*, 53 (1973) 162], complex(I) was reformulated as the dicarbonyl $Ru(CO)_2(TPP)$, with markedly bent (154°) Ru-C-O bonds. A detailed investigation reveals that the products are monocarbonyls, and that the supposed dicarbonyl is in fact the previously proposed ethanol adduct Ru(CO)(TPP)(EtOH) (119), in which the CO and EtOH groups are disordered.

Full details of the structure of $Mo[H_2B(Me_2pz)_2](\underline{h}^3\text{-}C_7H_7)(CO)_2$ (120) are now available.[133] In this complex, the molybdenum attains the favoured 18-electron configuration by forming a two-electron, three-centre B-H-Mo bridge bond. The six-membered chelate ring is markedly bent to accommodate this feature. In the solid state, the complex $[HB(pz)_3]Fe(CO)_2(COMe)$ has structure (121), in which the acetyl group is skewed relative to the rest of the molecule.[134] The Fe-N bond *trans* to acetyl is significantly longer than that *trans* to CO, probably as a result of the operation of a σ *trans* effect. In solution, the multiplicity of the ν(CO) bands indicates the presence of rotamers.

(c) Phosphorus or arsenic

Three phosphine (PH_3) complexes of chromium have been examined. The molecule *cis*-$Cr(CO)_3(PH_3)_3$ is octahedral, with a mean Cr-P distance of 2.346(3)Å. The monophosphine complex, $Cr(CO)_5(PH_3)$,



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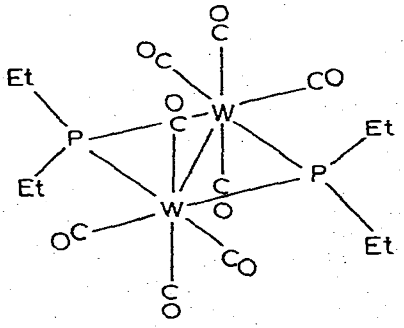


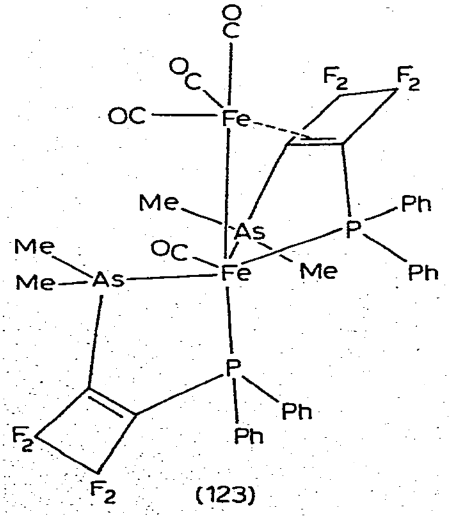
(122)

has very similar cell dimensions and structural parameters to those of $Cr(CO)_6$; the PH_3 group is disordered over three mutually cis positions.[135] The structure of cis-$Cr(CO)_4(PH_3)_2$ shows a near-octahedral coordination of the metal.[136] Derived hydrogen positions correspond statistically to two conformations rotated 60° about the Cr-P axis to monimise intramolecular contacts. Comparisons of Cr-P bond distances indicate the relative π-acceptor strengths: $P(OPh)_3 > PH_3 > PPh_3$.

Comparisons of structural parameters in the complexes $Cr(CO)_5L$ [L = PPh_3 or $P(OPh)_3$], which have the expected C_{4v} symmetry, has given information concerning the relative π-acceptor power of the ligands.[137] Thus, the Cr-P bonds are 2.422 and 2.309Å, while the Cr-C bonds trans to the ligand are 1.845 and 1.861Å, respectively. These values are those expected if $P(OPh)_3$ is a better π-acceptor than PPh_3, as indicated by earlier i.r. and n.m.r. studies.

The central W_2P_2 group in $[W(CO)_4PEt_2]_2$ (122) is planar, with a W-W bond [3.05(1)Å], and the angle at phosphorus decreased to 76.5(4)°.[138]

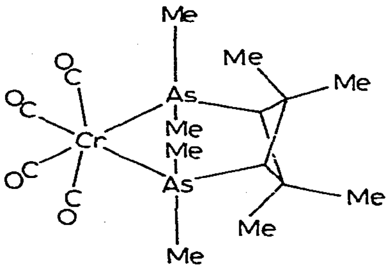
Irradiation of $(f_4asp)Fe_2(CO)_6$ with excess ligand for a prolonged period affords the unusual complex $(f_4asp)_2Fe_2(CO)_4$ (123).



(123)

One iron atom is chelated by two f$_4$asp ligands, the first occasion on which a ligand of this type has been shown to chelate. The second iron is bonded to three CO groups and an elongated [1.476(8)Å] C=C of one ligand [cf. the uncoordinated double-bond length of 1.326(8)Å]; the fifth coordination position is occupied by the metal-metal bond.[139]

A low-temperature (-150°) determination of the structure of the diarsine complex (124) reveals Cr-CO bond distances of 1.841(4) (trans) and 1.885(4)Å (cis to As), reflecting the superior π-acceptor character of the CO group.[140] The cyclobutane ring is non-planar. Although the two conformers of $Cr(CO)_4L$ [L = 1,3-bis(dimethylarsino)-propane, $Me_2As(CH_2)_3AsMe_2$] are equivalent, the related complex fac-$MnCl(CO)_3L$ exists as only one conformer (125), probably as a result of steric repulsion between the axial Me groups on the metal (ligand in



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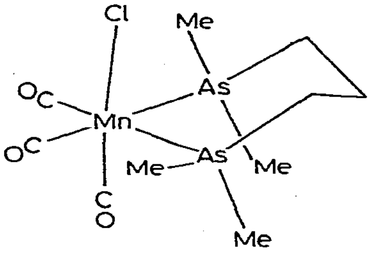

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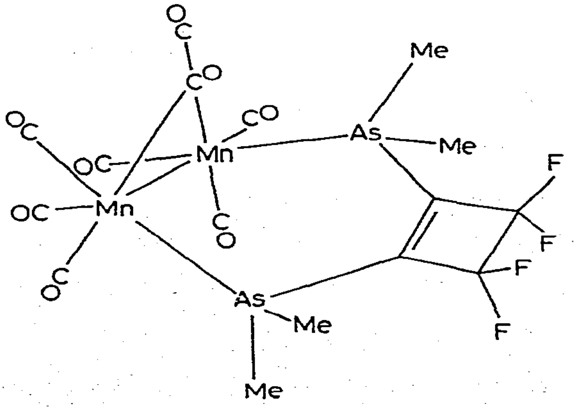
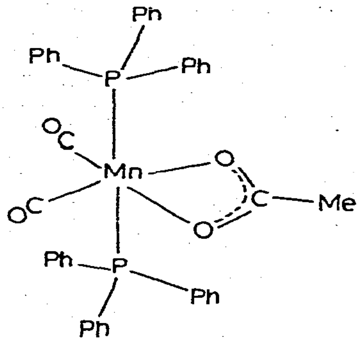


(126)

'equatorial' position).[141] The reaction between $Mn_2(CO)_{10}$ and $f_4$fars affords the binuclear complex $Mn_2(CO)_8(f_4fars)$ (126), in which the ligand bridges the two metal atoms; in spite of this feature, the two $Mn(CO)_4As$ groups are almost perfectly staggered.[142]

(d) Oxygen

The acetato complex $Mn(MeCO_2)(CO)_2(PPh_3)_2$ (127) contains a symmetrical bidentate carboxylate ligand, functioning primarily as a σ-donor.[143] Bond distance calculations suggest that some hydrogen bonding may occur between the acetate oxygens and two *ortho*-hydrogens, one from each PPh_3 group.



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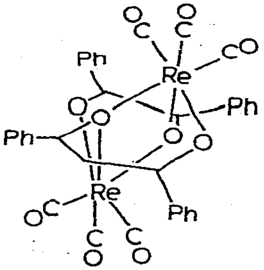

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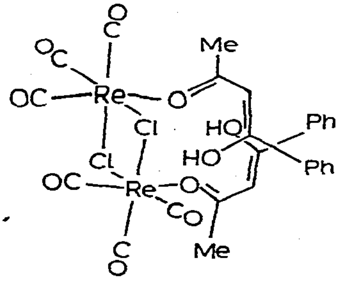


(129)

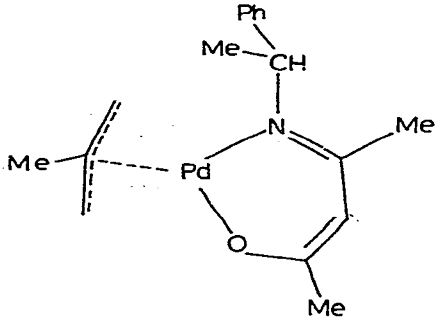
The reaction between $Re(CO)_5Cl$ and β-diketones affords $Re(CO)_3ClL$ and $Re_2(CO)_6(L)_2$ (L = β-diketonate). The dibenzoylmethane complex (L = dbm) has structure (128), in which one oxygen from each dbm ligand asymmetrically bridges the two metal atoms. No metal-metal bond is present.[144] Using benzoylacetone, a third type of complex, $[Re(CO)_3Cl(bzacH)]_2$ (129) was obtained, and shown to contain a monodentate neutral β-ketoenol ligand. The two $Re(CO)_3$ groups are bridged by halogen, and the β-ketoenol is bonded via the keto group.[145]

The structure determination of (π-methylallyl)[2-(*R*,*S*)-α-phenylethylimino-3-penten-4-olato]palladium (130) clearly distinguishes single and double bonds, and confirms the structure of the ketoimine ligand as shown.[146]

(e) Sulphur

The structure of $[PhSFe(CO)_3]_2$ (131) is similar to those of other related compounds, with the two phenyl groups being bent as shown (anti).[147]

The supposed cluster complex obtained from reactions between $Fe_2(CO)_6(SMe)_2$ and $S_2C_2(CF_3)_2$ has been shown[148] to be the salt $[Fe_2(SMe)_3(CO)_6][Fe_2\{S_2C_2(CF_3)_2\}_4]$. The structure is an interesting example (in fact, only the second such) of one solved by direct methods in the general space group P1. The cation (132) consists of two $Fe(CO)_3$ groups bridged by three SMe groups, with an Fe-Fe distance of 3.062(4)Å, implying essentially no metal-metal interaction. In contrast, the two metal atoms in the anion are separated by 2.767(4)Å, dimerisation occurring through the formation of two Fe-S bonds. Other structural features are similar to those found in other metal dithiolene dimers. Both the orange and violet isomers of $Ru(CO)(PPh_3)_2[S_2C_2(CF_3)_2]$ (133) have a square-pyramidal five-coordinate structure.[149] In the orange form, the CO group is at the apex, whereas in the violet isomer, one of the phosphines occupies this position. The former is most favoured and is also the most sterically hindered.



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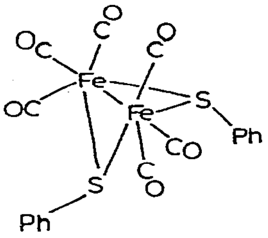

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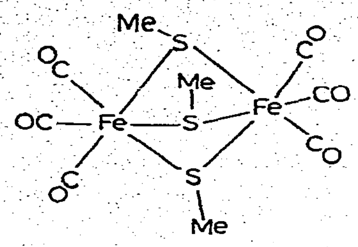

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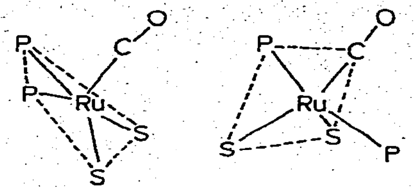
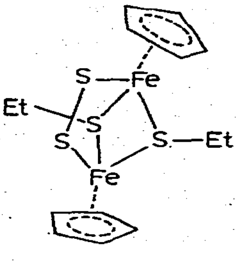


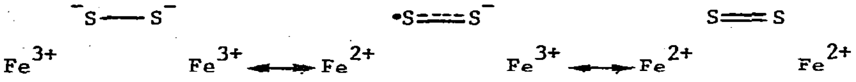
(133)

Bases of square pyramids indicated



(134)

The complex $[(\pi-C_5H_5)Fe(SEt)S]_2$ (134) contains a planar FeSSFe bridge, and the structure suggests that of the three resonance forms



$$\overset{^-S—S^-}{Fe^{3+}\qquad Fe^{3+}} \longleftrightarrow \overset{\bullet S{=}S^-}{Fe^{2+}\qquad Fe^{3+}} \longleftrightarrow \overset{S{=}S}{Fe^{2+}\qquad Fe^{2+}}$$

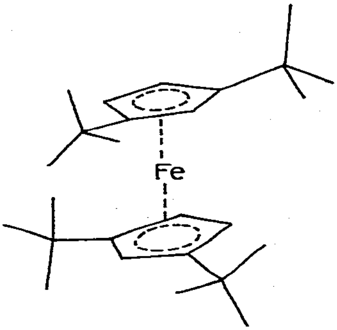
I II III

form II predominates for this diamagnetic compound.[150] Strong magnetic coupling between the Fe^{III} centres occurs via the bridge sulphur atoms. Possible relationships to structures of ferredoxins with two irons and two labile sulphurs are discussed. Although the complex anion $[Fe_4S_4(SR)_4]^{2-}$ is not an organometallic derivative, the paper[151] describing this structure includes a comparison of other tetranuclear cluster systems with a cubane-type structure, of which many organometallic examples have now been described. It is of interest that the $Fe_4S_4(SR)_4$ core is an analogue of the active sites of clostridial Fe-S proteins [see also the description of complex (28)].

Ferrocene and benchrotrene derivatives

The tetra-t-butylferrocene obtained from ferrocene and Bu^tCl in the presence of an $AlCl_3$-$LiAlH_4$ mixture has been shown[152] to be the 1,1',3,3'-isomer (135). To relieve steric strain, the rings have a 7° dihedral, and the rotation of the rings is 15 and 18° respectively in the two independent molecules. Stereospecific addition of ferrocenylcarbonium ions to cyclopentadiene gives a single cycloaddition product.[153] That obtained from $FcCMe_2^+$ has structure (136), with eclipsed C_5 rings in the ferrocene unit, and suggests that the diene adds to the cation in a formal ($6\pi+4\pi$) manner.

Full details of the synthesis and structure of (S,R,S)-2-(p-methoxyphenyl)hydroxymethyl-N,N-dimethyl-1-ferrocenylethylamine (137) are reported, and as mentioned previously [AS 72/1; 168], this result enables unequivocal structure assignments for a large number of optically active ferrocene derivatives to be made.[154]



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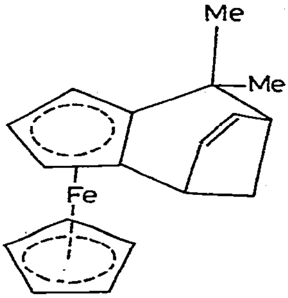
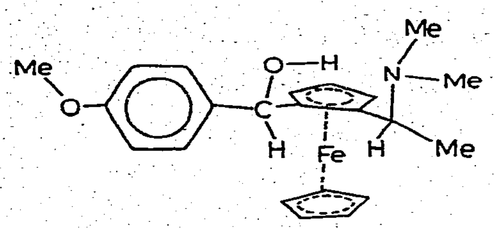


(136)

A complete discussion of the structure of 1,12-dimethyl-[1.1]ferrocenophane (138) has been given[155]; a preliminary account appeared in 1967.[156] In this molecule, the angles of twist lie almost midway between the eclipsed and staggered positions. The relative configuration of the bridged ferrocene alcohol ([3]ferrocenophanol) (139),



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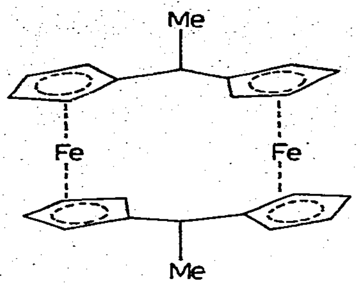

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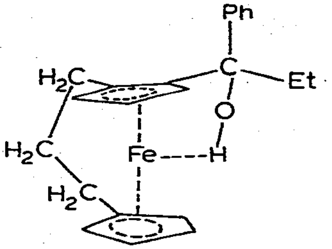
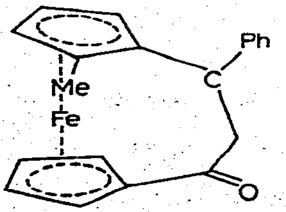


(139)

m.p. 122°, has been determined,[157] and is the same as that predicted by NMR methods. The molecular structure of the bridged ferrocenyl ketone (140) has been illustrated, but no other details are yet available.[158]

An ionic complex, obtained from $FcAuPPh_3$ and HBF_4, with the composition $[FcAu_2(PPh_3)_2]BF_4$, has the unusual structure (141), in which the metal atoms from an Fe-Au-Au chain.[159] The two gold atoms are bridged by one carbon of a cyclopentadienyl group, and this complex is also the first structurally characterised example of a ferrocene derivative with a direct Fe-M bond.



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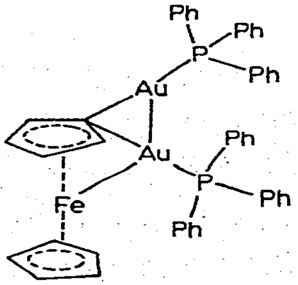

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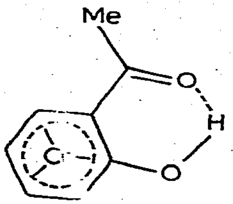

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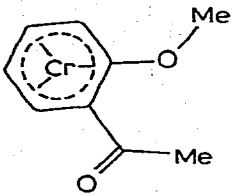


(143)
Carbonyl groups omitted

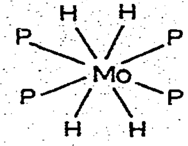
The difference of stereoselectivity in some reactions between o-hydroxy- and o-methoxyacetylbenchrotrenes (142 and 143) has been explained[160] on the basis of their structures. In particular, the two complexes are "quasi-enantiomeric", with the hydroxyl group hydrogen-bonded to the acetyl oxygen, while in the methoxy derivative, the acetyl oxygen points away from the alkoxy group. The projections also show a difference in the orientation of the $Cr(CO)_3$ groups (relative to acetyl).

Metal hydrides and related complexes

The stereochemically nonrigid hydride $H_4Mo(PMePh_2)_4$ (144) contains a D_{2d} dodecahedral metal-ligand coordination sphere with triangular faces.[161] The four hydride ligands form an elongated tetrahedron which penetrates the flattened tetrahedron formed by the phosphine ligands. The temperature-dependent ^1H and ^{31}P NMR spectra are related to the structure.

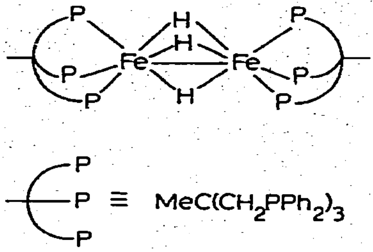
The unusual complex cation $[Fe_2H_3(triphos)_2]^+$ [triphos = $MeC(CH_2PPh_2)_3$] has been obtained from iron(II) halides and the triphosphine in the presence of $NaBH_4$.[162] The structure of the hexafluorophosphate salt is shown (145). The two iron atoms are bridged by three hydrogens, and also joined by a metal-metal bond (2.34Å).

The hydride $RuH_2(PPh_3)_4$, obtained from $Ru(C_6H_6)(C_6H_8)$ and PPh_3, contains the four phosphines arranged approximately tetra-



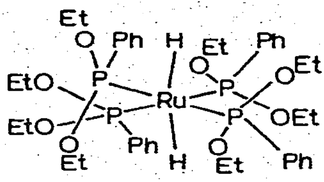
P = PMePh$_2$

(144)



≡ MeC(CH$_2$PPh$_2$)$_3$

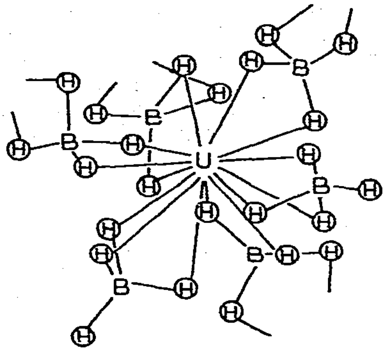
(145)



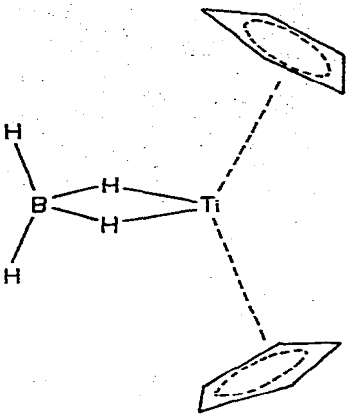
(146)

hedrally about the metal [angles P-Ru-P, 104.2-116.4(2)°].[163] Although the hydrogen atoms were not located, the H-Ru-H angle is calculated at 98°. The ruthenium coordination in *trans*-RuH$_2$[PPh(OEt)$_2$]$_4$ (146) consists of a flattened RuP$_4$ tetrahedron, with axial hydride ligands, which however, is much closer to octahedral than found in *cis*-FeH$_2$[PPh$_2$(OEt)$_2$]$_4$, which is closer to tetrahedral.[164] These differences are related to the larger Ru^{II} radius, and the larger number of P-M-P 90° angles in idealised *cis* (5) than in *trans* (4).

The strong *trans*-influence of hydrogen is indicated in the structure of *trans*-PdHCl(PEt$_3$)$_2$, where the Pd-Cl bond length is 2.427(5)Å (cf. PdCl$_4^{2-}$, 2.299Å; sum of covalent radii, 2.30Å).[165] An X-ray diffraction study[166] of U(BH$_4$)$_4$ (147) revealed a polymeric structure made up of interlocking helical chains in which a fourfold screw axis relates individual units. Each uranium atom is linked to six BH$_4$ groups (four bridging, two terminal). The structure has been further elucidated by a neutron-diffraction study, which enabled the hydrogens to be located.[167] Four BH$_4$ groups are attached via two hydrogens to one metal atom, bridging neighbouring uraniums with the others. The other two (*cis*) BH$_4$ groups are attached by three hydrogens, resulting in an overall coordination number of 14 for the uranium atom; a capped hexagonal antiprism is the ideal reference polyhedron. Comparisons with other M-BH$_4$ complexes show that the M-B distance can be correlated with the mode of attachment of the BH$_4$ group.



(147)



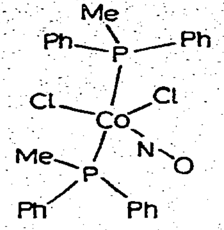
(148)

In $(\underline{h}^5\text{-}C_5H_5)_2TiBH_4$ (148), coordination of the tetrahydroborate group occurs via bridging hydrogen atoms, as found in $(Ph_3P)_2CuBH_4$, and with which comparison is made.[168] Disorder was found in the C_5 rings.

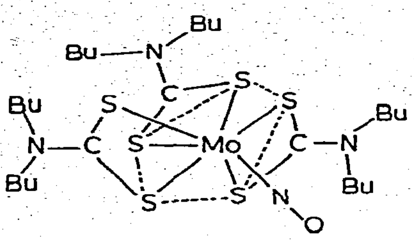
Nitrosyls

Recent structural results on metal-nitrosyl complexes have disclosed the existence of two types, in which the M-N-O moiety is either linear or bent. These observations have been correlated with coordination of nitric oxide as NO^+ or NO^-, respectively. In the complexes $CoCl_2(CO)L_2$ (L = tertiary phosphine), IR, NMR, and X-ray photoelectron spectra suggest the existence of conformational isomers.[169] One (A) has trigonal-bipyramidal geometry with a linear NO group, while the second (B) is thought to be square-pyramidal, with a bent NO at the apex. The structure of $CoCl_2(NO)(PMePh_2)_2$ (149) reveals a distorted trigonal bipyramid, with no evidence for isomer B. An extended discussion on the scope and limitations of the various spectroscopic methods fails to conclusively resolve this bent vs. linear nitrosyl situation, and further experiments are needed to clarify the earlier results which indicated the existence of a dynamic intramolecular redox equilibrium.

The nitrosyl $Mo(NO)(S_2CNBu^{\underline{n}}_2)_3$ (150) has pentagonal bipyramidal coordination about molybdenum, with an NO group occupying an axial position.[170] The latter is almost linear [angle Mo-N-O,



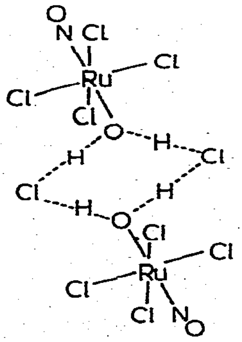
(149)



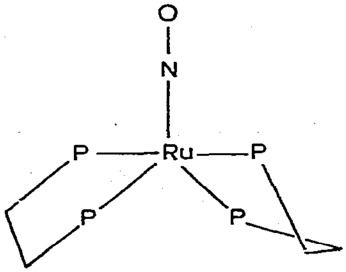
(150)

$173.2(7)^{\circ}$], indicating coordination as NO^+.

The compound previously described as $(NH_4)_2[Ru(NO)Cl_4(OH)]$ on the basis of an electron density projection[171] has been shown to have the composition $(NH_4)_2[Ru(NO)Cl_4(H_2O)]^-Cl^-H_2O$, with an almost linear Ru-N-O group.[172] The chloride ions are attached to the octahedral complex anion via O-H---Cl hydrogen bonds (151).



(151)



(152)

In $[Ru(NO)(dppe)_2]BPh_4$ (152), the equatorial NO group is linear, corresponding to a formally $\underline{d}^8$ Ru^0 complex of NO^+. An MO picture of the bonding of NO to metals in five-coördinate complexes is also discussed.[173] Comparisons of the structures of the nitrosyl $[RhClL(NO)](PF_6)$ with the parent complex [RhClL] [L = $PhP(CH_2CH_2CH_2PPh_2)_2$] have been made.[174] Minimal changes in the RhL environment occur, and the sixth potential site is crowded; in both complexes, all three phosphorus atoms are coordinated. The Rh-NO linkage is bent [131(1)°], and is interpreted as coordination in the sense $Rh^{III}-NO^{-}$.

Full details of the structure of $Pt_4(OAc)_6(NO)_2$ have been published;[175] the tetramer is solvated with two molecules of acetic acid. In this complex the nitrosyl group is formulated as NO^{-}. The two Pt-Pt distances [3.311 and 2.944Å] suggest that a metal-metal interaction occurs in the shorter separation.

Two isomers, red and black, of the $[Co(NH_3)_5(NO)]^{2+}$ cation have been prepared.[176] The structure of the black chloride revealed the presence of a bent Co-N-O group (120°). The red isomer is binuclear, and a study of the mixed bromide-nitrate salt shows that it is not a true nitrosyl complex, but that the two cobalt atoms are bridged by a hyponitrite group in the manner: Co-O-N-N(O)-Co.[177]

REFERENCES

1. M. Laing, E. Singleton and G. Kruger, J.Organometal.Chem., 54 (1973) C30.
2. M.B. Smith and R. Bau, J.Am.Chem.Soc., 95 (1973) 2388.
3. D.M. Bruce, J.H. Holloway and D.R. Russell, J.C.S.Chem.Comm., (1973) 321.
4. J.A. Ibers, D.S. Hamilton and W.H. Baddley, Inorg.Chem., 12 (1973) 229.
5. W. Clegg and P.J. Wheatley, J.C.S.Dalton, (1973) 90.
6. W.R. Robinson and D.P. Schussler, Inorg.Chem., 12 (1973) 848.
7. J. Rajaram and J.A. Ibers, Inorg.Chem., 12 (1973) 1313.
8. G. Hencken and E. Weiss, Chem.Ber., 106 (1973) 1747.
9. B.K. Nicholson, J. Simpson and W.T. Robinson, J.Organometal.Chem., 47 (1973) 403.
10. G.L. Simon and L.F. Dahl, J.Am.Chem.Soc., 95 (1973) 783.

11. R.D. Ball and D. Hall, J.Organometal.Chem., 52 (1973) 293.

12. J. Weaver and P. Woodward, J.C.S.Dalton, (1973) 1060.

13. C. Eaborn, P.B. Hitchcock, D.J. Tune and D.R.M. Walton, J.Organometal.Chem., 54 (1973) C1.

14. B. Crociani, M. Nicolini, D.A. Clemente and G. Bandoli, J.Organometal.Chem., 49 (1973) 249.

15. L.T.J. Delbaere, L.J. Kruczynski and D.W. McBride, J.C.S.Dalton, (1973) 307.

16. S.W. Ulmer, P.M. Skarstad, J.M. Burlitch and R.E. Hughes, J.Am.Chem.Soc., 95 (1973) 4469.

17. F.A. Cotton, B.A. Frenz and L. Kruczynski, J.Am.Chem.Soc., 95 (1973) 951.

18. M. Andrews, D.L. Tipton, S.W. Kirtley and R. Bau, J.C.S.Chem.Comm., (1973) 181.

19. A.S. Foust, W.A.G. Graham and R.P. Stewart, J.Organometal.Chem., 54 (1973) C22.

20. B.L. Barnett and C. Krüger, Cryst.Struct.Comm., 2 (1973) 347.

21. P. Singh, C.B. Dammann and D.J. Hodgson, Inorg.Chem., 12 (1973) 1335.

22. M.R. Churchill and S.W-Y. Ni, J.Am.Chem.Soc., 95 (1973) 2150.

23. G. Gervasio and G. Ferraris, Cryst.Struct.Comm., 3 (1973) 447.

24. M.R. Churchill and J. Wormald, Inorg.Chem., 12 (1973) 191.

25. C. Krüger, Angew.Chem., 81 (1969) 708; Int.Edit., 8 (1969) 678.

26. A.J. Deeming and M. Underhill, J.C.S.Chem.Comm., (1973) 277.

27. C.R. Eady, B.F.G. Johnson and J. Lewis, J.Organometal.Chem., 37 (1972) C39.

28. R. Mason, K.M. Thomas and D.M.P. Mingos, J.Am.Chem.Soc., 95 (1973) 3802.

29. V.G. Albano, M. Sansoni, P. Chini and S. Martinengo, J.C.S.Dalton, (1973) 651.

30. G.L. Simon and L.F. Dahl, J.Am.Chem.Soc., 95 (1973) 2175.

31. G.L. Simon and L.F. Dahl, J.Am.Chem.Soc., 95 (1973) 2164.

32. L.J. Guggenberger, Inorg.Chem., 12 (1973) 499.

33. B.L. Barnett and C. Krüger, Cryst.Struct.Comm., 2 (1973) 85.

34. M.C. Mazza and C.G. Pierpont, J.C.S.Chem.Comm., (1973) 207.

35. F.A. Cotton, J.N. Francis, B.A. Frenz and M. Tsutsui, J.Am.Chem.Soc., 95 (1973) 2483.

36. R.T. Kops, E. van Aken and H. Schenk, Acta Cryst., B29 (1973) 913.

37. C. Krüger and Y.H. Tsay, J.Organometal.Chem., 33 (1971) 59.

38. D.A. Whiting, Cryst.Struct.Comm., 1 (1972) 379.

39. T.C. van Soest, A. van der Ent and E.C. Royers, Cryst Struct.Comm., 3 (1973) 527.

40. A. Immirzi and G. Allegra, Acta Cryst., B25 (1969) 120.

41. G. Avitabile, P. Ganis, U. Leppore and A. Panunzi, Inorg.Chim.Acta, 7 (1973) 329.

42. J. Hubert, A.L. Beauchamp and T. Theophanides, Can.J.Chem., 51 (1973) 604.

43. N.G. Bokii, Y.V. Gatilov, Y.T. Struchkov and N.A. Ustynyuk, J.Organometal.Chem., 54 (1973) 213.

44. E. Ban, P.-T. Cheng, T. Jack, S.C. Nyburg and J. Powell, J.C.S.Chem.Comm., (1973) 368.

45. A.L. Beauchamp, F.D. Rochon and T. Theophanides, Can.J.Chem., 51 (1973) 126.

46. R.M. Kirchner and J.A. Ibers, J.Am.Chem.Soc., 95 (1973) 1095.

47. J. Browning and B.R. Penfold, J.C.S.Chem.Comm., (1973) 198.

48. J. Browning, M. Green, B.R. Penfold, J.L. Spencer and F.G.A. Stone, J.C.S.Chem.Comm., (1973) 31.

49. J.S. Ricci and J.A. Ibers, J.Organometal.Chem., 27 (1971) 261.

50. I.W. Bassi and R. Scordamaglia, J.Organometal.Chem., 51 (1973) 273.

51. S.Z. Goldberg, E.N. Duesler and K.N. Raymond, Inorg.Chem., 11 (1972) 1397.

52. R.A. Marsh, J. Howard and P. Woodward, J.C.S.Dalton, (1973) 778.

53. A.E. Smith, *Inorg.Chem.*, 11 (1972) 2306.

54. Y. Kitano, M. Kashiwagi and Y. Kinoshita, *Bull.Chem.Soc.Japan*, 46 (1973) 723.

55. M.D. McClure and D.L. Weaver, *J.Organometal.Chem.*, 54 (1973) C59.

56. G.G. Cash, J.F. Helling, M. Mathew and G. Palenik, *J.Organometal.Chem.*, 50 (1973) 277.

57. L.G. Kuz'mina, Y.T. Struchkov and A.I. Nekhaev, *Zh.strukt Khim.*, 13 (1972) 1115.

58. A. de Cian, P.M. L'Huillier and R. Weiss, *Bull.Soc.chim.France*, (1973) 451.

59. A. de Cian, P.M. L'Huillier and R. Weiss, *Bull.Soc.chim.France*, (1973) 457.

60. M.R. Churchill and B.G. de Boer, *Inorg.Chem.*, 12 (1973) 525.

61. F.A. Cotton, B.A. Frenz, G. Deganello and A. Shaver, *J.Organometal.Chem.*, 50 (1973) 227.

62. F.A. Cotton and J.M. Troup, *J.Am.Chem.Soc.*, 95 (1973) 3799.

63. C. Krüger, Y.H. Tsay, F.W. Grevels and E. Koerner von Gustorf, *Israel J.Chem.*, 10 (1972) 201.

64. M.J. Bennett, W.A.G. Graham, R.A. Smith and R.P. Stewart, *J.Am.Chem.Soc.*, 95 (1973) 1684.

65. A.A. Hock and O.S. Mills, *Acta Cryst.*, 14 (1961) 139.

66. J.A.D. Jeffreys, C.M. Willis, I.C. Robertson, G. Ferguson and J.G. Sime, *J.C.S.Dalton*, (1973) 749.

67. J.L. Atwood and K.D. Smith, *J.Am.Chem.Soc.*, 95 (1973) 1488.

68. C.H. Wong, T.Y. Lee and Y.T. Lee, *Acta Cryst*, 25B (1969) 2580.

69. J.L. Atwood, J.H. Burns and P.G. Laubereau, *J.Am.Chem.Soc.*, 95 (1973) 1830.

70. M. Tsutsui and H.J. Gysling, *J.Am.Chem.Soc.*, 91 (1969) 3175.

71. J. Leong, K.O. Hodgson and K.N. Raymond, *Inorg.Chem.*, 12 (1973) 1329.

72. C.H. Wong, Y.M. Lee and T.Y. Lee, *Acta Cryst.*, 18B (1965) 340.

73. J.H. Burns, J.Am.Chem.Soc., 95 (1973) 3815.

74. C.R. Lucas, M.L.H. Green, R.A. Forder and C.K. Prout, J.C.S.Chem. Comm., (1973) 97.

75. T.C. van Soest, J.C.C.W. Rappard and E.C. Royers, Cryst.Struct.Comm., 3 (1973) 451.

76. E.F. Epstein and I. Bernal, Inorg.Chem.Acta, 7 (1973) 211.

77. B.R. Davis and I. Bernal, J.Organometal.Chem., 30 (1971) 75.

78. V.I. Kulishov, N.G. Bokii and Y.T. Struchkov, Zh strukt.Khim., 13 (1972) 1110.

79. P. Corradini and A. Sirigu, Inorg.Chem., 6 (1967) 601.

80. F.N. Tebbe and L.J. Guggenberger, J.C.S.Chem.Comm., (1973) 227.

81. R. Hoxmeier, B. Deubzer and H.D. Kaesz, J.Am.Chem.Soc., 93 (1971) 536.

82. L.J. Guggenberger, Inorg.Chem., 12 (1973) 294.

83. N.I. Kirillova, A.I. Gusev and Y.T. Struchkov, Zh.strukt.Khim., 13 (1972) 473.

84. N.I. Kirillova, A.I. Gusev, A.A. Pasynskii and Y.T. Struchkov, Zh.strukt.Khim., 13 (1972) 880.

85. M.B. Dines and P.H. Bird, J.C.S. Chem.Comm., (1973) 12.

86. J.D. Zeinstra and J.L. de Boer, J.Organometal.Chem., 54 (1973) 207.

87. G.R. Clark and G.J. Palenik, J.Organometal.Chem., 50 (1973) 185.

88. K.O. Hodgson and K.N. Raymond, Inorg.Chem., 11 (1972) 3030.

89. K.O. Hodgson and K.N. Raymond, Inorg.Chem., 12 (1973) 458.

90. C.A. Bear, W.R. Cullen, J.P. Kutney, V.E. Ridaura, J. Trotter and A. Zanarotti, J.Am.Chem.Soc., 95 (1973) 3058.

91. E.W. Abel, I.W. Nowell, A.G.J. Modinos and C. Towers, J.C.S.Chem. Comm., (1973) 258.

92. Y. Dusausoy, J. Protas and R. Guilard, Acta Cryst., B29 (1973) 726.

93. Y. Dusausoy, J. Protas and R. Guilard, Acta Cryst., B29 (1973) 477.

94. J.J. Daly, F. Sanz, R.P.A. Sneeden and H.H. Zeiss, Helv.Chim.Acta, 56 (1973) 503.

95. J.J. Daly, F. Sanz, R.P.A. Sneeden and H.H. Zeiss, J.C.S.Dalton, (1973) 73.

96. M.R. Churchill and S.A. Bezman, Inorg.Chem., 12 (1973) 260.

97. M.R. Churchill and S.A. Bezman, Inorg.Chem., 11 (1972) 2243.

98. J.R. Shapley and J.A. Osborn, J.Am.Chem.Soc., 92 (1970) 6976.

99. M.R. Churchill and S.A. Bezman, Inorg.Chem., 12 (1973) 531.

100. A.J. Schultz, G.P. Khare, J.V. McArdle and R. Eisenberg, J.Am.Chem. Soc., 95 (1973) 3434.

101. M.R. Snow and J.A. Ibers, Inorg.Chem., 12 (1973) 224.

102. M.A. Bennett, G.B. Robertson, P.O. Whimp and T. Yoshida, J.Am. Chem.Soc., 95 (1973) 3028.

103. A. Chiesi Villa, A.G. Manfredotti and C. Guastini, Cryst.Struct. Comm., 2 (1973) 181.

104. R. Claverini, A. de Renzi, P. Ganis, A. Panunzi and C. Pedone, J.Organometal.Chem., 51 (1973) C30.

105. E. Benedetti, A. de Renzi, G. Paiaro, A. Panunzi and C. Pedone, Gazz Chim.Ital., 102 (1972) 744.

106. T. Blackmore, M.I. Bruce, F.G.A. Stone, R.E. Davis and N.V. Raghavan, J.Organometal.Chem., 49 (1973) C35.

107. M. Zocchi, G. Tieghi and A. Albinati, J.C.S.Dalton, (1973) 883.

108. J.A.J. Jarvis, A. Johnson and R.J. Puddephatt, J.C.S.Chem.Comm., (1973) 373.

109. R.G. Little and R.J. Doedens, Inorg.Chem., 12 (1973) 840.

110. R.G. Little and R.J. Doedens, Inorg.Chem., 12 (1973) 844.

111. F.W.B. Einstein and D. Sutton, J.C.S.Dalton, (1973) 434.

112. G.B. Robertson and P.O. Whimp, J.Organometal.Chem., 49 (1973) C27.

113. R.J. McKinney, B.T. Huie, C.B. Knobler and H.D. Kaesz, J.Am.Chem. Soc., 95 (1973) 633.

114. G. Perego, G. del Piero, M. Cesari, M.G. Clerici and E. Perrotti, J.Organometal.Chem., 54 (1973) C51.

115. A.J. Cheney, W.S. McDonald, K. O'Flynn, B.L. Shaw and B.L. Turtle, J.C.S.Chem.Comm., (1973) 128.

116. A.R. Fraser, P.H. Bird, S.A. Bezman, J.R. Shapley, R. White and J.A. Osborn, J.Am.Chem.Soc., 95 (1973) 597.

117. J.A. Evans, G.F. Everitt, R.D.W. Kemmitt and D.R. Russell, J.C.S.Chem.Comm., (1973) 158.

118. F.V. Hansen, R.G. Hazell, C. Hyatt and G.D. Stucky, Acta.Chem.Scand., 27 (1973) 1210.

119. M.R. Churchill and K. Gold, Inorg.Chem., 12 (1973) 1157.

120. D.C. Beer, V.R. Miller, L.G. Sneddon, R.N. Grimes, M. Mathew and G.J. Palenik, J.Am.Chem.Soc., 95 (1973) 3046.

121. J.W. Lott, D.F. Gaines, H. Shenhav and R. Schaeffer, J.Am.Chem.Soc., 95 (1973) 3042.

122. D.F. Gaines, J.W. Lott and J.C. Calabrese, J.C.S.Chem.Comm., (1973) 295.

123. J.P. Brennan, R. Schaeffer, A. Davison and S.S. Wreford, J.C.S. Chem.Comm., (1973) 354.

124. A.C. Sarapu and R.F. Fenske, Inorg.Chem., 11 (1972) 3021.

125. C.P. Casey, R.A. Boggs, D.F. Marten and J.C. Calabrese, J.C.S.Chem. (1973) 243.

126. W.M. Butler and J.H. Enemark, J.Organometal.Chem., 49 (1973) 233.

127. W.M. Butler, J.H. Enemark, J. Parks and A.L. Balch, Inorg.Chem., 12 (1973) 451.

128. W.M. Butler and J.H. Enemark, Inorg.Chem., 12 (1973) 540.

129. L.R. Nassimbeni and M.M. Thackeray, Inorg.Nucl.Chem.Letters, 9 (1973) 539.

130. W.H. Watson and C.-T. Lin, Inorg.Chem., 5 (1966) 1074.

131. V.L. Goedkin, J. Molin-Case and Y. Whang, J.C.S.Chem.Comm., (1973) 337.

132. J.J. Bonnet, S.S. Eaton, G.R. Eaton, R.H. Holm and J.A. Ibers, J.Am.Chem.Soc., 95 (1973) 2141.

133. F.A. Cotton, M. Jeremic and A. Shaver, Inorg.Chim.Acta, 6 (1972) 543.

134. F.A. Cotton, B.A. Frenz and A. Shaver, Inorg.Chim.Acta, 7 (1973) 161.

135. G. Huttner and S. Schelle, J.Organometal.Chem., 47 (1973) 383.

136. L.J. Guggenberger, U. Klabunde and R.A. Schunn, Inorg.Chem., 12 (1973) 1143.

137. H.J. Plastas, J.M. Stewart and S.O. Grim, Inorg.Chem., 12 (1973) 265.

138. M.H. Linck, Cryst.Struct.Comm., 3 (1973) 379.

139. F.W.B. Einstein and R.D.G. Jones, Inorg.Chem., 12 (1973) 255.

140. F.W.B. Einstein and R.D.G. Jones, Inorg.Chem., 12 (1973) 1148.

141. C.A. Bear and J. Trotter, J.C.S.Dalton, (1973) 673.

142. L.Y.Y. Chan and F.W.B. Einstein, J.C.S.Dalton, (1973) 111.

143. W.K. Dean, G.L. Simon, P.M. Treichel and L.F. Dahl, J.Organometal. Chem., 50 (1973) 193.

144. J.C. Barrick, M. Fredette and C.J.L. Lock, Can.J.Chem., 51 (1973) 317.

145. M.C. Fredette and C.J.L. Lock, Can.J.Chem., 51 (1973) 1116.

146. R. Claverini, P. Ganis and C. Pedone, J.Organometal.Chem., 50 (1973) 327.

147. W. Henslee and R.E. Davis, Cryst.Struct.Comm., 1 (1972) 403.

148. A.J. Schultz and R. Eisenberg, Inorg.Chem., 12 (1973) 518.

149. I. Bernal, A. Clearfield, E.F. Epstein, J.S. Ricci, A. Balch and J.S. Miller, J.C.S.Chem.Comm., (1973) 39.

150. G.T. Kubas, T.G. Spiro and A. Terzis, J.Am.Chem.Soc., 95 (1973) 273.

151. B.A. Averill, T. Herskowitz, R.H. Holm and J.A. Ibers, J.Am.Chem. Soc., 95 (1973) 3523.

152. Z.L. Kaluski, A.I. Gusev, A.E. Kalinin and Y.T. Struchkov, Zh.strukt.Khim., 13 (1972) 950.

153. T.S. Cameron, J.F. Maguire, T.D. Turbitt and W.E. Watts, J.Organometal.Chem., 49 (1973) C79.

154. L.F. Battelle, R. Bau, G.W. Gokel, R.T. Oyakawa and I.K. Ugi, J.Am.Chem.Soc., 95 (1973) 482.

155. J.S. McKechnie, C.A. Maier, B. Bersted and I.C. Paul, J.C.S.Perkin II, (1973) 138.

156. J.S. McKechnie, B. Bersted, I.C. Paul and W.E. Watts, J.Organometal. Chem., 8 (1967) P29.

157. C. Lecomte, Y. Dusausoy, J. Protas, C. Moise and J. Tirouflet, Acta Cryst., 29B (1973) 488.

158. C. Lecomte and Y. Dusausoy, unpublished work cited in: C. Moise, Y. Mugnier and J. Tirouflet, J.Organometal.Chem., 51 (1973) 346.

159. V.G. Andrianov, Y.T. Struchkov and E.R. Rossinskaya, J.C.S.Chem. Comm., (1973) 338.

160. Y. Dusausoy, J. Protas, J. Besancon and J. Tirouflet, Acta Cryst., B29 (1973) 469.

161. P. Meakin, L.J. Guggenberger, W.G. Peet, E.L. Muetterties and J.P. Jesson, J.Am.Chem.Soc., 95 (1973) 1467.

162. P. Dapporto, G. Fallani, S. Midollini and L. Sacconi, J.Am.Chem.Soc., 95 (1973) 2021.

163. A. Immirzi and A. Luccarelli, Cryst.Struct.Comm., 1 (1972) 317.

164. L.J. Guggenberger, Inorg.Chem., 12 (1973) 1317.

165. M.L. Schneider and H.M.M. Shearer, J.C.S.Dalton, (1973) 354.

166. E.R. Bernstein, T.A. Keiderling, S.J. Lippard and J.J. Mayerle, J.Am.Chem.Soc., 94 (1972) 2552.

167. E.R. Bernstein, W.C. Hamilton, T.A. Keiderling, S.J. LaPlaca, S.J. Lippard and J.J. Mayerle, Inorg.Chem., 11 (1972) 3009.

168. K.M. Melmed, D. Coucouvanis and S.J. Lippard, Inorg.Chem., 12 (1973) 232.

169. C.P. Brock, J.P. Collman, G. Dolcetti, P.H. Farnham, J.A. Ibers, J.E. Lester and C.A. Reed, Inorg.Chem., 12 (1973) 1304.

170. T.F. Brennan and I. Bernal, Inorg.Chim.Acta, 7 (1973) 283.

171. N.A. Parpiev and G.B. Bokii, Zh.neorg.Khim., 4 (1959) 2453.

172. T.S. Khodashova, M.A. Porai-Koshits, V.S. Sergienko, N.A. Parpiev and G.B. Bokii, Zh.strukt.Khim., 13 (1972) 1105.

173. C.G. Pierpont and R. Eisenberg, Inorg.Chem., 12 (1973) 199.

174. T.E. Napier, D.W. Meek, R.M. Kirchner and J.A. Ibers, J.Am.Chem.Soc. 95 (1973) 4194.

175. P. de Meester and A.C. Skapski, J.C.S.Dalton, (1973) 1194.

176. C.S. Pratt, B.A. Coyle and J.A. Ibers, J.Chem.Soc.(A), (1971) 2146.

177. B.F. Hoskins and F.D. Whillans, J.C.S.Dalton, (1973) 607.