STRUCTURES OF ORGANO-TRANSITION METAL COMPLEXES

ANNUAL SURVEY COVERING THE YEAR 1975*

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INTRODUCTION

This survey will follow the new pattern adopted last year, namely two sections comprising a collection of briefly annotated diagrams ordered according to structural type, and a molecular formula index of structure determinations published during the year. During 1975, some 310 structures of organo-transition metal complexes were determined by diffraction methods, a slight reduction in the 1974 total.

In addition to conventional organometallics, i.e. those compounds containing at least one metal-carbon bond (apart from cyanides), we have also summarised data pertaining to other complexes of interest to many organometallic chemists. These include hydride and boron hydride derivatives, nitrosyls, aryldiazo, aryldiimine and related complexes, dinitrogen and binary metal-tertiary phosphine complexes.

REVIEWS AND OTHER PAPERS OF GENERAL STRUCTURAL INTEREST

The second volume of the Chemical Society's Specialist Periodical Report *Molecular Structure by Diffraction Methods* has been published [1], with a format that closely follows that of the first volume. This

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*Annual survey 1974; M.I. Bruce, *J.Organometallic Chem.*, 115(1976)17-176.

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survey covers the period April 1972 – March 1973 (for X-ray studies), and to August (neutron diffraction) or mid-autumn 1973 (electron diffraction). Further volumes in the *Molecular Structures and Dimensions* series [2] take the bibliography to the first third of 1974.

A paper on correlations between angular deformations induced in the benzene ring by substitution of a hydrogen atom with a second-row element and Pauling electronegativity of the substituent includes a consideration of structural data for several metal carbonyl complexes containing appropriate ligands [3].

Non-parameterised molecular orbital calculations of ligand-bridged $Fe_2(CO)_6X_2$-type dimers containing metal-metal interactions make extensive use of the structural data which is available for a wide range of these complexes [4]. Comparative calculations indicate that variation of the bridging ligands does not markedly affect the Fe-Fe interaction. The HOMO in the neutral complexes is similar to the classical "bent" Fe-Fe bond, with the LUMO being its antibonding counterpart. Addition of electrons to give mono- and dianions $[Fe_2(CO)_6(PR_2)_2]^{n-}$ (n = 1 or 2) results in net one- and no-electron Fe-Fe bonds, respectively.

Single crystal EPR studies on $V(S_5)(C_5H_5)_2$ doped in the lattice of the titanium complex are claimed [5] to give the coup-de-grace to the Ballhausen-Dahl theory [6] of bonding in bent bis(η^5-cyclopentadienyl)metal complexes, and indicate that the later Alcock model [7] also is not an adequate interpretation. Instead, the quantitative results show that the unpaired electron resides in an MO which is mainly $3d_{z^2}$, with a small amount of $3d_{x^2-y^2}$, but no $4s$, character. These results were supported by crystal structures of $MCl_2(C_5H_4Me)_2$ (M = Ti and V) and EPR studies on the vanadium compound [8]. These studies are followed by non-parameterised MO calculations on several d^0, d^1 and d^2 $ML_2(C_5H_5)_2$ molecules, and the results, which agree with EPR and photo-electron spectral measurements, now provide

a sound theoretical basis for the interpretation and rationalisation of the various structural features [9].

A structural study of the two forms of $RhCl(PPh_3)_3$ (red and orange) has shown that in the latter, an *ortho* hydrogen atom (Rh-H, *ca.* 2.84Å) is approximately *trans* to the chlorine atom [10]. In the red isomer, a different *ortho* hydrogen is close to the metal atom (Rh-H, 2.77Å). All but one of the phenyl rings have similar orientations with respect to the mean coordination planes in both allotropes. Some discussion of contribution of non-primary valence interactions in achieving an 18-electron configuration is given, together with speculation regarding the role of the intermediate complex $RhCl(PPh_3)_2$. A trigonal bipyramidal arrangement (with two *ortho*-hydrogens as the two "extra" ligands) may be envisaged, with ready replacement by more conventional ligand electron pairs in the formation of $RhCl(L)(PPh_3)_2$ or the dimeric $[RhCl(PPh_3)_2]_2$.

It has been pointed out that the stereochemistry of the iron atom in 29 $FeY(CO)_2(\eta\text{-}C_5H_5)$ complexes is remarkably close to octahedral, and that there may be a certain rigidity in this arrangement [11]. If this is so, tautomerism in $[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$ and related complexes must involve simultaneous making or breaking of two CO-bridge systems. This observation provides an explanation for the mechanism used to rationalise NMR results.

Initial structure determinations of rhodium and iridium dioxygen complexes apparently showed a correlation between the O-O bond length and the degree of reversibility of uptake of dioxygen by the complexes. Structures of a series of related dioxygen salts, reported during the year [12], including a redetermination of the structure of $[Ir(O_2)(dppe)_2]PF_6$ [reported[13] O-O 1.625(23)Å] gave an O-O bond length of 1.52(1)Å for this complex, and indicated that systematic errors in the earlier intensity data, resulting from crystal decomposition, resulted in errors in atom coordinates [13]. The new results suggest that the O-O bond lengths

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probably lie in the range 1.45 - 1.50Å, with peroxide character, and that the deductions concerning O-O bond length and the bond between O_2 and the metal are not tenable.

An important paper, describing the structure of $Os(NO)_2(PPh_3)_2$ includes a full discussion of recent results on four-coordinate nitrosyl complexes, and eight rules of thumb for predicting the general coordination geometries in many nitrosyl complexes [14]. Although not inherently fundamental in nature, some simple assumptions concerning the NO group enable the generalisations to be understood. In contrast to the situation described in an earlier survey [15] and elsewhere [16], it would appear that this paper contains criteria which will be useful in predicting the stereochemistries and properties of nitrosyl compounds.

A paper comparing the nitrosyl and aryldiazo complexes $RuLCl_3(PPh_3)_2$ (L = NO or N_2tol-*p*) contains a detailed discussion on the N-O and N-N stretching frequencies found in complexes containing these isoelectronic ligands [17]. A number of empirical "corrections" applied to the observed ν(NO) frequencies result in the corrected frequencies falling into two groups, above and below 1606 - 1611 cm^{-1}. Bent nitrosyls fall in the lower range, while linear NO groups fall in the higher range. Application of aryldiazo compounds leads to two groups of ν(NN) frequencies lying above and below 1530 - 1550 cm^{-1}, arising from singly- and doubly-bent aryldiazo ligands, respectively.

A note discusses methods of twist angle calculations with reference to a number of complexes containing two approximately parallel faces (including three ferrocene derivatives). Requirements for complete descriptions of distortions in these molecules are summarised [18].

TRENDS IN 1975

The increasing use of X-ray diffraction as a routine analytical

tool is evident, as is the tendency to examine trends and relationships in more or less extensive series of compounds. Examples of the latter include $MMe_2(ind)_2$ (M = Ti, Zr, Hf), the isoelectronic nitrosyls $M(NO)_2(PPh_3)_2$ (M = Fe, Ru, Os, Co^+, Rh^+, Ir^+), and dioxygen complexes of rhodium and iridium (mentioned above). The rapid progress in several areas in which X-ray crystallographic structure determination is a prime necessity, such as metal cluster chemistry, metallocarborane reactions, and polynuclear hydrocarbon complexes of the Fe, Ru and Os carbonyls, is self-evident. Of just over 300 organometallic structures reported, no less than 40 originated from the Bristol group.

Noteworthy complexes and unusual ligands confirmed or revealed by structural determinations during the year, and detailed in the succeeding sections include: the first titanium- and copper carbonyl derivatives, the first selenocarbonyl group in $RuCl_2(CO)(CSe)(PPh_3)_2$, phenylphosphinidene and -arsinidene complexes $[Mn(CO)_3(C_5H_5)]_2PPh$ and $[Cr(CO)_5]_2AsPh$, the metalloacetylacetonato complex $Al[Mn(CO)_4(COMe)_2]_3$, and the unusual adduct from tetracyanoquinodimethan and $Pt(C_2Me)_2(PMe_3)_2$, containing the $PtC[:C(CN)_2]CMe[:C_6H_4C(CN)_2]$ group. Other interesting derivatives are the first unsubstituted methylene complex, $Ta(CH_2)Me(C_5H_5)_2$, tris-olefin complexes of platinum, and allyl and cyclopentadienyl groups bridging two palladium atoms, while reactions of hexafluorobut-2-yne with a wide variety of complexes have led to several new ligand types being derived from this versatile precursor.

ELECTRON DIFFRACTION RESULTS

A survey of organometallic compounds studied by gas-phase electron diffraction discusses only bis(cyclopentadienyl)metal derivatives in the section on transition metal derivatives [19]. Details of the structures reported during the year follow:

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$V(CO)_6$ An undistorted octahedral (O_h) structure was found [V-C, 2.015(2), C-O 1.138(2)Å] [20], with evidence for a dynamic Jahn-Teller effect, as predicted earlier.

$Cr(CO)_3(C_6H_6)$ In the vapour phase, the molecule is a nearly unhindered internal rotor, the vapour consisting of a mixture of several conformatons between eclipsed and staggered C_6H_6 and $Cr(CO)_3$ groups [21]. Bond distances: C-C 1.417(3), Cr-C(C_6H_6) 2.208(6), Cr-C(CO) 1.863(5)Å; angle OC-Cr-CO 88.6(11)°.

$M(C_5H_5)_2$ (M = V or Cr) Both molecules appear to have the eclipsed configuration, although a model with staggered rings cannot be definitely ruled out [22]. In the chromium complex, the C-H bonds are bent towards the metal atom by 2.9°. Some discussion of the structures of known $M(C_5H_5)_2$ (M = first row transition element) compounds with respect to their electronic structures is given; the M-C distances increase regularly with degree of electronic unsaturation.

$Mn(MH_3)(CO)_5$ (M = Si or Ge) In both complexes, the metal-metal bond distances are shorter than the sum of the covalent radii [23]. Although p_π-d_π interactions can be invoked to explain this observation, He-photoelectron spectra indicate that this effect is largely due to the better σ-acceptor characteristics of the Main Group hydride ligand.

$Mn(SiF_3)(CO)_5$ Again, an Mn-Si bond shorter than the sum of the covalent radii is consistent with the purely σ effects suggested by the PE spectral data [24].

NEUTRON DIFFRACTION RESULTS

Neutron diffraction studies of several key compounds have been used to define details not available from X-ray diffraction. In Zeise's salt, $K[PtCl_3(C_2H_4)].H_2O$, the Pt-Cl bond *trans* to C_2H_4[2.340(2)Å] is significantly longer (19σ) than the *cis* Pt-Cl bonds [2.302(2)Å] [25]. In

the ethylene ligand the C-C distance [1.375(4)Å] is 0.038Å longer than in free ethylene, and the four hydrogen atoms are bent away from the metal [angle between the normals to the CH_2 planes (α), 32.5°]. These data indicate some d_π-p_π* back bonding, but the changes are considerably smaller than those found in metal complexes of C_2F_4 and $C_2(CN)_4$.

A neutron diffraction study of $Cr(CO)_6$ at 78K has been reported as the first stage of a determination of the electron density distribution in the molecule [26]. The octahedron is significantly distorted, but there are no significant differences between chemically equivalent bond distances: Cr-C, 1.918; C-O, 1.141Å. Comparison with $Cr(CO)_3(C_6H_6)$ shows the CO groups are less strongly bonded to chromium in $Cr(CO)_6$, a result consistent with the larger electronegativity of CO compared to benzene.

STRUCTURAL DIAGRAMS

As in previous years, these have been assembled usually using the diagram appearing in the paper. The η symbol has been used to arrange the organic ligands, using the largest group where several different ones are present. Thus, the diagrams for $Ru[C(CO_2Me):CH(CO_2Me)](PPh_3)[C_5H_4C(OH)(CF_3)_2]$ and $Fe_2(CO)_5(COC_6H_6C_5H_4)$ are in the η^5 section. Further arrangement has usually been in order of Periodic Group. Suitable brief footnotes to each section draw attention to any unusual features noted in the structure, and reference numbers in square brackets [] refer to the list at the end of the article. The following headings have been used:

η^1-Ligands

(a) Simple carbonyls and carbonyl halides

(b) Carbonyls containing Group V donor ligands

(c) Carbonyl halides containing Group V donor ligands

(d) Carbonyls and carbonyl halides containing Group VI donor ligands

(e) Thiocarbonyls and selenocarbonyls

(f) Isocyanide complexes

(g) Carbene and carbyne complexes

(h) Alkyls, aryls and acyls

(i) Complexes containing chelating η^1-ligands

η^2-Ligands

(a) ($2\eta^1$)-Ligands (metallocycles)

(b) Olefin complexes

(c) Acetylene complexes

(d) Complexes containing other three-membered rings

η^3-Ligands

(a) ($\eta^1+\eta^2$)-Ligands

(b) η^3-Allyl complexes

η^4-Ligands

(a) ($2\eta^1+\eta^2$)-Ligands

(b) ($\eta^1+\eta^3$)-Ligands

(c) ($2\eta^2$)-Ligands

(d) η^4-Ligands (dienes)

η^5-Ligands

(a) Cyclopentadienyls

(b) Cyclopentadienyl metal halides

(c) Cyclopentadienyls containing other anionic ligands

(d) Cyclopentadienyls containing CO or PR_3 ligands

(e) Cyclopentadienyls containing other donor ligands

(f) Cyclopentadienyls containing other η-hydrocarbon ligands

(g) Substituted ferrocenes

(h) Acyclic η^5-Ligands

(i) ($\eta^2+\eta^3$)-Ligands

η^6-Ligands

(a) Cyclic η^6-ligands (arenes)

(b) Acyclic η^6-ligands

(c) $(2\eta^3)$-Ligands

η^7-Ligands

η^8-Ligands

η-Heteroatom Ligands

Silver Complexes

Polyhedral Metalloborane Complexes

Polyhedral Metallocarborane Complexes

Complexes Containing Metal-Metal Bonds

(a) Homobinuclear transition metal complexes

(b) Heterobinuclear transition metal complexes

(c) Binuclear complexes containing bridging hydrocarbon ligands

(d) Polynuclear clusters containing CO, CNR or PR_3 ligands

(e) Polynuclear clusters containing η-hydrocarbon ligands

(f) Complexes containing Transition Metal-Main Group metal bonds

(g) Polynuclear clusters containing Main Group elements

Hydride Complexes

Nitrosyls

Dinitrogen, Aryldiazo, Aryldiimine and Related Complexes

Binary Transition Metal-Tertiary Phosphine Complexes

ABBREVIATIONS

acac	acetylacetonate
cod	cycloocta-1,5-diene

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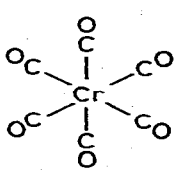
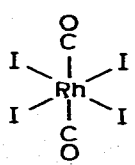
Cy	cyclohexyl
diars	1,2-bis(dimethylarsino)benzene
dme	1,2-dimethoxyethane
dmg	dimethylglyoximate
dmp	N,N-dimethylpiperazine
dmpe	1,2-bis(dimethylphosphino)ethane
dpam	bis(diphenylarsino)methane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
hfac	hexafluoroacetylacetonate
Meim	1-methylimidazole
Me_2ind	1,3-dimethylindenyl
nbd	norbornadiene (bicyclo[2.2.1]heptadiene)
oep	octaethylporphyrin
py	pyridine
pz	pyrazolyl
salpn	propane-1,2-salicylideneiminato
tcne	tetracyanoethylene
tcnq	tetracyanoquinodimethan
thf	tetrahydrofuran
tol	tolyl
tpp	*meso*-tetraphenylporphin

η^1-LIGANDS

(a) *Simple carbonyls and carbonyl halides*



(1) $Cr(CO)_6$

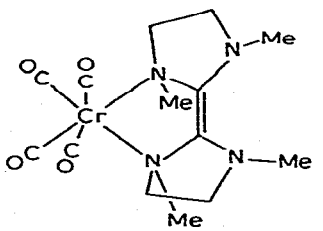


(2) $NPr_4[RhI_4(CO)_2]$

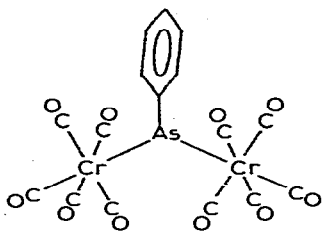
(*1*) Neutron diffraction study; octahedron distorted in crystal [26].

(*2*) Thermodynamically stable *trans*-$(CO)_2$, Rh-C 1.89, Rh-I 2.69Å [28].

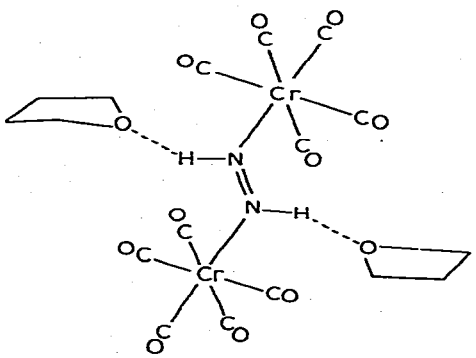
(b) *Carbonyls containing Group V donor ligands*



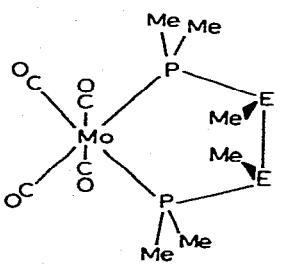
(3) $Cr(CO)_4\{[:CN(Me)(CH_2)_2N(Me)]_2\}$



(5) $PhAs[Cr(CO)_5]_2$



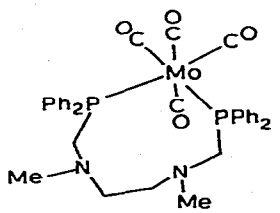
(4) $[Cr(CO)_5]_2N_2H_2$ 2 thf



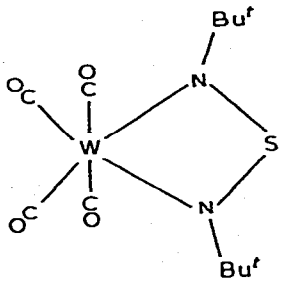
(6) $Mo(CO)_4(P_4Me_6)$ E = P

(7) $Mo(CO)_4(P_2As_2Me_6)$ E = As

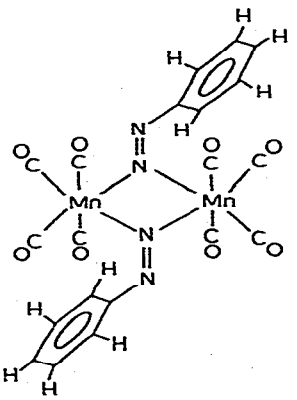
(*3*) Bond lengths in ligand indicate N atoms not bonded to Cr interact with C=C [113]. (*4*) Each proton of N_2H_2 ligand forms H bridge with O of tetrahydrofuran [50]. (*5*) Stabilised arsinidene (phenylarsanediyl), with strong metal→ligand back-bonding (Cr-As, 2.38Å), trigonal planar As^{I}. [compare analogous P compound (*159*)] [124]. (*6*) Short P-P [2.142(12)Å] contrasts with (Mo)P-P(P) [2.200(9)Å], and short



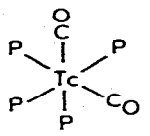
(8) $Mo(CO)_4[(Ph_2PCH_2NMeCH_2)_2]$



(9) $W(CO)_4[S(NBu^t)_2]$

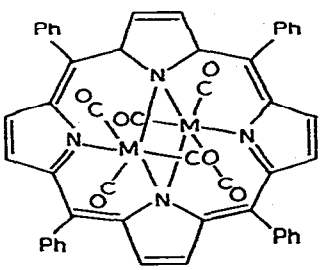


(10) $[Mn(N_2Ph)(CO)_4]_2$



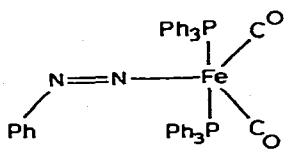
$P \equiv P(OEt)_2Ph$

(11) $\{cis\text{-}Tc(CO)_2[P(OEt)_2Ph]_4\}ClO_4$

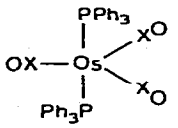


$(\mu\text{-tpp})[M(CO)_3]_2$

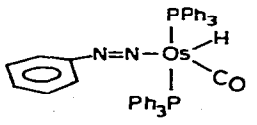
(12) M = Tc ; (13) M = Re



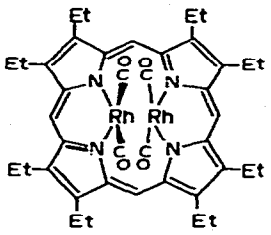
(14) $[Fe(CO)_2(N_2Ph)(PPh_3)_2]BF_4$



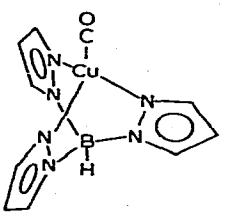
(15) $Os(CO)_2(NO)(PPh_3)_2$
X=N,C disordered



(16) $OsH(CO)(N_2Ph)(PPh_3)_2$



(17) $[Rh(CO)_2]_2(oep)$



(18) $Cu(CO)[HB(pz)_3]$

Mo-P[2.489(6)Å]; compare (*7*) [65]. (*7*) Chelate ring non-planar; very short As-As [2.343(7)Å], analogous to short P-P in (*6*), and short Mo-P, suggests some degree of π-delocalisation [64]. (*8*) Stable 9-membered ring, N not coordinated [245]. (*9*) Distorted octahedral with N-W-N, 64.1(5)°, and N-S-N, 93.4(7)° [compare with N-S-N, 113.6° in free ligand, and similar value in Pt complex containing monodentate $N(SBu^t)_2$] [92]. (*10*) Bridging PhN_2 group, with asymmetry Mn-N 2.031(2), 2.023(2), Mn-N-N 134.5(1), 119.5(1)°, probably arising from repulsions between Ph and CO; N=N 1.2332(23)Å [168]. (*11*) Confirms IR, NMR structure proposal [269]. (*12*) (*13*) Both have metals bonded to porphyrin nucleus above and below ligand plane; macrocycle considerably distorted from planarity; no evidence for metal-metal interactions [285]. (*14*) 5-coordinate TBP Fe with singly-bent PhN_2 ligand; bond parameters suggest multiple Fe-N, N-N bonds, i.e. complex of PhN_2^+ with Fe(0) [276]. (*15*) Linear NO, CO disordered [257]. (*16*) Distorted 5-coordinate TBP, steric requirements of H allow quasitetrahedral geometry; singly-bent PhN_2 ligand with long Os-N [1.867(6)Å] [271]. (*17*) Two square-planar

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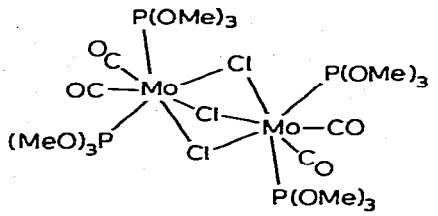
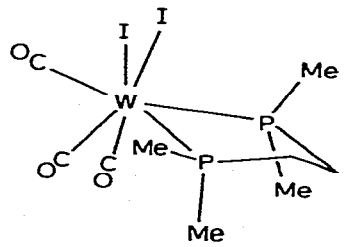
$Rh(CO)_2$ groups coordinated to deformed porphin skeleton, one above and one below macrocyclic plane; planes of adjacent pyrroles make angle of 18.3° [264]. (*18*) First structurally characterised Cu-CO link [av. Cu-CO, 1.765(14)Å]. [55].

(c) *Carbonyl halides containing Group V donor ligands*

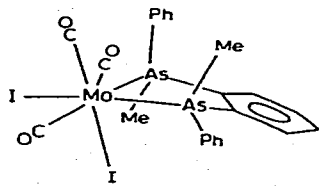


(19) $\left\{Mo_2Cl_3(CO)_4\left[P(OMe)_3\right]_4\right\}^{n+}$

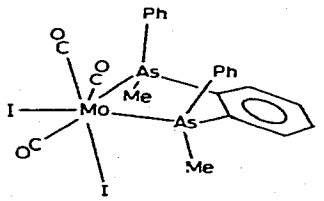


(22) $WI_2(CO)_3(dmpe)$

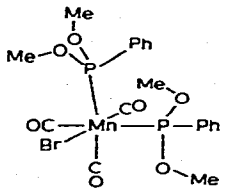
(*19*) From $MoCl_2(CO)_4$ + $P(OMe)_3$, counter-anion is $\{MoOCl_4[OP(OMe)_2]\}^{n-}$; value of n (and hence oxidation state) could not be determined from structural data [138]. (*20*) (*21*) *rac* and *meso* isomers; this reference contains theoretical description of stereochemistry of complexes [M(unidentate)$_5$(bidentate)] in terms of repulsion theory, and discussion of known structures in terms of the four different possible stereochemical types [272]. (*22*) Structures of two monoclinic forms give data on five independent molecules, which have essentially the same geometry, but show slight variations due to packing forces [123]. (*23*) (*24*) *fac* and *mer* isomers, both slightly distorted octahedral; no significant structural *trans* effect [161]. (*25*) Contains bridging dpam unit [234]. (*26*) *cis*-Diazene, Ru-N 2.086(5), N-N 1.218(7)Å, by protonation of aryldiazo complex; paper contains detailed discussion of ^{1}H NMR, Raman and IR spectra of aryldiazene and -diazo complexes [277]. (*27*) Double square planar coordination, with planes linked *via* Cl, and



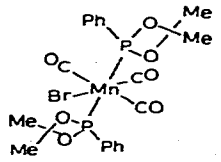
(20) $MoI_2(CO)_3[rac\text{-}o\text{-}C_6H_4(AsMePh)_2]$



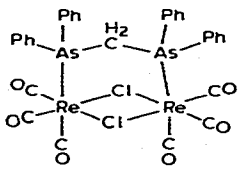
(21) $MoI_2(CO)_3[meso\text{-}o\text{-}C_6H_4(AsMePh)_2]$



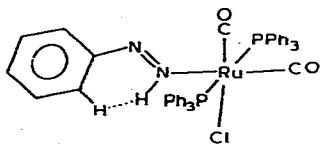
(23) $fac\text{-}MnBr(CO)_3[PPh(OMe)_2]_2$



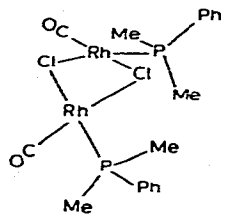
(24) $mer\text{-}MnBr(CO)_3[PPh(OMe)_2]_2$



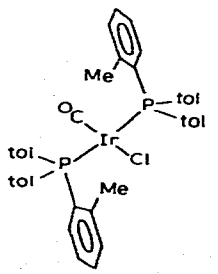
(25) $Re_2Cl_2(CO)_4(dpam)$



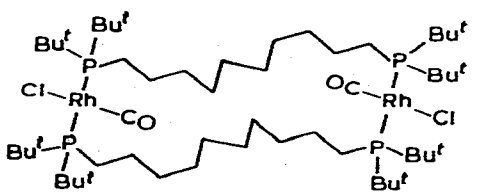
(26) $[RuCl(CO)_2(PPh_3)_2(HN_2Ph)]^+$



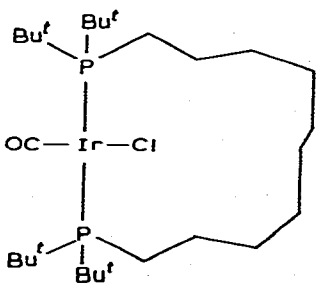
(27) $[RhCl(CO)(PMe_2Ph)]_2$



(29) $IrCl(CO)[P(o\text{-}tol)_3]_2$



(28) $\{RhCl(CO)[Bu^t_2P(CH_2)_{10}PBu^t_2]\}_2$

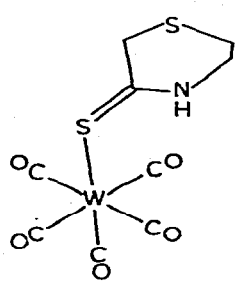


(30) $IrCl(CO)[Bu^t_2P(CH_2)_{10}PBu^t_2]$

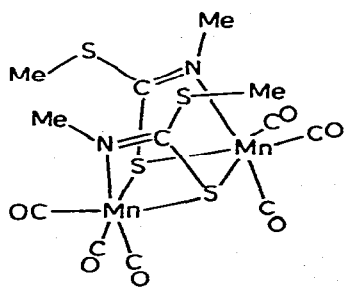
References p. 132

at an angle of 123°; phosphines occupy *cis* positions; only weak Rh...Rh interaction [3.167(1)Å] [152]. (*28*) 26-membered chelate ring, with 60:40 distribution of rotamers, Cl-*gauche* form predominating; Bu^t groups accurately eclipsed [222]. (*29*) Two of *o*-CH_3 groups located above and below square plane; general lack of reactivity (compared to PPh_3 analogue) ascribed to high activation energies rather than steric properties of P(*o*-tol)$_3$ [273]. (*30*) 13-membered chelate ring; CO groups *gauche* with respect to Bu^t group [222].

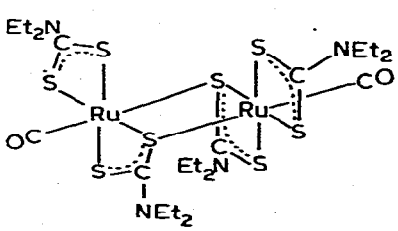
(d) *Carbonyls and carbonyl halides containing Group VI donor ligands*



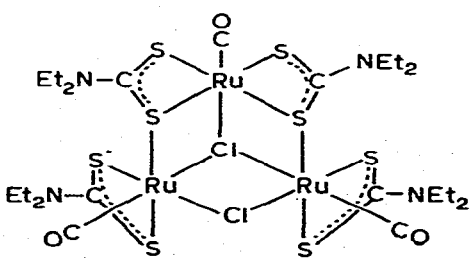
(31) $W(CO)_5(C_4H_7NS_2)$



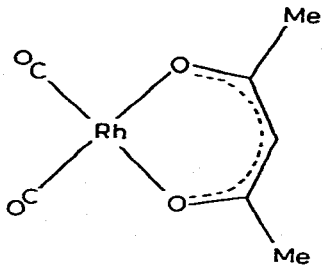
(32) $\{Mn(CO)_3[SC(SMe)NMe]\}_2$



(33) $[Ru(CO)(S_2CNEt_2)_2]_2$



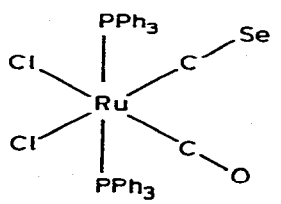
(34) $Ru_3Cl_2(CO)_3(S_2CNEt_2)_4$



(35) $Rh(acac)(CO)_2$

(*31*) Ligand S-bonded via thioketone group [44]. (*32*) Unusual bridging ligand from $[Mn(CO)_5]^-$ + MeNCS, followed by MeI [86]. (*33*) Originally reported as $[Ru(CS_2NEt_2)_2CO]$; short Ru-CO (*ca.* 1.80Å), bridging Ru-S (2.55Å) longer than others (mean, 2.399Å), asymmetric CS_2 geometry [196]. (*34*) From "carbonylated $RuCl_3$" + $MeCS_2NEt_2$; short Ru-CO (1.63 - 1.69Å) [202]. (*35*) Square planar molecules stack so that Rh atoms of neighbouring molecules occupy two remaining pseudo-octahedral positions (Rh....Rh, 3.253 and 3.271Å) [34].

(e) *Thiocarbonyls and selenocarbonyls*

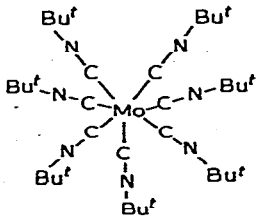


(36) $RuCl_2(CO)(CSe)(PPh_3)_2$

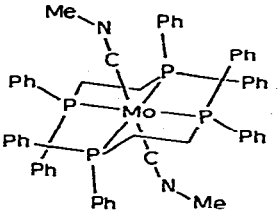
(*36*) First selenocarbonyl; Ru-Cl 2.427(5) (*trans* CO), 2.480(5)Å (*trans* CSe) indicate strong *trans* influence of this ligand; other bonds: Ru-C 1.89(2) (CO), 1.83(2) (CSe); C-O 1.21(3), C-Se 1.67(2)Å [256].

See also: *195*.

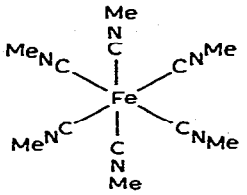
(f) *Isocyanide complexes*



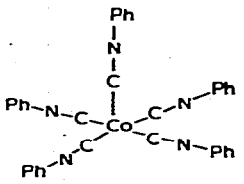
(37) $[Mo(CNBu^t)_7](PF_6)_2$



(38) *trans*-$Mo(CNMe)_2(dppe)_2$

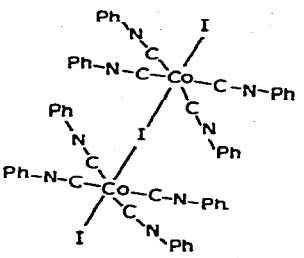


(39) $[Fe(CNMe)_6]^{2+}$

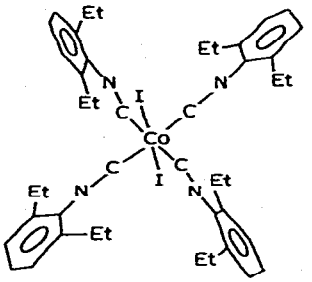


(40) $[Co(CNPh)_5]^+$

(41) $[Co(CNPh)_5]^{2+}$



(42) $[Co_2I_3(CNPh)_8]^-$

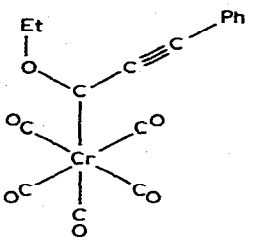


(43) $CoI_2(CNC_6H_3Et_2)_4$

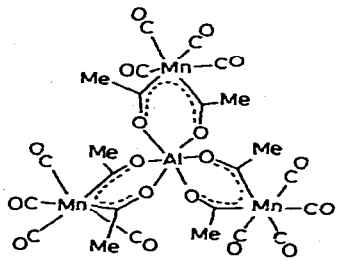
(*37*) Distorted capped trigonal prism (symmetry C_{2v}); three Mo-C bonds, range 2.051 - 2.171Å; similar to $[MoI(CNBu^t)_6]^+$, where I occupies capping position [251]. (*38*) Electron-rich Mo gives isocyanide some carbyne-like character, promoting ready electrophilic attack on N; Mo-C 2.101(7)Å, and Mo-C-N 156(1)° [294]. (*39*) Octahedral cation, Fe-C 1.874(4)Å [90]. (*40*) (*41*) Square pyramidal, comparison of Co(I) and Co(II) complexes shows change in effective coordination number and geometry; comparison with $Ni(CN)_5^{3-}$ shows better π-acceptor properties of PhNC over CN^-, increasing Co-C bond order; apical Co-C bond *shortens* on going from Co(I) to Co(II) [249,250]. (*42*) Reference [279]. (*43*) Nearly linear ICoICoI chain, diamagnetic via spin exchange in central CoICo group [279].

See also: *78, 83, 109, 224, 236, 237, 274, 275.*

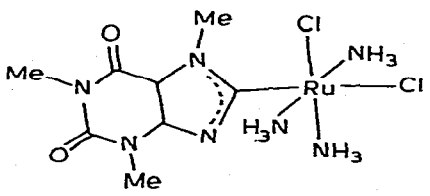
(g) *Carbene and carbyne complexes*



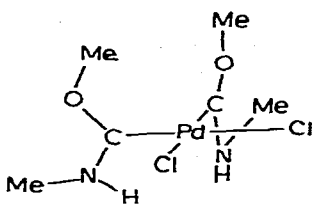
(44) $Cr(CO)_5[C(C_2Ph)(OEt)]$



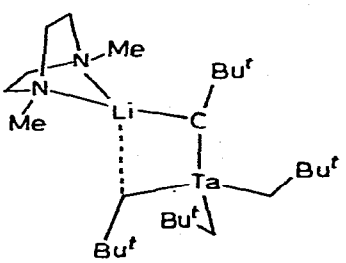
(45) $Al[Mn(CO)_4(COMe)_2]_3$



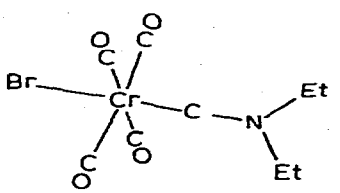
(46) $[RuCl_2(caffeine)(NH_3)_3]Cl$



(47) *cis*-$PdCl_2[C(OMe)(NHMe)]_2$



(48) $Li(dmp)[Ta(CH_2Bu^t)_3(CBu^t)]$



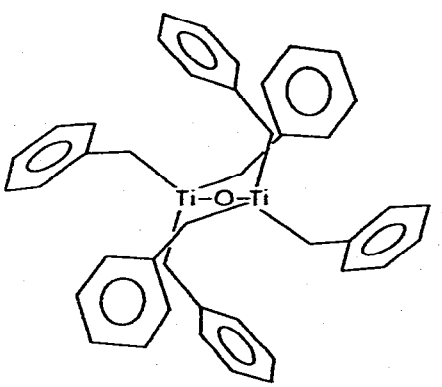
(49) *trans*-$Cr(CNEt_2)Br(CO)_4$

(*44*) All atoms of carbene ligand, including Ph group, are coplanar; Cr-C(carbene) 2.00(2)Å [128]. (*45*) New symmetrical "metallo-acac" anion [or bis(diacetyl)metallate], isolated as neutral Al chelate [206]. (*46*) Contains C-bonded purine derivative; no N-bonded complex obtained;

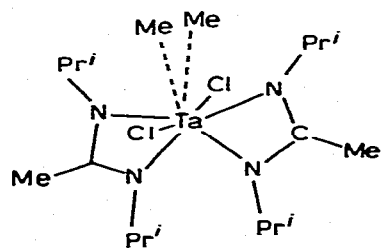
first Ru^{III}–C distance [2.03(1)Å], *trans* influence of carbene ligand shown in Ru–Cl distances, 2.427(3) (*trans*-C), 2.350(4)Å (*cis*-C) [37]. (*47*) *cis*-Bis-carbene complex; long Pd–Cl [2.387(1)Å] results from *trans* influence of carbene; bond distances indicate some delocalisation in O–C–N system [31]. (*48*) From "$Ta(CH_2Bu^t)_5$" + BuLi + diamine(N,N'-dimethylpiperazine); tetrahedral Ta, Ta–C(carbyne) 1.76, Ta–C(alkyl) 2.26Å; angle at carbyne C 165°; some interaction Li....CH_2Bu^t [179]. (*49*) Cr–C, 1.72(1); C–N 1.294(12)Å; indicates $Cr{\equiv}C{-}\ddot{N}R_2 \leftrightarrow \bar{C}r{=}C{=}\overset{+}{N}R_2$ [45].

See also: *157*, *178*, *240*.

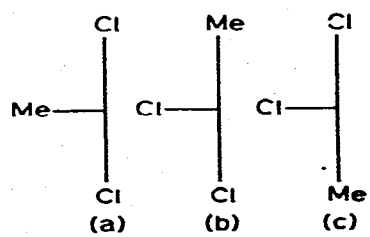
(h) *Alkyls, aryls and acyls*



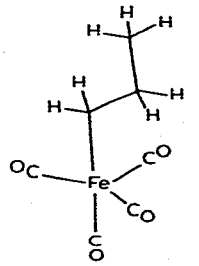
(50) $[Ti(CH_2Ph)_3]_2O$



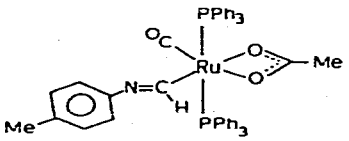
(51) $TaCl_2Me[MeC(NPr^i)_2]_2$



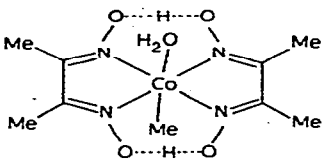
(*50*) Linear Ti–O–Ti, Ti–C 2.076(9)Å; no implication of Ti–C(β) π interaction [268]. (*51*) Distorted pentagonal bipyramid; 2Cl, Me occupy 2 axial and disordered equatorial site, arrangements (a),



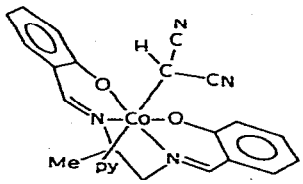
(52) $[Fe(CO)_4(C_3H_7)]^-$



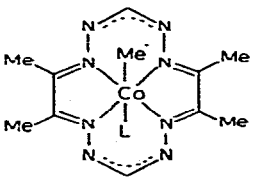
(53) $Ru(OAc)(CH{:}N\ tol\text{-}p)(CO)(PPh_3)_2$

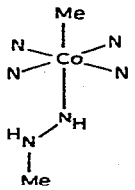


(54) $CoMe(OH_2)(dmg)_2$

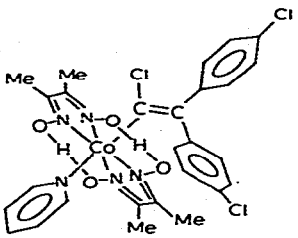


(56) $Co[CH(CN)_2](py)(salpn)$

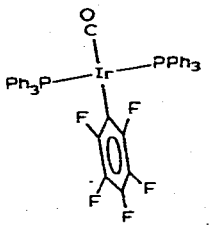




(55) $CoMe(N_2H_3Me)(C_{10}H_{14}N_8)$
L = NH_2NHMe

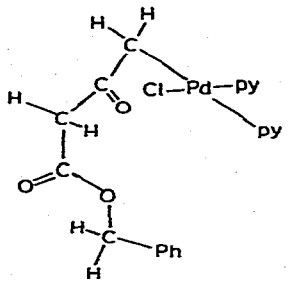


(57) $Co[CCl{:}C(C_6H_4Cl\text{-}p)_2](py)(dmg)_2$

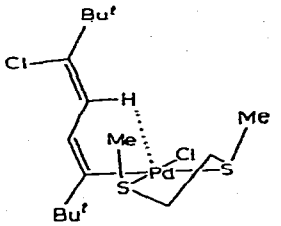


(58) $Ir(C_6F_5)(CO)(PPh_3)_2$

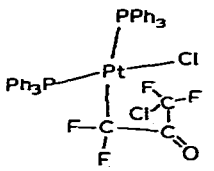
(b), (c) 69, 22, 9% from refinement [144]. (*52*) Alkyl in axial position of TBP; new conformation found in $N(PPh_3)_2^+$ cation [33]. (*53*) From $Ru(O_2)(CO)(CN\ tol\text{-}p)(PPh_3)_2$ + EtOH, via H transfer from Ru [284]. (*54*) Reference [48]. (*55*) Diamagnetic Co(III)-alkyl complex, but exhibits paramagnetic contact shifts [77]. (*56*) *Trans* influence of $CH(CN)_2$ group gives long Co-N(py), 2.06(1)Å [218]. (*57*) Reference [221]. (*58*) Ir-C(C_6F_5) 2.090(16)Å; reduced reactivity does not result from Ir-C_6F_5 π-bonding, but is probably steric in



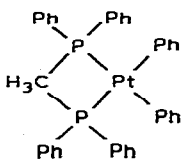
(59) $PdCl(CH_2COCH_2COCH_2Ph)(py)_2$



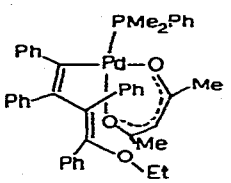
(60) $Pd(CBu^t{:}CHCH{:}CClBu^t)Cl(dth)$



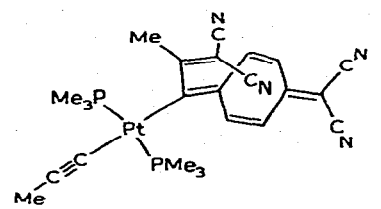
(61) $PtCl(CF_2COCF_2Cl)(PPh_3)_2$



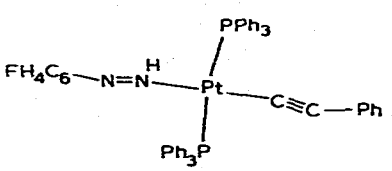
(62) $PtPh_2(dppm)$



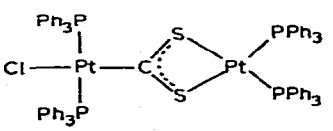
(63) $Pd[C_4Ph_4(OEt)](acac)(PMe_2Ph)$



(64) $Pt(C_2Me)\{C[CMe{=}C(CN)_2]{=}C_6H_4{=}C(CN)_2\}(PMe_3)_2$



(65) $[Pt(C_2Ph)(HNNC_6H_4F)(PPh_3)_2]^+$



(66) $[Cl(Ph_3P)_2Pt(CS_2)Pt(PPh_3)_2]BF_4$

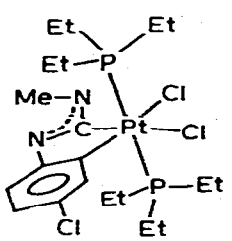
origin; C_6F_5 ring takes up edge-on position with respect to square plane [270]. (*59*) σ-Benzyl acetoacetate derivative, with normally unstable *cis*-$(py)_2$ configuration; ligand bent vertical to Pd square plane [189]. (*60*) *Cis*-chloropalladation product, intermediate in general mechanism of Pd^{II}-induced acetylene trimerisation; possible

interaction between Pd and H on C(5) [137]. (*61*) Rearrangement product from $Pt[OC(CF_2Cl)_2](PPh_3)_2$; very long Pt-P *trans* to C [260]. (*62*) Low J(PPt) results from distortion of valency angles at P and Pt, bond lengths normal [253]. (*63*) Formed by ring-opening of *endo*-alkoxycyclobutenyl complex [274]. (*64*) Addition of tcnq across C≡C, originally proposed as charge-transfer complex [210]. (*65*) From $Pt(HC_2Ph)(PPh_3)_2 + PhN_2^+$; Pt-C 1.95(3), C≡C 1.21(5)Å; compare ArN_2H ligand with that in (*346*) [286]. (*66*) Metallodithiocarboxylate ligand; Pt-C [1.950(15)Å] is one of shortest Pt-C(sp^2) known, suggesting some Pt-C π-bonding [296].

See also: *48, 98, 130, 151, 152, 172, 173, 174, 175, 176, 177, 178, 180, 181, 182, 187, 192, 213, 277, 310.*

(i) *Complexes containing chelating* η^1*-ligands*

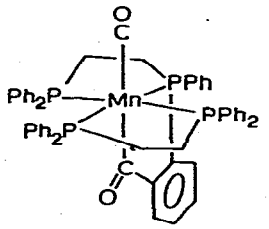
C-donors



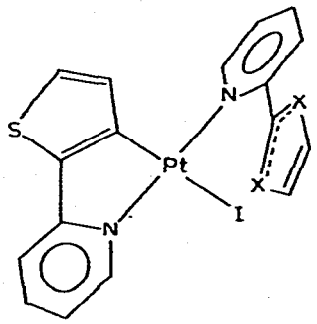
(67) $\left\{PtCl_2[(ClC_6H_3NH)C(NHMe)](PEt_3)_2\right\}^+$

(*67*) By chlorination of C(NHMe)(NHPh) complex; Pt^{IV}-C(Ph), 2.034(11); Pt^{IV}-C(carbene), 1.973(11)Å; *trans* influence on Pt^{IV}: Cl < carbene < σ-Ph [178].

N- or P-donors



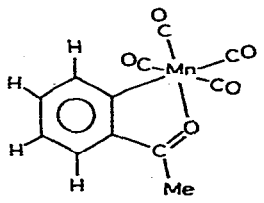
(68) $Mn[COC_6H_4P(Ph)(CH_2)_2PPh_2](CO)(dppe)$



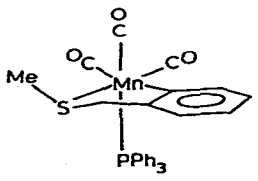
(69) PtI(tp)(tpH)
X = disordered C,S

(*68*) Reported as paramagnetic $Mn(CO)(dppe)_2$; contains acyl group formed by attack of $P(C_6H_4^-)$ on adjacent CO group [292]. (*69*) From K_2PtCl_4 + KI + 2-(2'-thienyl)pyridine(tp); coordination of one tp via pyridine N; second tp is metallated on thiophene ring in 3' position [145].

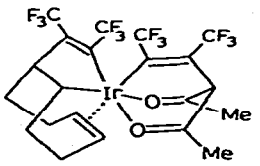
O- or S-donors



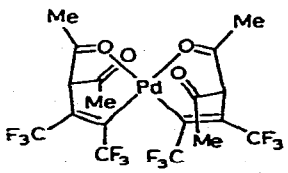
(70) $Mn[C_6H_4C(O)Me](CO)_4$



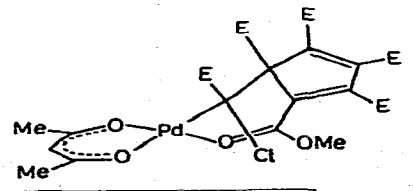
(71) $Mn(C_6H_4CH_2SMe)(CO)_3(PPh_3)$



(72) $Ir(acac\,C_4F_6)(cod\,C_4F_6)$

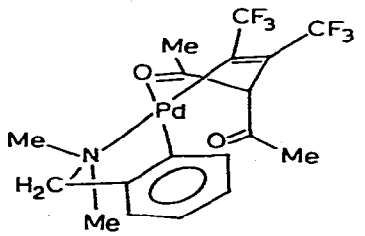


(73) $Pd(acac\,C_4F_6)_2$



(74) $Pd[CCl(CO_2Me)C_5(CO_2Me)_4C(O)OMe](acac)$

E = CO_2Me



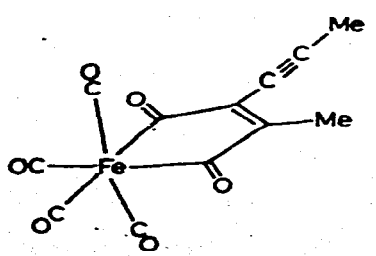
(75) $Pd(C_6H_4CH_2NMe_2)(acacC_4F_6)$

(*70*) Metallated acetophenone with long C=O distance *via* π-delocalisation, also reflected in *trans*-Mn-CO distance [81]. (*71*) Non-planar chelate ring, MnC_3S ring less strained than MnC_3N ring in analogous complex derived from $PhCH_2NMe_2$ [231]. (*72*) From Ir(acac)(cod) + $C_2(CF_3)_2$; contains ($acacC_4F_6$) ligand found in (*73*), and ligand formed by insertion of alkyne between Ir and one end of coordinated C=C [186]. (*73*) From $Pd(acac)_2$ + $C_2(CF_3)_2$ in 1,4-addition reaction, alkyne links γ-carbon of acac to Pd [146]. (*74*) From $PdCl_2$ + $C_2(CO_2Me)_2$, then acac; ligand contains planar $C_5(CO_2Me)_5$ ring, while PdC_4O chelate ring is considerably bent [200]. (*75*) Similar to (*73*); also contains *ortho*-metallated $PhCH_2NMe_2$ [146].

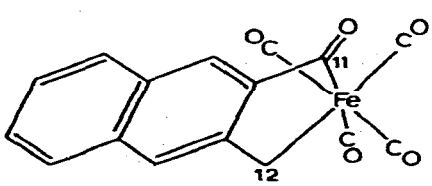
See also: *161, 167, 303.*

η^2-LIGANDS

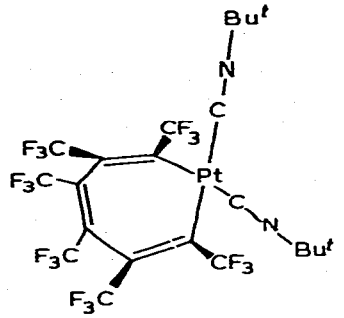
(a) *($2\eta^1$)-Ligands (Metallocycles)*



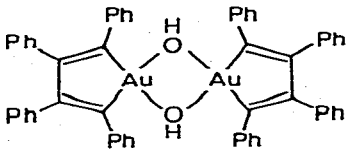
(76) $Fe(CO)_4[C(O)CMe{:}C(C{\equiv}CMe)CO]$



(77) $Fe(CO)_4(C_{12}H_8O)$



(78) $Pt[C(CF_3):C(CF_3)]_3(CNBu^t)_2$



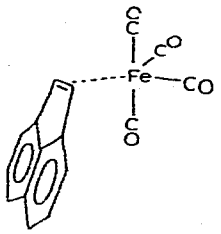
(79) $[Au(OH)(C_4Ph_4)]_2$

(*76*) From $MeC_2C_2Me + Fe(CO)_5$; axial CO groups bent towards metallocycle, with C-Fe-C 166° [79]. (*77*) From naphtho[*b*]cyclopropene + $Fe_2(CO)_9$; chelate ring bent along C(11) - C(12) by 15° [126]. (*78*) Formed by ring-opening of η^2-$C_6(CF_3)_6$ complex; *cis*, *cis*, *cis*-triene, cannot be converted thermally to previously reported *cis*, *trans*, *cis*-triene [194]. (*79*) Hydroxo-bridged dimer [224].

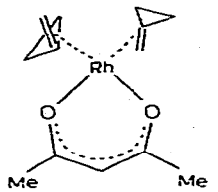
See also: *184*, *254*, *258*.

(b) *Olefin complexes*

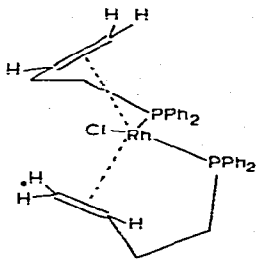
(*80*) η^2-Acenaphthylene complex,with C=C in equatorial position; fused C_6 rings exhibit alternating C-C distances as found with naphthalene; first accurate (olefin)$Fe(CO)_4$ structure [125]. (*81*) Olefins symmetrically bonded in converse orientations, with Rh-C(H_2) 2.131(12), Rh-C(C_2) 2.073(11)Å, angle between ring plane and C=C 153° [101]. (*82*) TBP Rh, with one P, 2C=C forming equatorial plane; orientation of one of the C=C bonds in this plane considerably distorts one butenyl group [239]. (*83*) TBP Rh, *trans* axial isocyanide ligands; fumaronitrile parameters: C=C 1.444(10)Å, substituents bent back by 20°; shows dynamic behaviour in solution [258]. (*84*) C_2H_4 perpendicular to $IrClP_2$



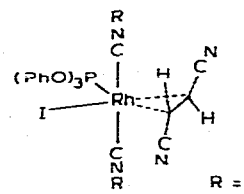
(80) $Fe(CO)_4(C_{12}H_8)$



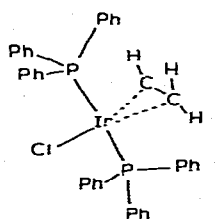
(81) $Rh(acac)(C_4H_6)_2$



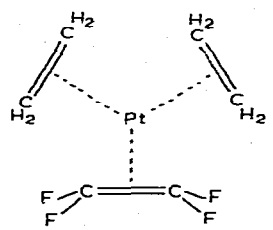
(82) $RhCl[P(CH_2CH_2CH{=}CH_2)Ph_2]_2$



(83) $RhI[CH(CN){:}CH(CN)][P(OPh)_3](CNC_6H_4OMe\text{-}p)_2$



(84) $IrCl(C_2H_4)(PPh_3)_2$
one C_2H_4 H-atom not shown



(85) $Pt(C_2H_4)_2(C_2F_4)$

plane with short C=C [1.375(10)Å], consistent with its lability; negligible *trans* influence on Ir–Cl bond [259]. (*85*) Confirms Hoffmann–Rösch predictions: C=C bonds 1.36 (C_2H_4), 1.44Å (C_2F_4) [30]. (*86*) 3 C=C, Pt coplanar; mean C=C 1.38Å; Pd complex isostructural [30]. (*87*) C_6 ring no longer planar, with alternate long and short bonds around ring; α 74° [214]. (*88*) Angle between normals of CF_2 planes 80°, indicating considerable rehybridisation; C=C 1.45Å [255].

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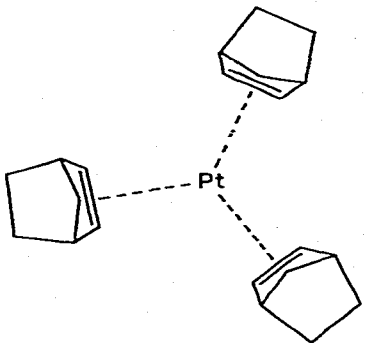
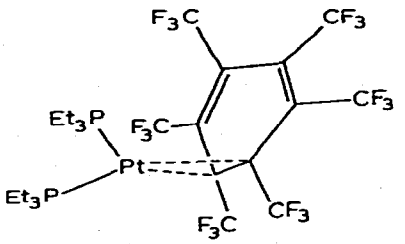
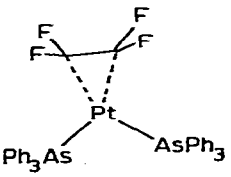


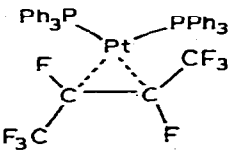
(86) $Pt(C_7H_{10})_3$



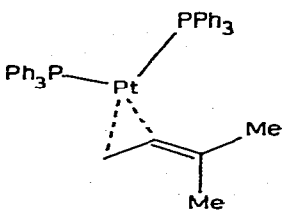
(87) $Pt[C_6(CF_3)_6](PEt_3)_2$



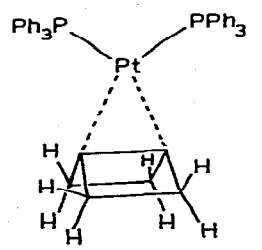
(88) $Pt(C_2F_4)(AsPh_3)_2$



(89) $Pt[CF(CF_3):CF(CF_3)](PPh_3)_2$

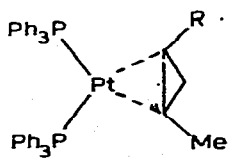


(90) $Pt(C_3H_2Me_2)(PPh_3)_2$



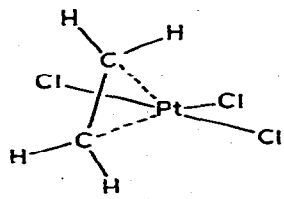
(91) $Pt(C_6H_8)(PPh_3)_2$

C_6H_8 = $\Delta^{1,4}$-bicyclo[2.2.0]hexene



(92) $Pt(C_3H_3Me)(PPh_3)_2$ R = H

(93) $Pt(C_3H_2Me_2)(PPh_3)_2$ R = Me

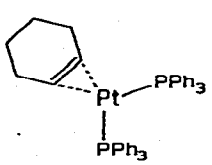


(94) $[PtCl_3(C_2H_4)]^-$

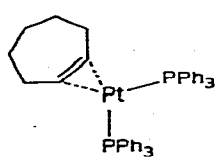
(*89*) Dihedral PtP_2/PtC_2 planes 10.8°; C=C 1.429(14)Å; dihedral between substituent planes 80°; discussion of bonding in this complex using ESCA data [262]. (*90*) Allene skeleton bent at central C by 140.8(8)°; C=C bonds: 1.430(11) (coordinated), 1.316(11)Å (free) [265]. (*91*) Olefin bent along coordinated C=C, angle between planes 56°; olefinic C=C 1.52(2)Å, dihedral PtP_2/PtC_2 3.2°; non-bonding contacts result in slight asymmetry in PtC_2 unit [267].
(*92*) (*93*) Cyclopropenes do not ring open; parameters for (*92*) inaccurate (disorder) [263]. (*94*) Neutron diffraction study; Pt-Cl distances show *trans* influence of olefin: 2.340(2) (*trans*-C=C), 2.302(2)Å (*trans*-Cl); C=C 1.375(4)Å; 4H bent away from Pt, angle between normals to CH_2 planes 32.5° [25].

See also: *158, 164.*

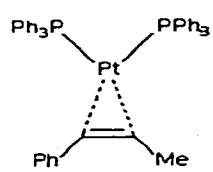
(c) *Alkyne complexes*



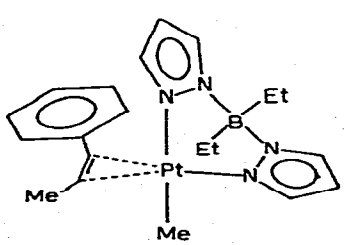
(95) $Pt(C_6H_8)(PPh_3)_2$



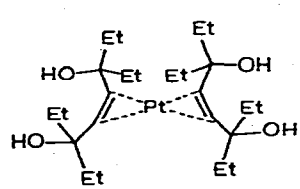
(96) $Pt(C_7H_{10})(PPh_3)_2$



(97) $Pt(MeC_2Ph)(PPh_3)_2$



(98) $PtMe(MeC_2Ph)[Et_2B(pz)_2]$

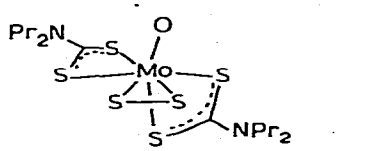


(99) $Pt\{C_2[CEt_2(OH)]_2\}_2$

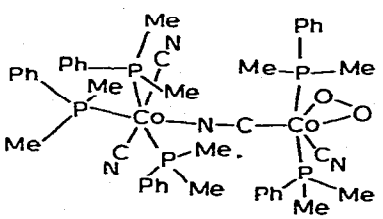
(*95*) (*96*) Complexes of small cyclic acetylenes; C≡C bond distances 1.297(8) (C_6), 1.283(5)Å (C_7), with C-C≡C angles 127.3 (C_6), 138.8° (C_7) [266]. (*97*) *cis*-bent alkyne, mean 40(1)°, with C≡C, 1.277(25)Å, consistent with Δν(C≡C) 478 cm^{-1} [281]. (*98*) Reference [174]. (*99*) Bis-alkyne-metal complex; Pt-C≡C dihedral 86°, C≡C 1.35Å; each molecule H-bonded to 4 neighbours [217].

See also: *127, 150, 245, 246, 247, 277, 278, 280, 281.*

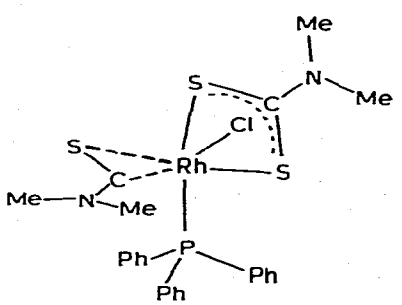
(d) *Complexes containing other three-membered rings and related systems*



(100) $MoO(S_2)(S_2CNPr_2)_2$

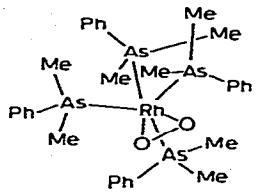


(101) $Co_2(CN)_4(PMe_2Ph)_5(O_2)$

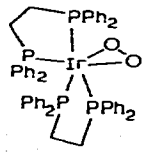


(102) $RhCl(SCNMe_2)(S_2CNMe_2)(PPh_3)$

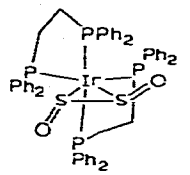
(*100*) From $MoO_2(S_2CNPr_2)_2 + H_2S$; S-S 2.018(8)Å [116]. (*101*) From $Co(CN)_2(PMe_2Ph)_3 + O_2$; 2 Co bridged by CN, with O_2 forming 3-membered ring [O-O, 1.441(11)Å] [280]. (*102*) η^2-Thiocarboxamido ligand has short Rh-C [1.895(16)Å] [212]. (*103-107*) See Table above. (*108*) Stabilisation of S_2O_2, from S_2 complex + $NaIO_4$; S-S 2.041Å [289]. (*109*) Irreversible oxygenation of $Ni(CNBu^t)_4$; O-O 1.45(1)Å [66]. (*110*) CO_2 has bent geometry, with O-C-O 133°, C-O bond lengths



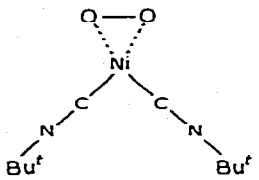
(103) $[Rh(O_2)(AsMe_2Ph)_4]ClO_4$



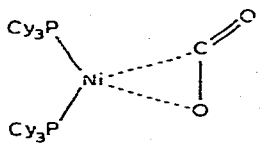
(107) $[Ir(O_2)(dppe)_2]^+$



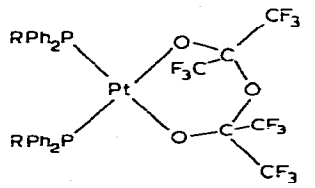
(108) $[Ir(S_2O_2)(dppe)_2]Cl$



(109) $Ni(O_2)(CNBu^t)_2$



(110) $Ni(CO_2)(PCy_3)_2$



$Pt[OC(CF_3)_2]_2O(PPh_2R)_2$

(111) R = Me; (112) R = Ph

Bond lengths in dioxygen complexes

	Complex	O-O(Å)	M-O(Å)	Reference
(*104*)	$[Rh(O_2)(PMe_2Ph)_4]BPh_4$	1.43	2.04, 2.03	[12]
(*103*)	$[Rh(O_2)(AsMe_2Ph)_4]ClO_4$	1.46	2.03, 2.03	[12, 240]
(*105*)	$[Ir(O_2)(PMe_2Ph)_4]BPh_4$	1.49	2.05, 2.04	[12]
(*106a*)	$[Ir(O_2)(dppm)_2]ClO_4$	1.49	2.06, 2.05	[12]
(*106b*)	$[Ir(O_2)(dppm)_2]PF_6$	1.45	2.00, 2.01	[12]
(*107*)	$[Ir(O_2)(dppe)_2]PF_6$	1.52	2.05, 2.05	[12, 288]

1.22 (coord.), 1.17Å (free) [254]. (*111*) (*112*) Pt incorporated in non-planar 6-membered ring, from condensation of $(CF_3)_2CO$; sequence of C-O bond lengths provides evidence for donation by O lone-pair into anti-bonding orbitals of $C(CF_3)_2$ group; Pt-P bonds are short [237].

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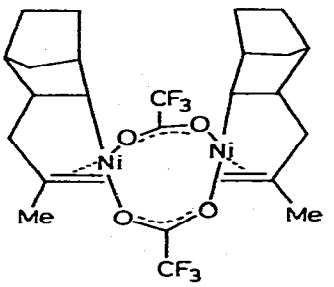
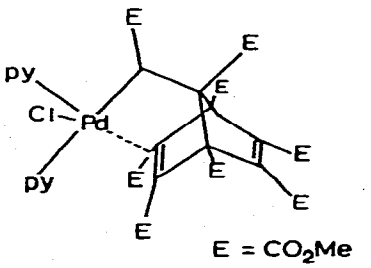
η^3-LIGANDS

(a) (η^1 - η^2)-*Ligands*



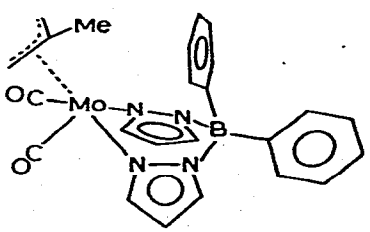
(113) $[Ni(O_2CCF_3)(C_{11}H_{17})]_2$



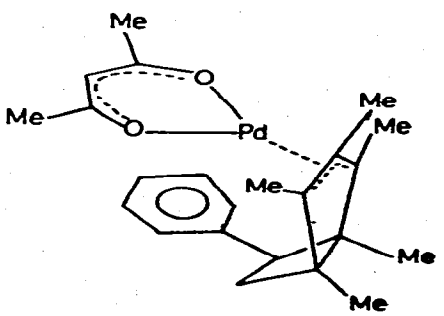
(114) $Pd[HC_8(CO_2Me)_8]Cl(py)_2$

(*113*) *Trans* influence of σ-C results in 2 CF_3CO_2 groups bonded differently; bond weakening in one related to formation of catalytically active intermediates [219]. (*114*) From $PdCl_2$ + $C_2(CO_2Me)_2$, then py; 5-coordinate Pd^{II}, distorted TBP with long Pd-N and Pd-Cl bonds [246].

(b) η^3-*Allyl complexes*



(115) $Mo(CO)_2(C_4H_7)[Ph_2B(pz)_2]$



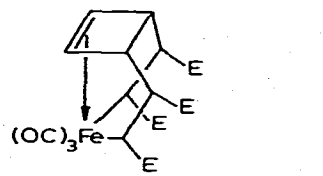
(116) $Pd(HC_7Me_5Ph)(acac)$

(*115*) 16-electron complex, no interaction with *ortho*-hydrogen; small C-C-C angles at phenyl carbons bonded to B [208]. (*116*) Cyclobutane ring formed by insertion of coordinated olefin into Pd-C σ bond; bonding of cyclopentenyl group relieves crowding from *endo*-Ph group and Pd [201].

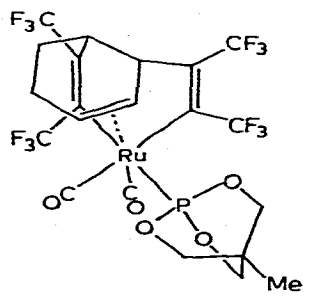
See also: *179, 263.*

η^4-LIGANDS

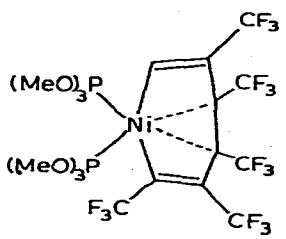
(a) $(2\eta^1 + \eta^2)$-*Ligands*



(117) $Fe(CO)_3(C_{16}H_{20}O_8)$



(118) $Ru(CO)_2[P(OCH_2)_3CMe]\{C_6H_8[C_2(CF_3)_2]_2\}$



(119) $Ni[C_6(CF_3)_6][P(OMe)_3]_2$

(*117*) Photo-adduct of $Fe(CO)_3(C_4H_4)$ + Me_2 maleate, with olefin formally inserting between Fe and 2 adjacent C atoms of C_4 ring to give 6-membered FeC_5 ring [160]. (*118*) Bis-adduct of $C_2(CF_3)_2$ + $Ru(CO)_3(C_6H_8)$, with alkyne formally inserting between Ru and both C atoms of original olefinic bond to give 7-membered rutheniacyclohepta-1,5-diene ring [184].

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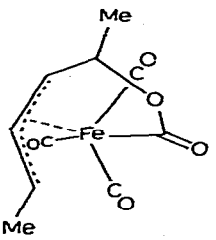
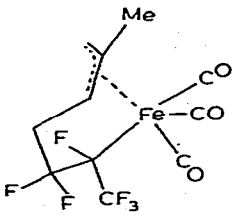
(*119*) *Cis, trans, cis*-triene, with central C=C also η^2-bonded to Ni [149].

(b) (η^1 + η^3)-*Ligands*



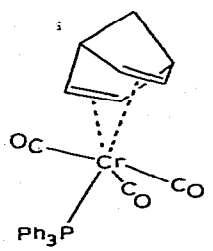
(120) $Fe(CO)_3[C(O)OC_4H_4Me_2]$



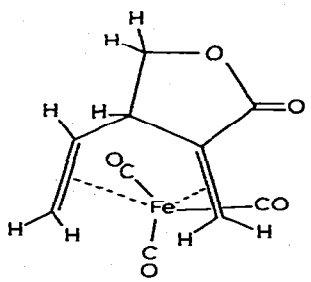
(121) $Fe(CO)_3[CF(CF_3)CF_2CH_2CHCMeCH_2]$

(*120*) From vinyloxirane + $Fe(CO)_5$, ferrelactone structure confirmed configuration [57]. (*121*) From $Fe(CO)_3(C_4H_6)$ + $CF_3CF{:}CF_2$; structure determines direction of addition as $FeCF(CF_3)CF_2$ [73].

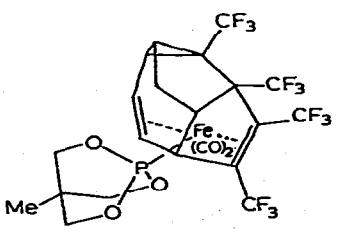
(c) ($2\eta^2$)-*Ligands*



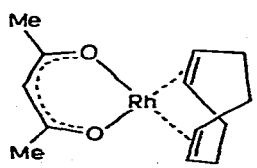
(122) $Cr(CO)_3(PPh_3)(nbd)$



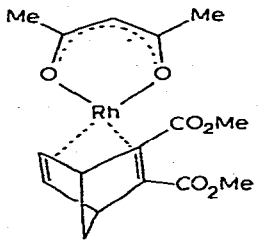
(123) $Fe(CO)_3(C_7H_8O_2)$



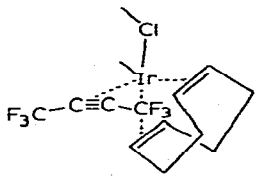
(124) $Fe(CO)_2\left[P(OCH_2)_3CMe\right]\left\{C_7H_8\left[C_2(CF_3)_2\right]_2\right\}$



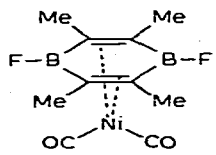
(125) Rh(acac)(cod)



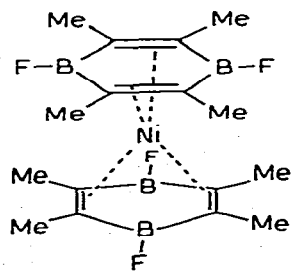
(126) Rh(acac)$[C_7H_6(CO_2Me)_2]$



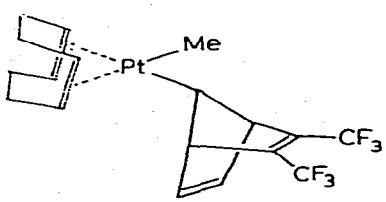
(127) $[IrCl(C_4F_6)(cod)]_2$
half of dimeric molecule



(128) $Ni(CO)_2(C_4Me_4B_2F_2)$



(129) $Ni(C_4Me_4B_2F_2)_2$



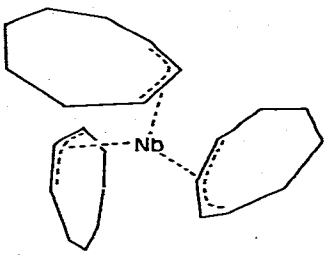
(130) $PtMe[C_7H_5(CF_3)_2](cod)$

(*122*) Double bond *trans* to P is bonded more strongly than the other, with Cr-C distances differing by *ca.* 0.13Å, and C=C bonds 1.407 (*trans* P), 1.350 (*trans* CO) [226]. (*123*) 3-Methylene-4-vinyldihydrofuran-2(3H)-one ligand formed by ring-opening of 2,3-bis(hydroxymethyl)methylenecyclopropane with $Fe_2(CO)_9$ [53]. (*124*) Bis-adduct of $C_2(CF_3)_2$ + $Fe(CO)_3(C_7H_8)$, with addition of alkyne on *endo*-face of C_7-ring to give one 3- and two 5-membered rings [184]. (*125*) Reference [100]. (*126*) Difference in C=C and Rh-C of substituted nbd ligand [134]. (*127*) Contains diene + alkyne coordinated to the same Ir atom; on heating forms isomer (*192*) [209]. (*128*) (*129*) Ligand from BF + C_2Me_2, isostructural with duroquinone (dq); these complexes obtained from ligand + $Ni(CO)_4$, and general properties and structures similar to

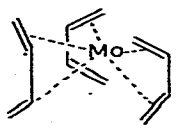
$Ni(dq)_2$ [60, 136]. (*130*) Diels-Alder adduct from $PtMe(cod)(C_5H_5)$ + $C_2(CF_3)_2$, with alkyne adding on opposite side to Pt, i.e. no metal interaction [151].

[See also: *185, 239, 242, 255.*

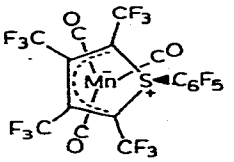
(d) η^4-*Ligands*



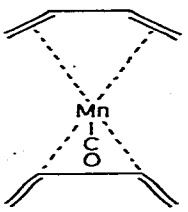
(131) $[Nb(C_8H_8)_3]^-$



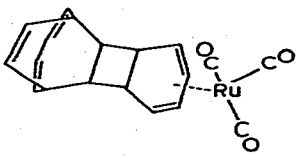
(132) $Mo(C_4H_6)_3$



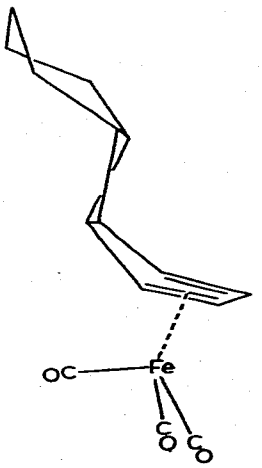
(134) $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$



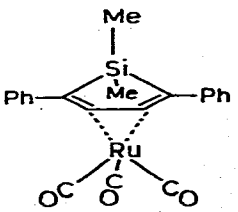
(133) $Mn(CO)(C_4H_6)_2$



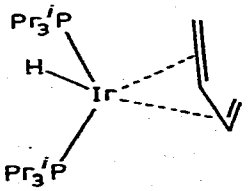
(136) $Ru(CO)_3(C_{16}H_{16})$



(135) $Fe(CO)_3(C_{12}H_{16})$



(137) $Ru(CO)_3(C_4H_2Ph_2SiMe_2)$



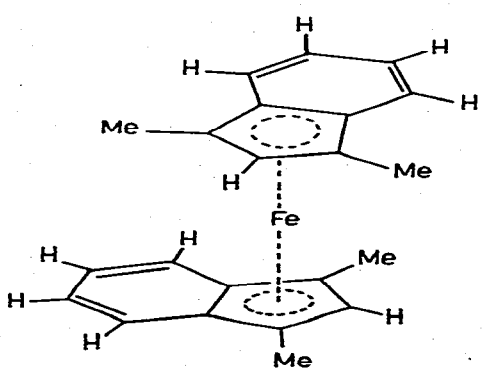
(138) $IrH(C_4H_6)(PPr^i_3)_2$

(*131*) 2 C_8 rings bonded via η^3 bonds, one via η^4; in solution all ring protons are equivalent, so detailed grometry probably determined by packing forces; formally Nb^I, 16-electron system [211]. (*132*) From Mo vapour + C_4H_6; trigonal prismatic arrangement of planar diene ligands around Mo [91]. (*133*) Paramagnetic, from $Mn(CO)_4(NO)$ + C_4H_6; planar diene ligands, H atom positions consistent with rehybridisation indicated by C-C distances [46]. (*134*) No Mn-S interaction; zwitterionic structure involving sulphonium ion and Mn(-I) species; fluorocarbon bonded via η^4 interaction [95]. (*135*) Cyclobutane ring non-planar, cyclohexane ring has twist-chair conformation [122]. (*136*) New C_8H_8 dimer, perhaps formed by Diels-Alder addition to $Ru(CO)_3(C_8H_8)$ [159]. (*137*) Comparison of free silole and $Ru(CO)_3$ derivative; Si atom above butadiene plane, opposite side from Ru, with dihedral 32° [185]. (*138*) Distorted TBP; central bond of C_4H_6 (1.408Å) shorter than outer two, which differ because of coordination to axial (1.442Å) and equatorial (1.433Å) positions; Ir-H, 1.77(12)Å [197].

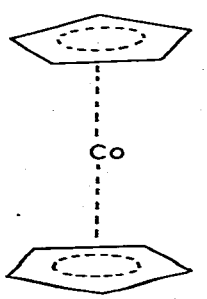
See also: *165, 166, 182, 183.*

η^5-LIGANDS

(a) *Cyclopentadienyls*



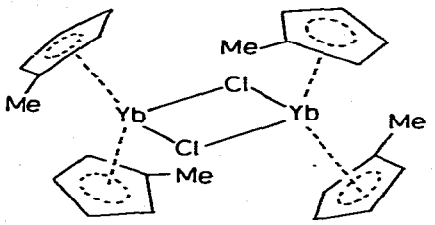
(139) $[Fe(C_9H_5Me_2)_2]PF_6$



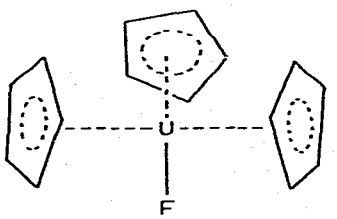
(140) $Co(C_5H_5)_2$

(*139*) Staggered, indenyl ring rotated about Fe-C_5 ring axis by 93.5°, resulting in rotation angle ϕ 21.7° [195]. (*140*) Accurate determination [56].

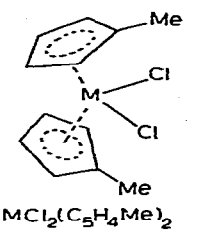
(b) *Cyclopentadienyl metal halides*



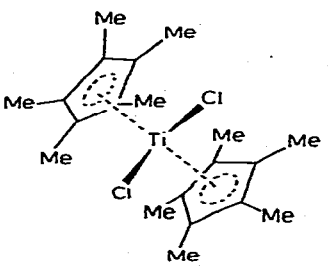
(141) $[YbCl(C_5H_4Me)_2]_2$



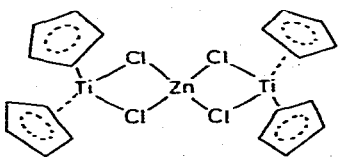
(142) $UF(C_5H_5)_3$



$MCl_2(C_5H_4Me)_2$
(143) M = Ti; (144) M = V



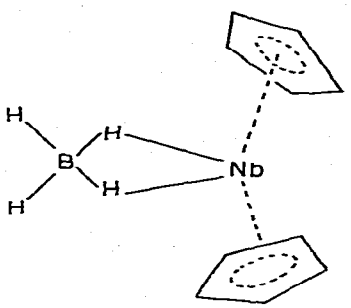
(145) $TiCl_2(C_5Me_5)_2$



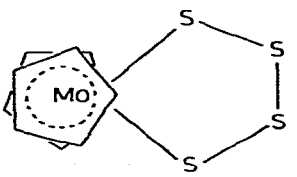
(146) $[TiCl(C_5H_5)]_2ZnCl_2$

(*141*) Distorted tetrahedral Yb, approximately square Yb_2Cl_2 moiety [213]. (*142*) Short U-F 2.11Å, evidence for ring C-H...F bonding linking adjacent molecules [120]. (*143*) (*144*) Main differences: Cl-M-Cl 87.1(V), 93.2°(Ti); M-Cl 2.398(2)(V), 2.360(2)(Ti), compared to shorter V-C; angles between ring normals 129.9(V), 133.4°(Ti) [8]. (*145*) Distorted tetrahedral Ti, several ring Me groups bent out of C_5 plane away from Ti to relieve Cl-Me and Me-Me crowding [175]. (*146*) More accurate determination [cf. C.G. Vonk, *J.Cryst.Molec.Struct.*, 3 (1973) 201] [170].

(c) *Cyclopentadienyls containing other anionic ligands*



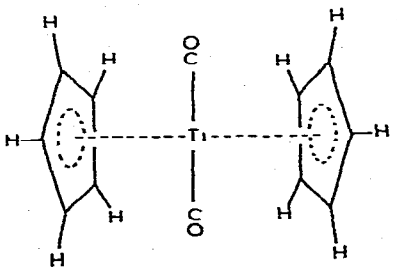
(147) $Nb(H_2BH_2)(C_5H_5)_2$



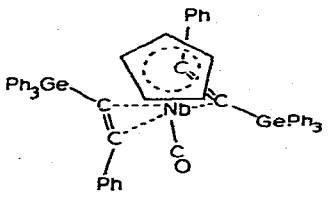
(148) $MoS_4(C_5H_5)_2$

(*147*) Nb-H 2.0(1)Å (high *R* value), Nb-B 2.26(6)Å, angle between ring normals 130°; comparisons made with $Ti(BH_4)(C_5H_5)_2$ and other $Nb(C_5H_5)_2$ derivatives [61]. (*148*) Central S-S bond [2.019(9)Å] significantly shorter than others [2.083(7)Å], S-S-S bond angles also small (av. 100.4°) (cf. 107.9° in S_8). Angle between normals to C_5 planes is 134° [58].

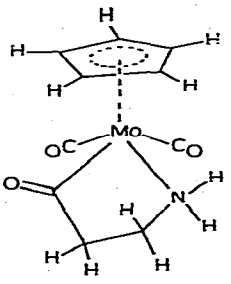
(d) *Cyclopentadienyls containing CO or PR_3 ligands*



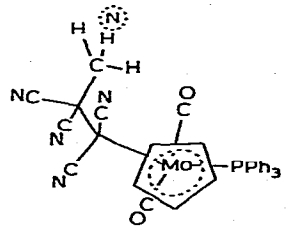
(149) $Ti(CO)_2(C_5H_5)_2$



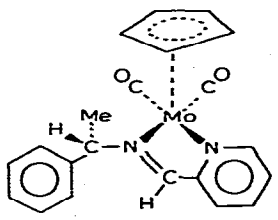
(150) $Nb(CO)(PhC_2GePh_3)_2(C_5H_5)$



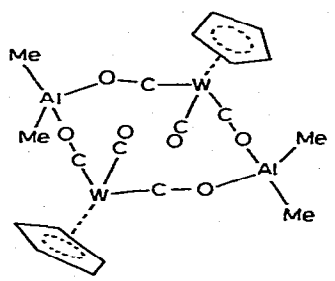
(151) $Mo(CO(CH_2)_2NH_2)(CO)_2(C_5H_5)$



(152) $Mo[C(CN)_2C(CN)_2Me](CO)_2(PPh_3)(C_5H_5)$
disorder in cyanopropyl ligand

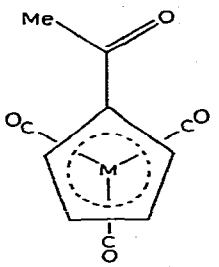


(153) $[Mo(CO)_2(C_{14}H_{14}N_2)(C_5H_5)]^+$

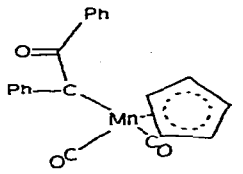


(154) $[W(CO)_3(C_5H_5)AlMe_2]_2$

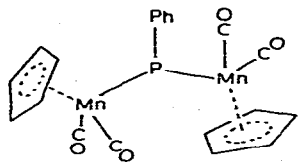
(*149*) First structural characterisation of Ti-CO link; Ti-CO [2.030(11)Å] longer than expected [84]. (*150*) From $Nb(CO)_4(C_5H_5)$ + PhC_2GePh_3; complex stabilised by bulky $GePh_3$ group (cf. C_2Ph_2 derivative which forms dimer); alkyne shows usual lengthened C≡C, substituents bent back [295]. (*151*) Intermolecular H-bonding between acyl acceptor and amine donor: N-H...O; chelating 3-aminopropionyl group [59]. (*152*) Disorder in Me, one CN; Mo-C (alkyl) 2.414(4)Å, longer than normal [236]. (*153*) Absolute configuration determined; α-phenylethyl group has *S* configuration, while that at Mo cannot be specified using present rules [187]. (*154*) $AlMe_2$ groups O-bonded to CO groups on different W atoms, to give slightly puckered 12-membered rings [172]. (*155*) (*156*) For $M(CO)_3(C_5H_4R)$, Mn, Re complexes are isostructural only for R=H; other pairs (R=COMe, COPh) differ in



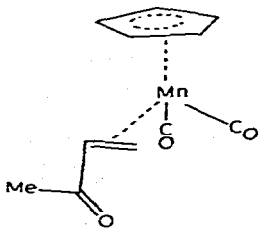
$M(CO)_3(C_5H_4COMe)$
(155) M = Mn; (156) M = Re



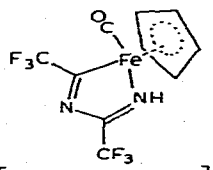
(157) $Mn(CO)_2[CPh(COPh)](C_5H_5)$



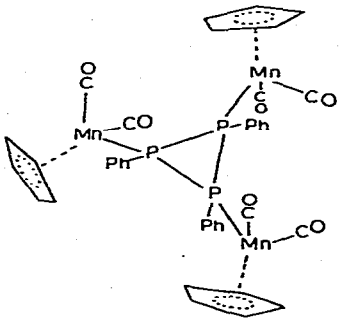
(159) $[Mn(CO)_2(C_5H_5)]_2PPh$



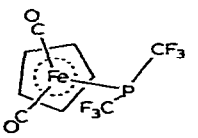
(158) $Mn(CO)_2(CH_2{=}CHCOMe)(C_5H_5)$



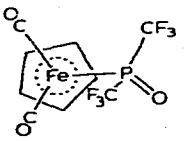
(161) $Fe[NH{:}C(CF_3)N{:}C(CF_3)](CO)(C_5H_5)$



(160) $[Mn(CO)_2(C_5H_5)]_3P_3Ph_3$

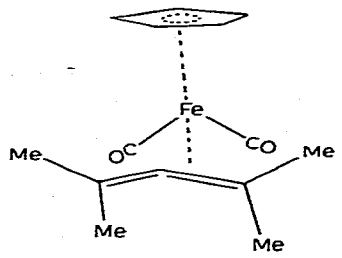


(162) $Fe(CO)_2[P(CF_3)_2](C_5H_5)$

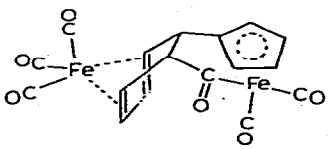


(163) $Fe(CO)_2[P(O)(CF_3)_2](C_5H_5)$

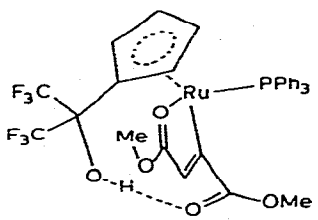
orientations of CO groups and ring [52]. (*157*) No heteroatoms bonded to carbene C; all carbene C-C distances equal [182]. (*158*) Olefin in *s-cis* configuration, but no interaction between CO group and metal [75]. (*159*) Phosphinidene complex obtained by heating (*160*) at 110°/10^{-2} torr; Mn_2CP coplanar, trigonal coordination stabilised by d_π–d_π bonds [169]. (*160*) By demetallation



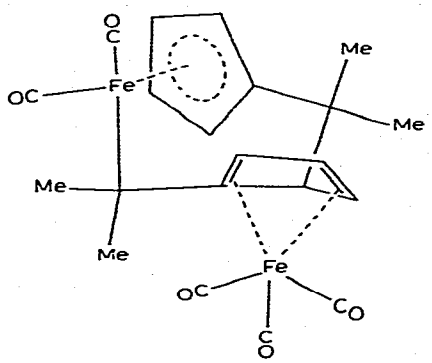
(164) $[Fe(C_3Me_4)(CO)_2(C_5H_5)]BF_4$



(165) $Fe_2(CO)_5[COC_6H_6C_5H_4]$



(167) $Ru[C_2H(CO_2Me)_2][C_5H_4C(OH)(CF_3)_2](PPh_3)$



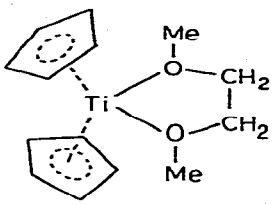
(166) $Fe_2(CO)_5(C_5H_4CMe_2)_2$

of $Mn(CO)_2(C_5H_5)(PPhLi_2)$ with N,N-dihaloamine to give trinuclear derivative of cyclotriphosphane ligand; 2Mn above, one below ring plane [261]. (*161*) From $FeMe(CO)_2(C_5H_5)$ + CF_3CN; planar delocalised FeNCNC ring, H attached to N not shared with other N; some bond shortening (C-CF_3, C-F) noted [51]. (*162*) (*163*) Covalent radius of P essentially same in both, and different Fe-P [2.265(3) and 2.191(3)Å, respectively] interpreted in terms of increased Fe→P d_π-d_π back-bonding in (*163*), also supported by shift in ν(CO) and Fe-C, C-O bond lengths consistent with decreased Fe→CO back bonding [41].

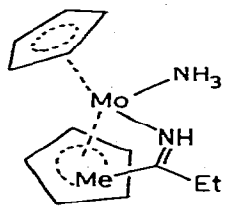
(*164*) Tetramethylallene has C=C=C angle 145.7(7)°, C=C (coord.) 1.367, C=C (free) 1.335Å; asymmetric distortions of Me groups arise from steric interactions [111]. (*165*) Fe-C (acyl) 1.9596(30)Å, significantly shorter than Fe-C(sp^3), but similer to acyl bond in $Fe(COMe)(CO)_2[HB(pz)_3]$ [142]. (*166*) From dimethylfulvene;

independent η^4, η^5 systems, in contrast to Fe–Fe bonded complex (*259*) obtained using diphenylfulvene [188]. (*167*) From $Ru[C(CF_3):CH(CF_3)](PPh_3)_2(C_5H_5) + (CF_3)_2CO$; intramolecular H-bond [235].

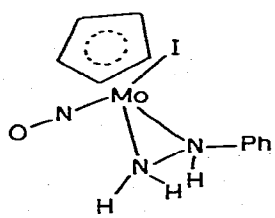
(e) *Cyclopentadienyls containing other donor ligands*



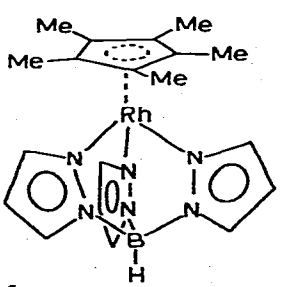
(168) $[Ti(dme)(C_5H_5)_2]Zn_2Cl_6$



(169) $[Mo(NH_3)(HNCMeEt)(C_5H_5)_2](PF_6)_2$



(170) $MoI(NO)(NH_2NHPh)(C_5H_5)$

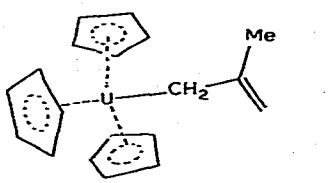


(171) $\left\{Rh(C_5Me_5)[HB(pz)_3]\right\}^+$

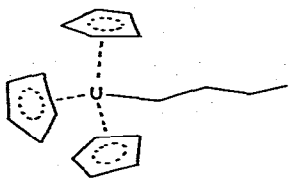
(*168*) Ti(III) cation with O-coordination; angle between ring normals 133.5°, O–Ti–O 76.6°, due to small bite of diether [170]. (*169*) Planar σ-ketimine ligand; angle between ring normals 134° [114]. (*170*) Both

N atoms of phenylhydrazine bonded to Mo; first complex with hydrazine bidentate to one metal atom; all H atoms located [76]. (*171*) C_5 ring planar, 4 Me groups displaced away from $HB(pz)_3$ ligand, latter is slightly twisted [148].

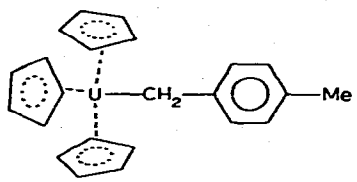
(f) *Cyclopentadienyls containing η-hydrocarbon ligands*



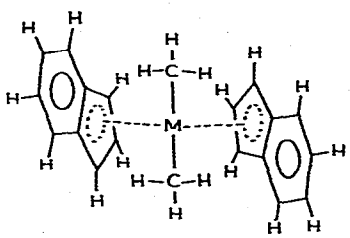
(172) $U(\eta^3\text{-}C_4H_7)(C_5H_5)_3$



(173) $U(C_4H_9)(C_5H_5)_3$

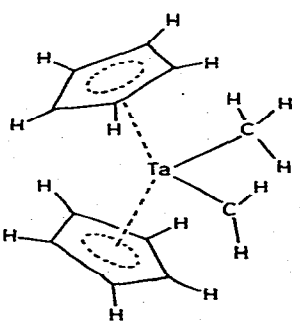


(174) $U(CH_2C_6H_4Me\text{-}p)(C_5H_5)_3$

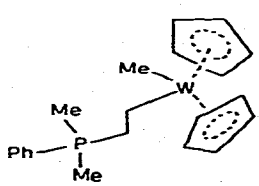


$MMe_2(ind)_2$

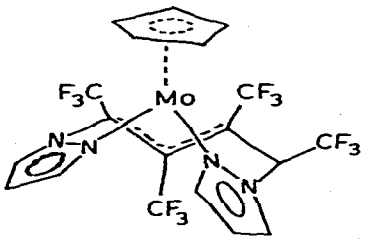
(175) M = Ti; (176) M = Zr; (177) M = Hf



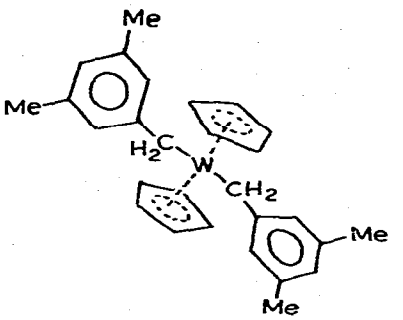
(178) $Ta(CH_2)Me(C_5H_5)_2$



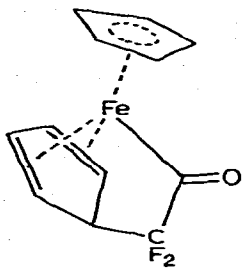
(180) $WMe[(CH_2)_2PMe_2Ph](C_5H_5)_2^+$



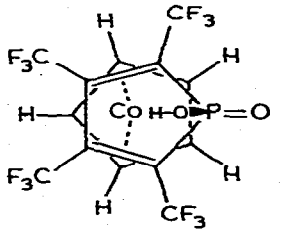
(179) $Mo[(pz)C_3(CF_3)_3CH(CF_3)](C_5H_5)$



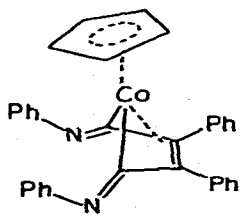
(181) $W(CH_2C_6H_3Me_2)_2(C_5H_5)_2$



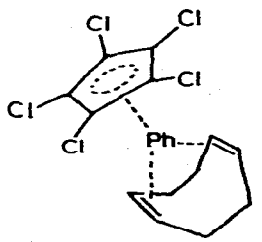
(182) $Fe(COCF_2C_5H_5)(C_5H_5)$



(183) $Co[C_4(CF_3)_4P(O)OH](C_5H_5)$



(184) $Co[(C_2Ph_2)(PhNC)_2]C_5H_5)$



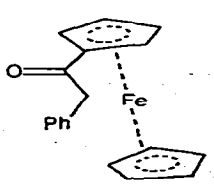
(185) $Rh(C_5Cl_5)(C_8H_{12})$

(172) η^1-2-Methylallyl group, U-C 2.48(3)Å; π-allyl structure not favoured, increase in coordinate bond energy less than reorganisational energy [162]. *(173)* *(174)* U-C 2.425(29), 2.553(22)Å; angle U-C-C 127.9(19), 128.5(13)°, respectively; large intramolecular interactions between C_5 groups and σ-alkyl [164]. *(175)* *(176)* *(177)* All

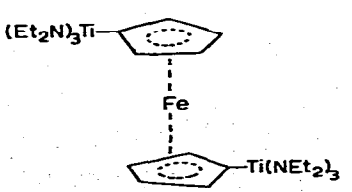
complexes isostructural, allow comparisons down the Group, lanthanide contraction results in unit cell of Hf compound being 5Å^3 *less* than Zr; indenyl groups in *gauche* configuration. Bond distances: M-C(Me) 2.21(2)(Ti), 2.51(6)(Zr), 2.332(12)Å(Hf); angles between normals to C_5 ring planes 119.8(Ti), 120.8(Zr), 121.0(9)°(Hf) [171]. (*178*) First isolable CH_2 complex; Ti-C(CH_2) 2.026(10), Ti-C(Me) 2.246(12)Å; angle between ring normals 135.7° [87]. (*179*) From $MoCl[C_2(CF_3)_2](C_5H_5)$ + $KHB(pz)_3$; contains unusual electronegatively-susbtituted η^3-allyl system, using 3 C atoms from dimerised $C_2(CF_3)_2$ [158]. (*180*) Formed by attack of PMe_2Ph on cationic C_2H_4 complex [191]. (*181*) Confirms structure, and explains inequivalence of methylene protons [229]. (*182*) From $Fe(CO)_2(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)$ + C_2F_4; formation involves cleavage of C=C in fluoro-olefin [83]. (*183*) Reaction product from $Co(PF_3)_2(C_5H_5)$ + $C_2(CF_3)_2$; P-heterocycle acts as 4-electron donor [95]. (*184*) Metallocycle from C_2Ph_2 + PhNC on cobalt, reacts with excess isocyanide to give a tris(arylimino)diphenylcyclopentene [243]. (*185*) Localised bonding in $\eta^5\text{-}C_5Cl_5$ ring with 2 short [1.399(6)Å], 3 long [1.436(5)Å] C-C bonds, bending of ring so that one carbon is brought closer to Rh, and 3 types of Rh-C bond; consistent with $(\eta^1 + 2\eta^2)\text{-}C_5Cl_5$ group [97].

Other complexes containing η-cyclopentadienyl groups: *216*, *218*, *222*, *223*, *226*, *232*, *233*, *236*, *241*, *242*, *243*, *244*, *246*, *247*, *253*, *262*, *263*, *277*, *279*, *282*, *285*, *286*, *287*, *288*.

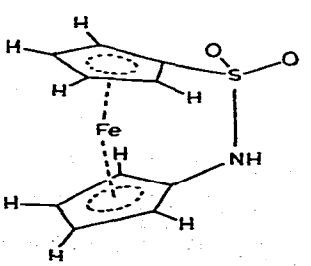
(g) *Substituted ferrocenes*



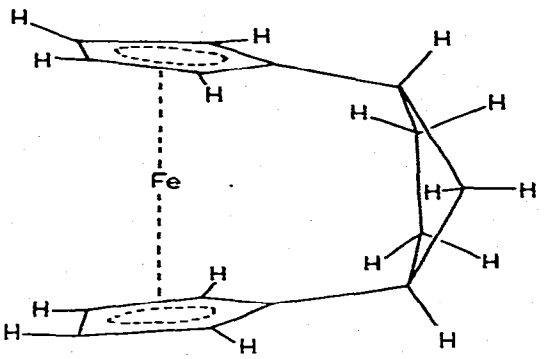
(186) $FcCOCH_2Ph$



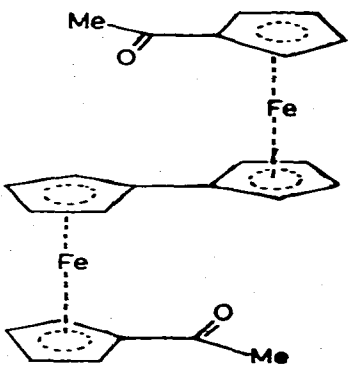
(187) $Fe[C_5H_4Ti(NEt_2)_3]_2$



(188) $Fe(C_5H_4SO_2NHC_5H_4)$



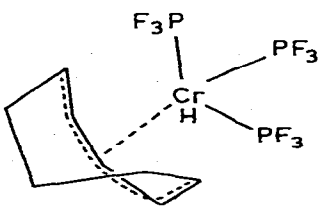
(189) $Fe(C_5H_4C_5H_8C_5H_4)$



(190) $[Fe(C_5H_4)(C_5H_4Ac)]_2$

(*186*) Reference [147]. (*187*) Angle of rotation ϕ 9.4°, average Ti-C 2.15Å [248]. (*188*) C_5 rings tilted by 23°; no evidence for delocalisation of ring electron density into SO_2NH bridge [54]. (*189*) From ferrocene + $AlCl_3$; C_5 ring eclipsed, with dihedral 11°, C_5 bridge distorted, asymmetric [121]. (*190*) Rotation angle ϕ 4.1° [207].

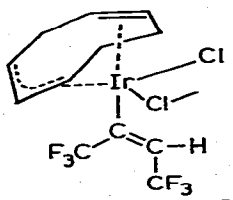
(h) *Acyclic* η^5*-Ligands*



(191) $CrH(PF_3)_3(C_8H_{11})$

(*191*) From Cr vapour + C_8H_{12} + PF_3; intermediate in conversion 1,3- to 1,5-C_8H_{12} via π-allyl-hydride mechanism [332].

(i) ($\eta^2 + \eta^3$)-*Ligands*

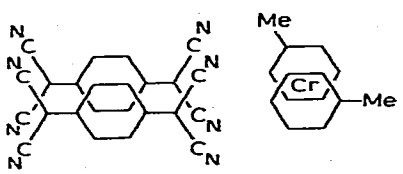


(192) $[IrCl[C(CF_3):CH(CF_3)](C_8H_{11})]_2$

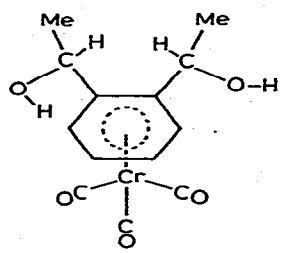
(*192*) Formed from (*127*); alkyne has abstracted H atom to give *cis*-vinylic group, while original C_8H_{12} is now bonded as 1,2-η^2-4,5,6-η^3 ligand [209].

η^6-LIGANDS

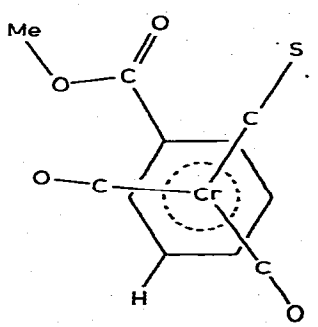
(a) *Cyclic* η^6-*Ligands (arenes)*



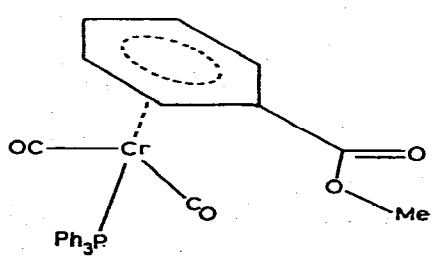
(193) $[Cr(PhMe)_2](tcnq)$



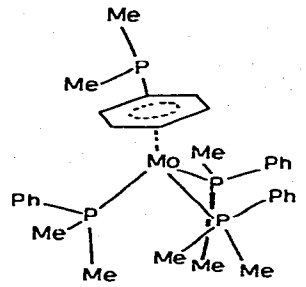
(194) $Cr(CO)_3\{C_6H_4[CHMe(OH)]_2\text{-}o\}$



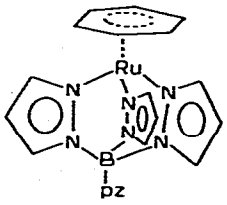
(195) $Cr(CO)_2(CS)(PhCO_2Me)$



(196) $Cr(CO)_2(PPh_3)(PhCO_2Me)$



(197) $Mo(\eta-PhPMe_2)(PMe_2Ph)_3$

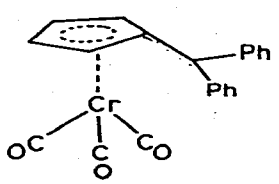


(198) $\{Ru(C_6H_6)[B(pz)_4]\}^+$

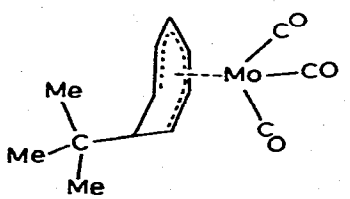
(*193*) Isolated infinite stacks of $CrAr_2^+$ and $(tcnq)^-$ ions [109]. (*194*) One of pseudoasymmetric forms, m.p. 144° [98]. (*195*) Cr-C(O), 1.849(3); Cr-C(S), 1.792(2)Å [72]. (*196*) Shortest Cr-P bond [2.337(1)Å]; no specific conformational features explain the unusually fast isotopic hydrogen exchange [227]. (*197*) Structural characterisation of $Mo(PMe_2Ph)_4$; short Mo-C bond indicates enhanced Mo-arene π-bonding in absence of strong π acids [241]. (*198*) Benzene ligand staggered with respect to $B(pz)_4$ ligand [148].

See also: *296*.

(b) *Acyclic* η^6*-Ligands*



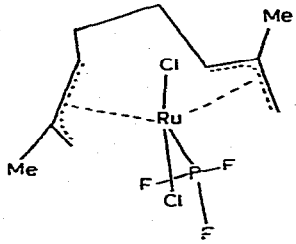
(199) $Cr(CO)_3(C_5H_4CPh_2)$



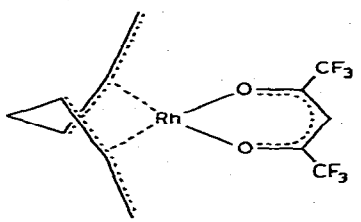
(200) $Mo(CO)_3(C_7H_7Bu^t)$

(*199*) Ph_2 fulvene complex, with Cr attached asymmetrically to C_5 ring and exocyclic double bond; ligand non-planar, unequal Cr-C distances [181]. (*200*) From $[Mo(CO)_3(C_7H_7)]^+ + Bu^tMgBr$ [110].

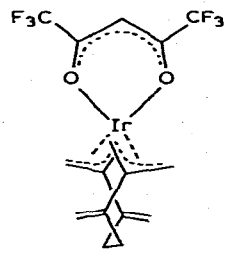
(c) ($2n^3$)-*Ligands*



(201) $RuCl_2(PF_3)(C_{10}H_{16})$



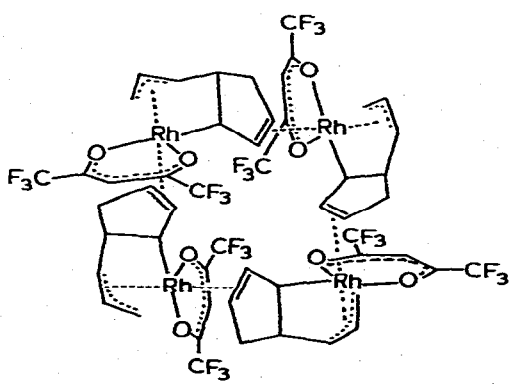
(202) $Rh(C_7H_{10})(hfac)$



(203) $Ir(hfac)(C_{12}H_{16})$

(*201*) TBP, with axial Cl ligands; organic ligand is tail-tail dimer of isoprene [62]. (*202*) From *trans*-divinylcyclopropane; C_3 ring has opened, and overall structure resembles $[RhCl(C_3H_5)_2]_2$; bridging atom increases extent of n-allyl localisation [85]. (*203*) From allene + $Ir(C_8H_{14})_2$ (hfac); ligand is allene tetramer [143].

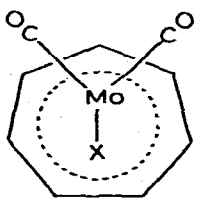
(d) ($n^1 + n^2 + n^3$)-*Ligands*



(204) $\left[Rh(hfac)(C_8H_{10})\right]_4$

(*204*) From *trans*-6-vinylbicyclo[3.1.0]hex-2-ene + $[RhCl(C_2H_4)_2]_2$ *via* cyclopropane ring-opening reaction; tetramer formed by (η^1 + η^3)-bonding to one Rh, η^2-bonding to the other; undergoes rearrangement in solution at 338K [287].

η^7-LIGANDS



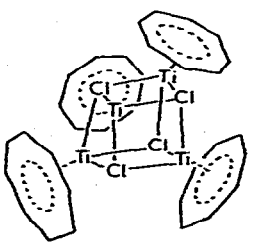
$MoX(CO)_2(C_7H_7)$

(205) X = Cl; (206) X = Br

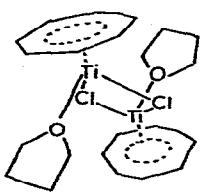
(*205*) (*206*) Isomorphous, Mo-Cl 2.598(5), Mo-Br 2.629(3)Å indicating greater d_π-d_π interaction in (*206*) [42].

See also: *284*.

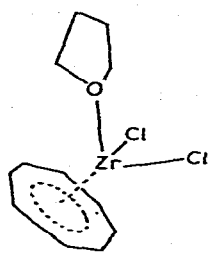
η^8-LIGANDS



(207) $[TiCl(C_8H_8)]_4$



(208) $[Ti(thf)(C_8H_8)]_2$

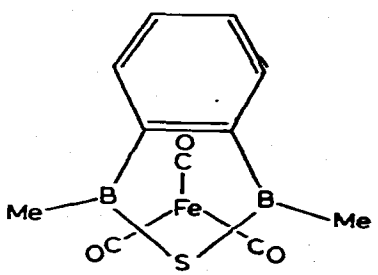


(209) $ZrCl_2(thf)(C_8H_8)$

(*207*) (*208*) Characterisation of Ti-cyclooctatetraene complexes as tetrameric (*207*) and dimeric (*208*); C_8H_8 ligands are perpendicular to body diagonals of Ti_4Cl_4 hexahedron in (*207*); in both, C_8H_8 ligands have umbrella shape by bending of H atoms towards Ti [216]. (*209*) From $Zr(C_8H_8)_2$ + HCl; C_8 ring approximately planar, with C-H bonds inclined towards Zr; thf bond parameters are most accurate so far reported [88].

See also: *131*, *280*.

η-HETEROATOM LIGANDS

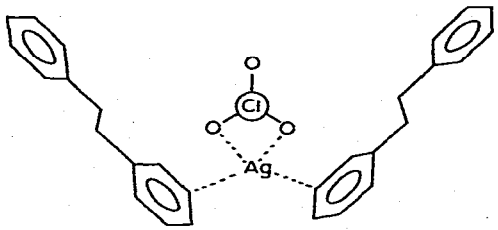


(210) $Fe(CO)_3[C_6H_4(BMe)_2S]$

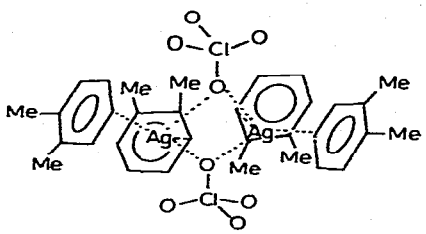
(*210*) Bonding to Fe fixes electron density in benzene ring; as shown by bond distances and electron density map, which also indicates π-electron density in ring B-C bonds [74].

Heterocyclic ligands attached via carbon atoms are present in: *128*, *129*, *134*, *137*, *183*.

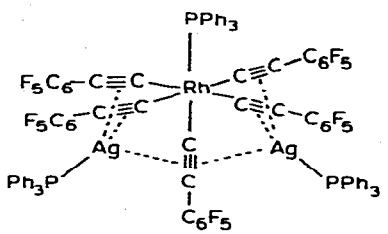
SILVER COMPLEXES



(211) $(PhCH_2CH_2Ph)_2AgClO_4$



(212) $(o\text{-}Me_2C_6H_4)_2AgClO_4$



(213) $RhAg_2(C_2C_6F_5)_5(PPh_3)_3$

(*211*) Ag disordered so that some are square pyramidal, others square planar, bonded to phenyl ring and O of ClO_4, resulting from small energy difference in long Ag-O interactions [108]. (*212*) Isolated O-bridged dimers; Ag coordinated to 2 O, 2 C_6 rings [135]. (*213*) From $RhCl(PPh_3)_3$ + $AgC_2C_6F_5$; no Rh-Ag bond, zwitterionic formulation $[Ag(PPh_3)]_3^+[Rh(C_2C_6F_5)_5(PPh_3)]^{3-}$ with additional π bonding between Ag and C≡C [298].

POLYHEDRAL METALLOBORANE COMPLEXES

(*214*) From (1- or 2-)-BrB_5H_8 + $IrCl(CO)(PMe_3)_2$; σ-B exerts strong *trans*-lengthening effect: Ir-Br 2.638(1) (*trans* B), 2.516(1)Å (*trans* CO); Ir-B 2.071(14)Å [35]. (*215*) Cu bonded to $B_{10}H_{10}^{2-}$ via CuHBBH chelate rings, with Cu-H 1.86(6), 2.08(7)Å; discussion of

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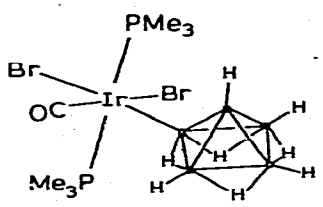
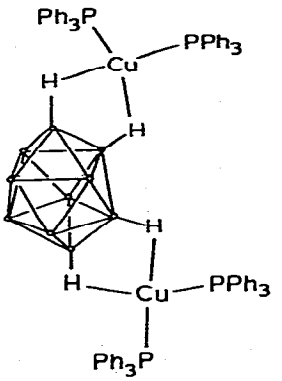


(214) $Ir(B_5H_8)Br_2(CO)(PMe_3)_2$



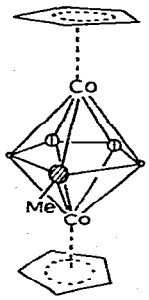
(215) $[(Ph_3P)Cu]_2B_{10}H_{10}$

bonding in relation to geometries and electronic requirements of related *nido*-metalloboranes [309].

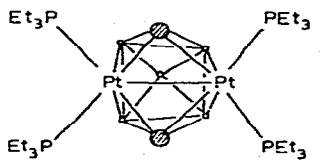
POLYHEDRAL METALLOCARBORANE COMPLEXES

In all structures ⊘ indicates carbon.

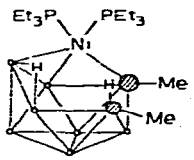
(*216*) Triple-decked sandwich, with one B, C disordered; outer C_5 rings tilted toward Me group on B_3C_2 ligand; also considered as 7-vertex polyhedron [99]. (*217*) From $Pt(styrene)(PEt_3)_2$ + *closo*-2,4-$C_2B_5H_7$; highly distorted tricapped trigonal prism [38]. (*218*) From polyhedral expansion of 4,5-$C_2B_7H_9$ + $FeCl_2$ + NaC_5H_5, diamagnetic isomer; new 10-vertex species derived from bicapped square antiprism [89]. (*219*) Carbadibora-allyl complex from $Ni(cod)(PEt_3)_2$ + *arachno*-5,9-C_2B_7 species [140]. (*220*) From Pt(*trans*-stilbene)$(PEt_3)_2$ + 1,6-Me_2-1,6-$C_2B_7H_7$; bicapped square antiprism, with non-bonding Pt-C distance giving *nido*-structure and open BCBPt face [139]. (*221*) Obtained from (*225*) by passing through activated charcoal; *nido*-geometry, with open CPtBCB face [38]. (*222*) (*223*) Products from Friedel-Crafts acetylation of



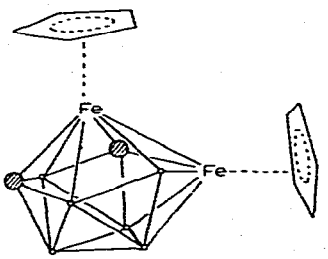
(216) $[(C_5H_5)Co]_2B_3C_2H_4Me$
Φ = disordered B,C



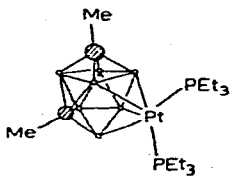
(217) *closo*-2,3-$[(Et_3P)_2]_2$-1,2,3,6-$CPtCB_5H_7$



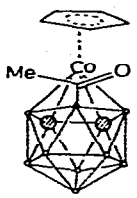
(219) 6,6-$(Et_3P)_2$-5,9-Me_2-6,5,9-$NiC_2B_7H_4$



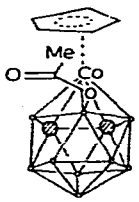
(218) 1,6-$(C_5H_5)_2$-1,6,2,3-$Fe_2C_2B_6H_8$



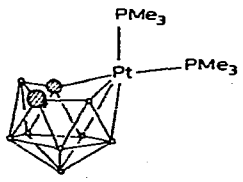
(220) 2,7-Me_2-9,9-$(Et_3P)_2$-2,7,9-$C_2PtB_7H_7$



(222) $(C_5H_5)CoB_9C_2H_{10}(COMe)$



(223) $(C_5H_5)CoB_9C_2H_{10}(OCOMe)$



(221) 8,8-$(Me_3P)_2$-7,8,10-$CPtCB_8H_{10}$

$(C_5H_5)Co[\eta$-(3)-1,2-$B_9C_2H_{11}]$ [47]. (*224*) Pd distorted square planar, little interaction Pd-C [2.600(6)Å]; zwitterionic formulation $(Me_3N)^+(PdCB_{10})^-$ [117]. (*225*) From $Pd(cod)(PMe_3)_2$ + *closo*-1,6-$C_2B_8H_{10}$; second Pt lies outside polyhedral framework [38]. (*226*) From Pt(*trans*-stilbene)$(PEt_3)_2$ + 1-(C_5H_5)-1,2,4-$CoC_2B_8H_{10}$; preliminary

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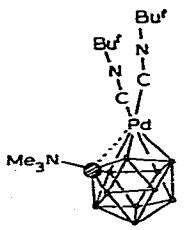
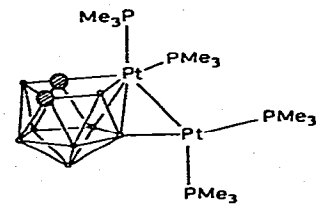
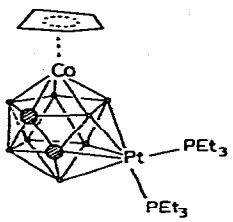


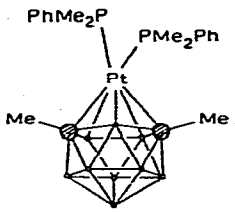
(224) 1,1-(Bu^{t}NC)-2-(NMe$_3$)-1,2-PdCB$_{10}$H$_{10}$



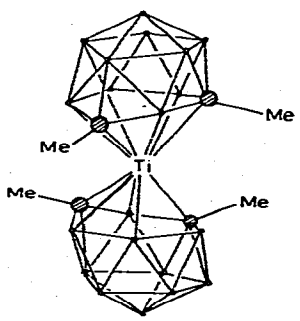
(225) *nido*-μ(4,8)-[(Me$_3$P)$_2$Pt]-8,8-(Me$_3$P)$_2$-7,8,10-CPtCB$_8$H$_{10}$



(226) 1-(C$_5$H$_5$)-8,8-(Et$_3$P)$_2$-1,2,7,8-CoC$_2$PtB$_8$H$_{10}$



(227) 1,1-(PhMe$_2$P)$_2$-2,4-Me$_2$-1,2,4-PtC$_2$B$_9$H$_9$

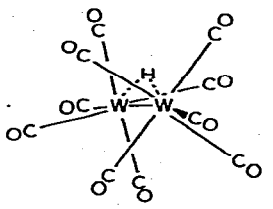


(228) [Ti(1,6-Me$_2$-1,6-C$_2$B$_{10}$H$_{10}$)$_2$]$^{2-}$

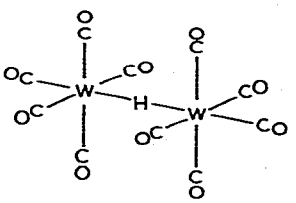
diagram only (R 8.1%) [117]. (*227*) From Pt(PMe$_2$Ph)$_4$ + 2,3-Me$_2$-2,3-$C_2B_9H_9$; *closo*-structure, with square planar Pt, P atoms *trans* to B atom, and mid-point of B-B bond; Pt-C bond long and very weak [176, 177]. (*228*) First metallocarborane with Group IVa metal; two 13-vertex closed polyhedra linked through Ti, with metal bonded to approximately parallel 6-membered rings; electron-deficient [39].

COMPLEXES CONTAINING METAL-METAL BONDS

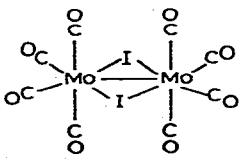
(a) *Homobinuclear transition metal complexes*



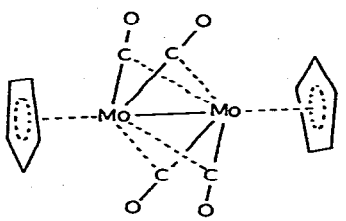
(229) $[N(PPh_3)_2][W_2H(CO)_{10}]$



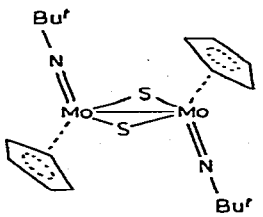
(230) $[NEt_4][W_2H(CO)_{10}]$



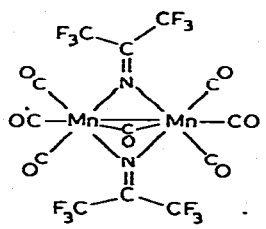
(231) $[MoI(CO)_4]_2$



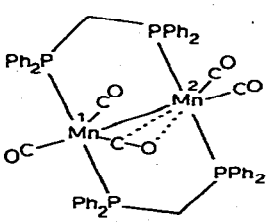
(232) $[Mo(CO)_2(C_5H_5)]_2$



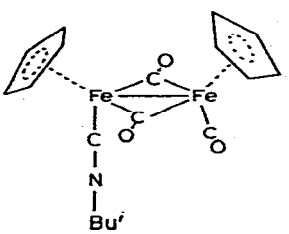
(233) $Mo_2(NBu^t)_2(C_5H_5)_2(\mu\text{-}S)_2$



(234) $Mn(CO)_7[N{:}C(CF_3)_2]_2$



(235) $Mn_2(CO)_5(dppm)_2$



(236) $Fe_2(CO)_3(CNBu^i)(C_5H_5)_2$

(*229*) (*230*) Linear eclipsed and bent staggered forms of anion in NEt_4^+ and $N(PPh_3)_2^+$ salts, respectively; linear W-H-W has W-W separation [3.504(1)Å] shorter than expected (*ca.* 3.75Å); bent W-H-W has W-W distance 3.391(1)Å. Configuration probably determined by crystal packing forces, in solution both salts give linear anion [49].

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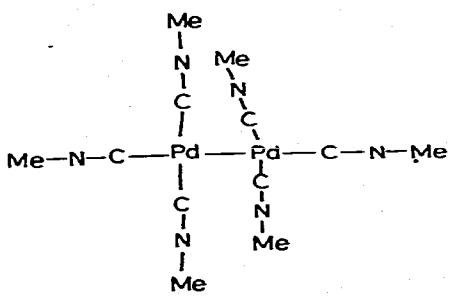
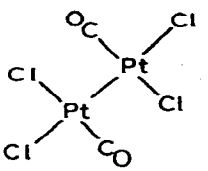
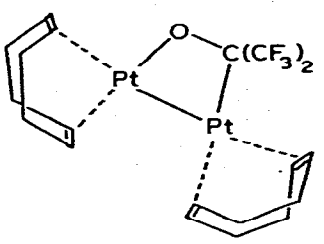


(237) $[Pd_2(CNMe)_6](PF_6)_2$



(238) $(NPr^n_4)_2[Pt_2Cl_4(CO)_2]$

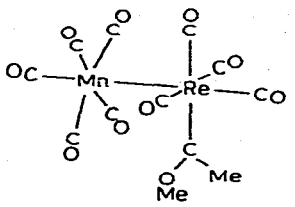


(239) $Pt_2[OC(CF_3)_2](C_8H_{12})_2$

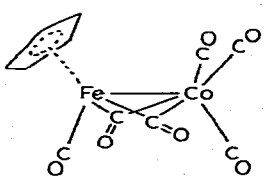
(*231*) Contains I-bridged Mo-Mo bond [333]. (*232*) From thermal decomposition of $[Mo(CO)_3(C_5H_5)]_2$, product has Mo≡Mo triple bond; CO groups probably interact with Mo-Mo bond, forming asymmetric bridging units [107]. (*233*) From $[Mo(CO)_3(C_5H_5)]_2 + S(NBu^t)_2$; planar Mo_2S_2 unit, with $Mo{=}NBu^t$ bond [1.733(4)Å]; some multiple bond character in Mo-Mo link; similar to isoelectronic $Mo_2(O)_2(S)_2(C_5H_5)_2$ [156]. (*234*) Asymmetric bridging alkylideneimino ligand balanced by asymmetric bridging CO, with Mn-Mn bond [102]. (*235*) Contains unusual CO group bonded conventionally to Mn(1), via C and O to Mn(2): Mn(1)-C 1.93, Mn(2)-C 2.01, Mn(2)-O 2.29Å; ν(CO) 1645 cm^{-1} [290, 291]. (*236*) Angle between $Fe(CO)_2Fe$ planes 165.6°; terminal isocyanide [150]. (*237*) From Na_2PdCl_4 + MeNC; both Pd square planar, dihedral 86.2° [93]. (*238*) Two slightly distorted $PtCl_2(CO)$ moieties

linked by unbridged Pt-Pt bond, dihedral 60°, CO in *transoid* configuration; long Pt-Cl [2.404(22)Å] *trans* to Pt-Pt bond, *cis* 2.337(10)Å [27]. (*239*) From $Pt(C_8H_{12})_2$ + $(CF_3)_2CO$; latter links 2#Pt to give cyclic Pt_2CO moiety; variation in ligands *trans* to η^2 bonds of C_8H_{12} gives 3 distinct Pt-C distances [163].

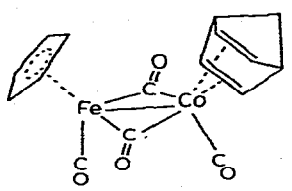
(b) *Heterobinuclear transition metal complexes*



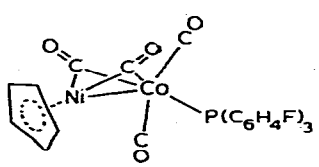
(240) $MnRe(CO)[CMe(OMe)]$



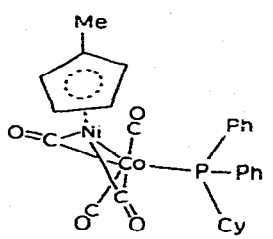
(241) $FeCo(CO)_6(C_5H_5)$



(242) $FeCo(CO)_4(nbd)(C_5H_5)$



(243) $(C_5H_5)NiCo(CO)_4[P(C_6H_4F\text{-}p)_3]$



(244) $(MeC_5H_4)NiCo(CO)_4(PCyPh_2)$

(*240*) From $MeMn(CO)_5$ + $Re(CO)_5^-$, followed by alkylation with $MeSO_3F$; carbene on Re, perhaps by rearrangement *via* bridging carbene ligand [80]. (*241*) Angle between $Fe(CO)_2Co$ planes 143.5°, asymmetry in bridge CO bonds to Fe, Co [69]. (*242*) Non-planar $Fe(CO)_2Co$, carbonyl O moves from Fe to Co; angle between planes 160.6° [130]. (*243*) (*244*) Angle between planes of $Co(CO)_2Ni$ system 133.9° (both) [220, 228].

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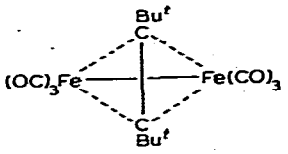
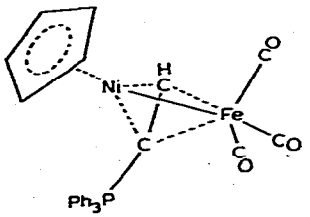
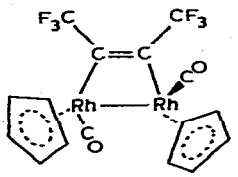
(c) *Binuclear complexes containing bridging hydrocarbon ligands*



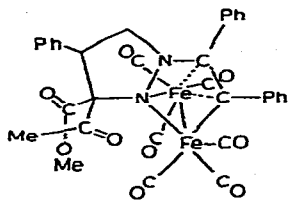
(245) $Fe_2(CO)_6(C_2Bu^t_2)$



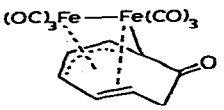
(246) $(C_5H_5)NiFe(CO)_3(HC_2PPh_3)$



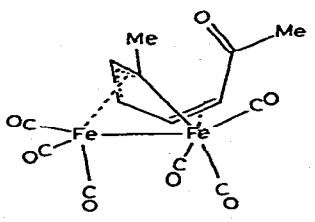
(247) $[Rh(CO)(C_5H_5)]_2C_2(CF_3)_2$



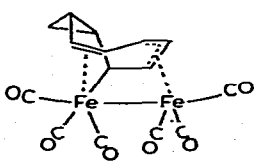
(248) $Fe_2(CO)_6(C_{27}H_{24}N_2)$



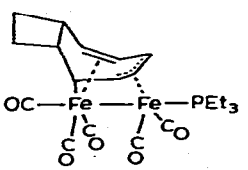
(249) $Fe_2(CO)_6(C_8H_8O)$



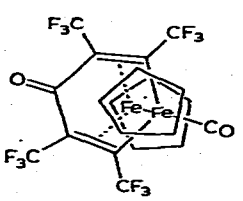
(250) $Fe_2(CO)_6(C_8H_{10}O)$



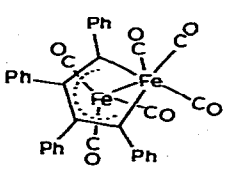
(251) $Fe_2(CO)_6(C_9H_{10})$



(252) $Fe_2(CO)_5(PEt_3)(C_{10}H_{12})$

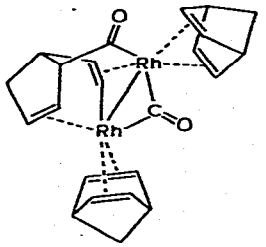


(253) $Fe_2(CO)[C_4(CF_3)_4CO](C_5H_5)_2$

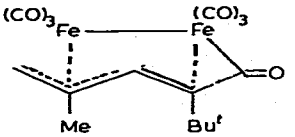


(254) $Fe_2(CO)_6(C_4Ph_4)$

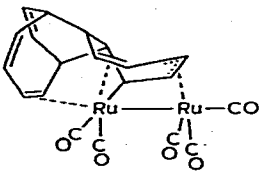
(*245*) From $Fe_2(CO)_9 + C_2Bu_2^t$; short Fe–Fe distance indicates multiple bond character [131]. (*246*) From $Fe_2(CO)_9 + Ni(C_2H)(PPh_3)(C_5H_5)$; structure shows migration of PPh_3 to acetylide, which bridges Fe, Ni atoms [225]. (*247*) Bridging alkyne σ-bonded to Rh leading to planar C_2Rh_2 moiety, and C≡C 1.285(44)Å [129]. (*248*) Cycloaddition product of C_2Ph_2 + pyrazoline-$Fe_2(CO)_6$ complex [242]. (*249*) Keto group adjacent



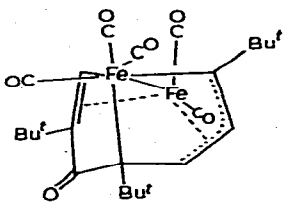
(255) $Rh_2(CO)(nbd)_2(C_8H_8O)$



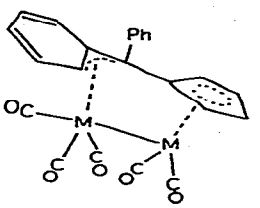
(256) $Fe_2(CO)_6(C_{10}H_{14}O)$



(257) $Ru_2(CO)_5(C_{16}H_{16})$

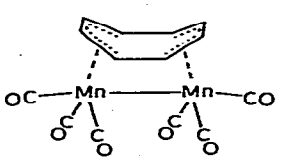


(258) $Fe_2(CO)_5[(HC_2Bu^t)_3CO]$

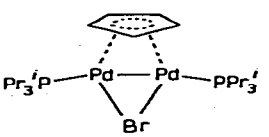


$M_2(CO)_5(C_5H_4CPh_2)$

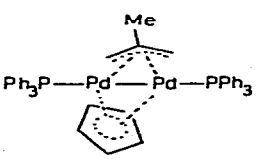
(259) M = Fe ; (260) M = Ru



(261) $Mn_2(CO)_6(C_8H_8)$



(262) $[Pd(PPr^i_3)]_2(Br)(C_5H_5)$



(263) $[Pd(PPh_3)]_2(C_4H_7)(C_5H_5)$

to Fe–C σ bond in solid state [104]. (*250*) Minor product from 2,7-Me_2-oxepin + $Fe(CO)_5$; ligand can be described formally as ketocarbene [106]. (*251*) Almost identical bond parameters in series (C_8H_{10}), (C_9H_{10}) and ($C_{10}H_{12}$)-$Fe_2(CO)_6$; *trans* influence of Fe–σ(C) shown by lengthening of Fe–CO(*trans*) [119]. (*252*) ^{13}C NMR and structural study enables fluxional processes in this and related complexes to be specified completely [190]. (*253*) From $[Fe(CO)_2(C_5H_5)]_2$ + $C_2(CF_3)_2$; ferracyclohexa-2,5-dienone has boat conformation, attached to second $Fe(C_5H_5)$ group by $2\eta^2$ bonds [83]. (*254*) Tetraphenylferrole complex from $Fe(CO)_3(C_7H_8)$ + C_2Ph_2; comparison with 5 related structures [244]. (*255*) From $Rh_6(CO)_{16}$ + nbd; ring-opening gives acylvinylcyclopentene

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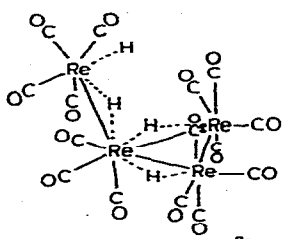
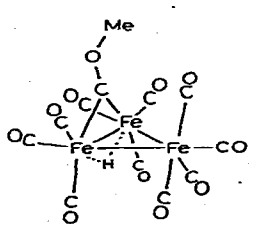
ligand bridging both Rh atoms; bridging CO is asymmetric, with Rh-C bonds 1.99, 2.15Å; nbd ligands also bonded asymmetrically [199]. (*256*) Contains coordinated C=C β to Fe-C(O) σ bond, and η^3-allyl group, one carbon of which is also part of the coordinated C=C [131]. (*257*) Contains valence tautomer of new C_8H_8 dimer; bonding to $Ru(CO)_2$ group involves one of two C=C of 1,3-diene unit; complex is fluxional in solution as expected [183]. (*258*) From $Fe_3(CO)_{12}$ + HC_2Bu^t; organic ligand formed from ($3HC_2Bu^t$ + CO), attached via $3\eta^1$ bonds to one Fe, and (η^2 + η^3) to second Fe [215]. (*259*) (*260*) From diphenylfulvene [188, 198]. (*261*) C_8 ligand bonded via η^4 bonds to each Mn, rather than the arrangement found in $Fe_2(CO)_5(C_8H_8)$ [105]. (*262*) From $PdBr(PPr^i_3)(C_5H_5)$ + Mg; C-C bonds in C_5 ring show partial localisation of π-electron density [115]. (*263*) From $Pd(C_4H_7)(C_5H_5)$ + PPh_3, hydrocarbon groups bridge Pd atoms [282].

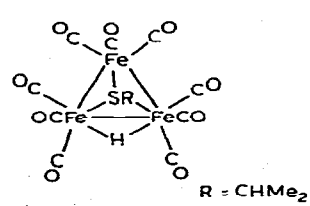
(d) *Polynuclear clusters containing CO, CNR or PR_3 ligands*



(264) $Re_4H_4(CO)_{15}^{2-}$

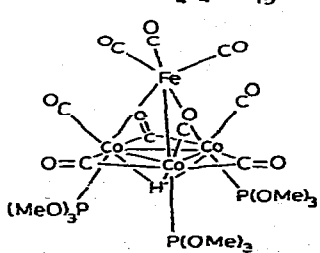


(265) $[Fe_3H(CO)_{10}(COMe)]^{2-}$

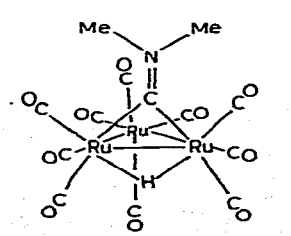


(266) $Fe_3H(CO)_9(SR)$

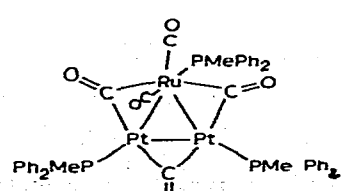
R = $CHMe_2$



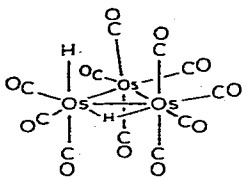
(267) $FeCo_3H(CO)_9[P(OMe)_3]_3$



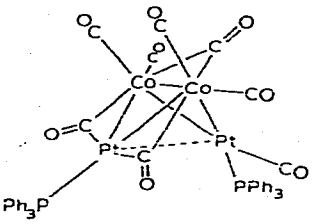
(268) $Ru_3H(C{:}NMe_2)(CO)_{10}$



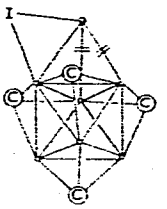
(269) $RuPt_2(CO)_5(PMePh_2)_3$



(270) $Os_3H_2(CO)_{11}$

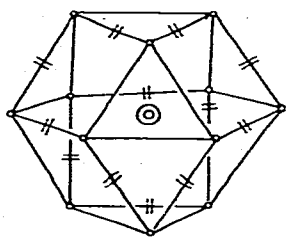


(271) $Co_2Pt_2(CO)_8(PPh_3)_2$



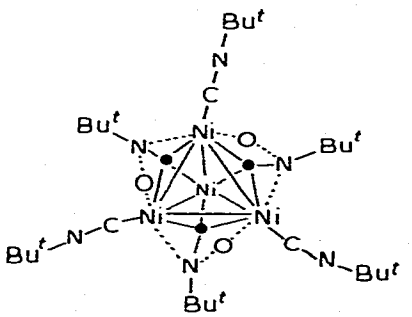
(272) $[Rh_7I(CO)_{16}]^{2-}$

© face-bridging CO
edges maked ≠ bridged by CO



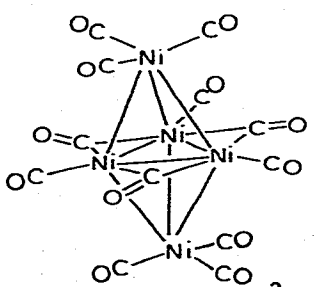
(273) $[Rh_{13}H_3(CO)_{24}]^{2-}$

μ-CO groups bridge marked edges
Terminal CO on each Rh
except Rh ◎) not shown)

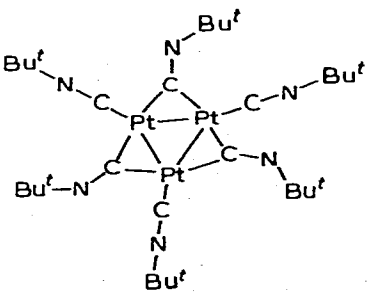


(274) $Ni_4(CNBu^t)_7$

● bridging isocyanide carbon sites
o terminal isocyanide carbon sites



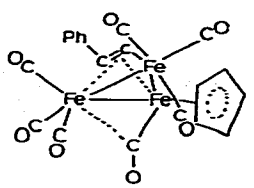
(275) $[Ni_5(CO)_{12}]^{2-}$



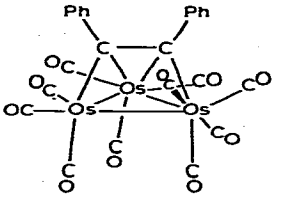
(276) $Pt_3(CNBu^t)_6$

(*264*) Cluster from $Re_2(CO)_{10}$ + KOH/MeOH; H atoms not located directly [118]. (*265*) Methylation of $Fe_3(CO)_{11}^{2-}$ with $MeSO_3F$, followed by protonation; bridging CO becomes stronger acceptor toward metal centres [78]. (*266*) Sulphido group bridges all three Fe atoms, with H bridging 2Fe on opposite side of cluster, such that Fe_2HS defines a plane [82]. (*267*) H-atom located above Co_3 plane of tetrahedron; all $P(OMe)_3$ axial, and each Co-Co bond is CO-bridged [155]. (*268*) From $Ru_3(CO)_{12}$ + $Me_2NCH_2SnMe_3$; H located bridging *shorter* Ru-Ru bond, as result of presence of bridging $Me_2N{=}C$ unit also [96]. (*269*) $RuPt_2$ cluster has all edges bridged by CO; differing Ru-Pt bonds result from asymmetric equatorial CO group on Ru, displaced by interaction with axial $PMePh_2$ ligand [278]. (*270*) Terminal and bridging H (not located) undergo mutual exchange; positions inferred from geometry of Os_3 cluster (one long Os-Os bond) [68]. (*271*) "Butterfly" Co_2Pt_2 cluster, with Co-Co hinge, one of faces bears 3 CO bridges [275]. (*272*) Monocapped octahedron, with 10 terminal, 2 edge-bonding, 4 face-bridging CO, and I bridges an edge; one electron pair in cluster antibonding orbital [141]. (*273*) From $[Rh_{12}(CO)_{30}]^{2-}$ + H_2; contains hexagonal close packed Rh atoms, with higher electron density in cluster than found for Rh metal [203]. (*274*) Fluxional, contains Bu^tNC ligands which may bridge face or edge; terminal sites become equivalent as bridging ligands traverse all edges or faces; exceptional reactivity and catalytic activity [252]. (*275*) From $Ni(CO)_4$ + Na/Hg; TBP arrangement of Ni atoms, with usual $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ unit forming the trigonal plane; cf. $[M_2Ni_3(CO)_{13}(\mu_2\text{-}CO)_2]^{2-}$ (M = Mo, W) [94]. (*276*) Pt_3 cluster bridged by 3 Bu^tNC ligands, which are bent (mean CNC angle, 143°) [233].

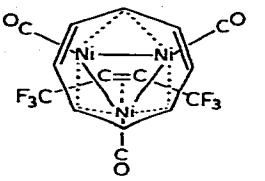
(e) *Polynuclear clusters containing η-hydrocarbon ligands*



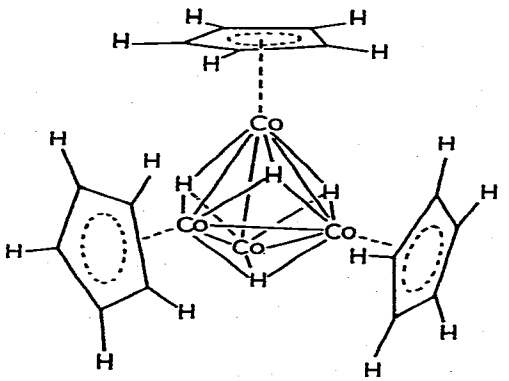
(277) $Fe_3(CO)_7(C_2Ph)(C_5H_5)$



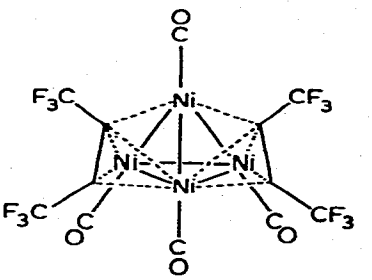
(278) $Os_3(CO)_{10}(C_2Ph_2)$



(280) $Ni_3(CO)_3[C_2(CF_3)_2](C_8H_8)$



(279) $Co_4H_4(C_5H_5)_4$
One C_5H_5 group not shown



(281) $Ni_4(CO)_4[C_2(CF_3)_2]_3$
Rear $C_2(CF_3)_2$ group not shown

(*277*) From $Fe(C_2Ph)(CO)_2(C_5H_5)$ + $Fe_2(CO)_9$; phenylethynyl group interacts with all Fe atoms; one CO forms asymmetric bridge [167]. (*278*) Intermediate in synthesis of osmiacyclopentadiene complexes; alkyne bonded via ($2\eta^1 + \eta^2$) interaction with cluster [204]. (*279*) Slightly distorted Co_4 tetrahedron, with face-bonded H atoms [173]. (*280*) From (*281*) + C_8H_8; $Ni_3(CO)_3$ plane lies between $C_2(CF_3)_2$ as 4e-donor and planar, highly delocalised η^8-C_8H_8 ligand; complex fluxional in solution; not frozen out at -90° [103]. (*281*) From $Ni(CO)_4$ + $C_2(CF_3)_2$, originally described as tricarbonyl; alkyne bonded via formal σ-bonds to apical Ni, and by 3-centre bonds to 2 adjacent basal Ni atoms [103].

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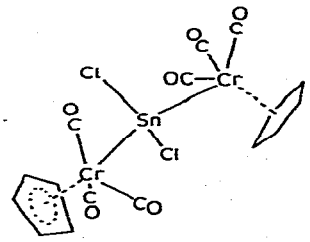
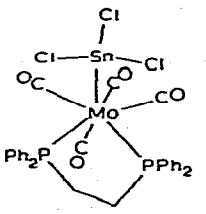
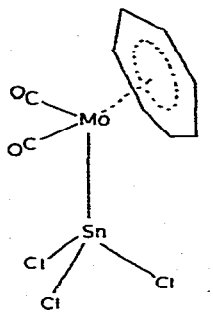
(f) *Complexes containing Transition Metal–Main Group Metal bonds*



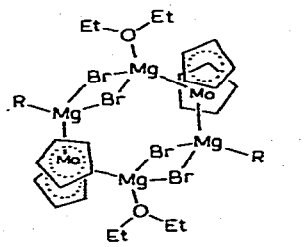
(282) $[Cr(CO)_3(C_5H_5)]_2SnCl_2$



(283) $[Mo(SnCl_3)(CO)_4(dppe)]^+$

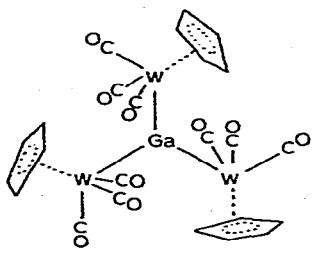


(284) $Mo(SnCl_3)(CO)_2(C_7H_7)$



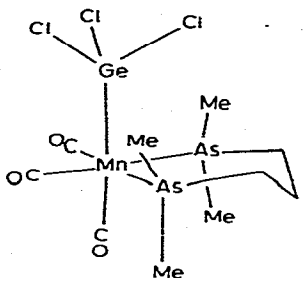
$[MoH(C_5H_5)_2]_2[Br_2MgR(OEt)]_2$

(285) R = Pr^i; (286) R = Cy

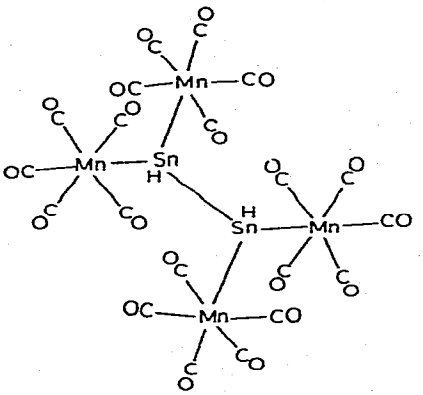


(287) $Ga[W(CO)_3(C_5H_5)]_3$

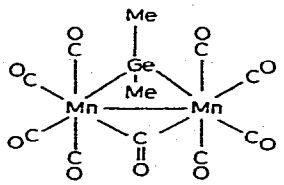
(*282*) Distorted tetrahedral Sn, Cr-Sn-Cr 130.2°, Cl-Sn-Cl 95.0° [127]. (*283*) Irregular capped (by $SnCl_3$) octahedral Mo, geometry minimises $SnCl_3$, dppe non-bonded repulsions [232]. (*284*) Comparison with $SnCl_2Ph$ and $SnClPh_2$ complexes described earlier [43]. (*285*) (*286*) Both complexes contain same $Mo_2(MgBr_2Mg)_2$ skeleton; H not located, but large Mg-Mo-Mg angle (109°) probably results from H atom in Mg-Mo-Mg plane [247]. (*287*) Individual Ga-W distances apparently significantly different from mean value, which is *ca.* 0.09Å shorter than sum of covalent radii [205]. (*288*) Chelate ring in chair conformation, flattened about As...As axis, while $GeCl_3$ group oriented to minimise interactions with $AsMe_2$ groups [63]. (*289*) Mn-Sn bond shorter than in Me or Ph derivatives; equatorial CO groups bent towards Sn. [29].



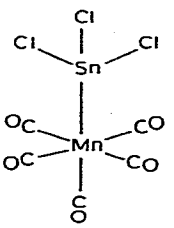
(288) $Mn(GeCl_3)(CO)_3[Me_2As(CH_2)_3AsMe_2]$



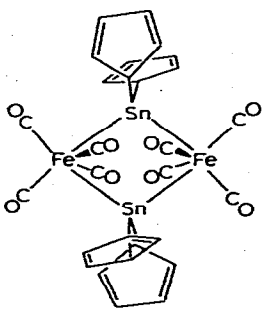
(290) $H_2Sn_2[Mn(CO)_5]_4$



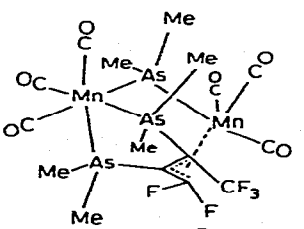
(291) $Mn_2(GeMe_2)(CO)_9$



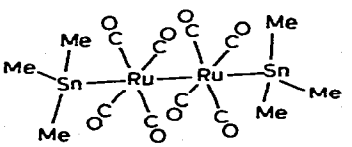
(289) $Mn(SnCl_3)(CO)_5$



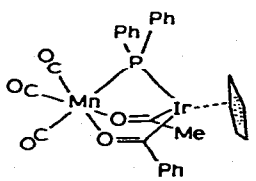
(294) $\{Fe[Sn(C_5H_5)_2](CO)_4\}_2$



(292) $Mn_2(CO)_6(AsMe_2)[C_3F_2(CF_3)(AsMe_2)_2]$



(295) $[Ru(SnMe_3)(CO)_4]_2$



(293) $(OC)_3Mn(PPh_2)(OCMe)(OCPh)Ir(C_5H_5)$

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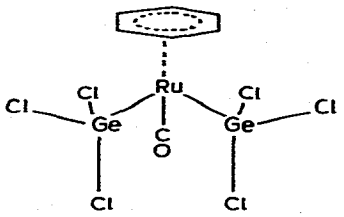
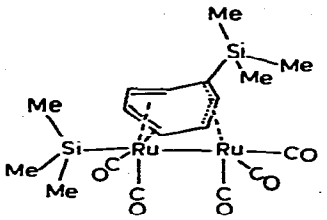
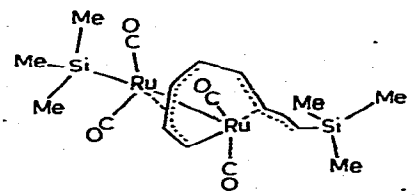


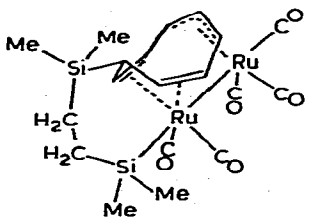
(296) $Ru(GeCl_3)_2(CO)(C_6H_6)$



(297) $Ru_2(SiMe_3)(CO)_5(C_7H_6SiMe_3)$



(298) $Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)$

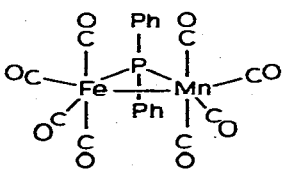


(299) $Ru_2(CO)_5[Me_2Si(CH_2)_2SiMe_2C_8H_8]$

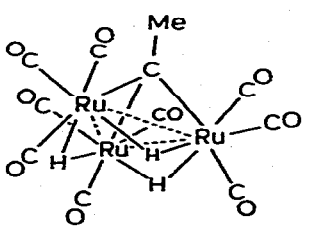
(*290*) From $Sn(C_5H_5)_2 + MnH(CO)_5$; shows expected distorted tetrahedral Sn geometry [165]. (*291*) Planar Mn_2Ge_2 rhombus; bridging Me_2Ge considered as bridging carbenoid ligand, strengthening and shortening Mn-Mn bond, which is shorter than in $Mn_2(CO)_{10}$ [70]. (*292*) From *cis*-$(Me_2As)C(CF_3):C(CF_3)(AsMe_2) + Mn_2(CO)_{10}$; unusual asymmetric η^3-$CF_2C(AsMe_2)C(CF_3)(AsMe_2)$ system formed by C-F bond cleavage; Mn-As bonds significantly different [133]. (*293*) From $MeMn(CO)_5 + Ir(CO)(PPh_3)(C_5H_5)$; 3 bridges involve formal Ir-acetyl and -benzoyl groups, and PPh_2; no Mn-Ir bond [230]. (*294*) From $Sn(\eta^5\text{-}C_5H_5)_2 + Fe_2(CO)_9$; complex contains $Sn(\eta^1\text{-}C_5H_5)_2$ groups, planar C_5H_5 but with diene bond distances; comparison with several related Sn-Fe compounds [223]. (*295*) Long Ru-Ru bond; unexpected eclipsed CO configuration; significantly non-linear Sn-Ru-Ru-Sn sequence may result from relation of 3-fold ($SnMe_4$) and 4-fold [$Ru(CO)_4$] symmetries to equalise Me-CO interactions [112]. (*296*) Eclipsed

conformation, planar C_6 ring; discussion in terms of similarities between CO and $GeCl_3$ electronically [32]. (*297*) From $[Ru(CO)_4(SiMe_3)]_2$ + cycloheptatriene; one $SiMe_3$ group migrates to ring which is attached via η^3 and η^4 bonds to the two metal atoms [153]. (*298*) Ring-opening of C_8H_8 and migration of $SiMe_3$ gives $[\eta^4 + (\eta^4 + \eta^1)]$ ligand [154]. (*299*) From $Ru[SiMe_2(CH_2)_2SiMe_2](CO)_4$ + C_8H_8; migration of one $SiMe_2$ from Ru to C_8H_8 with formation of $(\eta^3 + \eta^2)$ ligand [166].

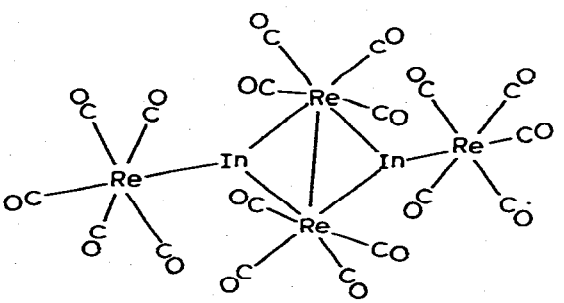
(g) *Polynuclear clusters containing Main Group elements*



(300) $MnFe(PPh_2)(CO)_8$

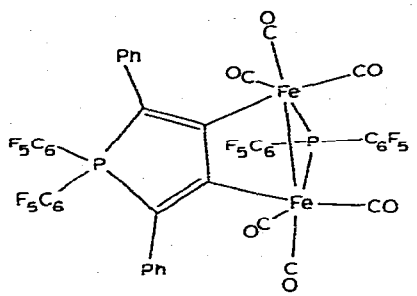


(304) $RuH_3(CMe)(CO)_9$

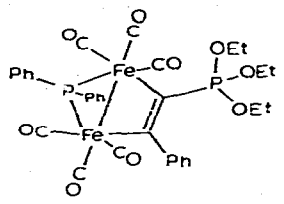


(301) $Re_2(CO)_8[InRe(CO)_5]_2$

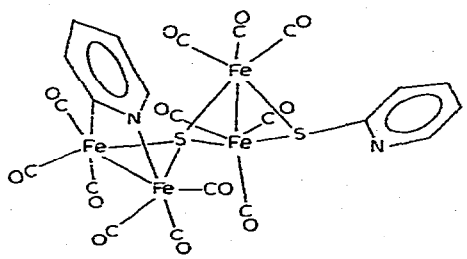
(*300*) Reference [166]. (*301*) Planar Re_2In_2 ring with Re-Re bond [157]. (*302*) From $PhC_2P(C_6F_5)_2$ + $Fe_2(CO)_9$; new P-heterocycle functions as symmetrical η^2, 3e-bridging ligand; bond parameters indicate ligand is a phosphoniadene rather than an ylide [283]. (*302a*) From nucleophilic attack on $Fe_2(PPh_2)(C_2Ph)(CO)_6$ by $P(OEt)_3$, formulated as phosphonium-betaine complex [238]. (*303*) Unusual cluster from $Fe_3(CO)_{12}$ + 2-mercaptopyridine, contains *o*-metallated pyridine nucleus bridging



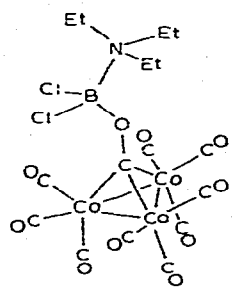
(302) $Fe_2(CO)_6[P(C_6F_5)_2][Ph_2C_4P(C_6F_5)_2]$



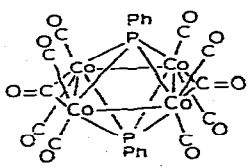
(302a) $Fe_2(CO)_6\{C[P(OEt)_3]CPh\}(PPh_2)$



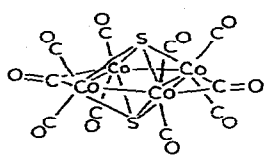
(303) $[Fe_2(CO)_6(C_5H_4N)](S)[Fe_2(CO)_6(SC_5H_4N)]$



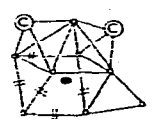
(305) $Co_3(COBCl_2NEt_3)(CO)_9$



(306) $Co_2(PPh)_2(CO)_{10}$



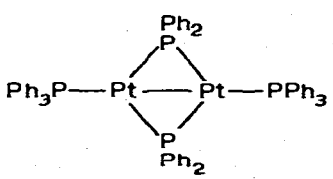
(307) $Co_4S_2(CO)_{10}$



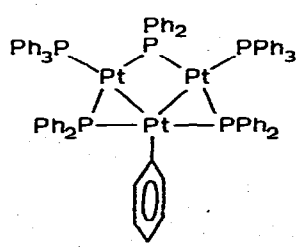
(308) $Rh_8C(CO)_{19}$

© face-bridging CO

edges marked ≠ bridged by CO



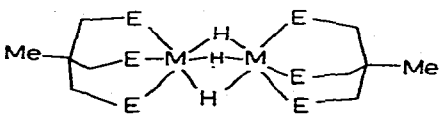
(309) $Pt_2(PPh_2)_2(PPh_3)_2$



(310) $Pt_3Ph(PPh_2)_3(PPh_3)_2$

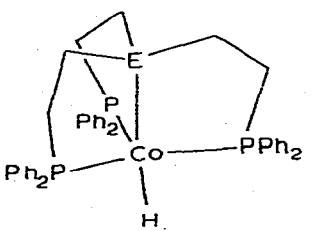
2 Fe atoms, and S tetrahedrally bridging 4 Fe atoms [192]. (*304*) Symmetrically-bridging H on opposite of Ru_3 plane from CMe, with Ru-H 1.72(7)Å, Ru-H-Ru 112(7)°; NMR values recalculated to give Ru-H 1.81Å Ru-H-Ru 103° [71]. (*305*) From $Co_2(CO)_8$ + Cl_3BNEt_3 [132]. (*306*) From $Co_2(CO)_8$ + Zn, followed by $PhPCl_2$; CO-bridged Co-Co bond shorter than unbridged bond; comparison with (*306*) indicates stronger P...P attractions [P···P 2.544(3), S···S 2.74(2)Å] [193]. (*307*) From $Co_2(CO)_8$ + S; S coordinates to 4 Co, with lone pair at apex [67]. (*308*) Rh_6C skeleton shown; 2 face-bonding, 6 edge-bonding, 11 terminal CO groups; probably formed by insertion of 2 $Rh(CO)_2^+$ units into $Rh_6C(CO)_{15}^{2-}$ anion [180]. (*309*) (*310*) Cluster complexes obtained by by continued refluxing of $Pt(PPh_3)_4$ in benzene; cleavage of P-C bond in (*309*) similar to e.g. pyrolysis of $Os_3(CO)_9(PPh_3)_3$ [297].

HYDRIDE COMPLEXES

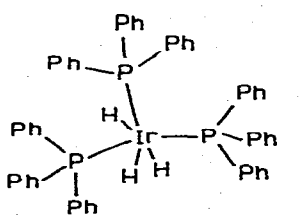


$[M_2H_3\{MeC(CH_2E)_3\}_2]^+$

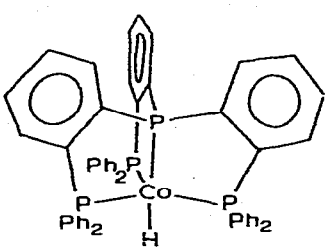
(311) M = Fe, E = PPh_2
(312) M = Co, E = $AsPh_2$



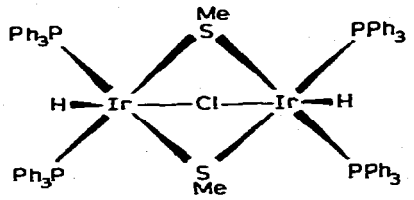
(313) $CoH[N(CH_2CH_2PPh_2)_3]$ E = N
(314) $CoH[P(CH_2CH_2PPh_2)_3]$ E = P
(315) $\{CoH[P(CH_2CH_2PPh_2)_3]\}^+$ E = P



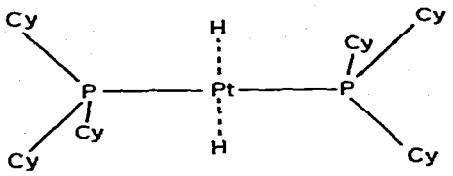
(317) *mer*-$IrH_3(PPh_3)_3$



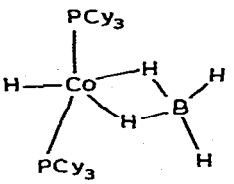
(316) $CoH[P(C_6H_4PPh_2)_3]$



(318) $[(Ph_3P)_2(H)Ir(SPh)_2ClIr(H)(PPh_3)_2]ClO_4$



(319) *trans*-$PtH_2(PCy_3)_2$
H-atom positions not determined

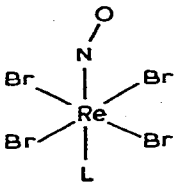


(320) $CoH(BH_4)(PCy_3)_2$

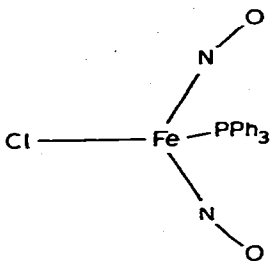
(*311*)(*312*) In both complexes, metal atoms bridged by 3H [1.83(Fe), 1.78Å(Co)] in shared octahedral face; metal-metal distances suggest multiple bond order [307]. (*313*) Comparison with $Ni(np_3)^+$; geometry of complexes imposed by tripod ligands, and virtually unaffected by H ligand; Co-H 1.45(5)Å [301]. (*314*)(*315*)(*316*) Systematic study of hydride complexes: Co-H 1.43(6) (*314*), 1.53(15) (*315*), 1.60(16)Å(*316*); all TBP structures, with axial H [302, 303, 304, 305]. (*317*) Very distorted octahedron, with P-Ir-P 103° (*cis*), 207° (*trans*); Ir-H 1.58-1.62Å, IrH_3 not coplanar [306]. (*318*) From $[IrHCl(SPh)(PPh_3)_2]_2 + AgClO_4$; no Ir-Ir bond, H not located [308]. (*319*) Two modifications, both refined, H not located [299]. (*320*) Paramagnetic; short Co-H, 1.34(9)Å and Co-B, 2.13(1)Å; borohydride attached via CoH_2BH_2 bridge. Co-H *ca.* 1.84Å [300].

See also: *16, 138, 147, 191, 229, 230, 264, 265, 266, 267, 268, 270, 273, 279, 285, 286, 304.*

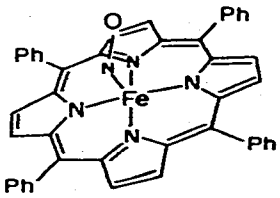
NITROSYLS



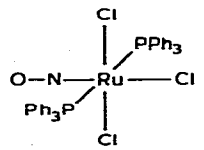
$[Re(NO)Br_4L]^-$
(321) L = MeCN
(322) L = EtOH



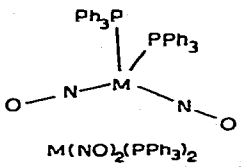
(323) $Fe(NO)_2(PPh_3)Cl$



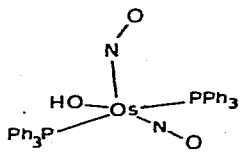
(324) Fe(NO)(tpp)



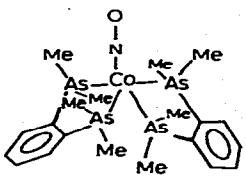
(325) $Ru(NO)Cl_3(PPh_3)_2$



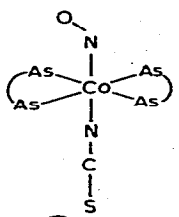
$M(NO)_2(PPh_3)_2$
(326) M = Ru, (327) M = Os



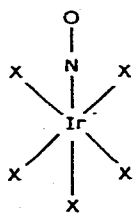
(328) $[Os(NO)_2(OH)(PPh_3)_2]PF_6$



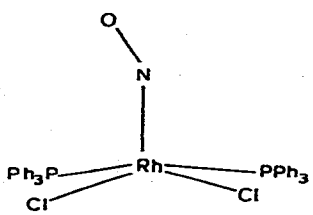
(329) $[Co(NO)(diars)_2](ClO_4)_2$



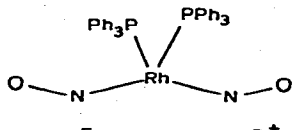
As As = diars
(330) $[Co(NO)(NCS)(diars)_2]SCN$
coordination of Co atom



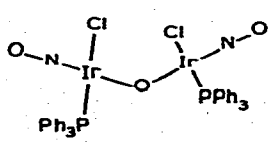
$[Ir(NO)X_5]^-$
(333) X = Br, (324) X = Cl



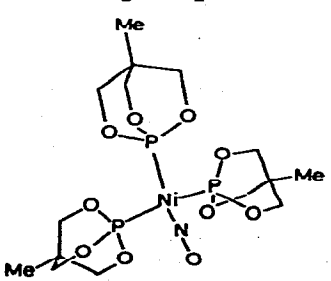
(331) $Rh(NO)Cl_2(PPh_3)_2$



(332) $[Rh(NO)_2(PPh_3)_2]^+$



(335) $[IrCl(PPh_3)(NO)]_2O$



(336) $\{Ni(NO)[P(OCH_2)_3CMe]_3\}BF_4$

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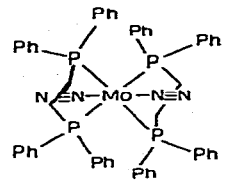
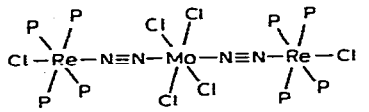
NITROSYLS (Continued)

(*321*)(*322*) Distorted octahedra, equatorial Br; short N-O bond in (*322*) probably disordered, both considered to have NO^+ ligands [310]. (*323*) Distorted trigonal pyramid, NO ligands bent towards each other [311]. (*324*) Square pyramidal Fe with apical NO [318]. (*325*) Comparison with aryldiazo complex (*343*); both N ligands good π acceptors, but NO is the better [17]. (*326*) Complements structure of C_6H_6 solvate reported last year; significant differences in P-Ru-P, Ru-N-O angles, and different conformation of PPh_3 groups [316]. (*327*) Very similar to Ru complex (hemibenzene solvate); extensive Os-N, N-O multiple bonding [14]. (*328*) Contains both linear and bent NO groups; hydroxyl hydrogen not located [317]. (*329*) 5-Coordinate Co, equatorial NO [312]. (*330*) 6-Coordinate Co, bent CoNO group, i.e. change from (*329*) to (*330*) represents formal 2e reduction of NO by addition of ligand [312]. (*331*) Distorted square pyramid, apical NO (bent) disordered; isomorphous and isostructural with Ir complex, but differs from Co complex [313]. (*332*) Rh geometry intermediate between tetrahedral and square planar; comparison with other isoelectronic complexes containing Fe, Ru, Os, Co^+ or Ir^+ [315]. (*333*)(*334*) Axial Ir-X shorter than equatorial Ir-X bond by 0.05(Cl), 0.06Å(Br) [319]. (*335*) From $[Ir(NO)(PPh_3)]_2O + HgCl_2$; Ir-O-Ir bridge retained, but Ir-Ir bond oxidatively cleaved [314]. (*336*) From $Ni[P(OCH_2)_3CMe]_4 + NOBF_4$; distorted tetrahedral Ni [319a].

See also: *15*, *170*.

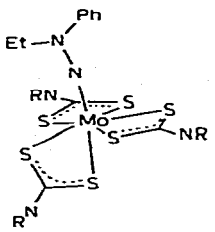


(337) $Mo(N_2)_2(dppe)_2$



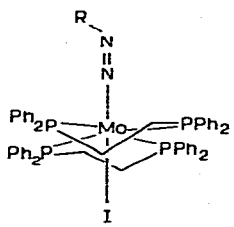
P = PMe_2Ph

(338) *trans*-$MoCl_4[(N_2)ReCl(PMe_2Ph)_4]_2$



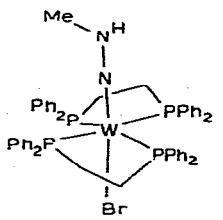
(339) $\{Mo(NNEtPh)[S_2CN(CH_2)_5]_3\}^+$

R = $(CH_2)_5$

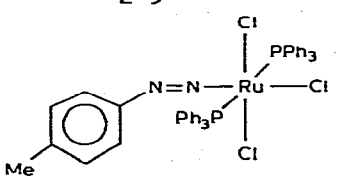


$Mo(N_2R)I(dppe)_2$

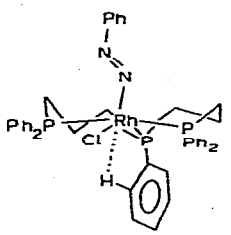
(340) R = Me, (341) R = Cy



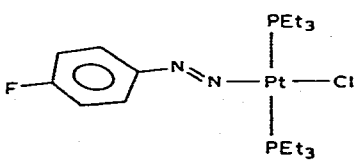
(342) $[WBr(NNHMe)(dppe)_2]^+$



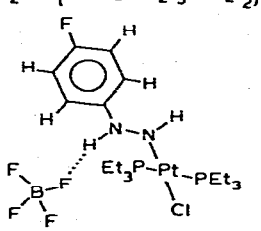
(343) $Ru(N_2tol\text{-}p)Cl_3(PPh_3)_2$



(344) $\left[RhCl(N_2Ph)\left\{PhP[(CH_2)_3PPh_2]_2\right\}\right]PF_6$



(345) $PtCl(N_2C_6H_4F)(PEt_3)_2$



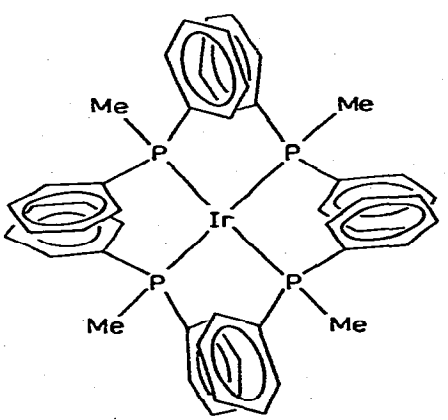
(346) $[PtCl(H_2NNHC_6H_4F)(PEt_3)_2]BF_4$

(*337*) *Trans* N_2-Mo-N_2, Mo-N 2.014(5), N-N 1.118(8)Å; slight distortions from octahedral geometry probably result from steric requirements of dppe, and packing effects [320]. (*338*) Linear Re-N-N-Mo-N-N-Re chain, with Re-N 1.75, Mo-N 1.99, N-N 1.28Å [321]. (*339*) Distorted pentagonal bipyramid, N=N 1.37(2), Mo-N 1.715(16)Å;

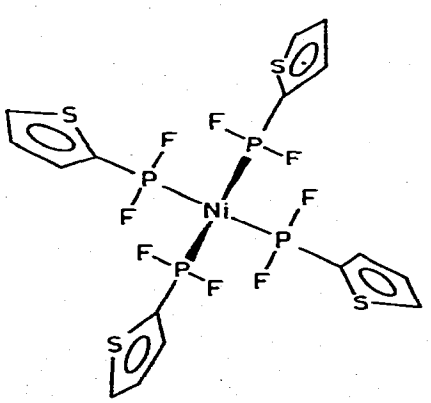
comparison with (*342*) shows decrease in M-N length accompanies increase in N-N distance [325]. (*340*)(*341*) From photochemical reactions of $Mo(N_2)_2(dppe)_2$ + MeI or CyI to give alkyldiazenido complexes; singly-bent Mo-N-N system [327]. (*342*) N=N 1.32(2), W-N 1.77Å; compare (*339*) [325]. (*343*) Comparison with nitrosyl (*325*); aryldiazo ligand singly bent, with Ru-N 1.784, N=N 1.158Å, Ru-N-N 171.9°, N-N-C 137.1° [17]. (*344*) Doubly-bent Rh-N-N-Ph formed by oxidative addition of PhN_2^+ to Rh^I; comparison with $[Rh(NO)ClL]^+$, and further discussion of NO^+/PhN_2^+ analogy [326]. (*345*) Disordered, leads to high R value; doubly-bent ArN_2Pt unit, represents another model compound [see (*346*)], with N=N 1.17(3)Å [323]. (*346*) Model compound in system proposed for reduction N_2→NH_3; N-N 1.436(11)Å, bond order 1, as expected for hydrazine complex [324].

See also: *10, 14, 16, 26, 65, 170.*

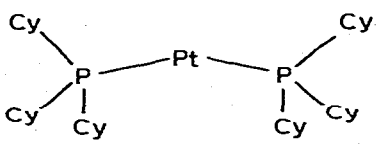
BINARY TRANSITION METAL-TERTIARY PHOSPHINE COMPLEXES



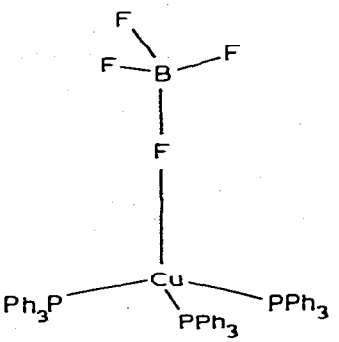
(347) $[Ir(PMePh_2)_4]BF_4$



(348) $Ni[PF_2(C_4H_4S)]_4$



(349) $Pt(PCy_3)_2$



(350) $Cu(PPh_3)_3BF_4$

(*347*) Very distorted square planar Ir, to reduce ligand-ligand interactions; Ir shielded from attack by reagents such as O_2 [330]. (*348*) Tetrahedral, short Ni-P [2.093(3)Å] because of d_π-d_π back-bonding to P [328]. (*349*) Closely similar to Pd complex, P-Pt-P angle 160.5(2)°; compare with *trans*-dihydride (*318*) [329]. (*350*) Weakly coordinated BF_4 *via* Cu-F-BF_3, Cu geometry trigonally distorted tetrahedral; absolute configuration *RSS* [331].

STRUCTURES ORDERED BY ELEMENT

TABULATED STRUCTURAL DATA (TABLES 1 AND 2)

As in previous years, some structural data of general interest has been collected. Such data, presented in Tables 1 and 2, includes metal-metal bond lengths, and parameters of coordinated NO ligands.

SUMMARY TABLES 3 AND 4

These Tables list most complexes whose structures have been reported during 1975, together with a small number reported during the previous year. The arrangement (in columns) is as follows:

1. *Reference number*, referring to the structural diagram in the preceding section.

2. *Molecular formula*, arranged in order of increasing C and H content. Other elements follow in alphabetical order of symbol. Ionic complexes are listed under the relevant ion, e.g. $K[PtCl_3(C_2H_4)].H_2O$ appears as $C_2H_4Cl_3Pt^-.K^+.H_2O$, and solvated molecules, if present, are listed last.

3. *Structural formula*, listed as far as is practicable, with metal atoms first, followed by attached ligand in increasing degree of electron donation. Thus, for some commonly found groups, the order is:

   M, H, M' (Main Group or Transition Metal)

   X (monodentate anionic ligand), R (σ-alkyl, aryl, etc.)

   η^1-ligands, ER_3(E = N, P, As, Sb), SR_2, acac (and anionic bidentates), NO

   η^2-ligands (olefin, acetylene),

   η^3-ligands (allyl, enyl),

   η^4-ligands (diene, cyclo-diene),

   η^5-ligands (dienyl, cyclo-dienyl),

   η^6-ligands (triene, arene),

   η^7-ligands (cyclo-trienyl),

   η^8-ligands (cyclo-tetraene)

   Of necessity, this order cannot be followed in all cases, particularly with cluster complexes.

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4-8. Crystal data, comprising *crystal class*, *space group*, Z and *unit cell dimensions*.

9-11. Number of *intensity data* (observed reflections) used in structural refinement, and lowest R value reported (as %). In an increasing number of cases, conventional (R) and weighted (R_w) values are being quoted; where appropriate, both are listed here.

12. *Miscellaneous notes*, often referring to low temperature determinations, etc. In this column, a number indicates the absolute temperature (K) at which data was collected, or cell constants determined. Other abbreviations used:

CD Cell data only given

ND Neutron diffraction study

SD Structural diagram only, which may be accompanied by some bond parameters.

Other comments are indicated in appropriate footnotes.

13. *Reference number* relating to the list of references at the end of the Survey.

TABLE 1 *Metal-metal bond distances reported in 1975*

Bond	Length(Å)	Complex		Structure	Reference
Cr-Sn	2.697(3)	$[Cr(CO)_3(C_5H_5)]_2SnCl_2$		(282)	127
Mo-Mg	2.737(6)	$\{MoH(C_5H_5)_2[Mg_2Br_2(OEt_2)Cy]\}_2$	Mo-Mg(Cy)	(285)	247
	2.76(3)	$\{MoH(C_5H_5)_2[Mg_2Br_2(OEt_2)Pr^i]\}_2$	Mo-Mg(Pr^i)	(286)	247
	2.81(3)		Mo-Mg(OEt_2)		
	2.853(7)	$\{MoH(C_5H_5)_2[Mg_2Br_2(OEt_2)Cy]\}_2$	Mo-Mg(OEt_2)	(285)	247
Mo-Sn	2.720(1)	$Mo(SnCl_3)(CO)_2(C_7H_7)$		(284)	43
	2.729(4)	$[Mo(SnCl_3)(CO)_4(dppe)]^+$		(283)	232
Mo-Mo	2.448(1)	$[Mo(CO)_2(C_5H_5)]_2$		(232)	107
	2.920(1)	$[Mo(NBu^t)(S)(C_5H_5)]_2$		(233)	156
	3.161	$[MoI(CO)_4]_2$		(231)	333
W-Ga	2.716-2.758(3)	$[W(CO)_3(C_5H_5)]_3Ga$		(287)	205
W-W	3.391(1)	$[W_2H(CO)_{10}]^-$	bent	(230)	49
	3.504(1)	$[W_2H(CO)_{10}]^-$	linear	(229)	49
Mn-Si	2.360(7)	$Mn(SiF_3)(CO)_5$		(ED)	24
	2.407(5)	$Mn(SiH_3)(CO)_5$		(ED)	23
Mn-Ge	2.381(3)	*fac*-$Mn(GeCl_3)(CO)_3[Me_2As(CH_2)_3AsMe_2]$		(288)	63
	2.432, 2.477(2)	$Mn_2(GeMe_2)(CO)_9$		(291)	70
	2.487(2)	$Mn(GeH_3)(CO)_5$		(ED)	23

Mn-Sn	2.590(av.)	$Mn(SnCl_3)(CO)_5$		(289)	29
	2.675, 2.730(5)	$[Mn(CO)_5]_4Sn_2H_2$		(290)	165
Mn-P	2.257(6)	$MnFe(PPh_2)(CO)_8$		(300)	166
	2.348(3)	$(OC)_3Mn(PPh_2)(COMe)(COPh)Ir(C_5H_5)$		(293)	230
Mn-As	2.455, 2.507(4)	$Mn_2(AsMe_2)_3(CO)_6(C_4F_5)$		(292)	133
Mn-Mn	2.5183(24)	$Mn_2(CO)_7[N{:}C(CF_3)_2]_2$		(234)	102
	2.854(2)	$Mn_2(GeMe_2)(CO)_9$		(291)	70
	2.934(6)	$Mn_2(CO)_5(dppm)_2$		(235)	290,291
	3.045(2)	$Mn_2(CO)_6(C_8H_8)$		(261)	105
Mn-Re	2.972(1)	$(OC)_5MnRe(CO)_4[CMe(OMe)]$		(240)	80
Mn-Fe	2.825(5)	$MnFe(PPh_2)(CO)_8$		(300)	166
Mn...Ir	3.543(2)	$(OC)_3Mn(PPh_2)(COMe)(COPh)Ir(C_5H_5)$	no bond	(293)	230
Re-In	2.738	$Re_2(CO)_8[InRe(CO)_5]_2$	$In-Re(CO)_5$	(301)	157
	2.754, 2.807(1)		$In-[Re(CO)_4]_2$		
Re-Re	3.032(8)	$[Re_4H_4(CO)_{15}]^{2-}$	non-bridged	(264)	118
	3.192, 3.211(8)		H-bridged, Re_3		
	3.232(1)	$Re_2(CO)_8[InRe(CO)_5]_2$		(301)	157
	3.288(8)	$[Re_4H_4(CO)_{15}]^{2-}$	H-bridged, $Re-Re_3$	(264)	118
Fe-Sn	2.651, 2.670(1)	$[(C_5H_5)_2SnFe(CO)_4]_2$		(294)	223

Fe-P	2.206(4), 2.226(3)	$Fe_2(PPh_2)(CO)_6\{C[P(OEt)_3]CPh\}$		(302a)	238
	2.212(4), 2.233(3)	$Fe_2[P(C_6F_5)_2](CO)_6[(C_6F_5)_2PC_4Ph_2]$		(302)	283
	2.239(6)	$FeMn(PPh_2)(CO)_8$		(300)	166
Fe-S	2.236-2.263(2)	$[Fe_2(CO)_6(C_5H_4N)](S)[Fe_2(CO)_6(SC_5H_4N)]$	Fe_4S	(303)	192
Fe-Fe	2.316(4)	$Fe_2(CO)_6(C_2Bu^t_2)$		(245)	131
	2.459	$Fe_2(CO)_6(C_{27}H_{24}N_2O_4)$		(248)	242
	2.496(2)	$Fe_2(CO)_5[(HC_2Bu^t)_3CO]$		(258)	215
	2.505(1)	$Fe_2(CO)_6(C_4Ph_4)$		(254)	244
	2.524(1)	$Fe_3(CO)_7(C_2Ph)(C_5H_5)$	CO-bridged	(277)	167
	2.524(3)	$Fe_2(CO)_3(CNBu^t)(C_5H_5)_2$		(236)	150
	2.532(1)	$[Fe_2(CO)_6(C_5H_4N)](S)[Fe_2(CO)_6(SC_5H_4N)]$	S-bridged	(303)	192
	2.571(1)	$1,6\text{-}(C_5H_5)_2\text{-}1,6,2,3\text{-}Fe_2C_2B_6H_8$		(218)	89
	2.590(2)	$Fe_2(CO)[C_4(CF_3)_4CO](C_5H_5)_2$		(253)	83
	2.598(1)	$[Fe_2(CO)_6(C_5H_4N)](S)[Fe_2(CO)_6(SC_5H_4N)]$	py-bridged	(303)	192
	2.634(1)	$Fe_3(CO)_7(C_2Ph)(C_5H_5)$		(277)	167
	2.640, 2.653(2)	$Fe_3H(CO)_9(SPr^i)$		(266)	82
	2.642(1)	$Fe_2(CO)_6(C_8H_{10}O)$		(250)	106
	2.671(2)	$Fe_2(PPh_2)(CO)_6\{C[P(OEt)_3]CPh\}$		(302a)	238
	2.678(2)	$Fe_3H(CO)_9(SPr^i)$	H,S-bridged	(266)	82
	2.697(2)	$Fe_2[PC_6F_5)_2](CO)_6[(C_6F_5)_2PC_4Ph_2]$		(302)	283
	2.740(3)	$Fe_2(CO)_6(C_{10}H_{14}O)$		(256)	131
	2.765(2)	$Fe_2(CO)_5(C_5H_4CPh_2)$		(259)	188

	2.773(1)	$Fe_2(CO)_6(C_9H_{10})$		(251)	119
	2.804(1)	$Fe_2(CO)_5(PEt_3)(C_{10}H_{12})$		(252)	190
Fe-Co	2.520(1)	$(C_5H_5)FeCo(CO)_4(nbd)$		(242)	130
	2.545(1)	$(C_5H_5)FeCo(CO)_6$		(241)	69
	2.560(2)	$HFeCo_3(CO)_9[P(OMe)_3]_3$		(267)	155
Fe-Ni	2.420(4)	$(C_5H_5)NiFe(CO)_3(HC_2PPh_3)$		(246)	225
Ru-C	2.082(12)	$Ru_3H_3(CMe)(CO)_9$		(304)	71
Ru-Si	2.437(5)	$Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)$		(298)	154
	2.452(3)	$Ru_2(SiMe_3)(CO)_5(C_7H_6SiMe_3)$		(297)	153
	2.458(4)	$Ru_2(CO)_5[MeSi(CH_2)_2(SiMe_2)C_8H_8]$		(299)	154
Ru-Ge	2.408(2)	$Ru(GeCl_3)_2(CO)(C_6H_6)$		(296)	32
Ru-Sn	2.691(1)	$[Me_3SnRu(CO)_4]_2$		(295)	112
Ru-Ru	2.7997(5) 2.828	$Ru_3H(CO)_{10}(CNMe_2)$	H,C-bridged	(268)	96
	2.841(6)	$Ru_3H_3(CMe)(CO)_9$	Ru-H-Ru	(304)	71
	2.845(1)	$Ru_2(CO)_5(C_5H_4CPh_2)$		(260)	198
	2.891(1)	$Ru_2(CO)_5(C_{16}H_{16})$		(257)	183
	2.909(2)	$Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)$		(298)	154
	2.935(2)	$Ru_2(CO)_5[Me_2Si(CH_2)_2(SiMe_2)C_8H_8]$		(299)	154
	2.937(1)	$Ru_2(SiMe_3)(CO)_5(C_7H_6SiMe_3)$		(297)	153
	2.943(1)	$[Me_3SnRu(CO)_4]_2$		(295)	112
Ru-Pt	2.707, 2.729(2)	$RuPt_2(CO)_5(PMePh_2)_3$		(269)	278

Os-Os	2.717, 2.855, 2.884(5)	$Os_3(CO)_{10}(C_2Ph_2)$		(278)	204
	2.8574(7)	$Os_3H_2(CO)_{11}$	Os-Os(H)	(270)	68
	2.9097(7)		Os-Os		
	2.9886(9)		H-bridged		
Co-C	1.89	$Co_3(COBCl_2NEt_3)(CO)_9$		(305)	132
Co-P	2.244	$Co_4(PPh)_2(CO)_{10}$		(306)	193
Co-S	2.26(1)	$Co_4S_2(CO)_{10}$		(307)	67
Co-Co	2.467	$Co_4H_4(C_5H_5)_4$		(279)	173
	2.47	$Co_3(COBCl_2NEt_3)(CO)_9$		(305)	132
	2.480(9)	$Co_4S_2(CO)_{10}$	CO-bridged	(307)	67
	2.488(12)	$HFeCo_3(CO)_9[P(OMe)_3]_3$		(267)	155
	2.519(2)	$Co_4(PPh)_2(CO)_{10}$	CO-bridged	(306)	193
	2.598(10)	$Co_4S_2(CO)_{10}$		(307)	67
	2.697(2)	$Co_4(PPh)_2(CO)_{10}$		(306)	193
Co-Ni	2.418(2)	$(C_5H_4Me)NiCo(CO)_4(PCyPh_2)$		(244)	228
	2.425(2)	$(C_5H_5)NiCo(CO)_4[P(C_6H_4F)_3]$		(243)	220
Co-Pt	2.528, 2.554(3)	$Co_2Pt_2(CO)_8(PPh_3)_2$		(271)	275
	2.540, 2.579(2)		CO-bridged		
Rh-C	2.127	$Rh_8C(CO)_{17}$		(308)	180
Rh-Rh	2.680(3)	$[Rh(CO)(C_5H_5)]_2C_4F_6$		(247)	129
	2.699-2.913(3)	$Rh_8C(CO)_{17}$		(308)	180

	2.77(av.)	$[Rh_7I(CO)_{16}]^{2-}$	octahedron } range	(272)	141	88
	2.93(av.)		tetrahedron } 2.740-3.000			
	2.81(av.)	$[Rh_{13}H_3(CO)_{24}]^{2-}$		(273)	203	
Ir-P	2.307(2)	$(C_5H_5)Ir(PPh_2)(COMe)(COPh)Mn(CO)_3$		(293)	230	
Ni-Ni	2.338	$Ni_4(CNBu^t)_7$		(274)	252	
	2.36	$[Ni_5(CO)_{12}]^{2-}$	Ni_3-plane	(275)	94	
	2.369, 2.385	$Ni_4(CO)_4(C_4F_6)_3$	Ni-Ni_3	(281)	103	
	2.458	$Ni_3(CO)_3(C_4F_6)(C_8H_8)$		(280)	103	
	2.669	$Ni_4(CO)_4(C_4F_6)_3$	Ni_3-base	(281)	103	
	2.703	$Ni_3(CO)_3(C_4F_6)(C_8H_8)$	C_4F_6-bridged	(280)	103	
	2.743-2.865(3)	$[Ni_5(CO)_{12}]^{2-}$	Ni-Ni_3	(275)	94	
Pd-Pd	2.5310(9)	$[Pd_2(CNMe)_6]^{2+}$		(237)	93	
	2.609(1)	$[Pd(PPr^i_3)]_2(Br)(C_5H_5)$		(262)	115	
	2.679	$[Pd(PPh_3)]_2(C_4H_7)(C_5H_5)$		(263)	282	
Pt-P	2.257-2.276	$Pt_3(PPh_2)_3(Ph)(PPh_3)_2$	bridging Pt-Pt	(310)	297	
	2.300-2.324	$Pt_2(PPh_2)_2(PPh_3)_2$		(309)	297	
	2.304	$Pt_3(PPh_2)_3(Ph)(PPh_3)_2$	bridging Pt...Pt	(310)	297	
Pt-Pt	2.584(2)	$[Pt_2Cl_4(CO)_2]^{2-}$		(238)	27	
	2.585(1)	$[Pt(cod)]_2OC(CF_3)_2$		(239)	163	
	2.604	$Pt_2(PPh_2)_2(PPh_3)_2$		(309)	297	
	2.632	$Pt_3(CNBu^t)_6$		(275)	94	

2.647(2)	$RuPt_2(CO)_5(PMePh_2)_3$	(269)	278
2.785	$Pt_3(PPh_2)_3(Ph)(PPh_3)_2$	(310)	297
2.820(2)	*nido*-μ(4,8)-[$(Me_3P)_2Pt$]-8,8-$(Me_3P)_2$-8,7,10-$PtC_2B_8H_{10}$	(225)	38
2.987(4)	$Co_2Pt_2(CO)_8(PPh_3)_2$	(271)	275
3.051(4)	*closo*-2,3-[$(Et_3P)_2$]$_2$-2,3,1,6-$Pt_2C_2B_5H_7$	(217)	38

TABLE 2 *M-N-O Bond Parameters in Nitrosyl Complexes*

Complex		M-N-O(°)	M-N(Å)	N-O(Å)	Reference
(a) *Bent nitrosyls*					
$Fe(NO)(tpp)$	(324)	149.2(6)	1.717(7)	1.122(12)	318
$[Os(NO)_2(OH)(PPh_3)_2]^+$ (apical)	(328)	133.6(12)	1.86(1)	1.17(2)	317
$[Co(NO)(SCN)(diars)_2]^+$	(330)	132.3(14)	1.85(1)	1.00(1)	312
$Rh(NO)Cl_2(PPh_3)_2$	(331)	124.8(16)	1.912(10)	1.15	313
$[Rh(NO)_2(PPh_3)_2]^+$	(332)	158.9(4)	1.818(4)	1.158(6)	315
(b) *Linear nitrosyls*					
$[Mo(NO)I(NH_2NHPh)(C_5H_5)]^+$	(170)	170.6(3)	1.780(4)	1.188(5)	76
$[Re(NO)Br_4(MeCN)]^-$	(321)	178(6)	1.771(11)	0.99(2)[a]	310
$[Re(NO)Br_4(EtOH)]^-$	(322)	169(3)	1.723(15)	1.19(2)	310
$Fe(NO)_2Cl(PPh_3)$	(323)	166.4(5)	1.679(5)	1.136(7)	311
		165.5(5)	1.681(5)	1.163(7)	
$Ru(NO)Cl_3(PPh_3)_2$	(325)	180	1.737(7)	1.142(8)	17
$Ru(NO)_2(PPh_3)_2$	(326)	168.0(15)	1.748(20)	1.215(18)	316
		174.7(16)	1.688(20)	1.229(18)	

$[Os(NO)(CO)_2(PPh_3)_2]^+$	(15)	178.3(10)	1.84(1)[b]	1.16(1)[b]	257
$Os(NO)_2(PPh_3)_2$	(327)	178.7(7)	1.776(7)	1.195(8)	14
		174.1(6)	1.771(6)	1.211(7)	
$[Os(NO)_2(OH)(PPh_3)_2]^+$ (basal)	(328)	177.6(12)	1.63(1)	1.24(2)	317
$[Co(NO)(diars)_2]^{2+}$	(329)	178(2)	1.68(3)	1.16(2)	312
$[Ir(NO)Br_5]^-$	(333)	170.3(26)	1.710(25)	1.166(42)	319
$[Ir(NO)Cl_5]^-$	(334)	174.3(11)	1.760(11)	1.124(17)	319
$[Ir(NO)Cl(PPh_3)]_2O$	(335)	177.2(10)	1.70(1)	1.18(2)	314
		174.2(10)	1.73(1)	1.14(2)	
$\{Ni(NO)[P(OCH_2)_3CMe]_3\}^+$	(336)	176.8(18)	1.581(12)	1.122(15)	319a

[a] Probably disordered, not resolved. [b] NO, CO disordered.

TABLE 3. ORGANOMETALLICS

No.	FORMULA	STRUCTURE	CRYSTAL CLASS	SPACE GROUP	Z
	C_2				
94	$C_2H_4Cl_3Pt^-.K^+.H_2O$	$K[PtCl_3(C_2H_4)].H_2O$	M	P2/c	4
238	$C_2Cl_4O_2Pt_2^{2-}.2C_{12}H_{28}N^+$	$(NPr_4)_2[Pt_2Cl_4(CO)_2]$	M	$P2_1/a$	4
2	$C_2I_4O_2Rh^-.C_{12}H_{28}N^+$	$NPr_4[RhI_4(CO)_2]$	M	$P2_1$	2
			M	$P2_1/c$	4
	C_5				
289	$C_5Cl_3MnO_5Sn$	$Mn(SnCl_3)(CO)_5$	M	$P2_1/c$	8
	C_6				
85	$C_6H_8F_4Pt$	$Pt(C_2H_4)_2(C_2F_4)$	M	A2/a	4
47	$C_6H_{14}Cl_2N_2O_2Pd$	*cis*-$PdCl_2[C(OMe)(NHMe)]_2$	Tri	$P\bar{1}$	2
1	C_5CrO_5	$Cr(CO)_5$	O	Pnma	4
	C_7				
296	$C_7H_5Cl_5Ge_2ORu$	$Ru(GeCl_3)_2(CO)(C_6H_6)$	O	Pnma	4
52	$C_7H_7FeO_4^-.C_{36}H_{30}NP_2^+$	$[N(PPh_3)_2][Fe(C_3H_7)(CO)_4]$	M	C2/c	8
35	$C_7H_7O_4Rh$	$Rh(CO)_2(acac)$	Tri	$P\bar{1}$	2
214	$C_7H_{26}B_5Br_2IrOP_2$	$Ir(B_5H_8)Br_2(CO)(PMe_3)_2$	M	$P2_1/c$	4
	C_8				
191	$C_8H_{12}CrF_9P_3$	$CrH(C_8H_{11})(PF_3)_3$			
46	$C_8H_{18}Cl_2N_7O_2Ru^+.Cl^-.H_2O$	*trans*-$[RuCl_2(C_8H_9N_4O_2)(NH_3)_3]Cl.H_2O$[a]	O	Pbca	8
221	$C_8H_{28}B_8P_2Pt$	*nido*-8,8-$(Me_3P)_2$-7,8,10-$CPtCB_8H_{10}$	Tri	$P\bar{1}$	2

[a] Crystal data from ref. 25a. [b] Needles. [c] Octahedra.

a	b	c	α	β	γ	DATA	R	R'	NOTES	REFERENCE
11.212(3)	8.424(6)	9.696(6)		107.52(4)		1210	7.0	7.6	ND,a	25
19.727(6)	9.176(3)	21.481(10)		113.72(3)		4448	10.9			27
12.764(8)	12.695(8)	7.737(5)		90.0(2)		2051	5.4		b	28
9.537(6)	15.551(9)	18.218(11)		108.4(2)					c	28
14.10(1)	13.38(5)	13.27(2)		97.39(21)		2581	9.98			29
8.884(4)	7.552(2)	12.934(6)		109.51(3)		765	8.5			30
8.45(1)	8.26(1)	9.19(1)	84.8(1)	105.2(1)	106.7(1)	1947	4.7			31
11.505(4)	10.916(3)	6.203(2)				422	2.9	4.9	ND,78	26
14.3071(6)	13.2024(6)	8.3497(5)				720	3.8	3.9		32
34.20(2)	9.38(1)	24.21(2)		97.22(8)		1597	7			33
6.5189(5)	7.7614(8)	9.2049(12)	106.04(1)	91.15(1)	100.21(1)	1456	3.8			34
13.8237(36)	10.6606(28)	13.6112(34)		104.90(2)		2558	4.84	4.88		35
									SD	332
11.341(3)	11.606(5)	26.673(7)				1314	5.9			37
9.551(3)	12.321(4)	10.156(2)	107.37(2)	123.29(2)	91.87(2)	3428	8			38

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228	$C_8H_{32}B_{20}Ti^{2-}.2C_4H_{12}N^+.2C_3H_6O$	$(NMe_4)_2[Ti(1,6\text{-}C_2B_{10}H_{10}Me_2)_2].2Me_2CO$	Tri	$P\bar{1}$	2
231	$C_8I_2Mo_2O_8$	$[MoI(CO)_4]_2$			

[a] $C_8H_9N_4O_2$ = caffeine.

C_9

162	$C_9H_5F_6FeO_2P$	$Fe(CO)_2[P(CF_3)_2](C_5H_5)$	M	$P2_1/c$	4
163	$C_9H_5F_6FeO_3P$	$Fe(CO)_2[P(O)(CF_3)_2](C_5H_5)$	M	$P2_1/c$	4
206	$C_9H_7BrMoO_2$	$MoBr(CO)_2(C_7H_7)$	O	$P2_12_12_1$	4
205	$C_9H_7ClMoO_2$	$MoCl(CO)_2(C_7H_7)$	O	$P2_12_12_1$	4
284	$C_9H_7Cl_3MoO_2Sn$	$Mo(SnCl_3)(CO)_2(C_7H_7)$	O		4
31	$C_9H_7NO_5S_2W$	$W(CO)_5(C_4H_7NS_2)$[a]	M	$P2_1/n$	4
49	$C_9H_{10}BrCrNO_4$	*trans*-$CrBr(CO)_4(CNEt_2)$			
133	$C_9H_{12}MnO$	$Mn(CO)(C_4H_6)_2$	Tet	$P\bar{4}2_1m$	2
222	$C_9H_{18}B_9CoO$	$Co(C_5H_5)[B_9C_2H_{10}(COMe)]$	M	Pc	4
223	$C_9H_{18}B_9CoO_2$	$Co(C_5H_5)[B_9C_2H_{10}(OCOMe)]$	M	$P2_1/c$	4
54	$C_9H_{19}CoN_4O_5$	$CoMe(OH_2)(dmg)_2$	O	Pnma	4

[a] $C_4H_7NS_2$ = thiomorpholin-3-thione

C_{10}

229	$C_{10}HO_{10}W_2^-.C_8H_{20}N^+$	$NEt_4[W_2H(CO)_{10}]$	Tri	$P\bar{1}$	1
230	$C_{10}HO_{10}W_2^-.C_{36}H_{30}NP_2^+$	$[N(PPh_3)_2][W_2H(CO)_{10}]$	Tri	$P\bar{1}$	2
4	$C_{10}H_2Cr_2N_2O_{10}.2C_4H_8O$	$[Cr(CO)_5]_2N_2H_2.2thf$	Tri	$P\bar{1}$	2
161	$C_{10}H_6F_6FeN_2O$	$Fe[NH{:}C(CF_3)N{:}C(CF_3)](CO)(C_5H_5)$	M	$P2_1/n$	4
155	$C_{10}H_7MnO_4$	$Mn(CO)_3(C_5H_4COMe)$	M	$P2_1/c$	4
156	$C_{10}H_7O_4Re$	$Re(CO)_3(C_5H_4COMe)$	M	$P2_1/a$	4
123	$C_{10}H_8FeO_5$	$Fe(CO)_3(C_7H_8O_2)$[a]	Tri	$P\bar{1}$	2

13.412(3)	9.325(2)	16.781(5)	95.21(2)	106.15(2)	81.55(2)	3214	5.6	5.9	113	39
									SD	333
8.602(7)	11.924(9)	12.859(9)		112.75(9)		1882	4.8			41
11.938(8)	7.603(6)	13.818(9)		100.97(8)		1777	4.5			41
6.4459(21)	11.8378(20)	13.2183(21)				1037	7.4			42
6.4276(20)	11.8527(19)	13.1114(18)				1179	12.5			42
11.8150(65)	9.4368(8)	11.8150(14)				1540	5.9			43
5.64(1)	23.17(3)	10.25(2)		91.7(3)		1919	5.3			44
						1609	4.7		SD	45
7.80(1)	7.80(1)	7.21(1)				425	7.7			46
12.030(1)	8.297(1)	15.509(1)		112.19(1)		2981	4.7	1.14		47
7.895(1)	12.592(1)	14.950(2)		99.30(1)		3107	4.8	1.28		47
13.136(5)	9.112(3)	12.114(4)				946	10	13		48
6.891(2)	10.196(5)	8.950(5)	102.25(3)	101.85(3)	86.27(3)	1411	6.0			49
11.433(3)	14.244(3)	16.791(3)	58.20(1)	96.55(1)	99.84(1)	3282	5.0			49
19.03(2)	10.27(1)	6.37(1)	97.3(1)	97.9(1)	95.9(1)	1310	6.8			50
8.975(7)	14.696(13)	9.785(4)		104.84(5)		1267	4.9	4.8		51
13.19	12.39	6.26		95		627	12			52
14.22	11.71	6.59		110		1480	8.9			52
7.745(5)	6.787(3)	9.873(4)	96.46(3)	86.79(4)	94.05(4)	1435	2.9			53

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188	$C_{10}H_9FeNO_2S$	$Fe(C_5H_4SO_2NHC_5H_4)$	M	$P2_1/c$	4
18	$C_{10}H_{10}BCuN_6O$	$Cu(CO)[HB(pz)_3]$	Rhomb	R3c	8
140	$C_{10}H_{10}Co$	$Co(C_5H_5)_2$	M	$P2_1/c$	2
120	$C_{10}H_{10}FeO_5$	$Fe(CO)_3[C(O)OCHMeCHCHCHMe]$	O	Pbca	8
148	$C_{10}H_{10}MoS_4$	$Mo(S_4)(C_5H_5)_2$	M	$P2_1/n$	4
151	$C_{10}H_{11}MoNO_3$	$Mo(COCH_2CH_2NH_2)(CO)_2(C_5H_5)$	O	$Pna2_1$	4
128	$C_{10}H_{12}B_2F_2NiO_2$	$Ni(CO)_2(C_4Me_4B_2F_2)$	M	A2/m	4
147	$C_{10}H_{14}BNb$	$Nb(BH_4)(C_5H_5)_2$	O	Fmm2	4
201	$C_{10}H_{16}Cl_2F_3PRu$	$RuCl_2(PF_3)(C_{10}H_{16})$[c]	M	C2/c	
288	$C_{10}H_{18}As_2Cl_3GeMnO_3$	$Mn(GeCl_3)(CO)_3[Me_2As(CH_2)_3AsMe_2]$	M	$P2_1/n$	4
7	$C_{10}H_{18}As_2MoO_4P_2$	$Mo(CO)_4[Me_2P(AsMe)_2PMe_2]$	O	Pbcn	4
6	$C_{10}H_{18}MoO_4P_4$	$Mo(CO)_4(P_4Me_6)$	O	Pbcn	4
109	$C_{10}H_{18}N_2NiO_2$	$Ni(O_2)(CNBu^t)_2$	O	Cmcm	4
307	$C_{10}Co_4O_{12}S_2$	$Co_4S_2(CO)_{10}$	M	$P2_1/n$	2

[a] $C_7H_9O_2$ = η^5-3-methylene-4-vinyldihydrofuran-2(3H)-one. [b] b not reported.

[c] $C_{10}H_{16}$ = 2,7-Me_2-2,6-octadien-1,8-diyl.

C_{11}

270	$C_{11}H_2O_{11}Os$	$Os_3H_2(CO)_{11}$	M	$P2_1/n$	4
241	$C_{11}H_5CoFeO_6$	$(C_5H_5)FeCo(CO)_6$	M	$P2_1/m$	2
291	$C_{11}H_6GeMn_2O_9$	$Mn_2(GeMe_2)(CO)_9$	M	C2/c	8
304	$C_{11}H_6O_9Ru$	$Ru_3H_3(CMe)(CO)_9$	O	Pnma	4
195	$C_{11}H_8CrO_4S$	$Cr(CO)_2(CS)(PhCO_2Me)$	Tri	$P\bar{1}$	2
121	$C_{11}H_8F_6FeO_3$	$Fe(CO)_3[CF(CF_3)CF_2CH_2CHCMeCH_2]$	O	$P2_12_12_1$	4
210	$C_{11}H_{10}B_2FeO_3S$	$Fe(CO)_3[C_6H_4(BMe)_2S]$[a]	Tri	$P\bar{1}$	2
158	$C_{11}H_{11}MnO_3$	$Mn(CO)_2(CH_2{:}CHCOMe)(C_5H_5)$	O	$P2_12_12_1$	4

10.566(7)	11.802(7)	7.671(6)		93.35(5)		978	5.1	5.0		54
13.8616(21)			91.37(1)			1726	2.85	3.20		55
5.926(4)	7.732(6)	10.618(8)		121.38(11)		765	7.6			56
12.0732(16)	b	12.2010(15)				2377	3.21	3.06		57
11.298(8)	12.166(9)	8.804(6)		92.73(3)		1600	5.8			58
18.932(35)	8.734(12)	6.472(18)				799	7.9			59
11.904(7)	15.505(8)	12.584(4)		110.07(4)		950	6.9	6.7		60
13.562(5)	9.327(5)	7.923(5)				239	12.8			61
12.575(10)	9.591(7)	12.051(9)		106.70(6)		1112	3.9			62
8.215(3)	14.279(7)	16.787(8)		90.46(1)		2133	8.3			63
8.138(1)	15.775(3)	14.701(3)				541	9.0	10.0		64
8.045(3)	15.766(4)	14.471(3)				560	6.6	5.1		65
11.53(1)	16.55(2)	7.05(5)				469	9.7	12.3	248	66
10.06(2)	6.81(1)	12.45(2)		97.25(33)		440	9.2	7.2		67
8.0744(16)	14.7265(29)	14.7770(28)		101.36(1)		2239	3.68	3.52		68
7.008(9)	10.941(17)	8.605(16)		104.7(1)		1240	5.5			69
8.742(2)	14.215(4)	27.221(7)		95.05(2)		2371	6.2	5.1		70
17.54(3)	14.55(2)	6.766(10)				1018	4.7			71
7.108(3)	10.340(4)	8.523(3)	89.75(6)	95.89(4)	105.50(4)	1963	3.0	3.8		72
23.020	8.497	6.546				1245	3.6			73
9.221(3)	9.322(2)	9.529(2)	69.66(2)	72.08(2)	60.71(3)	2848	2.62	3.64		74
7.718(2)	10.402(5)	13.723(4)				794	4.0	3.3		75

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170	$C_{11}H_{13}IMoN_3O^+.BF_4^-$	$[MoI(NO)(NH_2NHPh)(C_5H_5)]BF_4$	Tri	$P\bar{1}$	2
55	$C_{11}H_{23}CoN_{10}$	$CoMe(NH_2NHMe)(C_{10}H_{14}N_8)$[b]			

[a] $C_6H_4(BMe)_2S$ = η^5-benzothiadiborolane. [b] $C_{10}H_{14}N_8$ = a macrocyclic bis-α-diimine ligand.

C_{12}

265	$C_{12}H_4Fe_3O_{11}$	$Fe_3H(COMe)(CO)_{10}$	M	$P2_1/c$	4
76	$C_{12}H_6FeO_6$	$Fe(CO)_4[COCMe{:}C(C_2Me)CO]$	M	$P2_1/c$	4
240	$C_{12}H_6MnO_{10}Re$	*cis*-$MnRe(CO)_9[CMe(OMe)]$	Tri		2
70	$C_{12}H_7MnO_5$	$Mn[C_6H_4C(O)Me](CO)_4$	M	$C2/c$	8
266	$C_{12}H_8Fe_3O_9S$	$Fe_3H(CO)_9(SPr^i)$	M	$P2_1/c$	4
182	$C_{12}H_{10}F_2FeO$	$Fe(COCF_2C_5H_5)(C_5H_5)$	M	Cc	4
149	$C_{12}H_{10}O_2Ti$	$Ti(CO)_2(C_5H_5)_2$	O	$Pnma$	4
202	$C_{12}H_{11}F_6O_2Rh$	$Rh(C_7H_{10})(hfac)$[a]	O	$C222_1$	4
32	$C_{12}H_{12}Mn_2N_2O_6S_4$	$[Mn(CO)_3\{\mu\text{-}SC(SMe)NMe\}]_2$	M	$P2_1/n$	4
143	$C_{12}H_{14}Cl_2Ti$	$TiCl_2(C_5H_4Me)_2$	O	$Pnma$	4
144	$C_{12}H_{14}Cl_2V$	$VCl_2(C_5H_4Me)_2$	M	$C2/c$	4
178	$C_{12}H_{15}Ta$	$Ta(CH_2)Me(C_5H_5)_2$	M	$P2_1/c$	4
209	$C_{12}H_{16}Cl_2OZr$	$ZrCl_2(thf)(C_8H_8)$	O	$Cmca$	8
218	$C_{12}H_{18}B_6Fe_2$	$1,6\text{-}(C_5H_5)_2\text{-}1,6,2,3\text{-}Fe_2C_2B_6H_8$[b]	M	$P2_1/n$	4
39	$C_{12}H_{18}FeN_6^{2+}.2Cl_4Fe^-$	$[Fe(CNMe)_6](FeCl_4)_2$	M	$P2_1/c$	2
132	$C_{12}H_{16}Mo$	$Mo(C_4H_6)_3$	Hex	$P6_3/m$	2
9	$C_{12}H_{18}N_2O_4SW$	$W(CO)_4[S(NBu^t)_2]$	M	$P2_1/n$	4
237	$C_{12}H_{18}N_6Pd_2^{2+}.2F_6P^-.C_3H_6O$	$[Pd_2(CNMe)_6](PF_6)_2.Me_2CO$	Tri	$P\bar{1}$	2
275	$C_{12}Ni_5O_{12}^{2-}.2C_{36}H_{30}NP_2^+$	$[N(PPh_3)_2]_2[Ni_5(CO)_{12}]$	Tri	$A\bar{1}$	2
-	$C_{12}O_{12}Os_3$	$Os_3(CO)_{12}$	M	$P2_1/n$	4

[a] C_7H_{10} = (±)-*ZZ*-1,2,3-η^3-5,6,7-η^3-heptadienediyl. [b] Diamagnetic isomer.

10.737(5)	10.818(5)	7.451(2)	85.014(4)	110.272(13)	100.581(6)	3100	2.9			76
									SD	77
7.680(2)	16.363(3)	13.936(2)		103.55(2)		1440	6.1	8.5		78
6.848(2)	32.396(8)	7.361(2)		128.91(2)		989	4.2			79
8.999(5)	13.093(2)	8.202(2)	111.24(2)	112.22(3)	84.41(3)	1932	2.47	3.10		80
25.940(7)	5.993(1)	17.117(4)		115.63(2)		1921	3.1	3.7		81
9.59(1)	9.88(1)	19.59(2)		96.11(7)		1227	5.5	5.9		82
12.204(3)	8.386(4)	11.262(2)		120.11(2)			6.0			83
7.837(9)	11.475(8)	12.232(8)				648	8.6			84
8.599(1)	14.684(3)	11.264(2)				521	6.9			85
9.872(4)	13.784(3)	15.006(8)		98.20(4)		2525	5.6			86
11.928(5)	15.147(6)	6.848(4)				724	4.6	6.2		8
13.614(2)	6.720(1)	13.763(2)		105.99(1)		590	4.1	4.8		8
6.544(4)	11.685(2)	15.339(11)		117.13(5)		1279	2.6	3.2		87
12.328(2)	11.973(2)	17.581(3)				1364	2.5	3.4		88
8.999(7)	12.860(10)	11.989(4)		92.00(5)		1640	3.6	3.8	113	89
8.97(1)	8.83(1)	18.54(2)		97.83(17)		1474	5.5			90
7.208(11)		11.829(24)								91
10.374(1)	11.385(1)	14.546(1)		97.7		1615	6.7			92
12.281(2)	12.544(3)	10.388(2)	111.03(1)	111.12(1)	75.95(1)	3249	4.5	5.7		93
13.309(7)	23.804(14)	12.577(7)	91.73(5)	95.30(4)	77.63(4)	3482	7.5	9.7		94
8.0817(6)	14.7683(11)	14.5773(11)		100.56(1)					CD	68

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C_{13}

183	$C_{13}H_6CoF_{12}O_2P$	$Co(C_5H_5)[(C_4F_6)_2PO(OH)]$	O	$P2_12_12_1$	4
268	$C_{13}H_7NO_{10}Ru$	$Ru_3H(CO)_{10}(C{:}NMe_2)$	M	$P2_1/n$	8
185	$C_{13}H_{12}Cl_5Rh$	$Rh(cod)(C_5Cl_5)$	O	Pnma	4
194	$C_{13}H_{14}CrO_5$	$Cr(CO)_3[C_6H_4(CHOHMe)_2\text{-}o]$ [a]	Tri		
216	$C_{13}H_{17}B_3Co$	$[Co(C_5H_5)]_2C_2B_3H_4Me$ [b]	O	Pnam	4
125	$C_{13}H_{19}O_2Rh$	Rh(acac)(cod)	M	Cc	4
81	$C_{13}H_{19}O_2Rh$	$Rh(acac)(C_4H_6)_2$ [c]	M	$P2_1/n$	4
234	$C_{13}F_{12}Mn_2N_2O_7$	$Mn_2(CO)_7[N{:}C(CF_3)_2]_2$	M	$P2_1/c$	4

[a] Pseudoasymmetric, m.p. 144°. [b] 2-Me-1,7-$[Co(C_5H_5)]_2$-2,4-$C_2B_3H_4$. [c] C_4H_6 = η^2-methylenecyclopropane.

C_{14}

280	$C_{14}H_8F_6Ni_3O_3$	$Ni_3(CO)_3[C_2(CF_3)_2](C_8H_8)$	M	$P2_1/n$	4
249	$C_{14}H_8Fe_2O_7$	$Fe_2(CO)_6(C_8H_8O)$ [a]	Tri	$P\bar{1}$	
261	$C_{14}H_8Mn_2O_6$	$Mn_2(CO)_6(C_8H_8)$	O	Pbca	8
250	$C_{14}H_{10}Fe_2O_7$	$Fe_2(CO)_6(C_8H_{10}O)$ [b]	Tri	$P\bar{1}$	2
232	$C_{14}H_{10}Mo_2O_4$	$[Mo(CO)_2(C_5H_5)]_2$	O	Pbcm	4
211	$C_{14}H_{14}Ag^+.ClO_4^-$	$[Ph(CH_2)_2Ph]AgClO_4$ [c]	O	Pbnm	4
193	$C_{14}H_{14}Cr^+.C_{12}H_4N_4^-$	$[Cr(PhMe)_2](tcnq)$	M	$P2_1/n$	4
200	$C_{14}H_{16}MoO_3$	$Mo(CO)_3(C_7H_7Bu^t)$	Tri	$P\bar{1}$	2
164	$C_{14}H_{17}FeO_2^+.BF_4^-$	$[Fe(CO)_2(C_3Me_4)(C_5H_5)]BF_4$	M	$P2_1/c$	4
295	$C_{14}H_{18}O_8Ru_2Sn_2$	$[Ru(SnMe_3)(CO)_4]_2$	Tri	$P\bar{1}$	1
3	$C_{14}H_{20}CrN_4O_4$	$Cr(CO)_4[C(NMeCH_2)_2]_2$	M	$P2_1/c$	4
169	$C_{14}H_{22}MoN_2^{2+}.2F_6P^-$	$[Mo(NH_3)(HNCMeEt)(C_5H_5)_2](PF_6)_2$	M	$P2_1/c$	4
100	$C_{14}H_{28}MoN_2OS_6$	$MoO(S_2)(S_2CNPr_2)_2$	M	$P2_1/c$	
224	$C_{14}H_{37}B_{10}N_3Pd$	$1,1\text{-}(Bu^tNC)_2\text{-}2\text{-}NMe_3\text{-}1,2\text{-}PdCB_{10}H_{10}$	M	$P2_1/n$	4

9.353(7)	9.893(7)	17.923(10)				1922	6.3			95
9.3171(9)	35.8136(35)	11.9616(10)		97.06(1)		3702	2.41	3.45		96
10.437(1)	12.711(1)	11.646(1)				2841	5.3			97
7.80(1)	11.15(1)	8.74(1)	106.4(3)	104.53(33)	103.3(3)	1392	3.7			98
13.596(6)	9.968(3)	10.008(4)				294	4.6	5.3		99
6.854(5)	18.645(10)	9.864(7)		93.1(2)		1884	4.0			100
12.810(5)	9.054(3)	11.855(4)		103.09(3)		1684	6.6	7.5		101
9.298(5)	26.614(19)	9.543(8)		121.00(5)		1512	5.17	5.67		102
9.591(2)	11.994(3)	14.876(14)		99.57(2)		2114	5.4			103
11.93(1)	8.258(8)	7.729(8)				3687	3.2			104
10.096(3)	23.825(8)	11.472(4)				1252	8.64			105
7.5135(5)	8.5100(6)	12.8393(8)	72.132(6)	85.877(6)	83.514(8)	2984	4.2	5.1		106
6.485(2)	18.465(2)	11.639(3)				871	4.3	5.4		107
5.871(1)	12.575(2)	18.731(3)				447	7.6			108
7.00(2)	15.45(3)	20.50(6)		97.0(5)		1754	12.8			109
10.2260(7)	6.3869(27)	14.7800(19)	78.48(2)	131.049(8)	87.16(3)	2160	5.4			110
9.299	13.686	12.746		94.03		1984	6.8			111
6.886(1)	7.916(2)	11.358(2)	90.30(2)	107.73(1)	82.93(1)	1791	2.4	2.6		112
9.888(2)	15.806(3)	12.382(2)		118.87(2)		1225	3.4			113
9.647(6)	18.394(10)	13.988(5)		121.05(5)		3305	5.5			114
12.033(3)	11.813(3)	19.924(4)		125.04(2)		1166	7.6			116
10.947(3)	15.194(4)	15.804(4)		103.45(2)		3319	4.2	5.2		117

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225	$C_{14}H_{46}B_8P_4Pt_2$	*nido*-μ(4,8)-[$(Me_3P)_2$Pt]-8,8-$(Me_3P)_2$-7,8,10-CPtCB_8H_{10}	M	A2/a	8

[a] C_8H_8O = 2,3-η^2:4,5,6-η^3-cycloocta-2,4-dienone-6,7-diyl.

[b] $C_8H_{10}O$ = 2,3,4-η^3:5,6-η^2-7-oxo-3,5-octadien-2,2-diyl.

C_{15}

264	$C_{15}H_4O_{15}Re_4^{2-}.2C_8H_{20}N^+$	$(NEt_4)_2[Re_4H_4(CO)_{15}]$	M	$P2_1/c$	4
–	$C_{15}H_9MnO_4$	$Mn(CO)_3(C_5H_4COPh)$	M	$P2_1/c$	4
251	$C_{15}H_{10}Fe_2O_6$	$Fe_2(CO)_6(C_9H_{10})$[a]	Tri	$P\bar{1}$	2
142	$C_{15}H_{15}FU$	$UF(C_5H_5)_3$	Rhomb Hex	R3m	
189	$C_{15}H_{16}Fe$	$Fe(C_5H_4C_5H_8C_5H_4)$[b]	O	Pbca	8
135	$C_{15}H_{16}FeO_3$	$Fe(CO)_3(C_{12}H_{16})$[c]	M	$P2_1$	2
22	$C_{15}H_{32}I_2O_3P_4W$	$WI_2(CO)_3(dmpe)_2$	M	$P2_1/n$	4
			M	$P2_1/a$	16

[a] C_9H_{10} = 1,2,6-η^3:3,4,5-η^3-bicyclo[6.1.0]nona-1,3,5-triene. [b] 1,1'-(1'',3''-cyclopentylene)ferrocene.

[c] $C_{12}H_{16}$ = tricyclo[6.4.0.$0^{2,7}$]dodeca-3,5-diene.

C_{16}

5	$C_{16}H_5AsCr_2O_{10}$	$[Cr(CO)_5]_2AsPh$			
80	$C_{16}H_8FeO_4$	$Fe(CO)_4(C_{12}H_8)$[a]	M	$P2_1/c$	4
77	$C_{16}H_8FeO_5$	$Fe(CO)_4(C_{12}H_8O)$[b]	M	$P2_1/n$	4
282	$C_{16}H_{10}Cl_2Cr_2O_6Sn$	$[Cr(CO)_3(C_5H_5)]_2SnCl_2$	M	$P2_1/n$	4
44	$C_{16}H_{10}CrO_6$	$Cr(CO)_5[C(C_2Ph)(OEt)]$	M	$P2_1/c$	4
247	$C_{16}H_{10}F_6O_2Rh_2$	$Rh_2(CO)_2[C_2(CF_3)_2](C_5H_5)_2$	Tri	$P\bar{1}$	2
242	$C_{16}H_{13}CoFeO_4$	$(C_5H_5)FeCo(CO)_4(C_7H_8)$	M	$P2_1/c$	4
256	$C_{16}H_{14}Fe_2O_7$	$Fe_2(CO)_6(C_{10}H_{14}O)$[c]	M	$P2_1/n$	4
305	$C_{16}H_{15}BCl_2Co_3NO_{10}$	$Co_3(COBCl_2NEt_3)(CO)_9$	Tri	$P\bar{1}$	4

29.143(16)	10.058(7)	21.935(7)		90.54(4)		3153	7.6			38
11.60(1)	20.68(2)	17.97(2)		95.9(1)		777	8.7			118
12.47	6.42	16.49		96.7					CD	52
7.229(4)	14.699(4)	7.696(2)	87.53(2)	113.48(3)	102.08(2)	2651	3.4	3.3		119
8.156			114.23							120
13.698(4)		5.980(2)				763	3.04			120
16.250(7)	14.266(5)	10.337(2)				1570	5.7	5.7		121
6.176(1)	11.307(2)	9.781(2)		92.89(2)		1733	5.5	3.4		122
11.701(6)	15.680(9)	9.316(5)		95.36(5)		2226	7.2			123
25.772(14)	15.514(13)	17.432(14)		91.59(8)		3250	6.3			123
							5.8		SD	124
6.731(1)	21.311(2)	9.919(1)		99.716(9)		1869	3.4	4.9		125
9.446(3)	6.382(2)	23.464(4)		91.58(2)		1731	6.4	8.1		126
10.314(12)	15.646(20)	12.223(12)		93.25(10)		3458	5.7	8.6		127
7.188(8)	12.313(1)	18.778(1)		93.9(1)		795	8.8			128
9.322(5)	12.139(6)	8.671(5)	103.60(5)	68.98(5)	109.87(5)	2101	6.0			129
18.013(27)	6.553(17)	13.031(37)		103.2(1)		3936	6.3	7.5		130
10.025(4)	11.167(4)	16.482(8)		101.94(3)		1930	6.6			131
13.57	13.52	13.33	90.50	94.44	85.83	2724	5.9			132

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292	$C_{16}H_{18}As_3F_5Mn_2O_6$	$Mn_2(CO)_6[C_4F_5(AsMe_2)_3]$	Tri	$P\bar{1}$	2
245	$C_{16}H_{18}Fe_2O_5$	$Fe_2(CO)_6(C_2Bu_2^t)$	M	$P2_1/n$	4
126	$C_{16}H_{19}O_6Rh$	$Rh(acac)[C_7H_6(CO_2Me)_2]$	M	$P2_1/c$	4
212	$C_{16}H_{20}Ag^+.ClO_4^-$	$(o\text{-}Me_2C_6H_4)_2AgClO_4$	Tri	$P\bar{1}$	2
129	$C_{16}H_{24}B_4F_4Ni$	$Ni[C_4Me_4(BF)_2]_2$	M	$C2/c$	4
60	$C_{16}H_{33}Cl_2PdS_2$	$PdCl(CBu^t{:}CHCH{:}CClBu^t)[MeS(CH_2)_2SMe]$	Trig	$R\bar{3}$	18
19	$C_{16}H_{36}Cl_3Mo_2O_{16}P_4.^{n+}C_2H_6Cl_4MoO_4P^{n-}$	$\{Mo_2Cl_3(CO)_4[P(OMe)_3]_4\}$ - $\{MoOCl_4[OP(OMe)_2]\}$	Tri	$P\bar{1}$	2
220	$C_{16}H_{43}B_7P_2Pt$	$2,7\text{-}Me_2\text{-}9,9\text{-}(PEt_3)_2\text{-}2,7,9\text{-}C_2PtB_7H_7$	M	$P2_1/a$	4
219	$C_{16}H_{45}B_7NiP_2$	$6,6\text{-}(Et_3P)_2\text{-}5,9\text{-}Me_2\text{-}6,5,9\text{-}NiC_2B_7H_9$	M	$P2_1/n$	4
281	$C_{16}F_{18}Ni_4O_4$	$Ni_4(CO)_4[C_2(CF_3)_2]_3$	M	$P2_1/m$	2
272	$C_{16}IO_{16}Rh_7^{2-}.2C_8H_{20}N^+$	$(NEt_4)_2[Rh_7I(CO)_{16}]$	Tri	$P\bar{1}$	2

[a] $C_{12}H_8$ = η^2-acenaphthylene. [b] $C_{12}H_8FeO$ = naphtho[*b*]ferracyclopent-3-en-2-one.

[c] $C_{10}H_{14}O$ = 1,2,3-$\eta^3(Fe^1)$:3,4,5-$\eta^3(Fe^2)$-2-Me-4-Bu^t-5-oxopenta-1,3-diene-1,3,5-triyl.

C_{17}

165	$C_{17}H_{10}Fe_2O_6$	$Fe_2(CO)_5[COC_6H_6C_5H_4]$[a]	M	$P2_1/c$	4
203	$C_{17}H_{17}F_6IrO_2$	$Ir(hfac)(C_{12}H_{16})$[b]	M	$C2/c$	4
51	$C_{17}H_{37}Cl_2N_4Ta.C_6H_6$	$TaCl_2Me[MeC(NPr^i)_2]_2.C_6H_6$	M	$P2_1/n$	4
134	$C_{17}F_{17}MnO_3S$	$Mn(CO)_3[(C_4F_6)_2SC_5F_5]$	Tri	$P\bar{1}$	2

[a] $COC_6H_6C_5H_4$ = 1-(η^5-cyclopentadienyl)-2,3,4,5-η^4-cyclohexa-2,4-dien-1-oyl.

[b] $C_{12}H_{16}$ = 1,2,2'-η^3:7,7',8-η^3-(2,3,6,7-tetramethylene)octane-1,8-diyl.

C_{18}

69	$C_{18}H_{13}IN_2PtS_2$	$PtI(C_4H_2SC_5H_4N)(C_9H_7NS)$[a]	M	$P2_1/n$	4
73	$C_{18}H_{14}F_{12}O_4Pd$	$Pd(acac\ C_4F_6)_2$	M	$P2_1/n$	4
186	$C_{18}H_{16}FeO$	$FeCOCH_2Ph$	O	$P2_12_12_1$	

9.580(4)	15.279(6)	9.292(4)	93.07(2)	119.26(2)	82.80(2)	2233	7.8			133
13.824(4)	9.776(3)	13.826(5)		94.26(2)		1848	7.6			131
9.245(4)	9.003(4)	21.680(15)		113.41(5)		3010	6.60	6.9		134
8.595 (1)	10.766(1)	10.817(1)	86.21(1)	103.28(1)	113.70(1)	1236	10.3			135
17.569(3)	6.671(1)	17.270(3)		116.06(1)		2165	5.7			136
25.62		18.32				1306	7.0			137
11.714(13)	15.493(12)	15.038(13)	117.06(10)	99.43(13)	96.96(14)	3066	7.7			138
17.23(1)	18.86(1)	10.093(6)		126.96(4)		3185	3.5	4.3		139
9.144(2)	18.954(5)	15.021(3)		90.51(4)		3192	6.8	8.0		140
8.506(2)	16.05(1)	9.011(4)		100.52(3)		1033	12			103
20.06(2)	11.08(1)	10.42(1)	83.14(8)	96.46(8)	102.06(8)	2532	5.6	7.6		141
6.562(1)	21.690(5)	11.399(2)		96.78(2)		2852	5.02	4.24		142
9.850(2)	21.452(8)	8.583(2)		96.91(2)			6.4			143
11.772(12)	16.250(13)	15.632(13)		109.98(12)		1748	7.9			144
7.889(6)	11.737(8)	12.195(9)	91.45(10)	69.71(10)	81.55(9)	3229	4.5			95
17.360(3)	8.418(1)	13.556(2)		110.53(2)		2220	4.6	6.1		145
9.512(7)	23.294(13)	11.301(9)		114.9(2)		4302	5.7	6.9		146
9.47(4)	14.57(6)	9.94(4)				724	9			147

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198	$C_{18}H_{18}BN_8Ru^+.F_6P^-$	$\{Ru[B(pz)_4](C_6H_6)\}PF_6$	O	Cmca	8
119	$C_{18}H_{18}F_{18}NiO_6P_2$	$NiC_6(CF_3)_6[P(OMe)_3]_2$	O	Pbcn	4
75	$C_{18}H_{19}F_6NO_2Pd$	$Pd(C_6H_4CH_2NMe_2)(acac\ C_4F_6)$	M	$P2_1/c$	4
230	$C_{18}H_{19}Fe_2NO_3$	$Fe_2(CO)_3(CNBu^t)(C_5H_5)_2$	O	$P2_12_12_1$	4
130	$C_{18}H_{20}F_6Pt$	$PtMe[C_7H_5(CF_3)_2](cod)^b$	M	$P2_1/n$	4
27	$C_{18}H_{22}Cl_2O_2P_2Rh_2$	$[RhCl(CO)(PMe_2Ph)]_2$	Tri	$P\bar{1}$	2
297	$C_{18}H_{24}O_5Ru_2Si_2$	$Ru_2(SiMe_3)(CO)_5(C_7H_6SiMe_3)$	O	$P2_12_12_1$	4
298	$C_{18}H_{26}O_4Ru_2Si_2$	$Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)$	Tri	$P\bar{1}$	2
267	$C_{18}H_{28}Co_3FeO_{18}P_3$	$FeCo_3H(CO)_9[P(OMe)_3]_3$	M	$P2_1/c$	4
233	$C_{18}H_{28}Mo_2N_2S_2$	$Mo_2S_2(NBu^t)_2(C_5H_5)_2$	M	$P2_1/n$	2
301	$C_{18}In_2O_{18}Re_4$	$Re_2(CO)_8[InRe(CO)_5]_2$	M	$P2_1/n$	2

[a] C_5H_7NS = 2-thienylpyridine. [b] $C_7H_5(CF_3)_2$ = 7-η^1-1,2-$(CF_3)_2$-bicyclo[2.2.1]heptadienyl.

C_{19}

179	$C_{19}H_{12}F_{12}MoN_4$	$Mo[(pz)_2C_3(CF_3)_3CH(CF_3)](C_5H_5)$	M	$P2_1/n$	4
136	$C_{19}H_{16}O_3Ru$	$Ru(CO)_3(C_{16}H_{16})^a$	M	$P2_1/n$	4
117	$C_{19}H_{20}FeO_{11}$	$Fe(CO)_3(C_{16}H_{20}O_8)^b$	O	$P2_12_12_1$	8
23	$C_{19}H_{22}BrMnO_7P_2$	*fac-trans*-$MnBr(CO)_3[P(OMe)_2Ph]_2$	O	$P2_12_12_1$	4
24	$C_{19}H_{22}BrMnO_7P_2$	*mer-trans*-$MnBr(CO)_3[P(OMe)_2Ph]_2$	M	$P2_1/n$	8
172	$C_{19}H_{22}U$	$U(C_4H_7)(C_5H_5)_3$	O	$P2_12_12_1$	4
299	$C_{19}H_{24}O_5Ru_2Si_2$	$Ru_2(CO)_5[Me_2Si(CH_2)_2SiMe_2C_8H_8]$	Tri	$P\bar{1}$	2
239	$C_{19}H_{24}F_5OPt_2$	$Pt_2(cod)_2[(CF_3)_2CO]$	M	$P2_1/c$	4
173	$C_{19}H_{24}U$	$UBu(C_5H_5)_3$	O	$P2_12_12_1$	4
171	$C_{19}H_{25}BF_6Rh^+.F_6P^-$	$\{Rh(C_5Me_5)[HB(pz)_3]\}PF_6$	M	$P2_1/c$	4
226	$C_{19}H_{45}B_8CoP_2Pt$	$1-(C_5H_5)-8,8-(PEt_3)_2-1,2,7,8-CoC_2PtB_8H_{10}$	O	$P2_12_12_1$	4

13.472(5)	22.034(4)	14.718(2)				742	5.8	6.2		148
17.355(5)	11.014(3)	15.026(5)				804	5.0	5.4		149
8.789(7)	13.186(10)	17.237(14)		102.4(2)		3748	3.4	4.2		146
6.649(11)	13.062(35)	20.553(52)				1447	7.2			150
23.63(1)	8.354(4)	8.935(4)		93.20(1)		1483	9.5			151
10.495(9)	12.086(9)	10.337(7)	112.71(4)	97.50(4)	103.69(4)	2370	3.7	4.9		152
10.355(2)	12.380(5)	17.580(5)				2024	4.9			153
6.903(3)	7.669(3)	24.45(1)	92.41(3)	89.87(3)	116.45(3)	3600	7.0			154
15.992(6)	10.638(3)	18.403(4)		98.515(25)		6057	6.1		134	155
16.336(3)	10.896(2)	18.583(2)		97.259(12)					298	155
15.486(2)	8.839(1)	7.787(1)		93.882(5)		1244	2.4	4.2		156
6.788(2)	16.352(3)	12.519(3)		89.23(5)		3301	4.8			157
8.242(4)	17.537(9)	14.651(7)		97.62(5)		2512	6.5			158
12.801(4)	6.640(1)	19.678(5)		103.06		1991	3.6			159
15.646(2)	23.941(2)	11.033(1)				2779	5.1	6.1		160
17.19(2)	16.71(2)	8.27(1)				1498	4.1	4.8		161
14.94(2)	24.94(3)	13.34(1)		109.6(2)		3191	11.6			161
10.240(4)	8.747(4)	18.198(4)				3470	6.4	6.5		162
11.851(2)	8.761(2)	11.864(2)	100.54(2)	110.37(1)	92.25(1)	3658	6.6			154
9.917(3)	14.957(6)	13.358(3)		102.18(2)		2215	4.0			163
8.64(1)	22.69(2)	8.66(1)				1290	5.4			164
11.852(10)	14.962(5)	13.125(8)		92.27(8)		1448	11.7			148
18.654(8)	14.41(1)	12.800(35)					~8			117

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[a] $C_{16}H_{16}$ = 1,2,3,4-η^4-tetracyclo[4.4.2.$0^{5,16}0^{6,15}$]hexadeca-1,3,8,10,13-pentane.

[b] $C_{16}H_{20}O_8$ = cyclobutadiene-dimethyl maleate adduct.

C_{20}

290	$C_{20}H_2Mn_4O_{20}Sn_2$	$[Mn(CO)_5]_2Sn_2H_2$	M	C2/c	4
253	$C_{20}H_{10}F_{12}Fe_2O_2$	$Fe_2(CO)[COC_4(CF_3)_4](C_5H_5)_2$	O	$P2_12_12_1$	4
300	$C_{20}H_{19}FeMnO_8P$	$MnFe(PPh_2)(CO)_8$	O	Pbcn	8
277	$C_{20}H_{10}Fe_3O_7$	$Fe_3(CO)_7(C_2Ph)(C_5H_5)$	Tri	$P\bar{1}$	2
10	$C_{20}H_{10}Mn_2N_4O_8$	$[Mn(CO)_4(N_2Ph)]_2$	Tri	$P\bar{1}$	1
159	$C_{20}H_{15}Mn_2O_4P$	$[Mn(CO)_2(C_5H_5)]_2PPh$			
146	$C_{20}H_{20}Cl_4Ti_2Zn.2C_6H_6$	$[TiCl(C_5H_5)_2]_2ZnCl_2.2C_6H_6$	O	Pbcn	4
177	$C_{20}H_{20}Hf$	$HfMe_2(C_9H_7)_2$	O	$P2_12_12$	2
175	$C_{20}H_{20}Ti$	$TiMe_2(C_9H_7)_2$	O	$P2_12_12$	2
176	$C_{20}H_{20}Zr$	$ZrMe_2(C_9H_7)_2$	O	$P2_12_12$	2
154	$C_{20}H_{20}Al_2O_6W_2$	$[W(CO)_2(COAlMe_2)(C_5H_5)]_2$	M	C2/c	4
279	$C_{20}H_{24}Co_4$	$Co_4H_4(C_5H_5)_4$	M	C2/c	8
98	$C_{20}H_{27}BN_4Pt$	$PtMe(MeC_2Ph)[Et_2B(pz)_2]$	M	$P2_1/c$	4
145	$C_{20}H_{30}Cl_2Ti$	$TiCl_2(C_5Me_5)_2$	O	$P2_12_12_1$	4
227	$C_{20}H_{37}B_9P_2Pt$	1,1-$(PhMe_2P)_2$-2,4-Me_2-1,2,4-$PtC_2B_9H_9$	Tri	$P\bar{1}$	2
67	$C_{20}H_{38}Cl_3N_2P_2Pt^+.ClO_4^-$	$\{PtCl_2[C(NHC_6H_3Cl)(NHMe)](PEt_3)_2\}ClO_4$	M	$P2_1/a$	4
48	$C_{20}H_{42}Ta^-.C_6H_4LiN_2^+$	Li(dmp)$[Ta(CBu^t)(CH_2Bu^t)_3]$	O	$P2_12_12_1$	4
308	$C_{20}O_{19}Rh_8$	$Rh_8C(CO)_{19}$	Tri	$P\bar{1}$	2

C_{21}

199	$C_{21}H_{14}CrO_3$	$Cr(CO)_3(C_5H_4CPh_2)$	M	$P2_1/a$	4
157	$C_{21}H_{15}MnO_3$	$Mn(CO)_2[CPh(COPh)](C_5H_5)$	M	$P2_1/n$	4
257	$C_{21}H_{16}O_5Ru$	$Ru_2(CO)_5(C_{16}H_{16})$[a]	M	$P2_1/n$	8

15.71(5)	17.18(5)	12.51(5)		107.3(2)		2968	20			165
9.446(3)	13.708(6)	15.748(6)					4.6			83
16.768(9)	17.020(9)	15.359(8)				1331	8.0			166
12.635	9.457	9.033	94.64	109.10	99.60	2488	3.8			167
7.2358(13)	8.8893(17)	9.4677(18)	80.52(2)	77.38(1)	71.44(1)	1974	3.43	3.61		168
							5		SD	169
18.236(10)	15.513(8)	11.237(6)				1396	7.1	4.9		170
14.243(6)	8.215(4)	6.918(4)				965	3.0	3.9		171
14.124(7)	8.073(5)	6.844				280	7.0	7.8		171
14.248(4)	8.244(3)	6.929(3)				904	2.5	3.0		171
18.120(4)	6.188(2)	22.266(5)		93.29(2)		1175	4.2	5.1		172
27.68(2)	9.05(1)	15.25(1)		101.97(8)		1802	5.9			173
13.239(6)	11.077(5)	15.619(7)		114.53(2)		3289	3.62	3.55		174
10.816(1)	8.132(1)	22.259(1)				1429	3.2			175
9.324(3)	10.285(4)	14.208(8)	100.40(4)	94.32(4)	98.95(3)	4073	3.3	4.0		176,177
13.451(2)	21.381(5)	13.368(2)		130.73(1)		3811	4.8			178
17.196(6)	17.512(4)	10.503(3)				2192	7.1			179
9.18(1)	17.76(2)	10.46(1)	75.95(10)	69.07(10)	92.37(10)	3423	2.34			180
20.008(6)	6.504(2)	13.064(4)		94.36(2)		1019	9.6			181
7.11(2)	10.87(2)	21.94(2)		93.5(2)		799	8.5			182
7.010(1)	24.965(8)	22.021(7)		101.03(2)		4179	5.6			183

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118	$C_{21}H_{17}F_{12}O_5PRu$	$Ru(CO)_2[P(OCH_2)_3CMe](C_6H_8)(C_4F_6)_2$	M	$P2_1/c$	4
137	$C_{21}H_{16}O_3RuSi$	$Ru(CO)_3(CHCPhSiMe_2CPhCH)$	M	$I2/c$	8
72	$C_{21}H_{19}F_{12}IrO_2$	$Ir(cod\ C_4F_6)(acac\ C_4F_6)$	Tri	$P\bar{1}$	2
153	$C_{21}H_{19}MoN_2O_2^+.F_6P^-$	$(+)-[Mo(CO)_2(C_{14}H_{14}N_2)(C_5H_5)]PF_6$ [b]	O	$P2_12_12_1$	4
166	$C_{21}H_{20}Fe_2O_5$	$Fe_2(CO)_5(C_6H_4Me_2)_2$ [c]	M	$P2_1/c$	4
59	$C_{21}H_{21}ClN_2O_3Pd$	$PdCl(CH_2COCH_2COCH_2Ph)(py)_2$	Tri	$P\bar{1}$	2
252	$C_{21}H_{27}Fe_2O_5P$	$Fe_2(CO)_5(PEt_3)(C_{10}H_{12})$ [d]	O	$P2_12_12_1$	4
180	$C_{21}H_{28}PW^+.F_6P^-$	$[WMe(CH_2CH_2PMe_2Ph)(C_5H_5)_2]PF_6$	O	Pbca	16
-	$C_{21}H_{30}Pd$	$Pd(C_7H_{10})_3$	O	$P2_12_12_1$	4
86	$C_{21}H_{30}Pt$	$Pt(C_7H_{10})_3$	O	$P2_12_12_1$	4

[a] $C_{16}H_{16}$ = 3,4,5-η^3:1,2,6,9,10-η^5- tricyclo [6.4.2.$0^{7,16}$]hexadeca-1,3,9,11,14-pentaene-5,6-diyl.

[b] $C_{14}H_{14}N_2$ = PhCHMeN:CHpy. [c] $C_6H_4Me_2$ = dimethylpentafulvene.

[d] $C_{10}H_{12}$ = cis-1,2,6-η^3:3,4,5-η^3-bicyclo[6.2.0]dodeca-1,3,5-triene. [e] Isostructural with Pt complex.

C_{22}

303	$C_{22}H_8Fe_4N_2O_{12}S_3$	$[Fe_2(CO)_6SC_5H_4N]_2S$	M	$P2_1/n$	4
306	$C_{22}H_{10}Co_4O_{10}P_2$	$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PPh)_2$	Tri	$P\bar{1}$	2
124	$C_{22}H_{17}F_{12}FeO_5P$	$Fe(CO)_2[P(OCH_2)_3CMe](C_7H_8)(C_4F_6)_2$	M	$P2_1/n$	4
78	$C_{22}H_{18}F_{18}N_2Pt$	$PtC_6(CF_3)_6(CNBu^t)_2$	O	Pbca	8
139	$C_{22}H_{22}Fe^+.F_6P^-$	$[Fe(Me_2ind_2)_2]PF_6$	Tri	$P\bar{1}$	2
33	$C_{22}H_{40}N_4O_2Ru_2S_8$	$[Ru(CO)S_2CNEt_2)_2]_2$	Tri	$P\bar{1}$	2
138	$C_{22}H_{49}IrP_2$	$IrH(C_4H_6)(PPr^i_3)_2$	M	$P2_1/c$	4

C_{23}

259	$C_{23}H_{14}Fe_2O_5$	$Fe_2(CO)_5(C_6H_4Ph_2)$ [a]	M	$P2_1/c$	4
260	$C_{23}H_{14}O_5Ru_2$	$Ru_2(CO)_5(C_6H_4Ph_2)$ [a]	Tri	$P\bar{1}$	2
255	$C_{23}H_{24}O_2Rh_2$	$Rh_2(CO)(nbd)_2(C_8H_8O)$ [b]	M	$P2_1/c$	4

8.875(5)	17.841(9)	16.517(5)		94.51(3)		2418	7.7			184
11.112	8.013	27.455		97.22		3363	4.9			185
13.415(15)	11.448(12)	8.435(9)	70.2(4)	113.6(5)	103.5(5)	4642	4.8	5.0		186
12.245(5)	9.237(4)	20.693(7)				2359	7.3	9.0		187
16.039(3)	7.935(3)	16.057(6)		109.82(2)		1773	2.71			188
10.275(2)	11.849(3)	9.214(2)	75.16(2)	96.70(3)	100.02(4)	2689	4.4			189
13.744(8)	13.730(5)	11.922(7)				1910	4.9	6.7		190
12.286(7)	40.813(18)	18.302(8)				3120	5.6			191
5.705(1)	10.784(5)	28.770(15)							*e*,CD	30
5.720(1)	10.740(4)	28.771(12)				1695	10.6			30
9.053(4)	10.812(6)	29.27(12)		97.02(7)		2689	4.1	3.8		192
11.390(6)	14.257(10)	9.124(6)	97.99(6)	113.27(4)	96.13(5)	2661	4.3	6.5		193
8.647(3)	29.650(9)	9.371(3)		92.87(3)		3297	5.9			184
16.754(13)	23.211(20)	16.295(8)				1900	9.8			194
9.2586(16)	13.2849(22)	8.5681(16)	98.062(14)	91.311(14)	83.950(13)	2136	4.38	5.65		195
16.08(1)	11.907(5)	9.693(3)	103.04(3)	77.80(4)	94.15(4)	2997	5.2	5.6		196
12.55(1)	12.03(1)	16.69(2)		96.4(4)		4168	4.9			197
7.473(2)	15.156(7)	17.710(3)		94.30(7)		2040	3.97			188
11.557(8)	10.520(3)	8.992(3)	99.26(2)	102.26(21)	98.63(3)	3165	2.74			198
14.42	6.49	21.55		115.64		1408	4.4			199

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174	$C_{23}H_{24}U$	$U(CH_2C_6H_4Me\text{-}p)(C_5H_5)_3$	O	Pnma	
74	$C_{23}H_{25}ClO_{14}Pd.CHCl_3$	$Pd[CCl(CO_2Me)C_5(CO_2Me)_4C(O)OMe]$-(acac).$CHCl_3$	M	$P2_1/c$	4
116	$C_{23}H_{23}O_2Pd$	$Pd(acac)(C_7HMe_5Ph)$[c]	Tri	$P\bar{1}$	2
34	$C_{23}H_{40}Cl_2N_4O_3RuS_8$	$Ru_3Cl_2(CO)_3(S_2CNEt_2)_4$	Tri	$P\bar{1}$	2
262	$C_{23}H_{47}BrP_2Pd$	$[Pd(PPr^i_3)]_2Br(C_5H_5)$	M	$P2_1$	2

[a] $C_6H_4Ph_2$ = diphenylpentafulvene. [b] C_8H_8O = Acyl-2-vinylcyclopent-4-ene.

[c] C_7HMe_5Ph = 2,3,4-η^3-(1,2,3,4,5-Me$_5$-6$\bar{7}$-Ph-bicyclo[3.2.0]hept-2-enyl).

C_{24}

273	$C_{24}H_3O_{24}Rh_{13}^{2-}.2C_{36}H_{30}NP_2^+$	$[N(PPh_3)_2]_2[Rh_{13}H_3(CO)_{24}]$	M	$P2_1/c$	4
278	$C_{24}H_{10}O_{10}Os_3$	$Os_3(CO)_{10}(C_2Ph_2)$	Tri	$P\bar{1}$	2
287	$C_{24}H_{15}GaO_9W_3$	$[W(CO)_3(C_5H_5)]_3Ga$	M	$P2/n$	4
45	$C_{24}H_{18}AlMn_3O_{18}$	$Al[Mn(CO)_4(COMe)_2]_3$	M	$P2/n$	4
190	$C_{24}H_{22}Fe_2O_2$	$[Fe(C_5H_4)(C_5H_4Ac)]_2$	M	$P2_1/n$	2
115	$C_{24}H_{23}BMoN_4O_2$	$Mo(CO)_2(C_4H_7)[Ph_2B(pz)_2]$	M	$P2_1/c$	4
127	$C_{24}H_{24}Cl_2F_{12}Ir_2$	$[IrCl(cod)(C_4F_6)]_2$	M	$P2_1/n$	2
192	$C_{24}H_{24}Cl_2F_{12}Ir_2.2C_6D_6$	$\{IrCl[C(CF_3):CH(CF_3)](C_8H_{11})\}_2.2C_6D_6$	M	$P2_1/n$	2
64	$C_{24}H_{24}N_4P_2Pt$	*trans*-$Pt(C_2Me)\{C[:C(CN)_2]CMe$-$[:C_6H_4C(CN)_2]\}(PMe_3)_2$	M	$P2_1/c$	4
131	$C_{24}H_{24}Nb^-.C_{24}H_{20}As^+$	$AsPh_4[Nb(C_8H_8)_3]$	M	$P2_1/c$	4
102	$C_{24}H_{27}ClN_2PRhS_3.CHCl_3$	$RhCl(SCNMe_2)(S_2CNMe_2)(PPh_3).CHCl_3$	M	$P2_1/c$	4
141	$C_{24}H_{28}Cl_2Yb_2$	$[YbCl(C_5H_4Me)_2]_2$	M	C2/c	4
87	$C_{24}H_{30}F_{18}P_2Pt$	$Pt[C_6(CF_3)_5](PEt_3)_2$	M	$P2_1/n$	4
258	$C_{24}H_{36}Fe_2O_6$	$Fe_2(CO)_5[(HC_2Bu^t)_3CO]$	O	Pbca	8
208	$C_{24}H_{32}Cl_2O_2Ti_2$	$[TiCl(thf)(C_8H_8)]_2$	M	$P2_1/c$	4
99	$C_{24}H_{44}O_4Pt$	$Pt\{C_2[C(OH)Et_2]_2\}_2$	M	C2/c	4

19.64(2)	11.81(1)	8.19(1)				1148	5.3			164
8.78(1)	21.15(2)	16.76(2)		93.0(1)		2396	7.1	8.5		200
15.35(2)	8.34(1)	14.79(2)	100.5(1)	141.4(1)	97.3(1)	4417	4.4			201
13.904(5)	13.919(9)	11.073(5)	102.09(4)	109.91(3)	95.51(4)	1407	6.8	6.2		202
13.002(2)	15.551(2)	15.734(2)		116.7(1)		2672	3.5			115
15.90(3)	26.71(5)	25.13(5)		92.9(2)		2987	8.4			203
16.044(3)	8.947(3)	9.734(3)	113.99(5)	87.39(5)	92.03(5)	2165	8.2			204
13.464(4)	17.724(5)	11.296(3)		101.72(2)		2791	7.8	9.7		205
13.948(5)	12.182(6)	19.545(6)		90.51(2)		2099	4.9	7.0		206
8.576(15)	19.015(15)	5.826(15)		103.9		503	10.9			207
8.837(4)	10.785(3)	24.170(3)		97.93(2)		1677	5.2	7.1		208
9.58	12.61	12.54		114.7		2240	4.8			209
10.97	17.96	11.63		127.4		1755	7.1			209
14.934(2)	8.997(1)	20.221(3)		97.44(2)		1117	6.0			210
12.996(16)	22.377(26)	14.371(23)		115.51(11)		2663	7.7	6.9		211
9.275(7)	19.544(12)	17.153(11)		97.01(4)		1785	6.3			212
20.377(6)	9.185(2)	13.235(4)		108.97(2)		2751	3.46	3.69		213
9.937(6)	30.89(1)	11.398(8)		117.15(3)		2154	5.7	6.9		214
14.12(1)	19.99(1)	17.38(1)				2474	4.7			215
10.779(1)	14.304(1)	15.478(3)		100.84(2)		9206	5.88	5.44	100	216
21.751(5)	9.275(6)	17.079(9)		129.54(4)		2695	7.4	7.5		217

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C_{25}

56	$C_{25}H_{22}CoN_5O_2$	Co[CH(CN)$_2$](py)(salpn)	M	$P2_1/c$	4

C_{26}

113	$C_{26}H_{34}F_6Ni_2O_4$	[Ni(O_2CCF_3)($C_{11}H_{17}$)]$_2$	M	$P2_1/c$	4
217	$C_{26}H_{67}B_5P_4Pt_2$	*closo*-2,3-[(Et_3P)$_2$]$_2$-1,2,3,6-$CPt_2CB_5H_7$	M	$P2_1$ or $P2_1/m$	2

C_{27}

243	$C_{27}H_{17}CoF_3NiO_4P$	$(C_5H_5)NiCo(CO)_4[P(C_6H_4F\text{-}p)_3]$	M	I2/a	8
57	$C_{27}H_{27}Cl_3CoN_5O_4$	Co[CCl:C(C_6H_4Cl-p)$_2$](py)(dmg)	O	$Pn2_1a$	8
30	$C_{27}H_{56}ClIrOP_2$	IrCl(CO)[$Bu^t_2P(CH_2)_{13}PBu^t_2$]	O	Pbca	8

C_{28}

294	$C_{28}H_{20}Fe_2O_8Sn_2$	{Fe[Sn(C_5H_5)$_2$](CO)$_4$}$_2$	M	C2/c	4
79	$C_{28}H_{21}AuO$	$Au(OH)C_4Ph_4$	Tri	$P\bar{1}$	2
246	$C_{28}H_{21}FeNiO_3P$	$(C_5H_5)NiFe(CO)_3(HC_2PPh_3)$	M	$P2_1/c$	4
122	$C_{28}H_{23}CrO_3P$	$Cr(CO)_3(PPh_3)$(nbd)	O	$Pn2_1a$	4
196	$C_{28}H_{21}CrO_4P$	$Cr(CO)_2(PPh_3)(PhCO_2Me)$	M	$P2_1/n$	4
244	$C_{28}H_{28}CoNiO_4P$	$(C_5H_4Me)NiCo(CO)_4(PCyPh_2)$	M	$P2_1/c$	4
181	$C_{28}H_{32}W$	$W(CH_2C_6H_3Me_2)_2(C_5H_5)_2$	M	$P2_1/c$	4
168	$C_{28}H_{40}Cl_6O_4Ti_2Zn_2\cdot C_6H_6$	[Ti(dme)(C_5H_5)$_2$]$_2$$Zn_2Cl_6\cdot C_6H_6$	M	$P2_1/n$	4

C_{29}

293	$C_{29}H_{23}IrMnO_5P\cdot\frac{1}{2}C_6H_6$	$(C_5H_5)Ir(CPhO)(CMeO)(PPh_2)Mn(CO)_3\cdot\frac{1}{2}C_6H_6$	M	$P2_1/c$	4
71	$C_{29}H_{24}MnO_3PS$	Mn($C_6H_4CH_2SMe$)(CO)$_3$(PPh_3)	Tri	$P\bar{1}$	2

9.25(3)	18.14(6)	14.00(4)		105.3(1)		1369	6.1		218
16.431(3)	9.954(2)	16.614(3)		92.53(3)		1888	7.0		219
10.018(5)	18.54(1)	12.648(5)		126.54(5)		2172	10		38
16.396(42)	10.663(58)	29.260(84)		91.1(1)		2464	7.1		220
25.50(2)	23.13(2)	9.728(7)				3545	4.8	5.0	221
12.370(2)	34.154(4)	15.272(2)				2040	4.3		222
19.8031(41)	8.9385(11)	16.7219(14)		103.91(1)		2767	4.9		223
11.90(2)	30.10(3)	6.19(4)	90.0(5)	94.8(5)	90.8(5)	1565	11.8		224
10.674	12.294	20.351		110.13		1961	9.4		225
14.867(3)	14.475(5)	10.759(3)				1432	7.2		226
10.182(5)	18.884(6)	13.250(5)			108.64(2)	2192	4.0	3.6	227
14.261(22)	10.034(17)	18.508(32)		98.5(1)		3661	8.4		228
8.619(5)	22.278(12)	11.921(7)		95.0(1)		3586	3.2		229
11.810(4)	10.201(5)	17.284(7)		93.20(2)		2692	8.4	5.6	170
21.089(4)	8.576(2)	16.530(2)		102.50(1)		2906	3.5	4.0	230
11.022(7)	13.485(9)	9.123(6)	94.52(1)	109.90(1)	98.14(1)	3385	5.7	7.4	231

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C_{30}

283	$C_{30}H_{24}Cl_3MoO_4P_2Sn^+.H_2Cl_5OSn^-.C_6H_6$	$[Mo(SnCl_3)(CO)_4(dppe)][SnCl_5(OH_2)].-C_6H_6$	M	$P2_1/c$	4
276	$C_{30}H_{54}N_6Pt_3.C_7H_8$	$Pt_3(CNBu^t)_6.PhMe$	M	$P2_1/n$	4

C_{31}

25	$C_{31}H_{22}As_2Cl_2O_6Re_2.\frac{1}{2}C_6H_{14}$	$Re_2Cl_2(CO)_6(dpam).\frac{1}{2}C_6H_{14}$	Tri	$P\bar{1}$	4

C_{32}

167	$C_{32}H_{27}F_6O_5PRu$	$Ru[C_2H(CO_2Me)_2](PPh_3)[C_5H_4C(CF_3)_2OH]$	Tri	$P\bar{1}$	2
152	$C_{32}H_{23}MoN_4O_2P$	$Mo[C(CN)_2C(CN)_2Me](CO)_2(PPh_3)(C_5H_5)$	Tri	$P\bar{1}$	2
111	$C_{32}H_{26}F_{12}O_3P_2Pt$	$Pt\{[OC(CF_3)_2]_2O\}(PMePh_2)_2$	O	$Pca2_1$	4
302a	$C_{32}H_{30}Fe_2O_6P_2$	$Fe_2(CO)_6\{C[P(OEt)_3]CPh\}(PPh_2)$	M	$P2_1/n$	4
207	$C_{32}H_{32}Cl_4Ti_4$	$[TiCl(C_8H_8)]_4$	Tet	$I\bar{4}2m$	4
82	$C_{32}H_{34}ClP_2Rh$	$RhCl\{P[(CH_2)_2CH{:}CH_2]Ph_2\}_2$	M	$P2_1/c$	4
103	$C_{32}H_{44}As_4O_2Rh^+.ClO_4^-$	$[Rh(O_2)(AsMe_2Ph)_4]ClO_4$	Tri	$P\bar{1}$	2
105	$C_{32}H_{44}IrO_2P_4^+.C_{24}H_{20}B^-$	$[Ir(O_2)(PMe_2Ph)_4]BPh_4$			
197	$C_{32}H_{44}MoP_4$	$Mo(PMe_2Ph)_3(\eta\text{-}PhPMe_2)$	Tri	$P\bar{1}$	2
104	$C_{32}H_{44}O_2P_4Rh^+.C_{24}H_{20}B^-$	$[Rh(O_2)(PMe_2Ph)_4]BPh_4$			

C_{33}

248	$C_{33}H_{24}Fe_2N_2O_{10}$	$Fe_2(CO)_6[C_2Ph_2(C_{13}H_{14}N_2O_4)]$[c]	M	$P2_1/c$	4
184	$C_{33}H_{25}CoN_2$	$Co[C_2Ph_2(CNPh)_2](C_5H_5)$[b]	M	Cc	4

[c] Ligand = C_2Ph_2 - 3,3-$(CO_2Me)_2$-4-Ph-1-pyrazoline adduct.

[b] $CoC_2Ph_2(CNPh)_2$ = 2,5-bis(phenylimino)-3,4-diphenylcobaltacyclopentane.

21.846(5)	12.346(3)	20.486(6)		122.23(2)		2149	9.3	9.1		232
18.213(7)	11.811(7)	21.996(6)		110.21(3)		3680	6.1			233
15.763(1)	19.077(1)	12.233(1)	88.745(10)	110.506(5)	92.900(6)	7061	4.5	5.4		234
10.131(1)	15.107(2)	10.798(1)	102.14(1)	107.04(1)	89.64(1)	4457	4.0	4.1		235
8.6057(9)	12.1581(15)	13.9868(19)	85.60(2)	75.95(1)	88.37(1)	4346	3.98	4.76		236
22.040(20)	9.683(6)	16.235(3)				2611	8.5	10.8		237
10.368(11)	17.173(16)	20.110(15)		95.24(6)		2421	7.7			238
10.763		13.657				1011	6.8	5.7	100	216
10.697(5)	9.832(5)	36.44(2)		96.42(3)		4218	5.1			239
13.24(2)	17.42(2)	10.30(2)	89.9(1)	87.9(1)	128.6(1)	4404	6.0			12,240
						3312	5			12
11.424(2)	16.210(3)	9.413(2)	82.84(1)	111.02(1)	85.67(1)	1203	6.8	10.2		241
						3861	8			12
23.406(3)	8.551(1)	16.157(2)		98.73(1)		2108	5.3	6.3		242
19.756	10.904	12.986		114.43		2741	5.8			243

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C_{34}

254	$C_{34}H_{20}Fe_2O_6$	$Fe_2(CO)_6(C_4Ph_4)$[a]	M	$P2_1$	2
8	$C_{34}H_{34}MoN_2O_4P_2$	$Mo(CO)_4[(CH_2NMeCH_2PPh_2)_2]$	M	$P2_1/a$	4
114	$C_{34}H_{35}ClN_2O_{16}Pd$	$PdCl[HC_8(CO_2Me)_8](py)_2$	M	$P2_1$	2
285	$C_{34}H_{56}Br_4Mg_4Mo_2O_2$	$[(C_5H_5)_2Mo(H)(MgOEt_2)(MgPr^i)Br_2]_2$	M	$P2_1/c$	2
187	$C_{34}H_{68}FeN_6Ti_2$	$Fe[C_5H_4Ti(NEt_2)_3]_2$	M	$P2_1/n$	4

[a] C_4Ph_4Fe = tetraphenylferrole. [b] Decomposed, incomplete refinement.

C_{35}

40	$C_{35}H_{25}CoN_5^+.ClO_4^-.CHCl_3$	$[Co(CNPh)_5]ClO_4.CHCl_3$	M	$P2_1/m$	2
41	$C_{35}H_{25}CoN_5^{2+}.2ClO_4^-.\frac{1}{2}C_2H_4Cl_2$	$[Co(CNPh)_5](ClO_4)_2.\frac{1}{2}C_2H_4Cl_2$	M	$P2_1/c$	4
37	$C_{35}H_{63}MoN_7^{2+}.2F_6P^-$	$[Mo(CNBu^t)_7](PF_6)_2$	M	$P2/m$	8
274	$C_{35}H_{63}Ni_4N_7.C_6H_6$	$Ni_4(CNBu^t)_7.C_6H_6$	M	$P2_1/c$	4

C_{37}

62	$C_{37}H_{32}P_2Pt$	*cis*-$PtPh_2$(dppm)	M	$P2_1/c$	4
110	$C_{37}H_{66}NiO_2P_2.\frac{3}{4}C_7H_8$	$Ni(CO_2)(PCy_3)_2.\frac{3}{4}PhMe$	Tri	$P\bar{1}$	2

C_{38}

88	$C_{38}H_{30}As_2F_4Pt$	$Pt(C_2F_4)(AsPh_3)_2$	M	$P2_1/n$	4
36	$C_{38}H_{30}Cl_2OP_2RuSe$	$RuCl_2(CO)(CSe)(PPh_3)_2$	M	$P2_1/n$	4
15	$C_{38}H_{30}NO_3Os^+.ClO_4^-.CH_2Cl_2$	$[Os(CO)_2(PPh_3)_2(NO)]ClO_4.CH_2Cl_2$	M	$P2_1/n$	4
83	$C_{38}H_{31}IN_4O_5PRh$	RhI[*trans*-CH(CN):CH(CN)][P(OPh)$_3$]-(CNC$_6$H$_4$OMe-*p*)$_2$	M	$P2_1/c$	4
84	$C_{38}H_{34}ClIrP_2$	*trans*-$IrCl(C_2H_4)(PPh_3)_2$	M	$P2_1/c$	4

16.464(2)	7.822(2)	11.374(2)		98.14(1)		2465	6.1	5.1	233	244
16.955(5)	19.579(8)	10.057(4)		96.41(3)			6			245
11.588(5)	15.54(1)	10.362(5)		105.1(1)		3476	5.4			246
8.566(8)	12.955(12)	18.617(15)		93.9(1)		723	14[b]			247
9.408(5)	25.111(12)	18.448(18)		106.83(8)		2256	11.9			248
10.849(8)	17.741(14)	11.396(9)		121.00(3)		647	10.3	8.7		249
10.336(2)	13.939(6)	27.143(7)		95.589(11)		2358	7.1	9.3		250
25.220(10)	11.665(5)	38.013(17)		90.42(3)		3014	6.0	7.3		251
11.236(5)	11.036(4)	36.637(7)		101.39(3)		1656	10.7			252
15.390	10.138	22.380		119.4		4299	6.8	7.6		253
19.03(2)	12.18(1)	9.64(1)	96.3(1)	100.2(1)	99.1(1)	2448	11			254
11.291(10)	21.018(15)	14.380(10)		95.54(5)		5110	5.3	6.2		255
10.470(1)	23.446(2)	14.507(2)		94.75(1)		2214	7.7			256
17.031(2)	13.951(1)	17.270(1)		104.33(1)		4281	5.7	7.5		257
15.252(7)	11.454(6)	21.933(1)		103.62(2)		4357	4.0	4.8		258
12.334(2)	22.957(4)	14.039(2)		125.54(1)		4006		3.9		259

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C_{39}

61	$C_{39}H_{30}Cl_2F_4OP_2Pt$	*cis*-$PtCl(CF_2COCF_2Cl)(PPh_3)_2$	M	$P2_1/a$	4
160	$C_{39}H_{30}Mn_3O_6P_3$	$[Mn(CO)_2(C_5H_5)]_3(PPh)_3$			

C_{40}

89	$C_{40}H_{30}F_8P_2Pt$	$Pt(CF_3CF{:}CFCF_3)(PPh_3)_2$	M	$P2_1/c$	4
92	$C_{40}H_{36}P_2Pt$	$Pt(C_3H_3Me)(PPh_3)_2$	M	$P2_1/c$	4
			O	$P2_12_12_1$	4
17	$C_{40}H_{44}N_4O_4Rh_2$	$[Rh(CO)_2]_2$(oep)	M	$P2_1/c$	2
286	$C_{40}H_{62}Br_4Mg_4Mo_2O_2.C_4H_{10}O$	$[(C_5H_5)_2Mo(H)(MgOEt_2)(MgCy)Br_2]_2.Et_2O$	M	C2/m	2

[a] Disorder, space group problems.

C_{41}

90	$C_{41}H_{38}P_2Pt$	$Pt(C_3H_2Me_2)(PPh_3)_2$[a]	Tri	$P\bar{1}$	2
93	$C_{41}H_{38}P_2Pt$	$Pt(C_3H_2Me_2)(PPh_3)_2$[b]	M	$P2_1/c$	4

[a] $C_3H_2Me_2$ = 1,1-dimethylallene. [b] $C_3H_2Me_2$ = 1,2-dimethylcyclopropene.

C_{42}

112	$C_{42}H_{30}F_{12}O_3P_2Pt$	$Pt\{[OC(CF_3)_2]_2O\}(PPh_3)_2$	Tri	$P\bar{1}$	2
95	$C_{42}H_{38}P_2Pt$	$Pt(C_6H_8)(PPh_3)_2$[a]	Tri	$P\bar{1}$	2
91	$C_{42}H_{38}P_2Pt$	$Pt(C_6H_8)(PPh_3)_2$[b]	O	$P2_12_12_1$	4
50	$C_{42}H_{42}OTi_2$	$[Ti(CH_2Ph)_3]_2O$	Rhomb	$R\bar{3}$	1
11	$C_{42}H_{60}O_{10}P_4Tc^+.ClO_4^-$	*cis*-$\{Tc(CO)_2[PPh(OEt)_2]_4\}ClO_4$	Tri	$P\bar{1}$	2

[a] C_6H_8 = cyclohexyne. [b] C_6H_8 = $\Delta^{1,4}$-bicyclo[2.2.0]hexene.

C_{43}

58	$C_{43}H_{30}F_5IrOP_2$	*trans*-$Ir(C_6F_5)(CO)(PPh_3)_2$	M	$P2_1/c$	4

20.45(2)	18.66(2)	10.43(1)		114.0(4)		3956	9.5		260
						2300	7.4		261
11.635(2)	19.213(4)	18.107(3)		114.39(2)		3841	5.4		262
11.28(3)	20.74(4)	17.23(4)		124.5(2)		905	5.1		263
9.57(3)	19.66(4)	18.10(4)							263
8.778(2)	12.145(2)	19.134(3)		108.94(2)		2343	6.0		264
15.671(8)	11.996(5)	15.085(8)		109.55(8)		1531	8.3[a]		247
18.557(2)	10.216(2)	9.647(2)	98.29(3)	73.44(2)	88.34(2)	6033	4.5	4.3	265
12.49(1)	17.77(1)	16.38(1)		109.42(5)		2390	3.2		263
14.559(9)	12.287(6)	12.819(3)	107.62(3)	84.57(4)	105.74(4)	5296	6.8	8.6	237
9.875(2)	18.141(4)	10.081(2)	89.99(2)	80.68(2)	78.28(2)	5157	4.4	4.0	266
17.726(3)	9.748(2)	19.724(3)				3510	4.0	4.3	267
9.58(2)			83.6(2)			2234	11.2		268
17.708(15)	13.977(12)	10.185(10)	93.22(8)	90.48(9)	96.13(11)	3570	8.6		269
10.994(3)	13.459(2)	26.187(6)		108.49(3)		2145	3.94	3.94	270

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16	$C_{43}H_{36}N_2OOsP_2 \cdot CH_2Cl_2$	$OsH(CO)(N_2Ph)(PPh_3)_2 \cdot CH_2Cl_2$	Tri	$P\bar{1}$	2
20	$C_{43}H_{40}As_4I_2MoO_3$	*meso*-$MoI_2(CO)_3[C_6H_4(AsMePh)_2]_2$	Tri	$P\bar{1}$	2
21	$C_{43}H_{40}As_4I_2MoO_3 \cdot CHCl_3$	*rac*-$MoI_2(CO)_3[C_6H_4(AsMePh)_2]_2$	Tri	$P\bar{1}$	2
96	$C_{43}H_{40}P_2Pt$	$Pt(C_7H_{10})(PPh_3)_2$[a]	M	$P2_1/c$	4
29	$C_{43}H_{42}ClIrOP_2$	*trans*-$IrCl(CO)[P(o\text{-}tol)_3]_2$	M	$P2_1/n$	2
63	$C_{43}H_{43}O_3PPd$	$Pd(acac)(PMe_2Ph)[C_4Ph_4(OEt)]$			

[a] C_7H_{10} = cycloheptyne.

C_{44}

271	$C_{44}H_{30}Co_2O_8P_2Pt_2$	$Co_2Pt_2(CO)_8(PPh_3)_2$	Tri	$P\bar{1}$	1
14	$C_{44}H_{35}FeN_2O_2P_2^+ \cdot BF_4^-$	$[Fe(CO)_2(N_2Ph)(PPh_3)_2]BF_4$	M	$P2_1/c$	4
26	$C_{44}H_{36}ClN_2P_2Ru^+ \cdot ClO_4^- \cdot CH_2Cl_2$	$[RuCl(CO)_2(HN_2Ph)(PPh_3)_2]ClO_4 \cdot CH_2Cl_2$	M	$P2_1/c$	4
269	$C_{44}H_{33}O_5P_3Pt_2Ru$	$RuPt_2(CO)_5(PMePh_2)_3$	Tri	$P\bar{1}$	2
42	$C_{44}H_{52}CoI_2N_4$	$Co(CNC_6H_3Et_2)_4I_2$	M		
101	$C_{44}H_{55}Co_2N_4O_2P_5 \cdot \frac{1}{2}C_6H_6$	$Co_2(O_2)(CN)_4(PMe_2Ph)_5 \cdot \frac{1}{2}C_6H_6$		Fdd2	16

C_{45}

97	$C_{45}H_{38}P_2Pt$	$Pt(MeC_2Ph)(PPh_3)_2$	M	$P2_1$	2
263	$C_{45}H_{42}P_2Pd_2$	$Pd_2(PPh_3)_2(C_4H_7)(C_5H_5)$	Tri	$P\bar{1}$	1

C_{46}

302	$C_{46}H_{10}F_{20}Fe_2O_6P_2$	$Fe_2(CO)_6[P(C_6F_5)_2][(C_6F_5)_2PC_4Ph_2]$	M	$P2_1/c$	4

C_{47}

53	$C_{47}H_{40}NO_3P_2Ru$	$Ru(OAc)[CH{:}N(tol\text{-}p)](CO)(PPh_3)_2$	M	$P2_1/c$	4

13.440(2)	13.481(1)	12.528(2)	114.30(1)	101.82(1)	81.43(1)	5340	4.6	5.7		271
15.828(6)	10.505(1)	9.733(1)	120.604(8)	98.99(2)	97.69(2)	2371	11	13		272
14.985(5)	12.337(3)	9.654(1)	110.78(2)	101.90(2)	104.74(2)	2809	8.0	9.3		272
8.951(2)	33.523(8)	13.095(3)		114.24(2)		4918	3.0	2.4		266
15.689(6)	10.981(3)	10.739(4)		92.93(3)		1230	4.7	5.5		273
							8.3		SD	274
10.954(4)	11.090(4)	9.352(4)	98.40(2)	11.06(3)	82.17(2)	4421	4.6			275
13.447(4)	14.260(4)	22.755(16)		113.29(2)		3159	6.4	8.8		276
11.801(5)	17.752(8)	22.938(11)		110.96(2)		5074	5.3	6.7		277
10.694(3)	22.424(7)	8.938(2)	83.41(2)	90.02(2)	92.42(2)	5002	10.0			278
19.780(8)	10.885(6)	23.668(9)		118.8		1719	10.6			279
33.583(4)	30.471(4)	19.449(2)				2212	5.8	4.6		280
14.840(4)	9.558(3)	13.553(4)		102.74(2)		2843	4.2	5.5		281
9.663(4)	9.725(4)	10.863(3)	84.15(2)	81.01(2)	72.32(3)	2206	8.9			282
16.183(11)	11.524(18)	24.546(25)		98.76(14)		4296	8.7			283
9.947(4)	14.680(4)	28.014(5)		92.08(2)		2519	5.7	5.6		284

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C_{50}

13	$C_{50}H_{28}N_4O_6Re_2$	$[Re(CO)_3]_2(tpp)$	M	$P2_1/c$	2
12	$C_{50}H_{28}N_4O_6Tc_2$	$[Tc(CO)_3]_2(tpp)$	M	$P2_1/c$	2
65	$C_{50}H_{40}FN_2P_2Pt^+.BF_4^-$	$[Pt(C_2Ph)(HN_2C_6H_4F\text{-}p)(PPh_3)_2]BF_4$	O	$P2_12_12_1$	4
106	$C_{50}H_{44}IrO_2P_4^+.ClO_4^-$	$[Ir(O_2)(dppm)_2]ClO_4$			
106	$C_{50}H_{44}IrO_2P_4^+.F_6P^-$	$[Ir(O_2)(dppm)_2]PF_6$			

C_{51}

-	$C_{51}H_{56}Fe_2O_3$	$Fe_2(CO)_3(C_4Bu^t_2Ph_2)_2$	Tet	$I\bar{4}$	4

[a] Corrects entry 323 $C_{27}H_{28}Fe_2O_3$ in 1974 survey.

C_{52}

204	$C_{52}H_{44}F_{24}O_8Rh_4$	$[Rh(hfac)(C_8H_{10})]_4$[a]	M	$P2_1/c$	8
107	$C_{52}H_{48}IrO_2P_4^+.F_6P^-$	$[Ir(O_2)(dppe)_2]PF_6$	M	$P2_1/n$	4
108	$C_{52}H_{48}IrO_2P_4S_2^+.Cl^-$	$[Ir(S_2O_2)(dppe)_2]Cl$			

[a] C_8H_{10} = allylcyclopentene. [b] Redetermination.

C_{54}

235	$C_{54}H_{42}Mn_2O_5P_4.CH_2Cl_2.C_6H_{14}$	$Mn_2(CO)_5(dppm)_2.CH_2Cl_2.C_6H_{14}$	M	Cc	4
68	$C_{54}H_{47}MnO_2P_4$	$Mn(CO)[COC_6H_4PPh(CH_2)_2PPh_2](dppe)$	Tri	$P\bar{1}$	2
28	$C_{54}H_{112}Cl_2O_2P_4Rh_2$	$\{RhCl(CO)[Bu^t_2P(CH_2)_{10}PBu^t_2]\}_2$	M	$P2_1/c$	2

C_{55}

--	$C_{55}H_{60}FeN_{10}O$	$Fe(CO)(Meim)(C_{50}H_{54}N_8)$[a]	M	$P2_1/c$	2

[a] $C_{50}H_{54}N_8$ = substituted octaaza[14]annulene.

11.887(2)	16.363(2)	11.586(2)			117.02(1)		2385	4.5	4.4	285
11.934(1)	16.295(1)	11.596(1)			117.02(1)		3762	3.2	2.7	285
25.638(3)	16.250(2)	13.050(2)					2852	9		286
							3495	5		12
							3371	6		12
15.093(5)		18.641(4)					1484	6.1	α	
19.641	14.353	44.875			98.03		3288	7.7		287
17.18(1)	16.46(1)	16.97(1)			95.02		4007	4.4	β	12,288
									SD	298
19.650(3)	16.908(2)	22.253(4)			130.89(1)		1893	10.5	12.5	290,291
10.60(1)	13.37(1)	19.62(1)	99.1(1)		98.1(1)	112.3(1)	3800	9		292
8.474(1)	32.65(4)	12.307(2)			112.35(2)		2071	7.9		222
12.0	8.40	22.8			100				CD	293

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$C_{56} - C_{94}$

43	$C_{56}H_{40}Co_2I_3N_8^+.I^-$	$[Co_2I_3(CNPh)_8]I$	Tri		2
38	$C_{56}H_{54}MoN_2P_4$	*trans*-$Mo(CNMe)_2(dppe)_2$	Tri	$P\bar{1}$	1
150	$C_{58}H_{45}Ge_2NbO$	$Nb(CO)(PhC_2GePh_3)_2(C_5H_5)$	Tri	$P\bar{1}$	2
215	$C_{72}H_{70}B_{10}Cu_4P_4.CHCl_3$	$[Cu(PPh_3)_2]_2B_{10}H_{10}.CHCl_3$	Tri	$P\bar{1}$	2
66	$C_{73}H_{60}ClP_4Pt_2S_2^+.BF_4.0.2CH_2Cl_2$	$[Cl(Ph_3P)_2Pt(CS_2)Pt(PPh_3)_2]BF_4.0.2CH_2Cl_2$	M	$P2_1/c$	4
310	$C_{78}H_{65}P_5Pt_3.C_6H_6$	$Pt_3Ph(PPh_3)_2(PPh_2)_3.C_6H_6$	O	Pbcn	4
213	$C_{94}H_{45}F_{25}Ag_2P_3Rh$	$RhAg_2(C_2C_6F_5)_5(PPh_3)_3$	M	$P2_1/n$	4

11.058(3)	11.878(3)	12.462(3)	93.19(2)	107.69(2)	104.64(2)	4998	8.9		279
10.747	10.555	12.565	72.37	87.78	61.80	3579	6		294
24.262(5)	8.965(5)	11.106(5)	96.4(2)	85.1(2)	95.9(2)	2312	7.3		295
21.189(3)	13.438(2)	13.207(2)	102.61(1)	92.92(1)	88.4(1)	3405	6.1	7.3	309
15.577(1)	16.539(3)	27.190(2)		95.061(7)		5351	7		296
22.411(8)	17.940(7)	18.359(8)				2808	7.9		297
15.9023(19)	21.4974(27)	25.0411(33)		102.00(1)		7820	6.20	6.21	298

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TABLE 4. HYDRIDES, BOROHYDRIDES, NITROSYLS, DINITROGEN, ARYLDIAZO, ARYLDIIMINE AND TERTIAR

HYDRIDE AND BOROHYDRIDE COMPLEXES

No.	FORMULA	STRUCTURE		CRYSTAL TYPE	SPACE GROUP	Z
319	$C_{36}H_{68}P_2Pt$	*trans*-$PtH_2(PCy_3)_2$	I	Tri	$P\bar{1}$	2
			II	M	P2/c	4
320	$C_{36}H_{71}BCoP_2$	$CoH(BH_4)(PCy_3)_2$		M	$P2_1/a$	4
313	$C_{42}H_{43}CoP_3$	$CoH\{N(CH_2CH_2PPh_2)_3\}$		M	C2/c	8
314	$C_{42}H_{43}CoP_4 \cdot \frac{1}{2}C_3H_6O$	$CoH[P(CH_2CH_2PPh_2)_3] \cdot \frac{1}{2}Me_2CO$		Trig	$R\bar{3}$	6
315	$C_{42}H_{43}CoP_4^+ \cdot BF_4^-$	$\{CoH[P(CH_2CH_2PPh_2)_3]\}BF_4$		M	Cc	4
316	$C_{54}H_{43}CoP_4$	$CoH[P(C_6H_4PPh_2)_3]$		O	Pbca	8
317	$C_{54}H_{48}IrP_3 \cdot \frac{1}{2}C_6H_6$	$IrH_3(PPh_3)_3 \cdot \frac{1}{2}C_6H_6$		Tri	$P\bar{1}$	2
312	$C_{82}H_{81}As_6Co_2^+ \cdot C_{24}H_{20}B^-$	$\{Co_2H_3[MeC(CH_2AsPh_2)_3]_2\}BPh_4$		M	$P2_1/c$	4
311	$C_{92}H_{81}Fe_2P_5^+ \cdot F_6P^- \cdot 1\frac{1}{2}CH_2Cl_2$	$\{Fe_2H_3[MeC(CH_2PPh_2)_3]_2\}PF_6 \cdot 1\frac{1}{2}CH_2Cl_2$		M	P2/c	4
318	$C_{84}H_{72}ClIr_2P_4S_2^- \cdot ClO_4^- \cdot 3C_3H_6O$	$[(Ph_3P)_2(H)Ir(SPh)_2ClIr(H)(PPh_3)_2]$-$ClO_4 \cdot 3Me_2CO$		M	$P2_1$	2

NITROSYLS

No.	FORMULA	STRUCTURE	CRYSTAL TYPE	SPACE GROUP	Z
321	$C_2H_3Br_4N_2ORe^- \cdot C_8H_{20}N^+$	$NEt_4[Re(NO)Br_4(MeCN)]$	O	$Pn2_1a$	4
322	$C_2H_6Br_4NO_2Re^- \cdot C_8H_{20}N^+$	$NEt_4[Re(NO)Br_4(EtOH)]$	O	Pbca	8
336	$C_{15}H_{27}NNiO_{10}P_3^+ \cdot BF_4^-$	$\{Ni(NO)[P(OCH_2)_3CMe]_3\}BF_4$	M	C2/c	8
323	$C_{18}H_{15}ClFeN_2O_2P$	$Fe(NO)_2Cl(PPh_3)$	M	C2/c	8
329	$C_{20}H_{32}As_4CoNO^{2+} \cdot 2ClO_4^-$	$[Co(NO)(diars)_2](ClO_4)_2$	O	$P2_12_12_1$	4
330	$C_{21}H_{32}As_4CoN_2OS^+ \cdot CNS^-$	$[Co(NO)(NCS)(diars)_2]NCS$	M	C2/m	4
331	$C_{36}H_{30}Cl_2NOP_2Rh$	$Rh(NO)Cl_2(PPh_3)_2$	M	I2/c	4
335	$C_{36}H_{30}Cl_2Ir_2N_2O_3P_2$	$[Ir(NO)Cl(PPh_3)]_2O$	Tri	$P\bar{1}$	2

PHOSPHINE COMPLEXES.

a	b	c	α	β	γ	DATA	R	R_w	NOTES	REFERENCE
10.414(3)	9.906(3)	10.490(3)	100.60(2)	112.91(2)	89.73(2)	2225	4.4			299
23.576(3)	15.767(3)	10.218(3)		106.93(2)		1875	6.8			299
23.391(10)	12.614(4)	13.195(6)		106.93(3)		3707	6.2			300
24.278(5)	11.192(3)	28.027(5)		108.0(1)		2297	5.4	5.4		301
13.573(3)		36.404				1044	3.2	3.4		302,303
16.581	12.820	18.631		90.33		1348	5.8	5.6		304
17.040	22.312	22.581				1203	6.8	4.8		305
20.5703(15)	9.5385(9)	12.4486(6)	105.43(1)	82.70(1)	100.28(1)	3969	4.8	5.3		306
13.515(3)	18.286(4)	38.036(8)		95.40(2)		3327	8.2			307
22.669(2)	17.839(2)	20.106(2)		95.57(1)		4038	9.8			307
15.013(3)	12.918(1)	22.044(4)		91.94(1)		3726	4.7			308

a	b	c	α	β	γ	DATA	R	R_w	NOTES	REFERENCE
13.12(1)	8.71(1)	17.25(2)				930	3.0	3.5		310
16.41(2)	13.81(1)	16.91(2)				837	3.8	4.3		310
27.29(3)	12.63(1)	24.84(3)		135.55(2)		2216	8.5	9.0		319a
16.265(7)	14.495(7)	15.609(6)		96.86(2)		2266	5.52	5.64		311
12.565(9)	12.639(9)	19.491(13)				1788	5.4	6.1		312
20.48(2)	10.22(2)	14.75(3)		72.71(7)		1157	3.8	5.3		312
22.019(4)	9.604(2)	15.854(2)		104.57(1)		2598	5.14	5.69		313
16.828(8)	11.515(6)	10.667(5)	66.05(1)	107.37(1)	100.41(1)	5639	6.2	8.3		314

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325	$C_{36}H_{30}Cl_3NOP_2Ru$	$Ru(NO)Cl_3(PPh_3)_2$	M	I2/a	4
327	$C_{36}H_{30}N_2O_2OsP_2 \cdot \frac{1}{2}C_6H_6$	$Os(NO)_2(PPh_3)_2 \cdot \frac{1}{2}C_6H_6$	M	$P2_1/n$	4
332	$C_{36}H_{30}N_2O_2P_2Rh^+ \cdot ClO_4^-$	$[Rh(NO)_2(PPh_3)_2]ClO_4$	M	C2/c	4
326	$C_{36}H_{30}N_2O_2P_2Ru$	$Ru(NO)_2(PPh_3)_2$	M	$P2_1/n$	4
328	$C_{36}H_{31}N_2O_3OsP_2^+ \cdot F_6P^-$	$[Os(NO)_2(OH)(PPh_3)_2]PF_6$	M	$P2_1/c$	4
324	$C_{44}H_{28}FeN_5O$	Fe(NO)(tpp)	Tet	I4/m	2
333	$Br_5IrNO^- \cdot K^+ \cdot H_2O$	$K[Ir(NO)Br_5] \cdot H_2O$	O	Pnma	4
334	$Cl_5IrNO^- \cdot K^+ \cdot H_2O$	$K[Ir(NO)Cl_5] \cdot H_2O$	O	Pnma	4

DINITROGEN COMPLEXES

No.	FORMULA	STRUCTURE	CRYSTAL CLASS	SPACE GROUP	Z
337	$C_{52}H_{48}MoN_4P_4$	*trans*-$Mo(N_2)_2(dppe)_2$	Tri	$P\bar{1}$	1
338	$C_{64}H_{88}Cl_6MoN_4P_8Re_2$	*trans*-$MoCl_4[(N_2)ReCl(PMe_2Ph)_4]_2$	M	$P2_1/c$	2
–	$H_{15}N_7Os^{2+} \cdot 2Br^-$	$[Os(N_2)(NH_3)_5]Br_2$	Tet	$P4_2/mnc$	
–	$H_{15}N_7Os^{2+} \cdot 2Cl^-$	$[Os(N_2)(NH_3)_5]Cl_2$	Tet	$P4_2/nnm$	

ARYLDIAZO, ARYLDIIMINE AND RELATED COMPLEXES

No.	FORMULA	STRUCTURE	CRYSTAL CLASS	SPACE GROUP	Z
345	$C_{18}H_{34}ClFN_2P_2Pt$	*trans*-$PtCl(N_2C_6H_4F\text{-}p)(PEt_3)_2$	M	C2/c	4
346	$C_{18}H_{37}ClFN_2P_2Pt^+ \cdot BF_4^-$	$\{PtCl[H_2N_2H(C_6H_4F\text{-}p)](PEt_3)_2\}BF_4$	O	Pnma	4
339	$C_{26}H_{40}MoN_5S_6^+ \cdot C_{24}H_{20}B^-$	$\{Mo(N_2EtPh)[S_2CN(CH_2)_5]_3\}BPh_4$	M	$P2_1$	2
344	$C_{42}H_{42}ClN_2P_3Rh^+ \cdot F_6P^- \cdot CH_2Cl_2$	$[Rh(N_2Ph)Cl\{PhP[(CH_2)_3PPh_2]_2\}]$-$PF_6 \cdot CH_2Cl_2$	Tri	$P\bar{1}$	2
343	$C_{43}H_{37}Cl_3N_2P_2Ru \cdot CH_2Cl_2$	$Ru(N_2tol\text{-}p)Cl_3(PPh_3)_2 \cdot CH_2Cl_2$	M	$P2_1/c$	4
340	$C_{53}H_{51}IMoN_2P_4$	$Mo(N_2Me)I(dppe)_2$	Tri	$P\bar{1}$	1
342	$C_{53}H_{52}BrN_2P_4W^+ \cdot Br^-$	$[W(N_2HMe)Br(dppe)_2]Br$	M	$P2_1/c$	4
341	$C_{58}H_{59}IMoN_2P_4 \cdot \frac{1}{2}C_6H_6$	$Mo(N_2Cy)I(dppe)_2 \cdot \frac{1}{2}C_6H_6$	M	$P2_1/c$	4

15.877(3)	9.540(2)	22.326(4)		102.79(1)		2671	5.8	6.8	17
17.034(5)	18.735(5)	10.799(3)		96.81(1)		3455	3.1	3.9	14
17.134(4)	12.327(3)	17.166(4)		108.17		4649	6.1	9.0	315
9.96(1)	37.01(2)	9.31(1)		111.44(3)		927		4.85	316
18.433(2)	10.654(1)	18.952(4)		91.80(2)		3646	5.7	6.2	317
13.468(9)		9.755(8)				951	4.4	6.1	318
23.272(9)	7.261(5)	6.302(3)				1291	9.6	10	319
22.416(5)	6.935(1)	6.069(1)				1704	4.9	8.0	319

a	b	c	α	β	γ	DATA	R	R_w	NOTES	REFERENCE
10.662(3)	12.654(3)	10.527(3)	92.48(1)	118.89(2)	71.20(1)	3253				320
16.710	14.164	19.084		114.3		1306	7.4			321
17.45		16.73							CD	322
20.74		18.63							CD	322

a	b	c	α	β	γ	DATA	R	R_w	NOTES	REFERENCE
9.320(6)	20.244(9)	12.826(6)		97.59(1)		2011	8.5	10.1		323
16.062(7)	13.625(6)	12.085(5)				3015	4.5	5.4		324
15.467(2)	13.131(2)	12.895(2)		103.55(5)		1946	6.3			325
12.675(7)	13.254(7)	15.092(10)	94.78(5)	99.47(5)	112.40(8)	4031	5.7	7.8		326
12.406(8)	18.421(13)	18.565(13)		93.05(1)		5100	5.8	6.7		17
10.371(1)	10.628(1)	12.699(2)	103.81(1)	95.34(1)	118.12(1)	4211	9.8			327
13.463(2)	21.090(3)	18.933(3)		93.93(1)		4001	6.2			325
12.643(6)	21.351(7)	20.422(5)		98.91(3)		5400	8.2			327

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BINARY TERTIARY PHOSPHINE COMPLEXES

No.	FORMULA	STRUCTURE	CRYSTAL CLASS	SPACE GROUP	Z
348	$C_{16}H_{12}F_8NiP_4S_4$	$Ni[PF_2(C_4H_3S)]_4$	Tet	$P\bar{4}2_1c$	2
349	$C_{36}H_{66}P_2Pt$	$Pt(PCy_3)_2$	M	C2/c	4
347	$C_{52}H_{52}IrP_4^+.BF_4^-.C_6H_{12}$	$[Ir(PMePh_2)_4]BF_4.C_6H_{12}$	M	C2/c	12
350	$C_{54}H_{45}CuP_3^+.BF_4^-$	$[Cu(PPh_3)_3]BF_4$	Trig	P3	3
309	$C_{60}H_{50}P_4Pt.C_6H_6$	$Pt_2(PPh_3)_2(PPh_2)_2.C_6H_6$	M	$P2_1/n$	4

a	b	c	α	β	γ	DATA	R	R_w	NOTES	REFERENCE
10.120(2)		12.427(12)				573	5.0	5.3		328
16.801	9.659	22.310		92.396		3522	5.6			329
36.805(8)	22.93(2)	21.676(4)		121.41(1)		7905	6.0			330
18.749(3)		11.588(2)				2615	5.0			331
21.533(11)	16.933(16)	15.870(10)		97.34(6)		3694	6.7			297

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