STRUCTURES OF ORGANO-TRANSITION METAL COMPLEXES

ANNUAL SURVEY FOR 1973 (PART 2)*

MICHAEL I. BRUCE

Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001.

CONTENTS

---

*Part 1: M.I. Bruce, *J.Organometallic Chem.*, 75(1974)335.

ABBREVIATIONS

acac	acetylacetonate
bipy	2,2'-bipyridyl
cod	1,5-cyclooctadiene
Cy	cyclohexyl
dba	dibenzylideneacetone
dbms	monothiodibenzoylmethanate
diars	1,2-bis(dimethylarsino)benzene
rac-diars	$Ph(Me)As(CH)_2As(Me)Ph$
dmgH	dimethylglyoxime
gly	aminoacetate
nbd	norbornadiene

OEP	octaethylporphin
py	pyridine
pz	pyrazole
sp	(2-vinylphenyl)diphenylphosphine, *o*-CH_2:$CHC_6H_4PPh_2$
THF	tetrahydrofuran
tpp	$PhP(CH_2CH_2CH_2PPh_2)_2$
ms-TPP	*meso*-tetraphenylporphine
triphos	$PhP(CH_2CH_2PPh_2)_2$

GENERAL AND REVIEWS

Several papers have appeared which attempt to correlate recent structural results on a wide range of compounds. Thus, Churchill[1] has commented on C-H and N-H distances assumed in, and determined from X-ray diffraction studies. Anomalously short distances are found for bonds involving hydrogen atoms when X-ray diffraction methods are used, since the actual parameter determined is the distance between the centroids of electron density of the two atoms. From a survey of X-ray diffraction studies of inorganic molecules reported in *Inorganic Chemistry* during 1972, for which the positions of hydrogen atoms have been meaningfully refined, overall optimal (X-ray) C-H and N-H distances of 0.95 and 0.87Å, respectively, are found.

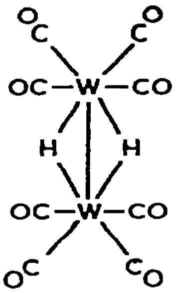
Consideration of the symmetry and electron occupacy of the appropriate MO's has enabled a satisfactory rationale to be given[2] for the geometries of bi- and polynuclear metal complexes with bridging ligands (halide, OR, SR, NR_2, PR_2, H and alkyl or aryl). However, detailed calculations of the extent of involvement of particular ligand orbitals in the bridge MO system are not yet possible.

Further volumes of *Molecular Structures and Dimensions* have been published[3]. The bibliography of organic and organometallic crystal structures has reached 1972 in volume 4, and volume A1 is a compilation of bond lengths, bond angles and torsion angles for structures reported between 1960 and 1965.[4] Specially prepared stereo diagrams have been used to illustrate the various structures. The publication supplements the well-known Chemical Society Special Publication *Tables of Interatomic Distances and Configuration in Molecules and Ions*, which covered the literature until the end of 1959.

Reviews appearing since the last summary[*] include surveys of five-coordinate and nitrosyl complexes of transition metals,[5] and some account of recent Russian crystal structure determinations, largely based on Struchkov's work.[6] An article on structural organotin chemistry[7] lists tin-metal bond lengths in organotin-transition metal compounds.

METAL CARBONYLS AND RELATED COMPOUNDS

The phosphine ligand in $Mn_2(CO)_9(PMe_2Ph)$ is attached axially, with the two $Mn(CO)_4$ moieties staggered.[8] The $AsMe_2Ph$ derivative is isostructural. The electron diffraction structure of $Re_2(CO)_{10}$ shows the molecule has D_{4h} symmet (eclipsed) in the gas phase.[9] The anion in $(NEt_4)_2[W_2H_2(CO)_8]$(1) contains a W-W bond bridged by two hydrogen atoms, which were located [W-H, 1.846(67)Å].[10] Crystal data for the mixed cluster carbonyls $Co_2Rh_2(CO)_{12}$, $Co_2Ir_2(CO)_{12}$, and $Co_2Rh_4(CO)_{16}$ have been tabulated.[12]



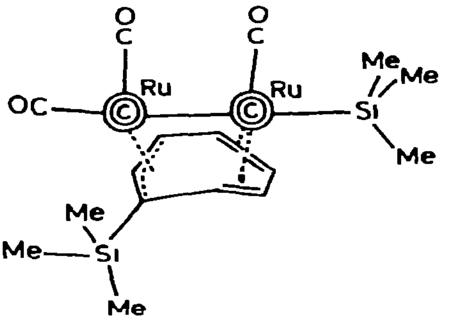
(1)

The cation in $[Ir(CO)_3[PMe_2Ph)_2]ClO_4$ has a trigonal bipyramidal structure, with phosphines in the axial positions.[11] The substituents on the two phosphines are mutually eclipsed, but staggered with respect to the CO groups.

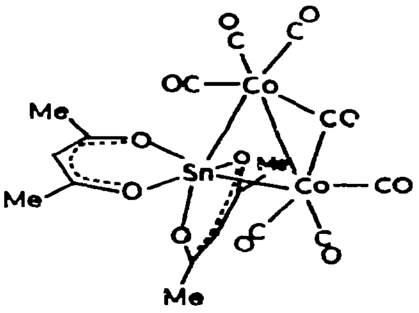
[*] AS72-2: M.I. Bruce, *J.Organometallic Chem.*, 1973, 58, 153.

COMPOUNDS CONTAINING METAL-METAL BONDS

(a) *Transition metal-Main Group metal bonds.* Reaction of cycloheptatrienes with $[Ru(CO)_4(SiMe_3)]_2$ affords the binuclear complexes $[Ru_2(CO)_5(SiMe_3)(C_7H_6R)]$; a minor product obtained from C_7H_8 contains the $C_7H_6SiMe_3$ ligand (2).[13] The structure of $(acac)_2SnCo_2(CO)_7$(3) consists of two $Co(CO)_3$ moieties joined by a Co-Co bond, and bridged by CO and $Sn(acac)_2$ groups.[14] The anion in $NMe_4[Pt(GeCl_3)_5]$ is a distorted trigonal bipyramid, with four Pt-Ge bonds having an average value of 2.406(8)Å, with the fifth(equatorial) bond at 2.480(3)Å. The geometry about platinum differs from that in $[Pt(SnCl_3)_5]^{3-}$, which is nearly regular trigonal-bipyramidal. The germanium atoms are also distorted from tetrahedral geometries.[15]



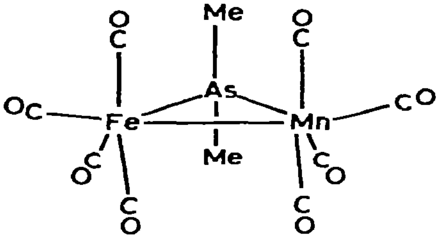
(2)



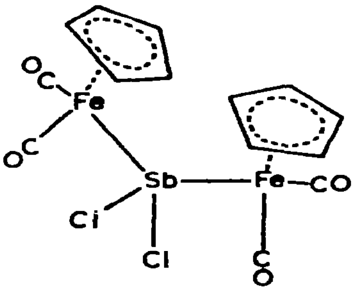
(3)

Irradiation of the arsenic-bridged complex $Me_2As[Fe(CO)_4][Mn(CO)_5]$ affords the trinuclear cluster $Me_2AsFeMn(CO)_8$(4).[16] In the molecule, the iron and manganese atoms are indistinguishable. The complex $[Cl_2Sb\{Fe(CO)_2(C_5H_5)\}_2]Sb_2Cl_7$ contains a very distorted tetrahedral antimony atom in the cation (5), while the anions form $Sb_4Cl_{14}^{2-}$ groupings via Sb-Cl contacts; the Sb and Cl atoms can be considered to form infinite chains if short contacts to 3.55Å are considered.[17]

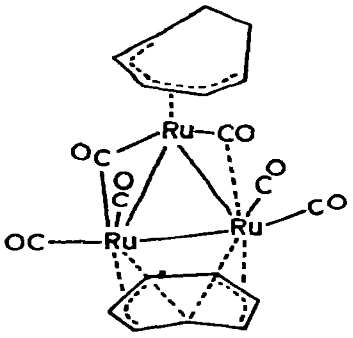
(b) *Metal clusters.* Cycloheptatriene reacts with $Ru_3(CO)_{12}$ affording the fluxional complex $Ru_3(CO)_6(C_7H_7)(C_7H_9)$ (6), in which the C_7H_7 ring bridges two of the metal atoms, while the C_7H_9 group is attached to the third ruthenium as an $\hbar^5$-cycloheptadienyl ligand.[18] In $Os_3(CO)_7(C_2Ph_2)(C_4Ph_4)$ (7),



(4)

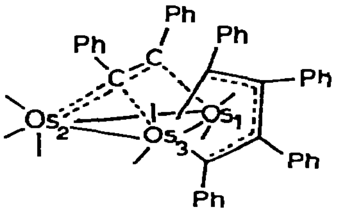


(5)



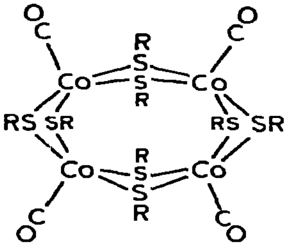
(6)

the diphenylacetylene ligand appears to be a four-electron donor to the whole cluster, while the C_4Os (osmacyclopentadiene) ring interacts with the other two metal atoms.[19]

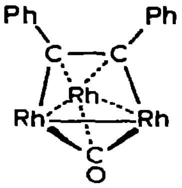


(7) CO groups omitted

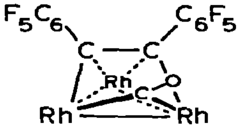
In $Co_4(CO)_4(SEt)_8$(8), the four metal atoms form a planar rectangular array, with pairs of atoms bridged by two mercapto groups.[20] Although the Co_4S_8 core would have an idealised tetragonal geometry, the formation of two short [2.498(5)Å] and strong Co-Co bonds results in the severe distortion found. Comparisons are made with the structurally analogous $[Ru\,(NO)Cl(PPh_2)]_4$, and with the structurally related $Fe_2(CO)_6(SEt)_2$ complexes. The X-ray structures



(8) $R = C_2H_5$



(9)

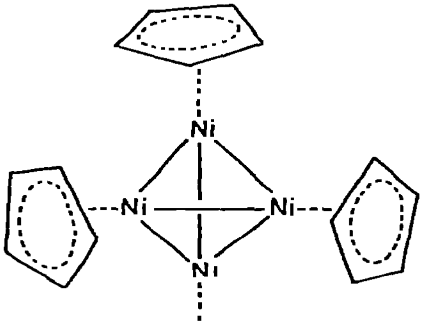


(10)

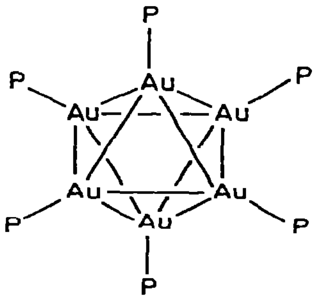
C_5H_5 groups omitted

of $[(C_5H_5)Rh]_3(CO)(C_2R_2)[R=Ph(9);\ C_6F_5(10)]$ have been reported briefly in connection with NMR studies.[21] The major difference lies in the position of the CO group. In (9), it is bridging two rhodium atoms and interacting less strongly with the third, while in (10), it bridges only two metal atoms.

Reduction of $Ni(NO)(C_5H_5)$ with $LiAlH_4/AlCl_3$ affords the tetranuclear cluster $[(C_5H_5)Ni]_4H_3$(11).[22] The three hydrogens form μ_3-bridges across three tetrahedral faces, as deduced from deviations from tetrahedral symmetry.



(11)



(12)

The cation in $[Au_6\{P(p\text{-tol})_3\}_6](BPh_4)_2$ (12) is a centrosymmetric octahedron which is deformed by squeezing along a three-fold axis passing through the centres of the two larger faces.[23] Two sets of Au-Au distances are found: two opposite faces [2.932(2)-2.990(2)Å], and the remaining edges [3.043(2)-3.091(2)Å] with a mean Au-Au distance of 3.019Å.

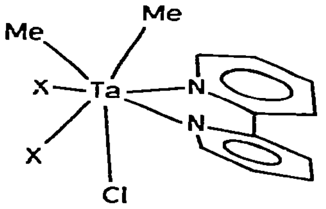
(c) *Metal-metal bond lengths reported during 1973*

Table 1 summarises metal-metal bond lengths determined throughout 1973, and is compiled from structural reports mentioned in both Parts of this Survey.

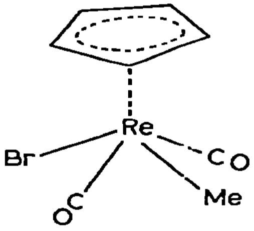
COMPLEXES CONTAINING METAL-CARBON σ BONDS

(a) *Alkyls, aryls and related compounds.* In $TaCl_2Me_3(bipy)$(13), tantalum has distorted capped trigonal prismatic coordination.[24] The geometry is rationalise in terms of ligand-ligand repulsions, and the bite of the bidentate ligand.

The coordination about chromium in $Cr(CH_2CMe_2Ph)_4$ is slightly distorted tetrahedral, in agreement with EPR results.[25] The octahedral cation in $[Cr(CH_2SiMe_3)_2(bipy)_2]I$ has the same Cr-C distance as found in two related aryl complexes. The Cr-N bonds *trans* to N [2.103(7)Å] are shorter than those *trans* to C[2.156(7)Å].[26] Full details of the structure of $WMe_4[ON(Me)NO]_2$ have been published.[27] The coordination geometry is intermediate between square antiprismatic and dodecahedral.

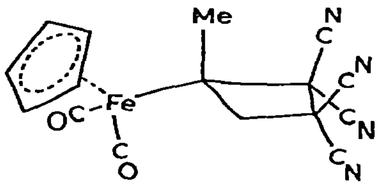


(13) X=disordered Cl,Me

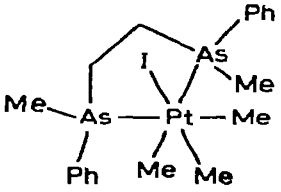


(14)

The structure of $ReBrMe(CO)_2(C_5H_5)$(14) shows that the two CO groups are *trans*; a strong *trans* effect of the methyl group results in a lengthened Re-Br distance (2.76$_9$Å; sum of covalent radii, 2.65Å).[28] Addition of tetracyanoethylene to $(C_5H_5)Fe(CO)_2CH_2CMe{=}CH_2$ affords the σ-cyclopentyl derivative (15). The crystal contains two independent molecules, which differ only in conformation, caused by rotation of the σ-bonded ligand about the Fe-C bond. The hydrogen atoms were successfully refined, and the Fe-C(sp^3) distance [2.0977(23)Å] was



(15)

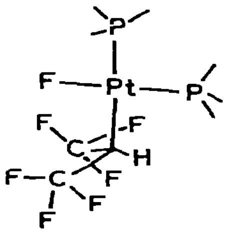


(16)

determined accurately for the first time.[29]

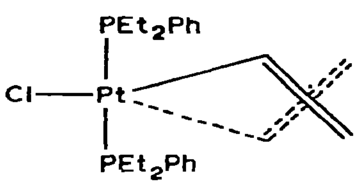
In *trans*-NiBr(C_6F_5)($PMePh_2$)$_2$, the Ni-C_6F_5 distance of 1.880(4)Å can be compared to values found in *trans*-Ni(C_6F_5)$_2$($PMePh_2$)$_2$ [1.939(3)Å] and in *trans*-Ni(C_6F_5)(C_6Cl_5)($PMePh_2$)$_2$ [1.978(10)Å], while the intra-ring angles of the C_6F_5 group show the marked deviations characteristic of the σ-bonded transition metal aryls.[30]

The structure of [PtMe$_3$(*rac*-diars)]I(16) provides several new parameters for platinum(IV) complexes; the mean Pt-Me bond length is 2.11Å, and the *trans* effect of the methyl group on the Pt-As and Pt-I bonds is about 0.1Å. The chelate ring has a distorted envelope conformation.[31] A minor product isolated from the reaction between Pt(stilbene)(PPh_3)$_2$ and (CF_3)$_2CN_2$ was shown to be *cis*-PtF[CH(CF_3)$_2$](PPh_3)$_2$ (17).[32] The Pt-F bond distance is 2.03(1)Å, and the two Pt-P distances differ significantly: that *trans* to F is 2.218(7)Å, which is among the shortest recorded. That *trans* to the hexafluoroisopropyl group is 2.310(7)Å.

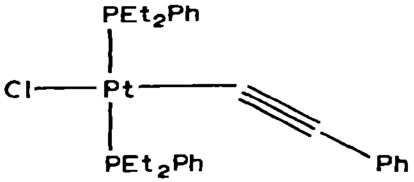


(17) Ph groups omitted

The *trans* influence of R in *trans*-PtClR(PEt_2Ph)$_2$ has only low sensitivity to hybridisation at carbon. The structures of complexes with R = $CH{=}CH_2$ (18), or $C{\equiv}CPh$ (19) reveal[33] Pt-Cl distances of 2.398(4) and 2.407(6)Å, respectively, which may be compared to a value of 2.415(5)Å found for R=CH_2SiMe_3.[34] In (18),



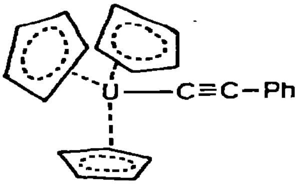
(18) showing disordered vinyl group



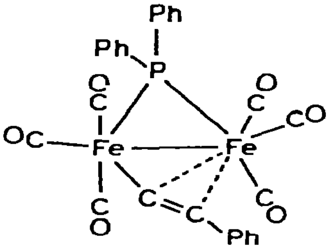
(19)

the vinyl group is disordered about the C_2 axis through Pt and Cl. The Pt-C≡C angle in (19) is 162(3)°.

Other acetylides which have been studied are $U(C_2Ph)(C_5H_5)_3$(20) and $Fe_2(C_2Ph)(CO)_6(PPh_2)$(21). In the former compound the U-C≡C angle is 175(2)°, and the U-C bond length is 2.33(2)Å.[35] The binuclear iron complex, which results from a reaction between $Fe_2(CO)_9$ and PhC_2PPh_2, contains a FeC_2Ph moiety π-bonded to the second iron group. The Fe-Fe bond is also supported by a bridging PPh_2 group.[36]

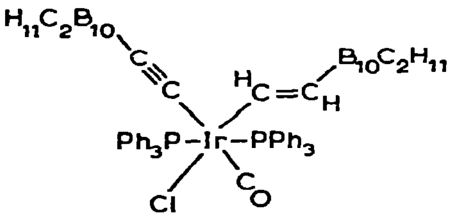


(20)

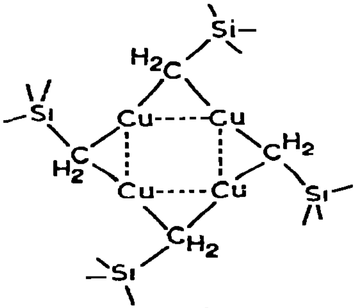


(21)

The 2:1 adduct obtained from ethynyldicarbadodecaborane(12) and *trans*-$IrCl(CO)(PPh_3)_2$ contains both substituted acetylide and vinyl groups (22). Oxidative addition of the acetylene affords a hydrido-acetylide, which reacts with the second acetylene to give the vinyl acetylide.[37]



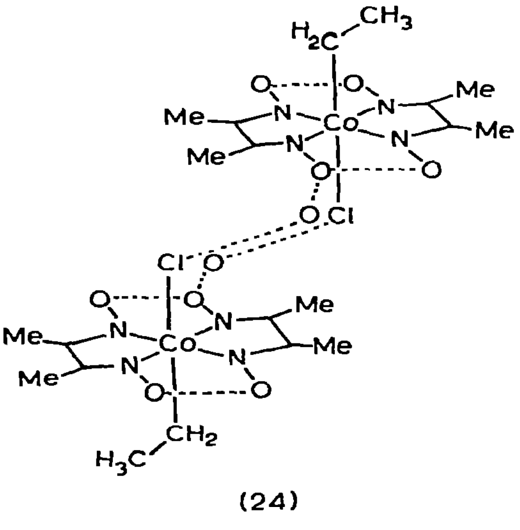
(22)



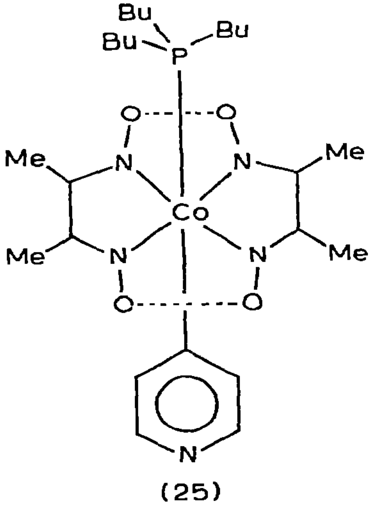
(23)

Trimethylsilylmethylcopper(I)(studied at -40°) is a tetramer (23), containing a square plane of copper atoms, the edges being bridged by the methylene carbons, which are also in the plane.[38] Metal-metal bonding is relatively unimportant. In square-planar gold(III) complexes, such as $AuCl_2Ph(SPr^n_2)$, the σ-phenyl group has a strong *trans* influence. The two Au-Cl bonds are 2.27(1) (*trans* to S) and 2.38(1)Å (*trans* to C_6F_5).[39]

The monoprotonated cobaloxime [EtCo(dmg)(dmgH)Cl].H_2O (24) crystallises as centrosymmetrically related pairs of molecules bridged via hydrogen-bonds to the water of crystallisation.[40] The two dimethylglyoxime O-H---O separations are different as a result of protonation of one oxygen, which then hydrogen-bonds to the water. The pyridine ligand in cobaloxime (25) is coordinated via a Co-C σ bond.[41] The major structural effect is on the C-C-C angle at the σ-bonded carbon, which decreases nearly 3°, while angles at adjacent carbons increase by 1.5°, both compared with N-coordinated pyridine.



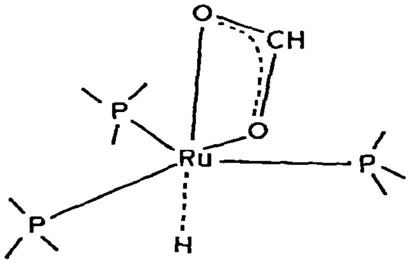
(24)



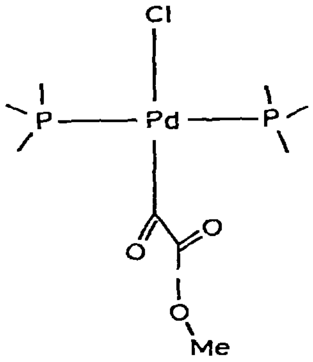
(25)

These changes probably result from contacts between the equatorial ligands and the pyridine ligand.

(b) *Other metal-carbon σ-bonded complexes.* The product of the reaction between CO_2 and $RuH_2(PPh_3)_4$ has been shown to be the formato complex (26) and does not contain any Ru-C σ bond.[42] Both monoclinic and triclinic



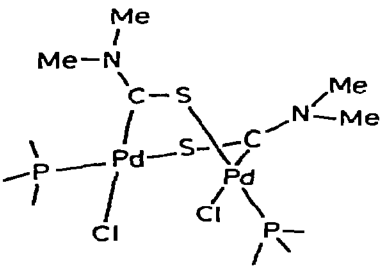
(26)

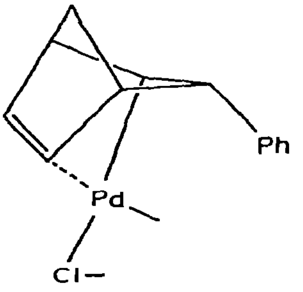


(27) Phenyl groups omitted

modifications exist. The methoxalyl complex *trans*-PdCl(COCO$_2$Me)(PPh$_3$)$_2$(27) contains the methoxalyl ligand in the *s-trans* planar conformation.[43]

In the absence of excess PPh$_3$, ready decarbonylation occurs, affording the methoxycarbonyl complex. The product from oxidative addition of ClC(S)NMe$_2$ to Pd[P(OMe)$_3$]$_4$ is the dimeric {PdCl(CSNMe$_2$)[P(OMe)$_3$]}$_2$ (28), in which bridging dimethylthiocarbamoyl groups link the two palladium atoms by coordination through C and S.[44]



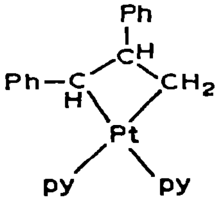


(28) OMe groups omitted

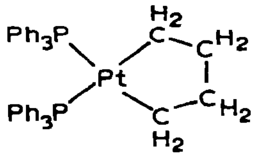
(29) Half of dimer

The reaction between HgPh$_2$ and PdCl$_2$(nbd) affords the *endo*-3-phenylnorbornen-2-yl-*endo*-palladium complex (29), probably via an intermediate σ-phenylpalladium complex which subsequently undergoes "*cis*-insertion".[45]

(c) *Metallocyclic complexes*. An area in which there is increasing interest as more examples are discovered, is the chemistry of complexes which contain a metallocyclic moiety. The complex PtCl$_2$(C$_3$H$_4$Ph$_2$)py$_2$(30), derived from 1,2-diphenylcyclopropane, contains a platinacyclobutane ring, although the attachment of the C_3 unit to the metal is best rationalised using a four-centre localised MO scheme.[46] There are two independent molecules: significant differences are found in the geometries. In one, the N-Pt-N angle is 92(1)°, with the plane of one of the Ph rings being perpendicular to the C_3 plane; in the second, the N-Pt-N angle is 82(1)°, with the planes of the C_3 and C_6 rings not being mutually perpendicular. Reaction of 1,4-dilithiobutane with *cis*-$PtCl_2(PPh_3)_2$ afforded the platinacyclopentane (31). The C_4Pt ring is puckered asymmetrically, a feature which is discussed in terms of possible intermediates in the olefin metathesis reaction.[47]

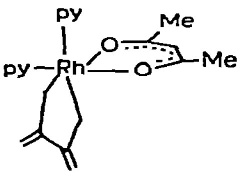


(30)

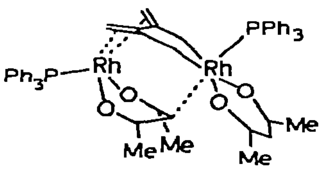


(31)

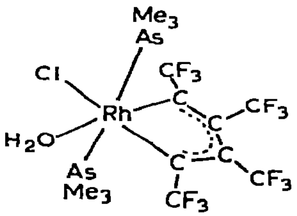
Rhodacyclopentane complexes have been obtained from allene and $Rh(acac)(C_2H_4)_2$; addition of pyridine to the unstable yellow complex so formed affords (32), which contains a chelating $CH_2C(=CH_2)C(=CH_2)CH_2$ group attached via σ bonds to the metal.[48] The first formed complex is unstable, and solutions slowly deposit an orange-red polymeric complex, which with PPh_3 affords the dimeric derivative (33). This complex contains a $Rh^{I}(acac)(PPh_3)$ group bonded to the two exocyclic methylene double bonds of the allene dimer unit which is σ bonded to the $Rh^{III}(acac)(PPh_3)$ unit. The latter also interacts with the electron pair on the central carbon atom of the $Rh^{I}(acac)$ group. Full details of the structure of $RhCl(H_2O)(AsMe_3)_2[C_4(CF_3)_4]$ (34) have appeared.[49] The fluorocarbon



(32)



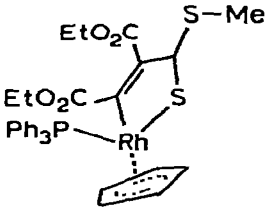
(33)



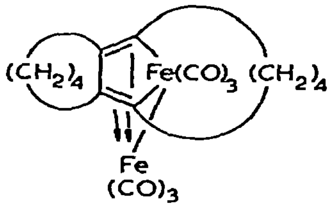
(34)

moiety exerts a strong *trans* influence on the Rh-Cl and Rh-O bonds. A heterocyclic five-membered metallo-ring complex of rhodium (35) has been obtained from the stepwise reaction between $(C_5H_5)Rh(PPh_3)_2$ and $C_2(CO_2Me)_2$, followed by CS_2.[50] Subsequent treatment of the product with iodomethane affords the methiodide, the structure of which was determined to confirm the presence of the $RhSC_3$ ring.

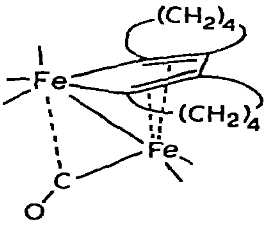
The reaction of 1,7-cyclododecadiyne with $Fe(CO)_5$ affords a major product, $C_{12}H_{16}Fe_2(CO)_6$, originally formulated as (36),[51] but shown by X-ray diffraction studies to be (36a).[52] In this, a major skeletal rearrangement has occurred involving fission of C-C bonds in a reaction probably related to the olefin metathesis reaction. One feature of interest in the structure is the CO group asymmetrically bridging the two iron atoms.



(35)

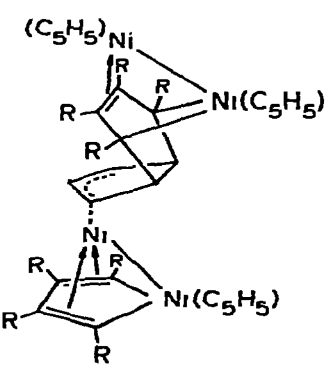


(36)



(36a)

The structure of $[(C_5H_5)Ni(CF_3C_2CF_3)]_4$(37)[one of the products obtained from $Ni(C_5H_5)_2$ and $C_2(CF_3)_2$] reveals the presence of four chemically distinct nickel atoms, and of h^1, h^2, h^3, h^4 and h^5 carbon donor units.[53] Unusual aspects of the structure include the bonding of a cyclohexene ring to a $[Ni(C_5H_5)]_2$ moiet



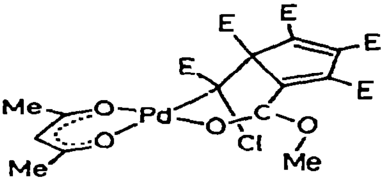
(37) $R=CF_3$

via a π-olefin and two C-Ni σ bonds, and the 1,2-addition of a C_4Ni unit to a cyclopentadienyl group.

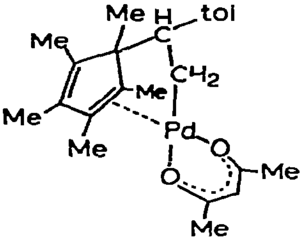
(d) *Compounds containing chelating σ-bonded groups*

The reaction between acetylenes and palladium complexes continues to be a source of complexes containing unusual structural features. Thus, the product from $PdCl_2(PhCN)_2$ and $C_2(CO_2Me)_2$, derivatised using acetylacetonate, has structure (38), in which the acetylene has oligomerised to a C_5 ring, chelated to the metal by a Pd-C σ bond, and the ester CO group.[54] A C_5 ring is also found in the product from $PdCl_2(NCPh)_2$, 2-butyne and $HgPh_2$ or $Hg(p\text{-tol})_2$; the structure of the p-tolyl product, again as the acetylacetonate (39), reveals chelation of the $C_5Me_5CH(p\text{-tol})CH_2$ group via a double bond and a Pd-C σ bond.[55]

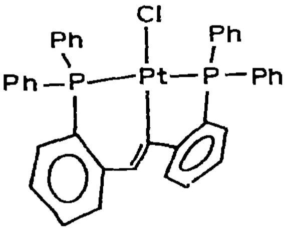
Metallation of 2,2'-bis(diphenylphosphino)stilbene occurs on reaction with halide derivatives of nickel, palladium or platinum, with elimination of HX. The chloroplatinum complex has structure (40), in which the ligand is metallated at an olefinic carbon atom.[56]



(38) E = CO_2Me



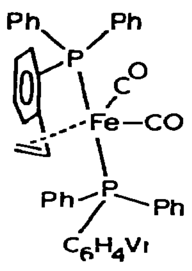
(39)



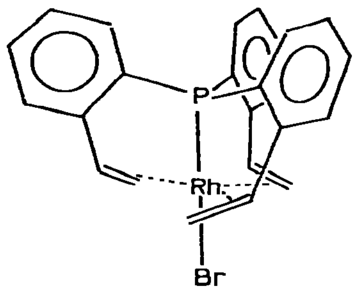
(40)

The stable iron(0) complex $Fe(CO)_2(sp)_2$(41) contains a chelating olefinic phosphine ligand, together with a second bonded through the phosphorus atom only.[57] Both phosphorus atoms occupy axial sites, the vinyl group being in an equatorial position. A related ligand, $P(C_6H_4Vi\text{-}o)_3$, acts as a tetradentate ligand in the rhodium complex (42); here also, the phosphorus atom occupies an axial site, with the three olefinic groups in equatorial positions.[58]

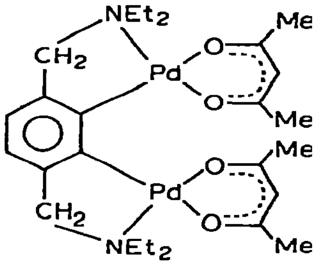
Crystal data for $3,6\text{-}C_6H_2(CH_2NEt_2)_2[Pd(acac)]_2$(43) have been reported.[59]



(41)



(42)



(43)

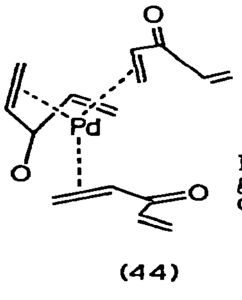
OLEFIN AND ACETYLENE COMPLEXES

In the system palladium-dibenzylideneacetone (dba), three complexes have been detected in the equilibria

$$\mathrm{Pd_2(dba)_3} \overset{\text{dba}}{\rightleftharpoons} \mathrm{Pd(dba)_2} \overset{\text{dba}}{\rightleftharpoons} \mathrm{Pd(dba)_3}$$

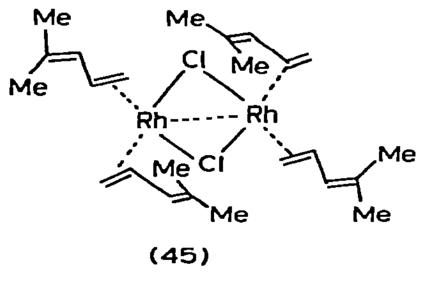
The structure of the binuclear complex was reported earlier (see Part 1), and that of the tris compound (44) later in the year.[60] Each dienone ligand is attached via one olefinic group, resulting in essentially trigonal coordination about the palladium.

The 4-methylpenta-1,3-diene complex $[\mathrm{RhCl(MeC_5H_7)_2}]_2$ (45), contains the diene attached to rhodium by only one of the two double bonds in each ligand, namely the less substituted one.[61] The $\mathrm{RhCl_2Rh}$ bridge is non-planar, as found for the complex $[\mathrm{RhCl(C_2H_4)_2}]_2$. The Rh-Rh separation is 3.090(3)Å, consistent with a weak interaction.



phenyl groups omitted

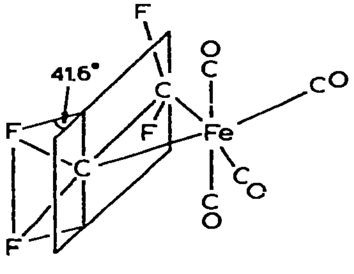
(44)



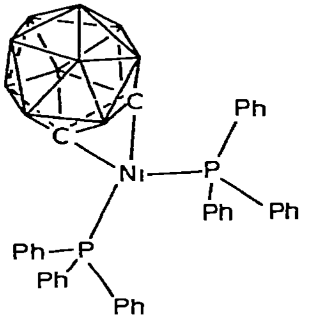
(45)

In $\mathrm{Fe(CO)_4(C_2F_4)}$(46), determined by gas-phase electron diffraction, the iron has distorted octahedral geometry, with the tetrafluoro ethylene occupying two adjacent equatorial sites[62] The C-C [1.530(15)Å] and Fe-C [1.989(10)Å] bond lengths, the angles involving the olefinic carbons [FCF, 111.3(1.1)°; CFeC, 104.2(1.4)°], and the supplement to the angle CCX(X=midpoint of vicinal F atoms)[41.6(1.1)°] all support a σ character for the Fe-C bonds.

The C-C bond involved in bonding to the nickel in $Ni(C_2B_{10}H_{10})(PPh_3)_2$(47), is shorter [at 1.57(3)Å] than the 1.64-1.67Å found in other *o*-carborane derivatives.[63]



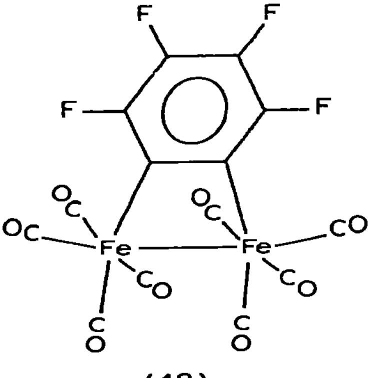
(46)



(47)

The anion in $PPh_4\{PtCl_3[Me_2C(OH)C_2C(OH)Me_2]\}$ has the expected square-planar structure, with the alkyne coordinated via the triple bond. The C and O atoms could not be distinguished. but there is no possible interaction between the OH groups and either the Pt or Cl atoms.[64]

The *o*-tetrafluorophenylene complex $C_6F_4Fe_2(CO)_8$(48) has been shown to be best formulated in this way, i.e. with two Fe-C bonds, and the Fe_2C_6 bicyclic



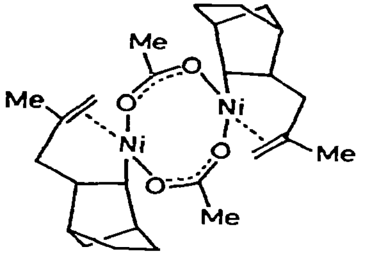
(48)

system coplanar, rather than the tetrafluorobenzyne derivative analogous to $(C_2R_2)Co_2(CO)_6$ complexes.[65]

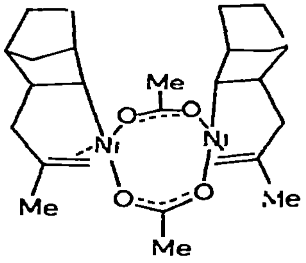
ALLYLIC AND DIENYL COMPLEXES

Two forms of di-μ-acetatobis[(2-methallyl-3-norbornyl)nickel] have been isolated and structurally characterised.[66-68] The orthorhombic form (49) is isostructural with the corresponding palladium complex,[69] and may be considered to be the transoid form, while the monoclinic crystal contains the cisoid isomer (50). As a result of the *trans* influence of the σ-bonded carbon, one of the acet groups in (50) is less strongly bonded.

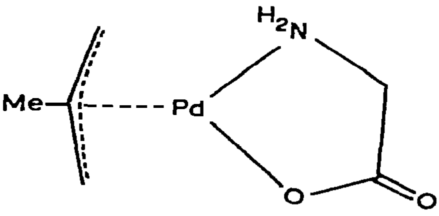
The unit cell of the aminoacid complex $Pd(C_4H_7)(gly)$ (51) contains two independent molecules differing only in the conformation of the glycinato moiety, which is planar in one, but twisted in the other.[70] The product of insertion of norbornadiene into the Pd-allyl bond of $Pd(C_4H_7)(dbms)$ has structure (52), in which the 2-methylallylnorbornenyl ligand chelates via the olefin and a Pd–C σ bond.[71]



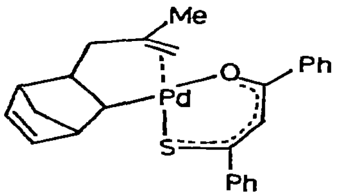
(49)



(50)

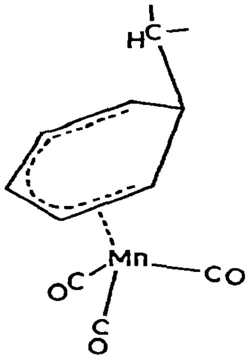


(51)



(52)

Nucleophilic attack of the anion $(CO_2Et)_2CH^-$ on $[Mn(CO)_3(C_6H_6)]^+$ affords the *exo*-substituted cyclohexadienyl complex (53). The C_6 ring is folded by 41°



(53)

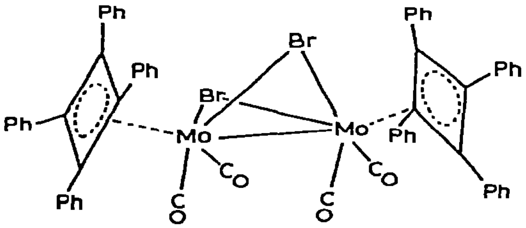
CO_2Et groups omitted

across the ends of the dienyl portion of the ligand.[72]

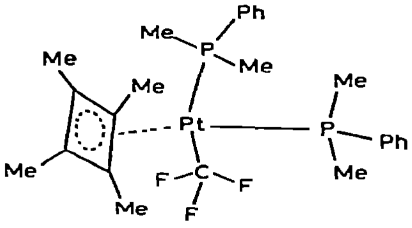
CYCLOBUTADIENE COMPLEXES

Dimeric $[MoBr(CO)_2(C_4Ph_4)]_2$ has structure (54), and contains a Mo-Mo bond, bridged by the two bromine atoms; the $MoBr_2Mo$ bridge unit is non-planar.[73]

Dimethylacetylene reacts with $[Pt(CF_3)(PMe_2Ph)_3]^+$ to give the cyclobutadiene derivative, $[Pt(CF_3)(C_4Me_4)(PMe_2Ph)_2]SbF_6$(55). The complex has a half-sandwich structure, with the C_4 ring being tilted away from the bulky phosphine ligands, and is best considered to be a platinum(II) complex with a distorted tetrahedral geometry.[74]



(54)

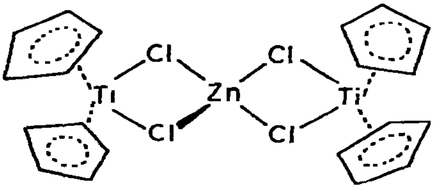


(55)

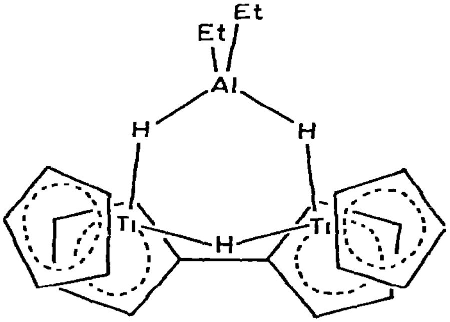
CYCLOPENTADIENYL COMPLEXES

Full details of the structure of $[ScCl(C_5H_5)_2]_2$ have been reported; two $Sc(C_5H_5)_2$ groups are linked by chlorine bridges.[75]

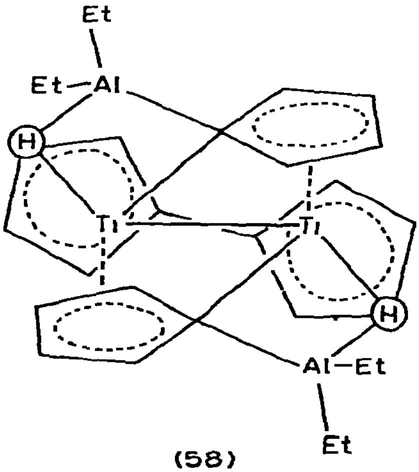
The structures of several cyclopentadienyl derivatives of titanium have been described. Green $Zn[Cl_2Ti(C_5H_5)_2]_2$, which forms a bis-benzene solvate, has structure (56), in which a central $ZnCl_4$ tetrahedron is linked along common Cl-Cl edges to two $TiCl_2(C_5H_5)_2$ tetrahedra, all somewhat distorted.[76] In the mixed complex $TiCl_2(C_5H_5)(C_5Me_5)$, the rings are staggered[77], although structural parameters are virtually the same as found in $TiCl_2(C_5H_5)_2$.[78] The aluminotitanium hydrides $[(C_5H_5)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)$ (57) and $[(C_5H_4)TiHAlEt_2]_2(C_{10}H_8)$ (58) both contain bridging h^5-C_5H_4-h^5-C_5H_4 ligands; the latter also contains an h^1:h^5-C_5H_4 ligand linking both titanium atoms.[79] The Ti-Ti distance (2.910Å) and the diamagnetism of (58) indicate the presence of a metal-metal bond in this complex. The relationship of (58) to "titanocene" (which is produced by hydrolysis), suggests a plausible structure for this



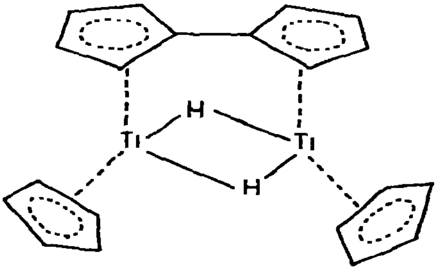
(56)



(57)



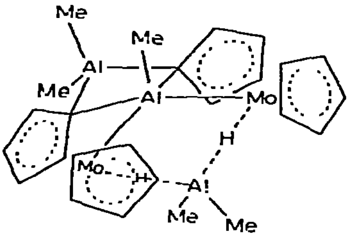
(58)



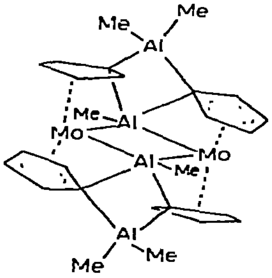
(59)

compound to be (59), as proposed originally by Brintzinger and Bercaw.[80]

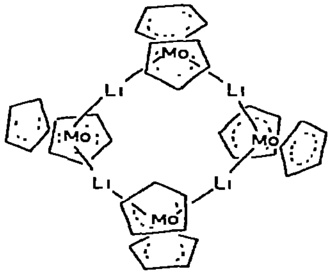
Related complexes containing molybdenum have been characterised recently. Excess $AlMe_3$ reacts with $MoH_2(C_5H_5)_2$ to give initially $[(C_5H_5)(C_5H_4)MoHAlMe_2]_2AlMe$ (60), and after prolonged refluxing, $[(C_5H_4)_2Mo(AlMe_2)(AlMe)]_2$ (61).[81] In both compounds, a planar Al-Me skeleton is bonded to two $Mo(C_5H_n)_2$ groups. In (60), two of the C_5 groups are bridged by aluminium, while in (61), all C_5 ligands are so bridged. Such groups are formulated as C_5H_4. Covalent Al-Mo bonds are also present. Using $LiBu^n$ in place of $AlMe_3$ in the initial reaction with $MoH_2(C_5H_5)_2$ afforded tetrameric $[(C_5H_5)Mo(H)Li]_4$(62), which contains an eight-membered $(MoLi)_4$ ring.[82] The geometry of the $Mo(C_5H_5)_2$ groups [Mo-Cp, 1.91Å; CpMoCp angle, 148°, compared with usual values of 1.96-1.99Å and *ca* 133°, respectively] is unusual, and the hydrogen atoms (not located, but indicated by ν(MoH) at 1847 cm^{-1}) are thought to be located one with each molybdenum atom.



(60)

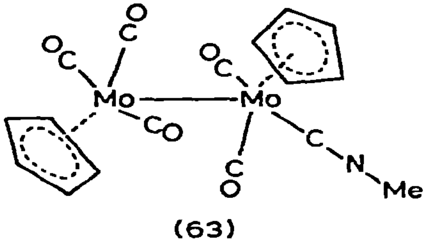


(61)



(62)

Intramolecular ligand scrambling in solutions of $Mo_2(CO)_5(CNMe)(C_5H_5)_2$ has been studied[83]; in the solid state, only the trans rotamer of the *trans* form (63) is found. Most structural features resemble those found in the unsubstituted $[Mo(CO)_3(C_5H_5)]_2$.

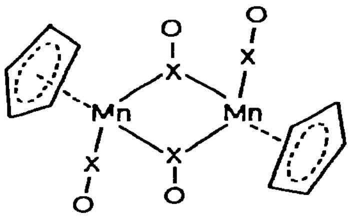


(63)

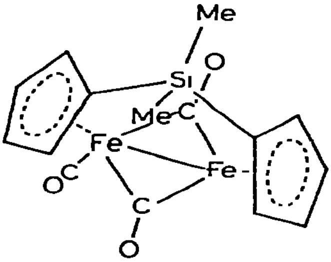
References p. 259

A detailed comparison of solution and solid state structural properties of the three isoelectronic complexes $[(C_5H_5)Cr(NO)_2]_2$, $[(C_5H_5)Mn(CO)(NO)]_2$ and $[(C_5H_5)Fe(CO)_2]_2$ was rendered possible by the structure determination of the manganese derivative (64).[84] Both bridging and terminal CO and NO ligands are disordered; the C_5 rings are *trans*. In the series, as the metal covalent radius increases, the M-M distance decreases [Cr, 2.615(1); Mn, 2.571(1); Fe, 2.534(2)Å].

The two cyclopentadienyl groups in $Fe_2(CO)_4(C_5H_4)_2SiMe_2$ (65) are linked by a silicon atom, which is displaced from the $Fe_2(CO)_2$(terminal) plane.[85] The Fe-Fe bond is bridged by two CO groups, with the Fe_2C_2 ring being folded along the Fe-Fe axis at *ca* 160°.



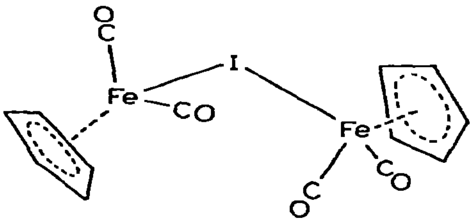
(64) X = disordered C,N



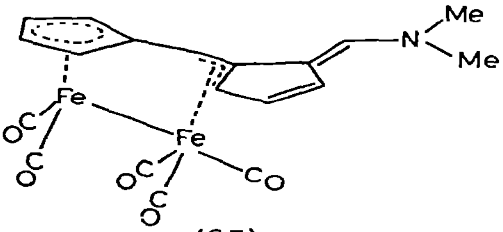
(65)

The structure of the cation in $[(C_5H_5)Fe(CO)_3]PF_6$ has been determined.[86] Comparisons show that Fe-C distances are longer, and C-O distances are shorter, than in neutral species, and that C-O distances are also shorter than in the isoelectronic $(C_5H_5)Mn(CO)_3$. There is a 12° rotation of the $M(CO)_3$ moiety about the $M(C_5H_5)$ axis, relative to the C_5 ring. The cation in $\{[(C_5H_5)Fe(CO)_2]_2I\}BF_4$ (66) contains conventional $Fe(CO)_2(C_5H_5)$ groups bonded to iodine [Fe-I distance, 2.588Å; angle FeIFe, 110.8(1)°]. The large angle probably results from the steric demands of the bulky iron complex groups in opposition to the tendency of iodine to form bonds at 90°, thereby maximising *p* character in its bonding orbitals[87]. Full details of the preparation and structure of $[Fe(CO)(\mu\text{-}COAlEt_3)(C_5H_5)]_2$ are now available.[88]

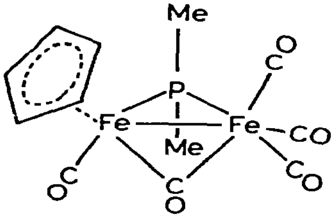
Small yields of the dinuclear pentacarbonyl (67) were obtained from



(66)



(67)



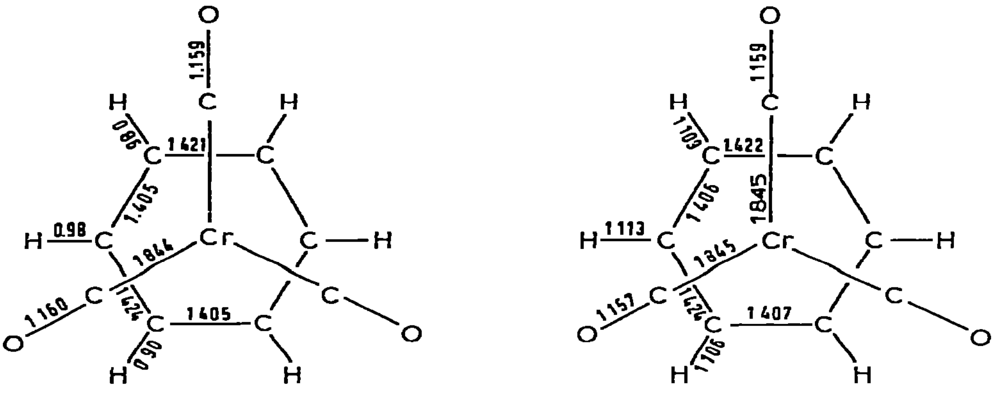
(68)

$Fe_2(CO)_9$ and 6-dimethylaminofulvene.[89] The complex contains a metal-metal bond; the two metal atoms are linked to an h^5-C_5 ring, and an exocyclic allylic group. Photolysis of $Me_2P[Fe(CO)_4][Fe(CO)_2(C_5H_5)]$ affords the pentacarbonyl (68), in which the Fe-Fe bond is bridged by CO and PMe_2 groups.[90]

ARENE COMPLEXES

Another contribution to the long-standing controversy over the symmetry of the complexed benzene ring in arene-chromium complexes is the report of the low temperature (78K) X-ray and neutron diffraction study of $Cr(CO)_3(C_6H_6)$ by Rees and Coppens.[91] Although the symmetry of the isolated molecule is C_{3v}, that of the benzene ring was determined to be D_{6h} in a room-temperature study. In $Cr(C_6H_6)_2$, the symmetry of the benzene rings was also finally determined to be D_{6h} by a variety of physico-chemical studies (X-ray diffraction, electron diffraction, i.r., thermodynamic studies).

Bond lengths and angles at 78K (corrected for thermal motion) are illustrated (69), and clearly the symmetry of the benzene is C_{3v}. Bonds intersecting the projections of the Cr-C-O bonds on the benzene plane (*cis*) are longer (av. 1.423Å) than those which do not (*trans*)(av. 1.406Å). The *cis* bonds do not differ significantly from those found in $Cr(C_6H_6)_2$, while



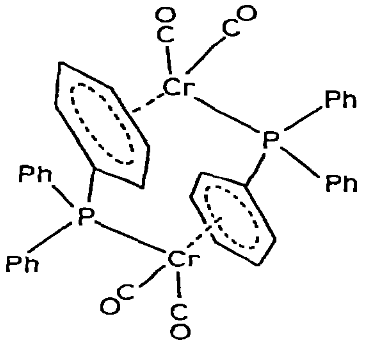
X-ray Neutron

(69) Bond lengths at 78°K, corrected for thermal motion

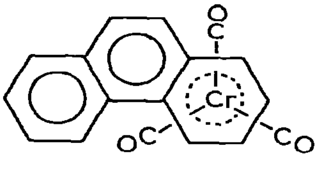
the *trans*bonds are 0.007Å longer than those in uncomplexed benzene. The hydrogen atoms are displaced by 0.03Å from the C_6 ring plane towards chromium. X-ray-neutron (X-N) difference density contours revealed overlap densities in the Cr-C,C-C,C-O and C-H bonds, and also the oxygen lone pairs; the Cr-C(O) peaks are nearer the carbon atoms, as predicted by theory. In addition, large residual density features near the metal nucleus are found, but cannot be explained at present.

An unusual example of a substituted benzene-chromium carbonyl complex is $[Cr(CO)_2(h^6-C_6H_5)PPh_2]_2$(70), in which the two chromium atoms are bridged by the two PPh_3 ligands.[92] Each is involved in P-bonding to one chromium, with one C_6H_5 group being h^6-bonded to the second metal atom.

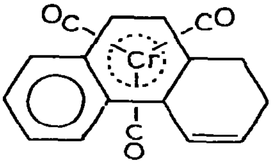
Reactions of $Cr(CO)_3(NCMe)_3$ with dehydro[14]annulene afford the $Cr(CO)_3$ complexes of the valence isomer, 1,4-dihydrophenanthrene (71), and of phenanthrene (72).[93] The latter formed a monoclinic polymorph, also described by Deuschl and Hoppe,[94] and compared with the orthorhombic form.[95] Bonding to the central ring in (71) is presumably a result of concentration of electron density in the C(9)-C(10) and C(11)-C(12) bonds by the cyclohexadiene fragment. The valence isomer of [14] annulene, *trans*-6a,12a-dihydrooctalene, is obtained coordinated to two $Cr(CO)_3$ moieties (73) when the annulene reacts with $Cr(CO)_3(NH_3)_3$. The chromium is bonded asymmetrically to the six carbon atoms.



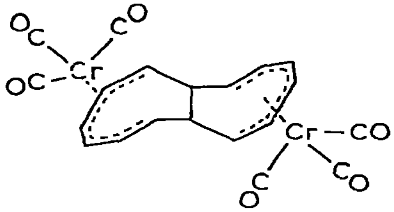
(70)



(71)



(72)



(73)

A systematic error apparently contributes to the central C-C bond length of 1.24Å: the vibration-corrected value is 1.48(4)Å.

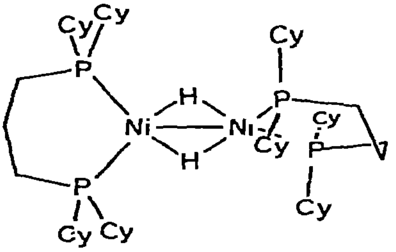
The structure of $Ru(C_6H_6)(C_6Me_6)$ illustrates a description of a general Fourier programme for X-ray crystal structure analysis utilising the Cooley-Tukey algorithm.[96] The unsubstituted C_6 ring is symmetrically bonded (h^6), while the hexamethylbenzene is attached in the 1,2,3,4-h^4 mode.

SOME NICKEL COMPLEXES FROM THE MÜLHEIM GROUP

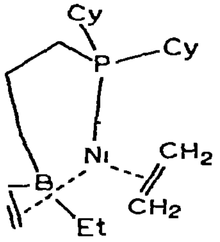
In the Karl Ziegler memorial issue of *Angewandte Chemie*, several articles by members of the Wilke's group at the MPI, Mülheim, contain structural diagrams of relevant nickel complexes. These contain a variety of interesting and unusual structural features, some of which are described below.

(a) Di-μ-hydridobis[trimethylenebis(dicyclohexylphosphine)nickel](74): contains a Ni-Ni bond bridged by two hydrogens (located during the analysis).[97]

(b) Ethylene[ethyl(vinyl)borylpropyldicyclohexylphosphine]nickel(75): formed in a reaction between Ni(cdt), C_2H_4, and $Et_2B(CH_2)_3PCy_2$, via $Ni(C_2H_4)_3$,



(74)



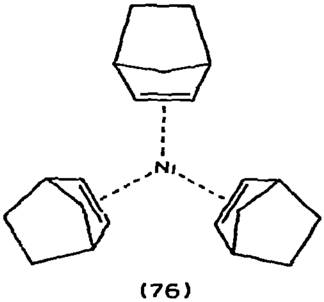
(75)

which reacts in a synchronous process whereby a hydrogen of a complexed C_2H_4 is transferred to the B-ethyl group, liberating ethane and forming a B-vinyl system.[98]

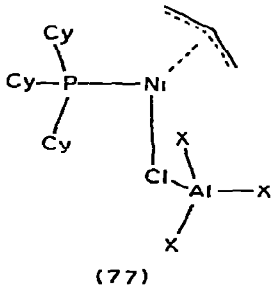
(c) Tris(bicycloheptene)nickel (76): related to the $Ni(C_2H_4)_3$ intermediate (above), in which the nickel is attached *exo* to the bicycloheptene double bond.[99]

(d) Tricyclohexylphosphine(allyl)nickel-μ-chloro-methyldichloroaluminium (77): related to catalysts used in asymmetric syntheses, although the allyl groups are lost in the first stages of the reactions.[100]

(e) Methyl(1-methyl-2-butenyl)-(-)-dimenthyl(methyl)phosphine nickel (78): the absolute configuration of this optically active complex was used to attempt a correlation between the absolute configuration of the phosphine and the optically active product (vinylnorbornane) from the norbornene-ethylene codimerisation reaction.[101]

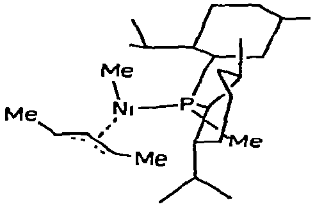


(76)



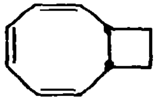
(77)

X = Cl,Me disordered

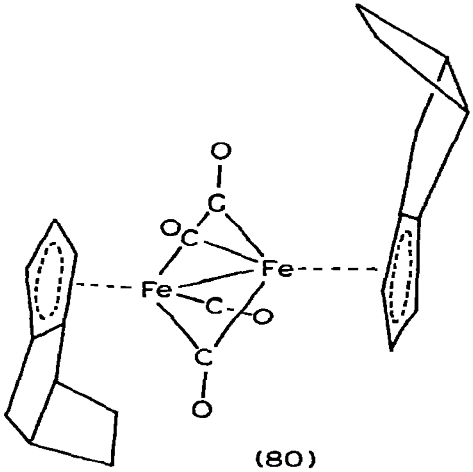


(78)

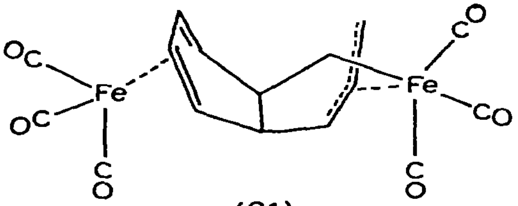
The structures of two of the products from reactions between $Fe_2(CO)_9$ and *cis*-bicyclo[6.2.0]deca-2,4,6-triene (79) have been reported in detail. The first, $[(C_{10}H_{11})Fe(CO)_2]_2$ (80), contains *h*^{5}-tricyclo[6.2.0.0^{2,6}]deca-2,4-dien-6-yl ligands.[102] Structural parameters are nearly identical with those found for *trans*-$[(C_5H_5)Fe(CO)_2]_2$. The second product, $(C_{10}H_{12})Fe_2(CO)_6$ (81), has an unusual structure containing a diene-$Fe(CO)_3$ group, an allyl-$Fe(CO)_3$ group and an Fe-C σ bond resulting from rearrangement and C-C bond cleavage in the original hydrocarbon.[103] No metal-metal bond is formed. The $Fe(CO)_3$ adduct of tricyclo[6.3.0.0^{2,7}]undeca-3,5-diene has structure (82), and is essentially a substituted 1,3-butadiene-$Fe(CO)_3$; eleven related structures containing this unit are compared.[104] The rings are fused *cis*, while the 5- and 6-membered rings have an *anti* relationship relative to the central planar 4-membered ring.



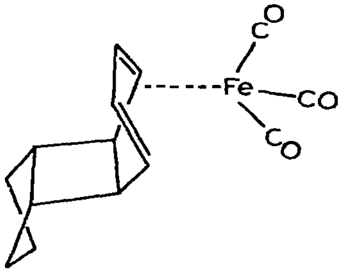
(79)



(80)



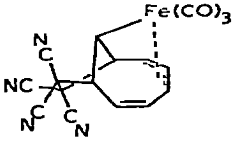
(81)



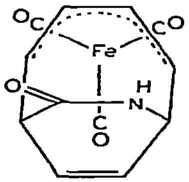
(82)

The mechanisms of cycloaddition to $(C_8H_8)Fe(CO)_3$ have often been postulated on the basis of unproven structures. For example, tetracyanoethylene was variously supposed to react via 1,2-, 1,3- or 1,4-addition. The structure of the adduct (83) shows that in fact 1,3-addition has occurred, giving a product in which the organic ligand is attached via h^3-allyl and h^1-carbon σ bonds. In contrast, addition of chlorosulphonyl isocyanate occurs 1,4, and after dechlorosulphonylation (PhSH and pyridine in cold acetone), the diene-$Fe(CO)_3$ complex (84) is obtained. Both products result from stereospecific attack of $(C_8H_8)Fe(CO)_3$ from its less hindered side.[105]

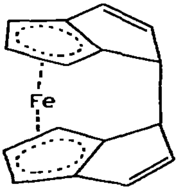
Bis(pentalenyl)iron(85) has a ferrocene-type structure, in which the two h^5-cyclopentadienyl rings are bridged by two carbon atoms, dimerisation of pentalene via 1-*endo*, 1'-*endo* carbon-carbon bond formation having occurred.[106] The short bridge bond [although significantly longer than a normal C(sp^3)-C(sp^3) bond, at 1.568(7)Å] results in tilting of the cyclopentadienyl rings (dihedral angle, 23.6°). The rotational angle is ∿10°, i.e. the ferrocene moiety is closer to eclipsed than staggered conformation. Reaction of *cis*-$Ru(GeMe_3)_2(CO)_4$ with cyclooctatetraene affords the pentalene complex (86), in which the bicyclic hydrocarbon is non-planar, and the Ge-Ru-Ru-Ge sequence is non-linear. The pentalene is attached to the two ruthenium atoms via two h^3-allyl units, and a four-electron multicentre interaction.[107]



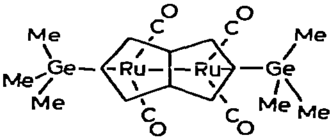
(83)



(84)



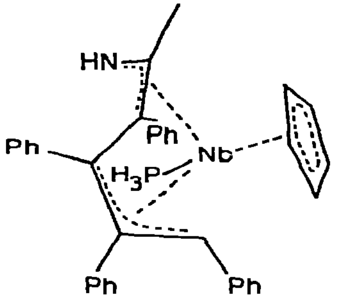
(85)



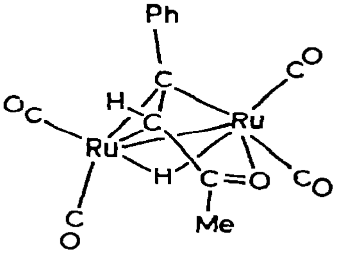
(86)

π-BONDED HETEROATOM LIGANDS

(a) *Acyclic groups*. The unusual complex $(C_5H_5)Nb(PH_3)[HCPh(CPh)_3C(:NH)Me]$(87) has been isolated from the photochemical reaction of $(C_5H_5)Nb(CO)(C_2Ph_2)_2$ with acetonitrile.[108] The acyclic ligand is formed by condensation of two C_2Ph_2



(87)

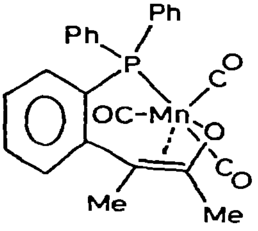


(88)

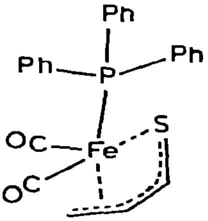
molecules with MeCN, and is a six-electron donor, formulated as an azaallylallyl ligand. The PH_3 is supposed to arise from the action of water on technical grade P_2O_5.

Benzylideneacetone reacts with $Ru(CO)_3(cod)$ to give the binuclear hydrido-complex $Ru_2H(CO)_6(C_{10}H_9O)$(88), in which the organic ligand is a 5-electron donor; the central C=C.C=O portion of the molecule is attached to one ruthenium via a π-olefinic bond, and to the other by an Ru-C σ bond, and an Ru-O dative σ bond.[109]

A similar interaction of an enone with manganese is found in the oxapropenyl complex (89) obtained from $MnMe(CO)_5$ and *o*-$ViC_6H_4PPh_2$.[110] The formation of (89) results from attack of an acylmanganese intermediate at the vinyl group of the phosphorus ligand, accompanied by hydride migration. A detailed comparison of the geometries of π-allyl and π-oxapropenyl systems is included.



(89)

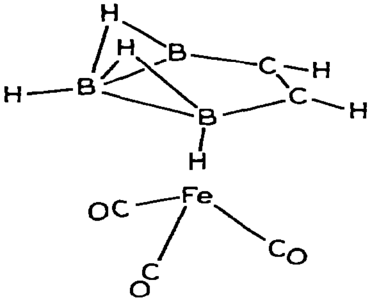


(90)

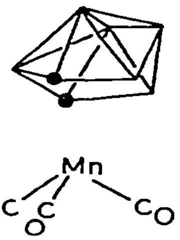
Opening of the thiete (thiacyclobutane) ring occurs on reaction with $Fe_2(CO)_9$ affording the thioacrolein derivative $[(C_3H_4S)Fe(CO)_3]_2$, which with

PPh_3 gives the monomeric complex (90)[111,112] The planar sulphur ligand acts as a four-electron donor (heterodiene).

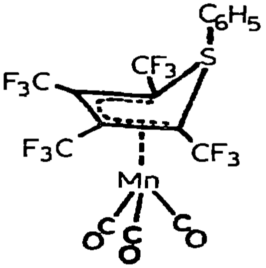
(b) *π-Complexed heterocycles.* The metallocarborane $(B_3C_2H_7)Fe(CO)_3$ (91), studied at −160°, contains a formally dianionic carborane ligand bonded to a dipositive $Fe(CO)_3$ moiety.[113] The anion in $PPh_3Me[(B_6C_2H_8)Mn(CO)_3]$(92) contains an $Mn(CO)_3$ group bonded to the B_6C_2 cage; the geometry of the MnB_6C_2 fragment is a tricapped trigonal prism.[114] Stabilisation of dihydropyridines by complex formation with $Cr(CO)_3$ groups has been achieved, and the structures of the 3-ethyl- and 5-ethyl derivatives have been reported in detail.[115] In both, the chromium interacts with the ring via the nitrogen lone pair, and the two double bonds. The major difference between the two structures in the location of the terminal ethyl carbon, either on the same side (3-isomer) or the opposite (5-isomer) to the chromium atom [see diagrams (76) and (77), AS 73-1].



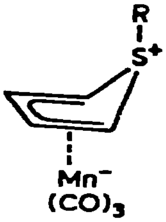
(91)



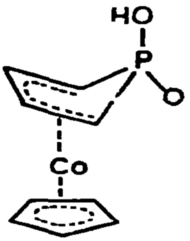
(92) Black circles = C



(93)



(93a)



(94)

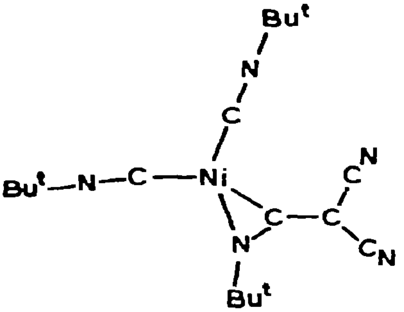
The reactions of $C_2(CF_3)_2$ with $[Mn(CO)_4SC_6F_5]_2$ and $(C_5H_5)Co(PF_3)_2$ have afforded the heterocyclic complexes (93) and (94), respectively.[116] In both, the heterocyclic rings have envelope conformations, the four carbon atoms in each being coplanar. Formally, the manganese complex is a sulphonium derivative [zwitterion structure (93a)]. The oxygen atoms in (94) result from hydrolysis of the $(C_4F_6)_2PF_3$ derivative initially formed.

THREE- AND FIVE-MEMBERED RINGS

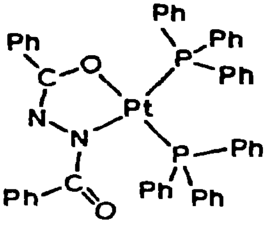
The full details of the structure of $[MoS(SCNPr^i_2)(S_2CNPr^i_2)]_2$, in which one dithiocarbamate ligand has been cleaved to give a thiocarboxamide group, are available.[117] The short Mo-C bond (2.069Å) suggests a Mo-C interaction related to that in $Pt(CS_2)(PPh_3)_2$. A strong Mo-Mo bond is also present.

Comparisons of the structure of $Ni(Ph_2N_2)[P(p\text{-tol})_3]_2$ with the analogous t-butyl isocyanide complex indicate the NiN_2 interaction is weaker in the phosphine complex.[118] Although the two N=N distances do not differ significantly [1.371(6)Å (phosphine), 1.385(5)Å (isocyanide)], the dihedral between the two C(Ph)NN planes is less in the phosphine derivative [23.5(3)° *vs* 26.8(4)°].

The ketenimine complex $Ni[Bu^tN{=}C{=}C(CN)_2](CNBu^t)_2$ (95) is probably formed via a metal-assisted carbene addition to coordinated isocyanide from the diazodicyanomethane complex, $Ni[N_2C(CN)_2](CNBu^t)_2$. The ketenimine is coordinated via the $N{=}C(CN)_2$ bond, resulting in the cumulene system being non-linear [angle N=C=C, 144.2(4)°].[119]



(95)



(96)

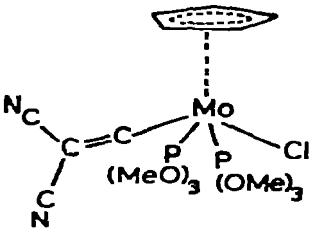
The dibenzoylhydrazine complex $Pt(PhCONNCOPh)(PPh_3)_2$ (96) contains a five-membered $\overline{PtOCNN}$ ring, with an envelope conformation,[120] instead of the symmetrically bonded diaroyldiazene ligand originally proposed.[121] The N-N bond distance [1.401(9)Å] is indicative of a single bond, although comparison with the bond length in a copper(I) complex (1.436Å) suggests that some degree of multiple bond character still remains.

COMPLEXES CONTAINING OTHER DONOR-ATOM LIGANDS

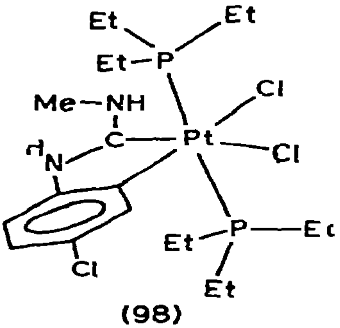
(a) *Carbene complexes*

The complex $(C_5H_5)Mo[C{=}C(CN)_2][P(OMe)_3]_2Cl$ (97) contains a terminal dicyanovinylidene (or dicyanomethylene carbene) ligand, related to CO by substitution of oxygen by $C(CN)_2$. The two phosphite ligands occupy mutually *trans* positions in the tetragonal plane. The Mo-C(carbene) bond length [1.833(6)Å] supports the idea that this ligand is a stronger π-acceptor than CO (typical distances, 1.93-1.99Å).[122]

Several platinum-carbene complexes have been studied. The cation in *trans*-$[PtMe\{CMe(OMe)\}(PMe_2Ph)_2]PF_6$ contains square-planar platinum, with the carbene ligand in the *trans* configuration.[123] The carbene is disordered, two ligands related by a 180° rotation about an axis Pt-C(Me). Chlorination of *trans*-$[PtCl\{C(NHMe)(NHPh)\}(PEt_3)_2]ClO_4$ affords the internally metallated complex (98).[124]



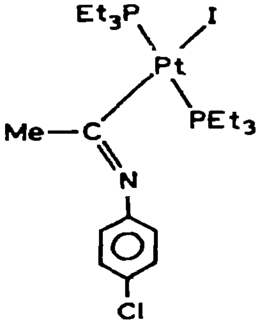
(97)



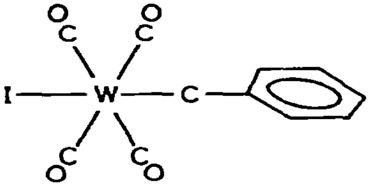
(98)

The acylimino complex *trans*-$PtI[C(Me){=}NC_6H_4Cl\text{-}p](PEt_3)_2$ (99), formed by "insertion" of isocyanide into the Pt-Me bond, has the four-coordinate structure shown, there being no interaction of the imine lone-pair with the metal.[125]

The unusual carbyne complex *trans*-WI(CO)$_4$(CPh)(100) has a pseudo-octahedral structure.[126] The W-C(carbyne) and W-CO distances are 1.88(10) and 2.14(10)Å, respectively.



(99)

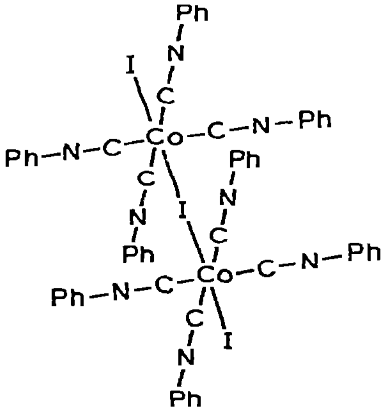


(100)

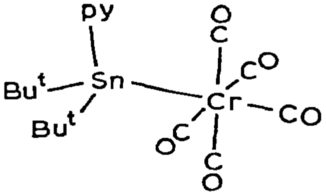
(b) *Other Group IV donor ligands*

A linear Co-I-Co bridge has been found in the diamagnetic form of CoI$_2$(CNPh)$_4$, which proves to contain the dimeric cation (101).[127] The Co-I distances are unusually long: terminal, 2.766(3); bridging, 2.890(2); sum of covalent radii, 2.65Å.

The di-t-butylstannylene complex Bu$^t_2$(py)SnCr(CO)$_5$ (102) contains unusually coordinated tin.[128] The Sn-C distances are long (at 2.24Å) compared to Me$_3$SnMn(CO)$_5$, and the Sn-Cr bond length is 2.654(3)Å. The bond angles



(101)



(102)

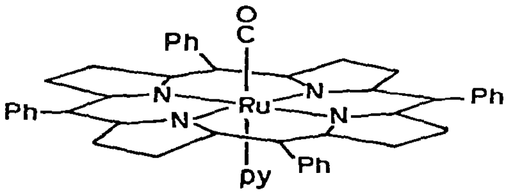
correspond to a situation intermediate between a planar $SnCrC_2$ group (with pyridine perpendicular) and a tetrahedral $SnCrC_2N$ group.

(c) *Nitrogen-donor ligands*

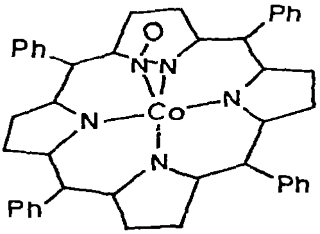
Porphyrin derivatives. In Ru(CO)(py)(TPP)(103), the metal atom lies 0.079Å out of the porphyrin plane on the CO side.[129] The *trans* effect of the CO group results in a long Ru-N distance [2.193(4)Å], compared to the Ru-N(porphy bond [2.052(9)Å]. Structural parameters for the porphyrin ring agree with those found for Ru(CO)(EtOH)(TPP).[130]

The nitrosylcobalt porphyrin, Co(NO)(TPP) (104), has a square pyramidal structure, with a bent NO group [angle Co-N-O, 135.2(8)°]. The molecule is disordered in the crystal. The metal atom is estimated to lie 0.094(52)Å above the porphyrin plane.[131]

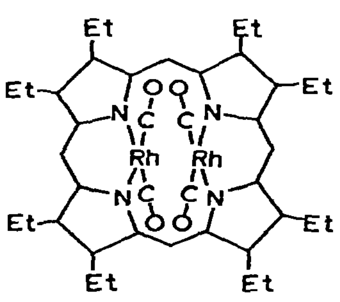
The dinuclear μ-OEP[$Rh(CO)_2]_2$ (105) contains the two metal atoms above and below the porphyrin plane, both having square-planar coordination. Oxidation in $CHCl_3$ affords the rhodium(III) complex, in which only one metal atom is associated with the porphyrin.[132]



(103)

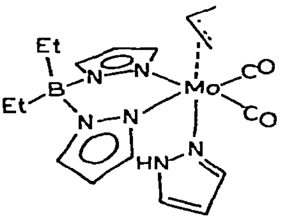


(104)

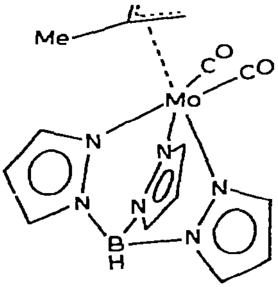


(105)

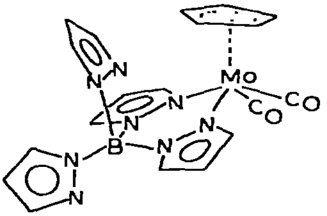
Poly(pyrazolyl)borate complexes. The structure of $Mo[Et_2B(pz)_2](C_3H_5)(CO)_2(Hpz)$ (106) was determined during attempts to study $Mo[Et_2B(pz)_2](C_3H_5)(CO)_2$.[133] The uncoordinated pyrazole nitrogen lies on the pyrazolylborate side of the molecule; the two CO groups are *trans* to the two pyrazolylborate nitrogens. The MoN_2BN_2 ring has a distorted chair conformation, in contrast to examples previously studied. No unusual features were found in the structures of $Mo[HB(pz)_3](CO)_2(C_4H_7)$ (107);[134] in $Mo[B(pz)_4](CO)_2(C_5H_5)$ (108), two of the four pyrazolyl rings are uncoordinated.[135] In both cases, the CO groups lie *trans* to coordinated nitrogens. The results of the present study of (107) correct a previous assignment of C and N atoms in one ring.[136]



(106)

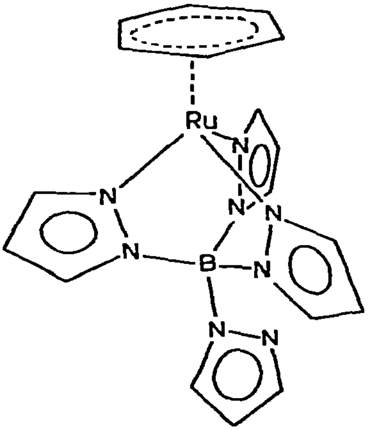


(107)

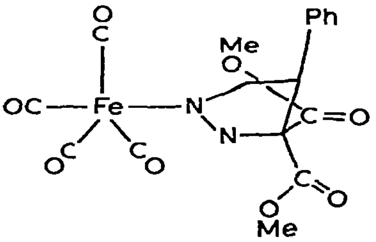


(108)

The mixed sandwich cation $\{(C_6H_6)Ru[B(pz)_4]\}PF_6$ (109) contains an h^6-benzene ligand, while the $B(pz)_4$ group is only tridentate.[137] The hydrocarbon ring is fully staggered with respect to the pyrazolylborate group.



(109)



(110)

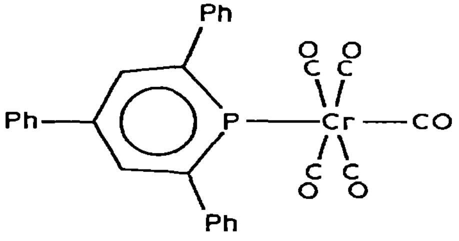
The structures of the cobalt derivatives, $Co[H_2B(pz)_2]_2$ (distorted tetrahedral)[138] and $Co[HB(pz)_3]_2$ (trigonally-distorted octahedral)[139] have been determined, and are of interest insofar as they represent examples of complexes containing pyrazolylborate ligands.

Miscellaneous. The geometry of the parent pyrazoline ligand is not altered on complexation to an $Fe(CO)_4$ moiety in (110), where it occupies an apical position.[140]

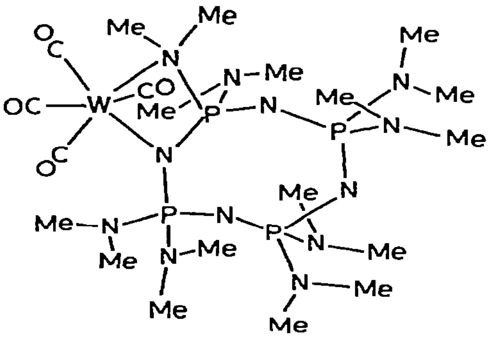
(d) *Phosphorus-donor ligands*

The structure determination[141] of 2,4,6-triphenylphosphorin-$Cr(CO)_5$ (111) complements that of the π-bonded tricarbonyl reported earlier.[142] The Cr-P bond is short [2.372(4)Å], and is inclined to the ring plane by 8°. The phosphorin ring is planar.

The eight-membered phosphonitrilic ligand in $P_4N_4(NMe_2)_8W(CO)_4$ (112) is coordinated via a ring nitrogen and an exocyclic N-NMe_2 nitrogen in *cis* positions to a distorted octahedral tungsten atom. Coordination results in changes from the near-saddle geometry of the uncomplexed ligand, to a ligand consisting of two nearly planar segments, with unequal ring bonds.[143]



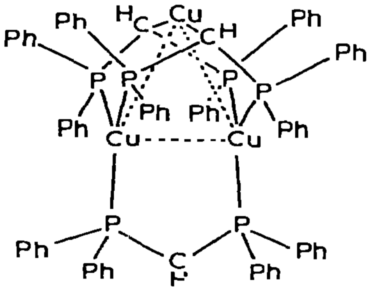
(111)



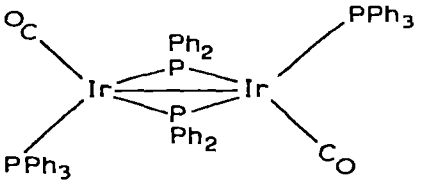
(112)

Reactions between arylcoppers and bis(diphenylphosphino)methane afford the arene and an unusual copper-phosphine complex, characterised structurally as $[Cu(Ph_2PCHPPh_2)]_3$ (113).[144] In this, one copper is attached to the methine carbons of two ligands which bridge the other two copper atoms by conventional P-Cu σ donor bonds. The three metal atoms thus form an isosceles triangle [basal Cu-Cu, 2.836(4); side Cu-Cu, 3.146(3) and 3.112(4)Å]. The structural non-equivalence of the copper atoms suggests a formulation [$Cu(Ph_2PCHPPh_2)_2.Cu_2(Ph_2PCHPPh_2)$], containing formally bi- and half-valent copper atoms. The complex can also be obtained from CuBr and $LiCH(PPh_2)_2$.

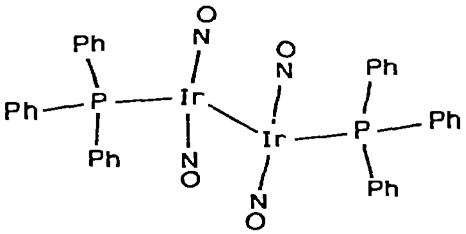
Pyrolysis of hydrido-iridium phosphine complexes in dimethylformamide affords $[Ir(CO)(PPh_3)(PPh_2)]_2$ (114), in which the Ir-Ir bond [2.551(1)Å] has a formal order of two.[145]* The structure is related to that of $[Ru(NO)(PMePh_2)(PPh_2)]_2$, full details of which have now been published,[146] and in which the Ru-Ru bond distance [2.629(2)Å] is also consistent with a double-bond. In $[Ir(NO)_2(PPh_3)]_2$ (115), the Ir-Ir bond has a normal single bond length [2.717(1)Å].[147] Apart from the shorter Ir-P distance in (115), all other structural parameters are comparable with those found in $[Ir(NO)_2(PPh_3)_2]^+$.[148]



(113)



(114)



(115)

Comparison of the structures of $[M(CO)_4(PEt_2)]_2$ (116; M=Mo or W) reveals

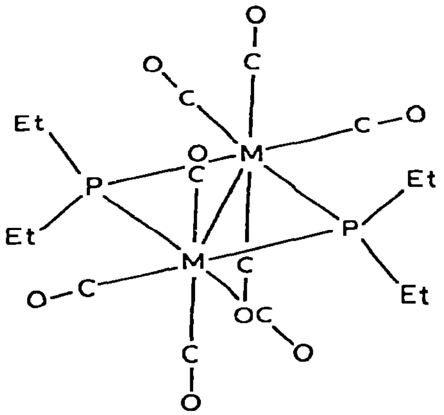
---

* See also the earlier report: R. Mason, L Søtofte, S.D. Robinson and M.F. Uttley, *J.Organometallic Chem.*, 46 (1972) C61.

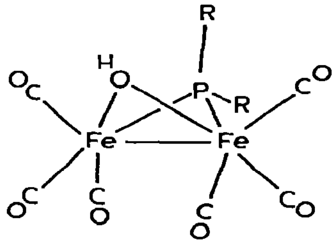
similar structural parameters for the M_2P_2 rings, with metal-metal bond lengths of *ca.* 3.05Å.[149]

A complex originally described as $Fe_2H(CO)_6[P(p\text{-}tol)_2]$ has been shown to contain a bridging hydroxy group (117), with an overall geometry typical of $Fe_2(CO)_6X_2$ complexes.[150] The two Fe–O distances are 1.969(6) and 1.974(6)Å.

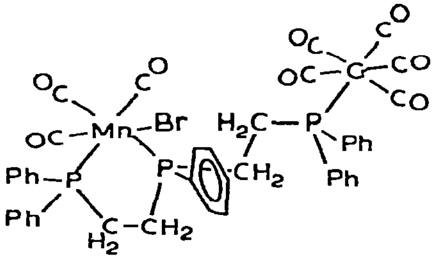
Two isomers of $Br(CO)_3Mn(triphos)Cr(CO)_5$ [triphos = $PhP(CH_2CH_2PPh_2)_2$] result from the phenyl ring attached to the central phosphorus atom being *trans*[α,(118)] or *cis*[β,(119)] to the bromine relative to the five-membered chelate PCCPMn ring. The chromium is bonded to the $-CH_2PPh_2$ group in both complexes.[151]



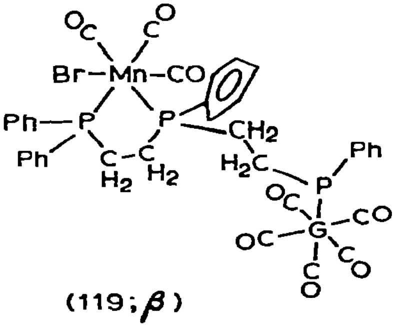
(116)



(117) R = *p*-tol

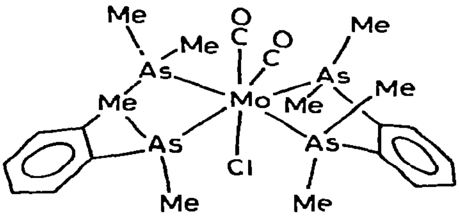


(118; *a*)



(119; *β*)

The structure of $Co(CO)_2(NO)(AsPh_3)$ has been reported[152]; the cobalt is approximately tetrahedrally coordinated, and the NO and CO groups are disordered. The complex cation in $[MoCl(CO)_2(diars)_2]I_3$ (120) forms a capped trigonal prism, with Cl in the capping position, and four arsines occupying the capped quadrilateral face.[153] Some comparisons with the coordination geometry in [Mo(CNBu^t)$_6$I]$^+$ are made.

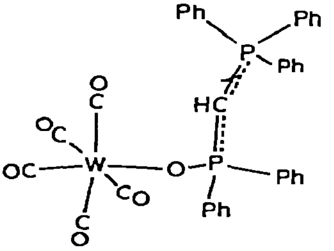


(120)

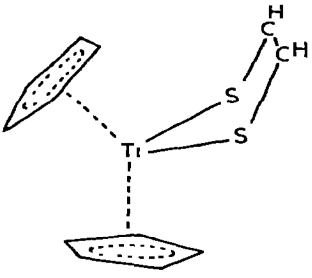
(e) *Group VI donor ligands*

The hydrolysis product of the complex obtained from W(CO)$_5$(THF) and Ph$_3$P:C:PPh$_3$ contains the Ph$_3$PCHP(O)Ph$_2$ ligand bonded to tungsten through oxygen (121).[154] The multiple bond is equally distributed over the two P-C bonds [1.690(10)Å], resulting in a longer P-O bond [1.523(8)Å] than in Ph$_3$PO. The W-O bond distance is 2.199(7)Å.

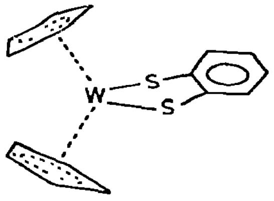
In (C$_5$H$_5$)$_2$TiS$_2$(CH)$_2$ (122), the TiS$_2$ plane is folded out from the S$_2$C$_2$H$_2$ plane by 46.1°. The C$_5$ rings are staggered, with their planes intersecting at an angle of 51.2°.[155] In the tungsten complex (C$_5$H$_5$)$_2$WC$_2$C$_6$H$_4$ (123), the sulphur ligand is folded by 8°.[156]



(121)

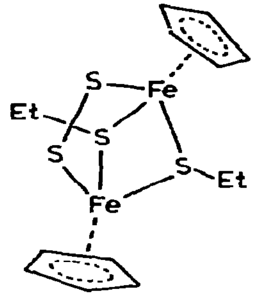


(122)



(123)

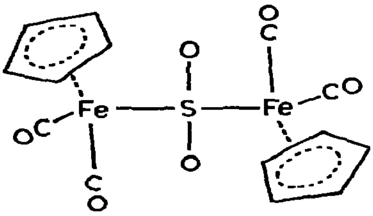
The complex [(C$_5$H$_5$)Fe(SEt)S]$_2$ (124) has been considered as a model compound for ferredoxin. The two iron atoms are joined by a planar Fe-S-S-Fe bridge, and by bridging SEt groups, but do not directly interact.[157]



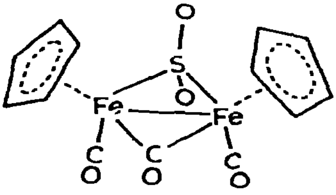
(124)

The Me_3PS ligand in $Cr(CO)_5(SPMe_3)$ acts as a simple S σ-donor ligand, with a Cr-S distance of 2.510(2)Å; its *trans* influence is reflected in the Cr-CO(*trans*) and Cr-CO(*cis*) bond lengths of 1.815(8) and 1.900(4)Å respectively.[158]

Sulphur dioxide complexes. The reaction between SO_2 and $NaFe(CO)_2(C_5H_5)$ affords two complexes containing sulphur dioxide bridging iron atoms. In $[(C_5H_5)Fe(CO)_2]_2SO_2$ (125), the SO_2 has "inserted" symmetrically between the two iron atoms.[159] The minor product $(C_5H_5)_2Fe_2(CO)_3(SO_2)$ (126) contains two $(C_5H_5)Fe(CO)$ groups linked by an Fe-Fe bond, bridged by one CO and the SO_2 ligand.[160] The cyclopentadienyl groups are *cis*. The Fe-Fe bond distances in the two indepent molecules differ by 0.013Å (or *ca.* 9σ), and are rather longer than those found in related molecules.

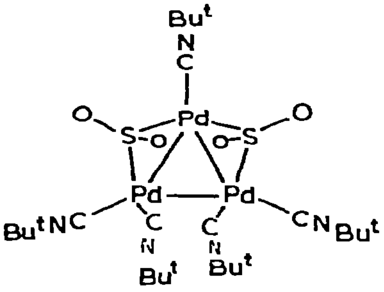


(125)



(126)

The complex $Pd_3(SO_2)_2(CNBu^t)_5$ (127), obtained from excess SO_2 and $Pd(CNBu^t)_2$, contains a triangular Pd_3 cluster, two sides of which are bridged by SO_2 ligands. Two of the isocyanides are nearly in a bridging conformation, which may offer an explanation for the solution n.m.r. behaviour (equivalent isocyanides) of the complex.[161] The platinum

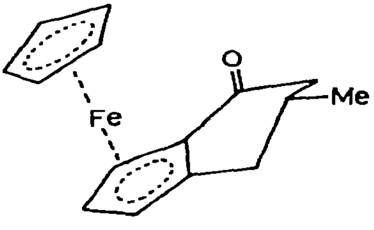


(127)

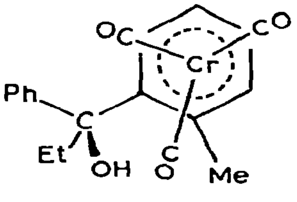
derivative $Pt(SO_2)(PPh_3)_3$ is a trigonal pyramid, with an apical SO_2 ligand. The absence of significant π-bonding is indicated by the long Pt-S bond [2.399(13)Å], while the open base results in easy electrophilic attack of the metal, e.g. by dioxygen.[162]

FERROCENE AND BENCHROTRENE DERIVATIVES

Recent structural investigations have been devoted to studies of absolute configurations of various optically active derivatives of the parent ferrocene and benzene-$Cr(CO)_3$ molecules. Homoannular cyclisation of ferrocenyl(methyl)butyric acids has given methylated ferrocenocyclohexenones; (-)-2,3-ferroceno-5-*exo*-methylcyclohex-2-en-1-one (128) has the absolute configuration 2*Rc*5*Sc*.[163] The two diastereomeric (racemic forms) ethylphenyl-*o*-methylbenchrotrenylmethanols have structures (129; m.p. 89°) (1*Rp*, *Rc* + 1*Sp*, *Sc*)

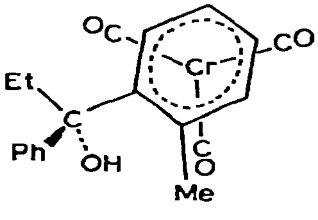


(128)

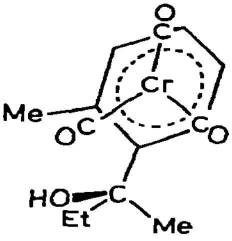


(129) m p. 89°

and (130; m.p. 163°) (1*Rp*,*Sc* + 1*Sp*, *Rc*)[164] and one racemic diastereoisomer of methylethyl-*o*-methylbenchrotrenylmethanol (m.p. 66°) has the configuration (131) (*RpSc* + *SpRc*); the isomer, m.p. 82°, is thus (*SpSc* + *RpRc*). These structures



(130) m.p 163°

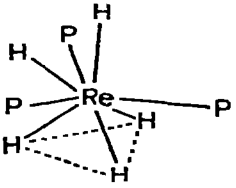


(131) mp 66°

confirm the major conclusions of an extensive discussion on asymmetric induction in the benchrotrene series.[165]

HYDRIDE COMPLEXES

The coordination geometry in $H_4Mo(PMePh_2)_4$ is a distorted dodecahedron, the hydrogen atoms (which were located) forming an elongated tetrahedron, while the four phosphorus atoms form a flattened tetrahedron, midway between the ideal tetrahedron and square planar. Two Mo-P distances [2.433(2) and 2.503(8)Å were found, and the average Mo-H bond length is 1.70(3)Å.[166] A structure for $ReH_5(PPh_3)_3$ (132) has also been proposed, based on the location of the four heavy atoms; the rhenium lies 0.49Å out of the P_3 plane. The hydrogen atoms



(132)

were not located.[167] Both complexes are fluxional in solution.

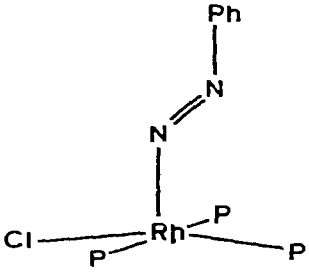
NITROSYLS, ARYLDIAZO COMPLEXES, AND RELATED COMPOUNDS

A further contribution to the discussion centred around the bonding of linear and bent transition metal nitrosyl complexes appeared recently.[168] The energetics of distortion are apparently determined to a large extent by the energies of only two MO's, and suggested energy level schemes for $M(NO)X_n$ (n=3 and 4) are given. From these, intermediate geometries (between 120° and

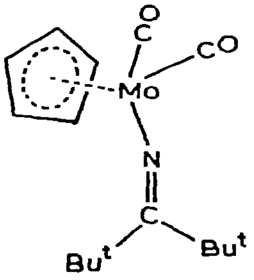
180°) appear unlikely for five-coordinate d^8 nitrosyls, whereas for four-coordinate complexes, the activation energy for interconversion is very low, giving the possibility of intermediate geometries. Such have been found, e.g. between 153 and 166° for some Co, Ir and Ni complexes. The importance of the low-lying π^* orbital in NO (unlike CO or N_2) in relation to this discussion is emphasised. In the review previously mentioned, eight complexes (out of 52) have M-N-O angles between 120 and 128°.

Several nitrosyl complexes have been mentioned previously in the above survey. In some of these, the NO group is linear [$\{Ru(NO)(PMePh_2)(PPh_2)\}_2$, 174°; $Co(CO)_2(NO)(AsPh_3)$(disordered with CO)] whereas in Co(NO)(TPP)(104), the angle Co-N-O is 135°, and in $[Ir(NO)_2(PPh_3)]_2$, it is 167°. In barium nitroprusside, $Ba[Fe(CN)_5(NO)].2H_2O$, the anion forms a highly distorted octahedron, with an Fe-N-O angle of 166(4)°.[169]

The analogies between NO^+ (linear M-N-O) and ArN_2^+, and between NO^- (M-N-O angle *ca.* 120°) and ArN_2^- have prompted structural studies of several aryldiazo complexes. Until 1973, the few examples of such complexes had linear M-N-N(Ar) groups [$ReCl_2(N_2Ph)(PMe_2Ph)_3$,[170] $Mo(N_2Ph)(CO)_2\{HB(pz)_3\}$[171] and $RuCl_3(N_2C_6H_4Me)(PPh_3)_2$[172]], or bent as part of a five-membered chelate ring [$\{IrCl(NHNC_6H_3F)(CO)(PPh_3)_2\}^+$[173]]. The structural parameters of the aryldiazo-metal moiety are summarised in Table 2. The first example of a bent M-N-N(Ar) group has been found in the cation $[RhCl(N_2Ph)(tpp)]^+$ (133) [tpp = $PhP\{(CH_2)_3PPh_2\}_2$], where the angle at the nitrogen atoms are 119° (NPh) and 125° (NRh).[174]



(133)



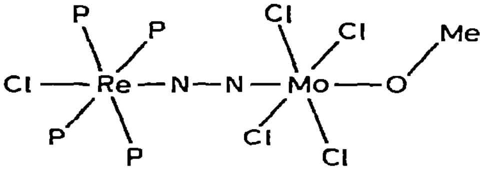
(134)

A further example of a three-electron nitrogen donor ligand is the dialkylmethyleneamino group. In $(C_5H_5)Mo(CO)_2(N{=}CBu^t_2)$ (134), the short Mo-N bond [1.892(5)Å] supports the idea of considerable back-bonding, as does the Mo-N-C angle [171.8(4)°], which indicates formal *sp* hybridisation.[175]

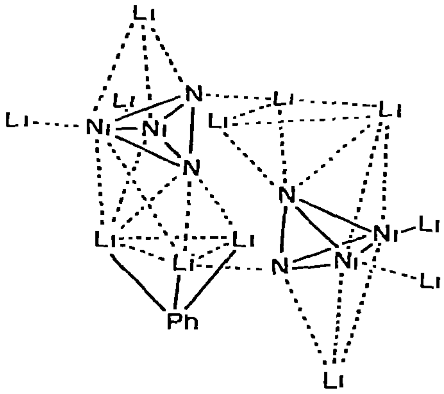
DINITROGEN COMPLEXES

A linear dinitrogen bridge between two different transition metals has been confirmed in $[(PhMe_2P)_4ClReN_2MoCl_4(OMe)]$ (135), prepared from $ReCl(N_2)(PMe_2Ph)_4$ and $MoCl_4(THF)_2$ in methanol. The lengthening of the N-N bond (1.21Å) anticipated from the low ν(NN) value of 1660 cm^{-1} is accompanied by shortening of the Re-N and Mo-N bonds (1.79 and 1.89Å, respectively).[176]

Although most dinitrogen complexes contain a linear M-N≡N moiety, side-bonded complexes have been assumed in the natural nitrogen fixation process. Such compounds would involve the nitrogen lone-pair in the formation of olefin-like complexes. The new complex $[(PhLi)_6Ni_2N_2(OEt_2)_2]_2$ (136), obtained from all-*trans*-1,5,9-cyclododecatrienenickel with phenyllithium and dinitrogen,[177] has been found to process a π-dinitrogen ligand. The Ni-Ni bond is bridged by the N_2 molecules, which are linked via two lithium atoms to form a six-membered $\overline{LiN_2LiN_2}$ ring; the two halves of the complex are linked via phenyl groups bridging lithium atoms. Each nickel atom is bonded to two phenyl groups. The electron acceptor character of the lithium enhances back-bonding



(135) P = PMe_2Ph



(136) Internal Li-Ni-N_2 skeleton

from nickel to the dinitrogen molecule, which is lengthened to 1.35Å. An important factor in the stability of the complex appears to be the interaction of the dinitrogen ligands with *both* the nickel (side-on) and the lithium (end-on) atoms.[178]

REFERENCES

1. M.R. Churchill, *Inorg.Chem.*, 12 (1973) 1213.
2. R. Mason and D.M.P. Mingos, *J.Organometallic Chem.*, 50 (1973) 53.
3. *Molecular Structures and Dimensions*, Volumes 3 (Bibliography, 1969-1971) and 4(Bibliography 1971-1972): Organic and organometallic crystal structures. Oosthoek, Utrecht, 1972, 1973.
4. *Molecular Structures and Dimensions*, Volume A1: Interatomic Distances 1960-1965. Organic and organometallic crystal structures. Oosthoek, Utrecht, 1973.
5. B.A. Frenz and J.A. Ibers, *MTP International Review of Science, Physical Chemistry*, Series I, volume 11, chapter 2, pp 35-57, (Five-coordination), 57-67 (Nitrosyls).
6. B.K. Vainshtein and G.N. Tishchenko, *MTP International Review of Science, Physical Chemistry*, Series I, volume 11, chapter 3, pp. 104-116.
7. B.Y.K. Ho and J.J. Zuckerman, *J.Organometallic Chem.*, 49 (1973) 1.
8. M. Laing, E. Singleton and R. Reimann, *J.Organometallic Chem.*, 56 (1973) C21
9. N.I. Gapotchenko, Y.T. Struchkov, N.V. Alekseev, and I.A. Ronova, *Zh.Strukt. Khim.*, 14 (1973) 419.
10. M.R. Churchill, S.W.-Y. Ni Chang. M.L. Berch and A. Davison, *J.C.S. Chem.Comm.*, (1973) 691.
11. G. Raper and W.S. McDonald, *Acta Cryst.*, B29 (1973) 2013.
12. S. Martinengo, P. Chini, V.G. Albano, F. Cariati and T. Salvatori, *J.Organometallic Chem.*, 59 (1973) 379.
13. A. Brookes, J. Howard, S.A.R. Knox, V. Riera, F.G.A. Stone and P. Woodward, *J.C.S. Chem.Comm.*, (1973) 727.

14. R.D. Ball and D. Hall, *J.Organometallic Chem.*, 56 (1973) 209.

15. E.D. Estes and D.J. Hodgson, *Inorg.Chem.*, 12 (1973) 2932.

16. H. Vahrenkamp, *Chem.Ber.*, 106 (1973) 2570.

17. F.W.B. Einstein and R.D.G. Jones, *Inorg.Chem.*, 12 (1973) 1690.

18. R. Bau, J.C. Burt, S.A.R. Knox, R.M. Laine, R.P. Phillips and F.G.A. Stone, *J.C.S. Chem.Comm.*, (1973) 726.

19. G. Ferraris and G. Gervasio, *J.C.S. Dalton*, (1973) 1933.

20. C.H. Wei, L. Marko, G. Bor and L.F. Dahl, *J.Amer.Chem.Soc.*, 95 (1973) 4840.

21. L.F. Dahl, unpublished work quoted in: T. Yamamoto, A.R. Garber, G.M. Bodner, L.J. Todd, M.D. Rausch and S.A. Gardner, *J.Organometallic Chem.*, 56 (1973) C23

22. J. Müller, H. Dormer, G. Huttner and H. Lorenz, *Angew.Chem.*, 85 (1973) 1117; *Angew.Chem.Internat.Edit.*, 12 (1973) 1005.

23. P. Bellon, M. Manassero and M. Sansoni, *J.C.S. Dalton*, (1973) 2423.

24. M.G.B. Drew and J.D. Wilkins, *J.C.S. Dalton*, (1973) 1830.

25. V. Gramlich and K. Pfefferkorn, *J.Organometallic Chem.*, 61 (1973) 247.

26. J.J. Daly, F. Sanz, R.P.A. Sneeden and H.H. Zeiss, *J.C.S. Dalton*, (1973) 1497.

27. S.R. Fletcher and A.C. Skapski, *J.Organometallic Chem.*, 59 (1973) 299.

28. G.G. Aleksandrov, Y.T. Struchkov and Y.V. Makarov, *Zh.Strukt.Khim.*, 14 (1973) 98

29. M.R. Churchill and S.W.-Y. Ni Chang, *J.Amer.Chem.Soc.*, 95 (1973) 5931.

30. M.R. Churchill, L.K. Kalra and M.V. Veidis, *Inorg.Chem.*, 12 (1973) 1656.

31. G. Casalone and R. Mason, *Inorg.Chim.Acta*, 7 (1973) 429.

32. J. Howard and P. Woodward, *J.C.S. Dalton*, (1973) 1840.

33. C.J. Cardin, D.J. Cardin, M.F. Lappert and K.W. Muir, *J.Organometallic Chem.*, 60 (1973) C70.

34. M.R. Collier, C. Eaborn, B. Jovanovic, M.F. Lappert, L. Manojlovic-Muir, K.W. Muir and M.M. Truelock, *J.C.S. Chem.Comm.*, (1972) 613.

35. J.L. Atwood, C.F. Hains, M. Tsutsui and A.E. Gebala, *J.C.S. Chem.Comm.*, (1973) 452.

36. H.A. Patel, R.G. Fischer, A.J. Carty, D.V. Naik and G.J. Palenik, *J.Organometallic Chem.*, 60 (1973) C49.

37. K.P. Callahan, C.E. Strouse, S.W. Layten and M.F. Hawthorne, *J.C.S. Chem.Comm.*, (1973) 465.

38. J.A.J. Jarvis, B.T. Kilbourn, R. Pearce and M.F. Lappert, *J.C.S. Chem.Comm.*, (1973) 475.

39. M. McPartlin and A.J. Markwell, *J.Organometallic Chem.*, 57 (1973) C25.

40. A.L. Crumbliss, J.T. Bowman, P.L. Gaus and A.T. McPhail, *J.C.S. Chem.Comm.*, (1973) 415.

41. W.W. Adams and P.G. Lenhert, *Acta Cryst.*, B29 (1973) 2412.

42. I.S. Kolomnikov, A.I. Gusev, G.G. Aleksandcv, T.S. Lobeeva, Y.T. Struchkov and M.E. Vol'pin, *J.Organometallic Chem.*, 59 (1973) 349.

43. J. Fayos, E. Dobrzynski, R.J. Angelici and J. Clardy, *J.Organometallic Chem.*, 59 (1973) C33.

44. S.K.Porter, H.White, C.R.Green, R.J. Angelici and J. Clardy, *J.C.S. Chem.Comm.*, (1973) 493.

45. A. Segnitz, P.M. Bailey and P.M. Maitlis, *J.C.S. Chem.Comm.*, (1973) 698.

46. J.A. McGinnety, *J.Organometallic Chem.*, 59 (1973) 429.

47. C.G. Biefield, H.A. Eick and R.H. Grubbs, *Inorg.Chem.*, 12 (1973) 2166.

48. G. Ingrosso, A. Immirzi and L. Porri, *J.Organometallic Chem.*, 60 (1973) C35.

49. J.T. Mague, *Inorg.Chem.*, 12 (1973) 2649.

50. Y. Wakatsuki, H. Yamazaki and H. Iwasaki, *J.Amer.Chem.Soc.*, 95 (1973) 5781.

51. R.B. King and I. Haiduc, *J.Amer.Chem.Soc.*, 94 (1972) 4044.

52. H.B. Chin and R. Bau, *J.Amer.Chem.Soc.*, 95 (1973) 5068.

53. J.L. Davidson, R. Kerak, L. Manojlovic-Muir, K.W. Muir and D.W.A. Sharp, *J.C.S. Chem.Comm.*, (1973) 864.

54. D.M. Roe, C. Calvo, N. Krishnamachari, K.Moseley and P.M. Maitlis, *J.C.S. Chem.Comm.*, (1973) 436.

55. T. Hosokawa, C. Calvo, H.B. Lee and P.M. Maitlis, *J.Amer.Chem.Soc.*, 95 (1973) 4914.

56. M.A. Bennett, P.W. Clark, G.B. Robertson and P.O. Whimp, *J.Organometallic Chem.*, 63 (1973) C15.

57. G.B. Robertson and P.O. Whimp, *J.C.S. Dalton*, (1973) 2454.

58. C. Nave and M.R. Truter, *J.C.S. Dalton*, (1973) 2202.

59. S. Trofimenko, *Inorg.Chem.*, 12 (1973) 1215.

60. M.C. Mazza and C.G. Pierpont, *Inorg.Chem.*, 12 (1973) 2955.

61. M.G.B. Drew, S.M. Nelson and M. Sloan, *J.C.S. Dalton*, (1973) 1484.

62. B. Beagley, D.G. Schmidling and D.W.J. Cruickshank, *Acta Cryst.*, B29 (1973) 1499.

63. A.A. Sayler, H. Beall and J.F. Sieckhaus, *J.Amer.Chem.Soc.*, 95 (1973) 5790.

64. R. Spagna and L. Zambonelli, *Acta Cryst.*, B29 (1973) 2302.

65. M.J. Bennett, W.A.G. Graham. R.P. Stewart and R.M. Tuggle, *Inorg.Chem.*, 12 (1973) 2944.

66. G. Tieghi and M. Zocchi, *J.Organometallic Chem.*, 57 (1973) C90.

67. G. Tieghi and M. Zocchi, *Cryst.Struct.Comm.*, 2 (1973) 557.

68. G. Tieghi and M. Zocchi, *Cryst.Struct.Comm.*, 2 (1973) 561.

69. M. Zocchi, G. Tieghi and A. Albinati, *J.Organometallic Chem.*, 33 (1971) C47.

70. E. Benedetti, G. Maglio, R. Palumbo and C. Pedone, *J.Organometallic Chem.*, 60 (1973) 189.

71. J.A. Sadownick and S.J. Lippard, *Inorg.Chem.*, 12 (1973) 2659.

72. A. Mawby, P.J.C. Walker and R.J. Mawby, *J.Organometallic Chem.*, 55 (1973) C39.

73. M. Mathew and G.J. Palenik, *J.Organometallic Chem.*, 61 (1973) 301.

74. D.B. Crump and N.C. Payne, *Inorg.Chem.*, 12 (1973) 1663.

75. J.L. Atwood and K.D. Smith, *J.C.S. Dalton*, (1973) 2487.

76. C.G. Vonk, *J. Cryst.Mol.Struct.*, 3 (1973) 201.

77. T.L. Khotsyanova and S.I. Kuznetsov, *J.Organometallic Chem.*, 57 (1973) 155.

78. V.V. Tkachev and L.O. Atomyan, *Zh.strukt.Khim.*, 13 (1972) 287.

79. L.J. Guggenberger and F.N. Tebbe, *J.Amer.Chem.Soc.*, 95 (1973) 7870.

80. H.H. Brintzinger and J.E. Bercaw, *J.Amer.Chem.Soc.*, 92 (1970) 6182.

81. R.A. Forder, M.L.H. Green, R.E. Mackenzie, J.S. Poland and K. Prout, *J.C.S. Chem.Comm.*, (1973) 426.

82. F.W.S. Benfield, R.A. Forder, M.L.H. Green, G.A. Moser and K. Prout, *J.C.S. Chem.Comm.*, (1973) 759.

83. R.D. Adams, M. Brice and F.A. Cotton, *J.Amer.Chem.Soc.*, 95 (1973) 6594.

84. R.M. Kirchner, T.J. Marks, J.S. Kristoff, and J.A. Ibers, *J.Amer.Chem.Soc.*, 95 (1973) 6602.

85. J. Weaver and P. Woodward, *J.C.S. Dalton*, (1973) 1439.

86. M.E. Gress and R.A. Jacobson, *Inorg.Chem.*, 12 (1973) 1746.

87. F.A. Cotton, B.A. Frenz, and J.A. White, *J.Organometallic Chem.*, 60 (1973) 147.

88. N.E. Kim, N.J. Nelson and D.F. Shriver, *Inorg.Chim.Acta*, 7 (1973) 393.

89. U. Behrens and E. Weiss, *J.Organometallic Chem.*, 59 (1973) 335.

90. H. Vahrenkamp, *J.Organometallic Chem.*, 63 (1973) 399.

91. B Rees and P. Coppens, *Acta Cryst.*, B29 (1973) 2515.

92. G.B. Robertson and P.O. Whimp, *J.Organometallic Chem.*, 60 (1973) C11.

93. J.M. Guss and R. Mason, *J.C.S. Dalton*, (1973) 1834.

94. H. Deuschl and W. Hoppe, *Acta Cryst.*, 17 (1964) 800.

95. K.W. Muir, G. Ferguson and G.A. Sim, *J.Chem.Soc.(B)*, (1968) 467.

96. A. Immirzi, *J.Appl.Cryst.*, 6 (1973) 246.

97. C Krüger, *Angew.Chem.*, 84 (1972) 412; *Angew.Chem.Internat.Edit.*, 11 (1972) 387.

98. B. Barnett and C. Krüger, unpublished work cited in: K. Fischer, K. Jonas, P. Misbach, R. Stabba and G. Wilke, *Angew.Chem.*, 85 (1973) 1002. *Angew.Chem.Internat.Edit.*, 12 (1973) 943.

99. C Krüger and Y.-H Tsay, unpublished work cited in: K. Fischer, K. Jonas, P. Misbach, R. Stabba and G. Wilke, *Angew.Chem.*, 85 (1973) 1002; *Angew.Chem.Internat.Edit.*, 12 (1973) 943.

100. C. Krüger and Y.-H. Tsay, unpublished work cited in: B. Bogdanovic, B. Henc, A. Lösler, B. Meister, H. Pauling and G. Wilke, *Angew.Chem.*, 85 (1973) 1013; *Angew.Chem.Internat.Edit.*, 12 (1973) 954.

101. B.L. Barnett and C. Krüger, unpublished work cited in: B. Bogdanovic, B. Henc, A. Lösler, B. Meister, H. Pauling and G. Wilke, *Angew.Chem.*, 85 (1973) 1013; *Angew.Chem.Internat.Edit.*, 12 (1973) 954.

102. F.A. Cotton, B.A. Frenz, J.M. Troup and G. Deganello, *J.Organometallic Chem.*, 59 (1973) 317.

103. F.A. Cotton, B.A. Frenz and J.M. Troup, *J.Organometallic Chem.*, 61 (1973) 337.

104. F.A. Cotton, V.W. Day, B.A. Frenz, K.I. Hardcastle and J.M. Troup, *J.Amer.Chem.Soc.*, 95 (1973) 4522.

105. L.A. Paquette, S.V. Ley, M.J. Broadhurst, D. Truesdell, J. Fayos and J. Clard *Tetrahedron Letters*, (1973) 2943.

106. M.R. Churchill and K-K. G. Lin, *Inorg.Chem.*, 12 (1973) 2274.

107. A. Brookes, J. Howard, S.A.R. Knox, F.G.A. Stone and P. Woodward, *J.C.S. Chem.Comm.*, (1973) 587.

108. N.I. Kirillova, A.I. Gusev, A.A. Pasynskii and Y.T. Struchkov, *J.Organometallic Chem.*, 63 (1973) 311.

109. A.J.P. Domingos, B.F.G. Johnson, J. Lewis and G.M. Sheldrick, *J.C.S. Chem.Comm.*, (1973) 912.

110. G.B. Robertson and P.O. Whimp, *Inorg.Chem.*, 12 (1973) 1740.

111. K. Takahashi, M. Iwanami, A. Tsai, P.L. Chang, R.L. Harlow, L.E. Harris, J.E. McCaskie, C.E. Pfluger and D.C. Dittmer, *J.Amer.Chem.Soc.*, 95 (1973) 6113.

112. R.L. Harlow and C.E. Pfluger, *Acta Cryst.*, B29 (1973) 2633.

113. J.P. Brennan, R.N. Grimes, R. Schaeffer and L.G. Sneddon, *Inorg.Chem.*, 12 (1973) 2266.

114. F.J. Hollander, D.H. Templeton and A. Zalkin, *Inorg.Chem.*, 12 (1973) 2262.

115. C.A. Bear and J. Trotter, *J.C.S. Dalton*, (1973) 2285.

116. M.J. Barrow, J.L. Davidson, W. Harrison, D.W.A. Sharp, G.A. Sim and F.B. Wilson, *J.C.S. Chem.Comm.*, (1973) 583.

117. L. Ricard, J. Estienne and R. Weiss, *Inorg.Chem.*, 12 (1973) 2182.

118. S.D. Ittel and J.A. Ibers, *J.Organometallic Chem.*, 57 (1973) 389.

119. D.J. Yarrow, J.A. Ibers, Y. Tatsuno and S. Otsuka, *J.Amer.Chem.Soc.*, 95 (1973) 8590.

120. S.D. Ittel and J.A. Ibers, *Inorg.Chem.*, 12 (1973) 2290.

121. A.S. Kasenally, *Proc.14 ICCC*, Toronto, (1972) 477.

122. R.M. Kirchner, J.A. Ibers, M.S. Saran and R.B. King, *J.Amer.Chem.Soc.*, 95 (1973) 5775.

123. R.F. Stepaniak and N.C. Payne, *J.Organometallic Chem.*, 57 (1973) 213.

124. K.W. Muir, R. Walker, J. Chatt, R.L. Richards and G.H.D. Royston, *J.Organometallic Chem.*, 56 (1973) C30.

125. K.P. Wagner, P.M. Treichel and J.C. Calabrese, *J.Organometallic Chem.*, 56 (1973) C33.

126. E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner and H. Lorenz, *Angew.Chem.*, 85 (1973) 618; *Angew.Chem.Internat.Edit.*, 12 (1973) 564.

127. D. Baumann, H. Endres, H.J. Keller and J. Weiss, *J.C.S. Chem.Comm.*, (1973) 853.

128. M.D. Brice and F.A. Cotton, *J.Amer.Chem.Soc.*, 95 (1973) 4529.

129. R.G. Little and J.A. Ibers, *J.Amer.Chem.Soc.*, 95 (1973) 8583.

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

131. W.R. Scheidt and J.L. Hoard, *J.Amer.Chem.Soc.*, 95 (1973) 8281.

132. A. Takenaka, Y. Sasada, T. Omura, H. Ogoshi, and Z.-I. Yoshida, *J.C.S. Chem.Comm.*, (1973) 792.

133. F.A. Cotton, B.A. Frenz and A.G. Stanislowski, *Inorg.Chim.Acta*, 7 (1973) 503.

134. E.M. Holt, S.L. Holt and K.J. Watson, *J.C.S. Dalton*, (1973) 2444.

135. E.M. Holt and S.L. Holt, *J.C.S. Dalton*, (1973) 1893.

136. J.L. Calderon, F.A. Cotton and A. Shaver, *J.Organometallic Chem.*, 37 (1972) 127.

137. R.J. Restivo and G. Ferguson, *J.C.S. Chem.Comm.*, (1973) 847.

138. L.J. Guggenberger, C.T. Prewitt, P. Meakin, S. Trofimenko and J.P. Jesson, *Inorg.Chem.*, 12 (1973) 508.

139. M.R. Churchill, K. Gold and C.E. Maw, *Inorg.Chem.*, 9 (1970) 1597.

140. C. Krüger, *Chem.Ber.*, 106 (1973) 3230.

141. H. Vahrenkamp and H. Nöth, *Chem.Ber.*, 106 (1973) 2227.

142. H. Vahrenkamp and H. Nöth, *Chem.Ber.*, 105 (1972) 1148.

143. H.P. Calhoun, N.L. Paddock and J. Trotter, *J.C.S. Dalton*, (1973) 2708.

144. A. Camus, N. Marsich, G. Nardin and L. Randaccio, *J.Organometallic Chem.*, 60 (1973) C39; see also corrigenda, *J.Organometallic Chem.*, 64 (1974) C55

145. P.L. Bellon, C. Bendicenti, G. Caglio and M. Manassero, *J.C.S. Chem.Comm.*, (1973) 946.

146. J. Reed, A.J. Schultz, C.G. Pierpont and R. Eisenberg, *Inorg.Chem.*, 12 (1973) 2949.

147. M. Angoletta, G. Ciani, M. Manassero and M. Sansoni, *J.C.S. Chem. Comm.*, (1973) 789.

148. D.M.P. Mingos and J.A. Ibers, *Inorg.Chem.*, 9 (1970) 1105.

149. M.B. Linck and L.R. Nassimbeni, *Inorg.Nucl.Chem.Letters*, 9 (1973) 1105.

150. P.M. Treichel, W.K. Dean and J.C. Calabrese, *Inorg.Chem.*, 12 (1973) 2908.

151. P.H, Bird, N.J. Coville, I.S. Butler and M.L. Schneider, *Inorg.Chem.*, 12 (1973) 2902.

152. G. Gilli, M. Sacerdoti and G. Reichenbach, *Acta Cryst.*, B29 (1973) 2306.

153. M.G.B. Drew and J.D. Wilkins, *J.C.S. Dalton*, (1973) 2664.

154. S.Z. Goldberg and K.N. Raymond, *Inorg.Chem.*, 12 (1973) 2923.

155. A. Kutoglu, *Acta Cryst.*, B29 (1973) 2891.

156. T. Debaerdemaeker and A. Kutoglu, *Acta Cryst.*, B29 (1973) 2664.

157. A. Terzis and R. Rivest, *Inorg.Chem.*, 12 (1973) 2132.

158. E.N. Baker and B.R. Reay, *J.C.S. Dalton*, (1973) 2205.

159. M.R. Churchill, B.G. de Boer and K.L. Kalra, *Inorg.Chem.*, 12 (1973) 1646.

160. M.R. Churchill and K.L. Kalra, *Inorg.Chem.*, 12 (1973) 1650.

161. S. Otsuka, Y. Tatsumo, M. Miki, T. Aoki, M. Matsumoto, H. Yoshioka and K. Nakatsu, *J.C.S. Chem.Comm.*, (1973) 445.

162. J.P. Linsky and C.G. Pierpont, *Inorg.Chem.*, 12 (1973) 2959.

163. C. Lecomte, Y. Dusausoy, J. Protas, B. Gautheron and R. Broussier, *Acta.Cryst.*, B29 (1973) 1504.

164. Y. Dusausoy, J. Protas and J. Besancon, *J.Organometallic Chem.*, 59 (1973) 29

165. J. Besancon, J. Tirouflet, Y. Dusausoy and A. Card, *J.Organometallic Chem.*, 59, (1973) 267.

166. L.J. Guggenberger, *Inorg.Chem.*, 12 (1973) 2295.

167. A.P. Ginsberg, S.C. Abrahams and P.B. Jamieson, *J.Amer.Chem.Soc.*, 95 (1973) 4751.

168. D.M.P. Mingos, *Inorg.Chem.*, 12 (1973) 1209.

169. A.H. Lanfranconi, A.G. Alvarez and E.E. Castellano, *Acta Cryst.*, B29 (1973) 1733.

170. V.F. Duckworth, P.G. Douglas, R. Mason and B.L. Shaw, *Chem.Comm.*, (1970) 1083.

171. G. Avitabile, P. Ganis and M. Nemiroff, *Acta Cryst.*, B27 (1971) 725.

172. J.V. McArdle, A.J. Schultz, B.J. Corden and R. Eisenberg, *Inorg.Chem.*, 12 (1973) 1676.

173. F.W.B. Einstein, A.B. Gilchrist, G.W. Rayner-Canham and D. Sutton, *J.Amer.Chem.Soc.*, 94 (1972) 645.

174. A.P. Gaughan, B.L. Haymore, J.A. Ibers, W.H. Myers, T.E. Nappier and D.W. Meek, *J.Amer.Chem.Soc.*, 95 (1973) 6859.

175. H.M.M. Shearer and J.D. Sowerby, *J.C.S. Dalton*, (1973) 2629.

176. M. Mercer, R.H. Crabtree and R.L. Richards, *J.C.S. Chem.Comm.*, (1973) 808.

177. K. Jonas, *Angew.Chem.*, 85 (1973) 1050; *Angew.Chem.Internat.Edit.*, 12 (1973) 997.

178. C. Krüger and Y.-H. Tsay, *Angew.Chem.*, 85 (1973) 1051; *Angew.Chem.Internat. Edit.*, 12 (1973) 998.

TABLE 1 *Metal-metal bond length determinations (1973)*

Bond	Length(Å)	Complex		Reference*
Ti-Si	2.159(13)	$[(C_5H_5)_2Ti(SiH_2)]_2$		1-8
Ti-Ti	2.910	$[(C_5H_4)Ti(H)AlEt_2]_2$		2-79
V-V	2.462(2)	$(C_5H_5)_2V_2(CO)_5$		1-17
Nb-Nb	3.115(3)	$[(C_5H_5)(C_5H_4)NbH]_2$		1-82
Cr-Sn	2.654(3)	$(py)Bu^t_2SnCr(CO)_5$		2-128
Cr-Re	3.435(1)	$HCrRe(CO)_{10}$	Cr-H-Re	1-19
Mo-Li	2.70(av.)	$[(C_5H_5)Mo(H)Li]_4$		2-82
Mo-Al	2.65-2.69	$[(C_5H_5)(C_5H_4)Mo(H)AlMe_2]_2AlMe$		2-81
	2.65-2.69	$[(C_5H_4)_2Mo(AlMe_2)(AlMe)]_2$		2-81

---

* Reference numbers relate to Parts 1 and 2, as denoted by prefix.
Part 1 J. Organometal. Chem., 75(1974)335-394.

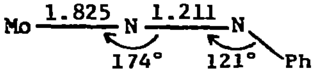
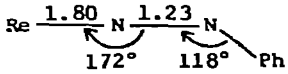
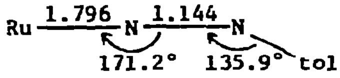
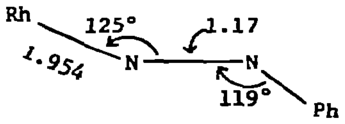
Mo-Tl	2.965(av.)	$Tl[Mo(CO)_3(C_5H_5)]_3$		1-7
Mo-Mo	2.705(2)	$[MoS(SCNPr^{i}_2)(S_2CNPr^{i}_2)]_2$		2-117
	2.954(1)	$[MoBr(CO)_2(C_4Ph_4)]_2$		2-73
	3.057(6)	$[Mo(CO)_4(PEt_2)]_2$		2-149
	3.230(1)	$Mo_2(CO)_5(CNMe)(C_5H_5)_2$		2-83
W-W	3.017(1)	$(NEt_4)_2[H_2W_2(CO)_8]$		2-10
	3.05(1)	$[W(CO)_4(PEt_2)]_2$		1-138, 2-149
	3.329	$HW_2(CO)_9(NO)$	W-H-W	1-18
Mn-Si	2.402(2)	$Mn_2(CO)_8(SiPh_2)_2$		1-10
	2.564(6)	$Mn[Si(SiMe_3)_3](CO)_5$		1-9
Mn-As	2.350(3)	$(Me_2As)FeMn(CO)_8$		2-16
Mn-Mn	2.571(1)	$[Mn(CO)(NO)(C_5H_5)]_2$		2-84
	2.871(2)	$Mn_2(CO)_8(SiPh_2)_2$		1-10
	2.904	$Mn_2(CO)_9(PMe_2Ph)$		2-8
	2.971(2)	$Mn_2(CO)_8(f_4fars)$		1-142
Mn-Fe	2.848(4)	$(Me_2As)FeMn(CO)_8$		2-16
Mn-Cd	2.760(4) 2.799(5)	$(terpy)Cd[Mn(CO)_5]_2$		1-5
Re-Re	3.04(05)	$Re_2(CO)_{10}$		2-9
Fe-As	2.348(2)(av.)	$As_2[Fe(CO)_3]_3$		1-15
	2.356(3)	$(Me_2As)FeMn(CO)_8$		2-16
Fe-Sb	2.440(2)	$\{Cl_2Sb[Fe(CO)_2(C_5H_5)]_2\}Sb_2Cl_7$		2-17
Fe-Fe	2.34	$[Fe_2H_3(triphos)_2]PF_6$		1-162
	2.462(3)	$(C_{12}H_{16})Fe_2(CO)_6$		2-52
	2.491(8)	$[Fe(CO)(\mu\text{-}COAlEt_3)(C_5H_5)]_2$		2-88
	2.500(3)	$C_4(OSiMe_3)_4Fe_2(CO)_6$		1-64
	2.511(2)	$Fe_2(CO)_6(OH)[P(\underline{p}\text{-}tol)_2]$		2-150
	2.512(3)	$Fe_2(CO)_4(C_5H_4)_2SiMe_2$		2-85
	2.516(2)	$[PhSFe(CO)_3]_2$		1-147
	2.525(3)	$(C_2H_2Br_2)Fe_2(CO)_6$		1-63

	2.553(2)	$[(C_{10}H_{11})Fe(CO)_2]_2$		2-102
	2.597(2)	$Fe_2(C_2Ph)(CO)_6(PPh_2)$		2-36
	2.597(1)	$Fe_2(CO)_3(SO_2)(C_5H_5)_2$		2-160
	2.615(2)	$(Me_2P)Fe_2(CO)_5(C_5H_5)$	molecule 1	2-90
	2.62	$\overline{C(OMe)CH.CH(:CPh_2)C(OMe)Fe}_2(CO)_6$		1-66
	2.623(4)	$As_2[Fe(CO)_3]_3$		1-15
	2.638(2)	$(Me_2P)Fe_2(CO)_5(C_5H_5)$	molecule 2	2-90
	2.739(3)	$Fe_2(CO)_5[Me_2NCH.C_5H_3CH.C_5H_4]$		2-89
	2.767(4)	$[Fe_2\{S_2C_2(CF_3)_2\}_4]^-$		1-159
	2.786(2)	$(C_{10}H_{12})Fe_2(CO)_6$		1-61
	2.797(1)	$(C_6F_4)Fe_2(CO)_8$		2-65
	2.869(1)	$(f_4asp)_2Fe_2(CO)_4$		1-139
	3.062(4)	$[Fe_2(SMe)_3(CO)_6]^+$		1-148
Fe-Ni	2.440(2)	$(C_5H_5)Ni(PPh_2)Fe(CO)_3(C_2Ph_2)$		1-20
Fe-Au	2.818(9)	$[FcAu_2(PPh_3)_2]BF_4$		1-159
Re-Si	2.456(4)	$Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)$		2-13
Ru-Ge	2.49	$(C_8H_6)[Ru(CO)_2(GeMe_3)]_2$		2-107
Ru-Ru	2.629(2)	$[Ru(NO)(PMePh_2)(PPh_2)]_4$		2-146
	2.741(1)(av.)	$(az)Ru_3(CO)_7$	CO-bridged	1-24
	2.794(2)	$Ru_3(CO)_9(HC_2Bu^t)$		1-23
	2.836, 2.840 2.86	$Ru_3(CO)_6(C_7H_7)(C_7H_9)$		2-18
	2.862(3)	$Ru_2H(CO)_6(C_{10}H_9O)$		2-109
	2.937(2)	$Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)$		2-13
	2.944(5)(av.)	$(az)Ru_3(CO)_7$		1-24
	3.05	$(C_8H_6)[Ru(CO)_2(GeMe_3)]_2$		2-107
Os-Os	2.680(2)	$Os_3(CO)_7(C_2Ph_2)(C_4Ph_4)$	Os(1)-Os(3)	2-19
	2.731	$Os_6(CO)_{18}$	Os^0-Os^0	1-28
	2.744(2)	$Os_3(CO)_7(C_2Ph_2)(C_4Ph_4)$	Os(2)-Os(3)	2-19
	2.757	$Os_6(CO)_{18}$	Os^I-Os^I	1-28

	2.793	$Os_6(CO)_{18}$	Os^0-Os^{-I}	1-28
	2.80	$H_2Os_3(CCH_2)(CO)_9$		1-26
	2.801	$Os_6(CO)_{18}$	Os^I-Os^C	1-28
	2.814	$Os_3(CO)_7(C_2Ph_2)(C_4Ph_4)$	Os(1)-Os(2)	2-19
	2.820	$Os_6(CO)_{18}$	Os^I-Os^{-I}	1-28
	2.89, 2.92	$H_2Os_3(CCH_2)(CO)_9$		1-26
Co-In	2.594(3)	$In[Co(CO)_4]_3$		1-6
Co-Sn	2.542(2)(av.)	$[Co(CO)(SnMe_2)(C_5H_5)]_2$		1-12
	2.564(3) 2.591(3)	$(acac)_2SnCo_2(CO)_7$		2-14
	2.602(6)	$BrSn[Co(CO)_4]_3$		1-11
Co-P	2.216(av.) 2.256(av.)	$Co_4P_4(C_5H_5)_4$		1-30
Co-Co	2.498(5)	$Co_4(CO)_4(SEt)_8$		2-20
	2.504(2)	$Co_4P_4(C_5H_5)_4$		1-30
	2.626(4)	$(acac)_2SnCo_2(CO)_7$		2-14
	3.172(5)	$[Co_4S_4(C_5H_5)_4]^+$		1-32
	3.295(av.)	$Co_4S_4(C_5H_5)_4$	bond order 0.5	1-32
	3.330(5)	$[Co_4S_4(C_5H_5)_4]^+$	non-bonding	1-32
Ru-C	2.134(6)	$[Rh_6C(CO)_{15}]^{2-}$		1-29
Rh-Rh	2.630(1)	$[Rh(CO)(PPh_3)_2]_2$		1-21
	2.776(3) 2.817(2)	$[Rh_6C(CO)_{15}]^{2-}$	basal	1-29
	2.9064(10)	$[(C_5Me_5)RhCl]_2HCl$		1-22
	3.090(3)	$[RhCl(MeC_5H_7)_2]_2$		2-61
Ir-Ir	2.551(1)	$[Ir(CO)(PPh_3)(PPh_2)]_2$		2-142
	2.717(1)	$[Ir(NO)_2(PPh_3)]_2$		2-147
Ni-Li	2.58-2.79	$[(PhLi)_6Ni_2N_2(OEt_2)]_2$		2-178
Ni-Ni	2.370, 2.466	$[Ni(C_4F_6)(C_5H_5)]_4$		2-53
	2.388(1)	$[Ni(C_2H_4)(PCy_2)]_2$		1-33
	2.444	$H_2[Ni(PCy_2)_2(CH_2)_3]_2$		2-97

	2.46(av.)	$H_3[Ni(C_5H_5)]_4$		2-22
	2.687	$[(PhLi)_6Ni_2N_2(OEt_2)]_2$		2-178
Pd-Pd	2.639(1)	$[Pd(C_5H_5)]_2C_2Ph_2$		1-44
	2.734(4) 2.760(3)	$Pd_3(SO_2)_2(CNBu^t)_5$	SO_2-bridged	2-161
Pt-Si	2.317(4)	$(+)$-$PtCl[SiMe(nap)Ph](PMe_2Ph)_2$		1-13
Pt-Ge	2.391(3)-2.424(3) 2.480(3)	$NMe_4[Pt(GeCl_3)_5]$		2-15
Pt-Pb	2.698(9)	$PtPh(PbPh_3)(PPh_3)_2$		1-14
Pt-Pt	2.944(2)	$Pt_4(OAc)_6(NO)_2$		1-175
	3.311(2)		non-bonding	
Cu-Cu	2.417	$[Cu(CH_2SiMe_3)]_4$		2-38
	2.836(4)	$[Cu(Ph_2PCHPPh_2)]_3$	basal	2-144
	3.112(4), 3.146(3)		side	
Au-Au	2.768(3)	$[FcAu_2(PPh_3)_2]BF_4$		1-159
	2.932(2)-2.990(2) 3.043(2)-3.091(2)	$\{Au_6[P(p\text{-tol})_3]_6\}(BPh_4)_2$		

TABLE 2 *Geometries of aryldiazo groups in metal complexes*

Complex	Aryldiazo group	Reference
$Mo(N{=}NPh)(CO)_2[HB(pz)_3]$		171
$Re(N{=}NPh)Cl_2(PMe_2Ph)_3$		170
$Ru(N{=}Ntol\text{-}p)Cl_3(PPh_3)_2$		172
$\{Rh(N_2Ph)Cl[PhP(CH_2)_3PPh_2]_2\}^+$		174