ORGANOMETALLIC STRUCTURES – TRANSITION METALS

ANNUAL SURVEY COVERING THE YEAR 1972 (PART 1)

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CONTENTS

ABBREVIATIONS

acac	acetylacetonate
asp	1-(dimethylarsino)-2-(diphenylphosphino)tetrafluorocyclobutene
bae	*N,N'*-ethylenebis(acetylacetoniminato)
bipy	2,2'-bipyridyl
CDT	1,5,9-cyclododecatriene
Cy	cyclohexyl

dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(dipenylphosphino)methane
dq	duroquinone
ffars	1,2-bis(dimethylarsino)tetrafluorocyclobutene
ind	indenyl
Me_2pz	3,5-dimethylpyrazolyl
ox	oxinate
PCy_3	tricyclohexylphosphine
phen	1,10-phenanthroline
py	pyridine
pz	pyrazolyl
THF	tetrahydrofuran

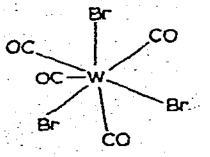
INTRODUCTION

During 1971, the number of molecular structures of interest to organo-transition metal chemists approached the 250 mark, and there is every likelihood that this figure will increase rapidly. In order to provide accounts that are both more manageable, and more timely, 1972 and later years will be covered by two surveys each year, appearing at approximately six-monthly intervals.

SIMPLE METAL CARBONYL DERIVATIVES

The anion in $NEt_4[WBr_3(CO)_4]$ (**1**) has C_{3v} (capped octahedral) symmetry[1], and bond lengths are similar to those reported for $WBr_2(CO)_3[(Ph_2As)_2CH_2]_2$ [AS71; p. 335] *. In this complex, the CO groups are mutually *cis* and thus avoid competing for metal d_π electron density. The compound $[WH(OH)(CO)_3]_4 \cdot 4OPPh_2Et$ (**2**) contains a distorted W_4O_4 cube, with non-bonding W· · ·W distances[2]. The hydride ligands are probably located between two of the CO groups, making the tungsten seven-coordinate. The adduct phosphine oxide molecules are linked to the cube via O–H· · ·O hydrogen bonds.

An independent determination[3] of the structure of $[(\pi\text{-}C_5H_5)W(CO)_3AlMe_2]_2$ [see AS71; p. 304] confirms the presence of CO groups bridging the two metal atoms: W–C–O–Al.



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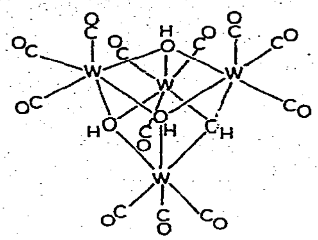
* AS71: M.I. Bruce, *J. Organometal. Chem.*, 48 (1973) p. 303–349.



(2)

Hydride atoms not shown

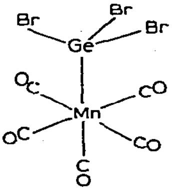
An electron diffraction determination[4] of the structure of $Re_2(CO)_{10}$ reveals that the equatorial CO groups are in the eclipsed conformation.

The anions in $[Ni(phen)_3][Mn(CO)_5]_2$ are trigonal bipyramidal, slightly distorted, especially in the equatorial plane, where C–Mn–C bond angles are 117.5(3) to 125.0(4)°. Although the difference in $Mn{-}C_{(axial)}$ and $Mn{-}C_{(eq)}$ bond lengths (~ 0.02 Å) is not significant, comparison with some other trigonal-bipyramidal complexes suggests a structural trend, for which an explanation is offered[5]. The iodocarbonyl anions in $[MnI(OPPh_3)_4]$ [*cis*-$MnI_2(CO)_4$] are disordered[6], as also found in other halo-carbonyls recently [AS71, p. 304; AS70, p. 54]*.

COMPOUNDS CONTAINING METAL–METAL BONDS

(a) Transition metal–Main Group metal bonds

The electron diffraction structure of $Br_3GeMn(CO)_5$ (3) reveals distorted tetrahedral and octahedral coordination about the germanium and manganese atoms, respectively, with the equatorial CO groups being bent towards the Group IV element[7]. The Ge–Mn bond is shorter than that found in $Ph_3GeMn(CO)_5$, explained by the greater electronegativity of the substituent.



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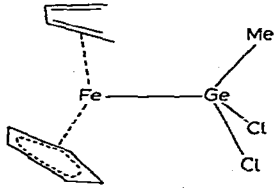

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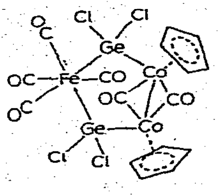
* AS70: M.I. Bruce, *Organometal. Chem. Rev. B.*, 9 (1972) p. 53–98.

In the two modifications of $(\pi\text{-}C_5H_5)(\pi\text{-}C_4H_6)FeGeCl_2Me$ (4), the metal–metal bonds are considerably shorter than the radius sum [2.28 *vs.* 2.56 Å], apparently as a result of significant $d_\pi(Fe) \rightarrow d_\pi(Ge)$ dative interaction[8]. The two hydrocarbon ligands are sterically hindered, and cause distortion of coordination about the two metal atoms.

Full details of the structure of $[(\pi\text{-}C_5H_5)Co(CO)]_2(GeCl_2)_2Fe(CO)_4$ (5), containing a five-atom metallocycle, have appeared[9]. The $\overline{\text{Co–Ge–Fe–Ge–Co}}$ ring is planar, and little strain is present in the ring.



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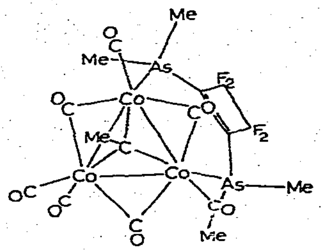
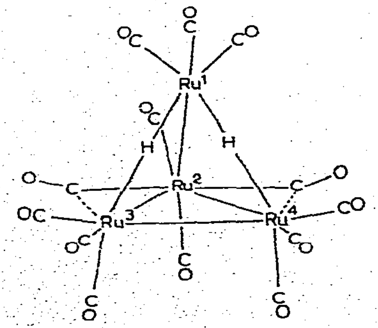


(6)

Also reported are details of the refinement of $[CCo_3(CO)_9]_2$, which consists of two tetrahedral CCo_3 units linked via the carbon atoms, in a configuration intermediate between eclipsed and staggered Co_3 atoms[10]. The formally single C–C bond length is 1.37(1) Å, indicating that the *p* character of the outwardly directed orbitals has been reduced. [See also AS71, p. 307; AS70, p. 61.] In the complex derived from $MeCCo_3(CO)_9$ and ffars, namely $MeCCo_3(CO)_7$(ffars) (6) three CO groups bridge the basal cobalt atoms; the arsenic ligand also bridges two of the metal atoms[11]. Two of the CO bridges are highly asymmetric.

(b) Complexes containing only transition metals

The account[12] of the structure of $\alpha\text{-}H_2Ru_4(CO)_{13}$ (7) complements that of the mixed hydride $H_2FeRu_3(CO)_{13}$ [AS71; p. 306]. Two separate sets of Ru–Ru distances are found. The two bridging CO groups are bonded asymmetrically, while the hydrogen atoms (not located) are assumed to bridge the Ru^1–Ru^3 and Ru^1–Ru^4 bonds.



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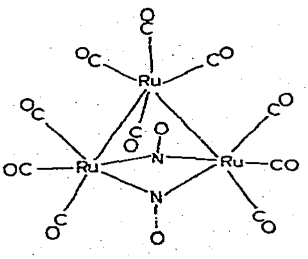
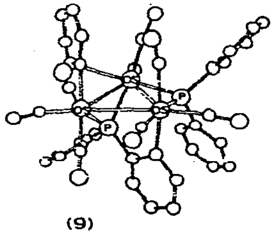


(8)

The ruthenium carbonyl nitrosyl, $Ru_3(CO)_{10}(NO)_2$, has structure (8). The Ru–Ru bond spanned by the two NO groups is 3.15 Å, and suggests a low bond-order. However, structures of related complexes suggest that the separation of two metal atoms in a cluster depends largely on the nature of the groups bridging these atoms[13].

The reaction between $Os_3(CO)_{12}$ and triphenylphosphine affords ten products, including the known complexes $Os_3(CO)_{12-n}(PPh_3)_n$ (n = 1–3). Six of the remaining complexes have been characterised by X-ray crystallographic methods, and several interesting structural features occur[14,15]. In all cases, the phosphine ligand has undergone some reaction with the Os_3 cluster. The complexes are $Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$ (9), $Os_3(CO)_7(PPh_2)_2(C_6H_4)$ (10), $HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$ (11), $HOs_3(CO)_7(PPh_3)(PPh_2)(C_6H_4)$ (12), $HOs_3(CO)_8(PPh_3)(PPh_2C_6H_4)$ (13), and $HOs_3(CO)_7(PPh_2)(PPh_2C_6H_4C_6H_3)$ (14). Major features include diphenylphosphido ligands bridging two metal atoms, *ortho*-metallated diphenylphosphido groups bridging two or three metal atoms, a phenyl group bridging two metal atoms via one carbon, a C_6H_4 group interacting with all three osmium atoms, and in (14), a ligand formed by addition of C_6H_4 to the phosphine. The formation of these complexes is considered to arise via oxidative addition reactions which occur on the cluster.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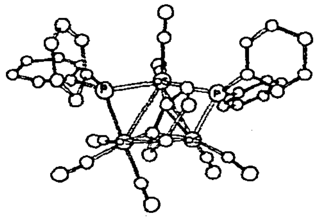
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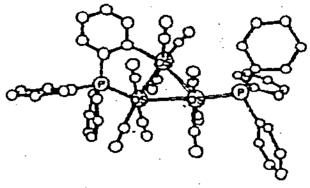
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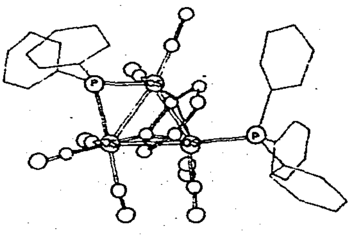
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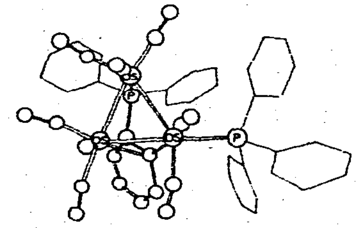
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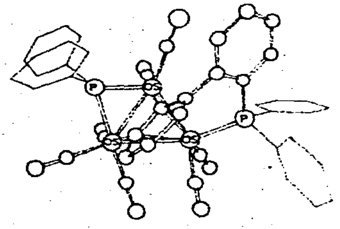
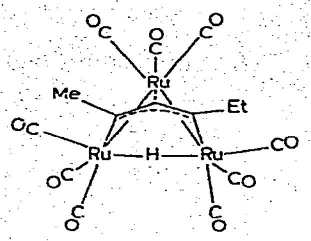

(14)

Another example of an allyl group acting as a five-electron donor is found in the complex $HRu_3(CO)_9(C_6H_9)$ (15), obtained from 2,4-hexadiene and $Ru_3(CO)_{12}$ [16]. The dimensions of the C_3Ru_3 set of atoms are very similar to those found in the complex $HRu_3(CO)_9(C_{12}H_{15})$

[AS71, p. 313; AS70, p. 63] and are consistent with the C_3 system π-bonding to one ruthenium, and σ-bonding to the other two metal atoms.



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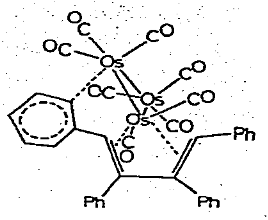

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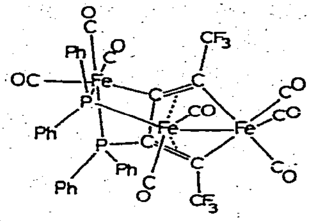
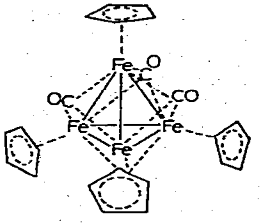


(17)

The reaction between $Os_3(CO)_{12}$ and tetraphenylbutadiene affords[17] the complex $Os_3(CO)_8(C_4Ph_4)$ (16), containing an Os_3 cluster bonded to the hydrocarbon via interaction of the diene system with two metal atoms, and of one of the phenyl groups to the third osmium. Reaction between $Ph_2PC{\equiv}CCF_3$ and $Fe_3(CO)_{12}$ affords complex (17), in which formation of a ferrole ring has occurred[18]. In addition, cleavage of a C—P bond to give a bridging PPh_2 group is found in a similar way to (ffars)$Fe_3(CO)_9$ [AS71: p. 337].



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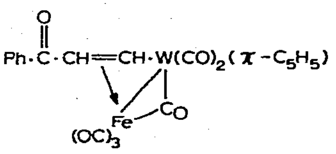
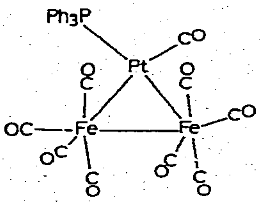


$Ph\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH{=}CH\text{-}W(CO)_2(\pi\text{-}C_5H_5)$, $Fe(CO)_3$ bridging, with CO

(19)

The first tetranuclear cyclopentadienylmetal complex, $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ (18), is another example of a molecule with a cubane-like M_4X_4 structure, with X being a symmetrically triply-bridging carbonyl group[19]. Although the four iron atoms form a bonded tetrahedron (Fe—Fe, 2.520 Å), this interlocks with the carbonyl group tetrahedron to give a distorted cube (Fe—C, 1.986 Å). The structure of the related paramagnetic monocation in $[(\pi\text{-}C_5H_5)_4Fe_4(CO)_4]PF_6$ reveals only a slight change in the $Fe_4(CO)_4$ nucleus (from cubic T_d in the neutral molecule toward distorted tetragonal D_{2d} in the cation). At the same time, the Fe—Fe bonds are shortened (to 2.484 Å). These and other bond length changes are rationalised on the basis of an MO correlation diagram, and suggest that oxidation involves removal of an electron from an MO which is somewhat antibonding between the iron atoms, and also antibonding between the carbon and oxygen atoms[20].

The Fe—W bond length (2.81 Å) in $(\pi\text{-}C_5H_5)(CH{=}CHCOPh)FeW(CO)_6$ (19) has been reported[21].



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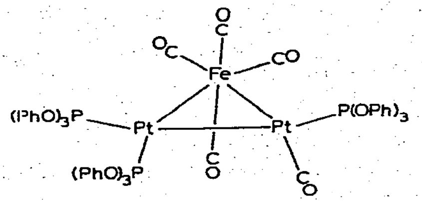
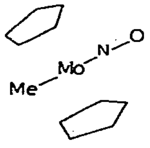


(21)

The mixed iron–platinum cluster complex $Fe_2Pt(CO)_9(PPh_3)$ (20) contains a $PtFe_2$ cluster with no bridging carbonyl groups[22]; the related compound $FePt_2(CO)_5[P(OPh)_3]_3$ (21) has also been studied[23]. In both cases, displacement of PPh_3 by CO has occurred on platinum. The stereochemistry of (20) suggests a simple bonding description involving a $[Pt(CO)(PPh_3)]^{2+}$ cation and two $[Fe(CO)_4]^-$ moieties, although it is likely that an MO description may be preferable. Qualitative MO calculations support the idea of some multiple bond character in the metal–metal bonds, which are shorter than expected.

COMPLEXES CONTAINING METAL–CARBON σ BONDS

Crystal data for the complex chromium aryl $Na_2CrPh_5 \cdot 3Et_2O \cdot THF$ have been reported[24]. The complex $(\pi\text{-}C_5H_5)_2Mo(NO)Me$ (22) contains a linear Mo–NO group, and asymmetric C_5H_5 groups containing two short, one intermediate, and two long Mo–C bond distances[25], which are analogous to those found in $(C_5H_5)_3Mo(NO)$ [AS69; 970]. The Mo–CH_3 bond length (2.20 Å) is markedly shorter than other reported examples. The crystal contains two independent discrete molecules which are approximate mirror-images of each other.



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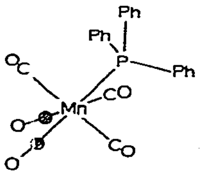
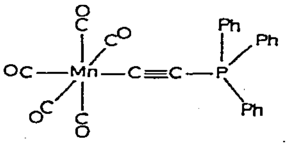


● Partial disorder between carbons of CO and CH_3 groups

(23)



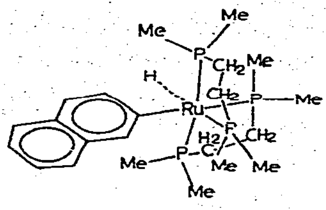
(24)

In the unit cell of $MnMe(CO)_4(PPh_3)$ (23), there are two molecules, one of which exhibits disorder with spatial occupation of two sites by both methyl and carbonyl groups, one *cis* and one *trans* to the PPh_3 ligand[26]. The second molecule exhibits no disorder, being the *cis* isomer. Full details of the structure of $Mn(CO)_4(C_2PPh_3)Br$ (24) have been published[27]. This complex, obtained from a reaction between $Mn(CO)_5Br$ and $Ph_3P{=}C{=}PPh_3$, is considered to contain the prominant resonance form $Ph_3P^+{-}C{\equiv}\bar{C}{-}Mn(CO)_4Br$. The ligand is essentially a tetraorganophosphonium molecule, with one of the organic groups being the acetylide anion.

In the system

$$M(C_{10}H_8)(dmpe)_2 \rightleftharpoons MH(C_{10}H_7)(dmpe)_2 \qquad (M = Ru, Os)$$

which behaves chemically as the Ru^0 complex, IR and NMP data suggest that the solid is the naphthyl hydride. This has been confirmed[28] by a crystal structure, which reveals the molecular configuration (25). The hydride is assumed to be *trans* to one of the phosphorus atoms in the vacant site. The major structural difference between the ruthenium and osmium complexes is in the fractional occupancy of sites for the bridging carbon atoms in the chelate rings.



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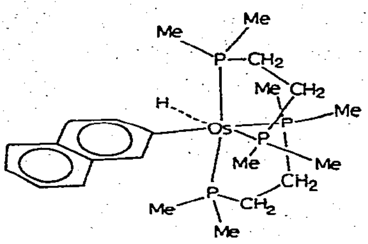
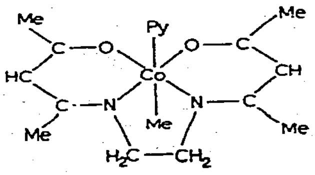


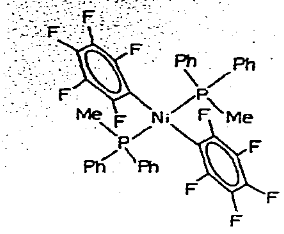
(25b)

Some preliminary data for the alkylcobalt complex MeCo(bae)(py) (26) have been given[29]. The Co—CH_3 bond length [1.99(1) Å] is similar to those found in related Schiff-base derivatives. Comparison with the five-coordinate complex MeCo(bae) shows that distortions in the macrocyclic ligand reflect interactions with the axial ligands. In (26) the metal atom remains in the coordination plane, whereas in MeCo(bae), the cobalt atom lies 0.12 Å out of the plane.



(26)

The complex *trans*-$Ni(C_6F_5)_2(PMePh_2)_2$ has structure (27)[30]. Comparison with *trans*-$Ni(C_6F_5)(C_6Cl_5)(PMePh_2)_2$ shows that in the latter, the Ni—C_6F_5 bond is longer by 0.039 Å, the Ni—P bond lengths increase by 0.024 Å, and the C—C—C angle at the nickel-bonded carbon decreases by 2.0°. The first two results suggest that σ-C_6Cl_5 is a better σ-donor than is σ-C_6F_5. Structural and spectroscopic data[31] for *trans*-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$ (28) lead to the conclusions that the *trans*-influence of YCH_2 is large compared with Cl, but smaller than Ph_2MeSi, and is not appreciably changed as Y changes in the series Y = H, Ph or $SiMe_3$. Dissolution of $PtIMe(PPh_3)_2$ in liquid SO_2, and removal of excess solvent, gives the adduct $PtIMe(PPh_3)_2SO_2$ (29), in which the SO_2 is attached to the iodine atom [I—S, 3.391(3) Å][32].



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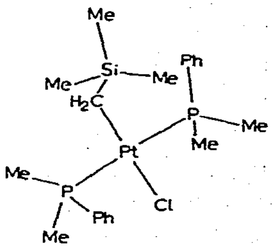

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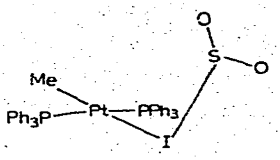
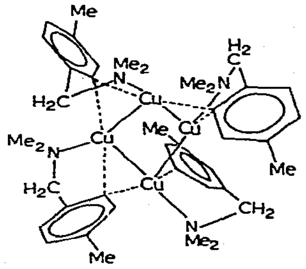


(29)

Aryl groups bridging two copper atoms are unusual features of the structure of $[Cu(Me_2NCH_2C_6H_3Me\text{-}p)]_4$ (**30**)[33]. Although the Cu–Cu bond distance is only 2.377 Å, bonding is considered to involve only the *s* and *p* valence orbitals. The four copper atoms form a distorted "butterfly" arrangement. In the related complex $[Cu(2\text{-}Me_2NC_6H_4)]_4(CuBr)_2$ (**31**), the six copper atoms form a distorted octahedron, with bridging bromines and 2-(dimethylamino)phenyl ligands[34]. Bonds from the copper atoms to the latter groups are asymmetric [2.08 and 1.97 Å].



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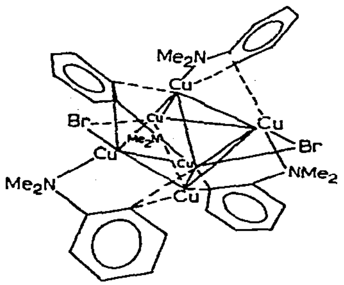
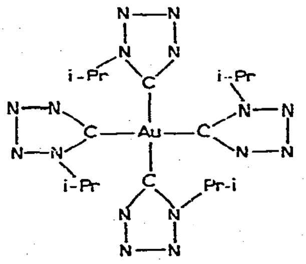


(31)

The complex anion in $AsPh_4[Au(CN_4R)_4]$ (R = i-Pr) (**32**), a complex obtained from $AsPh_4[Au(N_3)_4]$ and isopropylisonitrile, contains square-planar gold(III) σ-bonded to four tetrazolyl rings[35]. The latter form two *trans* coplanar pairs arranged so that the ring planes are mutually perpendicular.



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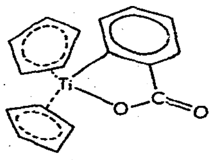
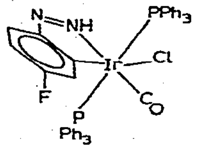


(33)

The reaction between $(\pi\text{-}C_5H_5)_2TiPh_2$ and CO_2 affords complex (33), in which CO_2 has formed an *ortho*-carboxylato group, with an intramolecular Ti–O bond, and formation of a five-membered metallocycle[36]. The second phenyl group is eliminated, presumably as benzene, together with the *ortho*-hydrogen atom.

One of the complexes obtained from $IrCl(CO)(PPh_3)_2$ and $p\text{-}FC_6H_4N_2^+BF_4^-$ is the metallated derivative (34), in which the *ortho*-hydrogen has migrated to the coordinated nitrogen atom. Deprotonation occurs on treatment with base[37].

Intramolecular metallations of olefins coordinated to platinum are substantiated in the cases of $PtCl(C_8H_{12}OMe)(py)$ (35), and of one diastereoisomer of $PtCl(C_5H_{10}O\cdot OMe)$ (amine) (36). In the former, obtained by a halogen bridge-splitting reaction, the pyridine is coordinated *trans* to the Pt–C σ bond[38]. In (36), obtained by a similar route from a diallylether complex, the absolute configurations of the asymmetric carbon atoms are indicated[39]



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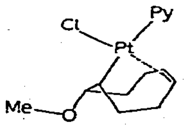

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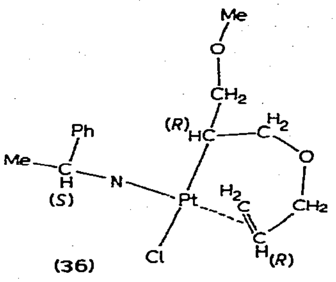

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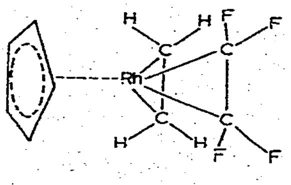
OLEFIN AND ACETYLENE COMPLEXES

Comparison of the ethylene and tetrafluoroethylene molecules bonded to a transition metal has been made in $(\pi\text{-}C_5H_5)Rh(C_2H_4)(C_2F_4)$ (37)[40]. The respective Rh–C and olefinic C–C bond distances for C_2H_4 and C_2F_4 are: 2.167(2), 1.358(9) and 2.024(2), 1.405(7) Å. The significant differences in metal–olefin bonding between the two ligands suggested by NMR work is borne out by the structural results. The Rh–C_2H_4 bond can be discussed in terms of the usual Dewar–Chatt–Duncanson (σ–π) approach, but the geometry of the Rh–C_2F_4 unit suggests a situation where there is a more or less pure π bond (or a



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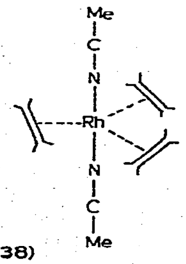
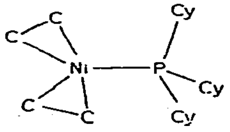


(38)

metallocyclopropane, in valence terms). Brief details have been given of the structure of the cation in $[Rh(C_2H_4)_3(MeCN)_2]BF_4$ (38); the three ethylene ligands are coplanar, and occupy the equatorial positions of a trigonal bipyramidal complex[41].

The diethylene–nickel complex $Ni(PCy_3)(C_2H_4)_2$ has structure (39), in which the metal has a distorted trigonal coordination, with an overall planar configuration of the bis-olefin–heavy atom framework[42]. A refinement[43] of $Ni(C_2H_4)(PPh_3)_2$ confirms the identity of the complex with that used by Dreissig and Dietrich[44] in their determination. Nearly twice as many intensity measurements result in a reduction in e.s.d. by a factor of three. The C_2H_4 double-bond length is 1.43(1) Å, and the bond is twisted out of the NiP_2 plane by 5.0°. The related complex $Pt(PPh_3)_2(C_2H_4)$ has a coplanar PtP_2C_2 arrangement, and the lengthening of the olefinic bonds in these complexes is similar to that found for other elements[45].



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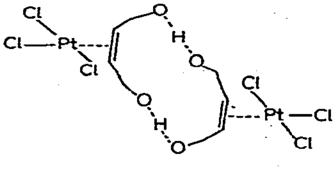
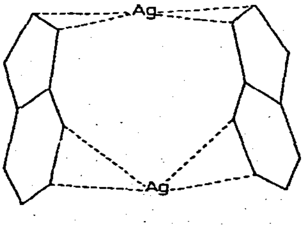


(40)

The structure of the Zeise's salt analogue $PPh_4[PtCl_3(C_4H_8O_2)]$ ($C_4H_8O_2$ = *cis*-2-buten-1,4-diol) has been reported[46]. The anions contain essentially square-planar platinum; the coordinated double bond has lengthened to 1.40(4) Å. In the crystal, dimerisation occurs by hydrogen bonding between two anions (40).

The differences found in silver-olefin and silver-aromatic coordination have been further discussed[47] with reference to the structure of the indene–$AgClO_4$ adduct (41). The dimeric units consist of two indene molecules linked by two silver atoms. One is coordinated only to olefinic double bonds, and the second to two aromatic rings and a perchlorate group. This metal atom has trigonal-planar coordination and is the first example of its type. For the adducts of $AgClO_4$ with acenaphthene (42) and acenaphthylene (43), the former consists of one-dimensional infinite chains of $AgClO_4$ with aromatic groups lying on either side[48]. Complex (43) consists of chains of alternating aromatic and perchlorate groups.



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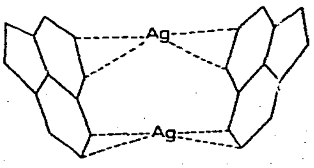
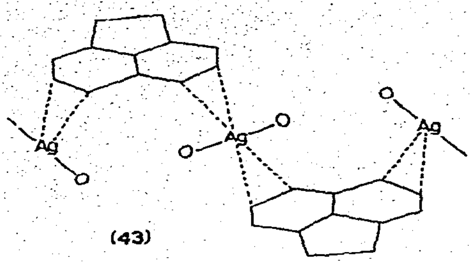


(42)

The structure of $W(CO)(C_2Ph_2)_3$ (44) has been determined[49], some eight years after the initial report of these interesting complexes. Three crystalline forms were characterised, all having similar molecular structures. Of essentially C_{3v} symmetry, the molecule contains three acetylene moieties tilted away from the W—C—O group by about 13.4°.



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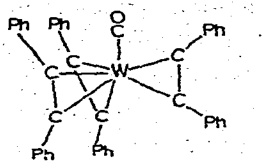

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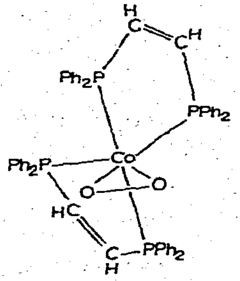
COMPLEXES FORMED BY OXIDATIVE ADDITION AND RELATED REACTIONS

A dioxygen adduct of a cobalt phosphine complex, $[Co(cis\text{-}Ph_2PCH{=}CHPPh_2)_2(O_2)]BF_4$, has structure (45)[50]. The O_2 ligand occupies an equatorial site, and the gross structural features are similar to those found in $[M(dppe)_2(O_2)]^+$ (M = Rh, Ir) [AS71; p. 322]. The disulphur analogue of the latter iridium complex, $[Ir(dppe)_2(S_2)]Cl$ (46) is nearly isostructural with the dioxygen complex[51]. The S—S bond [2.066(6) Å] is comparable with that in S_8 [2.060(3) Å], but significantly longer than the bond in free S_2 [1.889 Å].



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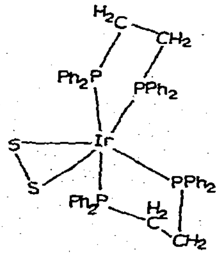

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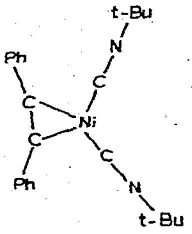
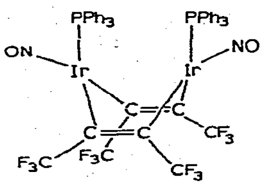


(47)

The complex $Ni(CN\text{-}t\text{-}Bu)_2(C_2Ph_2)$ has structure (47), with a small dihedral of about 2.6(7)° between the Ni—C—C (acetylene) and Ni—C—C (isocyanide) planes[52]. The C≡C triple bond length [1.284(16) Å] is intermediate between normal C=C and C≡C bonds; the phenyl groups are bent back by some 31°. Full details of the azobenzene complex $Ni(CN\text{-}t\text{-}Bu)_2(N_2Ph_2)$ are now available; the dihedral between the Ni—N—N and Ni—C—C planes is only 1.2(3)°, and the N—N bond distance [1.385(5) Å] is close to that of an N—N single bond[53].

The reaction between Ir(NO) $(PPh_3)_3$ and hexafluoro-2-butyne affords the unusual binuclear complex (48), in which the six-membered metallocycle has the boat conformation[54]. Addition of diphenylcyclopropenone to $Pt(PPh_3)_4$ affords the four-membered metallocycle (49), containing a platinacyclobutenone ring, a reaction which must involve C–C bond cleavage[55].



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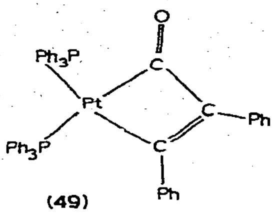


(49)

ALLYLIC AND RELATED COMPLEXES

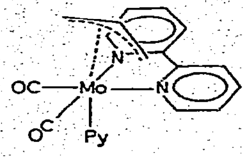
The cation in $[Mo(CO)_2(\pi\text{-}C_3H_5)(py)(bipy)]BF_4$ has structure (50), with approximate octahedral coordination about the molybdenum[56]. The compound is related to $Mo(CO)_2(\pi\text{-}C_3H_5)(NCS)(bipy)$ and $Mo(CO)_2(\pi\text{-}C_4H_7)(NCS)(phen)$, reported earlier [AS69, p. 964; AS70, p. 72].

The complex obtained from isoprene and $RuCl_3$ has structure (51), in which a linear tail-to-tail dimer of isoprene is coordinated to the metal atom via two allyl groups[57]. A similar coordination has also been reported for the analogous complex containing a butadiene trimer[58]. The Ru_2Cl_2 ring deviates appreciably from a perfect square, with the Ru–Cl bond opposite the π-allyl group being longer than that opposite to chlorine by some 0.09 Å.

The complex $(\pi\text{-}C_5H_5)NiC_3H_4 \cdot C_3H_4Ni(\pi\text{-}C_5H_5)$ (52) shows[59] some bond localisation in the C_5 rings, with "allyl" C–C bonds of 1.398, 1.394 Å separated by two "long" C–C bonds (1.438, 1.423 Å) from a "short" C–C bond of 1.401 Å. Extended Hückel MO calculations accord with this result. A *cis*-bis(π-allyl)nickel system is found[60] in the complex of nickel with tricyclohexylphosphine and allene trimer (53). The allylic C–C bonds are asymmetric, and suggest a formulation of the ligand as (53a).

A new phosphine derivative of $[(\pi\text{-}C_3H_5)PdI]_2$ has been obtained by treatment of the bridged iodide with excess PPh_3 in benzene[61]. The benzene solvate has structure (54), where two $Pd(PPh_3)$ moieties are linked by bridging halide, to give a Pd_2I triangle. The allyl group is parallel to the metal–metal bond, and randomly occupies two sites. Differences in C–C bond length in the C_3 group indicate different degrees of double bond character, while the Pd–C (terminal) bond distances suggest a certain degree of σ bond character.

The structure deduced for the palladium complex (55) by NMR methods has been confirmed by a single crystal X-ray study[62]. Full details of the structure determinations of $[Pt(C_3H_5)(acac)]_2$ (56) and $[Pt(C_3H_5)Cl]_4$ (57), in which the allyl groups act as σ,π-bridging ligands, are now available[63].



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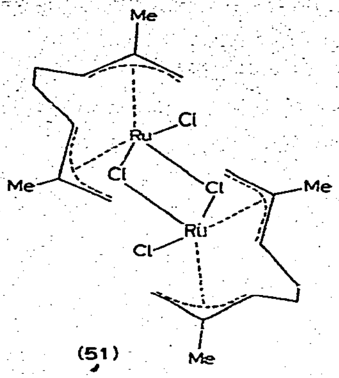

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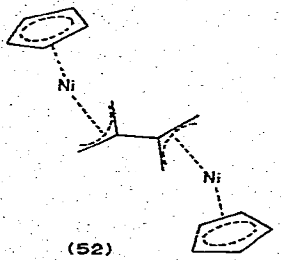

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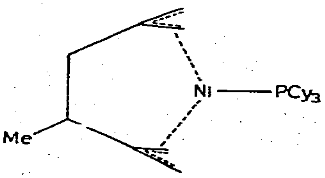

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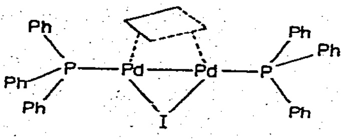

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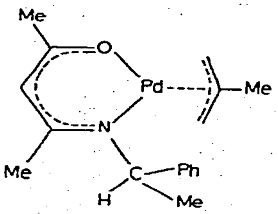

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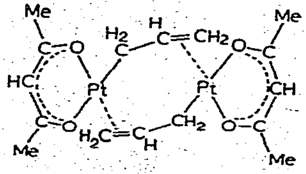

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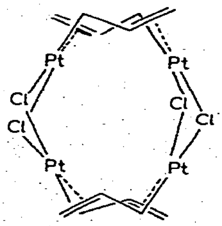
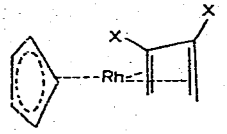


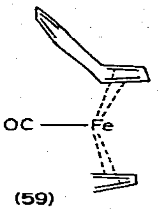
(57)

DIENE COMPLEXES

The structures of the complexes (π-C_5H_5)Rh(π-diene) **(58)** (diene = 2,3-dichlorobutadiene, 2,3-dimethylbutadiene) have been reported briefly[64]. While the diene systems show no unusual features, there is some evidence for localisation of bonding within the π-C_5H_5 ring, differences in Rh–C distances being matched by differences in the corresponding inter-ring C–C bond lengths.

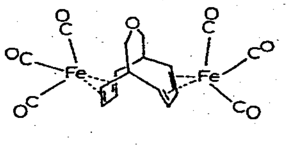


(58)
X = Me,Cl



(59)

The complex Fe(CO) (C_4H_6)(C_8H_8) **(59)** contains two diene units bonded to iron; the four terminal carbon atoms of these units form the base of a square pyramid, the apex being the carbonyl carbon atom[65]. The bonding of both units appears to be closer to the 2π than the π,2σ extreme. The structures of both the symmetrical[66] and unsymmetrical isomers[67] of the oxapropellatetraene–$Fe_2(CO)_6$ complex have been described. In the former **(60)**, m.p. 200–204°, each iron atom is complexed to a 1,3-diene system, with the central C–C bonds shorter than the outer ones. In the unsymmetrical isomer **(61)**, m.p. 135–138°, the ligand oxygen interacts with one of the diene systems, and consequences of this interaction are considered. In **(60)**, the oxygen atom has a large thermal vibration component, which may be explained by flipping of the atom to each side in the crystal, or by a statistical distribution of isomers in which the oxygen atom is bent to one or other side. A trinuclear complex of a cyclooctatetraene dimer, $C_{16}H_{16}Fe_3(CO)_9$, has structure **(62)**[68]. Apart from the normal 1,3-diene–$Fe(CO)_3$ unit, the other two iron atoms interact simultaneously with a vinyl radical and the allyl group in a bicyclo[3.2.1] octane moiety. The vinyl–Fe_2 interaction is a new feature in organoiron complexes.



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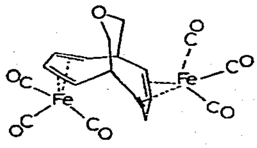

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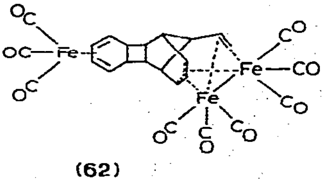
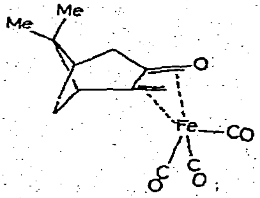


(62)

Spectroscopic and X-ray structural evidence has now established that α,β-unsaturated ketones complex to $Fe(CO)_3$ groups using only the π-systems. Pinocarvona–$Fe(CO)_3$ has structure **(63)**. The results are discussed on the basis of MO calculations, which are extended to the α,β-diketones[69].

An increasing number of complexes of the larger hydrocarbons are now being described, and a feature of their structures is the combination of well-established bonding modes, for example a π-allyl group and carbon–metal σ bond. The nomenclature of these complexes has been rendered easier by using the *hapto* system introduced by Cotton[70] some years ago. In the following section several complexes are mentioned which cannot be otherwise conveniently classified.



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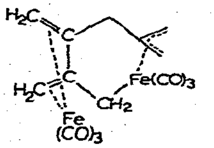

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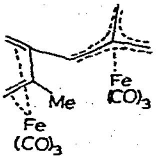
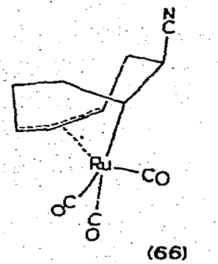


(65)

Three isomers of iron carbonyl derivatives of allene trimer, $(C_9H_{12})Fe_2(CO)_6$ have been isolated, and the structures of two of these have been reported[71]. In **(64)**, the C_9 hydrocarbon is attached via a 1,3-diene system to one $Fe(CO)_3$ group, while the second $Fe(CO)_3$ group is bonded to a π-allyl moiety and C(5). The other isomer **(65)** also contains a 1,3-diene–$Fe(CO)_3$ group, but the second iron atom is attached to a trimethylenemethane portion of the ligand.



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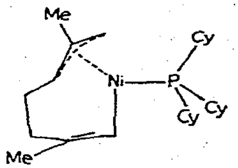

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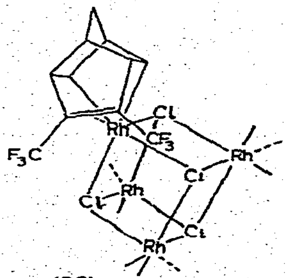

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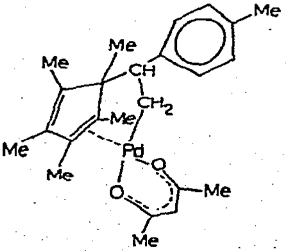


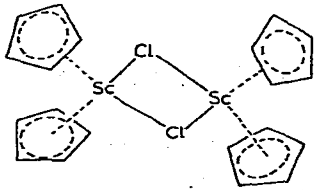
(69)

Hydride abstraction from $(C_8H_{12})Ru(CO)_3$, followed by addition of cyanide ion, affords the cyanocyclooctadienyl complex (66), in which the C_8 ring is attached to the $Ru(CO)_3$ group via a π-allyl group and a metal–carbon σ bond[72]. This type of attachment is described as a 1,2,3,6-*tetrahapto* system, and was first suggested by the author[73] for an isomer of $(C_8H_8)Os(CO)_3$ on the basis of NMR data.

Isoprene reacts with Ni(CDT) (PCy_3) to give the complex (67), containing an isoprene dimer attached to nickel again via a π-allyl system and a metal–carbon σ bond[74]. The 2,6-arrangement of methyl groups suggests that the two isoprene units are not symmetrically bonded to the metal atom before coupling.

An unusual tetrameric rhodium complex is obtained from hexafluoro-2-butyne and $[Rh(C_7H_8)Cl]_2$, and has structure (68)[75]. In this, the acetylene and diene have undergone a homo Diels–Alder addition; the resulting ligand is attached to rhodium via the double bond and two Rh–C σ bonds.

The insertion product from an intermediate "*p*-tolyl-palladium chloride" and 2-butyne, derivatised with acetylacetonate, has structure (69)[76]. The molecule unusually contains a cyclopentadiene coordinated to the metal by only one double bond, and a Pd–C σ bond to a $CH(p\text{-tol})CH_2$ group attached to the C_5 ring.



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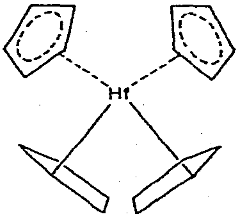


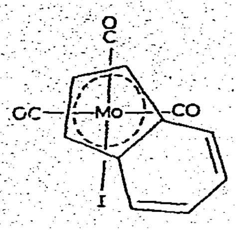
(71)

CYCLOPENTADIENYL AND RELATED COMPLEXES

The first structural study of an organoscandium complex is provided by $[(\pi\text{-}C_5H_5)_2ScCl]_2$ (70), which is a chloro-bridged dimer, containing symmetrically-bonded (*pentahapto*) C_5 rings[77]. In the crystal, $Hf(C_5H_5)_4$ (71) has two *pentahapto*-C_5H_5 groups, and two *monohapto* groups[78], and is thus similar to the titanium complex, but differs from the zirconium analogue.

The complex originally formulated as $MoI(CO)_2(ind)$ has now been shown[79] to be the tricarbonyl complex (72). Structurally, it is similar to the corresponding C_5H_5 compounds. The structure of $(Me_3Si\text{-}\pi\text{-}C_5H_4)Re(CO)_3$ (73) has also been reported[80], but gives no further information concerning the unusual solution ^1H NMR spectrum.

Reactions between ruthenocene and mercury(II) halides have given two compounds, $[(\pi\text{-}C_5H_5)_2Ru]_2 \cdot 3HgCl_2$ (74) and $(\pi\text{-}C_5H_5)_2Ru \cdot HgBr_2$ (75)[81]. In the former, Ru–Hg bonds are present; in addition, molecules of $HgCl_2$ are bonded via bridging chlorines, as shown. In (75), metal–metal bonds are also present, the adduct being a bromide-bridged



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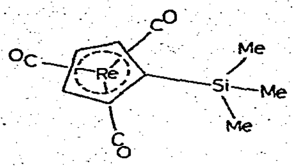

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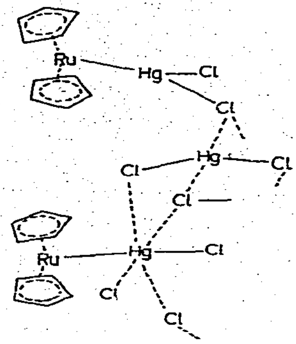

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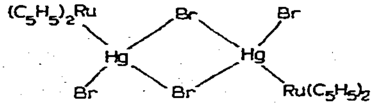
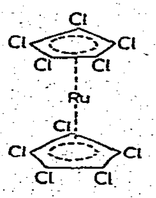


(75)

dimer. A similar compound has been described during electrochemical studies of the ruthenocene–ruthenicinium system[82]. Following the successful syntheses of perchloroferrocene and related molecules, the structures of decachlororuthenocene (76) is of interest[83]. The molecule has nearly perfect D_{5h} symmetry, with eclipsed rings, and the chlorine atoms are displaced outward from the planar C_5 ring by about 0.1 Å. This apparently results from directed valence forces. The metal–ring distance (2.170 Å) is shorter than that found in ruthenocene (2.21 Å).

Further results of studies of quinone π-complexes of the Co–Rh–Ir triad include details of the structures of (π-ind)Rh(dq) (77)[84] and of (π-C_5H_5)Ir(dq) (78)[85]. In the former, a pronounced distortion of the duroquinone ligand to the boat form occurs, with a dihedral angle of 25°. The iridium complex is similar to the rhodium analogue [AS70; p.70], with a dihedral angle of 26° for the complexed quinone molecule.



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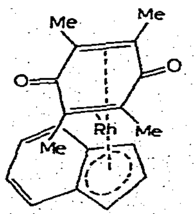

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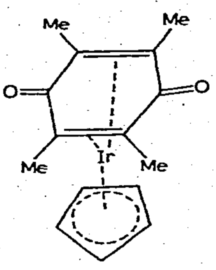

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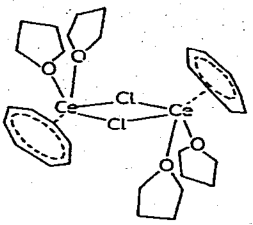

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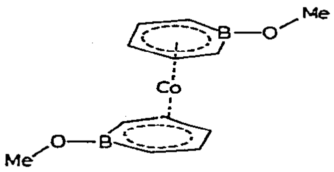
LARGE RING HYDROCARBON COMPLEXES

Several complexes with the cyclooctatetraene dianion are now known, and details of the structures of three of these have been described. Cerium forms a dimeric chloro-bridged complex, $[Ce(C_8H_8)Cl(THF)_2]_2$, which has structure **(79)**[86]. The thorium and uranium complexes, $M(C_8H_8)_2$ (M = Th, U) both have D_{8h} symmetry, with symmetrically bonded C_8 rings[87]. In all cases, the hydrocarbon ligand is considered to be the 10π cyclooctatetraene dianion.



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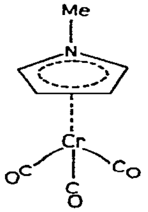

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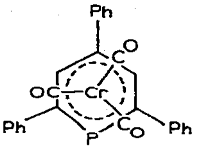

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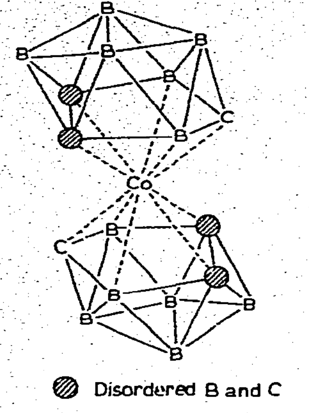
π-BONDED HETEROCYCLIC SYSTEMS

The structure of a derivative of the hydridoborinate anion, $Co(C_5H_5BOMe)_2$ **(80)**, confirms the presence of almost planar C_5B rings attached to the metal, with the boron atom involved in bonding[88]. The *N*-methylpyrrole π-complex **(81)** resembles other arene–$Cr(CO)_3$ derivatives[89]. The ring is planar, although the methyl group is bent away from the metal by 8–9°. In the chromium complex of 2,4,6-triphenylphosphorin **(82)**, the metal is bonded to the central C_5P ring, and bond distances suggest the ligand behaves as an aromatic system[90].



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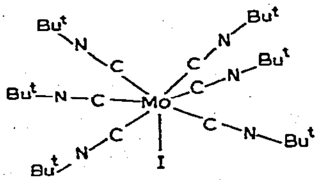
COMPLEXES CONTAINING DONOR ATOM LIGANDS

(a) Boron

The anion in $NEt_4 [Co(B_7C_2H_9)_2]$ has structure (83), with bicapped square anti-prismatic geometry[91]. Half the carbon atoms are disordered as shown, and no conclusions can be drawn concerning the existence of optical isomers in the crystal.



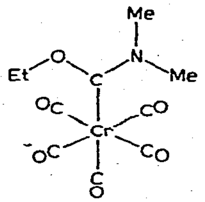
(84)

(b) Carbon

The cation in $[Mo(CN\text{-}t\text{-}Bu)_6I]I$ (84) has monocapped trigonal prismatic geometry, with an iodine atom above one of the square faces[92]. This paper also includes a discussion of the distribution of seven-coordinate structures among the three polyhedra found for this group of complexes.

Full details of the structures of *cis*-$[PtCl_2(CNEt)(PEt_2Ph)]$ [93] and of *cis*-$[PtCl_2(CNPh)_2]$ [94] have now been published [see AS71; p. 325], and a brief report[95] of the structure determination of *trans*-[$PdI_2(CN\text{-}t\text{-}Bu)_2$] has appeared. Bond length data on the platinum complexes suggest the *trans*-influence of isocyanide is appreciably smaller than that of tert-phosphine, and that there is appreciable metal→isocyanide back bonding.

Recent studies of carbene complexes have included: $Cr(CO)_5C(OEt)NMe_2$ **(85)**, with a higher π character for the C–N bond than for the C–O bond[96]; $Cr(CO)_5C(SPh)Me$ **(86)**, the first complex of this type with sulphur as the heteroatom[97]; and the manganese complex $Mn_2(CO)_9C(OMe)Ph$ **(87)**[98]. In the latter, one of the equatorial carbonyl groups in $Mn_2(CO)_{10}$ is replaced by the carbene ligand. In all complexes, there is some shortening of the axial M–CO bond (referred to the equatorial carbonyl).



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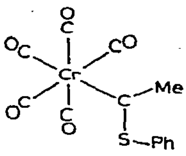

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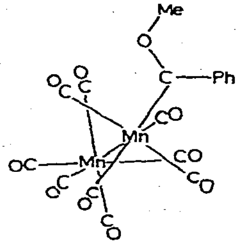
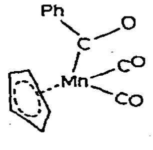


(87)

The anion in $NMe_4[(\pi\text{-}C_5H_5)Mn(CO)_2COPh]$ **(88)**, an intermediate in the formation of carbene complexes, contains a carbene bonded to manganese (1.96 Å)[99]. Slight shortening of the Mn–C bond, and lengthening of the C–O bond, are found. Treatment of $Fe(CO)_5$ with $C_6H_3(OMe)_2Li$, followed by $Et_3O^+BF_4^-$, gave a small amount of complex **(89)**, shown to consist of a carbene–$Fe(CO)_4$ moiety linked to an $Fe(CO)_3$ group by the metal–carbene system[100]. This is the first occasion on which the four-electron three-centre π-system associated with a metal–carbene ligand has been found to act as a π-ligand.



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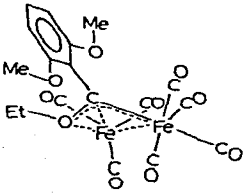

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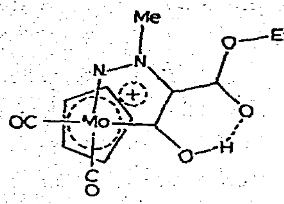
The chelate carbene complex **(90)** is obtained from ethyl diazoacetate and $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$, followed by methylation, protonation, and isolation of the hexafluorophosphate[101]. The carbene ligand forms a planar MoC_2N_2 ring, which can be represented as a non-classical ion, analogous to that formed by a sydnone.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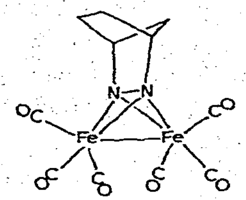
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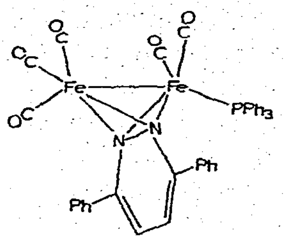
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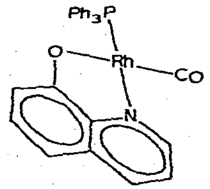
(c) Nitrogen

The structures of two complexes containing $Fe(CO)_3$ or $Fe(CO)_2(PPh_3)$ groups linked by an N–N bridge have been determined. In the derivative obtained from 2,3-diazabicyclo[2.2.1]heptane (**91**), the N–N bond length [1.404(9) Å] is close to an N–N single bond[102]. In the 3,6-diphenylpyridazine complex (**92**), the N–N bond length is 1.43 Å. In both molecules, an Fe–Fe bond is present, and contributes to the Fe_2N_2 framework[103].

Complexes of 8-hydroxyquinoline (oxH) with rhodium carbonyl moieties have been investigated[104]. In $Rh(ox)(CO)_2$, metal–metal bonds occur in the crystal, but substitution of the CO *trans* to nitrogen, giving $Rh(ox)(CO)(PPh_3)$ (**93**), results in an Rh–Rh separation of 6.68 Å. A full set of data was not obtained for the dicarbonyl, the final R value being 0.24. The nickel carbonyl derivative of diacetylbis(dimethylhydrazone) (**94**) has distorted tetrahedral coordination about the metal, the ligand forming an almost planar five-membered chelate ring[105].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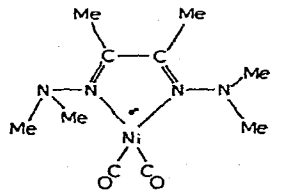
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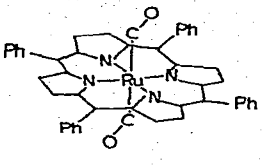
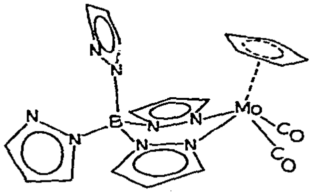
The reaction between $Ru_3(CO)_{12}$ and *meso*-tetraphenylporphine has been found to give the dicarbonyl (**95**)[106], rather than the ethanol adduct of a monocarbonyl[107]. The complex is centrosymmetric, with two mutually *trans* CO groups, and is of interest because of the ease of displacement of one of these groups by other ligands. Unusually for metal carbonyl derivatives, this complex has highly non-linear CO groups [angle Ru-C-O, 153.3(9)°].

There has been much interest in structures of molybdenum complexes of the poly(pyrazolyl)borate ligands, some of which exhibit fluxional behaviour. In $Mo(CO)_2(C_5H_5)[B(pz)_4]$



(95)

(96), the tetrakis(pyrazolyl)borate ligand is bidentate[108]. The six-membered chelate ring, which in the crystal has a somewhat flattened boat conformation, can exist in two conformations in solution, giving rise to a temperature-variable proton NMR spectrum. In the analogous complex $Mo(CO)_2(C_7H_7)[H_2B(3,5\text{-}Me_2pz)_2]$ (97), which contains a *trihapto* C_7 ring, the boron ligand is bidentate as expected[109]. However, the chelate ring is severely bent, as a result of the formation of a two-electron, three-centre B–H–Mo bond. The coordination about molybdenum in the related complex $[H_2B(Me_2pz)_2]Mo(CO)_2(C_3H_5)$ (98) is distorted octahedral, the sixth position being occupied by a B–H hydrogen atom, and a possible interaction between these two atoms has also been suggested, allowing the 18-electron configuration to be achieved[110]. The complex $[HB(pz)_3]Mo(CO)_2N_2Ph$ (99) has the expected structure, with a short Mo–N (diazo) bond explained in terms of a contribution from $Mo{=}\overset{+}{N}{=}N{\smallsetminus}_{Ph}$; the tris(pyrazolyl)borate ligand has C_{3v} symmetry[111].



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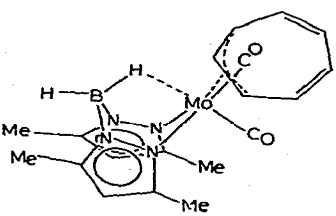
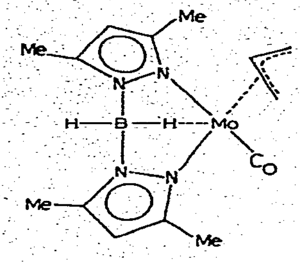


(97)

(d) Phosphorus

The effect of a Group V donor ligand on the Cr–CO bond lengths in $Cr(CO)_4(dppe)$ (100) has been studied[112]. The Cr–CO bonds *trans* to Cr–P bonds [1.831(7) Å] are shorter than those *trans* to Cr–CO [1.884(7) Å], and these data support conventional ideas concerning the relative π-accepting abilities of arylphosphine and carbonyl ligands. An account of the structure of *trans*-$Cr(CO)_4[P(OPh)_3]_2$ shows that the complex has the expected distorted octahedral structure (101)[113]. Molybdenum carbonyl halides react with Group V donor ligands to give seven-coordinate complexes. The complex $MoCl_2(CO)_2(PMe_2Ph)_3$



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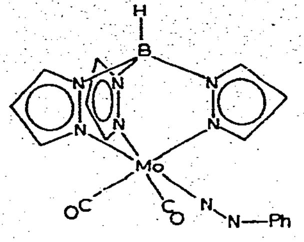
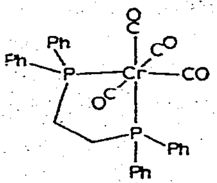


(99)

(102) has one unusually long Mo–P bond, and it is suggested that solvated methanol forms a bifurcated hydrogen bond to the two chlorine atoms[114]. In $MoBr_2(CO)_2[(Ph_2As)_2CH_2]_2$ **(103)**, one of the diarsine ligands is monodentate while the second is bidentate[115].



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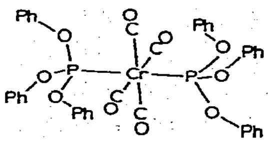

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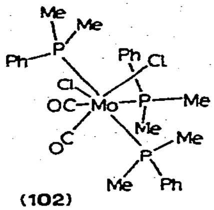

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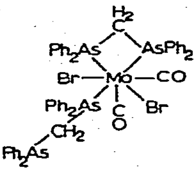
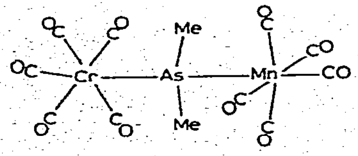


(103)

In $(CO)_5CrAsMe_2Mn(CO)_5$ **(104)**[116], the two metal atoms are crystallographically practically indistinguishable, bonds to arsenic being nearly equal, and other molecular parameters similar to those of $[(CO)_5CrICr(CO)_5]^-$. Complex **(104)** thus can be considered a member of the pseudosymmetric class of molecules.

The mixed tert-phosphine-arsine $Ph_2P\overline{CF{=}CF(AsMe_2)CF_2C}F_2$ (asp) behaves as a monodentate ligand in (asp)Fe(CO)$_4$ **(105)**, being bonded to iron via phosphorus in an axial position[117]. The structure of *cis*-$H_2Fe[PhP(OEt)_2]_4$ **(106)** has been reported[118], in which the FeP_4 geometry is intermediate between tetrahedral and octahedral (including the two hydride ligands). The latter were located, giving Fe–H distances of 1.51(4) Å.



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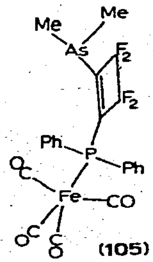

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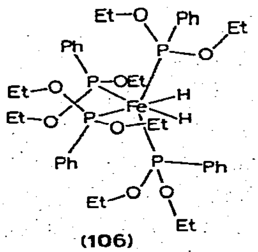
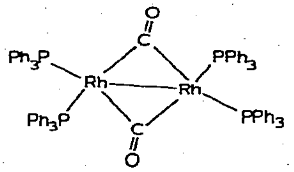


(106)

The structures of $Co(CO)_2(NO)(PPh_3)$ and $Co(CO)(NO)(PPh_3)_2$ have been compared[119], and a second, independent determination on the former complex has appeared[120]. The CO and NO groups are disordered, and the most significant difference between the two compounds is found in the (C/N)–Co–(C/N) angles, which are 113.4° and 120.0°, respectively, and is explained in terms of different π electron repulsions. Solvated dimeric complexes of stoichiometry $[Rh(CO)(PPh_3)_2(S)]$ have been shown[121] to be the five-coordinate dimers **(107)**, in which the solvent does not interact with the metal. The metal–metal bond length is 2.630(2) Å.



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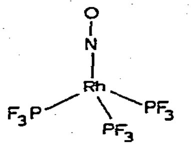
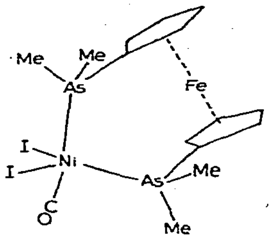


(108)

An electron-diffraction study of $Rh(NO)(PF_3)_3$ **(108)** reveals a linear Rh–N–O system[122]. The Rh–P bond lengths [2.245(5) Å] are compared with those found in twelve other rhodium–phosphine complexes, and correlations between bond length and the nature of the substituent on phosphorus are noted.



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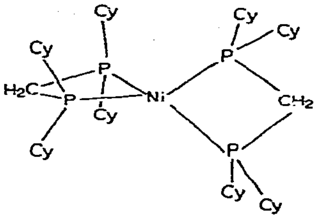

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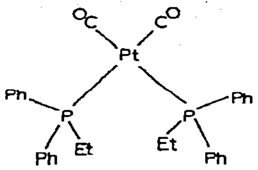
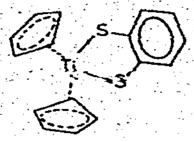


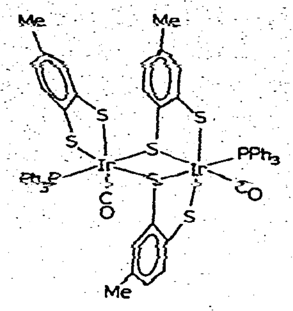
(111)

The complex derived from ferrocene-1,1′-bis(dimethylarsine) (fdma) and nickel carbonyl, followed by addition of iodine, has the structure **(109)**[123]. This five-coordinate complex has nearly regular trigonal bipyramidal stereochemistry. The unusual bidentate ligand coordinates in a stepped configuration, with eclipsed cyclopentadienyl rings. The fluxional NMR behaviour may be explained by a flipping of the $Ni(CO)_2I_2$ moiety from one side of the $FeAs_2$ plane to the other. The low-valent nickel complex $Ni[CH_2(PCy_2)_2]_2$ **(110)** contains a heterocyclic four-membered spirane ring system, in which the nickel has a distorted tetrahedral coordination[124]. The P–Ni–P angles (77°) indicate that orbital overlap occurs via bent Ni–P bonds.

The structure of $Pt(CO)_2(PEtPh_2)_2$ **(111)** has been reported; some disorder was found in the Pt–CO interactions[125].



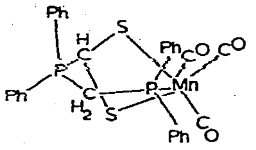
(112)



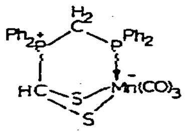
(113)

(e) Sulphur

The $S_2C_6H_4$ plane in $(\pi\text{-}C_5H_5)_2TiS_2C_6H_4$ (**112**) is folded out of the TiS_2 plane by some 46°[126]; this value is similar to those reported earlier in related complexes. Full details of the structure of $(\pi\text{-}C_5H_5)_2Mo(S\text{-}n\text{-}Bu)_2FeCl_2$ are available[127] [AS71, p. 339]. This complex serves as a model compound for the nitrogenase system. There is no evidence for any metal—metal bond, and indeed the acute S—Mo—S (72.6°) and S—Fe—S angles (75.4°) suggest that metal—metal repulsion occurs. The iridium—dithiolene complex $Ir_2(tdt)_3(CO)_2(PPh_3)_2$ (**113**) (tdt = toluene-3,4-dithiolate) consists of iridium atoms linked by bridging sulphurs which are part of ligands chelating to one iridium only[128]. No metal—metal interaction occurs.



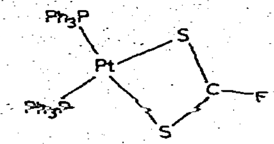
(114)



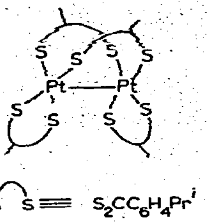
(114a)

Addition of CS_2 to *cis*-$MnH(CO)_3(dppm)$ [dppm = $CH_2(PPh_2)_2$] results in hydrometallation of a C=S bond followed by internal attack on the thiocarbonyl sulphur atom after fission of an Mn—P bond[129]. The resulting complex has structure (**114**). The valence-bond structure (**114a**) can be written, although the metal carbonyl groups will prevent any significant charge remaining on the metal. Insertion of CS_2 into the Pt—F bond in $[PtF(PPh_3)_3]HF_2$ affords the cationic dithiofluoroformate complex (**115**)[130]. The dithiocumate complex (**116**) is of some interest because of the metal—metal bond [2.870(3) Å], supported by two bridging ligands[130a].

Cyclopentamethylenethiuram disulphide reacts with $Fe(CO)_5$ to give the dicarbonyl derivative (**117**); in this paper[131], structural data for some twelve other dithiocarbamates

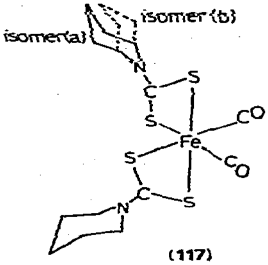


(115)



(116)

are reviewed. The structure of Co(NO)(S_2CNMe_2)$_2$ (118) has also been reported[132]; the Co–N–O angle is 135°. The nitrosyl group is disordered.



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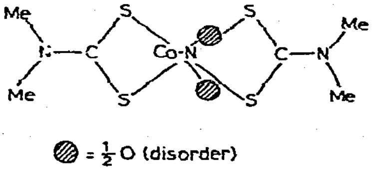

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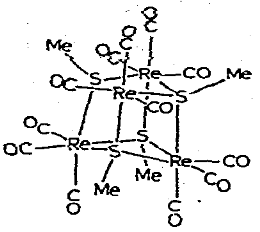
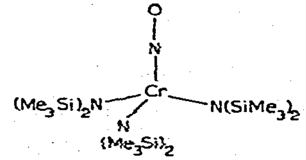


(119)

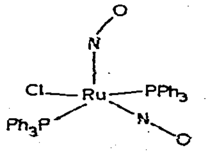
The tetrameric [Re(CO)$_3$(SMe)]$_4$ (119) belongs to the cubane class of molecules although the Re_4S_4 unit is considerably distorted, and long Re–Re distances (3.85–3.95 Å) confirm the absence of any formal metal–metal interaction[133] [see AS70; p. 90].

Nitrosyl complexes

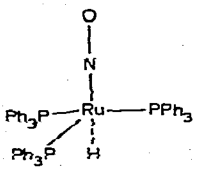
A pseudo-tetrahedral coordination about chromium is found in Cr(NO)[N(SiMe$_3$)$_2$]$_3$ (120)[134], contrasting with the square-planar geometry of the related complex Cr[N(SiMe$_3$)$_2$]$_2$(THF)$_2$. The Cr–N–O system is linear.



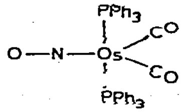
(120)



(121)



(122)

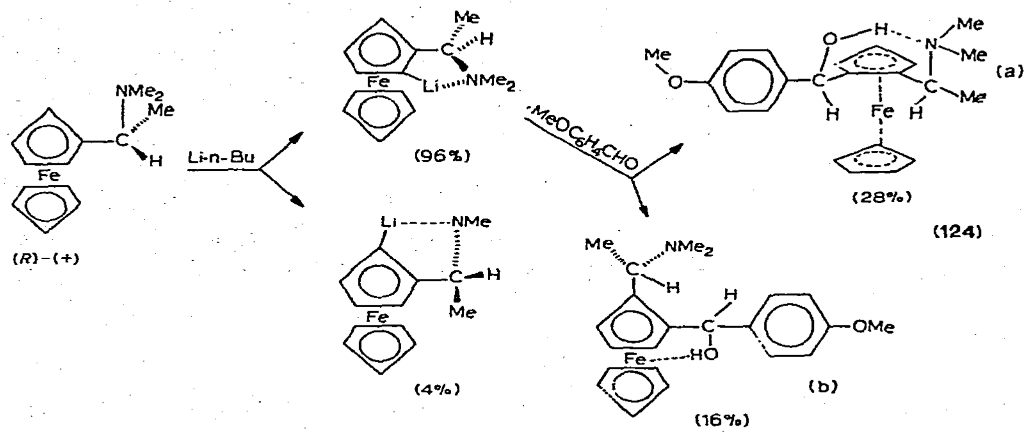


(123)

Full details of the structures of [RuCl(NO)$_2$(PPh$_3$)$_2$]PF$_6$ (121)[135] and of RuH(NO)(PPh$_3$)$_3$ (122)[136] are now available, together with a discussion of the bonding of the NO groups in complexes of this type. The former complex contains both bent and linear Ru—N—O systems, whereas in (122), the angle Ru—N—O is 176(1)°. In the osmium derivative $[Os(NO)(CO)_2(PPh_3)_2]ClO_4$ (123), the Os—N—O system is linear (it is bent in the related cations $[IrCl(CO)(NO)(PPh_3)_2]^+$ and $[Os(OH)(NO)_2(PPh_3)_2]^+$), and the structure is similar to that of $Os(CO)_3(PPh_3)_2$ and $[Mn(NO)(CO)_2(PPh_3)_2]$[137]. In contrast with most linear M—N—O systems, which are usually associated with shorter M—NO bonds, the Os—NO bond is rather long [1.89(1) Å]. It is evident that generalisations concerning the preferred geometry of the M—N—O system in any given situation seem to have little predictive power at present.

FERROCENE AND BENCHROTRENE DERIVATIVES

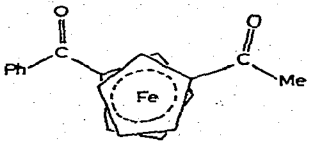
The absolute configurations of a large number of optically active ferrocenes have been established[138] via the structure determination of compound (124a), obtained by the following route:



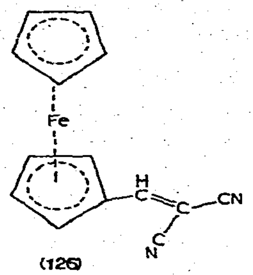
The conformations about the two asymmetric carbons are determined by hydrogen bond formation between the OH and NMe_2 groups, a factor which also contributes to the increased stability of (124a) over (124b).

The orientation of the C_5 rings in 1-acetyl-1′-benzoylferrocene (125) is midway between fully eclipsed and staggered[139]. The two acyl groups are removed as far as possible from one another, with the phenyl ring rotated out of the C_5 ring plane. In 2,2-dicyanovinylferrocene (126), close intermolecular approaches are found [*e.g.* C···C, 3.28 Å], but it is not clear whether these represent "self-complexing" of the type found in the ferrocene-tetracyanoethylene adduct, or merely repulsive contacts allowing more efficient packing. The C_5 rings are rotated by 7° from the eclipsed conformation[140].

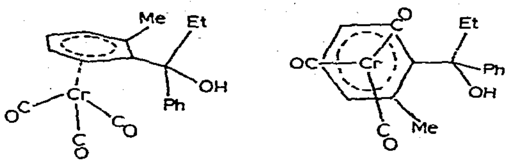
The structures of the two racemic diastereoisomers of methyl-2-(1′-hydroxy-1′-phenylpropyl)benchrotrene (127) have been determined[141], and consequently also their absolute configurations. The *endo* hydroxy group is compatible with the Cr· · ·H–O hydrogen bond suggested by the IR spectrum.



(125)



(126)



m.p. 89° m.p. 163°

(127)

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