STRUCTURES OF ORGANO-TRANSITION METAL COMPLEXES

ANNUAL SURVEY COVERING THE YEAR 1974.

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INTRODUCTION

The advent of modern computer-controlled X-ray diffractometers has resulted in a dramatic increase in the number of reported structures of organo-transition metal complexes determined by this means. For example, the yearly totals of structures reported in these surveys for the years 1968 and 1973 were about 140 and 290; the following summary gives details of over 400.

During the year under review, it became obvious that our previous discursive method of reviewing those structures of interest to organometallic chemists would have to be changed for two reasons: firstly, the sheer magnitude of the time and effort involved, and secondly, the fact that many of the structures were being discussed in the sections devoted to the particular elements involved. Consequently, we have decided to present this survey in two sections, comprising a collection of briefly annotated diagrams, based on the reported illustrations of structures, and ordered according to structural type, together with a molecular formula index of structures published during the year. This summary presents details of these complexes, including some reported during 1972 and 1973 which had escaped our previous notice.

It is of some interest that the year produced only two duplicate

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Organometallic Structures parts I and II covering the year 1973 see J. Organometal. Chem., 75(1974)335-394 and 89(1975)215-272.

determinations, while several compounds of long standing were either reexamined, or structurally characterised for the first time. Examples include $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ (further refinement), $[M(CO)_3C_5H_5)]_2$ (M = Cr, Mo, W), and $Ni(CO)_2(PPh_3)_2$.

In addition to conventional organometallics, small Tables at the end refer to other complexes of interest to many organometallic chemists. These include hydride and boron hydride derivatives, nitrosyls, dinitrogen, aryldiazo, aryldiimine and related complexes, and binary metal-tertiary phosphine complexes.

REVIEWS AND OTHER PAPERS OF STRUCTURAL INTEREST

The first volume of a new Chemical Society Specialist Report, Molecular Structure by Diffraction Methods has appeared,[1] and includes sections on structure determinations of organometallic and inorganic compounds by electron diffraction, and surveys of X-ray diffraction results on a Group basis, together with a chapter on mixed cluster complexes. This survey covers the period January 1971 to March 1972.

The use of bond length data in considering the *trans* influence of ligands in a series of platinum complexes containing a linear C-Pt-Cl array has been examined.[2] The Pt-C bond lengths depend on the nature of the C-donor ligand, and increase in the order CO < RNC < carbene < σ-carbyl; when account is taken of the hybridisation of the carbon atom involved, an increase in the effective radius of platinum is found (and paralleled by an increase in Pt-Cl distances), a variation resulting from changes in the extent of Pt-C multiple bonding. In another series, where the ligand *trans* to Cl has negligible π-acidity, a similar range of Pt-Cl bond lengths is found. These observations are rationalised in a qualitative explanation of the *trans* influence which allows for the effects of both σ and π components.

The conformations of cyclobutane rings in a variety of complexes

containing this moiety have been compared with a large number of purely organic compounds.[3] In organometallic compounds the dihedral ranges from 0.2(3)° to 16.4(12)°, as a result of the differing ring systems fused to the cyclobutane ring. In contrast, the preferred angle for simple substituted cyclobutanes appears to be ca. 26 ± 3°.

Non-parametised MO calculations on the dimeric series $[Cr_2(CO)_8(PR_2)_2]^{n-2}$ and $[Mn_2(CO)_8(PR_2)_2]^n$ (n = 0, +1, +2) have indicated that the electrons are added to an orbital with largely in-plane antibonding σ^*-type dimetal orbital character (rather than out-of-plane π^*-type or bridging ligand).[4] Available X-ray and spectral data support this interpretation.

Of some interest were two papers in the W.C. Hamilton Memorial Symposium, held at the Brookhaven National Laboratory on 15 June 1973. Coppens[5] has discussed the implications of combined X-ray and neutron diffraction studies. A survey of ten combined studies, including $Cr(CO)_3(C_6H_6)$, has shown that experimental measurements (X-N difference densities) yield results comparable with the more sophisticated electron density calculations, and that third row elements can be studied successfully. Abrahams[6] has considered the reliability of crystallographic structural information, analysing objective methods for assessing quality of intensity measurements, errors in theoretical models used in crystal structure refinements and associated computing methods, and assessing the significance of the final parameters.

On cooling to 80K, the unit cell of ferrocene changes to triclinic from the monoclinic cell found at room temperature, as a result of shortening of the *b* and *c* axes.[7]

Much of the current discussion on structures of nitrosyl complexes has been summarised in a recent review.[8] Russian workers have considered the occurrence of linear or bent M-N-O groups in 29 octahedral and square pyramidal complexes,[9] and the mutual influences of ligands in a series of

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complexes MXL_5 with metal-ligand multiple bonds including 27 nitrosyl complexes and dinitrogen derivatives.[10]

There has been further discussion[11], on the basis of the early structure determination[12], concerning Cu-H-B interactions in $Cu_2B_{10}H_{10}$. The IR spectra of this compound, and also of $[(Ph_3P)Cu]_2B_{10}H_{10}$, contain bands consistent with Cu-H-B stretching modes. On the basis of observed Cu and B positions (Cu-B distances range from 2.06 to 2.33 Å), there are both Cu-B and Cu-H-B interactions present, the possible Cu-H distances indicating less than full bridge bonds.

ELECTRON DIFFRACTION STUDIES

The electron diffraction structures of $Cr(C_5H_5)_2$ and $Mg(C_5H_5)_2$ have been compared; the eclipsed configuration seems to be preferred, but the barriers to internal rotation are less than the thermal energy available (0.8 $kcal.mol^{-1}$). In $Cr(C_5H_5)_2$, the C-H bonds are bent toward the metal atom by 2.9° out of the C_5 plane.[13] Re-evaluation of the gas phase electron diffraction data, together with spectroscopic parameters for $Fe(CO)_5$, given[14] the following values for the bond lengths: FeC(av), 1.8205 + 0.0010; CO(av), 1.1531 ± 0.0011 Å, with the difference between equatorial and axial bonds, 0.0204 ± 0.0055 Å.

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 $Fe(SnPh_3)(CO)(C_2Ph_2)(C_5H_5)$ and $Mo(CO)(NO)(C_3H_5)(S_2CNMe_2)(C_5H_5)$ 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.

The following headings have been used:

η^1-*Ligands*

(a) Simple carbonyls, carbonyl hydrides, halides and pseudohalides

(b) Carbonyls containing Group V donor ligands

(c) Carbonyl hydrides and halides containing Group V donor ligands

(d) Carbonyls containing Group VI donor ligands

(e) Thiocarbonyls

(f) Isocyanide complexes

(g) Carbene and carbyne complexes

(h) Alkyls, aryls and acyls

(i) Complexes containing chelating η^1-ligands

η^2-*Ligands*

(a) Ligands bonded by two η^1 groups (metallocycles)

(b) Olefin complexes

(c) Acetylene complexes

(d) Complexes containing other three-membered rings

η^3-*Ligands*

(a) η^3-Allyl complexes

(b) Ligands bonded via $\eta^1 + \eta^2$ groups

η^4-*Ligands*

(a) Ligands bonded via $2\eta^1 + \eta^2$ groups

(b) Ligands bonded via η^1 and/or η^2 groups

(c) Acyclic η^4 ligands

(d) 1,2,3,4-η^4 dienes

(e) 1,2,3,n-η^4 ligands

(f) 1,2,3,4-η^4 + 1,2,3,n-η^4 ligands

(g) Cyclobutadienes

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η^5-Ligands

(a) Cyclopentadienyls

(b) Cyclopentadienyl metal halides

(c) Cyclopentadienyls containing other anionic ligands

(d) Cyclopentadienylmetal thiolate complexes as ligands

(e) Cyclopentadienyl complexes containing CO, PR_3 or NO ligands

(f) Cyclopentadienyl complexes containing other η-hydrocarbon ligands

(g) Substituted ferrocenes

(h) Acyclic η^5-ligands

η^6-Ligands

(a) Cyclic η^6-ligands (arenes)

(b) Acyclic η^6-ligands

η^7-Ligands

η^8-Ligands

η-Heteroatom Ligands

Copper and silver Complexes

Polyhedral Metalloborane Complexes

Polyhedral Metallocarborane Complexes

Complexes Containing Metal-Metal Bonds

(a) Homobinuclear transition metal complexes

(b) Heterobinuclear transition metal complexes

(c) Polynuclear clusters containing CO or PR_3 ligands

(d) Polynuclear clusters containing Main Group elements

(e) Polynuclear clusters containing η-hydrocarbon ligands

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

Hydride Complexes

Nitrosyls

Dinitrogen, Aryldiazo, Aryldiimine and Related Complexes

Binary Transition Metal-Tertiary Phosphine Complexes

TABULATED STRUCTURAL DATA

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 3-7

These Tables list most complexes whose structures have been reported during 1974, together with a small number reported during the previous two years. 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. $[(Ph_3P)_2N][Fe(CN)(CO)_4]$ appears as $C_5FeNO_4^-.C_{36}H_{30}NP_2^+$, 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. In addition, it has not proved possible to indicate bridging ligands (μ-L) in all cases.

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. Note: n.d. = neutron diffraction study.

13. *Reference number* relating to the reference list at the end of Section 2.

Abbreviations

In column 3, several commonly used abbreviations appear, while in other cases, simple formulae have been used. These are summarised below. Where the ligand is complex, the ligand formula is explained in a footnote.

acac	acetylacetonate
apo	2C,N-acetophenonoxime
bipy	2,2'-bipyridyl
Cy	cyclohexyl
dba	dibenzylideneacetone
dbm	dibenzoylmethanate
diars	1,2-bis(dimethylarsino)benzene

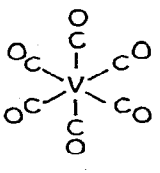
diglyme	$(MeOCH_2CH_2)_2O$
diox	dioxan
dme	1,2-dimethoxyethane
dmg	dimethylglyoximate
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dq	duroquinone
Fc	ferrocenyl
ind	indenyl
Meim	2,3-dimethylimidazolyl
Memnt	S-methylmaleonitriledithiolate
men	menthyl
Mepaphy	(E)-5-methylpyridine-2-carboxyldehyde-2′-pyridylhydrazone
nbd	norbornadiene
$oepH_4$	octaethylporphyrin dication
pda	pyridazinedicarboxylate
phen	1,10-phenanthroline
py	pyridine
pz	pyrazolyl
sal:NPh	$[PhN{:}CHC_6H_4O\text{-}o]^-$
salen	ethylene-1,2-bis(salicylideniminato)
salophen	*o*-phenylenebis(salicylideniminato)
tcne	tetracyanoethylene
thf	tetrahydrofuran
tol	tolyl

η^1-LIGANDS

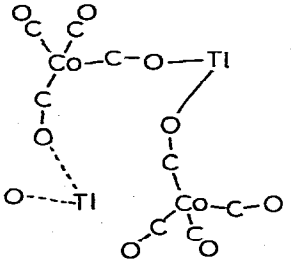
(a) *Simple carbonyls, carbonyl hydrides, halides and pseudohalides*

[Structures *1* - *5*]

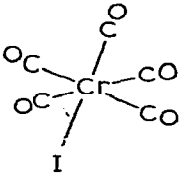
(*1*) V-C 1.931(9)Å, linear P-N-P in cation. (*2*) NaCl-type ionic structure, no Tl-Co interaction [Tl-Co, 3.55(1)Å], but CO directed at Tl. (*3*) Cr-CO *cis* and *trans* to I, 1.893, 1.859Å, respectively. (*4*) Fe-CO(ax) - Fe-CO(eq), 0.045(12)Å; Fe-CN, 1.928(8)Å. (*5*) From $oepH_2$ + $[RhCl(CO)_2]_2$, essentially planar $[oepH_4]^{2+}$ cation.



(1) $[(Ph_3P)_2N][V(CO)_6]$ [31]



(2) $Tl[Co(CO)_4]$ [21]



(3) $(N_4P_4Me_9)[CrI(CO)_5]$ [23]

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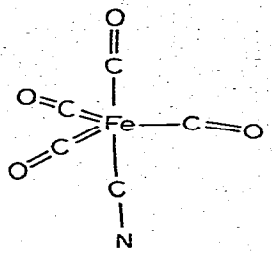
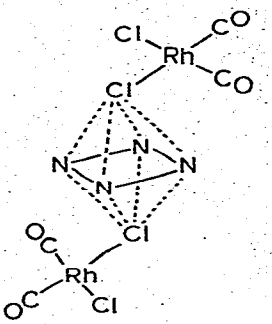




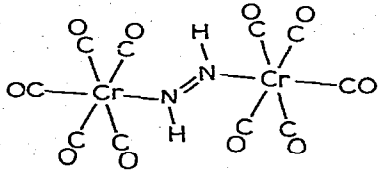
(4) $(Ph_3P)_2N[Fe(CO)_4(CN)]$ [24] (5) $[oepH_4]^{2+}2[RhCl_2(CO)_2]^-$ [15]

(b) *Carbonyls containing Group V donor ligands*

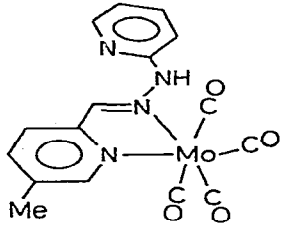
[Structures *6* - *28*]

(*6*) First structurally characterised *trans*-diimine complex.

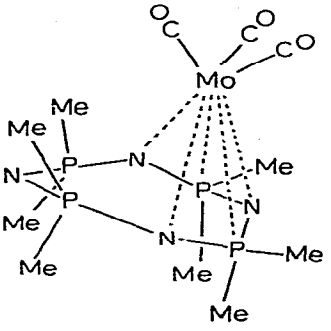
(*7*) Intramolecular C-H...N bond; coordination mode of chelating ligand determined. (*9*) Bridging phosphinimine ligands in zwitterionic $(Ph_3\overset{+}{P} - \overset{-}{N}H)$ form. (*11*) From $Cr(CO)_6$ + $Me_2As(O)OH$, Cr_2As_4 metallocycle in chair form. (*12*) From $W(CO)_5$ + P_5Me_5, 'skew-boat' conformation for P_6 skeleton. (*15*) First bridging PhN_2 group. (*16*) Unsymmetrical CO bridge compensated by less unsymmetrical μ-amido ligands. (*19*) Confirms internal asymmetry in $P(OMe)_3$ groups found by IR. (*20*) Geometry intermediate between TBP and SP, shows rapid site exchange of 3 CO groups. (*22*) CO, NO disordered. (*23*) Ordered model suggested by bond parameters: Co-$C(N)^2$, 1.70; Co-$C(N)^{1,3}$, 1.76Å. (*25*) Ligand H-bonded to coordinated water. (*25a*) From $RhCl(CO)(PPh_3)_2$ + $K^+[TCNE^-]$, cyanocarbon bonded via N, slight delocalisation (cf. delocalised $K_2[cis\text{-}C_4(CN)_6]$); one Rh severely distorted square planar. (*26*) Unusual $IrNC_4N$ metallocycle from condensation of CF_3CN and CH_2CMeCH_2 ligands on Ir. (*28*) Some Ni-Ni interaction; bridging CO.



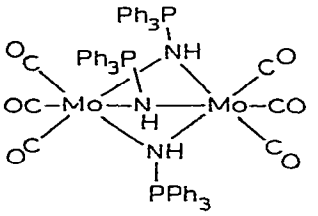
(6) $[Cr(CO)_5]_2N_2H_2$[55]



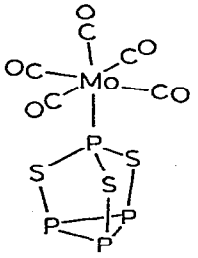
(7) $Mo(CO)_4$(Mepaphy) [158]



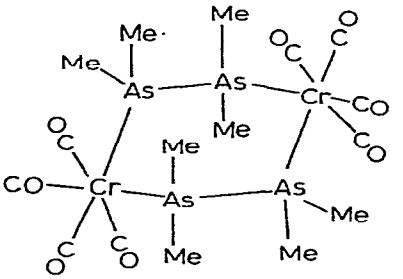
(8) $Mo(CO)_3[NPMe_2]_4$ [35]



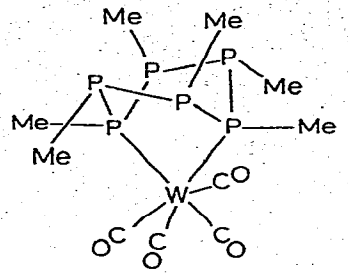
(9) $Mo_2(CO)_6(NHPPh_3)_3$ [365]



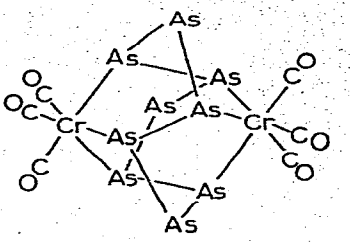
(10) $Mo(CO)_5(P_4S_3)$ [25]



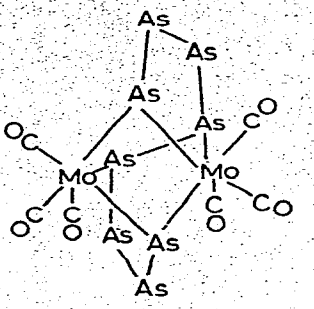
(11) $[Cr(CO)_4]_2(AsMe_2)_4$ [170]



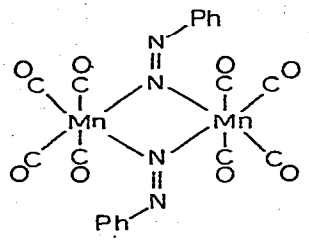
(12) $W(CO)_4[P_6Me_6]$ [68]



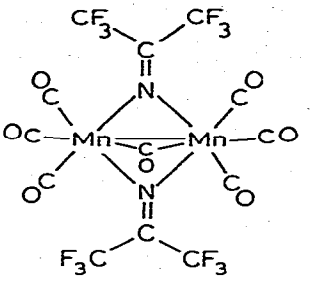
(13) $Cr_2(CO)_6(AsMe)_9$ [151]
Me groups omitted



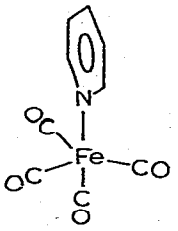
(14) $Mo_2(CO)_6(AsPr^n)_8$ [151]
alkyl groups omitted



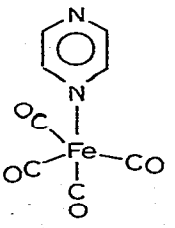
(15) $[Mn(CO)_4(N{=}NPh)]_2$ [207]



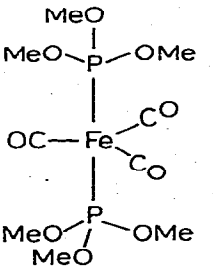
(16) $Mn_2(CO)_7[N{=}C(CF_3)_2]_2$ [120]



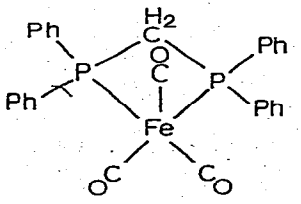
(17) $Fe(CO)_4(py)$ [41]



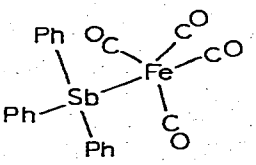
(18) $Fe(CO)_4$(pyrazine) [41]



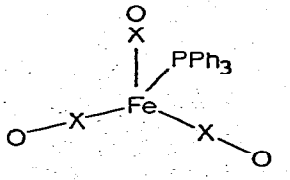
(19) *trans*-$Fe(CO)_3[P(OMe)_3]_2$ [51]



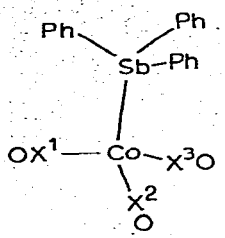
(20) $Fe(CO)_3$(dppm) [285]



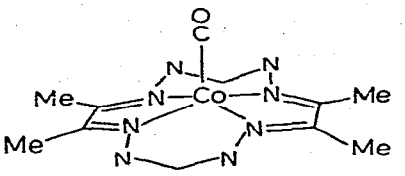
(21) $Fe(CO)_4(SbPh_3)$ [235]



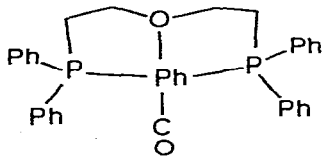
(22) $Fe(CO)(PPh_3)(NO)_2$ [199]
CO,NO indistinguishable



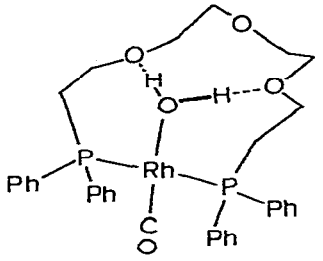
(23) $Co(CO)_2(NO)SbPh_3$ [210]
CO, NO not distinguishable



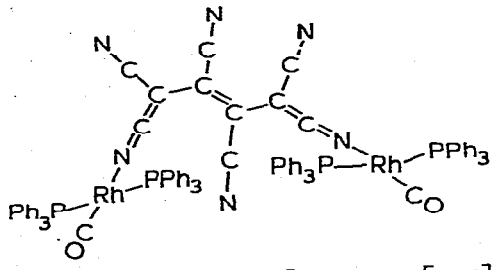
(23a) $Co(CO)(C_{10}H_{17}N_8)$ [80]



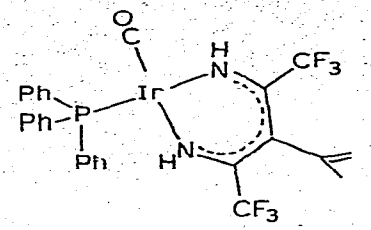
(24) $[Rh(CO)\{O[(CH_2)_2PPh_2]_2\}]PF_6$ [291]



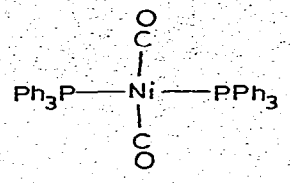
(25) $[Rh(CO)(H_2O)\{O[(CH_2)_2O(CH_2)_2PPh_2]_2\}]PF_6$ [291]



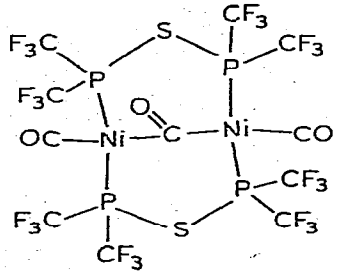
(25a) $[Rh(CO)(PPh_3)_2]_2C_4(CN)_6$ [370]



(26) $Ir(CO)(PPh_3)\{[NHC(CF_3)]_2C(C_3H_5)\}$ [275]



(27) $Ni(CO)_2(PPh_3)_2$ [318]



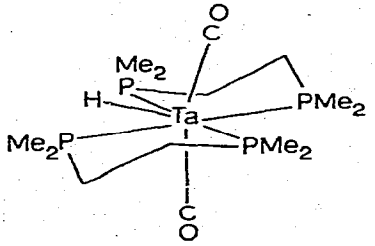
(28) $Ni_2(CO)_3\{S[P(CF_3)_2]_2\}_2$ [81]

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

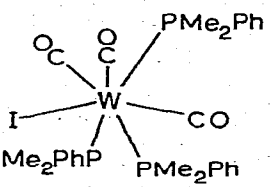
[Structures *29* - *38*]

(*29*) Distorted octahedron capped by H; dmpe ligands disordered.

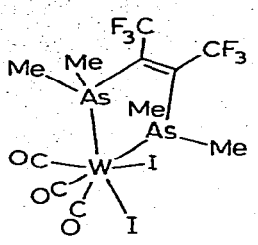
(*30*) 1/2/2/2 geometry, intermediate between capped trigonal prism and capped octahedron, I in unique position. (*32*) I caps trigonal prism. (*33*) CO, NO disordered, long Ru-I, 2.828(2)Å. (*35*) ν(CO), 1885 cm^{-1}, long Ir-Cl, 2.619(6)Å, leads to ready formation of $[Ir(CO)(PMe_2Ph)_3]^+$.



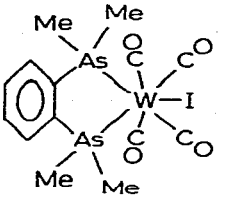
(29) $TaH(CO)_2(dmpe)_2$ [134]



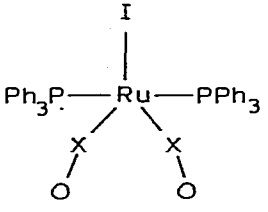
(30) $[WI(CO)_3(PMe_2Ph)_3]BPh_4$ [281]



(31) $\{WI_2(CO)_3[Me_2AsC(CF_3)=C(CF_3)AsMe_2]\}^+$ [73]

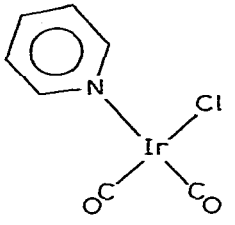


(32) $[WI(CO)_4(das)]I_3$ [129]

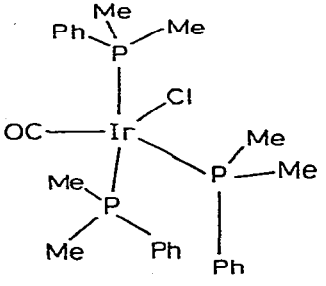


(X = C, N)

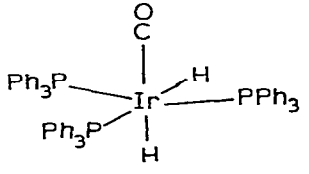
(33) $RuI(CO)(NO)(PPh_3)_2$ [313]



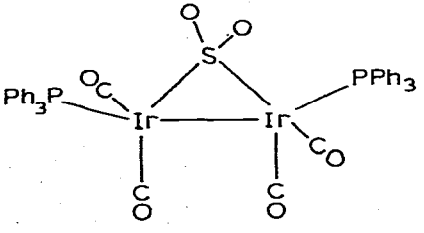
(34) $IrCl(CO)_2(py)$ [32]



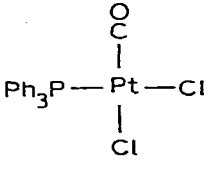
(35) $IrCl(CO)(PMe_2Ph)_3$ [262]



(36) $[IrH_2(CO)(PPh_3)_3]SiF_5$ [362]



(37) $[IrH(CO)_2(PPh_3)]_2SO_2$ [328]



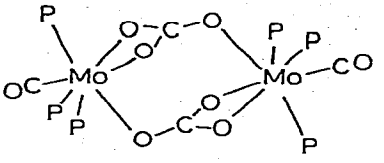
(38) $PtCl_2(CO)(PPh_3)$ [198]

(d) *Carbonyls containing Group VI donor ligands*

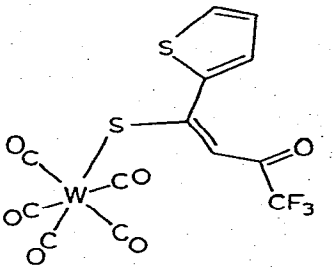
[Structures *39* - *48*]

(*39*) From $Mo(N_2)(PMe_2Ph)_4 + CO_2$, *via* spontaneous reaction of $Mo(CO_2)_2(PMe_2Ph)_4$. (*40*) Monodentate β-thiodiketonate. (*41*) Ligand S-bonded, intermolecular N-H...O bond. (*43*) Distorted pentagonal bipyramid, axial CO; for dtc with S in both positions, Re-S(eq), Re-S(ax) 2.433, 2.518Å, respectively. (*45*) From $Re(CF_3)(CO)_5 + CS_2$. (*46*) Orange isomer. (*47*) Rh-O, 2.049(7); P-O, 1.52(1)Å; latter retains considerable bond character. (*48*) Chelating pyridazinedicarboxylate; solvated H_2O forms 3 O-H...O hydrogen bonds.

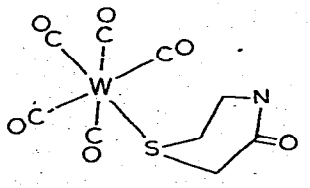
See also: *210*, *211*, *212*.



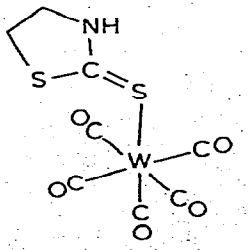
(39) $[Mo(CO_3)_2(CO)(PMe_2Ph)_3]_2$ [358]



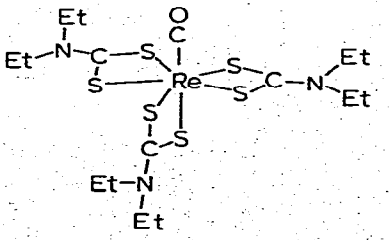
(40) $\{W(CO)_5[SC(C_4H_3S)=CHCOCF_3]\}^-$ [104]



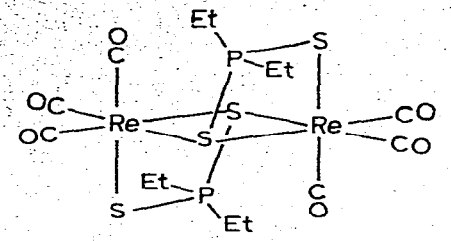
(41) $W(CO)_5[\overline{S(CH_2)_2NHCOCH_2}]$ [59]



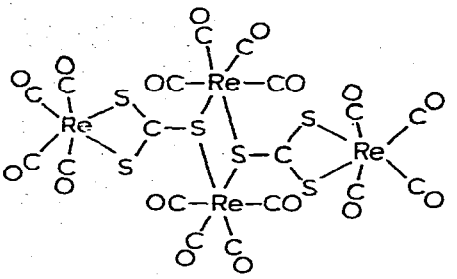
(42) $W(CO)_5[S=\overline{CNH(CH_2)_2S}]$ [42]



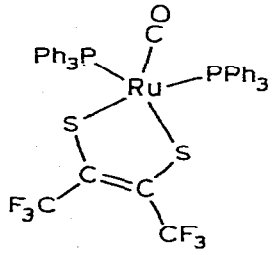
(43) $Re(CO)(S_2CNEt_2)_3$ [172]



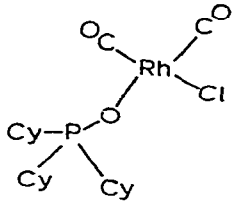
(44) $[Re(CO)_4(S_2PEt_2)]_2$ [132]



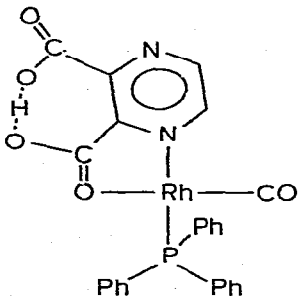
(45) $Re_4(CO)_{16}(CS_3)_2$ [197]



(46) $Ru(CO)(PPh_3)_2[S_2C_2(CF_3)_2]$ [334]
orange isomer



(47) $RhCl(CO)_2(OPCy_3)$ [222]

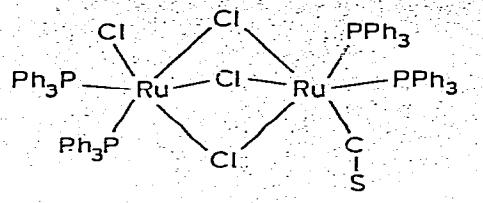


(48) $Rh(pda)(CO)(PPh_3)$ [258]

(e) *Thiocarbonyls*

[Structure *49*]

(*49*) Disordered CS, Cl (terminal).



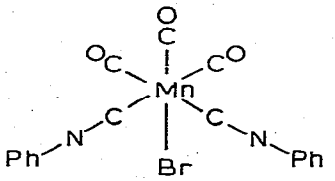
(49) $Ru_2Cl_4(CS)(PPh_3)_4$ [368]

(f) *Isocyanide complexes*

[Structure *50*]

(*50*) Mn-CO, 1.74(3); Mn-CNPh, 1.92(3)Å.

See also: *52*, *108*, *215*, *317*, *321*, *328*.



(50) $MnBr(CO)_3(CNPh)_2$ [177]

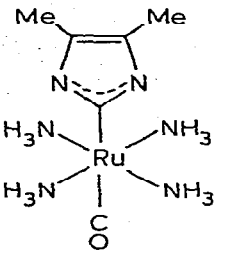
(g) *Carbene and carbyne complexes*

[Structures *51* - *64*]

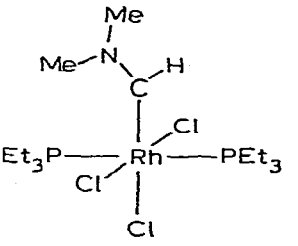
(*51*) Planar C-bonded imidazole confirmed, Ru-C 2.128(4)Å. (*52*) Ru-C bond lengths: 2.045 (carbene), 1.979 (isocyanide), 1.825Å(CO). (*53*) High *trans* influence of secondary carbene: Rh-Cl(*trans*-Cl), 2.36; (*trans*-carbene), 2.445Å. (*55*) Planar chelating carbene. (*57*) Ylid formulation favoured (tetrahedral C) with organophosphonium ion, Ni-C 2.096, P-C 1.745Å. (*58*)(*59*) Comparison of *cis-trans* isomers; Pt-C bond order ∿ 1, *trans* influence: carbene ∿ PR_3 > Cl. (*61*) Carbene almost planar, perpendicular to Pt square plane. (*62*)(*63*)(*64*) Comparison of three

carbyne complexes: M≡C, 1.69(1), 1.68(3), 1.90(5)Å respectively; Cr(W)–I both near covalent radii sum.

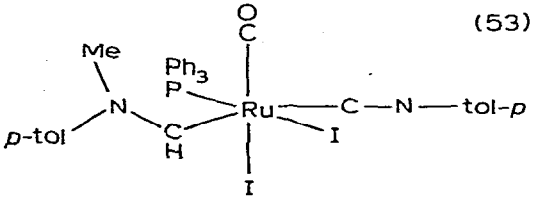
See also: *108*, *220*, *228*, *318*, *321*, *389*.



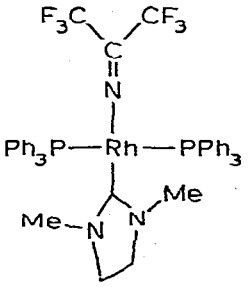
(51) *trans*-$[Ru(CO)(C\text{-}Meim)(NH_3)_4]PF_6$ [30]



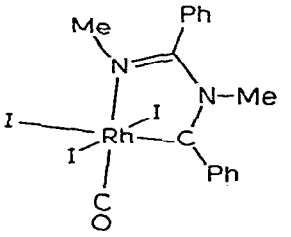
(53) $RhCl_3(CHNMe_2)(PEt_3)_2$ [152]



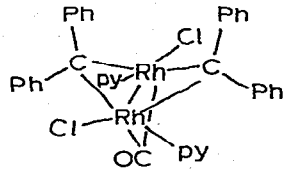
(52) $RuI_2(CO)(PPh_3)(CN\ tol\text{-}p)(CHNMe\ tol\text{-}p)$ [307]



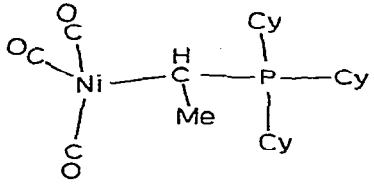
(54) $Rh[C(NMeCH_2)_2][N{=}C(CF_3)_2](PPh_3)_2$ [346]



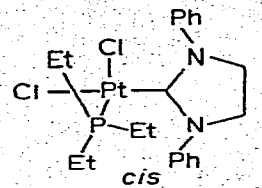
(55) $RhI_3(CO)(CPhNMeCPh{=}NMe)$ [180]



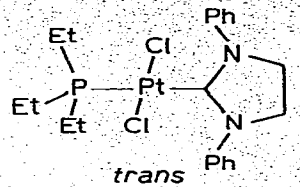
(56) $[RhCl(py)(CPh_2)]_2CO$ [312]



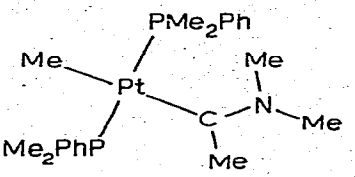
(57) $Ni(CO)_3[CHMePCy_3]$ [247]



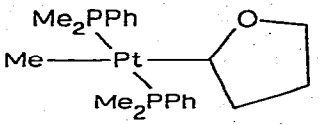
(58) $PtCl_2[C(PhNCH_2)_2](PEt_3)$ [230]



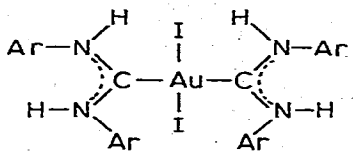
(59)



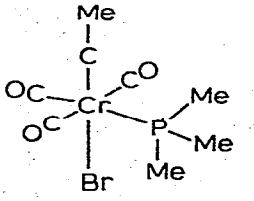
(60) *trans*-$\{PtMe[CMe(NMe_2)](PMe_2Ph)_2\}PF_6$ [233]



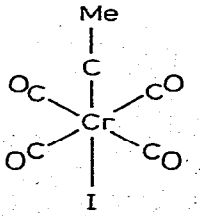
(61) *trans*-$[PtMe(CO(CH_2)_2CH_2)(PMe_2Ph)_2]PF_6$ [231]



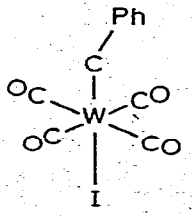
(61a) $[AuI_2\{C(NHtol\text{-}p)_2\}_2]^+$ [295]
Ar = *p*-tol



(62) $CrBr(CMe)(CO)_3(PMe_3)$ [26]



(63) $CrI(CMe)(CO)_4$ [26]



(64) $WI(CPh)(CO)_4$ [26]

(h) *Alkyls, aryls and acyls*

[Structures *65* - *97*]

(*65*) Slightly distorted pentagonal bipyramid, axial Cl.

(*67*) Li interaction at three edges of octahedron, Li...Me, 2.17Å; tetrahedral Li, dioxan connects Cr anions, i.e. $\{Cr[Me_2Li\text{-}2(diox)_{\frac{1}{2}}]_3\}_n$.

(*68*) Eclipsed (D_{4h}) structure attributed to δ component of quadruple Mo-Mo bond. (*74*) Non-symmetrical intramolecular H-bond, no evidence for *cis*-influence on Co-C bond. (*77*) From $[Co(py)(dmg)_2]^-$ + DDT.

(*78*) Distorted octahedral, axial Me; Co-C 2.047Å (*cis* influence).

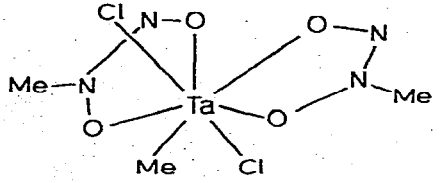
(*79*) Co-C σ bonding favoured. (*84*) Equivalence of Et protons in ^1H NMR spectrum accidental. (*85*) Unusual product from $NiCl(Br)_2$ + NAs_3 + $NaBPh_4$ in refluxing EtOH; TBP. (*86*) Tilted ligand suggests pseudo-phospha-allyl type interaction. (*87*) C-bonded acac, 2 CO groups not parallel. (*88*) $HB(pz)_3$ group bidentate. (*90*) *trans*-Styryl group indicates stereospecific oxidative addition. (*91*) Acylimino complex from $PtIMe(PEt_3)_2$ + *p*-tolNC, refutes 5-coordinate structure proposed from NMR.

(*93*) Strong *trans* influence of aryl on Pt-CO, 1.97Å (cf. $[PtCl(CO)(PEt_3)_2]^+$, 1.78Å). (*94*) Unexpected *trans* configuration; long Pt-P 2.302Å.

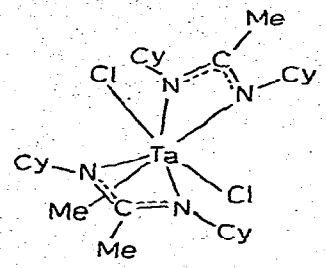
(*95*) Cubane type, triple-bridging N_3 groups. (*96*) Eight-membered $(PCCuC)_2$ ring, linear C-Cu-C, weak Cu-Cu interaction (2.843Å).

(*97*) Planar anion, tetrahedral Ag coordinated by N, O of NO, and N of CN; infinite 2-dimensional layers.

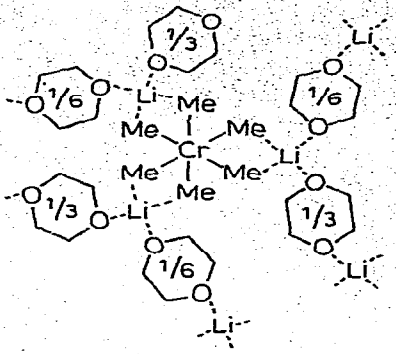
See also: *60*, *61*, *134*, *178*, *218*, *235*, *236*, *237*, *238*, *241*, *247*, *260*, *301*, *302*. Structures *182*, *183*, *366a*, *382a*, *382b* contain $\eta^1{:}\eta^5$ - C_5H_5 groups.



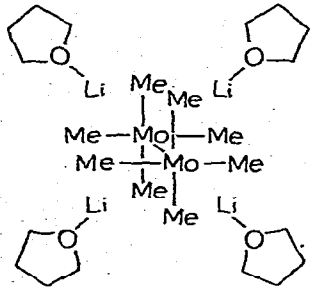
(65) $TaCl_2Me[ON(Me)NO]_2$ [16]



(66) $TaCl_2Me[MeC(NCy)_2]_2$ [292]

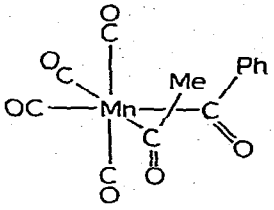


(67) $[Li(diox)]_3CrMe_6$ [29]

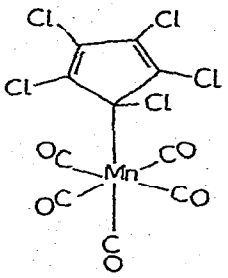


(68) $[Li(thf)]_4[Mo_2Me_8]$ [45]

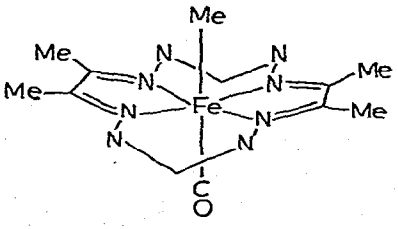
(69) No structure



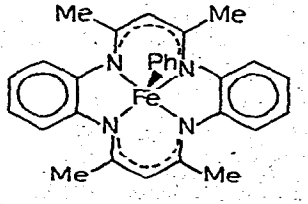
(70) *cis*-$[Mn(COMe)(COPh)(CO)_4]$ [108]



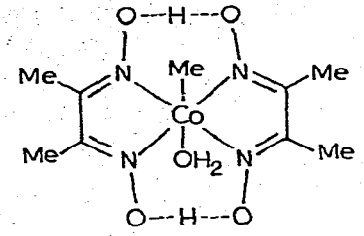
(71) $Mn(CO)_5(C_5Cl_5)$ [69]



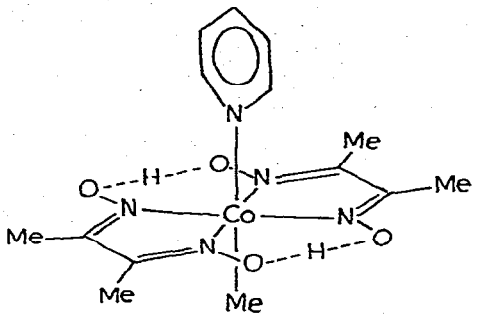
(72) $FeMe(CO)(C_{10}H_{19}N_8)$ [96]



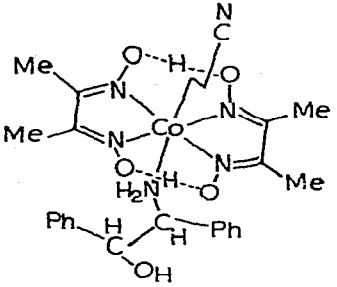
(73) $FePh(C_{22}H_{22}N_4)$ [286]



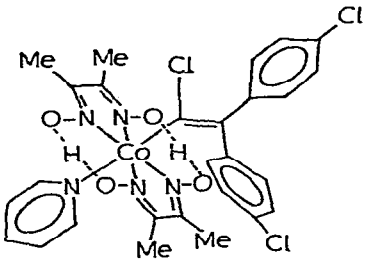
(74) $CoMe(H_2O)(dmg)_2$ [52]



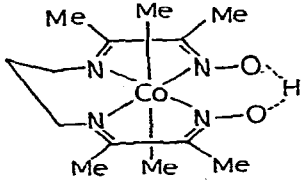
(75) $CoMe(py)(dmg)_2$ [133]



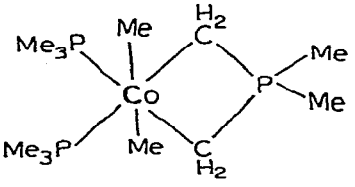
(76) $Co(CH_2CH_2CN)(CHPhNH_2CHPhOH)(dmg)_2$ [263]



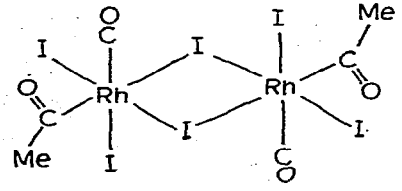
(77) $Co[CCl=C(C_6H_4Cl_2](py)(dmg)_2$ [276



(78) $CoMe_2(C_{11}H_{19}N_4O_2)$ [118]

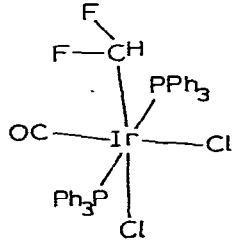


(79) $CoMe_2[(CH_2)_2PMe_2](PMe_3)_2$ [98]

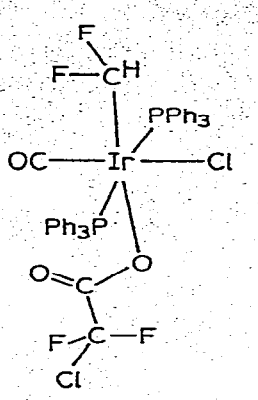


(80) $(Me_3PhN)_2[Rh_2I_6(COMe)_2(CO)_2]$ [27]

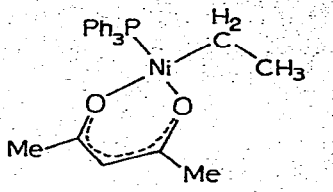
(81) No structure



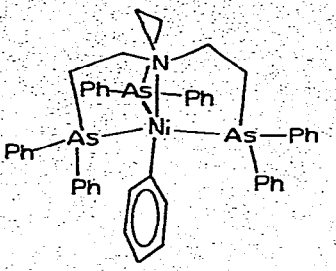
(82) $IrCl_2(CHF_2)(CO)(PPh_3)_2$ [319]



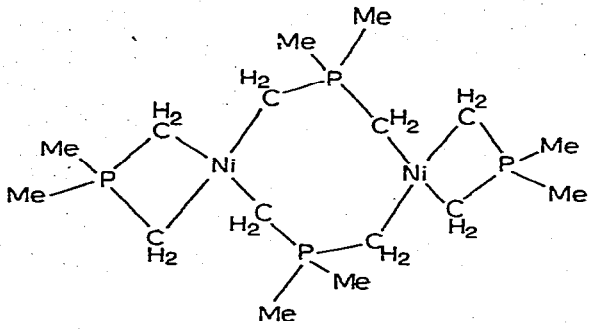
(83) $IrCl(OCOCF_2Cl)(CHF_2)(CO)(PPh_3)_2$ [327]



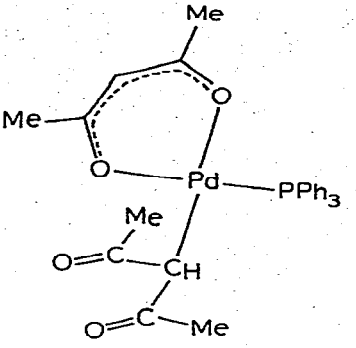
(84) $NiEt(acac)(PPh_3)$ [344]



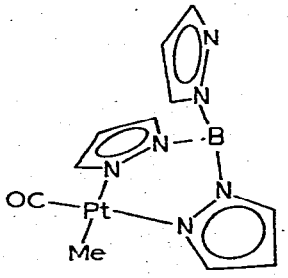
(85) $[NiPh(NAs_3)]BPh_4$ [352]



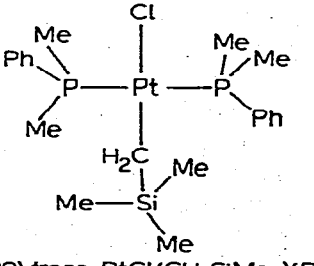
(86) $\{Ni[(CH_2)_2PMe_2]_2\}_2$ [98]



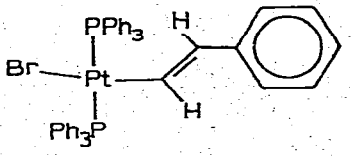
(87) $Pd(acac)_2(PPh_3)$ [283]



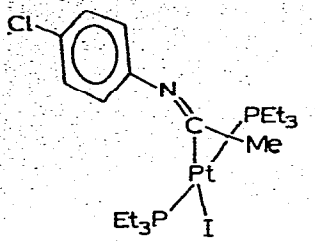
(88) $PtMe(CO)[HB(pz)_3]$ [74]



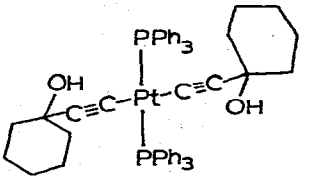
(89) *trans*-$PtCl(CH_2SiMe_3)(PMe_2Ph)_2$ [?]



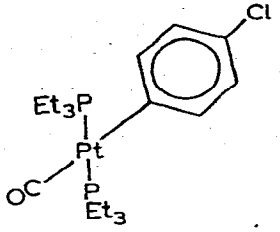
(90) *trans*-$PtBr(CH{=}CHPh)(PPh_3)_2$ [345]



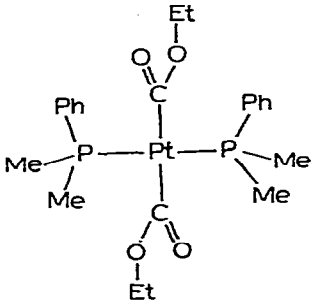
(91) *trans*-PtI(CMe:NC$_6$H$_4$Cl)(PEt$_3$)$_2$ [223]



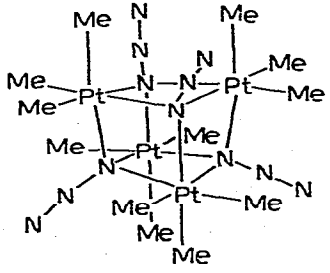
(92) *trans*-Pt(C$_2$C$_6$H$_{10}$OH)$_2$(PPh$_3$)$_2$ [357]



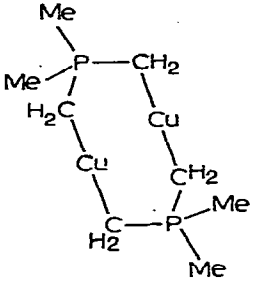
(93) *trans*-[Pt(C$_6$H$_4$Cl)(CO)(PEt$_3$)$_2$]$^+$ [203]



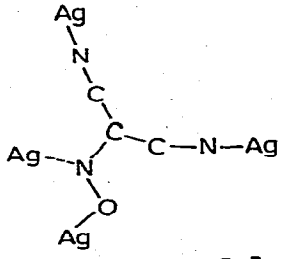
(94) *trans*-Pt(CO$_2$Et)$_2$(PMe$_2$Ph)$_2$ [340]



(95) [PtMe$_3$(N$_3$)]$_4$ [99]



(96) [Cu(CH$_2$)$_2$PMe$_2$]$_2$ [44]



(97) AgC(CN)$_2$(NO) [18]

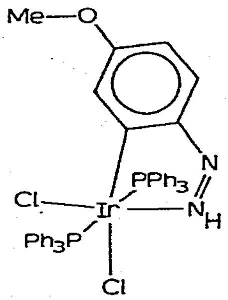
(98) No structure

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

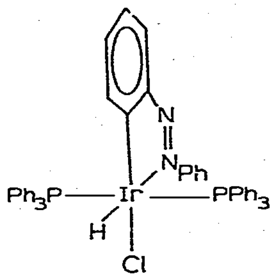
[Structures *99 - 109*]

(99) Metallated diimide, planar chelate ring, NH located in difference Fourier. *(102)* Confirms *trans* nitrogens; puckered chelate ring. *(103)* Identity of "Ru(dmpe)$_2$"; previous unit cell in error, giving insoluble Patterson. *(104)* Ir-P(*trans* H), 2.396; others 2.346, 2.362Å. *(105)* Chelate ring strained. *(106)* *Trans*-chelation by P; Pt-P-C 103° (deformed, expected 116°). *(106a)* *ortho*-Metallated phenyldioxolane ligand; complex formed by Grignard route. *(107)* Addition of $C_2(CF_3)_2$ to acac ligand [cf. *(159)*]. *(108a)* From TCNE oxide. *(109)* First structurally characterised *ortho*-metallated S-donor ligand.

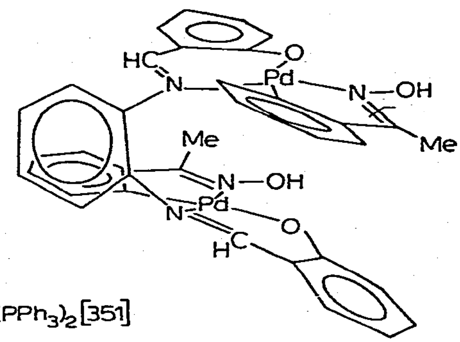
See also: *231, 302.*



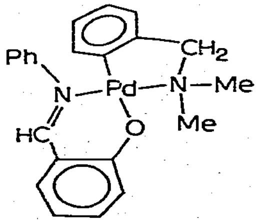
(99) $IrCl_2[C_6H_3(OMe)N{=}NH](PPh_3)_2$ [343]



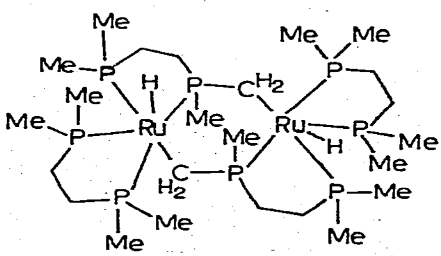
(100) $IrHCl(C_6H_4N{=}NPh)(PPh_3)_2$ [351]



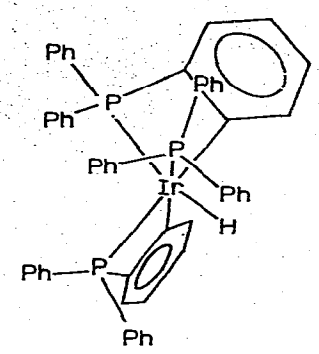
(101) [Pd(apo)]$_2$salophen [306]



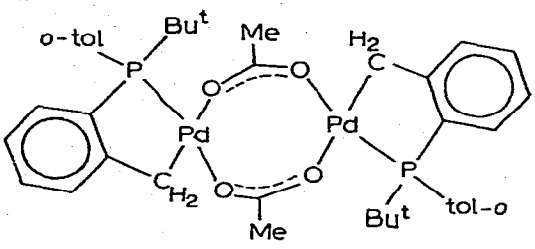
(102) $Pd(C_6H_4CH_2NMe_2)$(sal=NPh) [239]



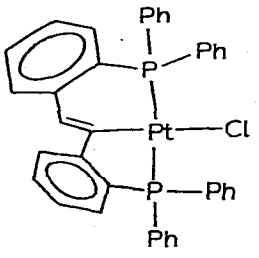
(103) $\{RuH[CH_2PMe(CH_2)_2PMe_2](dmpe)\}_2$ [255]



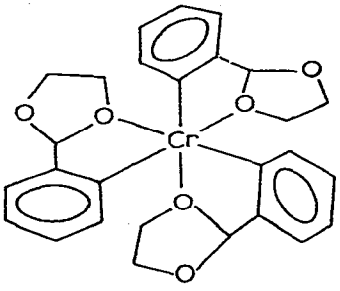
(104) $IrH(C_6H_4PPh_2)_2(PPh_3)$ [359]



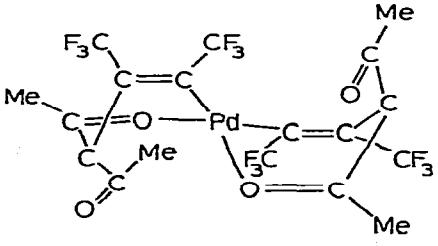
(105) $\{Pd(OAc)[CH_2C_6H_4PBu^t(o\text{-}tol)]\}_2$ [332]



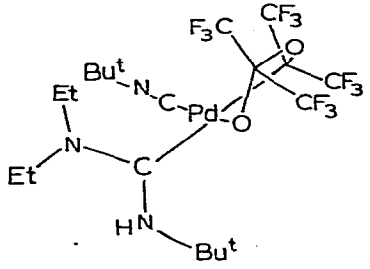
(106) $PtCl(Ph_2PC_6H_4C{=}CHC_6H_4PPh_2)$ [316]



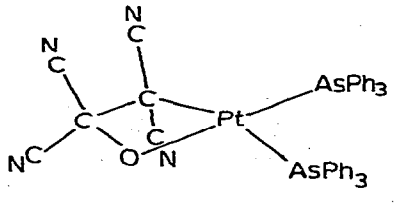
(106a) $Cr(C_6H_4C_3H_5O_2)_3$ [277]



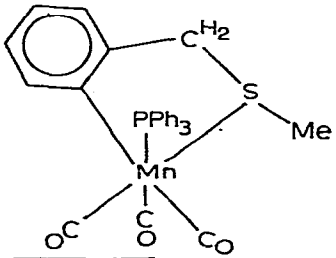
(107) Pd(acac C_4F_6)$_2$ [184]



(108) $[Pd\,OC(CF_3)_2OC(CF_3)_2](CNBu^t)[C(NHBu^t)(NEt_2)]$ [218]



(108a) $Pt[C_2(CN)_4O](AsPh_3)_2$ [335]



(109) $Mn(C_6H_4CH_2SMe)(CO)_3(PPh_3)$ [289]

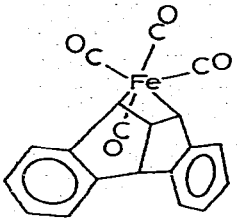
η^2-LIGANDS

(a) *Ligands bonded by two* η^1 *groups (metallocycles)*

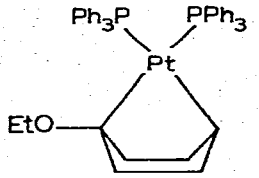
[Structures *110* - *112*]

(*110*) From dibenzosemibullvalene, planar ferretane ring. (*110a*) Ligand formed by allene dimerisation. (*111*) From OEt^- + bicyclo[2.2.0]hexene complex (*128*). (*112*) From $Pt(PPh_3)_4$ + 1,1,2,2-$(CN)_4$cyclopropane, puckered C_3Pt ring.

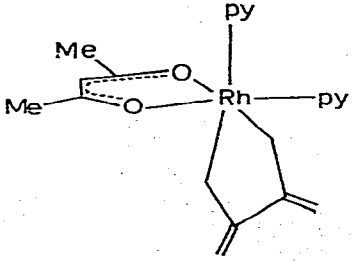
See also: *232*, *325*, *326*, *364*, *365*, *366*, *370*.



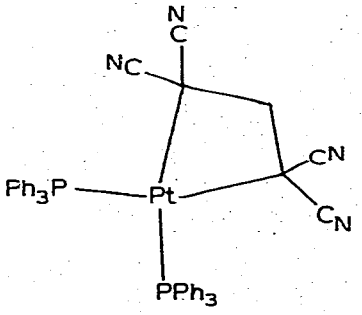
(110) $Fe(CO)_4(C_{16}H_{12})$ [191]



(111) $Pt(C_6H_9OEt)(PPh_3)_2$ [339]



(110a) $Rh(acac)(py)_2(C_6H_8)$ [229]



(112) $Pt[C_3H_2(CN)_4](PPh_3)_2$ [342]

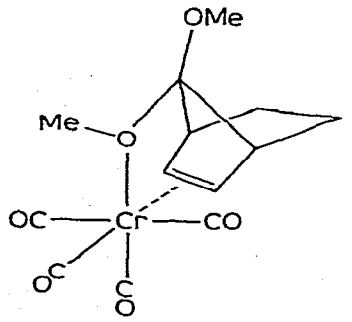
(b) *Olefin complexes*

[Structures *113* - *129*]

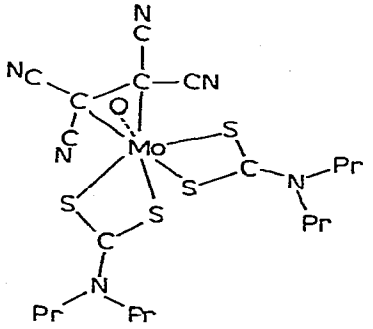
(*115*) Feist's ester complex, *cis* Fe, ester groups results in C_2 tilted out of C_3-ring plane by 37.6°. (*118*) 2 enantiomorphs in crystallographic unit; short Rh-P, 2.162Å; C=C inclined 13.7° to mid-point plane.

(*119*) Comparison with azobenzene derivative. (*121*) Allene C=C: 1.30 (free); 1.40Å (complexed); H atoms bent back 26°. (*122*) 2 s-*cis*,*trans*, 1 S-*cis*,*cis*; C_6H_6 solvate contains 3 *cis*,*trans* dba ligands. (*123*)(*124*) Rings essentially unchanged by complexation. (*126*) Establishes absolute configuration of chiral centre formed by olefin coordination. (*127*) Zwitterion; crystal racemic with C(2)(*R*):C(3)(*R*) and C(2)(*S*):C(3)(*S*) (latter illustrated). (*128*) Reacts with ethoxide to give (111). (*129*) Steric effects cause substituents to be bent away 33, 5°, leading to differing Pt-C and Pt-P bonds.

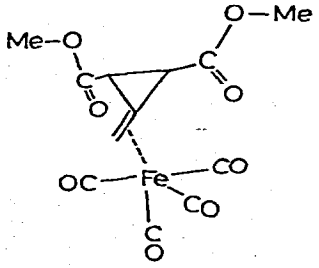
See also: *185* (η^2-C_5H_5), *217*, *236*, *239*, *242*, *243*, *364*, *365*, *366*.



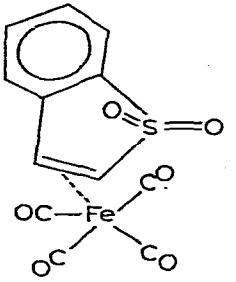
(113) $Cr(CO)_4[C_7H_8(OMe)_2]$ [113]



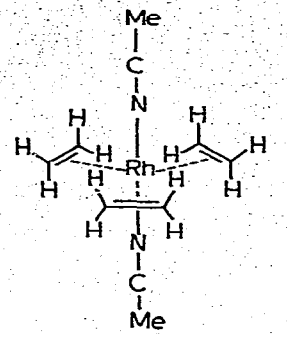
(114) $MoO(S_2CNPr_2)_2(tcne)$ [217]



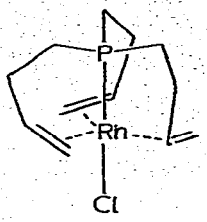
(115) $Fe(CO)_4[C_4H_4(CO_2Me)_2]$ [86]



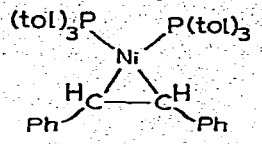
(116) $Fe(CO)_4(C_8H_6SO_2)$ [82]



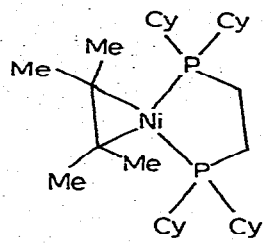
(117) $[Rh(C_2H_4)_3(NCMe)_2]^+$ [67]



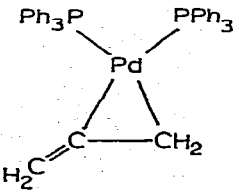
(118) RhCl $P(CH_2CH_2CH{=}CH_2)_3$ [94]



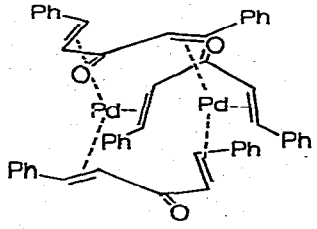
(119) Ni(*trans* CHPh=CHPh)$(P(tol)_3)_2$ [363]



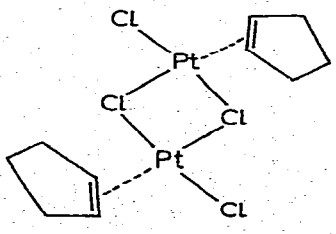
(120) $Ni(C_2Me_4)[(Cy_2PCH_2)_2]$ [300]



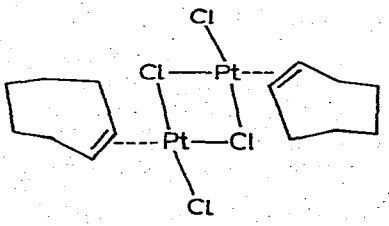
(121) $Pd(C_3H_4)(PPh_3)_2$ [323]



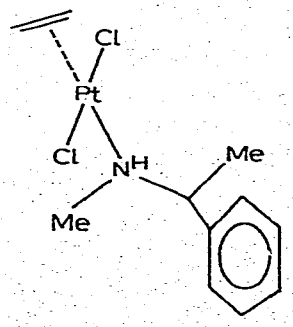
(122) $Pd_2(dba)_3$ [355,356]



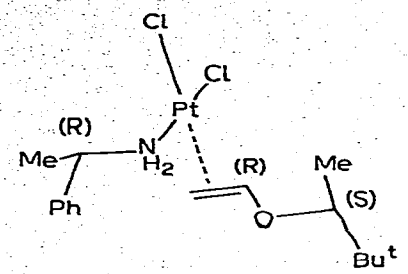
(123) $[PtCl_2(C_5H_8)]_2$ [66]



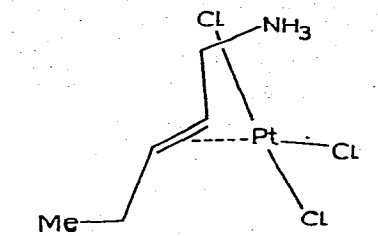
(124) $[PtCl_2(C_7H_{12})]_2$ [66]



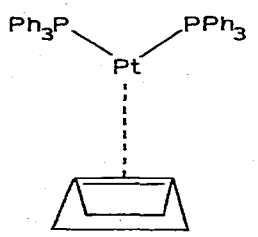
(125) $PtCl_2(C_2H_4)$(NHMeCHMePh) [79]



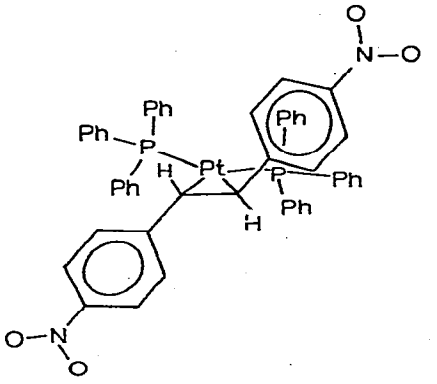
(126) *cis*-$PtCl_2[(R)NH_2CHMePh][(R)CH_2{:}CHOCHMeBu^t(S)]$ [171]



(127) $PtCl_3(C_5H_9NH_3)$ [22]



(128) $Pt(C_6H_8)(PPh_3)_2$ [839]



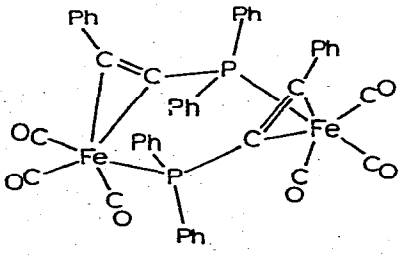
(129) $Pt(NO_2C_6H_4CH{=}CHC_6H_4NO_2)(PPh_3)_2$ [354]

(c) *Acetylene complexes*

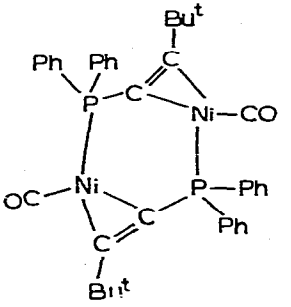
[Structures *129a - 138*]

(*131*) Dihedral PdP_2/PdC_2 9.7°. (*137*)(*138*) Zwitterionic complexes, no Re-Cu or Rh-Ag interactions.

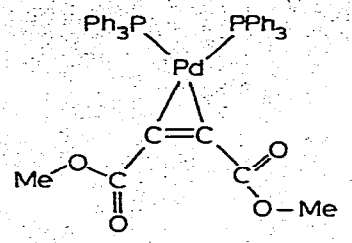
See also: *226*, *230*, *239*, *240*, *322*, *373*, *392*.



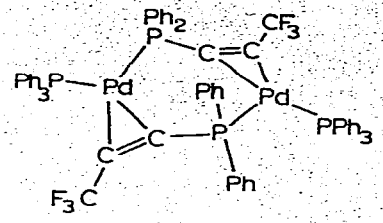
(129a) $Fe_2(CO)_6(PhC_2PPh_2)_2$ [320]



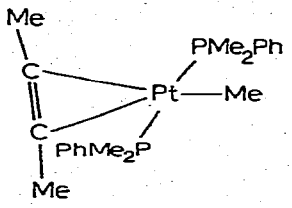
(130) $Ni_2(CO)_2(Ph_2PC_2Bu^t)_2$ [320]



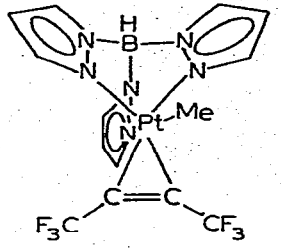
(131) $Pd[C_2(CO_2Me)_2](PPh_3)_2$ [337]



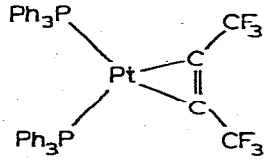
(132) $[Pd(CF_3C_2PPh_2)(PPh_3)]_2$ [366]



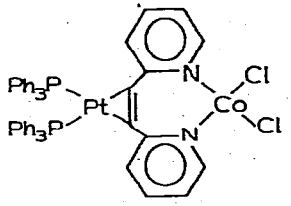
(133) $[PtMe(C_2Me_2)(PMe_2Ph)_2]PF_6$ [232]



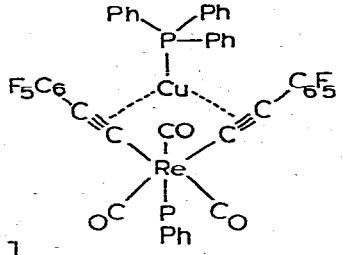
(134) $PtMe[C_2(CF_3)_2][HB(pz)_3]$ [126]



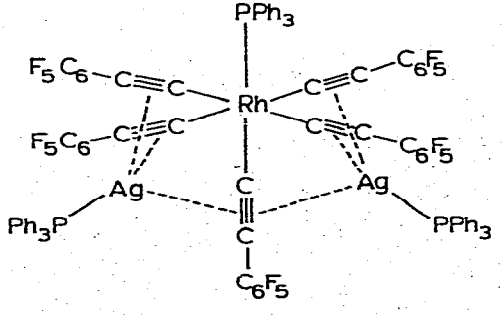
(135) $Pt[C_2(CF_3)_2](PPh_3)_2$ [325]



(136) $Pt[C_2(C_5H_4N)_2CoCl_2](PPh_3)_2$ [350]



(137) $ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2$ [361]



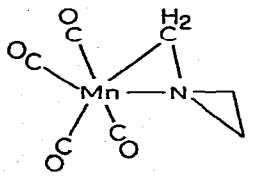
(138) $RhAg_2(C_2C_6F_5)_5(PPh_3)_3$ [371]

(d) *Complexes containing other three-membered rings*

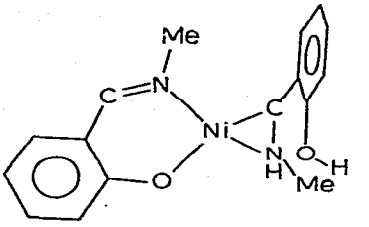
[Structures *139* - *142*]

(*139*) First stable aminomethylene derivative. (*140*) Hydroxyl H of one ligand transferred to the other, which bonds via π-bond of >CH=NHMe group. (*141*) P_2NiCO approximately coplanar. (*142*) Crown structure.

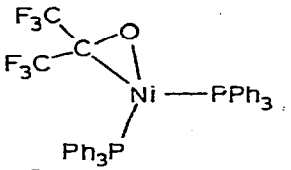
See also: *219*, *302*.



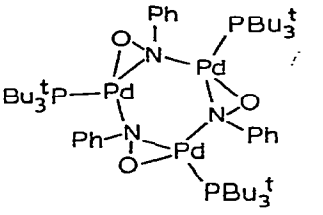
(139) $Mn(CO)_4(CH_2{=}NC_2H_4)$ [34]



(140) $Ni(sal{=}NMe)_2$ [167]



(141) $Ni[(CF_3)_2CO](PPh_3)_2$ [322]



(142) $[Pd(PhNO)(PBu^t_3)]_3$ [402]

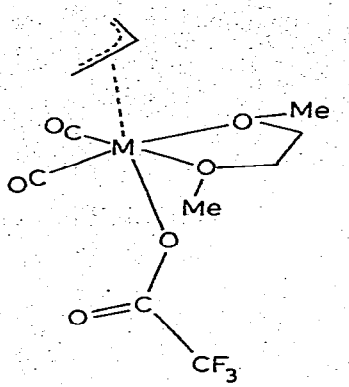
η^3-LIGANDS

(a) η^3-*Allyl complexes*

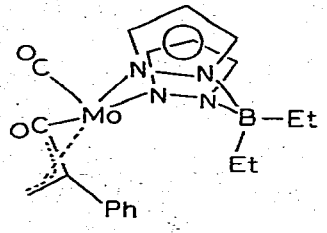
[Structures *143* - *155*]

(*145*) Stronger C-H...Mo interaction than (*146*), with Mo-H 2.27 (possibly 2.15Å). (*146*) Interaction of aliphatic C-H competes with formation of η^5-C_7H_7. (*147*) Confirms *endo* attack of diene-$Fe(CO)_3$ under Friedel-Crafts conditions. (*148a*) Two P atoms form *trans* chelate. (*149*) Allyl occupies 2 positions statistically. (*149a*) Ligand = η^3-pinenyl. (*152*) Absolute configuration *R*. (*153*) Conformation of allyl may indicate Ni-H(Me)

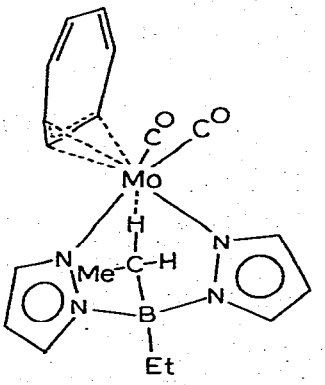
interaction. (*154*) Slight differences in C-C bond lengths *trans* to O, N. (*155*) Resolves structure of long-known Bu^tC_2H-trimer from acetylene + $PdCl_2$. See also: *195*, *207*, *216*, *244*, *245*, *264*, *355*.



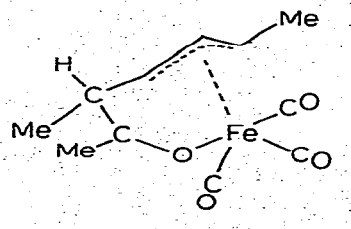
(143) M = Mo [77]
$M(O_2CCF_3)(CO)_2(C_3H_5)(dme)$ (144) M = W



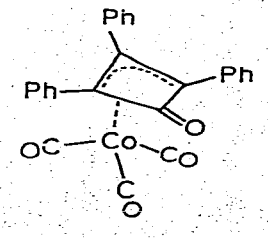
(145) $Mo(CO)_2(CH_2CPhCH_2)[Et_2B(pz)_2]$ [227]



(146) $Mo(CO)_2(C_7H_7)[Et_2B(pz)_2]$ [201]

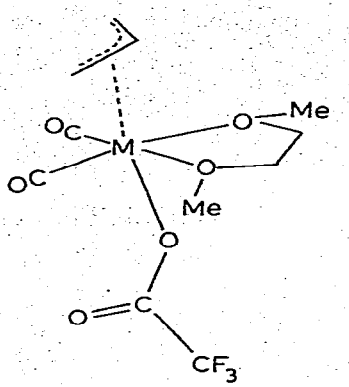


(147) $[Fe(CO)_3(CHMe(CH)_2CHMeCMeO)]^+$ [75]

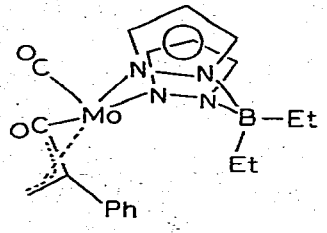


(148) $Co(CO)_3(C_3Ph_3CO)$ [256]

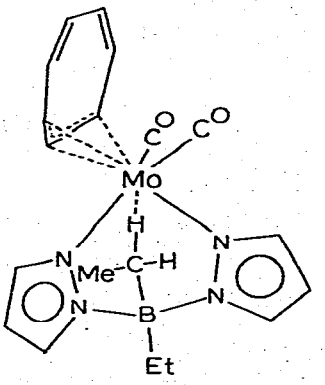
interaction. (*154*) Slight differences in C-C bond lengths *trans* to O, N. (*155*) Resolves structure of long-known Bu^tC_2H-trimer from acetylene + $PdCl_2$. See also: *195*, *207*, *216*, *244*, *245*, *264*, *355*.



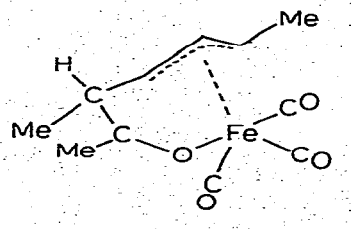
(143) M = Mo [77]
$M(O_2CCF_3)(CO)_2(C_3H_5)(dme)$ (144) M = W



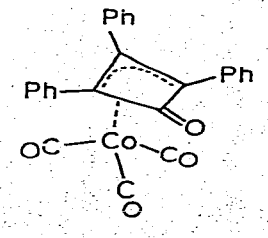
(145) $Mo(CO)_2(CH_2CPhCH_2)[Et_2B(pz)_2]$ [227]



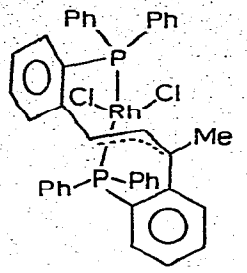
(146) $Mo(CO)_2(C_7H_7)[Et_2B(pz)_2]$ [201]



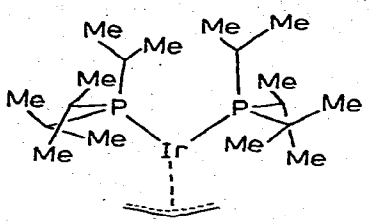
(147) $[Fe(CO)_3(CHMe(CH)_2CHMeCMeO)]^+$ [75]



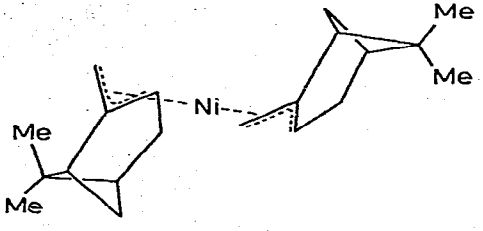
(148) $Co(CO)_3(C_3Ph_3CO)$ [256]



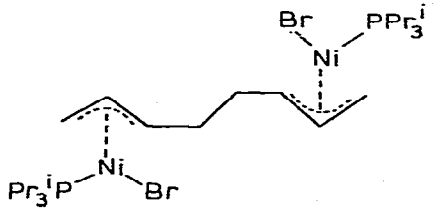
(148a) $RhCl_2(Ph_2PC_6H_4CHCHCMeC_6H_4PPh_2)$ [329]



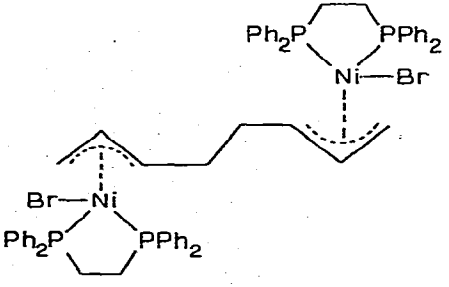
(149) $Ir(C_3H_5)(PPr^i_3)_2$ [97]



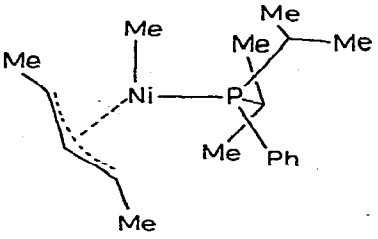
(149a) (+)-$Ni(C_{10}H_{15})_2$ [220]



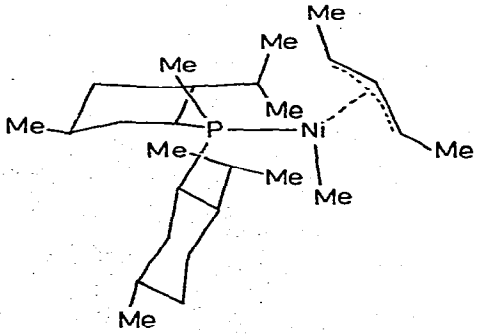
(150) $[NiBr(PPr^i_3)]_2C_8H_{12}$ [271]



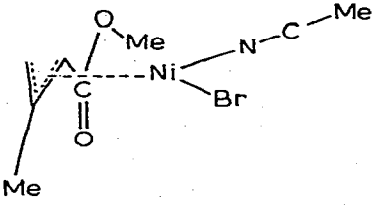
(151) $[NiBr(dppe)]_2C_8H_{12}$ [271]



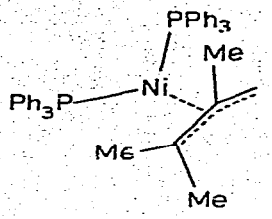
(151a) NiMe(CHMeCHCHMe)(PPr^i_2Ph) [194]



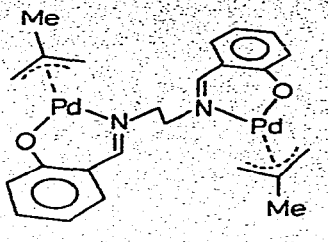
(152) NiMe(CHMeCHCHMe)[PPr^i(men)$_2$] [194]



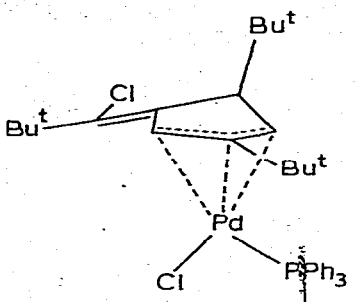
(152a) NiBr(NCMe)($CH_2CMeCHCO_2Me$) [43



(153) $[Ni(C_6H_{11})(PPh_3)_2]ZnCl_3$ [341]



(154) $[Pd(C_4H_7)]_2$salen [251]



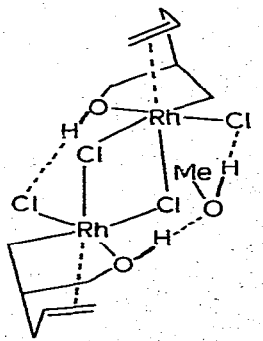
(155) $PdCl(PPh_3)\{Cl(HC_2Bu^t_3)\}$ [308]

(b) *Ligands bonded via* $\eta^1 + \eta^2$ *groups*

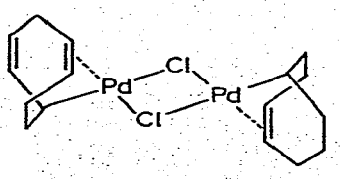
[Structures *156* - *157*]

(*156*) From $RhCl_3$ + allyl alcohol; Rh_2Cl_2 dihedral 162°; H-bonding O-H...O or O-H...Cl with solvent MeOH and coordinated OH.

See also: *239*, *248*.



(156) $[RhCl_2(C_6H_{11}O)]_2MeOH$ [95]



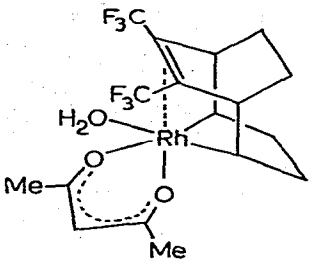
(157) $[PdCl(C_8H_{11})]_2$ [169]

η^4-LIGANDS

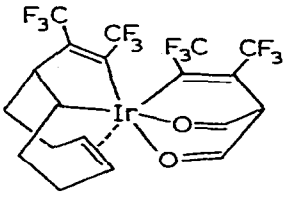
(a) *Ligands bonded via* $2\eta^1 + \eta^2$ *groups*

[Structures *158* - *159*]

(*158*) From $C_2(CF_3)_2$ + Rh(acac)(C_8H_{12}); fluxional in solution, probably involving labile H_2O. (*159*) From $C_2(CF_3)_2$ + Ir(acac)(C_8H_{12}), mode of addition differs from (*158*); alkyne also adds to acac group [cf. (*107*)].



(158) Rh[$C_8H_{12}C(CF_3)_2$](acac)(OH_2) [181]



(159) Ir[$C_8H_{12}C_2(CF_3)_2$][acac$C_2(CF_3)_2$] [181]

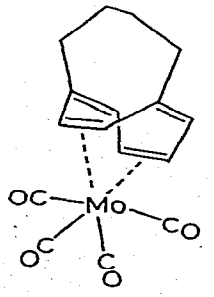
(b) *Ligands attached by* η^1 *and/or* η^2 *groups*

[Structures *162* - *165a*]

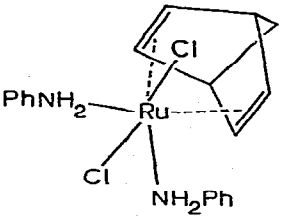
(*162*) Normal rearrangement of tricyclic precursor redirected in presence of Mo, which interacts with 6π system in intermediate. (*164*) From [Rh(mmt)(C_8H_{12})]$^-$ + MeI. (*165a*) Duroquinone has boat conformation.

See also: *398*.

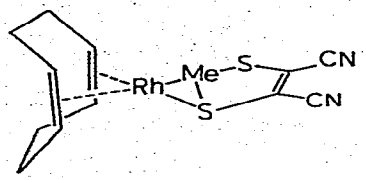
(160)
(161)
} No structures



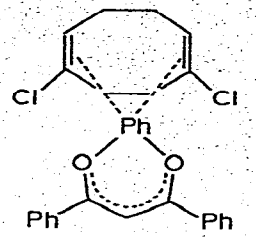
(162) $Mo(CO)_4(C_{12}H_{14})$ [125]



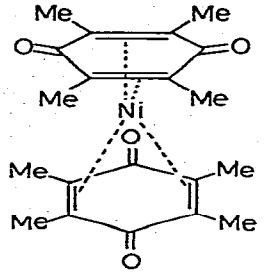
(163) $RuCl_2(NH_2Ph)_2$(nbd) [200]



(164) Rh(cod)(Memnt) [117]



(165) Rh(dbac)($C_8H_{10}Cl_2$) [117]



(165a) $Ni(dq)_2$ [216]

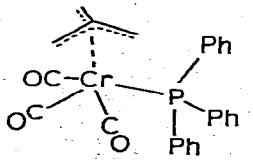
(c) *Cyclic* η^4 *ligands (cyclobutadienes)*

See: *250*, *251*, *252*, *323*.

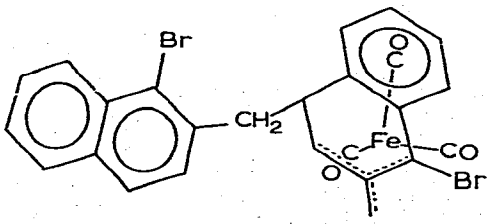
(d) *Acyclic* η^4 *ligands*

[Structures *166* – *167*]

(*166*) Non-planar $C(CH_2)_3$ ligand; discussion of X-ray *trans* influence with Cr, Mn, Fe complexes, σ, π donor-acceptor properties, using M-CO bond lengths, ν(CO). (*167*) From 1-bromo-2-bromomethylnaphthalene and $Fe_2(CO)_9$.



(166) $Cr(CO)_3(PPh_3)[C(CH_2)_3]$ [261]



(167) $Fe(CO)_3(C_{22}H_{16}Br_2)$ [257]

(e) *1,2,3,4-η⁴ dienes*

[Structures *168 - 178*]

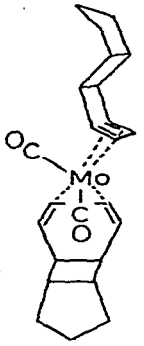
(*168*) Conformation of tricyclic ligand similar to iron complex (*173*).

(*169*)(*170*) Confirmation of *syn*, *anti* geometries established by NMR studies; H located: *anti*-H 30° away from metal, *syn*-H 20° toward metal.

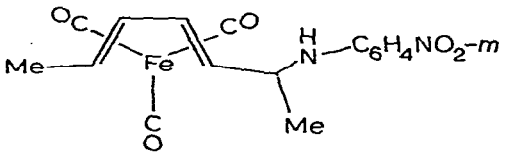
(*171*) From thermal ring-closure of cyclooctatetraene complex. (*172*) From $Fe(CO)_3(C_7H_8)$ + $C_2(CO_2Me)_2$ in (2_π + 6_π) cycloaddition. (*174*) Complex resulted from attempted synthesis of heptafulvene derivative.

(*176*) Bond lengths indicate π,2σ geometry illustrated. (*178*) Hydrocarbon ligand is allene dimer, also forms metallocycle with second Rh atom; latter bonded to γ-C of acac ligand.

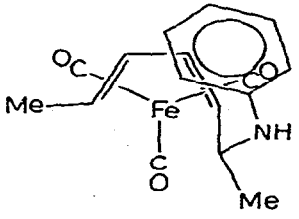
See also: *241*, *247*, *269*, *332*.



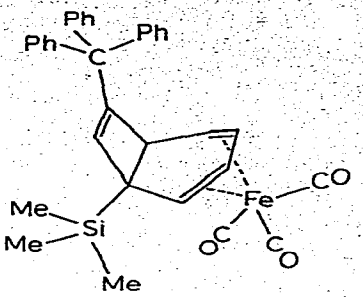
(168) $Mo(CO)_2(C_{11}H_{14})_2$ [250]



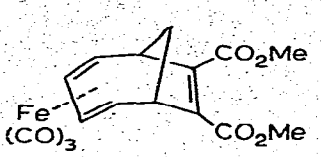
(169) *syn*-$Fe(CO)_3(MeC_4H_4CHMeNHC_6H_4NO_2$-*m*) [161]



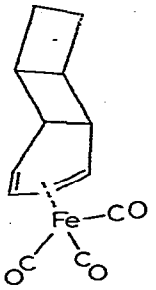
(170) *anti*-$Fe(CO)_3(MeC_4H_4CHMeNHPh)$ [161]



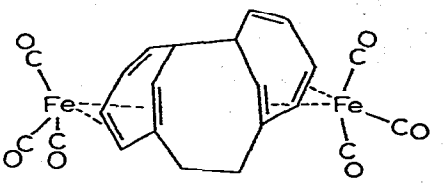
(171) $Fe(CO)_3[C_8H_6(SiMe_3)(CPh_3)]$ [305]



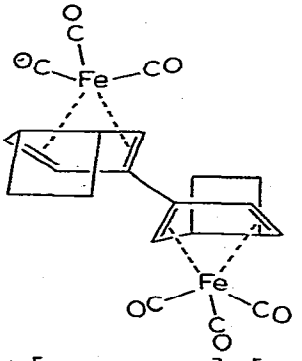
(172) $Fe(CO)[C_7H_8C_2(CO_2Me)_2]$ [146]



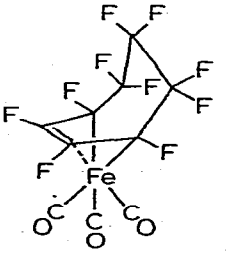
(173) $Fe(CO)_3(C_{10}H_{12})$ [114]



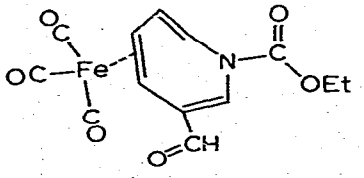
(174) $[Fe(CO)_3]_2C_{16}H_{14}$ [234]



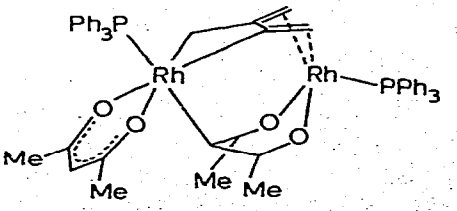
(175) $[C_8H_9Fe(CO)_3]_2$ [236]



(176) $Fe(CO)_3(C_7F_{10})$ [70]



(177) $Fe(CO)_3[C_6H_5(CHO)N(CO_2Et)]$ [112]

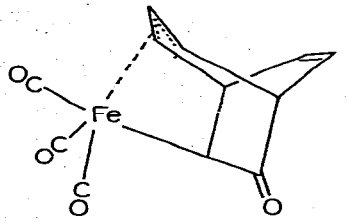


(178) $Rh_2(acac)_2(PPh_3)_2(C_6H_8)$ [229]

(f) *1,2,3,n-η^4 ligands (allyl + σ)*

[Structure *179*]

(*179*) From barbaralone + $Fe_2(CO)_9$; ref. 85 suggests 'homobutadiene' structure, whereas ref. 84 says broad features at variance with this form.

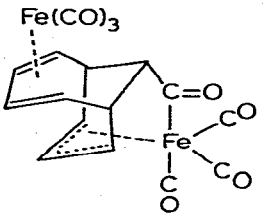


(179) $Fe(CO)_3(C_9H_8O)$ [84,85]

(180) No structure

(g) *1,2,3,4-η^4 + 1,2,3,n-η^4 ligands*

[Structure *181*]



(181) $Fe_2(CO)_6(C_{11}H_{10}O)$ [85]

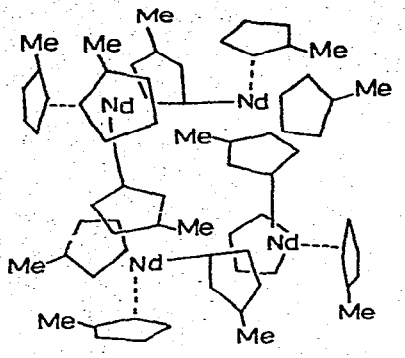
η^5-LIGANDS

(a) *Cyclopentadienyls*

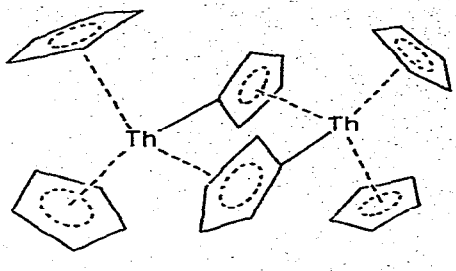
[Structures *182 - 190*]

(*182*) Tetramer formed by η^1 interaction of C_5H_5 groups with a second Nd; mainly ionic bonds, spatial arrangement results from maximum cation-anion contacts. (*183*) Dimer formed by bridging η^1; η^5 - C_5H_5 groups. (*184*) Random mixture of enantiomorphic pair of molecules. (*185*) Two η^5-C_5H_5 rings; third forms 3-electron η^2 linkage. (*189*) Migration of

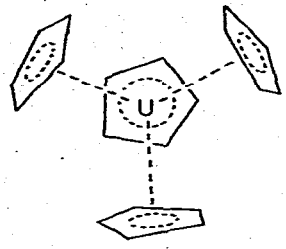
carboranyl group to C_5 ring; note H bridging five atoms. (*190*) First characterisation of triple-decker sandwich cation.



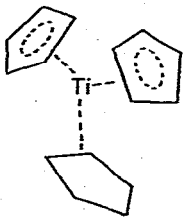
(182) $[Nd(C_5H_4Me)_3]_4$ [367]



(183) $[Th(C_5H_5)_2(C_5H_4)]$ [294]

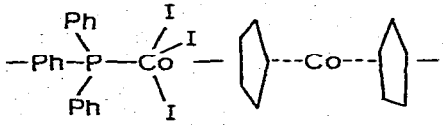


(184) $U(C_5H_5)_4$ [213,214]

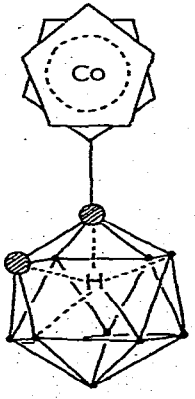


(185) $Ti(C_5H_5)_3$ [145]

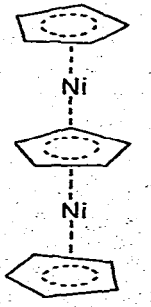
(186)
(187)
} No structures



(188) $[Co(C_5H_5)_2][CoI_3(PPh_3)]$ [61]



(189) $Co(C_5H_5)(C_5H_4C_2B_9H_{11})$ [93]

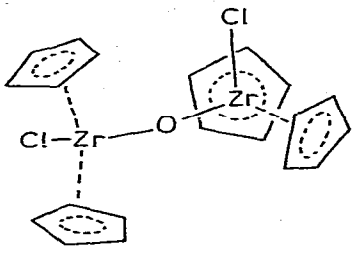


(190) $[Ni_2(C_5H_5)_3]^+$ [144]

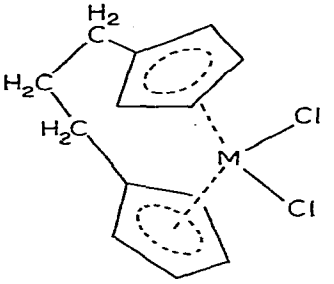
(b) *Cyclopentadienyl metal halides*

[Structures *191* - *201*]

(*191*), (*196*) - (*200*) Structures determined in connection with discussion of bonding in bent $M(C_5H_5)_2$ systems. (*192*) Twinned, angle Zr-O-Zr 168.9° (cf. linear Ti-O-Ti). (*193*)(*194*) Isomorphous, Hf compound contains 12.3% : (*195*) Steric interactions in expected $(\eta^5\text{-fluorenyl})_2Zr$ complex eased by opening of ring planes angle to 125.6°, and displacement to give η^3 and η^5-fluorenyl ligands. (*201*) From ruthenocene + I_2, rings eclipsed, ring planes at 32.2°.

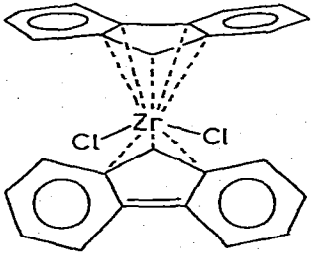


(192) $[ZrCl(C_5H_5)_2]_2O$ [212]



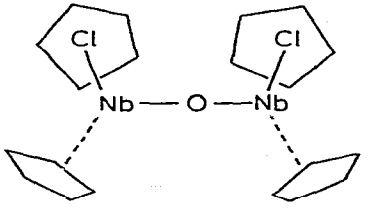
$MCl_2[(C_5H_4)_2(CH_2)_3]$

(193) M = Zr [116] (194) M = Hf [115]

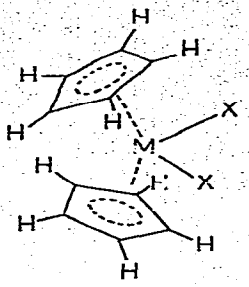


(195) $ZrCl_2(\eta^3\text{-}C_{13}H_9)(\eta^5\text{-}C_{13}H_9)$ [266]

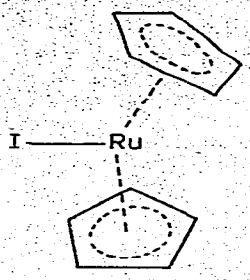
(196) See under (191)



(197) $\{[(C_5H_5)_2NbCl]_2O\}^+$ [60]



(191) M = Zr, X = Cl [60]
(196) M = Nb, X = Cl
(198) M = Mo, X = Cl
(199) M = Mo^+, X = Cl
(200) M = Re, X = Br
(203) M = Ti, XX = S_5 [65]

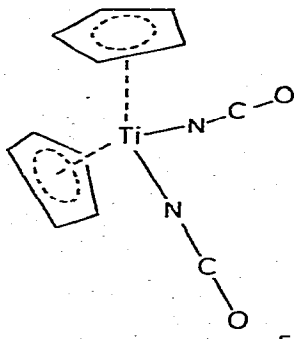


(201) $[RuI(C_5H_2)_2]I_3$ [64]

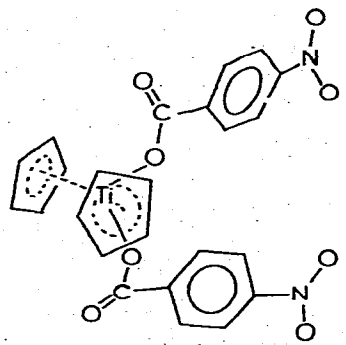
(c) *Cyclopentadienyls containing other anionic ligands*

[Structures *202* - *206*]

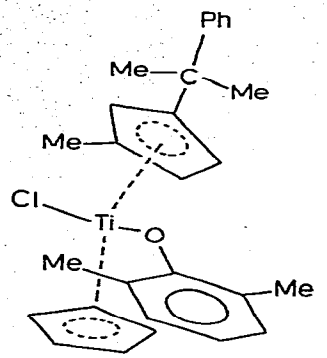
(*202*) N-bonded cyanate confirmed. (*203*) EPR on complex doped with 0.2%V; MO calculations, bonding model considered. (*205*) Racemic form, m.p. 164°; mixture of $[S_{Ti}S_p + R_{Ti}R_p]$ forms.



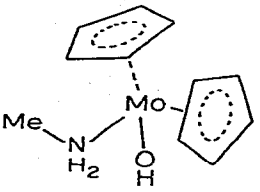
(202) $Ti(NCO)_2(C_5H_5)_2$ [87]



(204) $Ti(OCOAr)_2(C_5H_5)_2$ [248]
Ar = $C_6H_4NO_2$-*p*



(205) $TiCl(OC_6H_3Me_2)(C_5H_5)(C_5H_3MeCMe_2Ph)$ [287]

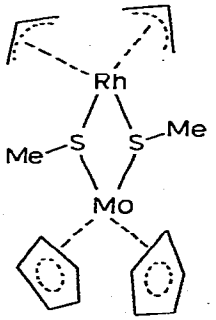


(206) $[(C_5H_5)_2Mo(OH)NH_2Me]^+$ [60]

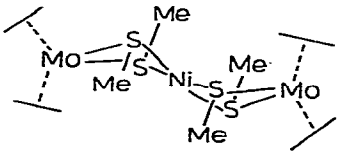
(d) *Cyclopentadienylmetal thiolate complexes as ligands*

[Structures *207 - 212*]

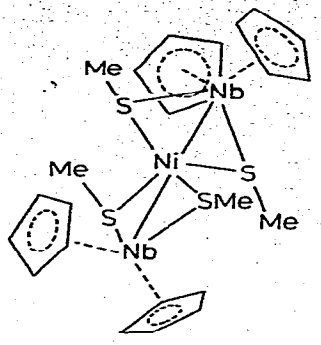
All studied to seek evidence for metal–metal bond; no unusual features found in $Rh(C_3H_5)_2$ or $M(CO)_4$ groups. (*208*) Formally contains Mo(IV), square planar Ni(II), long Mo–Ni separation (3.39Å). (*209*) Formally contains Nb(V), tetrahedral Ni(0), short Nb–Ni contact (2.78Å).



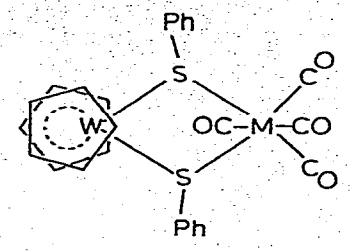
(207) $[(C_5H_5)_2Mo(SMe)_2Rh(C_3H_5)_2]$ [192]



(208) $\{[(C_5H_5)_2Mo(SMe)_2]_2Ni\}^{2+}$ [253]



(209) $\left\{[(C_5H_5)_2Nb(SMe)_2]\,Ni\right\}^{2+}$ [253]



$(C_5H_5)_2W(\mu\text{-}SPh)_2M(CO)_4$ [268]

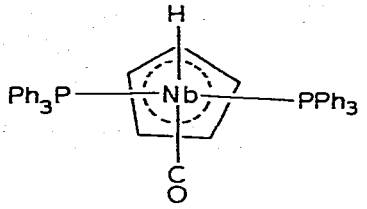
(210) M = Cr; (211) M = Mo; (212) M = W

(e) *Cyclopentadienyl complexes containing CO, PR_3 or NO ligands*

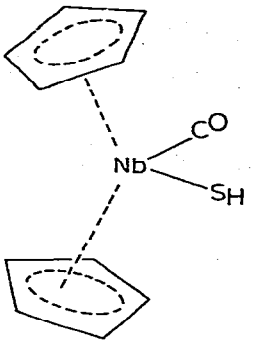
[Structures *213 – 234*]

(*214*) Dethiocarbonylation of dithioformate from hydride + CS_2.

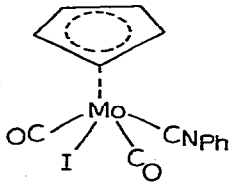
(*216*) Both rotational isomers in crystal. (*217*) Stereochemically rigid, with η^1-allyl group. (*218*) Dithiocarbamate attached to η^2-allyl group. (*219*) Asymmetric bridging hydrazide. (*220*) Contains dicyanomethylenecarbene ligand, extremely strong π-acceptor [cf. bridging $C{=}C(CN)_2$ group in (*318*)], through space C_5H_5 – $C{=}C(CN)_2$ interaction, Mo-C(carbene) 1.833Å (bond order 3), asymmetric Mo-carbene π-back-bonding, Mo-C=C, 166.6°. (*223*)(*224*) Comparative study of P^{III} and P^{V} derivatives. (*225*)(*226*) Comparison of phenylethynyl complex with CuCl derivative. (*228*) Carbene complex from Bu^tNC and product from $FeMe(CO)_2(C_5H_5)$ + CyNC. (*229*) Confirms S-sulphinate. (*229a*) No Fe-Sb bond; distorted octahedral Sb, 4e,3-centre Sb-Cl bonds. (*231*) Complex contains ligand *ortho*-metallated ly fluorine abstraction, and first example of $(\eta\text{-}C_5H_4C_5H_4)PPh_2$ ligand. (*232*) Metallocycle from $Co(PPh_3)(PhC_2CO_2Me)(C_5H_5)$ + Me_2 maleate. (*233*) Linear Co_3, bridging phosphonate ligands.



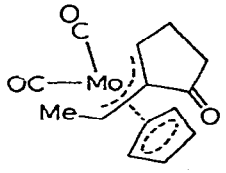
(213) $NbH(CO)(PPh_3)_2(C_5H_5)$ [338]



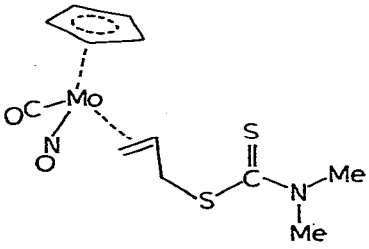
(214) $Nb(SH)(CO)(C_5H_5)_2$ [72]



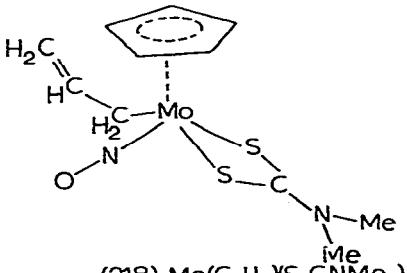
(215) $MoI(CO)_2(CNPh)(C_5H_5)$ [124]



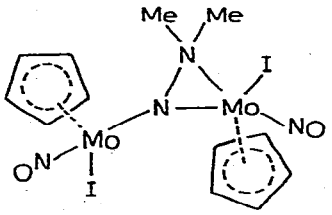
(216) $Mo(CO)_2(C_5H_6MeO)(C_5H_5)$ [128]



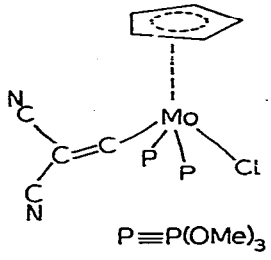
(217) $Mo(CO)(NO)(C_3H_5SC(S)NMe_2)$ [78]



(218) $Mo(C_3H_5)(S_2CNMe_2)(NO)(C_5H_5)$ [78]

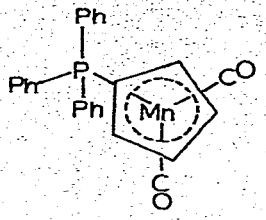


(219) $[MoI(NO)(C_5H_5)]_2NNMe_2$ [89]

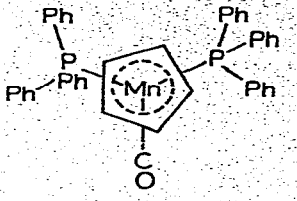


$P{\equiv}P(OMe)_3$

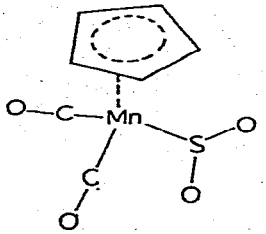
(220) $MoCl[C{=}C(CN)_2][P(OMe)_3]_2(C_5H_5)$ [150]



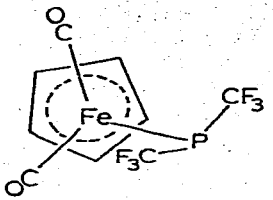
(221) $Mn(CO)_2(PPh_3)(C_5H_5)$ [260]



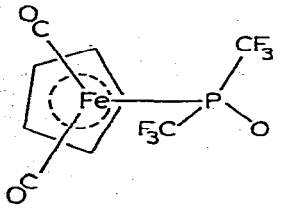
(222) $Mn(CO)(PPh_3)_2(C_5H_5)$ [336]



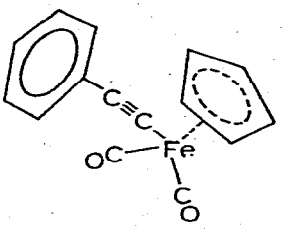
(222a) $Mn(CO)_2(SO_2)(C_5H_5)$ [33]



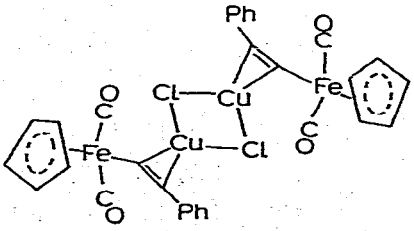
(223) $Fe(CO)_2[P(CF_3)_2](C_5H_5)$ [49]



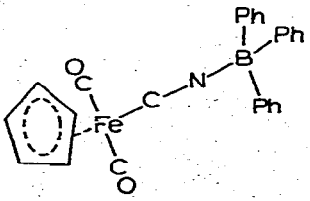
(224) $Fe(CO)_2[PO(CF_3)_2](C_5H_5)$ [49]



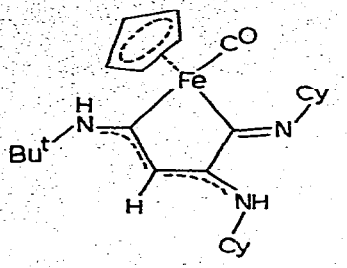
(225) $Fe(C_2Ph)(CO)_2(C_5H_5)$ [139]



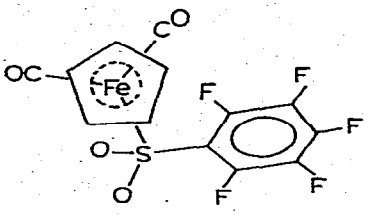
(226) $[Fe(C_2PhCuCl)(CO)_2(C_5H_5)]_2$ [293]



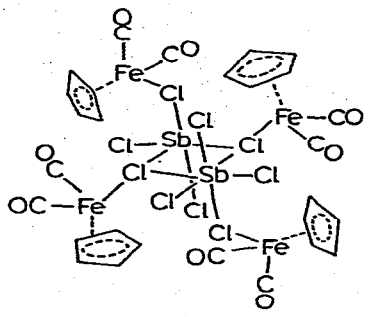
(227) $Fe(CNBPh_3)(CO)_2(C_5H_5)$ [267]



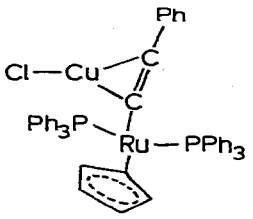
(228) $(C_5H_5)Fe(CO)$(carbene) [270]



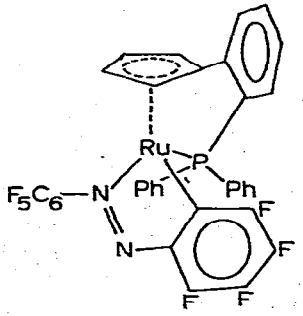
(229) $Fe(SO_2C_6F_5)(CO)_2(C_5H_5)$ [106]



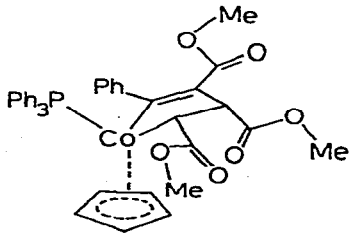
(229a) $[Fe(CO)_2(C_5H_5)Cl]_4 Sb_2Cl_6$ [284]



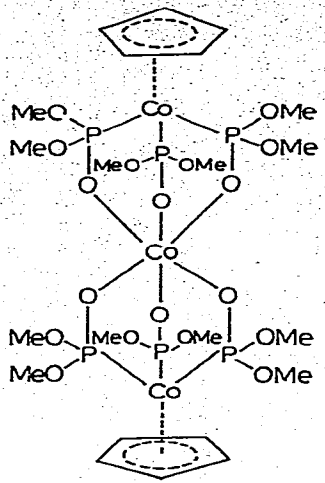
(230) $Ru(C_2Ph)(PPh_3)_2(C_5H_5)CuCl$ [353]



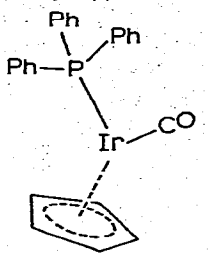
(231) $RuC_6F_4N{=}NC_6F_5(Ph_2PC_6H_4C_5H_4)$ [305]



(232) $Co[(PhC_2CO_2Me)(CHCO_2Me)_2](PPh_3)(C_5H_5)$ [314]



(233) $Co_3[P(O)(OMe)_2]_6(C_5H_5)_2$ [241]



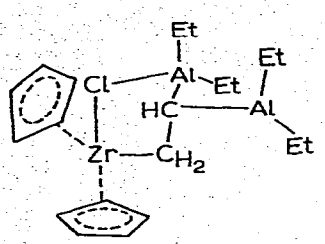
(234) $Ir(CO)(PPh_3)(C_5H_5)$ [249]

(f) *Cyclopentadienyl complexes containing other* η*-hydrocarbon ligands*

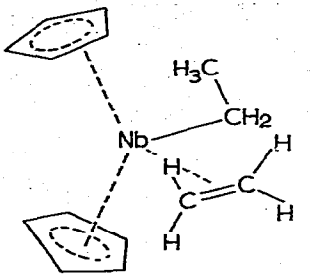
[Structures *235 - 252*]

(*236*) Nb–C_2H_4 bond comparable to later transition metals, with H bent back from Nb. (*238*) From irradiation of $WH_2(C_5H_5)_2$ in mesitylene. (*239*)(*240*) Products from $C_2(CF_3)_2$ and $MCl(CO)_3(C_5H_5)$ (M=Mo, W, respectively). (*241*) From $Fe_2(CO)_9$ + *spiro*[2,4-cyclopentadiene-1,7'-norcara-2',4'-diene]. (*244*)(*245*) Complexes from 6,6-diphenylpentafulvene and appropriate carbonyl. (*247*) No Fe-Fe bond, complex from 6,6-dimethylpentafulvene. (*248*) From nickelocene and dimethylketene. (*250*)(*251*)(*252*) Some rotational disorder in CN group; Ph groups bent away from Co, in propeller configuration (twisted about axes 35°).

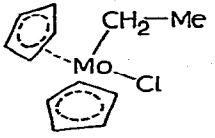
Other complexes containing η^5-C_5H_5 groups: *266, 293, 294, 297, 299, 300, 305, 306, 307, 308, 309, 310, 317, 318, 319, 321, 327, 328, 330, 331, 332, 333, 351, 352, 353, 354, 359, 359a, 361, 362, 369, 379, 380, 381, 382, 382a, 382b, 383, 390, 392, 393.*



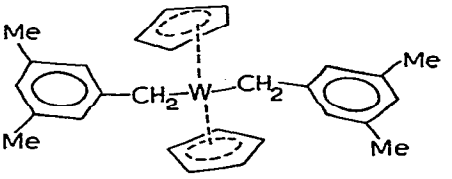
(235) $ZrCl[CH_2CH(AlEt_2)_2](C_5H_5)_2$ [221]



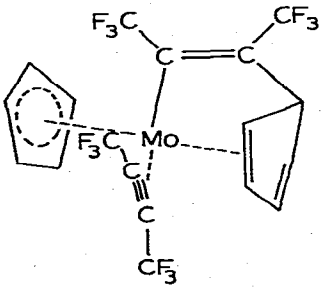
(236) $NbEt(C_2H_4)(C_5H_5)_2$ [131]



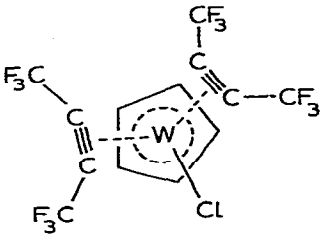
(237) $(C_5H_5)_2MoClEt$ [60]



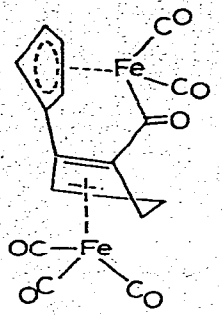
(238) $W(CH_2C_6H_3Me_2)_2(C_5H_5)_2$ [288]



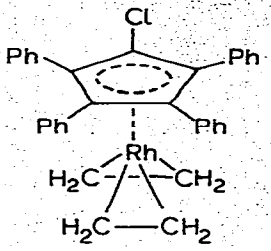
(239) $Mo[C(CF_3)=C(CF_3)C_5H_5][C_2(CF_3)_2](C_5H_5)$ [105]



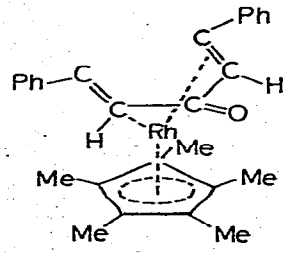
(240) $WCl[C_2(CF_3)_2]_2(C_5H_5)$ [105]



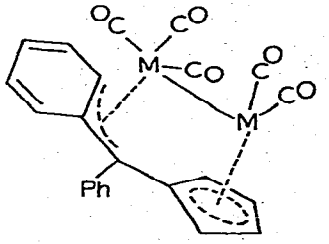
(241) $Fe(CO)_2COC_6H_6Fe(CO)_3(C_5H_4)$ [179]



(242) $Rh(C_2H_4)(C_5Ph_4Cl)$ [302]

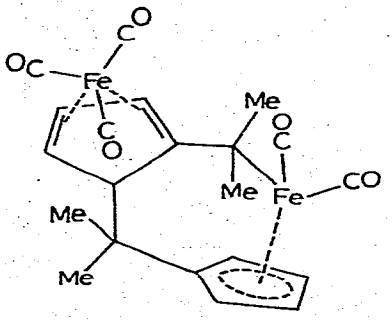


(243) $Rh(dba)(C_5Me_5)$ [279]

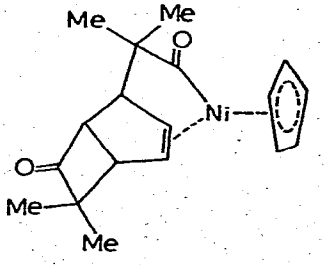


$M_2(CO)_5(C_5H_4{=}CPh_2)$
(244) M = Fe [226]; (245) M = Ru [242]

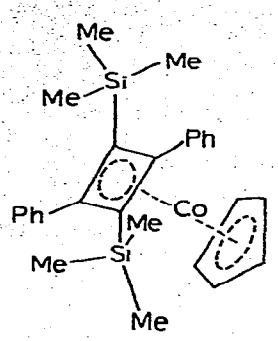
(246) No structure



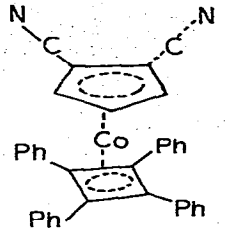
(247) $Fe_2(CO)_5(Me_2CC_5H_4)_2$ [226]



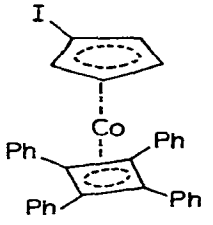
(248) $Ni(C_5H_5)[C_5H_5(C_2Me_2O)_2]$ [191]



(249) $Co[C_4Ph_2(SiMe_3)_2](C_5H_5)$ [280]

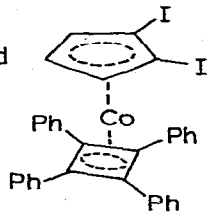


(250) $Co(C_4Ph_4)(C_5H_4CN)$ [301]



(251) $Co(C_4Ph_4)(C_5H_4I)$ [301]

CN group disordered



(252) $Co(C_4Ph_4)(C_5H_3I_2)$ [301]

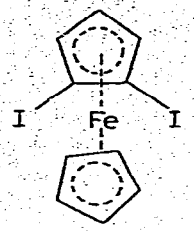
(g) *Substituted ferrocenes*

[Structures *253* - *258*]

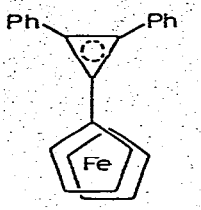
(*253*) 4 independent molecules: 2 nearly prismatic (ϕ 8°), 2 intermediate (ϕ 21°). (*255*) Racemic form, m.p. 288°, rings totally eclipsed, dihedral 10°. (*256*) Twinned; confirms structure formed from $FcCMe_2^+ + C_5H_6$ stereospecifically; ring planes inclined 7° by H atom repulsion.

(*257*) Confirmation and refinement using automatic diffractometer data; rings rotated by 8.5° from fully eclipsed. (*258*) Deformation of molecule to accommodate two *endo*-Me groups.

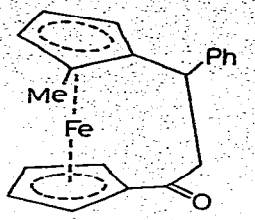
See also: *366a*.



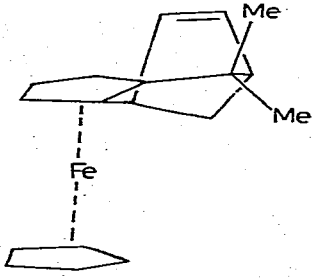
(253) $Fe(C_5H_5)(C_5H_3I_2)$ [58]



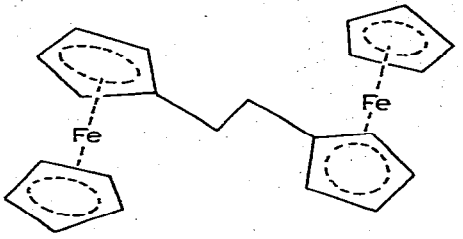
(254) $[FcC_3Ph_2]BF_4$ [259]



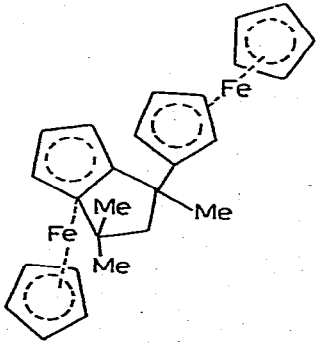
(255) $Fe[C_5H_3(Me)CH{-}nCH_2COC_5H_4]$ [211]



(256) $Fe(C_5H_5)(C_{13}H_{15})$ [186]



(257) $Fc(CH_2)_2Fc$ [238]



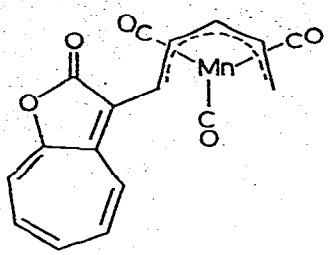
(258) $Fe(C_5H_3CMe_2CH_2CMeFc)(C_5H_5)$ [269]

(h) *Acyclic* η^5*-ligands*

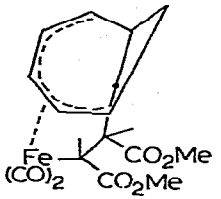
[Structures *259* - *260*]

(*259*) From $Mn_2(CO)_{10}$ and 2 trcpone molecules, one opened to give first acyclic η^5-dienyl-Mn complex. (*260*) Product from $Fe(CO)_3(C_7H_8)$ + Me_2 maleate.

See also: *394*.



(259) $Mn(CO)_3(C_{14}H_{11}O_2)$ [183]



(260) $Fe(CO)_2[C_7H_8C_2H_2(CO_2Me)_2]$ [146]

η^6-LIGANDS

(a) *Cyclic η^6-ligands (arenes)*

[Structures *261* - *268*]

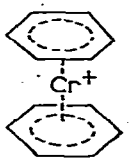
(*262*) Structural studies in conjunction with NMR correlations, particularly axial Me located above naphthalene ring; some asymmetry in C_6-Cr bond.

(*263a*) Formed by pyrolysis of As-donor complex; one As disordered.

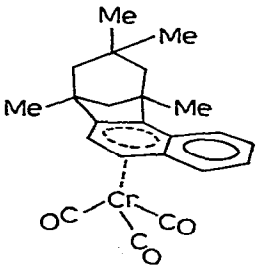
(*264*) Planar Mo_2Cl_2 unit. (*265*) Dinitrogen complex, mesitylene not quite planar. (*266*) Zwitterionic complex from $RuCl(PPh_3)_2(C_5H_5)$ + BPh_4^-.

(*267*) H located at ∿ 1.7Å from Ru.

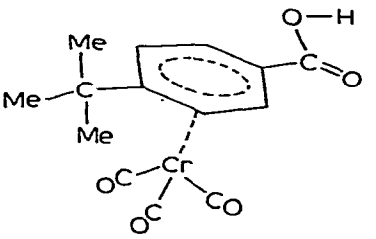
See also: *360*, *371*, *372*.



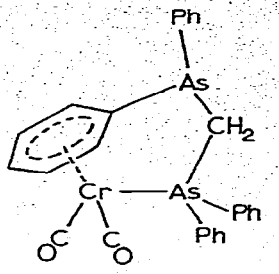
(261) $[Cr(C_6H_6)]^+$



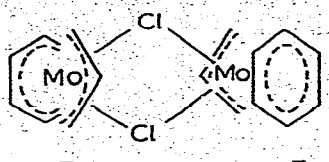
(262) $Cr(CO)_3(C_{20}H_{24})$ [245]



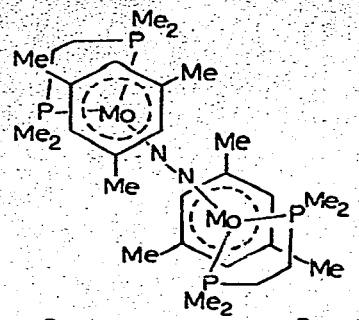
(263) $Cr(CO)_3[C_6H_4(CO_2H)Bu^t]$ [127]



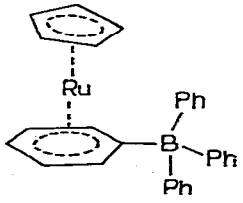
(263a) $Cr(CO)[(\eta^6\text{-}Ph)AsPhCH_2AsPh_2]$ [274]



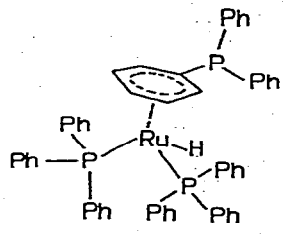
(264) $[MoCl(C_3H_5)(C_6H_6)]_2$ [189]



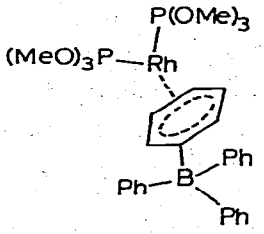
(265) $[Mo(dmpe)(C_6H_3Me_3)]_2N_2$ [297]



(266) $Ru(C_5H_5)(\eta\text{-}PhBPh_3)$ [290]



(267) $[RuH(PPh_3)_2(\eta\text{-}PhPPh_2)]^+$ [360]

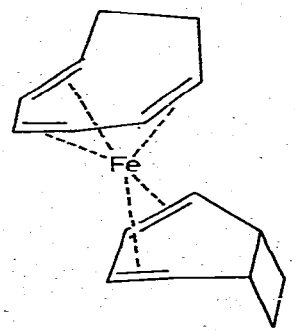


(268) $Rh[P(OMe)_3]_2(\eta\text{-}Ph)BPh_3$ [296]

(b) *Acyclic* η^6*-ligands*

[Structure *269*]

(*269*) Complex contains two valence tautomers of cycloocta-1,3,5-triene as η^4 and η^6 ligands.



(269) $Fe(C_8H_{10})_2$ [168]

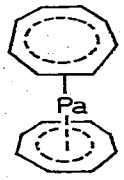
η^7-LIGANDS

See *369*, *377*, *378*.

η^8-LIGANDS

[Structure *270*]

(*270*) Shown to be isostructural with U, Th derivatives by powder pattern only.



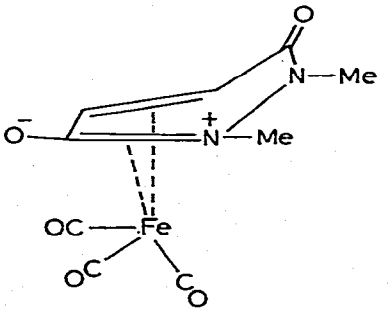
(270) $Pa(C_8H_8)_2$ [163]

η-HETEROATOM LIGANDS

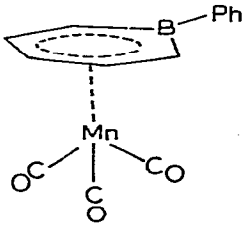
[Structures *271* - *273*]

(*271*) Zwitterionic heterodiene, non-planar pyridazine ring.

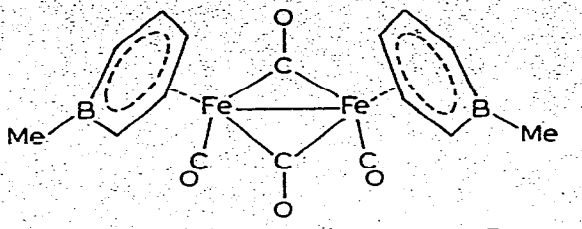
(*272*)(*273*) Further examples of η-borabenzene complexes; Fe complex *cis*; in both M-B > M-C bond length.



(271) $Fe(CO)_3(C_5H_5N_2O_2)$ [50]



(272) $Mn(CO)_3(C_5H_5BPh)$ [123]



(273) $[Fe(CO)_2(C_5H_5BMe)]_2$ [123]

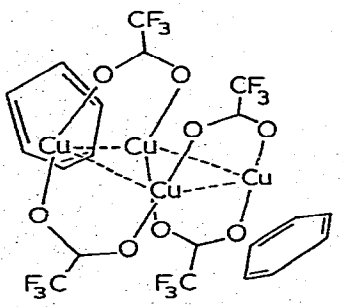
COPPER AND SILVER COMPLEXES

[Structures *274* - *281*]

Complexes containing these elements have been listed separately because they often contain structural features not generally found with the other transition elements.

(*274*) Aromatic weakly bonded, displaced by olefin (indene) to give (*275*). (*275*) Not fully refined; indicates one benzene replaced by two olefins. (*277*) 2 parallel linear chains of Ag atoms, 3- and 4-coordinate, bridged by CF_3CO_2 and C_6H_6. (*278*)(*279*) Ag interacts with localised double bonds. (*280*) No Ag-aromatic interaction; polymer formed by Ag-NO_3 chain. (*281*) Ag bonded to active CH_2 of one acac ring, also to ClO_4 and H_2O via O.

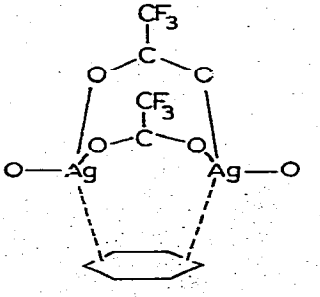
See also: *97*, *137*, *138*, *226*, *230*, *373*.



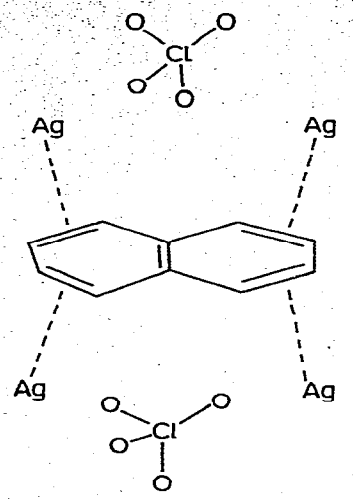
(274) $Cu_4(O_2CCF_3)_4(C_6H_6)_2$ [208]

(275) No diagram available

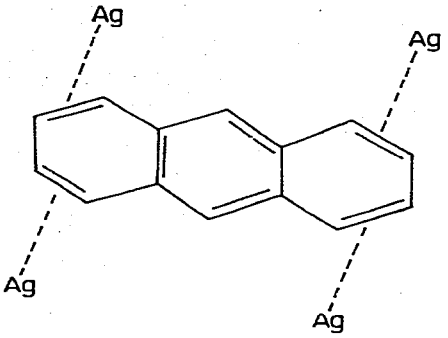
(276) No structure



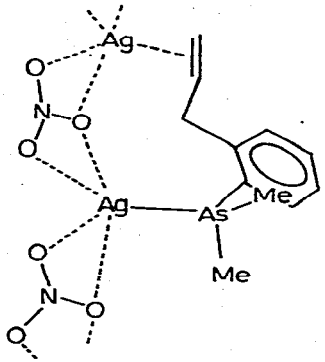
(277) $C_6H_6(AgO_2CCF_3)_2$ [56]



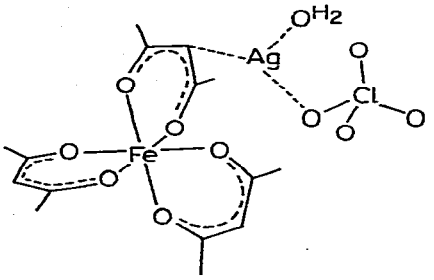
(278) $C_{10}H_8(AgClO_4)_4 4H_2O$ [57]



(279) $C_{14}H_{10}(AgClO_4)_4$ [122]



(280) $\left\{Ag_2[C_6H_4(CH_2CH=CH_2)AsMe_2]\right\}^{2+}$ [76]



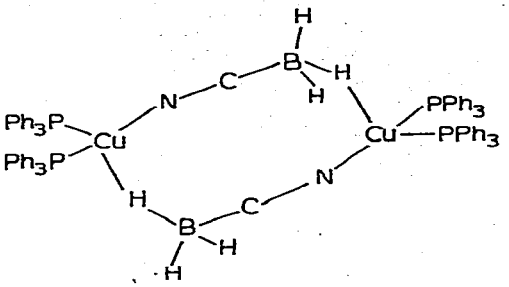
(281) $Fe(acac)_3 AgClO_4 H_2O$ [149]

POLYHEDRAL METALLOBORANE COMPLEXES

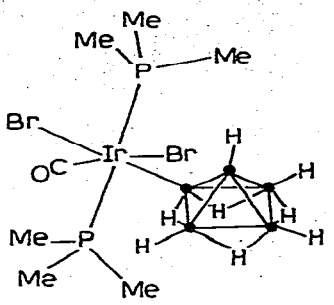
[Structures *282* - *288*]

(*282*) Ligand attached by *one* H and *CN* to different Cu atoms. (*283*) Product from oxidative addition of B_5H_8Br + $IrBr(CO)(PMe_3)_2$; *trans* influence B_5H_8 > CO (Ir-Br, 2.638, 2.516Å, resp.); (*284*) Stabilisation of B-H species by electron-withdrawing group; (*285*) Mn bonded via 3 Mn-H-B bridges, 2 to

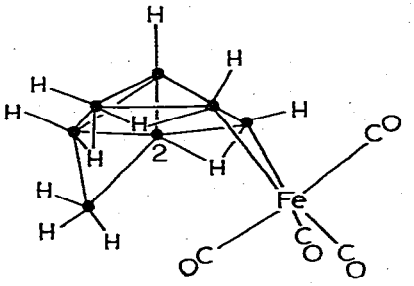
open face, 1 to base of cage; H_a rapidly exchanges between three B atoms. (*286*) Unit cell has *dl* pair of 5- and 7-THF isomers; open MnB_9 cluster. (*287*) Crystal contains pairs of 8- and 10-substituted isomers; ether cleaved, with rearrangement of MnB_9 in (*286*); (*288*) Earlier structure omitted from previous surveys; Fe bonded to B_4S; S and one B disordered.



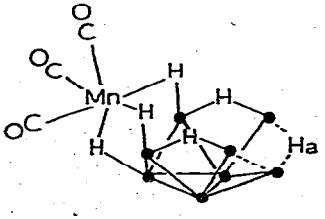
(282) $[Cu(NCBH_3)(PPh_3)_2]_2$ [369]



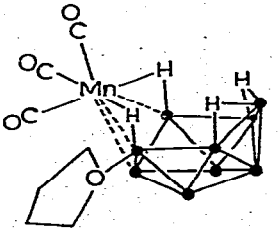
(283) 2-$[IrBr_2(CO)(PMe_3)_2]$ B_5H_8 [39]



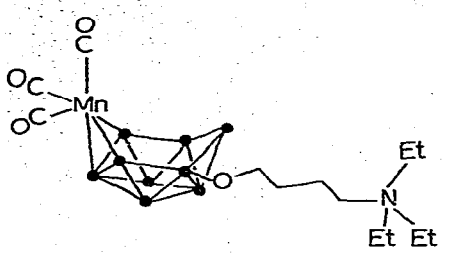
(284) $\{[Fe(CO)_4]B_7H_{12}\}^-$ [19]
one H hidden behind B(2)



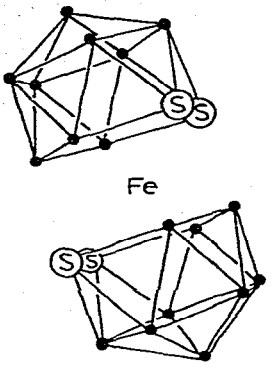
(285) $(CO)_3MnB_8H_{13}$ [17]



(286) 5-thPf)-6-$[Mn(CO)_3]B_9H_{12}$ [38]



(287) 6-$[Mn(CO)_3]$-10-$[Et_3N(CH_2)_4O]$ B_9H_{12} [119]



(288) $[Fe(B_9H_{10}S_2)_2]^{2-}$ [378] one B and S atoms disordered

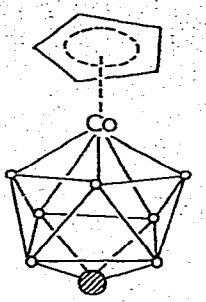
POLYHEDRAL METALLOCARBORANE COMPLEXES

In all structures ⊘ indicates carbon atoms.

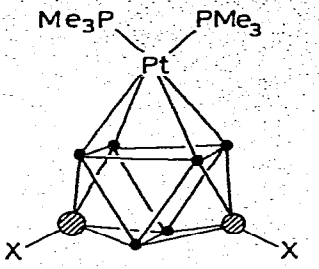
[Structures *289* - *302*]

(*289*) Approximate tricapped (by 2B,C) trigonal prism, Co bonded to 5B.

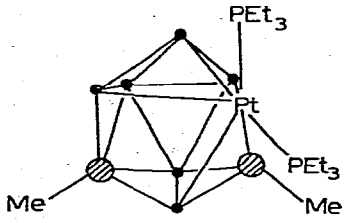
(*291*) Cyclobutadiene analogue, Pt caps prism. (*292*) *Nido* derivative, Pt in prism. (*294*) Distorted bicapped square antiprism. (*295*) 1,2,3-η^3-Carbadiboraallyl ligand. (*296*) *nido*-Polyhedron, fluxional with mirror image. (*297*) Terminal 11-vertex octahedron ($CoC_2B_8H_{10}$). (*298*) *closo*-Icosahedron, bicapped square antiprism. (*299*) Short Co-Co bond, distorted icosahedron. (*300*) 13-Apex docosahedron, Co bonded to non-planar 6-atom ring; fluxional. (*301*) Carborane bonded via Rh-C σ bond, Rh-H-B bridge bond. (*302*) C-bonded carborane; one PPr^n_3 ligand metallated to give 3-membered ring Pt-P-C, considered to be stabilised Pr_2P=CHEt ligand.



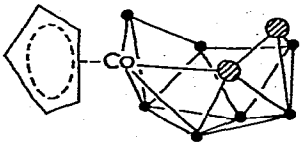
(289) Cs $[Co(C_5H_5)CB_7H_8]$ [28]



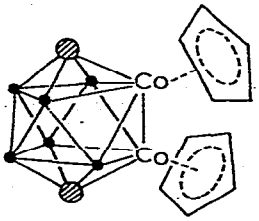
closo-1-$[(Me_3P)_2Pt]$-6,8-$X_2C_2B_6H_6$ [46]
(290) X = H ; (291) X = Me



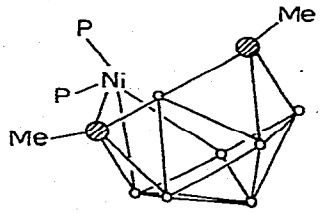
(292) *nido*-6-$[(Et_3P)_2Pt]$-5,8-$Me_2C_2B_6H_6$ [46]



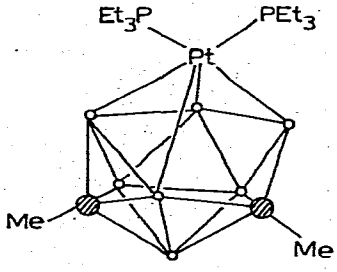
(293) 8-$[Co(C_5H_5)]$-6,7-$C_2B_7H_{11}$ [36]



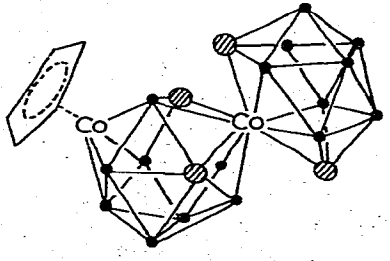
(294) 2,9-$[Co(C_5H_5)]_2$-1,10-$C_2B_6H_8$ [91]



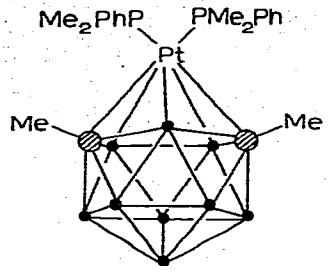
(295) $Ni(PEt_3)_2(Me_2C_2B_7H_9)$ [175]
P ≡ PEt_3



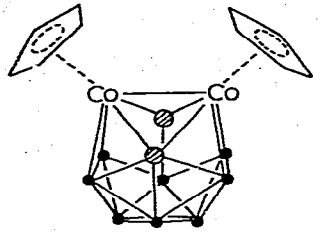
(296) $[Pt(PEt_3)_2]Me_2C_2B_7H_7$ [174]



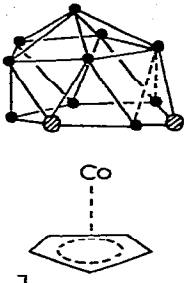
(297) $[(C_5H_5)Co(C_2B_8H_{10})Co(C_2B_8H_{10})]^-$ [53]



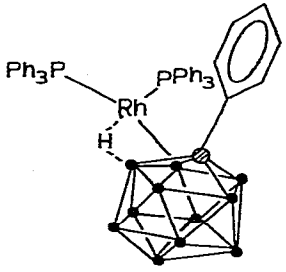
(298) 1-[Pt(PMe$_2$Ph)$_2$]-2,4-Me$_2$C$_2$B$_9$H$_9$[174]



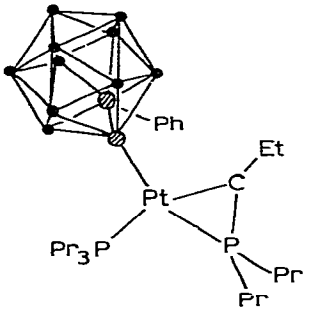
(299) 2,3-[Co(C$_5$H$_5$)]$_2$-1,7-C$_2$B$_8$H$_{10}$[92]



(300) Co(C$_5$H$_5$)(7,9-C$_2$B$_{10}$H$_{12}$)[37]



(301) Rh(CB$_{10}$H$_{10}$CPh)(PPh$_3$)$_2$[347]



(302) 1-[Pt(CHEtPPr$_2$)(PPr$_3$)]-2-PhC$_2$B$_{10}$H$_{10}$[272]

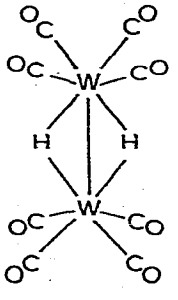
COMPLEXES CONTAINING METAL-METAL BONDS

(a) *Homobinuclear transition metal complexes*

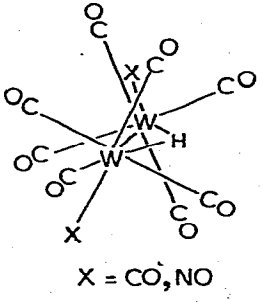
[Structures *303* - *328*]

(*303*) H atoms located, planar W(μ-H)$_2$W unit, short W-W interaction. (*304*) X-ray and n.d., single bent W-H-W 2e,3-centre bond; NO disordered over 2 axial positions. (*305*) Short Cr≡Cr triple bond, *trans* C_5 groups. (*306*)(*307*)(*308*) Classical structures redetermined to provide more accurate M-M bond lengths, in conjunction with NMR studies; bond lengths Cr >> Mo > W; Cr complex shows internal strain, steric crowding, giving Cr-Cr 0.06Å longer than Mo-Mo. (*310*) From [Mo(CO)$_3$(C$_5$H$_5$)]$_2$ + S(NBu^t)$_2$. (*311*) Another

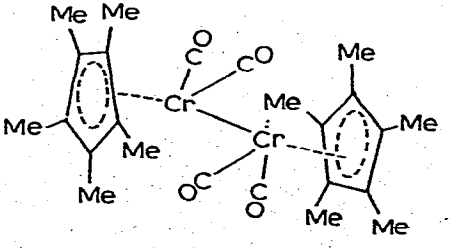
classical structure redetermined, removing previous inconsistencies e.g. Fe-CO(terminal) < Fe-CO(bridge); record low angle at μ-CO (77.6°). (*312*) With (*329*) completes isoelectronic series of binuclear Co_2, $FeCo^-$, Fe_2^{2-} carbonyls; Fe_2 dianion staggered (D_{3d}). (*313*) Contains semi-bridging CO group. (*314*) Long Fe-Fe bond, overall structure related to that suggested for $Os_2(CO)_9$; bridge CO symmetrical, all CO's rapidly scrambled. (*316*) Comparison with Fe_2N_2, Fe_2S_2 systems. (*317*)(*319*)(*321*) Series of structures determined in connection with NMR studies of intramolecular dynamics (*cis-trans* equilibria). (*318*) *cis*-C_5 groups; contains bridging $C{=}C(CN)_2$ group, similar π-acceptor properties to bridge CO; compare with (*220*). (*322*)(*323*) Contain short Fe≡Fe triple bonds. (*325*)(*326*) Both from benzocyclobutadiene-$Fe(CO)_3$ + $Fe_3(CO)_{12}$; *sym* and *unsym* isomers not interconverted. (*327*) Identity of Fischer's "$Rh_2(CO)_4(C_5H_5)_2$" with this complex confirmed. (*328*) Early structure omitted from previous surveys; characterisation of bridging MeNC group, dihedral between 2 Ni_2CN planes 121.1°; short Ni-Ni bond.



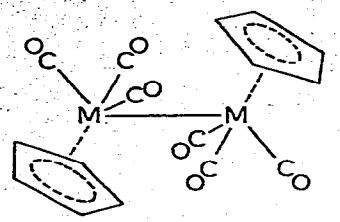
(303) $(NEt_4)_2[W_2H_2(CO)_8]$ [40]



(304) $W_2H(CO)_9(NO)$ [48]

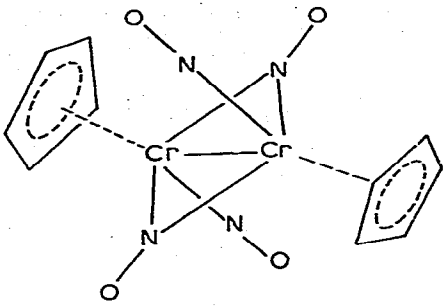


(305) $[Cr(CO)_2(C_5Me_5)]_2$ [252]

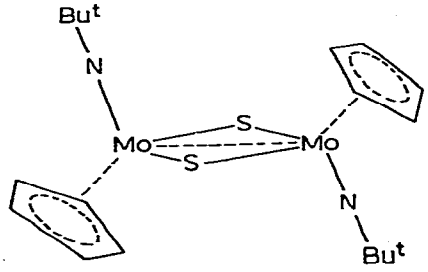


$M_2(CO)_6(C_5H_5)$

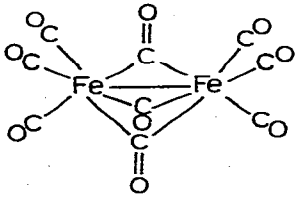
(306) M = Cr [154]; (307) M = Mo [155]
(308) M = W [155]



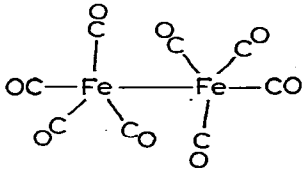
(309) $[Cr(NO)_2(C_5H_5)]_2$ [62]



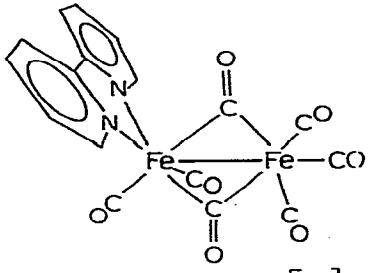
(310) $[MoS(NBu^t)(C_5H_5)]_2$ [193]



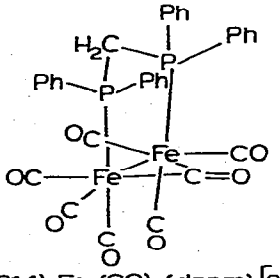
(311) $Fe_2(CO)_9$



(312) $[(Ph_3P)_2N]_2[Fe_2(CO)_8]$ [47]

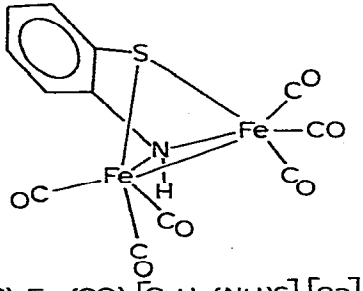


(313) $Fe_2(CO)_7(bipy)$ [176]

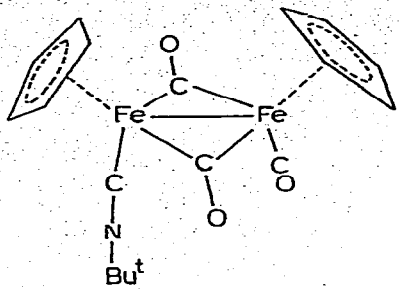


(314) $Fe_2(CO)_7(dppm)$ [299]

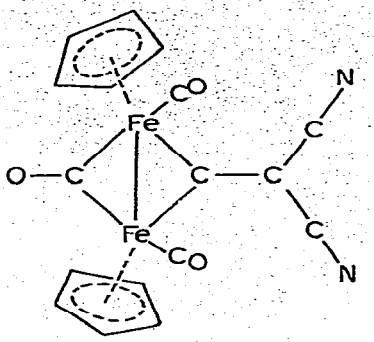
(315) No structure



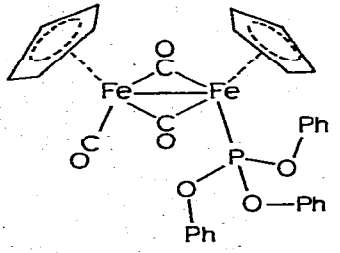
(316) $Fe_2(CO)_6[C_6H_4(NH)S]$ [83]



(317) $Fe_2(CO)_3(CNBu^t)(C_5H_5)_2$ [185]

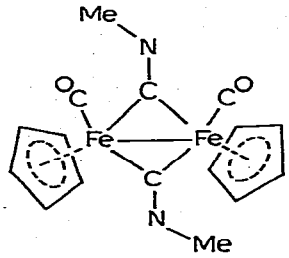


(318) $Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2](C_5H_5)_2$ [178]

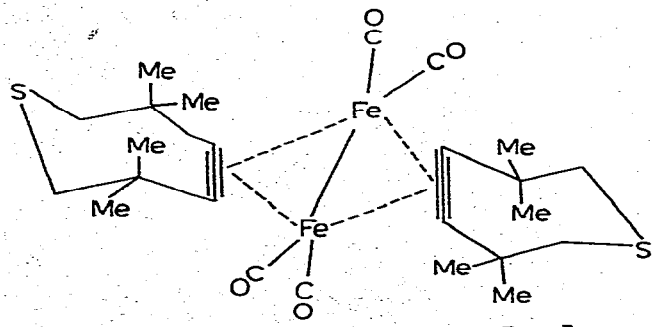


(319) $Fe_2(CO)_3[P(OPh)_3](C_5H_5)_2$ [298]

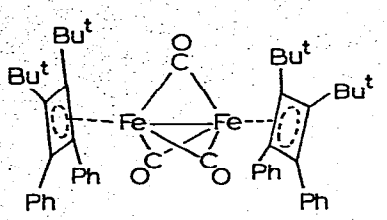
(320) No structure



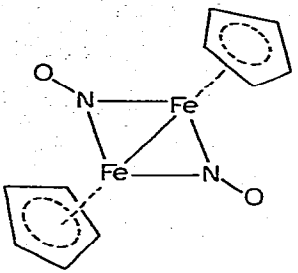
(321) $[Fe(CO)(CNMe)(C_5H_5)]_2$ [160]



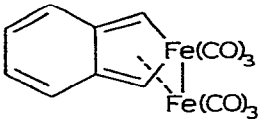
(322) $[Fe_2(CO)_4(C_6H_6Me_4S)]_2$ [254]



(323) $Fe_2(CO)_3(C_4Bu^t_2Ph_2)_2$ [278]

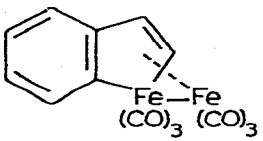


(324) $[Fe(NO)(C_5H_5)]_2$ [63]

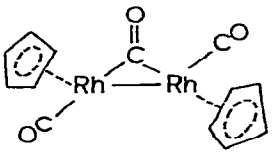


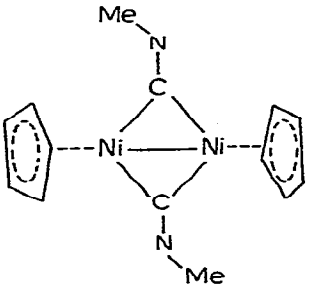
sym

(325) $Fe_2(CO)_6(C_8H_6)$ [121]



unsym





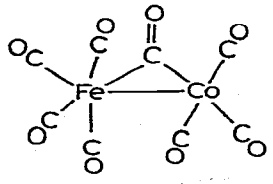
(326) $Fe_2(CO)_6(C_8H_6)$ [121] (327) $Rh_2(CO)_3(C_5H_5)_2$ [109] (328) $[Ni(CNMe)(C_5H_5)]_2$ [130]

(b) *Heterobinuclear transition metal complexes*

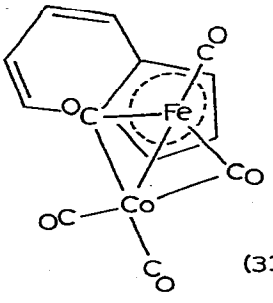
[Structures *329* - *333*]

(*329*) Comparison with (*312*), $Co_2(CO)_8$ revealed unusual differences, Co, Fe not distinguished, illustrated arrangement favoured.

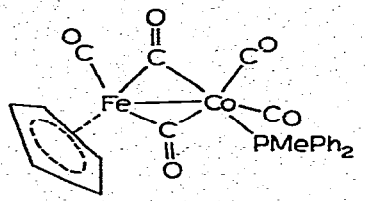
(*330*)(*331*)(*332*)(*333*) Series of complexes studied in connection with IR studies of bridge-terminal CO equilibria; non-planar distorted $M(CO)_2M'$ units, dihedral 148.0° (*330*), 154.6° (*331*), 133.7° (*333*).



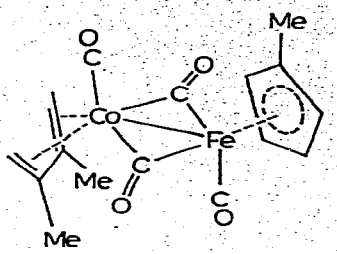
(329) $[(Ph_3P)_2N][FeCo(CO)_8]$ [47]



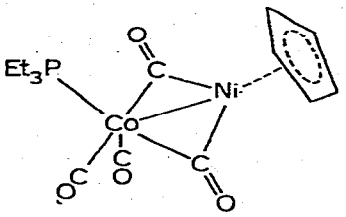
(330) $FeCo(CO)_5(ind)$ [138]



(331) $FeCo(CO)_5(PMePh_2)$ (C_5H_5) [243]



(332) $FeCo(CO)_4(C_4H_4Me_2)$ (C_5H_4Me) [141]



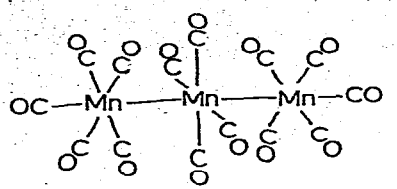
(333) $CoNi(CO)_4(PEt_3)(C_5H_5)$ [148]

(334) No structure

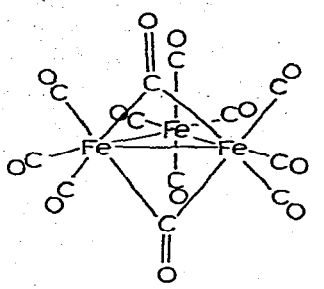
(c) *Polynuclear clusters containing CO, PR_3 ligands*

[Structures *335* - *346*]

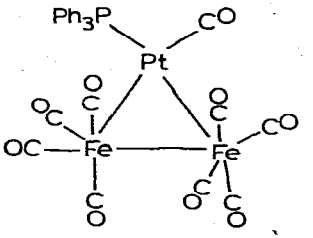
(*335*) Corrects $[H_2Mn_3(CO)_{12}]^-$ formulation; comments on linear *vs* bent M-M-M and M-H-M bonds. (*336*) Increased precision, 2 disordered 'half-molecules' resolved; unsymmetrical CO bridges, solution dynamic behaviour discussed. (*337*)(*338*) M-M bond lengths discussed in terms of *closo* structure or electron deficiency. (*340*) Twinned, disordered; Ir prefers apical position with only terminal CO. (*341*) Co, Ni not distinguished in octahedral cluster, statistical distribution. (*342*) Comparison with (*343*) shows unprecedented differences in geometries adopted by congener elements as result of steric requirements. (*343*)(*344*)(*345*)(*346*) Series of cluster anions formed by stacking triangular $Pt(CO)_3(\mu\text{-}CO)_3$ units; resulting Pt-Pt bonds same as in metal; steric requirements cause twisting of stack.



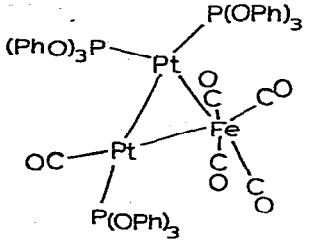
(335) $[Mn_3(CO)_{14}]^-$ [136]



(336) $Fe_3(CO)_{12}$ [101]

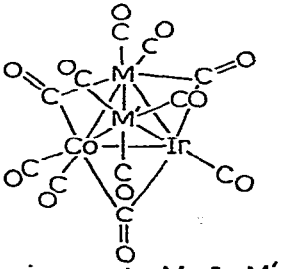


(337) $Fe_2Pt(CO)_9(PPh_3)$ [273]



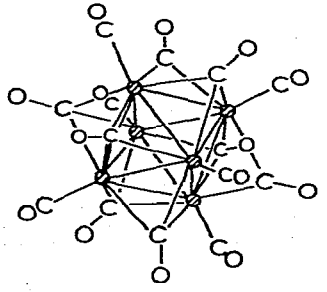
(338) $FePt_2(CO)_5[P(OPh)_3]_3$ [364]

(339) No structure

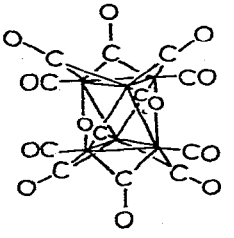


isomer A M = Ir, M′ = Co
isomer B M = Co, M′ = Ir
Proportion A:B = 1:5

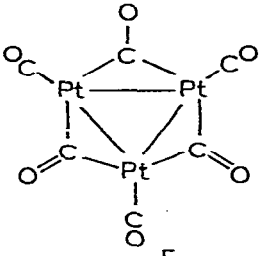
(340) $Co_2Ir_2(CO)_{12}$ [100]



(341) $[Co_4Ni_2(CO)_{14}]^{2-}$ [135]



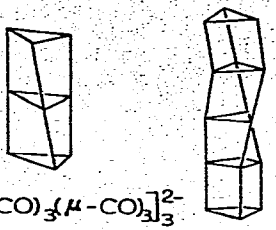
(342) $[Ni_3(CO)_3(\mu\text{-}CO)_3]_2^{2-}$



Building block in $[Pt_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ [103]

(343)

$[Pt_3(CO)_3(\mu\text{-}CO)_3]_2^{2-}$



(344) $[Pt_3(CO)_3(\mu\text{-}CO)_3]_3^{2-}$

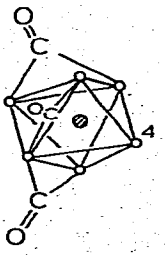
(345) $[Pt_3(CO)_3(\mu\text{-}CO)_3]_4^{2-}$

(346) $[Pt_3(CO)_3(\mu\text{-}CO)_3]_5^{2-}$

(d) *Polynuclear clusters containing Main Group Elements*

[Structures *347* - *359a*]

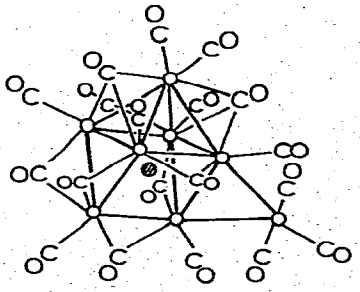
(*347*) 3 semi-bridging CO groups, octahedrally coordinated C atom. (*348*) First completely asymmetric cluster. (*349*) Central Rh linked to 12 other metal atoms. (*351*) Paramagnetic, from $Ni(C_5H_5)_2 + S(NBu^t)_2$. (*352*) 3 of 4 faces bridged by H. (*353*) N.d.; symmetrical bridging H, bent 3-centre Mo-H-Mo bond. (*354*) Ligands crowd Mn_2As nucleus, result in bent Mn-C-O (160°). (*355*) From isomer by insertion of bridging $AsMe_2$ group. (*356*) From *cis*-$CF_3C(AsMe_2)=C(CF_3)AsMe$. (*357*)(*358*) Planar Mn_2M_2 ring. (*359*) *Cis* form, structure determined in connection with IR, NMR studies of molecular dynamic properties. (*359a*) Open Fe-Rh-Fe system confirms prediction of unstable *closo*-cluster resulting from substitution of CO by highly basic PPh_2 groups.



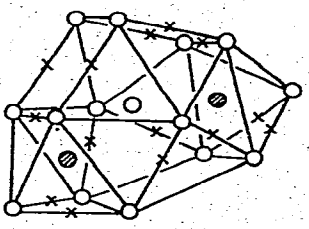
(347) $[Fe_6C(CO)_{15}]^{2-}$

Fe^4 has 3 terminal CO; all other Fe have 2

3 semi-bridging CO shown

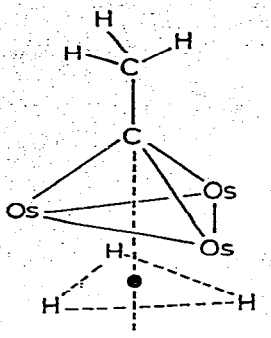


(348) $Rh_8C(CO)_{19}$ [224]

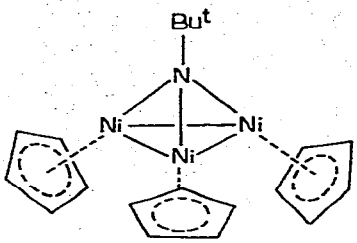


(349) $[Rh_{15}C_2(CO)_{28}]^-$ [224]

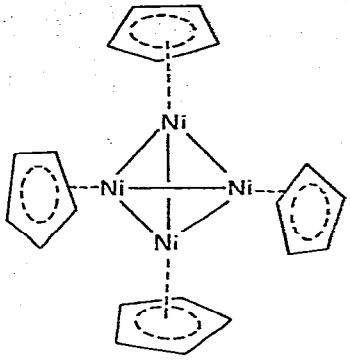
X denotes bridging CO group



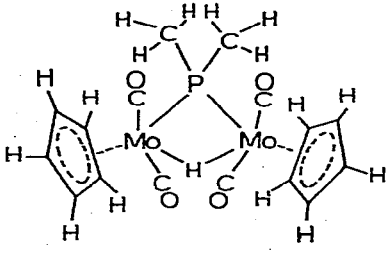
(350) $Os_3H_3(CMe)(CO)_9$ [71]



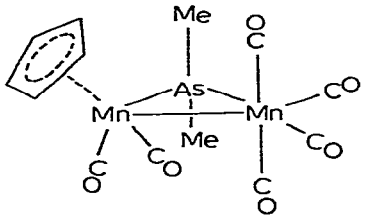
(351) $Ni_3(NBu^t)(C_5H_5)_3$ [202]



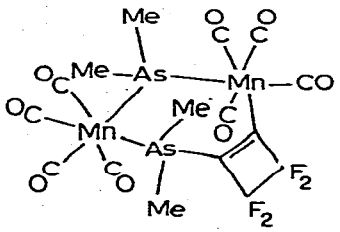
(352) $Ni_4H_3(C_5H_5)_4$ [215]



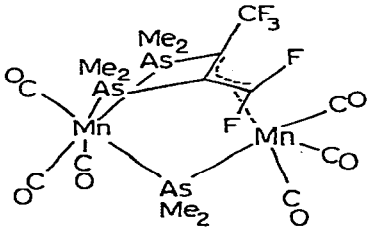
(353) $Mo_2H(CO)_4(PMe_2)(C_5H_5)$ [164]



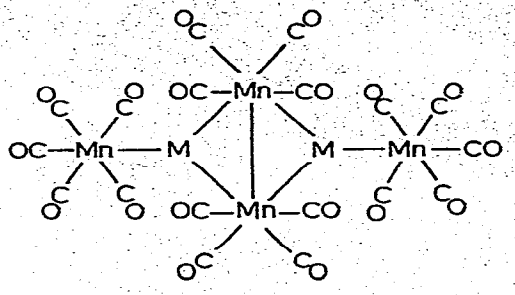
(354) $Mn_2(CO)_6(AsMe_2)(C_5H_5)$ [111]



(355) $Mn_2(CO)_8(AsMe_2)[C_4F_4(AsMe_2)]$ [157]

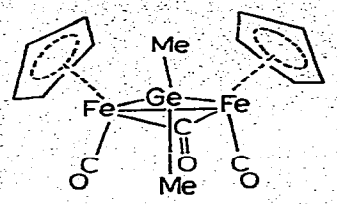


(356) $Mn_2(CO)_6(AsMe_2)[(Me_2As)_2C_4F_5]$ [165]

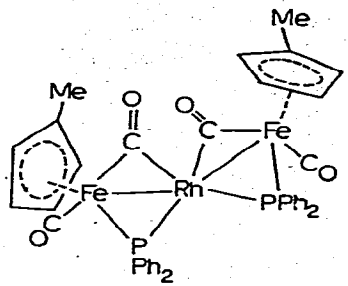


$M_2Mn_4(CO)_{18}$

(357) M = Ga ; (358) M = In [195,196]



(359) $Fe_2(GeMe_2)(CO)_3(C_5H_5)_2$ [147]



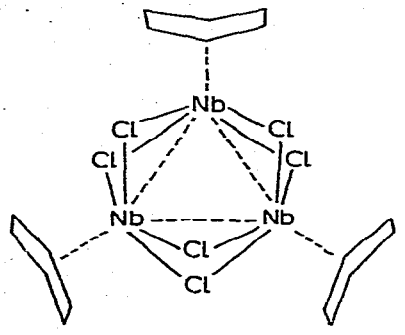
(359a) $[Fe_2Rh(CO)_4(PPh_2)_2(C_5H_4Me)_2]^+$ [330]

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

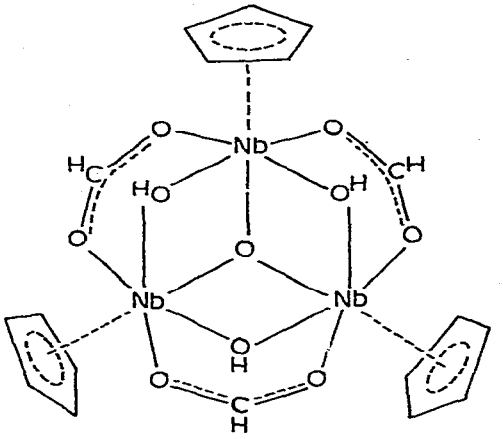
[Structures *360* - *373*]

(*360*) Apparent folding of arene molecules not significant from disorder; Nb-Nb bond order $\frac{1}{3}$. (*361*) Little Nb-Nb interaction, paramagnetic, cluster held by formate, OH and O bridges. (*362*) Solved by direct methods gives no evidence of disorder (cf. ref. 143). (*363*) 2 unsymmetrical bridging CO; correlation of Fe-Fe bond lengths with degree of symmetry of CO bridge in several Fe complexes. (*364*)(*365*) Formation of (*364*) from (*365*) involves CO elimination, M-M bond formation, and changes in PPh_2 bridge (see diagram); (*364*) contains ferracyclobutene system. (*366*) CO_2Me group derived from methanol + CO group. (*366a*) First ferrocene derivative with metal-metal bond involving central iron atom; C_5H_5 group also bridges Au atoms.

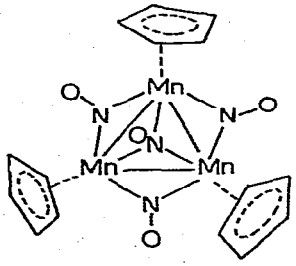
(*367*)(*368*) Stabilisation of pentalene and derivatives on Ru_3 clusters. (*369*) One C_8H_9 is η^5-tetrahydropentalenyl; second apparently attached to two Ru by 7 out of 8 carbons, geometry indicates isolated CH_2 group. (*370*) Same structure in 2 crystal forms. (*373*) Non-linear *transoid* Ir-C≡C-Ph (not *cis* bent); formal M-M bond order $\frac{3}{4}$.



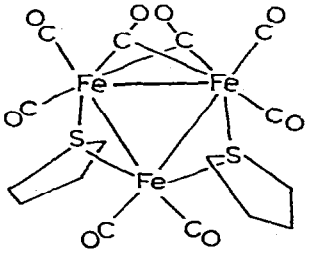
(360) $[Nb_3Cl_6(C_6Me_6)_3]^+$ [309]



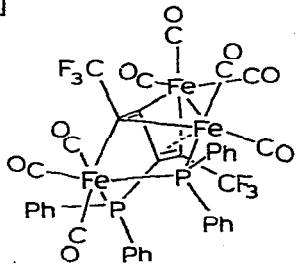
(361) $[(C_5H_5)Nb(O_2CH)(OH)]_3O$ [187,188]



(362) $Mn_3(NO)_4(C_5H_5)_3$ [142]

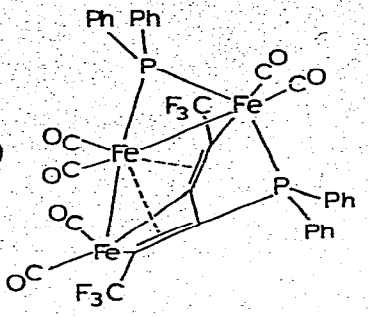


(363) $Fe_3(CO)_8(C_4H_8S)_2$ [162]

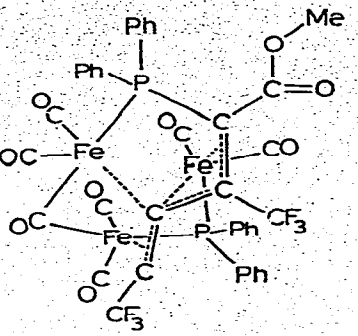


(364) $Fe_3(CO)_8(PPh_2)[Ph_2PC_4(CF_3)_2]$ [315]

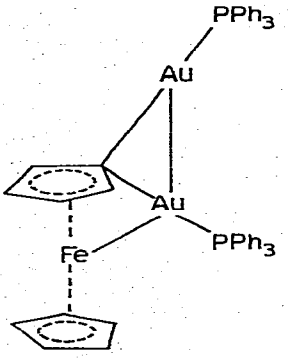
See separate diagram for relationships between (364) and (365)



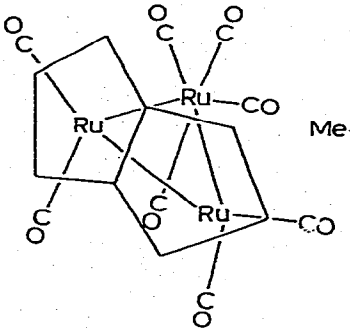
(365) $Fe_3(CO)_7[Ph_2PC_4(CF_3)_2](PPh_2)$ [310]



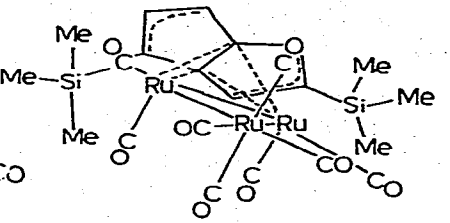
(366) $Fe_3(CO)_7\{Ph_2PC_4(CF_3)_2\}(CO_2Me)(PPh_2)$ [321]



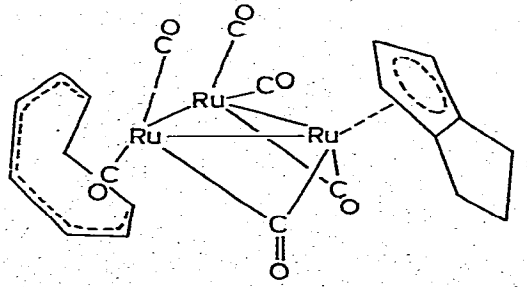
(366a) $[FcAu_2(PPh_3)_2]^+$ [348, 349]



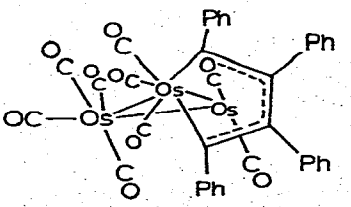
(367) $Ru_3(CO)_8(C_8H_6)$ [153]



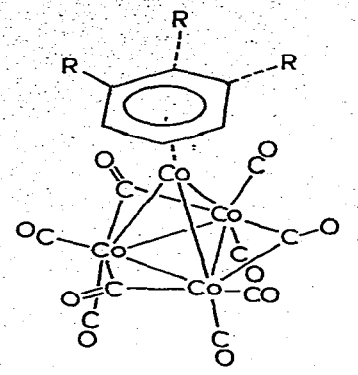
(368) $Ru_3(CO)_8[C_8H_4(SiMe_3)_2]$ [240]



(369) $Ru_3(CO)_6(\eta^5\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)$ [237]

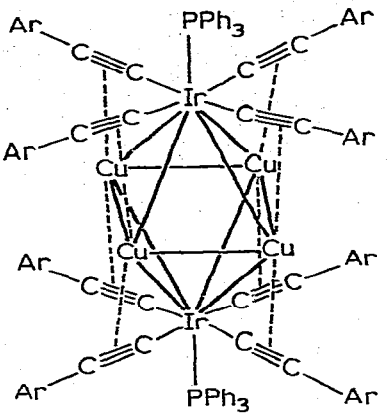


(370) $Os_3(CO)_9(C_4Ph_4)$ [311]



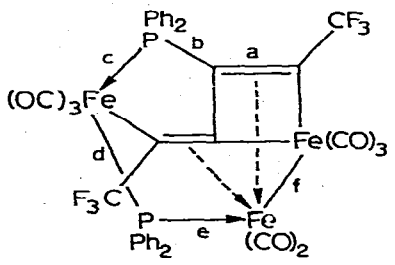
$Co_4(CO)_9(C_6H_4R_2)$ [137]

(371) R = H; (372) R = Me (disordered mixture of *o*- and *m*-isomers)



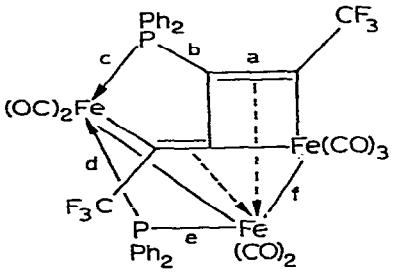
Ar = Ph

(373) $Ir_2Cu_4(C_2Ph)_8(PPh_3)_2$ [372]



(364)

a	1.240 (14) Å	1.39 (3) Å
b	1.905 (9)	1.84 (3)
c	2.305 (4)	2.241 (6)
d	2.330 (3)	2.173 (9)
e	2.277 (4)	2.292 (5)
f	2.514 (3)	2.532 (11)



(365)

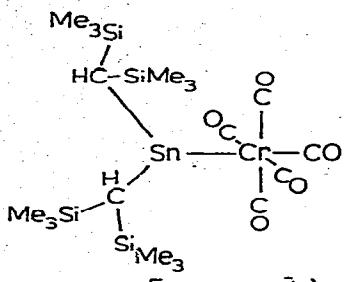
(f) *Complexes containing Transition Metal-Main Group metal bonds*

[Structures *375* - *398*]

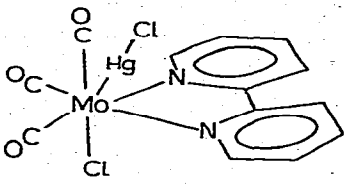
(*375*) 3-coordinate planar Sn in new ligand R_2Sn (R = bulky group).

(*376*) Capped (Cl) trigonal prism. (*380*) Covalent Mo-Mg bond, H not located. (*384*) (*385*) (*386*) Cd-Mn bond gives distorted octahedral Mn; comparison 4- and 5-coordinate Cd, effective increase of ∿ 0.1Å in

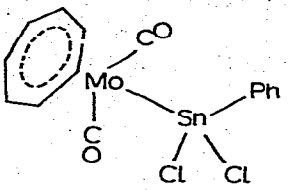
covalent radius. (*389*) Planar carbene, 8-membered $(ReGeOC)_2$ ring. (*390*) 2 rotational isomers (88:12) disordered in unit cell; show interconversion by NMR. (*392*) Ph-C≡C, 153°. (*393*) "Inorganic Grignard". (*394*) *Exo* Configuration for migrant $SiMe_3$ group [from $Ru(SiMe_3)_2(CO)_4$]. (*395*) Linear Sn-Os-Sn sequence. (*398*) Intermediate geometry (between TBP and SP); all H atoms located (in presence Cl, P, Sn, Ir).



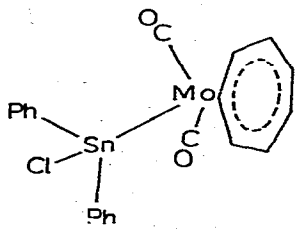
(375) $Cr\{Sn[CH(SiMe_3)_2]_2\}(CO)_5$ [204]



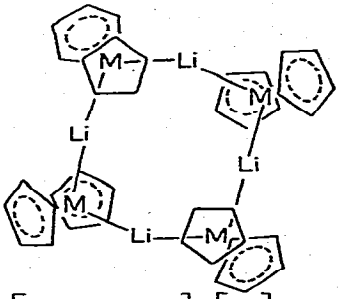
(376) $MoCl(HgCl)(CO)_3(bipy)$ [107]



(377) $Mo(SnCl_2Ph)(CO)_2(C_7H_7)$ [140]

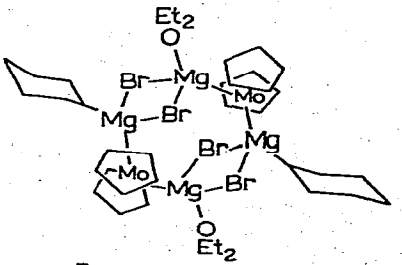


(378) $Mo(SnClPh_2)(CO)_2(C_7H_7)$ [140]

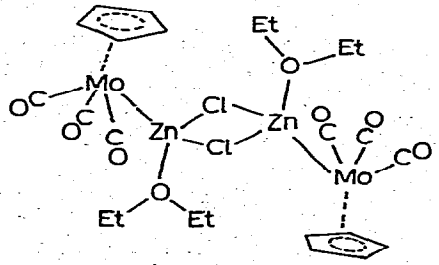


$[(C_5H_5)_2MLiH]_4$ [331]

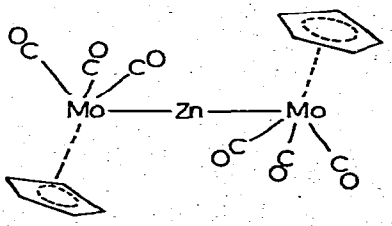
(379) M = Mo; (383) M = W



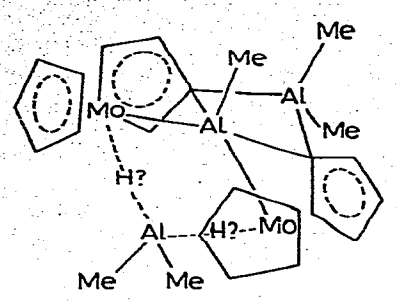
(380) $[(C_5H_5)_2MoHMgCyBr_2Mg(OEt_2)]_2$ [333]



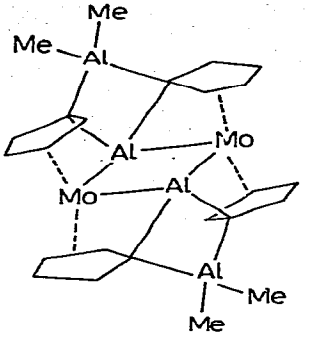
(381) $[(C_5H_5)(CO)_3Mo\text{-}ZnCl(OEt_2)]_2$ [156]



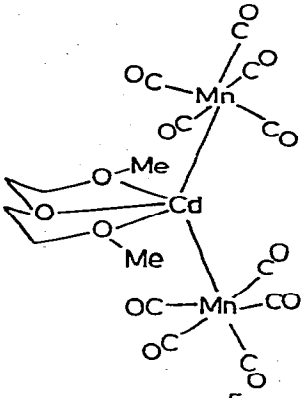
(382) $[Mo(CO)_3(C_5H_5)]_2Zn$ [156]



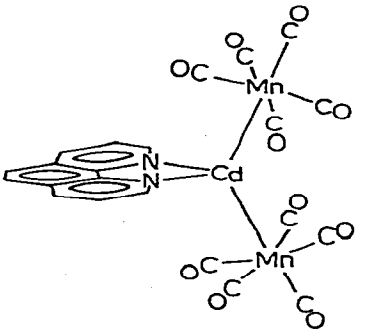
(382a) $[MoH(C_5H_4)(C_5H_5)]_2Al_3Me_5$ [264, 265]



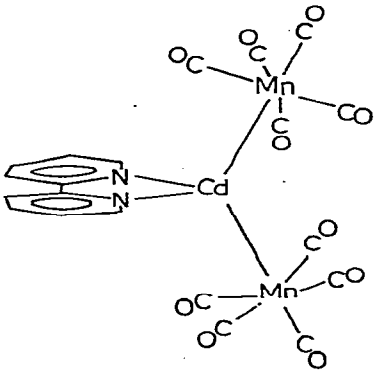
(382b) $[Mo(C_5H_4)_2Al_2Me_3]_2$ [264]



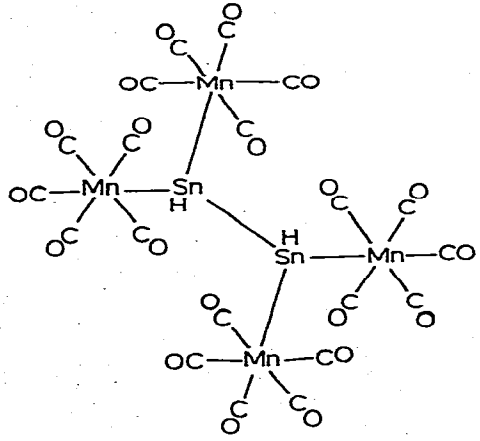
(384) Cd(diglyme)$[Mn(CO)_5]_2$ [159]



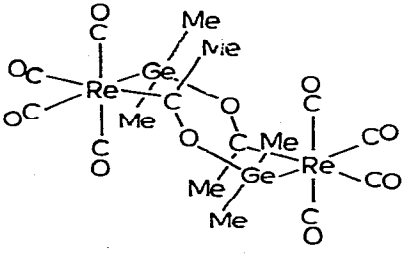
(385) Cd(phen)$[Mn(CO)_5]_2$ [206]



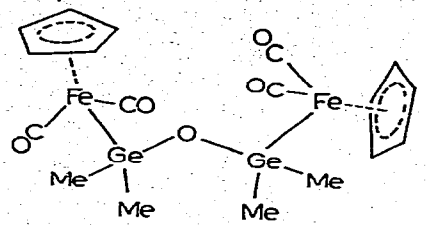
(386) Cd(bipy)$[Mn(CO)_5]_2$ [206]



(387) $H_2Sn_2[Mn(CO)_5]_4$ [205]

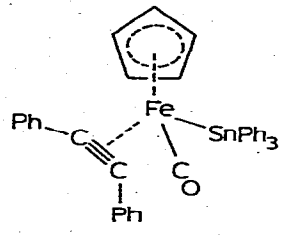


(389) $[Re(CO)_4(Me_2GeOCMe)]_2$ [166]

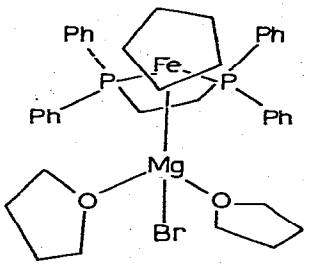


(390) $[Fe(CO)_2(C_5H_5)GeMe_2]_2O$ [190]

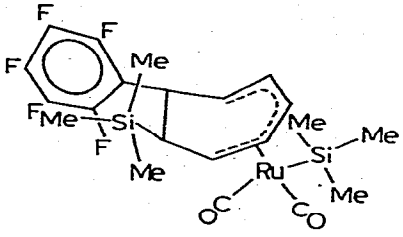
(388) (391) (397) No structures



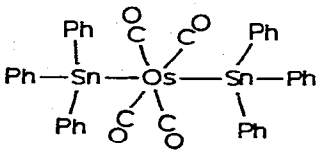
(392) $Fe(SnPh_3)(CO)(C_2Ph_2)$ [317]



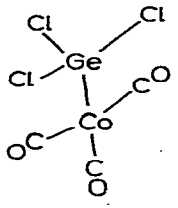
(393) $(C_5H_5)(dppe)FeMgBr$ [324]



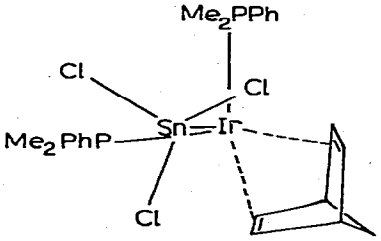
(394) $Ru(SiMe_3)(CO)_2[C_7H_7(C_6F_5)SiMe_3]$ [228]



(395) $Os(CO)_4(SnPh_3)_2$ [326]



(396) $Co(GeCl_3)(CO)_4$ [20]



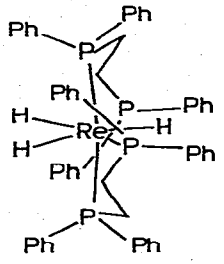
(398) $Ir(SnCl_3)(C_7H_8)(PMe_2Ph)_2$ [246]

HYDRIDE COMPLEXES

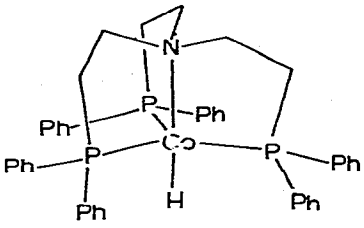
[Structures *399* - *403*]

(*399*) H not located, but H-H interactions indicate they occupy 3 equatorial positions in pentagonal bipyramid. (*401*) Non-stoichiometric Ni complex ($n \sim 0.5$), all molecules identical whether containing H or not, i.e. statistical 1:1 occupancy. (*402*) (*403*) H located in latter only.

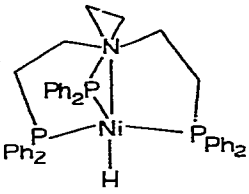
See also: *29*, *36*, *37*, *100*, *103*, *104*, *213*, *267*, *282*, *285*, *286*, *287*, *303*, *304*, *350*, *352*, *353*, *379*, *380*, *382a*, *383*, *423*.



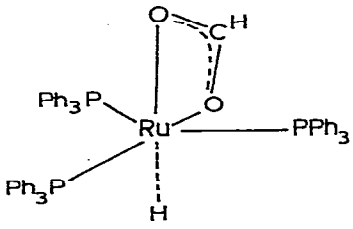
(399) $ReH_3(dppe)_2$ [375]



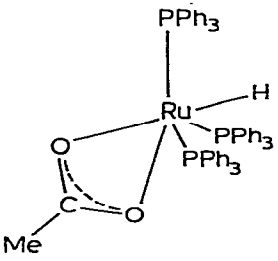
(400) $CoH(np_3)$ [373]



(401) $[NiH(np_3)]BF_4$ [374]



(402) $RuH(O_2CH)(PPh_3)_3$ [376]



(403) $RuH(OAc)(PPh_3)_3$ [377]

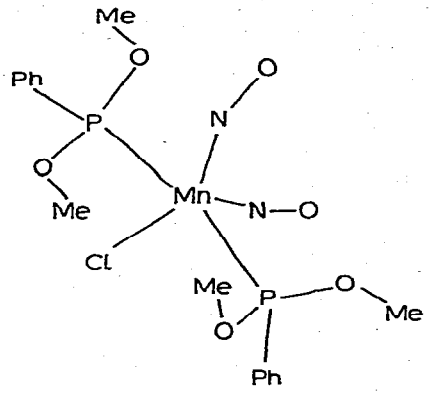
NITROSYLS

[Structures *404* - *424a*]

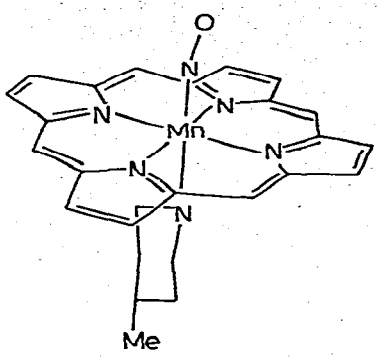
(*404*) 3 independent measurements (2 crystal forms, one having 2 independent molecules). (*405*) Linear NO, isoelectronic with Fe-CO in carbonyl-haem. (*407*) From one-electron reduction of $[Fe(NO)(CN)_5]^{3-}$, with dissociation of CN. (*408*) From NO^+ and dimeric $[FeL]_2$ complex. (*410*)(*411*) Cubane geometry [see also (*422*)]; comparison with $Fe_4S_4(C_5H_5)_4$ and $[Fe_4(SR)_4S_4]^{2-}$ shows gross dissimilarities in bonding. (*413*) Pseudoperiodicity hampers identification NO, Cl; best R 22%. (*417*) Ru-N bond lengths in similar complexes indicate NO^+ stronger π-acid than ArN_2^+. (*418*) Cl, NO disordered. (*419*) Both NO disordered

between positions A, B. (*422*) From $Co(NO)(CO)_2(PPh_3)$ + $S(NBu^t)_2$; distorted cube disagrees with first-order Jahn-Teller predictions. (*423*) Brown isomer, H not located, both P apical (cf. black isomer apical NO, H). (*424*) Close approach of 2 O from NO indicates possible NO^+–NO^- interaction.

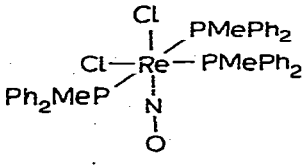
See also: *22*, *23*, *33*, *217*, *218*, *219*, *304*, *309*, *324*, *362*.



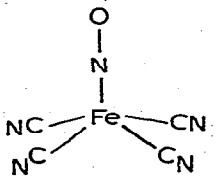
(404) $MnCl(NO)_2[PPh(OMe)_2]_2$ [382]



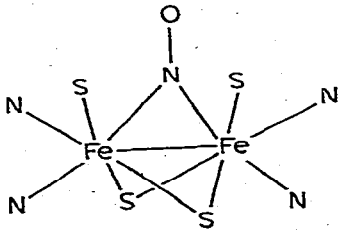
(405) Mn(NO)(Mepip)TPP [391]
(Ph groups omitted)



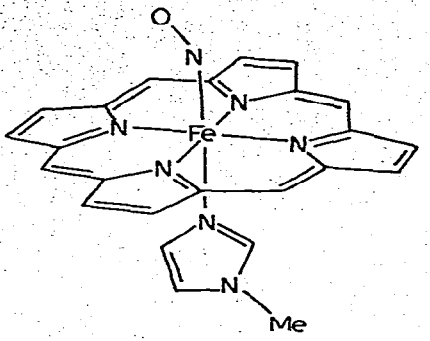
(406) $Re(NO)Cl_2(PMePh_2)_3$ [390]



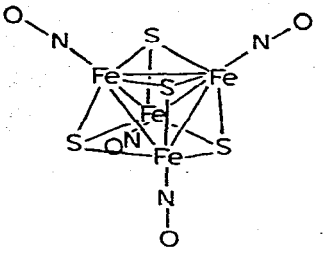
(407) $Na_2[Fe(NO)(CN)_4]$ [379]



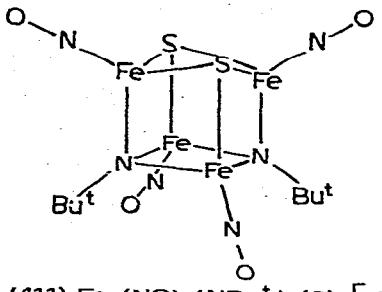
(408) Inner coordination sphere of $[(FeL)_2NO]PF_6$
$[L = S(CH_2)_2NMe_2(CH_2)_2NMe(CH_2)_2S]$
[348]



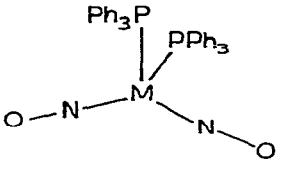
(409) Fe(NO)(MeIm)(TPP) [391]
(Ph groups omitted)



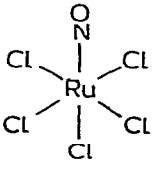
(410) $Fe_4(NO)_4(S)_4$ [380]



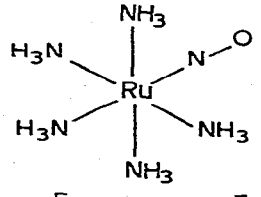
(411) $Fe_4(NO)_4(NBu^t)_2(S)_2$ [380]



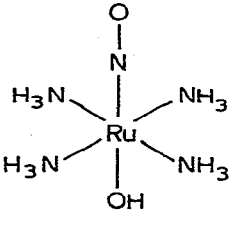
$M(NO)_2(PPh_3)_2$
(412) M = Fe [388];
(416) M = Ru [389]



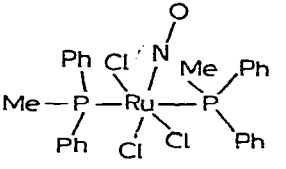
(413) $[RuCl_5(NO)]^{2-}$ [394]



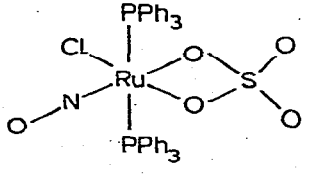
(414) $[Ru(NO)(NH_3)_5]Cl_3$ [393]



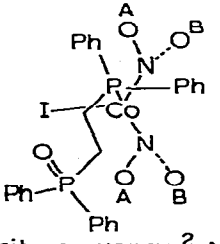
(415) $[Ru(NO)(OH)(NH_3)_4]Cl_2$ [393]



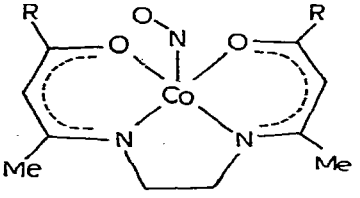
(417) $RuCl_3(NO)(PMePh_2)_2$ [386]



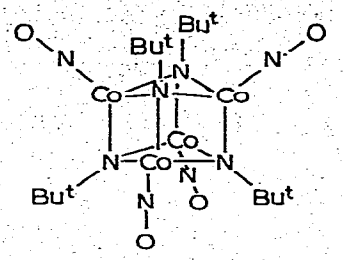
(418) $RuCl(SO_4)(NO)(PPh_3)_2$ [387]



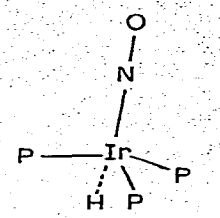
site occuancy $\frac{2}{3}A\frac{1}{3}B$
(419) $CoI(NO)_2[Ph_2P(O)(CH_2)_2PPh_2]$ [385]



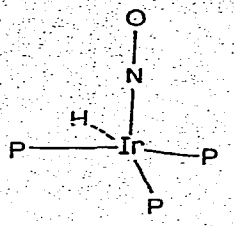
(420) R = Me Co(NO)(ea) [381]
(421) R = Ph Co(NO)(eb)



(422) $Co_4(NO)_4(NBu^t)_4$ [383]

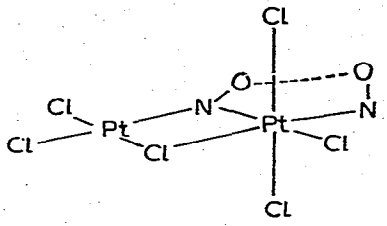


black

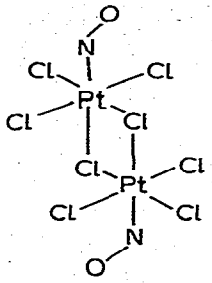


brown

(423) $[IrH(NO)(PPh_3)_3]ClO_4$ [392]



(424) $(NEt_4)_2[Pt_2Cl_6(NO)_2]$ [395]



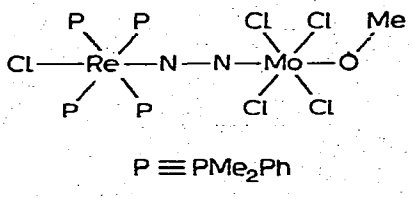
(424a) $[Pt_2(NO)_2Cl_8]^-$ [396]

DINITROGEN, ARYLDIAZO, ARYLDIIMINE AND RELATED COMPLEXES

[Structures *425* - *429*]

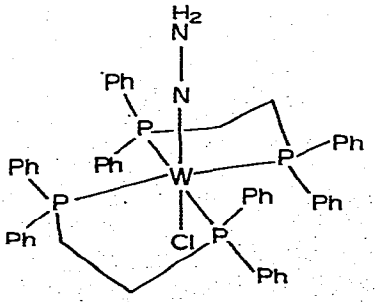
(*425*) Almost linear Re-N-N-Mo system. (*426*) Linear W-N-N indicates W=N-NH , N-N bond order 1.5. (*427*) Linear Re-N-N indicates Re-N-NHPh. (*428*) *Cis* diazene, N-H refined; model complex in proposed N_2-fixation reaction. (*429*) Linear Cl-Re-N-Me.

See also: *265*.

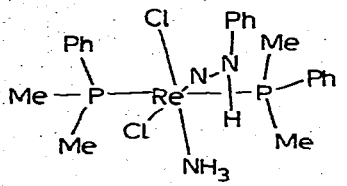


P ≡ PMe_2Ph

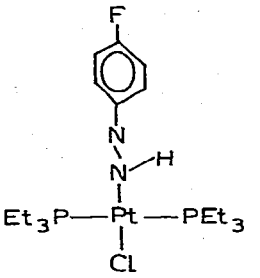
(425) $[(PhMe_2P)_4ClReN_2MoCl_4(OMe)]$ [397]



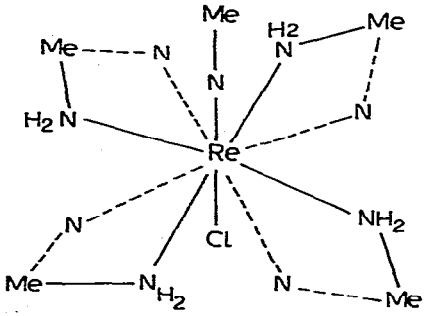
(426) $[W(N_2H_2)Cl(dppe)_2]BPh_4$ [400]



(427) $[ReCl_2(NH_3)(N_2HPh)(PMe_2Ph)_2]Br$ [399]



(428) $[PtCl(NHNC_6H_4F)(PEt_3)_2]^+$ [398]



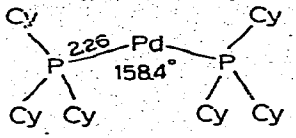
alternative positions of N indicated

(429) $[Re(NMe)Cl(NH_2Me)_4](ClO_4)_2$ [401]

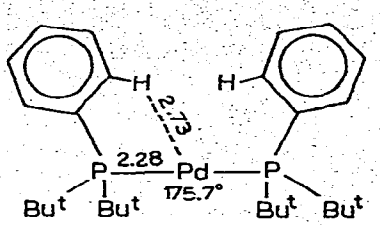
BINARY TRANSITION METAL - TERTIARY PHOSPHINE COMPLEXES

[Structures *430* - *432*]

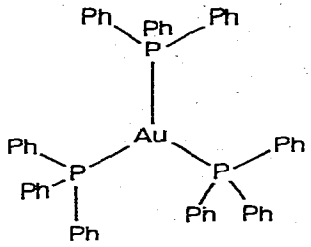
(*430*) Short Pd-P (2.278Å), P-Pd-P 176.8°; interaction of two *ortho* hydrogens with each other (2.4Å), and with Pd (2.73, 2.79Å), suggests 3-centre bond. (*431*) P-Pd-P 158.4°, no H...H interactions less than 2.32A; differing geometry [from (*430*)] not explained. (*432*) Cation trigonal, nearly planar, with minimal Au-P π-bonding; anion is open icosahedral $B_9H_{12}S^-$ fragment.



(431) $Pd(PCy_3)_2$ [404]



(430) $Pd(PBu^t_2Ph)_2$ [403,404]



(432) $[Au(PPh_3)_3]^+$ [405]

Structures ordered by metal

Nd: *182.*

Th: *183.*

Pa: *270.*

U: *184.*

Ti: *185, 202, 203, 204, 205.*

Zr: *191, 192, 193, 195, 235.*

Hf: *194.*

V: *1.*

Nb: *196, 197, 209, 213, 214, 236, 360, 361.*

Ta: *29, 65, 66.*

Cr: *3, 6, 11, 13, 62, 63, 67, 106a, 113, 166, 210, 261, 262, 263, 263a, 305, 306, 309, 375.*

Mo: *7, 8, 9, 10, 14, 39, 68, 114, 143, 145, 146, 162, 168, 198, 199, 206, 207, 208, 211, 215, 216, 217, 218, 219, 220, 237, 239, 264, 265, 307, 310, 353, 376, 377, 378, 379, 380, 381, 382, 382a, 382b.*

W: *12, 30, 31, 32, 40, 41, 42, 64, 144, 210, 211, 212, 238, 240, 303, 304, 308, 383, 426.*

Mn: *15, 16, 50, 70, 71, 109, 139, 221, 222, 222a, 259, 272, 285, 286, 287, 335, 354, 355, 356, 357, 358, 362, 384, 385, 386, 387, 404, 405.*

Re: *43, 44, 45, 137, 200, 389, 399, 406, 425, 427, 429.*

Fe: *4, 17, 18, 19, 20, 21, 22, 72, 73, 110, 115, 116, 129a, 147, 167, 169, 170, 171, 172, 173, 174, 175, 176, 177, 179, 181, 223, 224, 225, 226, 227, 228, 229, 229a, 241, 244, 247, 253, 254, 255, 256, 257, 258, 260, 269, 271, 273, 284, 288, 311, 312, 313, 314, 316, 317, 318, 319, 321, 322, 323, 324, 325, 326, 329, 330, 331, 332, 336, 337, 338, 347, 359, 359a, 363, 364, 365, 366, 366a, 390, 392, 393, 407, 408, 409, 410, 411, 412.*

Ru: *33, 46, 49, 51, 52, 103, 163, 201, 230, 231, 245, 266, 267, 367, 368, 369, 394, 402, 403, 413, 414, 415, 416, 417, 418.*

Os: *350, 370, 395.*

Co: *2, 23, 23a, 74, 75, 76, 77, 78, 79, 136, 148, 188, 189, 232, 233, 249, 250, 251, 252, 289, 293, 294, 297, 299, 300, 329, 330, 331, 332, 333, 340, 341 371, 372, 396, 400, 419, 420, 421, 422.*

Rh: *5, 24, 25, 25a, 47, 48, 53, 54, 55, 56, 80, 110a, 117, 118, 138, 148a, 156, 158, 164, 165, 178, 207, 242, 243, 268, 301, 327, 348, 349, 359a.*

Ir: *26, 34, 35, 36, 37, 82, 83, 99, 100, 104, 159, 234, 283, 340, 373, 398, 423.*

Ni: *27, 28, 57, 84, 85, 86, 119, 120, 130, 140, 141, 149a, 150, 151, 151a, 152,*

152a, 153, 165a, 190, 208, 209, 248, 295, 328, 333, 341, 342, 351, 352, 401.

Pd: *87, 101, 102, 105, 107, 108, 121, 122, 131, 132, 142, 154, 155, 157, 430, 431*

Pt: *39, 58, 59, 60, 61, 88, 89, 90, 91, 92, 93, 94, 95, 106, 108a, 111, 112, 123, 124, 125, 126, 127, 128, 129, 133, 134, 135, 136, 290, 291, 292, 296, 298, 302, 337, 338, 343, 344, 345, 346, 424, 424a, 428.*

Cu: *96, 137, 226, 230, 274, 275, 282, 373.*

Ag: *97, 138, 277, 278, 279, 280, 281.*

Au: *366a, 432.*

TABLE 1 *Metal–metal bond length determinations (1974)*

Bond	Length (Å)	Complex		Reference
Nb–Nb	3.140(av.)	$[Nb(O_2CH)(C_5H_5)]_3(OH)_2O_2$		187,188
	3.334(6)	$[Nb_3Cl_6(C_6H_3Me_3)_3]^+$		309
Nb–Ni	2.771(5)	$\{[(C_5H_5)_2Nb(SMe)_2]_2Ni\}^{2+}$		253
Cr–Sn	2.562(5)	$Cr\{Sn[CH(SiMe_3)_2]_2\}(CO)_5$		204
Cr–As	2.480(1)	$[Cr(CO)_4]_2(AsMe_2)_4$		170
Cr–Cr	2.280(2)	$[Cr(CO)_2(C_5Me_5)]_2$		252
	2.615(1)	$[Cr(NO)_2(C_5H_5)]_2$		62
	3.281	$[Cr(CO)_3(C_5H_5)]_2$		154
Mo–Li	2.70(av.)	$[MoHLi(C_5H_5)]_4$		331
Mo–Mg	2.74	$[(C_5H_5)_2MoHMgCyBr_2Mg(OEt_2)]_2$	Mo–MgCy	333
	2.85		$Mo–Mg(OEt_2)$	
Mo–Al	2.656(av.)	$[MoH(C_5H_5)(C_5H_4)]_2Al_3Me_5$		264,265
	2.656,2.685(3)	$[Mo(C_5H_4)_2Al_2Me_3]_2$		264
	2.973(av.)	$[MoH(C_5H_5)(C_5H_4)]_2Al_3Me_5$	Mo–H–Al	264,265
Mo–Sn	2.717(1)	$Mo(SnCl_2Ph)(CO)_2(C_7H_7)$		140

	2.739(1)	$Mo(SnClPh_2)(CO)_2(C_7H_7)$		140
Mo-Mo	2.148(2)	$Li_4[Mo_2Me_8].4C_4H_8O$		45
	2.920(1)	$[Mo(NBu^t)S(C_5H_5)]_2$		193
	3.105(5)	$Mo_2(CO)_6(AsPr^n)_8$		151
	3.235(1)	$[Mo(CO)_3(C_5H_5)]_2$		155
	3.267(2)	$Mo_2(CO)_4(C_5H_5)_2H(PMe_2)$	Mo-H-Mo	164
Mo-Hg	2.700(7)	$MoCl(HgCl)(CO)_3(bipy)$		107
Mo-Zn	2.538(1)	$Zn[Mo(CO)_3(C_5H_5)]_2$		156
	2.632(1)	$[(C_5H_5)Mo(CO)_3ZnCl(OEt_2)]_2$		156
W-Li	2.69(av.)	$[WHLi(C_5H_5)]_4$		331
W-W	3.0162(11)	$[W_2H_2(CO)_8]^{2-}$		40
	3.222(1)	$[W(CO)_3(C_5H_5)]_2$		155
	3.328(3)	α-$W_2H(CO)_9(NO)$	W-H-W (n.d.)	48
	3.3292(12)	α-$W_2H(CO)_9(NO)$	(x-ray)	48
	3.330(3)	β-$W_2H(CO)_9(NO)$	(n.d.)	48
Mn-Ga	2.451(1)	$Mn_2(CO)_8[GaMn(CO)_5]_2$		195,196
Mn-In	2.605(1)	$Mn_2(CO)_8[InMn(CO)_5]_2$		195,196
Mn-Sn	2.67,2.73	$[Mn(CO)_5]_4Sn_2H_2$		205
Mn-As	2.350(4)	$Mn_2(AsMe_2)(CO)_6(C_5H_5)$	As-Mn(CO)$_4$	111
	2.362(4)		As-Mn(C_5H_5)	111
Mn-Mn	2.506(3)	$Mn_3(NO)_4(C_5H_5)_3$		142
	2.518(2)	$Mn_2(CO)_7\{N{:}C(CF_3)_2\}_2$		120
	2.895(av.)	$[Mn_3(CO)_{14}]^-$		136
	2.912(4)	$Mn_2(AsMe_2)(CO)_6(C_5H_5)$		111
	3.052(1)	$Mn_2(CO)_8[GaMn(CO)_5]_2$		195,196
	3.227(1)	$Mn_2(CO)_8[InMn(CO)_5]_2$		195,196
Mn-Cd	2.681(av.)	$(phen)Cd[Mn(CO)_5]_2$		206

	2.683(av.)	(bipy)Cd[Mn(CO)$_5$]$_2$		206
	2.711(av.)	(diglyme)Cd[Mn(CO)$_5$]$_2$		159
Re-Ge	2.591(3)	[Re(GeMe$_2$)(CO)$_4$C(O)Me]$_2$		166
Re-Cu	3.078(3)	ReCu(C$_2$C$_6$F$_5$)$_2$(CO)$_3$(PPh$_3$)$_2$	(non-bonding)	361
Fe-Mg	2.593(7)	(C$_5$H$_5$)Fe(dppe)MgBr(thf)$_2$		324
Fe-C	1.805(38)-1.968(38)	[Fe$_6$C(CO)$_{16}$]$^{2-}$		183
Fe-Ge	2.346(1)	Fe$_2$(GeMe$_2$)(CO)$_3$(C$_5$H$_5$)$_2$		147
	2.372(av.)	[Fe(GeMe$_2$)(CO)$_2$(C$_5$H$_5$)]$_2$O		190
Fe-Sn	2.56	Fe(SnPh$_3$)(CO)(C$_2$Ph$_2$)(C$_5$H$_5$)		317
Fe-Fe	2.177(3)	Fe$_2$(CO)$_3$(C$_4$Bu$^t_2$Ph$_2$)$_2$		278
	2.326(4)	[Fe(NO)(C$_5$H$_5$)]$_2$		63
	2.411(1)	Fe$_2$(CO)$_6$[C$_6$H$_4$(NH)S]		83
	2.468(2)	[(FeL)$_2$NO]$^{+a}$		384
	2.496(1)	Fe$_4$(NO)$_4$S$_2$(NBu^t)$_2$	Fe$_2$N$_2$	380
	2.511(4)	Fe$_2$(CO)$_3$[C:C(CN)$_2$](C$_5$H$_5$)$_2$		118
	2.514(3)	Fe$_3$(CO)$_8$[Ph$_2$PC$_4$(CF$_3$)$_2$](PPh$_2$)		315
	2.523(1)	Fe$_2$(CO)$_9$		54
	2.523(2)	Fe$_2$(CO)$_3$(CNBu^t)(C$_5$H$_5$)$_2$		185
	2.532(11)	Fe$_3$(CO)$_7$[Ph$_2$PC$_4$(CF$_3$)$_2$](PPh$_2$)		310
	2.538(1)	[Fe(CO)(CNMe)(C$_5$H$_5$)]$_2$		160
	2.545(2)	Fe$_2$(CO)$_3$[P(OPh)$_3$](C$_5$H$_5$)$_2$		298
	2.553-2.632	[Fe$_6$C(CO)$_{16}$]$^{2-}$	bridged	183
	2.558(1)	Fe$_3$(CO)$_{12}$	CO-bridged	101
	2.562(1)	Fe$_4$(NO)$_4$S$_2$(NBu^t)$_2$	Fe$_2$SN	380
	2.574(2)	[Fe(CO)$_2$(C$_5$H$_5$BMe)]$_2$		123
	2.611	Fe$_2$(CO)$_7$(bipy)		176
	2.611(2)	Fe$_3$(CO)$_8$(C$_4$H$_8$S)$_2$		162

	2.628(1)	$Fe_2(GeMe_2)(CO)_3(C_5H_5)_2$		147
	2.634(av.)	$Fe_4(NO)_4S_4$		380
	2.642(1)	$Fe_4(NO)_4S_2(NBu^t)_2$	Fe_2S_2	380
	2.645(2)	$Fe_3(CO)_8(C_4H_8S)_2$	CO-bridged	162
	2.646-2.743(10)	$[Fe_6C(CO)_{16}]^{2-}$	non-bridged	183
	2.665(8)	$Fe_3(CO)_7[Ph_2PC_4(CF_3)_2](PPh_2)$		310
	2.677,2.683	$Fe_3(CO)_{12}$		101
	2.681(av.)	$Fe_3(CO)_7[Ph_2PC_4(CF_3)_2](CO_2Me)(PPh_2)$		321
	2.709(2)	$Fe_2(CO)_7(dppm)$		299
	2.758(8)	$Fe_2Pt(CO)_9(PPh_3)$		273
	2.765	$Fe_2(CO)_5(Ph_2fulvene)$		226
	2.787(2)	$[Fe_2(CO)_8]^{2-}$		47
Fe-Co	2.540(4)	$FeCo(CO)_5(PMePh_2)$		243
	2.5460(10)	$FeCo(CO)_3(Me_2C_4H_4)(C_5H_4Me)$		141
	2.552(2)	$FeCo(CO)_6(ind)$		138
	2.585(3)	$[FeCo(CO)_8]^-$		47
Fe-Rh	2.659,2.674(1)	$\{[Fe(PPh_2)(CO)(C_5H_4Me)]_2Rh\}^+$		330
Fe-Pt	2.530(5)	$Fe_2Pt(CO)_9(PPh_3)$	'*cis*'-PPh_3	273
	2.550(5)	$FePt_2(CO)_5[P(OPh)_3]_3$	Fe-Pt(CO)P	364
	2.583(6)	$FePt_2(CO)_5[P(OPh)_3]_3$	Fe-PtP_2	364
	2.597(5)	$Fe_2Pt(CO)_9(PPh_3)$	'*trans*'-PPh_3	273
Fe-Au	2.819(9)	$[FeAu_2(PPh_3)_2]^+$		348,349
Ru-Si	2.43	$Ru(SiMe_3)(CO)_2[C_7H_7(C_6F_5)SiMe_3]$		228
Ru-Ru	2.806(1)	$Ru_3(CO)_8[C_8H_4(SiMe_3)_2]$		240
	2.81	$Ru_3(CO)_6(C_8H_6)$		153
	2.835	$Ru_3(CO)_6(C_8H_9)_2$	CO-bridged	237
	2.845	$Ru_2(CO)_5(Ph_2fulvene)$		242

	2.853	$Ru_3(CO)_6(C_8H_9)_2$	C_8H_9-wrapped	237
	2.930(1)	$Ru_3(CO)_8[C_8H_4(SiMe_3)_2]$	$C_8H_4R_2$-bridged	240
	2.94	$Ru_3(CO)_6(C_8H_6)$	C_8H_6-bridged	153
Os-Sn	2.711(1)	$Os(SnPh_3)_2(CO)_4$		326
Os-Os	2.732(2); 2.741(2)*	$Os_3(CO)_9(C_4Ph_4)$	$(CO)_2Os$-$Os(CO)_4$	311
	2.729(2); 2.739(1)*	$Os_3(CO)_9(C_4Ph_4)$	$(CO)_2Os$-$Os(CO)_3$	311
	2.84	$Os_3H_3(CMe)(CO)_9$		71
	2.917; 2.894(1)*	$Os_3(CO)_9(C_4Ph_4)$	$(CO)_3Os$-$Os(CO)_4$	311
	[* values for (orthorhombic; monoclinic) modifications]			
Co-Ge	2.310(7)	$Co(GeCl_3)(CO)_4$		20
Co-Co	2.387(2)	$(C_5H_5Co)_2C_2B_8H_{10}$		92
	2.454(2)	$Co_4(CO)_9(C_6H_4Me_2)$		137
	2.457(2)	$Co_4(CO)_9(C_6H_6)$	basal	137
	2.460(2)	$Co_4(NO)_4(NBu^t)_4$		383
	2.472-2.491(2)	$Co_4(CO)_9(C_6H_4Me_2)$	base-apex	137
	2.485(1)	$Co_4(CO)_9(C_6H_6)$	base-apex	137
	2.489(1)	$(C_5H_5Co)_2C_2B_6H_8$		91
	2.544(2)	$Co_4(NO)_4(NBu^t)_4$		383
M-M (Co,Ir)	2.594-2.693	$Co_2Ir_2(CO)_{12}$		100
Co-Ni	2.4097(8)	$CoNi(CO)_4(PEt_3)(C_5H_5)$		148
M-M (Co,Ni)	2.487(1)	$[Co_4Ni_2(CO)_{14}]^{2-}$	basal	135
	2.519(1)	$[Co_4Ni_2(CO)_{14}]^{2-}$	between	135
Rh-C	2.06	$[Rh_{15}C_2(CO)_{28}]^{2-}$		224
	2.127	$Rh_8C(CO)_{19}$		224
Rh-Rh	2.51	$[Rh(CPh_2)Cl(py)]_2CO$		312
	2.699-2.913(3)	$Rh_8C(CO)_{19}$		224

	2.738–3.091(3)	$[Rh_{15}C_2(CO)_{28}]^{2-}$	31 edges	224
	3.332(3)	$[Rh_{15}C_2(CO)_{28}]^{2-}$	2 edges	224
Rh–Ag	3.086,3.102	$RhAg_2(C_2C_6F_5)_5(PPh_3)_3$	non-bonding	371
Ir–Sn	2.5867(6)	$Ir(SnCl_3)(C_7H_8)(PMe_2Ph)_2$		246
Ir–Ir	2.759(2)	$[IrH(CO)_2(PPh_3)]_2SO_2$		328
Ir–Cu	2.776–2.959(4)	$Ir_2Cu_4(C_2Ph)_8(PPh_3)_2$		372
Ni–Ni	2.3217(8)	$[Ni(CNMe)(C_5H_5)]_2$		130
	2.364(av.)	$Ni_3(Bu^t)(C_5H_5)_3$		202
	2.38	$\{[Ni_3(CO)_6]_2\}^{2-}$	intra-Δ	102
	2.464	$Ni_4H_3(C_5H_5)_4$		215
	2.577(5)	$Ni_2(CO)_3\{S[P(CF_3)_2]_2\}_2$		81
	2.77	$\{[Ni_3(CO)_6]_2\}^{2-}$	inter-Δ	102
Pt–Pt	2.633(1)	$FePt_2(CO)_5[P(OPh)_3]_3$		364
	2.66	$\{[Pt_3(CO)_6]_n\}^{2-}$ (n = 2,3,5)	intra-Δ	103
	3.04(av.)	$\{[Pt_3(CO)_6]_2\}^{2-}$	inter-Δ	103
	3.05(av.)	$\{[Pt_3(CO)_6]_3\}^{2-}$	inter-Δ	103
	3.08(av.)	$\{[Pt_3(CO)_6]_5\}^{2-}$	inter-Δ	103
Cu–Cu	2.665–2.823	$Ir_2Cu_4(C_2Ph)_8(PPh_3)_2$		372
	2.843(3)	$Cu_2[(CH_2)_2PMe_2]_2$		44
	3.07(1)	$Cu_4(O_2CCF_3)_4(C_6H_6)_2$		208
Au–Au	2.768(3)	$[FcAu_2(PPh_3)_2]^+$		348,349

[a] L = $S(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2S$.

TABLE 2 *Parameters for M-N-O Groups*

Complex	M-N(Å)	N-O(Å)	M-N-O(°)	Reference
(i) *Terminal NO*				
$[Cr(NO)_2(C_5H_5)]_2$ (terminal)	1.690(3)	1.181(4)	175.6(5)	62
Mn(NO)(Mpip)(TPP)	1.644(5)	1.176(7)	176.2(5)	391
$Mn(NO)_2Cl[PPh(OMe)_2]_2$	1.63	1.20	165	382
$Re(NO)Cl_2(PMePh_2)_3$	1.775(10)	1.182(14)	178.8(14)	390
$[Fe(NO)(CN)_4]^-$	1.565	1.161	177.1	379
Fe(NO)(Meim)(TPP)	1.743(4)	1.121(8)	142.1(6)	391
$Fe(NO)_2(CO)(PPh_3)$ [a]	1.690(8)–1.732(8)	1.147(12)–1.150(8)	177.3(11)–178.9(6)	199
$Fe(NO)_2(PPh_3)_2$	1.650(7)	1.190(10)	178.2(7)	388
$Fe_4(NO)_4S_4$	1.661(5) 1.666(5)	1.143(6)–1.171(6)	176.9(5)–178.7(5)	380
$Fe_4(NO)_4S_2(NBu^t)_2$	1.653(6)–1.668(6)	1.158(8)–1.173(7)	177.8(4)–179.4(7)	380
$Ru(NO)_2(PPh_3)_2$	1.762(6) 1.776(6)	1.190(7) 1.194(7)	177.7(6) 170.6(5)	389
$Ru(NO)I(CO)(PPh_3)_2$	1.80(4)	1.15(5)	159(2)	313
$Ru(NO)Cl_3(PMePh_2)_2$	1.744(6)	1.132(6)	176.4(6)	386
$Ru(NO)Cl(SO_4)(PPh_3)_2$	1.80(3)	1.07(4)	175(3)	387
$[Ru(NO)(NH_3)_5]^{3+}$	1.735(3)	1.159(5)	173.8(3)	393
$[Ru(NO)(OH)(NH_3)_4]^{2+}$	1.770(9)	1.172(14)	172.8(9)	393
Co(NO)(ea)	1.821(9)	1.093(16)	122.4(9)	381
Co(NO)(eb)	1.831(11)	1.136(26)	122.9(8)	381
Co(NO)I(dppeO)	1.677(20)	1.052(17)	[b]	385
$Co_4(NO)_4(NBu^t)_4$	1.645(9) 1.662(10)	1.16(1) 1.15(1)	174(1) 168(1)	383
$[Ir(NO)H(PPh_3)_3]^+$ [c]	1.80(2)	1.14(3)	174.5(21)	392
$[Pt_2(NO)_2Cl_6]^-$	1.98(6)	1.05(6)	122(5)	396

$[Pt_2(NO)_2Cl_8]^-$	2.15	1.18	112	395
(ii) *Bridging NO*				
$[Cr(NO)_2(C_5H_5)]_2$	1.960	1.193(4)	136.4(3)	62
$[Fe(NO)(C_5H_5)]_2$	1.768	1.254(12)	138.8(8)	63
$[(FeL)_2NO]^+$ [d]	1.818(5)	1.193(8)	137.2	384
$[Pt_2(NO)_2Cl_6]^-$	1.89(4) 1.93(3)	1.27(5)	123(3) 118(3)	395

[a] CO, NO disordered.

[b] Disordered O atoms in 2 positions, A:B = 67:33; bond angles: O(1A), 120.5(19); O(1B), 166.3(26); O(2A), 154.6(43); O(2B), 149.0(57).

[c] Brown isomer.

[d] L = $S(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2S$.

TABLE 3 Crystal structure data: Organometallics

Number	Formula	Structure	Crystal Type	Space Group	Z
5	$2C_2Cl_2O_2Rh^-.C_{36}H_{46}N_4^+$	$oepH_4[RhCl_2(CO)_2]_2$	Tet	$P4/n$	4
65	$C_3H_9Cl_2N_4O_4Ta$	$TaCl_2Me[ON(Me)NO]_2$	M	$P2_1/n$	4
285	$C_3H_{13}B_8MnO_3$	$Mn(CO)_3(B_8H_{13})$	O	Pmcn	4
97	C_3AgN_3O	$AgC(CN)_2(NO)$	O	Pbca	8
284	$C_4H_{12}B_7FeO_4^-.C_{16}H_{36}N^+$	$NBu_4[Fe(CO)_4(B_7H_{12})]$	M	$P2_1/c$	4
396	$C_4Cl_3CoGeO_4$	$Co(GeCl_3)(CO)_4$	M	Cc	8
2	C_4CoO_4Tl	$Tl[Co(CO)_4]$	Cub	$P2_13$	4
127	$C_5H_{12}Cl_3Pt$	$PtCl_3(C_5H_9NH_3)^a$	M	$P2_1/c$	4
3	$C_5CrIO_5^-.C_9H_{27}N_4P_4^+$	$N_4^3{}^4Me_9[CrI(CO)_5]$	Tri	$P\bar{1}$	2
4	$C_5FeNO_4^-.C_{36}H_{30}NP_2^+$	$N(PPh_3)_2[Fe(CN)(CO)_4]$	M	$P2_1/c$	4
10	$C_5MoO_5P_4S_3$	$Mo(CO)_5(P_4S_3)$	M	$P2_1/c$	8

[a] $C_5H_9NH_3$ = *trans*-pent-2-enylammonium.

63	$C_6H_3CrIO_4$	$CrI(CMe)(CO)_4$	O	Cmcm	4
80	$C_6H_6I_6O_4Rh_2^{2-}.2C_9H_{14}N^+$	$(NMe_3Ph)_2[Rh_2I_6(COMe)_2(CO)_2]$	M	$P2_1/c$	2
289	$C_6H_{13}B_7Co^-.Cs^+$	$Cs[Co(C_5H_5)(CB_7H_8)]$	M	C2/c	8
67	$C_6H_{18}Cr^{3-}.3Li^+.3C_4H_8O_2$	$Li_3CrMe_6.3C_4H_8O_2$	Trig	$R\bar{3}c$	6
51	$C_6H_{20}N_6ORu^{2+}.2F_6P^-.C_2D_6OS$	$[Ru(CO)(C_5H_8N_2)(NH_3)_4](PF_6)_2.(CD_3)_2SO$[a]	M	C2/m	4
1	$C_6O_6V^-.C_{36}H_{30}NP_2^+$	$N(PPh_3)_2[V(CO)_6]$	Trig	$R\bar{3}$	1

[a] $C_5H_8N_2$ = C-bonded 4,5-dimethylimidazolium

34	$C_7H_5ClIrNO_2$	$IrCl(CO)_2(py)$	M	$P2_1/a$	4
222a	$C_7H_5MnO_4S$	$Mn(CO)_2(SO_2)(C_5H_5)$	M	$P2_1/c$	4

Unit cell constants						Data	R	R_w	Notes	Reference
a	b	c	α	β	γ					
24.604(3)		8.231(1)				1439	8.9			15
9,78(1)	15.10(1)	7.74(1)		97.18(6)		1336	8.7			16
11.549(2)	5.506(1)	19.260(3)				928	3.3	4.1		17
11.729(14)	10.299(4)	7.868(5)				463	7.0			18
10.891(5)	11.656(6)	23.803(9)		90.34(1)		2283	11			19
26.238(3)	6.623(5)	12.969(2)		106.20(3)		1647	9.8			20
8.869(3)						135	8.3	4.4		21
11.215(3)	8.729(2)	10.259(3)		90.0(1)		1560	4.0	4.7		22
14.632(21)	10.364(10)	10.765(9)	89.65(9)	106.98(13)	63.72(7)	2112	5.3			23
10.749(4)	12.909(6)	26.801(9)		97.98(5)		2313		4.55		24
6.764(4)	34.98(4)	12.59(2)		97.7(1)		1476	8.2			25
7.911(9)	11.795(10)	10.747(10)				425	5			26
9.663(8)	15.050(12)	12.399(10)		92.42(10)		2867	10.0			27
12.643(2)	11.815(2)	16.376(2)		90.34(1)		1521	4.0	4.6		28
17.69(7)		13.20(5)				278	12.3			29
22.725(5)	8.500(2)	12.307(3)		94.22(3)		2426	3.2	3.8		30
9.761(6)			91.93			595	7.5			31
17.58(6)	7.16(2)	11.65(4)		142.9(1)		838	2.5	2.9		32
10.98(2)	10.63(2)	7.43(2)		100.75(8)		1512	9.3			33

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139	$C_7H_6MnNO_4$	$Mn(CO)_4(CH_2{:}NC_2H_4)$	M	$P2_1/n$	4
8	$C_7H_{12}MoN_4O_3P_4$	$Mo(CO)_3(NPMe)_4$	O	$P2_12_12_1$	4
293	$C_7H_{16}B_7Co$	$Co(C_5H_5)(C_2B_7H_{11})$	M	$P2_1/n$	4
300	$C_7H_{17}B_{10}Co$	$Co(C_5H_5)(C_2B_{10}H_{12})$[b]	O	$Pca2_1$	4
300a	$C_7H_{17}B_{10}Co$	$Co(C_5H_5)(C_2B_{10}H_{12})$[c]	O		4
300b	$C_7H_{17}B_{10}Co$	$Co(C_5H_5)(C_2B_{10}H_{12})$[d]	O		4
286	$C_7H_{20}B_9MnO_4$	$Mn(CO)_3(B_9H_{12}C_4H_8O)$	Tri	$P\bar{1}$	2
283	$C_7H_{26}B_5Br_2IrOP_2$	$IrBr_2(CO)(PMe_3)_2(B_5H_8)$	M	$P2_1/c$	4

[a] Disordered; not fully refined. [b] 'Red II' isomer. [c] 'Orange III' isomer; cell data only; probably twinned M, space group Cc. [d] 'Red-orange IV' isomer; cell data only; probably twinned M, space group Cc.

303	$C_8H_2O_8W_2^{2-}.2C_8H_{20}N^+$	$(NEt_4)_2[W_2H_2(CO)_8]$	M	C2/m	2
18	$C_8H_4FeN_2O_4$	$Fe(CO)_4(C_4H_4N_2)$[a]	M	$P2_1/c$	4
42	$C_8H_5NO_5S_2W$	$W(CO)_5(C_3H_5NS_2)$[b]	M	$P2_1/a$	4
62	$C_8H_{12}BrCrO_3P$	$CrBr(CMe)(CO)_3(PMe_3)$	M	$P2_1$	4
152a	$C_8H_{12}BrNNiO_2$	$NiBr(MeCN)[CH(CO_2Me)CMeCH_2]$	Tri	$C\bar{1}$	4
96	$C_8H_{20}Cu_2P_2$	$Cu_2[(CH_2)_2PMe_2]_2$	M	C2/c	4
68	$C_8H_{24}Mo_2^{4-}.4C_4H_8LiO^+$	$[Li(OC_4H_8)]_4[Mo_2Me_8]$	M	$P2_1/n$	2
290	$C_8H_{26}B_6P_2Pt$	$(Me_3P)_2PtC_2B_6H_8$	M	A2	2
329	$C_8CoFeO_8^-.C_{36}H_{30}N^+$	$N(PPh_3)_2[FeCo(CO)_8]$	Tri	$P\bar{1}$	2
312	$C_8Fe_2O_8^{2-}.2C_{36}H_{30}N^+.2C_2H_3N$	$[N(PPh_3)_2]_2[Fe_2(CO)_8].2MeCN$	Tri	$P\bar{1}$	1

[a] $C_4H_4N_2$ = pyridazine. [b] $C_3H_5NS_2$ = $\overbrace{S(CH_2)_2NHC{=}S}$.

304	$C_9HNO_{10}W_2$	$W_2H(CO)_9(NO)$	α	Tri	$P\bar{1}$	2
			β	M	C2/c	4
223	$C_9H_5F_6FeO_2P$	$Fe(CO)_2[P(CF_3)_2](C_5H_5)$		M	$P2_1/c$	4

10.803(1)	13.812(2)	6.347(1)		93.99(1)		1314	7.8			34
16.22(1)	14.90(1)	8.194(7)				1498	α			35
6.811(2)	15.678(2)	10.949(5)		104.91(3)		1323	3.2		-160°	36
13.744(4)	7.047(2)	13.620(3)				2344	3.02	3.81		37
7.259(3)	16.194(6)	11.052(2)								37
7.249(3)	16.258(7)	11.199(5)								37
9.828(3)	13.305(5)	6.937(2)	90.81(2)	104.23(2)	109.7(3)	1803	4.5	5.5		38
13.824(4)	10.661(3)	13.611(3)		104.90(2)		2546	4.64	4.25		39
15.863(4)	12.129(3)	8.145(2)		105.28(2)		1051	3.34	3.18		40
7.760(2)	10.593(3)	12.801(3)		105.69(2)		1437	3.4	4.5		41
16.91(2)	10.73(1)	7.07(1)		98.93(2)		1862	6.0			[illegible]
6.8[illegible](8)	13.667(10)	14.261(10)		96.55(7)		1128	7			26
14.23(1)	11.02(1)	7.41(1)	88.3(1)	104.6(1)	89.8(1)	1239	9.9			43
10.17(8)	9.72(7)	13.19(9)		94.0(5)		775	11			44
11.473(3)	12.766(3)	12.373(3)		116.32(1)		1160	4.3	5.3		45
5.716(2)	9.785(4)	15.329(8)		94.24(3)		767	12			46
10.58(2)	15.35(3)	12.66(3)	96.3(1)	97.4(1)	92.3(1)	2193	9.8			47
17.942(4)	12.944(3)	10.532(3)	93.21(2)	115.35(1)	106.72(2)	3765	8.8			47
12.228(4)	9.634(4)	6.925(3)	112.83(3)	91.28(3)	97.38(3)	1932	6.1			
12.284(14)	9.621(5)	6.921(4)	112.84(2)	91.31(5)	97.34(4)	2518	6.0		n.d.	48
14.582(8)	6.771(4)	15.627(9)		102.336(6)		919	6.6		n.d.	
8.602(7)	11.924(9)	12.959(9)		112.75(9)		1882	4.8			49

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224	$C_9H_5F_6FeO_3P$	$Fe(CO)_2[P(O)(CF_3)_2](C_5H_5)$	M	$P2_1/c$	4
17	$C_9H_5FeNO_4$	$Fe(CO)_4(py)$	M	$P2_1/n$	4
41	$C_9H_7NO_6SW$	$W(CO)_5(C_4H_7NOS)$[a]	M	$P2_1/c$	4
271	$C_9H_8FeN_2O_5$	$Fe(CO)_3(C_6H_8N_2O_2)$[b]	M	$P2_1/b$	4
19	$C_9H_{18}FeO_9P_2$	*trans*-$Fe(CO)_3[P(OMe)_3]_2$	M	C2/c	4
74	$C_9H_{19}CoN_4O_5$	$CoMe(H_2O)(dmg)_2$	O	Pnma	4
297	$C_9H_{25}B_{16}Co_2^-.C_8H_{20}N^+$	$NEt_4[Co_2(C_5H_5)(C_2B_8H_{10})_2]$	M	$P2_1/c$	4
311	$C_9Fe_2O_9$	$Fe_2(CO)_9$	Hex	$P6_3/m$	1

[a] C_4H_7NOS = thiomorpholin-3-one.

[b] $C_6H_8N_2O_2$ = 1,2-Me_2-1,2-dihydropyridazine-3,6-dione.

6	$C_{10}H_2Cr_2N_2O_{10}.2C_4H_8O$	$[Cr(CO)_5]_2N_2H_2.2thf$	Tri	$P\bar{1}$	2
277	$C_{10}H_6Ag_2F_6O_4$	$[Ag(CF_3CO_2)]_2C_6H_6$	M	A2/m	8
278	$C_{10}H_8Ag_4^{4+}.4ClO_4^-.4H_2O$	$C_{10}H_8(AgClO_4)_4.4H_2O$	Tri	$P\bar{1}$	2
253	$C_{10}H_8FeI_2$	$Fe(C_5H_5)(C_5H_3I_2)$	Tri	P1	4

200	$C_{10}H_{10}Br_2Re^+.BF_4^-$	$[ReBr_2(C_5H_5)_2]BF_4$	O	Pmmn	2
198	$C_{10}H_{10}Cl_2Mo$	$MoCl_2(C_5H_5)_2$	M	$P2_1/b$	8
199	$C_{10}H_{10}Cl_2Mo^+.BF_4^-$	$[MoCl_2(C_5H_5)_2]BF_4$	O	Pmmn	2
196	$C_{10}H_{10}Cl_2Nb$	$NbCl_2(C_5H_5)_2$	M	$P2_1/b$	8
191	$C_{10}H_{10}Cl_2Zr$	$ZrCl_2(C_5H_5)_2$	Tri	$P\bar{1}$	4
188	$C_{10}H_{10}Co^+.C_{18}H_{15}CoI_3P^-$	$[Co(C_5H_5)_2][CoI_3(PPh_3)]$	Cub	Pa3	8
309	$C_{10}H_{10}Cr_2N_4O_4$	$[Cr(NO)_2(C_5H_5)]_2$	Tri	P1	
324	$C_{10}H_{10}Fe_2N_2O_2$	$[Fe(NO)(C_5H_5)]_2$	M	$P2_1/c$	2
201	$C_{10}H_{10}IRu^+.I_3^-$	$[RuI(C_5H_5)_2]I_3$	O	Pnma	4
203	$C_{10}H_{10}S_5Ti(V)$	$TiS_5(C_5H_5)_2$[a]	M	$P2_1/n$	4
123	$C_{10}H_{16}Cl_4Pt_2$	$[PtCl_2(C_5H_8)]_2$	O	Ibam	4

11.938(8)	7.603(6)	13.818(9)		100.97(8)		1777	4.5		49
8.198(6)	10.488(5)	12.080(8)		98.74(6)		1410	5.4	7.0	41
16.97(3)	6.43(2)	11.84(3)		110.7(4)		1899	7.0		59
14.412(8)	13.103(7)	6.334(5)			112.69(8)	1430	9.8		50
11.964(4)	11.208(4)	13.406(5)		108.80(4)		1193	4.4	4.4	51
13.182(12)	9.115(6)	12.132(7)				1070	3.9		52
13.070(7)	12.442(5)	18.183(13)		99.34(4)		2895	5.4	7.5	53
6.436(1)		16.123(2)				604	4.0	5.0	54
19.03	10.27	6.37	97.3	97.9	95.9	1310	6.8		55
15.253(5)	9.674(1)	15.882(6)		95.667(4)		2824	8.7		56
11.870(1)	9.247(1)	11.123(1)	88.93(1)	96.88(1)	101.21(1)	1796	6.1	7.0	57
10.779(15)	10.708(15)	10.050(15)	89.25(25)	93.57(25)	96.95(25)	1800	16		58
9.50(1)	9.38(1)	7.03(1)				690	5.4		60
13.29(2)	12.09(2)	12.99(2)			106.9(1)	2101	6.8		60
9.55(1)	9.34(1)	6.79(1)				539	2.6		60
14.74(2)	12.21(2)	13.16(2)			107.7(1)	2832	6.8		60
14.06(1)	8.09(1)	13.15(1)	113.7(1)	117.9(1)	99.5(1)	3478	9.5		60
18.272(6)						1087	6.0		61
7.174(1)	6.069(1)	7.927(1)	106.73(1)	102.52(1)	85.18(1)	708	2.7		62
7.8257(9)	5.9998(9)	11.9875(13)		105.548(9)		547	6.3		63
7.632(7)	14.080(10)	14.186(7)				1093	8.9		64
9.019	13.089	11.294		93.62					65
9.537(4)	18.703(7)	8.290(5)				819	8.1		66

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117	$C_{10}H_{18}N_2Rh^+.BF_4^-$	$[Rh(C_2H_4)_3(MeCN)_2]BF_4$	Hex	$P6_3/mmc$	2
12	$C_{10}H_{18}O_4P_6W$	$W(CO)_4(PMe)_6$	M	C2/c	4
292	$C_{10}H_{30}B_6P_2Pt$	$[(Me_3P)_2Pt]Me_2C_2B_6H_6$ α	M	A2/a	4
		β	M	$P2_1/c$	4
71	$C_{10}Cl_5MnO_5$	$Mn(C_5Cl_5)(CO)_5$	M	$P2_1/n$	4
176	$C_{10}F_{10}FeO_3$	$Fe(CO)_3(C_7F_{10})$	O	Pnma	4

[a] Doped with 0.2% $VS_5(C_5H_5)_2$.

64	$C_{11}H_5IO_4W$	$WI(CPh)(CO)_4$	O	Pbca	8
350	$C_{11}H_6O_9Os_3$	$Os_3H_3(CMe)(CO)_9$	O	Pnma	
214	$C_{11}H_{11}NbOS$	$Nb(SH)(CO)(C_5H_5)_2$	O	$P2_12_12_1$	4
31	$C_{11}H_{12}As_2F_6I_2O_3W$	$WI_2(CO)_3[Me_2AsC(CF_3):C(CF_3)AsMe_2]$	M	$P2_1/c$	4
88	$C_{11}H_{13}BN_6OPt$	$PtMe(CO)[HB(pz)_3]$	M	$P2_1/c$	4
147	$C_{11}H_{13}FeO_4^+.F_6P^-$	$\{Fe(CO)_3[CHMe(CH)_2CHMeC(O)Me]\}PF_6$	M	$P2_1/c$	4
280	$[C_{11}H_{15}Ag_2As^{2+}.2NO_3^-]_n$	$[C_6H_4(CH_2CH:CH_2)(AsMe_2)(AgNO_3)_2]_n$	O	$P2_12_12_1$	4
143	$C_{11}H_{15}F_3MoO_6$	$Mo(O_2CCF_3)(CO)_2(C_3H_5)(dme)$	O	Pnam	4
144	$C_{11}H_{15}F_3O_6W$	$W(O_2CCF_3)(CO)_2(C_3H_5)(dme)$	O	Pnam	4
206	$C_{11}H_{16}MoNO^+.F_6P^-$	$[Mo(OH)(NH_2Me)(C_5H_5)_2]PF_5$	M	$P2_1/n$	4
218	$C_{11}H_{16}MoN_2OS_2$	$Mo(NO)(C_3H_5)(S_2CNMe_2)(C_5H_5)$	M	$P2_1/c$	4
125	$C_{11}H_{17}Cl_2NPt$	*trans*-$[PtCl_2(C_2H_4)(S)$-NHMeCHMePh]			
23a	$C_{11}H_{17}CoN_8O$	$Co(CO)(C_{10}H_{17}N_8)$[c]	O	Cmca	8
28	$C_{11}F_{24}Ni_2O_3P_4S_2$	$Ni_2(CO)_3[(CF_3)_2PSP(CF_3)_2]_2$	O	Pbcn	4

[a] Combination X-ray powder data and nematic phase ^1H n.m.r., isostructural with Ru complex.
[b] No crystal data given, diagram only.
[c] $C_{10}H_{17}N_8$ = 6,7,13,14-tetramethyl-1,2,4,5,8,9,11,12-octaazacyclotetradeca-2,5,7,12,14-pentaenato.

316	$C_{12}H_5Fe_2NO_6$	$Fe_2(CO)_6[C_6H_4(NH)S$-$\sigma]$	M	$P2_1/c$	4
116	$C_{12}H_6Fe_2O_6S$	$Fe(CO)_4(C_8H_6SO_2)$[a]	M	$P2_1/c$	4

7.30(1)		16.25(2)			668	7		67
9.29(2)	16.88(2)	12.92(2)	96.0(1)		1091	9.3		68
12.002(5)	10.415(7)	16.559(7)	102.47(3)		1162	7		46
11.892(4)	9.280(4)	18.724(8)	106.17(3)		2613	5		
13.701(2)	8.758(1)	13.329(1)	107.78(1)		1560	4.1		69
11.305(10)	12.110(10)	9.075(10)			1066	3.7		70
20.10(2)	12.12(1)	11.26(1)			688	7.8		26
17.55(3)	14.57(2)	6.76(1)						71
6.544(5)	12.815(5)	12.531(5)			823	9		72
15.37(2)	9.529(1)	15.967(3)	112.03(2)		1823	6.9		73
14.416(1)	7.951(1)	12.990(1)	104.35(1)		2124	3.9	3.3	74
9.363(6)	12.174(9)	16.547(10)	121.60(5)		1538	8.0		75
7.17	10.16	22.02			774	7.8		76
16.10(2)	9.87(2)	9.68(2)			855	11.8		77
15.84(3)	9.76(3)	9.67(4)			1016	14.0		77
9.98(1)	13.07(1)	10.88(1)		100.4(1)	2138	4.9		60
15.247(4)	12.419(3)	7.729(3)	98.71(2)		772	5.6		78
								79
14.313(14)	14.009(9)	13.720(8)			1782	5.0	4.2	80
10.49(1)	14.26(1)	18.77(1)			948	8.7		81
8.982(3)	14.443(5)	11.597(5)	94.39(5)		1058	3.5	4.5	83
9.81(2)	10.81(2)	13.18(2)	111.92(33)		827	6.1		82

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179	$C_{12}H_8FeO_4$	$Fe(CO)_3(C_9H_8O)$[b]	Tri	$P\bar{1}$	2
			O	$Pna2_1$	4
115	$C_{12}H_{10}FeO_8$	$Fe(CO)_4(C_8H_{10}O_4)$[c]	O	Pcmn	4
202	$C_{12}H_{10}N_2O_2Ti$	$Ti(NCO)_2(C_5H_5)_2$	O	Pbca	8
261	$C_{12}H_{12}Cr^+.I^-$	$[Cr(C_6H_6)_2]I$	Tet	$I\bar{4}m2$	2
			O	Immm?	
237	$C_{12}H_{15}ClMo$	$MoClEt(C_5H_5)_2$	M	$P2_1/b$	4
219	$C_{12}H_{16}I_2Mo_2N_4O_2$	$[MoI(NO)(C_5H_5)]_2(\mu\text{-}N_2Me_2)$	M	$P2_1/c$	4
217	$C_{12}H_{16}MoN_2O_2S_2$	$Mo(CO)(NO)(C_3H_5)(S_2CNMe_2)(C_5H_5)$	M	$P2_1/c$	4
294	$C_{12}H_{18}B_6Co_2$	2,6-$[Co(C_5H_5)]_2$-1,10-$C_2B_6H_8$	M	C2/c	8
299	$C_{12}H_{20}B_8Co_2$	2,3-$[Co(C_5H_5)]_2$-1,7-$C_2B_8H_{10}$	M	$P2_1/n$	4
189	$C_{12}H_{20}B_9Co$	$Co(C_5H_5)(C_5H_4B_9C_2H_{11})$	M	$P2_1/c$	4
118	$C_{12}H_{21}ClPRh$	$RhCl[P(CH_2CH_2CH{:}CH_2)_3]$	M	$P2_1/c$	8
156	$C_{12}H_{22}Cl_4O_2Rh_2.CH_4O$	$[RhCl_2(C_6H_{11}O)]_2$.MeOH[e]	O	$Pc2_1n$	→
72	$C_{12}H_{22}FeN_8O$	$FeMe(CO)(C_{10}H_{19}N_8)$[f]	O	Cmcm	4
79	$C_{12}H_{34}CoP_3$	$CoMe_2[(CH_2)_2PMe_2](PMe_3)_2$	M	$P2_1/m$	2
95	$C_{12}H_{36}N_{12}Pt_4$	$[Pt(N_3)Me_3]_4$	Trig	$P\bar{3}c1$	4
340	$C_{12}Co_2Ir_2O_{12}$	$Co_2Ir_2(CO)_{12}$	M	$P2_1/c$	4
336	$C_{12}Fe_3O_{12}$	$Fe_3(CO)_{12}$	M	$P2_1/n$	2
342	$C_{12}Ni_6O_{12}^{2-}.2C_4H_{12}N^+$	$(NMe_4)_2[Ni_3(CO)_6]_2$	Trig	$P\bar{3}$	1
343	$C_{12}O_{12}Pt_6^{2-}.2C_{24}H_{20}P^+$	$(PPh_4)_2[Pt_3(CO)_6]_2$	M	C2/c	4

[a] $C_8H_6SO_2$ = benzo[*b*]thiophene-1,1-dioxide. [b] C_9H_8O = 2,3,4,8-η^4-bicyclo[3.2.2]nona-3,6-dien-2,8-yl-9-one. [c] $C_8H_{10}O_4$ = η^2-*cis*-2,3-dicarbomethoxymethylenecyclopropane. [d] Rings disordered at room temperature (RT), become ordered at low temperatures. [e] $C_6H_{11}O$ = 2-(hydroxymethyl)pent-4-enyl. [f] $C_{10}H_{19}N_8$ = 6,7,13,14-tetramethyl-1,2,4,5,8,9,11,12-octaazacyclotetradeca-5,7,12,14-tetraenato. [g] Twinned to give apparent O unit cell of some dimensions. [h] Disordered.

7.476(2)	11.912(4)	6.606(2)	94.55(2)	110.17(2)	92.38(3)	1283	2.1	3.1		84
14.800(8)	8.775(4)	8.412(4)				727	6.1			85
7.047(1)	13.690(3)	14.510(2)				882	4.3			86
9.689(3)	13.265(4)	17.500(6)				2338	5.3			87
7.031(3)		11.754(5)				225	5.5		RT	88
6.82	7.04	11.64							−100°	
8.66(1)	13.87(1)	10.94(2)			120.1(2)	1560	5.0			60
14.673(2)	7.732(1)	16.867(2)		02.30(2)		3837	6.9			89
11.614(3)	7.155(4)	19.068(4)		104.5(2)		1702	10			78
28.101(5)	8.351(2)	15.154(5)		129.28(2)		1372	3.4	4.3	−150	91
28.47(2)	8.46(1)	15.28(1)		129.43(3)					23	
14.940(4)	9.006(2)	11.503(3)		93.08(2)		1435	6.7	6.0		92
10.0216(9)	10.9918(11)	14.5535(13)		98.57(1)		5197	4.60	3.36		93
14.087(4)	13.986(6)	14.887(5)		117.76(2)		2807	4.0			94
11.88(1)	15.00(2)	10.70(1)				2948	7.6			95
8.277(2)	13.929(4)	13.418(4)				872	4.2	3.4		96
9.0217(11)	11.767(2)	9.0769(9)		109.12(1)		1341	6.2	5.6		98
10.082(6)		31.49(7)				1030	9.9		273K	99
9.98		31.25							203 ± 4K	
9.12(1)	11.62(1)	17.31(2)		90		570	5.1		g	100
8.359(2)	11.309(2)	8.862(2)		97.00(2)		1354	4.6	6.0	h	101
11.003(1)		045(1)				614	3.9	4.0		102
18.882(4)	14.677(3)	22.860(7)		110.67(2)		1506	5.6	5.9		103

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40	$C_{13}H_4F_3O_7SW^-.C_8H_{20}N^+$	$NEt_4[W(CO)_5(C_8H_4F_3O_2S)]$[a]	O	$C222_1$	8
240	$C_{13}H_5ClF_{12}W$	$WCl[C_2(CF_3)_2]_2(C_5H_5)$	Tri	$P\bar{1}$	2
229	$C_{13}H_5F_5FeO_4S$	$Fe(SO_2C_6F_5)(CO)_2(C_5H_5)$	M	$P2_1/c$	4
376	$C_{13}H_8Cl_2HgMoN_2O_3$	$MoCl(HgCl)(CO)_3(bipy)$	M	$P2_1/c$	4
70	$C_{13}H_8MnO_6^-.C_4H_{12}N^+$	$NMe_4[MnAcBz(CO)_4$-*cis*$]$	M	$P2_1/c$	4
327	$C_{13}H_{10}O_3Rh_2$	$Rh_2(CO)_3(C_5H_5)_2$			
354	$C_{13}H_{11}AsMn_2O_6$	$Mn_2(AsMe_2)(CO)_6(C_5H_5)$	O	Pbca	8
177	$C_{13}H_{11}FeNO_6$	$Fe(CO)_3(C_{10}H_{11}NO_3)$[c]	Tri	$P\bar{1}$	2
173	$C_{13}H_{12}FeO_3$	$Fe(CO)_3(C_{10}H_{12})$[d]	O	$P2_12_12_1$	4
194	$C_{13}H_{14}Cl_2Hf$	$HfCl_2[(C_5H_4)_2(CH_2)_3]$	O	Pbca	8
193	$C_{13}H_{14}Cl_2Zr$	$ZrCl_2[(C_5H_4)_2(CH_2)_3]$	O	Pbca	8
113	$C_{13}H_{14}CrO_6$	$Cr(CO)_4[C_7H_8(OMe)_2]$	O	$P2_12_12_1$	4
164	$C_{13}H_{15}N_2RhS_2$	$Rh(C_8H_{12})(Memnt)$[e]	M	$P2_1/a$	4
78	$C_{13}H_{25}CoN_4O_2$	$CoMe_2(C_{11}H_{19}N_4O_2)$[f]	M	Pc	2
287	$C_{13}H_{35}B_9MnNO_4$	6-$Mn(CO)_3$-8-$Et_3N(CH_2)_4OB_9H_{12}$	Tri	$P\bar{1}$	2
16	$C_{13}F_{12}Mn_2N_2O_7$	$Mn_2[N{:}C(CF_3)_2]_2(CO)_7$	M	$P2_1/c$	4

[a] $C_8H_4F_3O_2S$ = $CF_3COCHCOC_4H_3S$. [b] Identity of Fischer's "$[Rh(CO)_2(C_5H_5)]_2$"; cell data only; cf. Mills and Nice (ref. 110) [c] $C_{10}H_{11}NO_3$ = 3-formyl-N-carbethoxyazepine.
[d] $C_{10}H_{12}$ = 3,4,5,6-η^4-tricyclo[6.2.0.$0^{2,7}$]deca-3,5-diene [e] Memnt = 1-methylthiomaleonitrile-2-thiolate
[f] $C_{11}H_{19}N_4O_2$ = 3,3'-(trimethylenedinitrilo)bis(butan-2-one oximato)

325	$C_{14}H_6Fe_2O_6$	$Fe_2(CO)_6(C_8H_6)$[a] sym	Tri	P1	4
326	$C_{14}H_6Fe_2O_6$	$Fe_2(CO)_6(C_8H_6)$[a] unsym	M	$P2_1/c$	4
279	$C_{14}H_{10}Ag_4^{4+}.4ClO_4^-.H_2O$	$C_{14}H_{10}(AgClO_4)_4.H_2O$	M	$P2_1/n$	2
272	$C_{14}H_{10}BMnO_3$	$Mn(CO)_3(C_5H_5BPh)$	O	Pbca	8
215	$C_{14}H_{10}IMoNO_2$	$MoI(CO)_2(CNPh)(C_5H_5)$	O	Pbca	8
134	$C_{14}H_{13}BF_6N_6Pt$	$PtMe[HB(pz)_3][C_2(CF_3)_2]$	O	Pnma	4
263	$C_{14}H_{14}CrO_5$	$Cr(CO)_3[C_6H_4(CO_2H)Bu^t$-*p*$]$	M	$P2_1/c$	4

8.82	18.62	31.99				2559	4.4			104
7.942(1)	9.302(1)	12.828(2)	93.76(1)	104.76(1)	111.57(1)	2406	7.9			105
10.97(2)	12.12(2)	12.06(2)		117.6(2)		754	10.7			106
12.685(4)	12.494(4)	11.925(3)		118.70(2)		1407	8.0			107
10.35	15.58	12.09		100.99		1249	6.85			108
8.06(3)	9.04(2)	9.45(3)	73.8(2)	80.7(2)	83.3(2)				*b*	109
11.157(8)	12.665(8)	22.507(14)				730	3.9			111
7.022(3)	10.550(4)	9.500(3)	92.82(3)	94.53(3)	96.13(3)	2363	4.6			112
11.758(3)	16.987(7)	6.032(2)				1359	3.3	2.9		114
8.177(3)	13.916(4)	22.425(9)				1797	2.9			115
8.277(2)	13.922(4)	22.568(5)				1049	2.64	2.58		116
14.786(2)	10.137(1)	9.440(1)				840	4.7			113
14.78(1)	10.69(1)	9.20(1)		106.09(5)		2127	3.2	4.5		117
7.600(8)	8.301(8)	13.675(6)		113.5(3)		1342	3.4			118
10.018(2)	12.843(3)	9.305(2)	99.661(15)	94.545(4)	96.918(15)	1803	5.6	6.1		119
9.298(5)	26.614(19)	9.543(8)		121.00(5)		1512	5.2			120
8.714	14.926	12.174	99.04	102.06	68.96	3337	6.3	5.5		121
8.076	14.188	12.408		113.57		2093	7.2	5.8		121
24.189(6)	9.325(2)	5.304(1)		90.35(5)		2151	4.9			122
10.47(1)	15.54(2)	16.36(2)				1084	4.8			123
12.035(4)	17.284(5)	14.510(5)				1471	4.0			124
18.424(5)	13.385(3)	7.568(2)				1917	3.5	5.0		126
12.230(5)	7.509(3)	18.099(6)		117.91(4)		1717	4.76			127

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216	$C_{14}H_{14}MoO_3$	$Mo(CO)_2(C_7H_9O)(C_5H_5)$ [b]	M	Cc	16
32	$C_{14}H_{16}As_2IO_4W^+ \cdot I_3^-$	$[WI(CO)_4(diars)]I_3$	M	$P2_1/m$	2
328	$C_{14}H_{16}N_2Ni_2$	$[Ni(CNMe)(C_5H_5)]_2$	M	$P2_1/c$	4
236	$C_{14}H_{19}Nb$	$NbEt(C_2H_4)(C_5H_5)_2$	Tet	$I4_1/a$	16
44	$C_{14}H_{20}O_6P_2Re_2S_4$	$[Re(CO)_3(S_2PEt_2)]_2$	Tri	$P\bar{1}$	1
75	$C_{14}H_{22}CoN_5O_4$	$CoMe(py)(dmg)_2$	Tri	$P\bar{1}$	2
124	$C_{14}H_{24}Cl_4Pt_2$	$[PtCl_2(C_7H_{12})]_2$	M	$P2_1/c$	2
29	$C_{14}H_{33}O_2P_4Ta$	$TaH(CO)_2[(CH_2PMe_2)_2]_2$	M	$P2_1/c$	2
341	$C_{14}Co_4Ni_2O_{14}^{2-} \cdot 2C_4H_{12}N^+$	$(NMe_4)_2[CO_4Ni_2(CO)_{14}]$	Trig	$R\bar{3}$	3
335	$C_{14}Mn_3O_{14}^- \cdot C_{24}H_{20}As^+$	$AsPh_4[Mn_3(CO)_{14}]$	Tri	$P\bar{1}$	2

[a] C_8H_6Fe = benzoferrole [b] C_7H_9O = 1,1',2'-η^3-[(oxo-5'-cyclopent-1'-ene)yl]-1-ethyl

371	$C_{15}H_6Co_4O_9$	$Co_4(CO)_9(C_6H_6)$	Trig	$R\bar{3}$	2
330	$C_{15}H_7CoFeO_6$	$FeCo(CO)_6(C_9H_7)$	M	$P2_1/c$	4
225	$C_{15}H_{10}FeO_2$	$Fe(C_2Ph)(CO)_2(C_5H_5)$	M	$P2_1/n$	4
377	$C_{15}H_{12}Cl_2MoO_2Sn$	$Mo(SnCl_2Ph)(CO)_2(C_7H_7)$	M	$P2_1/n$	4
332	$C_{15}H_{15}CoFeO_4$	$FeCo(CO)_4(C_4H_4Me_2)(C_5H_5)$	M	C2/c	8
362	$C_{15}H_{15}Mn_3N_4O_4$	$Mn_3(NO)_4(C_5H_5)_3$	M	$P2_1/c$	4
190	$C_{15}H_{15}Ni_2^+ \cdot BF_4^-$	$[Ni_2(C_5H_5)_3]BF_4$	O	$P2_12_12_1$	4
185	$C_{15}H_{15}Ti$	$Ti(C_5H_5)_3$	O	Pbca	8
260	$C_{15}H_{16}FeO_6$	$Fe(CO)_2[C_7H_8C_2H_2(CO_2Me)_2]$	M	$P2_1/c$	4
359	$C_{15}H_{16}Fe_2GeO_3$	$Fe_2(GeMe_2)(CO)_3(C_5H_5)_2$	O	$P2_12_12_1$	4
333	$C_{15}H_{20}CoNiO_4P$	$CoNi(CO)_4(PEt_3)(C_5H_5)$	M	$P2_1/c$	4
281	$C_{15}H_{21}AgFeO_6^+ \cdot NO_3^- \cdot H_2O$	$Fe(acac)_3AgNO_3 \cdot H_2O$	M	$P2_1/c$	4
220	$C_{15}H_{23}ClMoN_2O_6P_2$	$MoCl[C{:}C(CN)_2][P(OMe)_3]_2(C_5H_5)$	M	$P2_1/n$	4
13	$C_{15}H_{27}As_3Cr_2O_6$	$Cr_2(CO)_6(AsMe)_3$	M	$P2_1/c$	4

16.070(6)	41.48(2)	10.854(4)		134.67(3)		~2300	11			128
14.43(1)	10.86(1)	8.01(1)		93.51(8)		1544	7			129
6.999(2)	22.07(1)	9.130(3)		93.433(5)		2416	3.7	3.7		130
16.481(2)		18.186(2)				1247	4.4	4.9		131
13.14(5)	12.34(2)	7.20(1)	131.76(9)	132.13(42)	47.15(9)	922	6.2			132
14.38(1)	10.02(1)	9.41(1)	56.3(1)	127.3(1)	106.6(1)	3094	6.4			133
6.035(2)	8.030(3)	19.355(8)		91.03(3)		1982	9.3			66
8.963(5)	12.467(4)	12.552(5)		125.53(6)		935	13			134
11.283(6)		21.106(12)				725	3.3			135
11.614(11)	9.646(12)	18.022(22)	100.89(5)	96.66(6)	90.96(5)	1414	9.2			136
9.798(3)			82.95(1)			491	3.3	3.0		137
12.076(14)	9.905(10)	12.683(12)		97.5(1)		1899	9.8			138
9.473(2)	9.796(2)	13.887(3)		109.70(2)		1696	6.0			139
6.937	14.883	19.086		90.585		2926	5.0			140
17.730(16)	7.404(14)	23.861(40)		95.5(1)		3066	7.2	6.0		141
13.341(4)	7.951(2)	16.837(7)		107.73(3)		1338	3.2	1.2	*a*	142
17.019(2)	11.454(2)	8.074(1)				1216	6.3			144
13.468(6)	10.229(5)	17.180(7)				1461	5.2	5.5		145
11.781	12.891	15.407		139.7			*b*			146
13.503(1)	14.162(2)	8.229(1)				2141	3.5	4.8		147
8.945(8)	10.462(14)	20.005(25)		107.5(1)		2853	5.2			148
12.274(5)	11.761(5)	17.235(5)		120.64(12)		1672	6.6			149
9.127(2)	18.515(2)	12.923(2)		91.56(1)		3037	4.3	6.1		150
17.92	10.40	17.00		90.3		955	6.3			151

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53	$C_{15}H_{37}Cl_3NP_2Rh$	$RhCl_3(CHNMe_2)(PEt_3)_2$	O	$P2_12_12_1$	4

[a] New determination; see also ref. 143. [b] Disordered, partial refinement.

367	$C_{16}H_6O_8Ru_3$	$Ru_3(CO)_8(C_8H_6)$[a]	Tri	$P\bar{1}$	2
306	$C_{16}H_{10}Cr_2O_6$	$[Cr(CO)_3(C_5H_5)]_2$	M	$P2_1/c$	2
307	$C_{16}H_{10}Mo_2O_6$	$[Mo(CO)_3(C_5H_5)]_2$	M	$P2_1/c$	2
382	$C_{16}H_{10}Mo_2O_6Zn$	$Zn[Mo(CO)_3(C_5H_5)]_2$	M	$P2_1/n$	2
308	$C_{16}H_{10}O_6W_2$	$[W(CO)_3(C_5H_5)]_2$	M	$P2_1/c$	2
355	$C_{16}H_{12}As_2F_4Mn_2O_8$	$[Mn(CO)_4]_2(AsMe_2)(C_4F_4AsMe_2)$	M	$P2_1/n$	4
7	$C_{16}H_{12}MoN_4O_4$	$Mo(CO)_4$(Mepaphy)[b]	M	$P2_1/c$	4
384	$C_{16}H_{14}CdMn_2O_{13}$	Cd(diglyme)$[Mn(CO)_5]_2$	M	$P2_1/n$	4
172	$C_{16}H_{14}FeO_7$	$Fe(CO)_3[C_7H_8C_2(CO_2Me)_2]$	M	$P2_1/c$	4
162	$C_{16}H_{14}MoO_4$	$Mo(CO)_4(C_{12}H_{14})$[c]	M	$P2_1/n$	4
273	$C_{16}H_{16}B_2Fe_2O_4$	$[Fe(CO)_2(C_5H_5BMe)]_2$	O	Cmcm	4
169	$C_{16}H_{16}FeN_2O_5$	$Fe(CO)_3(MeC_4H_4CHMeNHC_6H_4NO_2\text{-}m)$	Tri	$P\bar{1}$	2
321	$C_{16}H_{16}Fe_2N_2O_2$	$Fe_2(CO)_2(\mu\text{-}CNMe)_2(C_5H_5)_2$	Tri	$P\bar{1}$	2
363	$C_{16}H_{16}Fe_3O_8S_2$	$Fe_3(CO)_8(C_4H_8S)_2$[d]	M	C2/c	4
270	$C_{16}H_{16}Pa$	$Pa(C_8H_8)_2$			
170	$C_{16}H_{17}FeNO_3$	$Fe(CO)_3(MeC_4H_4CHMeNHPh)$	M	$P2_1/c$	4
353	$C_{16}H_{17}Mo_2O_4P$	$Mo_2H(CO)_4(PMe_2)(C_5H_5)_2$	Tri	$C\bar{1}$	4
356	$C_{16}H_{18}As_3F_5Mn_2O_5$	$Mn_2(CO)_6(AsMe_2)[C_4F_5(AsMe_2)_2]$	Tri	P1	2
389	$C_{16}H_{18}Ge_2O_{10}Re_2$	$[Re(CO)_4C(O)Me(GeMe_2)]_2$	M	I2/m	2
			Tri	$P\bar{1}$	
140	$C_{16}H_{18}N_2NiO_2.C_7H_8$	$Ni(MeN{:}CHC_6H_4OH)_2.C_7H_8$	M	$P2_1/n$	4
269	$C_{16}H_{20}Fe$	$Fe(C_8H_{10})_2$	M	$P2_1/$	4
157	$C_{16}H_{22}Cl_2Pd_2$	$[PdCl(C_8H_{11})]_2$	Hex	$R\bar{3}$	9

1.84(1)	12.26(1)	15.72(2)				2112	5.0	5.6		152
9.824(2)	8.866(2)	12.665(3)	83.82(2)	93.97(2)	125.90(2)		7.7			153
10.468(1)	7.625(1)	12.227(2)		127.22(1)		1269	2.7	3.3		154
10.387(1)	8.031(1)	12.039(2)		125.58		1471	2.1	2.9		155
11.101(4)	7.548(2)	11.726(4)		64.43(2)		2101	4.0	5.8		156
10.374(1)	7.971(1)	12.047(2)		125.83(1)		1548	2.3	3.9		155
9.040(3)	13.552(4)	18.517(5)		90.52(2)		1728	3.6			157
8.326(8)	11.916(12)	18.056(18)		93.15(10)		1336	8.8			158
10.161(10)	23.010(20)	9.718(9)		91.80(2)		2191	4.31			159
12.360	9.295	14.195		102.2		2583	5.6	5.0		146
17.962(5)	11.944(3)	7.125(2)		93.65(2)		1477	7.7			125
9.80(1)	8.47(1)	19.96(2)				556	5.3			123
11.743(2)	9.755(2)	7.914(1)	94.66(1)	89.55(1)	109.46(1)	2206	2.6			161
8.660(2)	12.682(4)	7.993(2)	101.72(2)	116.28(1)	83.28(2)	1370	3.9	4.7		160
15.251(3)	8.402(2)	17.445(4)		104.91(2)		1024	4.5	6.5		162
7.09(4)	8.75(4)	10.62(4)		98.5(4)					*e*	163
11.789(2)	14.528(3)	9.259(2)		96.61(1)		1998	2.4			161
9.192(11)	16.631(20)	11.592(14)	93.06(6)	97.56(7)	90.68(9)	2318	7.6	7.7	*f*	164
9.580(4)	15.279(6)	9.292(3)	93.07(2)	119.26(2)	82.80(2)	2234	8.0			165
9.639(8)	11.504(9)	11.140(9)		97.22(1)		692	3.9		*g*	166
9.05	9.05	9.63	106.9	118.0	101.0					
13.776(2)	12.159(2)	12.724(2)		91.97(2)		1340	6.0			167
8.61(1)	21.31(2)	11.39(1)		143.0(08)		1064	5.9			168
27.155(7)		6.669(6)				731	5.1			169

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11	$C_{16}H_{24}As_4Cr_2O_8$	$[Cr(CO)_4]_2(AsMe_2)_4$	M	I2/m	2
126	$C_{16}H_{27}Cl_2NOPt$	$PtCl_2[(R)\text{-}NH_2CHMePh]\text{-}[(S)\text{-}Bu^tCHMeO\text{-}(R)\text{-}CH{:}CH_2]$	O	$P2_12_12_1$	4
43	$C_{16}H_{30}N_3ORe S_6$	$Re(CO)(S_2CNEt_2)_3$	Tri	$P\bar{1}$	2
86	$C_{16}H_{40}Ni_2P_4$	$Ni_2[(CH_2)_2PMe_2]_4$	M	C2/m	2
291	$C_{16}H_{42}B_6P_2Pt$	6-$Pt(PEt_3)_2$-5,8-$Me_2C_2B_6H_6$	O	Pbca	16
296	$C_{16}H_{43}B_7P_2Pt$	10-$Pt(PEt_3)_2$-2,8-$Me_2C_2B_7H_7$	M	$P2_1/a$	
295	$C_{16}H_{45}B_7NiP_2$	$[Ni(PEt_3)_2]Me_2C_2B_7H_9$	M	$P2_1/n$	4

[a] C_8H_6 = pentalene. [b] Mepaphy = (E)-5-methylpyridine-2-carboxaldehyde-2'-pyridylhydrazone. [c] $C_{12}H_{14}$ = η^4-1,2:5,6-bicyclo[4.3.3]dodeca-1,3,5,7-tetraene. [d] C_4H_8S = tetrahydrothiophene. [e] Crystal data only, from powder pattern; data for U, Th compounds also listed. [f] Neutron diffr.; cf. X-ray study, ref.406. [g] Apparent space group and unit cell is composite of two orientations of triclinic cell; refinement in I2/m.

313	$C_{17}H_8Fe_2N_2O_7$	$Fe_2(CO)_7(bipy)$	Tri	$P\bar{1}$	2
50	$C_{17}H_{10}BrMnN_2O_3$	$MnBr(CO)_3(CNPh)_2$	M	$P2_1/n$	4
372	$C_{17}H_{10}Co_4O_9$	$Co_4(CO)_9(C_6H_4Me_2)$	M	$P2_1/c$	4
318	$C_{17}H_{10}Fe_2N_2O_3$	*cis*-$Fe_2(CO)_3[C{:}C(CN)_2](C_5H_5)_2$	M	$P2_1/c$	2
241	$C_{17}H_{10}Fe_2O_6$	$Fe(COC_6H_6[Fe(CO)_3]C_5H_4)(CO)_2$ [b]	M	$P2_1/c$	4
181	$C_{17}H_{10}Fe_2O_7$	$Fe_2(CO)_6(C_{11}H_{10}O)$ [c]	M	$P2_1/c$	4
55	$C_{17}H_{16}I_3N_2ORh$	$RhI_3[CPh(NMe)CPh{:}NMe](CO)$	M	$P2_1/n$	4
158	$C_{17}H_{21}F_6O_{\frac{1}{2}}Rh.\frac{1}{2}H_2O$	$Rh(H_2O)(acac)[C_8H_{12}C_2(CF_3)_2].\frac{1}{2}H_2O$	M	C2/c	8
259	$C_{17}H_{22}MnO_5$	$Mn(CO)_3(C_{14}H_{11}O_2)$ [d]	M	$P2_1/c$	4
347	$C_{17}Fe_6O_{16}^{2-}.2C_4H_{12}N^+$	$(NMe_4)_2[Fe_6C(CO)_{16}]$	O	Pnma	8

[a] Ligand is disordered mixture of *o*-, *m*-xylenes. [b] $COC_6H_6C_5H_4$ = 1-(η^5-cyclopentadienyl)-2,3,4,5-η^4-cyclohexa-2,4-dien-1-oyl. [c] $C_{11}H_{10}O$ = 2,3,4,11-η^4-bicyclo[4.3.1]undeca-2,6,8-triene-4,11-yl-11-one. [d] $C_{14}H_{11}O_2$ = 1-*syn*-(1',2'-dihydro-2'-oxo-1'-oxa-azulen-3'-yl)-η^5-pentadienyl.

239	$C_{19}H_{10}F_{12}Mo$	$Mo[C_2(CF_3)_2C_5H_5][C_2(CF_3)_2](C_5H_5)$	M	$P2_1/n$	4
107	$C_{18}H_{14}F_{12}O_4Pd$	$Pd[acacC_2(CF_3)_2]_2$	M	$P2_1/n$	4

9.920(2)	10.976(2)	13.240(2)		118.14(1)		727	2.9	4.7	170
25.56(3)	11.37(1)	6.84(1)				1764	7.1		171
15.666(1)	9.933(1)	9.507(1)	107.61(1)	93.04(1)	114.63(1)	2660	2.75		172
11.8445(6)	10.7782(8)	9.3078(6)		99.672(6)		2500	3.7	4.4	98
18.868(8)	17.143(7)	31.07(2)				4569	7		46
16.955(10)	18.879(18)	10.066(16)		125.66(8)		2810	10.7		174
9.144(3)	18.954(5)	15.021(4)		90.51(4)		3449	10.4		175
10.447(6)	12.447(6)	7.047(2)	84.49(3)	97.50(4)	101.26(4)				176
18.03(5)	5.93(5)	16.83(5)		107.33		555	11.1		177
10.03(1)	9.86(1)	20.24(2)		96.40(5)		1883	5.6	5.4	137
7.218(1)	33.275(6)	13.364(2)		99.71(1)		1441	8.4		178
6.562(1)	21.690(5)	11.399(2)		96.78(2)		2852	5.0	4.2	179
12.007(6)	11.842(7)	12.742(7)		107.47(2)		1632	5.2		85
10.83(1)	17.24(2)	11.52(1)		97.3(2)		2400	4.7		180
8.84	19.34	22.61		102.8		1388	9.1		181
13.249(5)	7.178(4)	15.662(6)		96.66(3)		1009	6.6		182
10.098(15)	18.788(20)	36.712(36)				1584	11.9		183
12.905(6)	9.461(3)	15.302(6)		106.34(4)		2249	9.5		105
9.512	23.29	11.30		114.9		4302	5.8		184

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317	$C_{18}H_{19}Fe_2NO_3$	$Fe_2(CO)_3(CNBu^t)(C_5H_5)_2$	M	$P2_1/c$	4
256	$C_{18}H_{20}Fe$	$Fe(C_5H_5)(C_{13}H_{15})^a$	M	$P2_1/c$	4
361	$C_{18}H_{20}Nb_3O_{10}$	$[Nb(HCO_2)(C_5H_5)]_3(OH)_2(O)_2$	M	$B2/m$	4
264	$C_{18}H_{22}Cl_2Mo_2$	$[MoCl(C_3H_5)(C_6H_6)]_2$	M	$P2_1/b$	2
390	$C_{18}H_{22}Fe_2Ce_2O_5$	$[Fe(CO)_2(C_5H_5)CeMe_2]_2O$	M	$P2_1/n$	4
248	$C_{18}H_{22}NiO_2$	$Ni[C_5H_5(Me_2C_2O)_2](C_5H_5)^b$	Tri	$P\bar{1}$	2
207	$C_{18}H_{26}MoRhS_2^+.F_6P^-$	$[(C_5H_5)_2Mo(SMe)_2Rh(C_3H_5)_2]PF_6$	M	$P2_1/b$	4
310	$C_{18}H_{28}Mo_2N_2S_2$	$Mo_2(NBu^t)_2S_2(C_5H_5)_2$	M	$P2_1/n$	2
151a	$C_{14}H_{31}NiP$	$NiMe(CHMeCHCHMe)(PPr^i_2Ph)$	M	$P2_1/c$	4
357	$C_{18}Ga_2Mn_4O_{18}$	$Mn_2(CO)_8[\mu\text{-}GaMn(CO)_5]_2$	Tet	$I4_1/a$	8
358	$C_{18}In_2Mn_4O_{18}$	$Mn_2(CO)_8[\mu\text{-}InMn(CO)_5]_2$	Tet	$I4_1/a$	8
45	$C_{18}O_{16}Re_4S_6$	$Re_4(CO)_{16}(SCS_2)_2$	Tri	$P\bar{1}$	1
344	$C_{18}O_{18}Pt_9^{2-}.2C_{24}H_{20}P^+$	$(PPh_4)_2[Pt_3(CO)_6]_3$	M	$C2/c$	4

^{a} $C_{13}H_{15}$ = 2,3-*exo*-η^5-cyclopentadieno-4,4-dimethylbicyclo[3.2.1]octa-2,6-diene.
^{b} $C_5H_5(Me_2C_2O)_2$ = 1,3',4'-η^3-2-methyl-2-(6',6'-dimethylbicyclo[3.2.0]hept-3'-en-7'-on-2'-yl)propionyl.

38	$C_{19}H_{15}Cl_2OPPt$	*cis*-$PtCl_2(CO)(PPh_3)$	Tri	$P\bar{1}$	2
22	$C_{19}H_{15}FeN_2O_3P$	$Fe(CO)(NO)_2(PPh_3)$	Tri	$P\bar{1}$	2
163	$C_{19}H_{22}Cl_2N_2Ru$	$RuCl_2(C_7H_8)(NH_2Ph)_2$	O	$Cmc2_1$	4
146	$C_{19}H_{23}BMoN_4O_2$	$Mo(CO)_2[Et_2B(pz)_2](C_7H_7)$	M	$P2_1/n$	4
351	$C_{19}H_{24}NNi_3$	$Ni_3(C_5H_5)_3(NBu^t)$	M	$C2/c$	8
93	$C_{19}H_{34}ClOP_2Pt^+.F_6P^-$	$[Pt(C_6H_4Cl\text{-}p)(CO)(PEt_3)_2]PF_6$	O	$Pnam$	4
375	$C_{19}H_{38}CrO_5Si_4Sn$	$Cr(CO)_5Sn[CH(SiMe_3)_2]_2$	M	$P2_1/c$	4
387	$C_{20}H_2Mn_4O_{20}Sn_2$	$[Mn(CO)_5]_4Sn_2H_2$	M	$C2/c$	4
386	$C_{20}H_8CdMn_2N_2O_{10}$	$[Mn(CO)_5]_2Cd(bipy)$	M	$P2_1/n$	4
15	$C_{20}H_{10}Mn_2N_4O_8$	$[Mn(CO)_4N{:}NPh]_2$	Tri	$P\bar{1}$	1
274	$C_{20}H_{12}Cu_4F_{12}O_8$	$Cu_4(O_2CCF_3)_4(C_6H_6)_2$	M	$P2_1/n$	4

15.571(8)	9.518(9)	12.162(7)		101.74(4)		907	3.1	3.5	185
10.733(3)	8.122(1)	16.873(5)		110.95(1)		842	9.1		186
13.150	8.901	17.467			102.7		11.5		187,188
9.29(2)	12.49(2)	7.65(2)			104.3(3)	961	4.9		189
8.056(2)	12.506(2)	22.631(3)		98.01		1780	5.1	6.8	190
9.0048(16)	15.5241(33)	6.0445(12)	94.17(2)	109.94(1)	94.04(2)	2794	3.04	3.05	191
8.23(2)	17.71(3)	15.33(3)			96.5(2)	1917	9.8		192
15.486(2)	8.839(1)	7.787(1)		93.882(5)		1244	2.4		193
8.927(3)	26.031(9)	8.718(2)		110.88(2)		1404	6.26	4.56	194
13.50(2)		28.26(3)				2392	3.2		195,196
13.72(2)		28.54(3)				3172	4.0		195,196
7.121(1)	8.540(2)	14.502(3)	89.07(1)	108.75(1)	104.53(1)	1477	8.3		197
20.123(3)	14.311(3)	26.433(5)		115.22(6)		2436	6.3	6.8	103
10.482(1)	9.593(1)	11.007(1)	97.57(1)	117.96(1)	93.80(1)	4150	6.7	7.5	198
10.96(1)	10.20(1)	10.45(1)	115.84(8)	117.38(8)	78.90(8)	1448	5.0	6.5	199
17.162(4)	12.589(3)	8.522(2)				2642	2.5		200
16.242(7)	9.602(5)	12.777(7)		94.45(4)		2023	9.5		201
28.40(3)	9.16(2)	15.28(2)		100.5(2)		1620	13.8		202
12.453(15)	15.282(17)	14.360(16)				1872	14.24		203
9.340(4)	13.548(8)	24.272(10)		90.33(1)		1591	7.1		204
15.71(5)	17.18(5)	12.51(5)		107.4(1)		2968	20		205
14.429(15)	15.805(16)	10.423(10)		94.62(2)		2041	5.27		206
7.2358(13)	8.8893(17)	9.4677(18)	80.52(2)	77.38(1)	71.44(1)	1974	3.43		207
24.581(6)	10.586(1)	11.603(2)		113.13(1)		2342	10.6		208

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110	$C_{20}H_{12}FeO_4$	$Fe(CO)_4(C_{16}H_{12})$[a]	M	$P2_1/n$	
23	$C_{20}H_{15}CoNO_3Sb$	$Co(CO)_2(SbPh_3)(NO)$	M	$P2_1/n$	
255	$C_{20}H_{18}FeO$	$Fe(MeC_5H_3CHPhCH_2COC_5H_4)$[b]	O	Aba2	8
197	$C_{20}H_{20}Cl_2Nb_2O^{2+}.2BF_4^-$	$\{[NbCl(C_5H_5)_2]_2O\}(BF_4)_2$	O	Pnn2	2
192	$C_{20}H_{20}Cl_2OZr_2$	$[ZrCl(C_5H_5)_2]_2O$	M	Cz	4
184	$C_{20}H_{20}U$	$U(C_5H_5)_4$	Tet	$I\bar{4}2m$	2
352	$C_{20}H_{23}Ni_4$	$Ni_4H_3(C_5H_5)_4$	M	C2/c	8
165a	$C_{20}H_{24}NiO_4$	$Ni(C_6Me_4O_2)_2$[c]	M	P2/a	4
114	$C_{20}H_{28}MoN_6OS_4$	$MoO(S_2CNPr_2)_2C_2(CN)_4$	O	Pbca	8
108	$C_{20}H_{29}F_{12}N_3O_2Pd$	$Pd[OC(CF_3)_2OC(CF_3)_2](CNBu^t)$ $[C(NHBu^t)(NEt_2)]$	M	$P2_1/a$	4
89	$C_{20}H_{30}ClP_2PtSi$	*trans*-$PtCl(CH_2SiMe_3)(PMe_2Ph)_2$	M	Cc	4
220	$C_{20}H_{30}Ni$	$(+)$-$Ni(C_{10}H_{15})_2$[d]	M	$P2_1$	2
235	$C_{20}H_{33}Al_2ClZr$	$ZrCl[CH_2CH(AlEt_2)_2](C_5H_5)_2$	O	$P2_12_12_1$	
89	$C_{20}H_{33}ClP_2PtSi$	*trans*-$PtCl(CH_2SiMe_3)(PMe_2Ph)_2$	M	Cc	4
47	$C_{20}H_{33}ClO_3PPh$	*cis*-$RhCl(CO)_2[P(O)Cy_3]$	M	$P2_1/c$	4
298	$C_{20}H_{37}B_9P_2Pt$	*closo*-1-$Pt(PMe_2Ph)_2$-2,4-$Me_2C_2B_9H_9$	Tri		
291	$C_{20}H_{37}ClINP_2Pt$	*trans*-$PtI(CMe{:}NC_6H_4Cl\text{-}p)(PEt_3)_2$	M	$P2_1/c$	4
348	$C_{20}O_{19}Rh_8$	$Rh_8C(CO)_{19}$	Tri	$P\bar{1}$	2

[a] $C_{16}H_{12}$ = dibenzosemibullvalene [b] m.p. 228° [c] $C_6Me_4O_2$ = durroquinone
[d] $C_{10}H_{15}$ = η^3-pinenyl (7,7-dimethyl-1a,1,2-η^3-1-methylenebicyclo[3.1.1]hept-1-enyl)

378	$C_{21}H_{17}ClMoO_2Sn$	$Mo(SnClPh_2)(CO)_2(C_7H_7)$	M	$P2_1/n$	4
159	$C_{21}H_{19}F_{12}IrO_2$	$Ir[acacC_2(CF_3)_2][C_8H_{12}C_2(CF_3)_2]$	Tri	$P\bar{1}$	2
247	$C_{21}H_{20}Fe_2O_5$	$Fe_2(CO)_5(C_5H_4CMe_2C_5H_4CMe_2)$	M	$P2_1/c$	4
145	$C_{21}H_{25}BMoN_4O_2$	$Mo(CO)_2(CH_2CPhCH_2)[Et_2B(pz)_2]$	O	$P2_12_12_1$	4
394	$C_{21}H_{25}F_5O_2RuSi_2$	$Ru(SiMe_3)(CO)_2[C_7H_7(C_6F_5)SiMe_3]$	M	Cc	4
110a	$C_{21}H_{25}N_2O_2Rh$	$Rh(acac)(C_8H_8)(py)_2$[a]	Tri	$P\bar{1}$	2
58	$C_{21}H_{29}Cl_2N_2PPt$	*cis*-$PtCl_2[C(NPhCH_2)_2](PEt_3)_2$	O	Pnam	4

9.365(4)	18.355(8)	9.816(4)		106.0(1)		2849	4.4		209
15.697(4)	9.416(3)	13.624(3)		90.04(2)		3532	3.7	4.4	210
14.45(2)	25.08(3)	8.13(1)				658	6.1		211
11.55(1)	8.12(1)	12.93(1)				1293	3.0		60
13.88(1)	7.82(1)	19.05(2)		98.88(10)		1015	5.7		212
8.635(2)		10.542(3)				700	2.07		213,214
28.32(2)	9.23(1)	15.03(1)		102.77(8)		1227	6.4		215
16.653(6)	17.070(6)	6.797(2)			115.8(1)	1200	9.5		216
13.033(5)	18.289(8)	23.805(10)				3093	5.0		217
20.093(3)	9.519(2)	201(3)		96.77(2)		4123	9.9		218
8.919(4)	21.723(8)	13.865(6)		113.88(3)		2573	3.9		219
14.91	7.38	8.04		90.03		1893	11.4		220
14.976(2)	18.607(2)	8.278(1)				1712	10		221
8.919(4)	21.723(8)	13.865(6)		113.88(3)		2573	3.9		219
9.168(10)	13.410(8)	18.271(24)		100.84(9)		1905	6.5		222
9.424(3)	10.285(4)	14.208(8)	100.40(4)	94.32(4)	98.95(3)	4330	4.2		174
20.903(3)	8.531(1)	15.176(2)		107.760(10)		1791	3.8		223
9.18(1)	17.76(2)	10.46(1)	75.95(10)	69.05(10)	92.35(10)				224
8.479	18.295	12.795		90.751		3725	3.0		140
13.445	11.389	8.472	69.5	114.1	104.2	4642	4.8		181
16.083(3)	7.935(3)	16.057(6)		109.82(2)		1773	2.7		226
10.085(2)	10.219(2)	20.654(4)				2397	4.4	5.3	227
6.798(2)	17.057(5)	21.157(6)		91.61(2)			7.0		228
13.167(1)	9.108(1)	9.185(1)	107.93(1)	81.12(1)	93.17(1)	3373	3.3		229
15.991(2)	8.601(2)	16.703				1822	4.8	6.0	230

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59	$C_{21}H_{29}Cl_2N_2PPt$	*trans*-$PtCl_2[C(NPhCH_2)_2](PEt_3)_2$	Tri	$P\bar{1}$	2
61	$C_{21}H_{31}OP_2Pt^+.F_6P^-$	*trans*-{PtMe[$\overbrace{CO(CH_2)_2CH_2}$](PMe$_2$Ph)$_2$}$PF_6$	O	Pcca	8
133	$C_{21}H_{31}P_2Pt^+.F_6P^-$	[PtMe(C_2Me_2)(PMe$_2$Ph)$_2$]PF_6	O	Pnma	4
60	$C_{21}H_{34}NP_2Pt^+.F_6P^-$	*trans*-{PtMe[CMe(NMe$_2$)](PMe$_2$Ph)$_2$}PF_6	M	$P2_1/c$	4
149	$C_{21}H_{47}IrP_2$	Ir(C_3H_5)(P^{i}Pr$_3$)$_2$	Tet	$P\bar{4}2_1c$	4

[a] C_6H_8 = 2,3-bis(methylene)butane-1,4-diyl.

385	$C_{22}H_8CdMn_2N_2O_{10}$	[Mn(CO)$_5$]$_2$Cd(phen)	M	$P2_1/n$	4
174	$C_{22}H_{14}Fe_2O_6$	[Fe(CO)$_3$]$_2C_{16}H_{14}$[a]	O	Pbca	8
21	$C_{22}H_{15}FeO_4Sb$	Fe(CO)$_4$(SbPh$_3$)	Tri	$P\bar{1}$	2
175	$C_{22}H_{18}Fe_2O_6$	[Fe(CO)$_3$]$_2C_{16}H_{18}$[b]	Tri	$P\bar{1}$	1
369	$C_{22}H_{18}O_6Ru_3$	Ru$_3$(CO)$_6$(η^5-C_8H_9)(η^7-C_8H_9)[c]	M	C2/m	2
257	$C_{22}H_{22}Fe$	$FcCH_2CH_2Fc$	O	Pbca	4
102	$C_{22}H_{22}N_2OPd$	$\overbrace{Pd(C_6H_4CH_2NMe_2)}$(sal:NPh)	M	$P2_1$	2
368	$C_{22}H_{22}O_8Ru_3Si_2$	Ru$_3$(CO)$_8$[C_8H_4(SiMe$_3$)$_2$][d]	M	$P2_1/a$	4
233	$C_{22}H_{46}Co_3O_{18}P_6$	Co$_3$(C_5H_5)$_2$[P(O)(OMe)$_2$]$_6$	M	$P2_1/c$	2

[a] $C_{16}H_{14}$ = 3,3'-ethano-1,1'-bis(2,3,4,5-η^4-cyclohepta-2,4,6-trienyl).
[b] $C_{16}H_{18}$ = bis(2,3,4,5-η^4-bicyclo[4.2.0]octa-2,4-dien-3-yl).
[c] η^5-C_8H_9 = η^5-tetrahydropentalenyl; η^7-C_8H_9 = η^7-cyclooctatrienyl.
[d] $C_8H_4(SiMe_3)_2$ = η-1,5-bis(trimethylsilyl)pentalene.

244	$C_{23}H_{14}Fe_2O_5$	Fe$_2$(CO)$_5$($C_5H_4CPh_2$)[a]	M	$P2_1/c$	4
245	$C_{23}H_{14}O_5Ru_2$	Ru$_2$(CO)$_5$($C_5H_4CPh_2$)[a]	Tri	$P\bar{1}$	4
			M	$P2_1/c$	4
331	$C_{23}H_{18}CoFeO_5P$	FeCo(CO)$_5$(PMePh$_2$)(C_5H_5)	Tri	$P\bar{1}$	2
165	$C_{23}H_{21}Cl_2O_2Rh$	Rh(PhCOCHCOPh)($C_8H_{10}Cl_2$)[b]	O	Pnma	4
262	$C_{23}H_{24}CrO_3$	Cr(CO)$_3$($C_{20}H_{24}$)[c]	M	C2/c	8
398	$C_{23}H_{30}Cl_3IrP_2Sn$	Ir($SnCl_3$)(C_7H_8)(PMe$_2$Ph)$_2$	M	$P2_1/c$	4
57	$C_{23}H_{37}NiO_3P$	Ni(CO)$_3$(CHMePCy$_3$)	M	$P2_1/n$	4

13.961(6)	11.782(4)	10.659(5)	92.98(3)	125.29(3)	114.54(3)	2382	4.8	6.5	230
15.503(7)	18.81(1)	17.66(1)				1763	4.4		231
15.447(5)	15.344(4)	11.005(3)				1060	3.6		232
8.515(2)	10.934(2)	28.549(7)		93.93(1)		1865	4.1		233
11.62(1)		18.39				1090	3.6		97
14.574(15)	16.258(16)	10.453(10)		96.87(2)		1431	5.76		206
13.59(3)	15.11(3)	20.32(4)				771	7.0	6.9	234
10.557(1)	10.043(1)	11.230(1)	114.22(1)	91.95(1)	92.25(1)	3217	2.4		235
8.178(2)	6.800(3)	9.729(3)	101.98(3)	106.99(2)	95.83(3)	1788	3.0	3.9	236
24.934(11)	12.632(6)	14.669(8)		114.31(2)		2211	5.9		237
10.063(8)	10.434(4)	16.226(5)				1202	4.5		238
8.629(5)	10.755(8)	11.116(9)		107.2(1)		1967	4.8		239
13.298(8)	10.793(2)	19.812(6)		97.35(4)			5.7		240
11.787(5)	12.519(6)	13.646(6)		111.63(2)			9		241
7.473(2)	15.156(7)	17.710(13)		94.30(7)		2040	4.0		226
11.557(8)	10.520(3)	8.992(3)	99.26(2)	102.26(21)	98.63(4)	3165	2.8		242
12.55(1)	8.96(1)	18.32(9)		90.6(1)					
6.948(9)	11.551(18)	14.618(19)	100.9(1)	86.9(1)	104.3(1)	1466	8.5		243
9.56(1)	20.50	10.65(1)				1482	4.0		244
19.663(3)	14.350(5)	16.443(3)		120.10(1)		1946	4.6	5.3	245
9.616(1)	28.620(6)	9.765(1)		96.72(1)		4704	3.93	3.37	246
10.670(1)	13.879(2)	16.222(2)		91.80(1)		4099	9.4		247

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[a] $C_5H_4CPh_2$ = 6,6-diphenylpentafulvene(α,1,2-η^3-α-phenylbenzyl-η^5-cyclopentadienyl). [b] $C_8H_{10}Cl_2$ = 1,6-dichloro-1,5-cyclooctadiene. [c] $C_{20}H_{24}$ = 1,3,3,5-tetramethyl-6-(1',2'-naphtho)bicyclo[3.2.1]octene.

204	$C_{24}H_{18}N_2O_8Ti$	$Ti(OCOC_6H_4NO_2\text{-}p)_2(C_5H_5)_2$	Tri	$P\bar{1}$	2
234	$C_{24}H_{20}IrOP$	$Ir(CO)(PPh_3)(C_5H_5)$	Tri	$P\bar{1}$	2
168	$C_{24}H_{28}MoO_2$	$Mo(CO)_2(C_{11}H_{14})_2$[a]	M	$P2_1/c$	4
154	$C_{24}H_{28}N_2O_2Pd_2$	$[Pd(CH_2CMeCH_2)]_2$salen	M	$P2_1/c$	2
381	$C_{24}H_{30}Cl_2Mo_2O_8Zn$	$[Mo\{ZnCl(OEt_2)\}(CO)_3(C_5H_5)]_2$	Tri	$P\bar{1}$	1
305	$C_{24}H_{30}Cr_2O_4$	$[Cr(CO)_2(C_5Me_5)]_2$	M	$P2_1/n$	2
208	$C_{24}H_{32}Mo_2NiS_4^{2+}.2BF_4^-$	$\{Ni[(MeS)_2Mo(C_5H_5)_2]_2\}(BF_4)_2$	M	$P2_1/a$	2
209	$C_{24}H_{32}Nb_2NiS_4^{2+}.2BF_4^-.2H_2O$	$\{Ni[(MeS)_2Nb(C_5H_5)_2]_2\}(BF_4)_2.2H_2O$	M	$P2_1/b$	4
322	$C_{24}H_{36}Fe_2O_4S_2$	$[Fe(CO)_2(C_6H_6Me_4S)]_2$[b]	M	$P2_1/c$	4
103	$C_{24}H_{64}P_8Ru_2$	$\{RuH[CH_2PMe(CH_2)_2PMe_2](dmpe)\}_2$	Tri	$P\bar{1}$	2
345	$C_{24}O_{24}Pt_{12}^{2-}.2C_{24}H_{20}As^+$	$(AsPh_4)_2[Pt_3(CO)_6]_4$	Tri	$P\bar{1}$	

[a] $C_{11}H_{14}$ = tricyclo[6.3.0.$0^{2,7}$]undeca-3,5-diene. [b] $C_6H_6Me_4S$ = 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne. [c] Previous unit cell had only half correct volume, leading to insoluble Patterson function. [d] Not fully refined.

148	$C_{25}H_{15}CoO_4$	$Co(CO)_3(C_3Ph_3CO)$	M	$P2_1/a$	8
167	$C_{25}H_{16}Br_2FeO_3$	$Fe(CO)_3(C_{22}H_{16}Br_2)$[a]	M	$P2_1/n$	4
48	$C_{25}H_{18}N_2O_5P.H_2O$	$Rh(C_6H_3N_2O_4)(CO)(PPh_3).H_2O$[b]	M	$P2_1/a$	4
254	$C_{25}H_{19}Fe^+.BF_4^-$	$[FcC_3Ph_2]BF_4$	M	$P2_1/c$	4
221	$C_{25}H_{20}MnO_2P$	$Mn(CO)_2(PPh_3)(C_5H_5)$	Tri	$P\bar{1}$	2
166	$C_{25}H_{21}CrO_3P$	$Cr(CO)_3(PPh_3)[C(CH_2)_3]$	M	$C2/c$	16
35	$C_{25}H_{33}ClIrOP_3$	$IrCl(CO)(PMe_2Ph)_3$	M	$P2_1/c$	4
76	$C_{25}H_{33}CoN_6O_5$	$Co(CH_2CH_2CN)[NH_2CHPhCH(OH)Ph](dmg)_2$	M	$P2_1$	4
382a	$C_{25}H_{35}Al_3Mo_2$	$[MoH(C_5H_5)(C_5H_4)]_2Al_3Me_5$	O	$P2_12_12_1$	4
			O	$P2_12_12_1$	4

12.90(5)	11.48(5)	7.70(5)	94.00(1)	95.00(1)	90.05(1)	~1500	16.3			248
10.028(2)	10.578(4)	11.291(4)	72.06(4)	81.56(4)	62.53(4)	2525	3.3			249
11.608(2)	12.533(3)	13.759(2)		101.01(1)		3595	3.0	4.0		250
9.701(5)	10.060(5)	11.993(6)		99.38		985	7.8			251
8.524(3)	9.092(3)	13.152(4)	56.03(2)	110.13(2)	103.96(2)	2578	4.3	5.2		156
8.717(6)	14.716(4)	9.867(5)		112.00(5)		1411	5.3	6.1		252
10.15(1)	18.82(2)	7.85(1)		95.0(1)		1839	7.2			253
11.44(1)	33.56(3)	8.33(1)			92.7(1)	1595	8.6			253
16.364(3)	18.015(3)	8.859(3)		92.28(3)	...	2052	7.7			254
10.028(4)	13.880(6)	15.018(6)	95.87(3)	101.27(3)	112.02(3)		5.8	8.9	*c*	255
15.239(5)	19.377(14)	14.628	106.66(4)	101.10(3)	85.65(5)	5322	*d*			103
18.336	11.537	21.243		111.68		2016	9.9			256
19.597(8)	8.232(6)	13.770(7)		89.38(5)		838	14.5			257
11.200(5)	27.87(1)	7.695(1)		99.5(1)		2136	6.2			258
8.219(3)	14.708(3)	17.857(3)		103.60(5)		1410	5.7	4.6		259
9.41(2)	10.60(2)	11.36(2)	103.47(16)	79.47(16)	101.72(16)	2931	10.8			260
36.955(3)	10.789(1)	22.799(3)		100.80(1)		4731	8.8	8.7		261
16.25(2)	10.38(1)	30.07(5)		147.30(3)		1331	3.3	4.5		262
13.31	8.84	23.90		108.0		2127	14			263
19.383(7)	14.458(6)	9.009(5)				2670	6.9			264
19.398(4)	14.438(9)	9.035(2)				1213	6.6	6.3		265

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[a] $C_{22}H_{16}Br_2$ = 1,2,2a,3-η^4-1-bromo-2-methylene-3-naphthyl(1'-bromo-2'-naphthyl)methane.
[b] $C_6H_3N_2O_4$ = pyrazine-2,3-dicarboxylate.

195	$C_{26}H_{18}Cl_2Zr$	$ZrCl_2(\eta^3\text{-}C_{13}H_9)(\eta^5\text{-}C_{13}H_9)$[a]	M	$P2_1/n$	4
227	$C_{26}H_{20}BFeNO_2$	$Fe(CNBPh_3)(CO)_2(C_5H_5)$	Tri	P1	2
210	$C_{26}H_{20}CrO_4S_2W$	$(C_5H_5)_2W(SPh)_2Cr(CO)_4$	M	B2/b	8
211	$C_{26}H_{20}MoO_4S_2W$	$(C_5H_5)_2W(SPh)_2Mo(CO)_4$	M	B2/b	8
212	$C_{26}H_{20}O_4S_2W_2$	$(C_5H_5)_2W(SPh)_2W(CO)_4$	M	B2/b	8
26	$C_{26}H_{22}F_6IrN_2OP$	$Ir[NHC(CF_3)CMe(CH_2)C(CF_3)NH](CO)(PPh_3)$	M	$P2_1/c$	4
258	$C_{26}H_{28}Fe_2$	$Fe(C_5H_4CMe_2CH_2CMeFcC_5H_4)$	O	Pbca	8
383	$C_{26}H_{34}Al_4Mo_2$	$[Mo(C_5H_4)_2Al_2Me_3]_2$	Tri	$P\bar{1}$	1
228	$C_{26}H_{39}FeN_3O$	$Fe[C(NCy)C(NHCy)CHC(NHBu^t)](CO)(C_5H_5)$	M	$P2_1/c$	4
150	$C_{26}H_{54}Br_2Ni_2$	$[NiBr(PPr^i_3)]_2C_8H_{12}$	Tri	$P\bar{1}$	1
302	$C_{26}H_{56}B_{10}P_2Pt$	$1\text{-}Pt(CHEtPPr_2)(PPr_3)\text{-}2\text{-}PhC_2B_{10}H_{10}$	Tri	$P\bar{1}$	2

[a] η^3-$C_{13}H_9$ = 9,9a,8a-η^3-fluorenyl; η^5-$C_{13}H_9$ = 9,9a,4a,4b,8a-η^5-fluorenyl

337	$C_{27}H_{15}Fe_2O_9PPt$	$Fe_2Pt(CO)_9(PPh_3)$	M	$P2_1/c$	4
263a	$C_{27}H_{22}As_2CrO_2$	$Cr(CO)_2[(\eta^6\text{-}Ph)PhAsCH_2AsPh_2]$	Tri	$P\bar{1}$	2
77	$C_{27}H_{27}Cl_3CoN_5O_4$	$Co[CCl{:}C(C_6H_4Cl\text{-}p)_2](py)(dmg)_2$	O	$Pn2_1a$	8
106a	$C_{27}H_{27}CrO_6$	$Cr(C_6H_4C_3H_5O_2)_3$[a]	O	$Pna2_1$	4
323	$C_{27}H_{28}Fe_2O_3$	$Fe_2(CO)_3(C_4Bu^t_2Ph_2)$	Tet	$I\bar{4}$	4
243	$C_{27}H_{29}ORh$	$Rh(dba)(C_5Me_5)$	M	$P2_1/a$	4
249	$C_{27}H_{33}CoSi_2$	$Co[C_4Ph_2(SiMe_3)_2](C_5H_5)$	O	Pbca	8
30	$C_{27}H_{33}IO_3P_3W^+.C_{24}H_{20}B^-$	$[WI(CO)_3(PMe_2Ph)_3]BPh_4$	Tri	P1	1
152	$C_{27}H_{53}NiP$	$NiMe(CHMeCHCHMe)[PMe(menthyl)_2]$	O	$P2_12_12_1$	4

[a] $C_6H_4C_3H_5O_2$ = 2'-(2-phenyl-1,3-dioxolano).

12.347	13.771	11.922		98.2		2697	5.8		266
11.58(1)	10.20(1)	10.25(1)	111.7(1)	79.9(1)	97.4(1)	3520	5.		267
17.85(3)	18.23(3)	15.83(3)			112.8(3)	2724	7.5		268
18.07(3)	18.33(3)	16.23(3)			112.6(3)	2702	7.0		268
17.90(3)	18.37(3)	15.93(3)			112.3(3)	2576	9.0		258
15.615(9)	10.418(6)	17.816(11)		113.68(5)		3277	4.5		275
14.719(7)	24.630(12)	11.354(5)				4075	11.7		269
9.029(5)	9.125(5)	9.748(5)	64.86(2)	70.34(2)	86.88(2)	2379	9.7		264
11.732	10.380	22.831		112.97		3298	6.4		270
13.72(1)	7.93(1)	7.89(1)	103.1(1)	83.8(1)	103.3(1)	1960	10.2		271
11.77(1)	10.20(1)	15.84(1)	82.5(1)	95.2(1)	106.5(1)	3407	5.3		272
11.88	14.13	17.49		106.9		1626	7.2		273
7.609(3)	8.563(3)	18.677(5)	83.16(2)	82.52(2)	81.66(2)	3208	3.2	4.2	274
25.50(2)	27.13(2)	9.728(7)				3545	4.9		276
21.804	8.651	12.702				1812	6.8		277
15.093(5)		18.641(4)				1484	6.1		278
14.348(12)	14.063(13)	11.393(10)		104.42(3)		2100	3.5		279
29.622(7)	9.967(2)	17.140(3)				3173	3.8	4.4	280
12.216(9)	10.100(8)	10.287(11)	100.55(9)	104.87(12)	89.31(8)	3866	5.2		281
14.446(1)	13.727(1)	11.895(1)				2689	3.65	4.55	194

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229a	$C_{28}H_{20}Cl_{10}Fe_4O_8Sb_2$	$[FeCl(CO)_2(C_5H_5)]_4(SbCl_3)_2$	Tri	$P\bar{1}$	2
20	$C_{28}H_{22}FeO_3P_2$	$Fe(CO)_3(dppm)$	Tri	$P\bar{1}$	2
73	$C_{28}H_{27}FeN_4$	$FePh(C_{22}H_{22}N_4)^a$	Tri	$P\bar{1}$	2
87	$C_{28}H_{29}O_4PPd.\frac{1}{2}C_6H_6$	$Pd[CH(COMe)_2](acac)(PPh_3).\frac{1}{2}C_6H_6$	M	C2/c	8
205	$C_{28}H_{31}ClOTi$	$TiCl(OC_6H_3Me_2)(C_5H_5)[C_5H_3(Me)CMe_2Ph]$	M	$P2_1/n$	
238	$C_{28}H_{32}W$	$W[CH_2(C_6H_3Me_2)]_2(C_5H_5)_2$	M	$P2_1/c$	4

[a] $C_{22}H_{22}N_4$ = 2,3:9,10-dibenzo-1,4,8,11-tetraazacyclotetradeca-2,5,9,12-tetraenato.
[b] Racemic, m.p. 164°.

109	$C_{29}H_{24}MnO_3PS$	$Mn(C_6H_4CH_2SMe)(CO)_3(PPh_3)$	Tri	$P\bar{1}$	2
266	$C_{29}H_{25}BRu$	$Ru(C_5H_5)(\eta^6\text{-}Ph)BPh_3]$	M	$P2_1/c$	4
24	$C_{29}H_{28}O_2P_2Rh^+.F_6P^-$	$\{Rh(CO)[O(CH_2CH_2PPh_2)_2]\}PF_6$	Tri	$P\bar{1}$	2
66	$C_{29}H_{53}Cl_2N_4Ta$	$TaCl_2Me[(NCy)_2CMe]_2$	M	$P2_1/c$	4
226	$C_{30}H_{20}Cl_2Cu_2Fe_2O_4$	$[Fe(C_2PhCuCl)(CO)_2(C_5H_5)]_2$	M	$P2_1/a$	2
183	$C_{30}H_{28}Th_2$	$[Th(C_5H_4)(C_5H_5)_2]_2$	O	Pnnm	4
61a	$C_{30}H_{32}AuI_2N_4^+.ClO_4^-.C_4H_{10}O$	$\{AuI_2[C(NHC_6H_4Me\text{-}p)_2]_2\}ClO_4.Et_2O$	M	$P2_1/c$	4
268	$C_{30}H_{38}BO_6P_2Rh$	$Rh[P(OMe)_3]_2(\eta^6\text{-}Ph)BPh_3$	M	$P2_1/c$	4
14	$C_{30}H_{56}As_8Mo_2O_6$	$Mo_2(CO)_6(AsPr^n)_8$	M	$P2_1/n$	4
265	$C_{30}H_{56}Mo_2N_2P_4$	$[Mo(dmpe)(C_6H_3Me_3)]_2N_2$	O	Pbca	4
349	$C_{30}O_{28}Rh_{15}^-.H_3O^+$	$H_3O[Rh_{15}C_2(CO)_{28}]$	O	Pbca	4
346	$C_{30}O_{30}Pt_{15}^{2-}.2C_{24}H_{20}As^+$	$(AsPh_4)_2[Pt_3(CO)_6]_5$	Tri	$P\bar{1}$	2
319	$C_{31}H_{25}Fe_2O_6P$	*cis*-$Fe_2(CO)_3[P(OPh)_3](C_5H_5)_2$	Tri	$P\bar{1}$	4
314	$C_{32}H_{22}Fe_2O_7I$	$Fe_2(CO)_7(dppm)$	M	$P2_1/c$	4
120	$C_{32}H_{60}NiP_2$	$Ni(C_2Me_4)[Cy_2P(CH_2)_2PCy_2]$	M	$P2_1/n$	4
252	$C_{33}H_{23}CoI_2$	$Co(C_4Ph_4)(C_5H_3I_2)$	M	$P2_1/c$	4
251	$C_{33}H_{24}CoI$	$Co(C_4Ph_4)(C_5H_4I)$	O	Pbcn	16

12.513(3)	18.618(5)	10.899(3)	104.20(2)	115.50(2)	92.15(2)	2001	7.4			284
12.08(1)	9.63(1)	11.35(1)	101.02(3)	90.92(2)	101.13(3)	2060	6.3	6.5		285
9.645(1)	12.544(1)	9.969(1)	88.26(1)	76.82(1)	72.22(1)	4206	6.6	4.7		286
36.444(8)	11.836(2)	16.170(4)		124.70(4)		2806	7.8	8.1		283
14.16(2)	12.91(2)	13.18(2)		96.9(5)		1939	6.2		b	287
8.619	22.278	11.921		94.97		3586	3.4			288
11.029(22)	13.485(26)	9.123(18)	94.52(3)	109.90(3)	98.14(3)	3385	5.7			289
9.527(4)	15.381(6)	15.518(7)		105.09(5)		2048	3.2	3.6		290
10.907(3)	11.048(2)	13.405(3)	94.19(2)	82.30(2)	107.98(2)	2384	6.9			291
13.521(8)	13.084(8)	17.916(8)		93.78		3198	8.0			292
12.57(1)	18.27(2)	7.15(1)		115.3(1)		1578	7.1			293
9.758(4)	8.528(3)	14.397(5)				790		7		294
10.03	15.915	25.21		101.63		3521	5.4	6.2		295
15.59(1)	11.51(1)	19.74(1)		120.72(7)		2540	5.1			296
21.17	16.97	12.98		103.2		2780	6.3			151
13.309(7)	16.582(9)	16.438(9)				3291	3.1			297
15.01(2)	17.34(2)	18.85(2)								224
14.783(8)	26.426(13)	13.835(4)	102.73(3)	118.16(3)	95.28(4)	3558	5.9	6.3		103
14.331(5)	17.335(9)	12.482(7)	102.12(4)	92.02(4)	66.44(4)	3605	7.5	9.0		298
11.257(2)	11.926(3)	22.911(8)		100.22(2)		2388	6.0	7.7		299
17.1306(7)	16.9016(7)	11.4899(8)		100.082(5)		4995	3.3	5.3		300
10.95(1)	14.39(1)	17.56(1)		97.3(1)		2382	8.3			301
21.31(1)	15.25(1)	32.25(1)				1920	6.1			301

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242	$C_{33}H_{28}ClRh$	$Rh(C_2H_4)_2(C_5Ph_4Cl)$	M	$P2_1/n$	4
171	$C_{33}H_{30}FeO_3Si$	$Fe(CO)_3[C_8H_6(CPh_3)(SiMe_3)]$	Tri	$P\bar{1}$	2
25	$C_{33}H_{38}O_5P_2Rh^+.F_6P^-$	$(Rh(CO)(H_2O)[O(CH_2CH_2OCH_2CH_2PPh_2)_2]\}-PF_6$	Tri	$P\bar{1}$	2

[a] $C_8H_6(CPh_3)(SiMe_3)$ = 2,3,4,5-η^4-1-trimethylsilyl-7-triphenylmethylbicyclo[4.2.0]octa-2,4,7-triene.

250	$C_{34}H_{24}CoN$	$C_o(C_4Ph_4)(C_5H_4CN)$	M	$P2_1/c$	4
231	$C_{35}H_{18}F_9N_2PRu$	$\overline{Ru(C_6F_4N:NC_6F_5)}(C_5H_4C_6H_4PPh_2)$	M	$P2_1/c$	4
101	$C_{36}H_{30}N_4O_4Pd_2$	$[Pd(apo)]_2$salophen	M	$P2_1/c$	4
52	$C_{36}H_{33}I_2N_2OPRu$	$RuI_2[CH{:}NMe(C_6H_4Me\text{-}p)](CO)(CNC_6H_4Me\text{-}p)(PPh_3)$	Tri	$P\bar{1}$	2
155	$C_{36}H_{45}Cl_2PPd.C_2H_4O_2$	$PdCl[(HC_2Bu^t)_3Cl](PPh_3).MeCO_2H$	M	$P2_1/c$	4
360	$C_{36}H_{54}Cl_6Nb_3^+.Cl^-$	$[Nb_3Cl_6(C_6Me_6)_3]Cl$	Hex	P6/m	1
365	$C_{37}H_{20}F_6Fe_3O_7P_2$	$Fe_3(CO)_7[Ph_2PC_4(CF_3)_2](PPh_2)$	M	$P2_1/c$	4
370	$C_{37}H_{20}O_9Os_3$	$Os_3(CO)_9(C_4Ph_4)$	M	$P2_1/c$	4
			O	Iba2	8
56	$C_{37}H_{30}Cl_2N_2ORh_2$	$[Rh(CPh_2)Cl(py)]_2(CO)$	M	C2	2
33	$C_{37}H_{30}INO_2P_2Ru$	$RuI(CO)(NO)(PPh_3)_2$	O	Pbcn	4
364	$C_{36}H_{20}F_6Fe_3O_8P_2.C_6H_6$	$Fe_3(CO)_8[Ph_2PC_4(CF_3)_2](PPh_2).C_6H_6$	Tri	$P\bar{1}$	2
106	$C_{36}H_{29}ClP_2Pt$	$\Delta\text{-}\overline{Pt}Cl[o\text{-}Ph_2PC_6H_4C:CHC_6H_4PPh_2\text{-}o]$	M	$P2_1$	2
392	$C_{36}H_{30}FeOSn$	$Fe(SnPh_3)(CO)(C_2Ph_2)(C_5H_5)$	M	$P2_1/c$	4
27	$C_{36}H_{30}NiO_2P_2$	$Ni(CO)_2(PPh_3)_2$	M	P2/c	2
82	$C_{36}H_{31}Cl_2F_2IrOP_2$	$IrCl_2(CHF_2)(CO)(PPh_3)_2$	M	$P2_1/c$	4
130	$C_{36}H_{38}Ni_2O_2P_2$	$Ni_2(CO)_2(Ph_2PC_2Bu^t)_2$	M	$P2_1/n$	4
366	$C_{39}H_{23}F_6Fe_3O_9P_2.2C_6H_6$	$Fe_3(CO)_7[Ph_2PC_4(CF_3)_2](CO_2Me)(PPh_2).2C_6H_6$	Tri	$P\bar{1}$	2

15.846(2)	10.593(2)	16.081(2)		104.95(1)		4285	5.9		302
10.968(4)	11.496(4)	12.213(5)	95.63(3)	108.56(3)	91.60(3)	3626	5.2		303
9.837(2)	11.416(2)	17.554(3)	94.08(1)	79.64(1)	111.98(1)	3106	8.9		291
10.19(1)	15.24(1)	16.85(1)		107.0(1)		1718	5.3		301
15.650(14)	13.338(11)	14.741(11)		97.38(3)		3092	7.5		305
7.109(4)	25.321(3)	17.979(8)		107.8(4)		3122	6.9		306
11.640(1)	10.9139(8)	16.587(2)	87.98	90.67	62.25	2731	5.5		307
10.738(5)	9.725(5)	36.46(2)		90.2(1)		3056	6.7		308
12.2571(13)		8.0377(13)				413	12		309
12.325(4)	21.075(4)	19.701(9)		133.54(1)		2925	6.3		310
12.148(5)	9.796(4)	29.565(16)		91.79(5)		4807	9.5		311
18.45(8)	18.59(4)	9.80(2)				1916	8.0		
19.14(1)	10.05(1)	11.41(1)		121.17(3)		1831	7		312
19.26(2)	10.77(2)	16.13(3)				1066	13.7		314
11.738(6)	14.110(6)	14.753(4)	97.26(3)	92.35(4)	112.31(4)	4059	7.9		315
10.633(4)	16.934(6)	9.957(4)		119.02(2)		4872	4.2	4.0	316
11.050(3)	15.676(1)	17.881(4)		92.0(1)			17		317
11.770(1)	8.2663(4)	17.056(4)		105.711(8)		2240	4.0	4.2	318
10.47(1)	14.45(2)	24.58(2)		97.68(5)		1945	5.9	7.1	319
16.733	12.233	19.677		118.31		2268	7.0		320
10.319(8)	14.516(12)	17.944(9)	90.13(5)	110.34(5)	95.44(6)	4396	6.7		321

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141	$C_{39}H_{30}F_6NiOP_2$	$Ni[(CF_3)_2CO](PPh_3)_2$	M	$P2_1/n$	4
121	$C_{39}H_{34}P_2Pd$	$Pd(C_3H_4)(PPh_3)_2$	Tri	$P\bar{1}$	2
232	$C_{39}H_{36}CoO_6P$	$Co[(PhC_2CO_2Me)(MeO_2CCH)_2](PPh_3)(C_5H_5)$	Tri	$P\bar{1}$	2
393	$C_{39}H_{45}BrFeMgO_2P_2.C_4H_8O$	$Fe[BrMg(C_4H_8O)_2](dppe)(C_5H_5).THF$	M	$P2_1/c$	4
135	$C_{40}H_{30}F_6P_2Pt$	$Pt[C_2(CF_3)_2](PPh_3)_2$	Tri	$P\bar{1}$	2
395	$C_{40}H_{30}O_4OsSn_2$	*trans*-$Os(SnPh_3)_2(CO)_4$	M	$C2/c$	8
83	$C_{40}H_{31}Cl_2F_4IrO_3P_2.C_6H_6$	$IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2.C_6H_6$	Tri	$P\bar{1}$	2
37	$C_{40}H_{32}Ir_2O_6P_2S$	$[IrH(CO)_2(PPh_3)]_2SO_2$	M	$C2/c$	4
148a	$C_{40}H_{33}Cl_2P_2Rh.CH_4O$	$RhCl_2[o\text{-}Ph_2PC_6H_4CHCHCMeC_6H_4PPh_2\text{-}o].MeOH$	M	Cc	4
359a	$C_{40}H_{34}Fe_2O_4P_2Rh^+.F_6P^-$	$\{Rh[Fe(C_5H_4Me)(CO)_2(PPh_2)]_2\}PF_6$	O	$Pbca$	8
379	$C_{40}H_{44}Li_4Mo_4$	$[MoHLi(C_5H_5)_2]_4$	M	$C2/c$	4
383	$C_{40}H_{44}Li_4W_4$	$[WHLi(C_5H_5)_2]_4$	M	$C2/c$	4
105	$C_{40}H_{50}O_4P_2Pd_2$	$\{Pd(OAc)[CH_2C_6H_4PBu^t(o\text{-}tol)]\}_2$	Tri	$P\bar{1}$	2
380	$C_{40}H_{64}Br_4Mg_4Mo_2O_2.C_4H_{10}O$	$[(C_5H_5)_2MoHMgCyBr_2Mg(OEt_2)]_2.Et_2O$	M	$C2/m$	2
46	$C_{41}H_{30}F_6OP_2RuS_2$	$Ru(CO)(PPh_3)_2[S_2C_2(CF_3)_2]$[a]	M	$P2_1/c$	4
108a	$C_{42}H_{30}As_2N_4OPt$	$Pt[C_2(CN)_4O](AsPh_3)_2$	M	$P2_1/c$	4
222	$C_{42}H_{35}MnOP_2.C_6H_6$	$Mn(CO)(PPh_3)_2(C_5H_5).C_6H_6$	Tri	$P\bar{1}$	2
131	$C_{42}H_{36}O_4P_2Pd$	$Pd[C_2(CO_2Me)_2](PPh_3)_2$	M	$P2_1/c$	4
213	$C_{42}H_{37}NbOP_2$	$NbH_2(CO)(PPh_3)_2(C_5H_5)$	M	Bb	4
128	$C_{42}H_{38}P_2Pt$	$Pt(C_6H_8)(PPh_3)_2$[a]	O	$P2_12_12_1$	8
94	$C_{42}H_{40}O_4P_2Pt$	*trans*-$Pt(CO_2Et)_2(PPh_3)_2$	Tri	$P\bar{1}$	1
153	$C_{42}H_{41}NiP_2^+.Cl_3Zn^-$	$[Ni(C_6H_{11})(PPh_3)_2]ZnCl_3$[b]	O	$Pbca$	8

[a] C_6H_8 = 1,4-η^2-$\Delta^{1,4}$-bicyclo[2.2.0]hexene. [b] C_6H_{11} = 1,1,2-trimethylallyl.

18.123(5)	19.879(5)	9.745(2)		93.46(2)		1406	8.7		322
19.475(2)	10.204(2)	18.341(2)	108.46(2)	85.46(1)	118.80(1)	4096	5.1		323
12.330	17.834	8.955	98.12	116.13	81.13	4673	10.6		314
12.258(4)	13.027(4)	26.577(11)		102.48(2)		1505	8		324
11.799(2)	16.062(3)	9.723(1)	99.33(1)	101.47(1)	96.75(1)	6153	3.7	5.7	325
47.55(3)	9.313(7)	31.97(2)		148.87(2)		2785	6.3	8.1	326
18.31(2)	12.15(1)	10.92(1)	106.98(5)	94.75(5)	108.98(5)	3759	4.8		327
14.80(1)	16.22(1)	16.56(1)		107.67(5)		2031	3.5		328
9.833(2)	19.430(5)	18.898(5)		93.18(2)		3811	2.3		329
19.92	25.96	15.82				2541	6.2		330
26.39(2)	7.72(1)	22.43(2)		124.8(5)		1624	7.1		331
26.24(1)	7.759(5)	22.35(1)		124.6(4)		2744	3.5		331
12.989	15.643	20.325	130.85	117.91	94.08	5436	4.4	5.8	332
15.671	11.996	15.085		109.55		1530	8.1		333
10.147(3)	10.081(4)	38.627(9)		102.27(3)		2337	4.7	7.2	334
9.913(2)	20.477(3)	18.634(3)		95.42(1)		4819	3.9		335
9.83(2)	14.79(1)	11.36(2)	69.44(8)	66.48(8)	67.57(10)	4554	8.7		336
11.816(3)	15.331(4)	21.891(6)		113.22(1)		3365	5.2		337
15.745(5)	21.319(5)	10.935(5)			99.4(2)	1517	9.0		338
17.726(3)	9.748(2)	19.724(3)				1512	2.8		339
10.204(8)	11.602(8)	8.363(7)	106.04(8)	88.04(7)	108.98(7)	3435	3.8		340
18.968(3)	19.497(3)	21.363(3)				2321	10.3		341

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112	$C_{43}H_{32}N_4P_2Pt$	$Pt[C_3H_2(CN)_4](PPh_3)_2$	Tri	$P\bar{1}$	2
99	$C_{43}H_{37}Cl_2IrN_2OP_2.CHCl_3$	$IrCl_2(MeOC_6H_3N{:}NH)(PPh_3)_2.CHCl_3$	Tri	$P\bar{1}$	2
84	$C_{43}H_{42}NiO_2P_2$	$NiEt(acac)(PPh_3)_2$	Tri	$P\bar{1}$	2
275	$C_{44}H_{32}Cu_4F_{12}O_8$	$Cu_4(O_2CCF_3)_4(C_9H_8)_4$[a]	M	$P2_1/m$	2
90	$C_{44}H_{37}BrP_2Pt$	$PtBr(CH{:}CHPh)(PPh_3)_2$	M	$P2_1/c$	4
54	$C_{44}H_{40}F_6N_3P_2Rh$	*trans*-$Rh[N{:}C(CF_3)_2]$-$[C(NMeCH_2)_2](PPh_3)_2$	M	$P2_1/n$	4
111	$C_{44}H_{44}OP_2Pt.\frac{1}{2}X$	$Pt(C_6H_9OEt)(PPh_3)_2.\frac{1}{2}X$[c]	M	C2/c	8
301	$C_{44}H_{45}B_{10}P_2Rh$	$[Rh(PPh_3)_2]PhC_2B_{10}H_{10}$	O	Pbca	8

[a] C_9H_8 = indene. [b] No refinement reported. [c] C_6H_9OEt = 1,4-n^2-1-ethoxycyclohexyl; X = unknown solvent molecule.

129a	$C_{46}H_{30}Fe_2O_6P_2$	$Fe_2(CO)_6(Ph_2PC_2Ph)_2$	M	$P2_1/n$	4
366a	$C_{46}H_{39}Au_2FeP_2^+.BF_4^-$	$[FcAu_2(PPh_3)_2]BF_4$	M	$P2_1/a$	4
136	$C_{48}H_{38}Cl_2CoN_2P_2Pt$	$Pt[C_2(2\text{-}C_5H_4N)_2CoCl_2](PPh_3)_2$	M	$P2_1/c$	4
170	$C_{48}H_{40}ClIrN_2P_2.C_6H_{14}$	$IrHCl(C_6H_4N{:}NPh)(PPh_3)_2.C_6H_{14}$	M	$P2_1/n$	4
85	$C_{48}H_{47}As_3NNi^+.C_{24}H_{20}B^-$	$\{NiPh[N(CH_2CH_2AsPh_2)_3]\}BPh_4$	Tri	$P\bar{1}$	2
230	$C_{49}H_{40}ClCuP_2Ru$	$Ru(C_2PhCuCl)(PPh_3)_2(C_5H_5)$	M	$P2_1/c$	4
129	$C_{50}H_{40}N_2O_4P_2Pt$	$Pt[trans\text{-}C_2H_2(C_6H_4NO_2\text{-}p)_2](PPh_3)_2$	Tri	$P\bar{1}$	2
122	$C_{51}H_{42}O_3Pd$	$Pd_2(dba)_3$	Tri	$P\bar{1}$	2
122	$C_{51}H_{42}O_3Pd.CHCl_3$	$Pd_2(dba)_3.CHCl_3$	M	$P2_1/c$	4
122	$C_{51}H_{42}O_3Pd.C_6H_6$	$Pd_2(dba)_3.C_6H_6$	M	$P2_1/c$	

[a] Similar disorder to $CHCl_3$ solvate.

92	$C_{52}H_{52}O_2P_2Pt$	$Pt(C_2C_6H_{10}OH)_2(PPh_3)_2$	M	$P2_1/n$	2
178	$C_{52}H_{52}O_4P_2Rh_2$	$Rh_2(acac)_2(C_6H_8)(PPh_3)_2$[a]	Tri	$P\bar{1}$	2

11.422(5)	17.001(8)	10.478(5)	107.27(3)	110.72(2)	82.50(2)	4553	3.5			342
12.55(2)	12.38(2)	15.55(2)	103.07(7)	91.73(7)	116.28(7)	3699	3.5			343
9.297(2)	11.026(7)	13.188(6)	106.05(4)	110.37(3)	101.38(4)	1437	6.8	8.2		344
13.6(3)	20.30(5)	9.28(2)		100(1)			*b*			208
14.857(3)	16.339(5)	16.980(4)		118.30(1)		3123	3.1			345
20.228(4)	20.714(4)	9.836(2)		96.08(7)		2853	6.7			346
26.242(8)	12.161(3)	26.744(8)		115.76(2)		953	4.4			339
18.895	18.424	24.522				1950	7.5			347
12.032	19.155	17.644		91.39		3400	6.5			120
14.460(11)	30.539(27)	9.509(12)		92.61(15)		2082	11.2			348, 349
9.392(1)	22.591(3)	23.729(3)		101.41						350
15.824(1)	25.903(1)	10.871(1)		88.227(2)		4615	11.5			351
18.132(3)	13.377(2)	13.162(2)	84.65(2)	73.80(2)	86.93(2)	3008	6.9			352
12.914	22.111	16.534		110.77		5895	8.2	7.4		353
12.955(3)	15.012(3)	11.169(3)	96.65(1)	97.93(1)	93.00(1)	2785	6.6			354
12.400(5)	15.149(5)	12.956(5)	115.01(5)	95.23(5)	97.30(5)	2911	6.8			355
13.536(3)	13.474(2)	25.415(4)		109.5(1)		3819	6.7			356
13.745(5)	23.589(5)	15.434(5)		66.04(3)			8.5		*a*	356
8.992	23.012	11.585		105.35		2898	5.2			357
17.866(4)	14.993(4)	10.297(3)	99.22(2)	91.19(2)	108.26(2)	4473	4.1			229

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39	$C_{52}H_{66}Mo_2O_8P_6$	$[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$			

[a] C_6H_8 = 1,4-η^2:2,2a,3,3a-η^4-2,3-bis(methylene)butan-1,4-diyl. [b] No crystal data reported.

104	$C_{54}H_{45}IrP_3$	$IrH(C_6H_4PPh_2)_2(PPh_3)$	M	$P2_1/c$	4
267	$C_{54}H_{46}P_3Ru^+.BF_4^-$	$[RuH(PPh_3)_2(\eta^6\text{-}Ph)PPh_2]BF_4$	M	$P2_1/c$	4
137	$C_{55}H_{30}CuF_{10}O_3P_2Re$	$ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2$	Tri	$P\bar{1}$	2
36	$C_{55}H_{47}IrOP_3^+.F_5Si^-$	$[IrH_2(CO)(PPh_3)_3]SiF_5$	Tri	$P\bar{1}$	2
119	$C_{56}H_{54}NiP_2.\frac{1}{2}C_4H_8O$	$Ni(CHPh{:}CHPh)[P(C_6H_4Me\text{-}p)_3]_2.\frac{1}{2}C_4H_8O$	O	Pccn	8
338	$C_{59}H_{45}FeO_{14}P_3Pt_2$	$FePt_2(CO)_5[P(OPh)_3]_3$	Tri	$P\bar{1}$	2
9	$C_{60}H_{48}Mo_2N_3O_6$	$Mo_2(CO)_6(NHPPh_3)_3$	M	$P2_1/c$	4
151	$C_{60}H_{60}Br_2Ni_2P_4.8CHCl_3$	$[NiBr(dppe)]_2C_8H_{12}.8CHCl_3$	M	A2/a	4
132	$C_{66}H_{50}F_6P_4Pd_2$	$Pd_2(Ph_2PC_2CF_3)_2(PPh_3)_2$	M	$P2_1/c$	4
182	$C_{72}H_{84}Nd_4$	$[Nd(C_5H_4Me)_3]_4$	M	$P2_1/c$	2
49	$C_{73}H_{60}Cl_4P_4Ru_2S$	$Ru_2Cl_4(CS)(PPh_3)_4$	O	$Pn2_1a$	4
282	$C_{74}H_{66}B_2Cu_2N_2$	$[Cu(BH_3CN)(PPh_3)_2]_2$	A	$P2_1/n$	4
25a	$C_{84}H_{60}N_6O_2P_4Rh_2$	$[Rh(CO)(PPh_3)_2]_2C_4(CN)_6$	Tri	$P\bar{1}$	2
138	$C_{94}H_{45}Ag_2F_{25}P_3Rh$	$RhAg_2(C_2C_6F_5)_5(PPh_3)_3$	M	$P2_1/n$	4
373	$C_{100}H_{70}Cu_4Ir_2P_2$	$Ir_2Cu_4(C_2Ph)_8(PPh_3)_2$	M	$P2_1$	2

						5506	7.9		(b)	358
11.81(1)	22.81(2)	20.52(2)		128.1(5)		5384	4.0			359
20.755	12.784	18.609		109.06		4658	5.4			360
15.96	13.60	11.70	84.1	80.6	93.0	2683	7.7			361
16.69(3)	12.78(2)	16.65(2)	101.15(1)	95.66(1)	101.60(1)	3855	5.8			362
19.548(8)	26.145(12)	19.718(9)				2417	9.2			363
22.80(2)	12.31(1)	10.55(1)	105.2(1)	78.0(1)	88.6(1)	2353	6.2			364
19.605(9)	13.507(10)	24.045(11)		91.15(3)		2154	9.6	5.0		365
18.08(1)	22.18(1)	17.02(1)			110.2(1)	1248	9.3			271
17.547(4)	13.088(4)	28.152(7)		102.14(2)		5465	9.1			366
14.257(5)	26.85(1)	9.286(3)		120.28(8)		3463	4.0			367
21.53	23.40	14.20				1258	11.5			368
18.100(1)	27.407(5)	13.615(1)		104.43(1)		2921	6.0	7.2		369
16.483(2)	18.580(3)	12.813(2)	105.02(1)	103.83(1)	82.26(1)	7028	5.8			370
15.902(2)	21.497(3)	25.041(3)		102.00(1)		7820	6.8			371
14.86(2)	22.04(4)	13.62(2)		105.04(10)		4584	8.2			372

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TABLE 4 Crystal structure data: Hydrides

Number	Formula	Structure	Crystal Type	Space Group	Z
400	$C_{42}H_{43}CoNP_3$	$CoH[N(CH_2CH_2PPh_2)_3]$	M	C2/c	8
401	$C_{42}H_{43}NNiP_3^+ \cdot BF_4^-$	$\{NiH[N(CH_2CH_2PPh_2)_3]\}BF_4$ [a]	M	Cc	4
399	$C_{52}H_{51}P_4Re$	$ReH_3(dppe)_2$	M	$P2_1/c$	2
402	$C_{55}H_{47}O_2P_3Ru$	$RuH(O_2CH)(PPh_3)_3$	Tri	P1 or $P\bar{1}$	2
			M	$P2_1/c$	4
403	$C_{56}H_{49}O_2P_3Ru$	$RuH(O_2CMe)(PPh_3)_3$	M	$P2_1/c$	4
288	$H_{20}B_{20}FeS_2^{2-} \cdot 2C_4H_{12}N^+$	$(NMe_4)_2[Fe(B_{10}H_{10}S)_2]$	O	Ibam	4

[a] Non-stoichiometric hydride; mixture of trigonal bipyramidal cation (N,H axial) with trigonal pyramidal cation (N axial); cell data refer to approximately $NiH_{0.5}$.

Unit cell constants a	b	c	α	β	γ	Data	R	R_w	Notes	Reference
24.278	11.192	28.027		107.99		2297	5.6			373
16.739(2)	12.666(1)	18.064(2)		90.41(2)		1440	7.0	9.0		374
16.09(2)	10.27(1)	19.11(2)		128.0(1)		656	7.5			375
12.633	12.646	18.468	78.77	103.90	68.66				}	376
20.272	14.260	20.944		122.77		1357	13.6			
20.68(4)	9.636(20)	26.59(4)		119.58(8)		4080	8.9			377
15.585(5)	12.324(4)	14.806(6)				962	4.2	4.4		378

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TABLE 5 Crystal structure data: Nitrosyls

Number	Formula	Structure	Crystal type	Space Group	Z
407	$C_4FeN_5O^{2-}.2Na^+$	$Na_2[Fe(NO)(CN)_4]$	O	$Pna2_1$	4
411	$C_8H_{18}Fe_4N_6O_4S_2$	$Fe_4(NO)_4S_2(NBu^t)_2$	M	$P2_1/m$	2
420	$C_{12}H_{18}CoN_3O_3$	Co(NO)(ea)	O	$P2_12_12_1$	4
404	$C_{16}H_{22}ClMnN_2O_6P_2$	$Mn(NO)_2Cl[PPh(OMe)_2]_2$	Tri	$P\bar{1}$	4
			M	C2/c	8
422	$C_{16}H_{36}Co_4N_8O_4$	$Co_4(NO)_4(NBu^t)_4$	Tet	$P4_12_12$	4
408	$C_{16}H_{36}Fe_2N_5OSi_4^+.F_6P^-.C_3H_6O$	$[\{Fe[S(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2S]\}_2(NO)]PF_6.Me_2CO$	O	Ama2	4
421	$C_{22}H_{22}CoN_3O_3$	Co(NO)(eb)	O	$P2_12_12_1$	4
419	$C_{26}H_{24}CoIN_2O_3P_2$	$Co(NO)_2I[Ph_2P(CH_2)_2P(O)Ph_2]$	M	C2/c	8
417	$C_{26}H_{26}Cl_3NOP_2Ru$	$Ru(NO)Cl_3(PMePh_2)_2$	M	$P2_1/c$	4
418	$C_{36}H_{30}ClNO_5P_2RuS$	$Ru(NO)Cl(SO_4)(PPh_3)_2$	O	Pbcn	4
412	$C_{36}H_{30}FeN_2O_2P_2$	$Fe(NO)_2(PPh_3)_2$	M	P2/c	2
416	$C_{36}H_{30}N_2O_2P_2Ru.\frac{1}{2}C_6H_6$	$Ru(NO)_2(PPh_3)_2.\frac{1}{2}C_6H_6$	M	$P2_1/n$	4
406	$C_{39}H_{39}Cl_2NORe$	$Re(NO)Cl_2(PMePh_2)_3$			
409	$C_{48}H_{34}FeN_7O.CHCl_3$	Fe(NO)(NMeIm)(TPP).$CHCl_3$	O	$P2_12_12_1$	4
405	$C_{50}H_{41}MnN_6O.CHCl_3$	Mn(NO)(Mpip)(TPP).$CHCl_3$	O	$P2_12_12_1$	4
423	$C_{54}H_{46}IrNOP_3^+.ClO_4^-$	$[Ir(NO)H(PPh_3)_3]ClO_4$	O	Pbca	8
415	$H_{13}N_5O_2Ru^{2+}.2Cl^-$	*trans*-$[Ru(NO)(OH)(NH_3)_4]Cl_2$	M	C2/m	4
414	$H_{15}N_6ORu^{3+}.3Cl^-.H_2O$	$[Ru(NO)(NH_3)_5]Cl_3.H_2O$	O	$Pn2_1a$	4
413	$Cl_5NORu^{2-}.2C_5H_6N^+$	$(pyH)_2[Ru(NO)Cl_5]$	O	Pnma	8
424	$Cl_6N_2O_2Pt_2^-.C_8H_{20}N^+$	$NEt_4[Pt_2(NO)_2Cl_6]$	M	$P2_1/c$	8
424a	$Cl_8N_2O_2Pt_2^{2-}.2C_9H_8N^+$	$(quinH)[Pt_2(NO)_2Cl_8]$	Tri	$P\bar{1}$	2
410	$Fe_4N_4O_4S_4$	$Fe_4(NO)_4S_4$	M	$P2_1/n$	4

[a] Form A, from EtOH/$CHCl_3$. [b] Form B, from C_6H_6. [c] No crystal data, diagram only.
[d] Reinvestigation. [e] Space group: *Pnma* or $Pna2_1$, best R for former; pseudoperiodicity.

Unit cell constants a	b	c	α	β	γ	Data	R	R_w	Notes	Reference
33.92(2)	7.604(2)	9.832(2)				1796	10.2			379
11.140(2)	11.013(2)	7.921(1)		91.82(1)		1194	3.3	4.6		380
17.308(10)	12.725(7)	6.316(4)				1232	5.6	7.0		381
15.727(5)	15.198(5)	9.405(5)	90.97(1)	89.04(1)	97.21(1)	3711	6.5		*a*	382
25.863(5)	11.863(5)	14.563(5)		90.96(1)		2265	5.8		*b*	
11.725(7)		20.606(5)				861	4.2	4.6		383
24.18(2)	15.670(7)	8.011(4)				1345	3.2	3.7		384
22.188(10)	11.935(5)	3.708(2)				1130	7.0	7.9		381
29.139(15)	9.002(5)	24.096(13)		117.67(2)		1499	7.43			385
12.308(4)	16.579(6)	14.700(4)		114.82(2)		3120	4.4	5.1		386
19.65(1)	10.79(1)	15.73(1)				1192	5.4			387
11.70(1)	8.20(1)	17.24(2)		106.60(8)		1198	5.2	6.4		388
17.031(2)	18.792(2)	10.800(1)		97.03(1)		2985	4.3			389
									c	390
17.733(13)	25.339(22)	9.752(10)				4148	5.2	7.4		391
17.561(6)	25.580(3)	10.175(6)				3440	5.3	7.8		391
23.245(2)	21.308(2)	19.441(5)				2654	8.9	11.2		392
11.422(3)	7.365(2)	11.157(2)		109.09(2)		2398	3.1		*d*	393
11.864(7)	6.878(5)	14.192(9)				971	4.7		*d*	393
7.21	32.1	14.77				~800	22		*e*	394
20.704(2)	10.390(1)	14.408(2)		106.994(8)		1688	7			395
8.103(5)	10.687(7)	8.772(6)	113.04(5)	93.33(3)	77.21(5)	1626	10.1			396
12.350(3)	9.627(7)	10.407(4)		103.66(3)		1376	3.2	4.2		380

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TABLE 6 Crystal structure data: Dinitrogen, aryldiazo, aryldiimine and related complexes.

Number	Formula	Structure	Crystal type	Space Group	Z
425	$C_{33}H_{47}Cl_5MoN_2OP_4Re.CH_4O.ClH$	$(Me_2PhP)_4ClReN_2MoCl_4(OMe).MeOH.HCl$	M	$P2_1/c$	4
428	$C_{18}H_{35}ClFN_2P_2Pt$	*trans*-$Pt(HN_2C_6H_4F\text{-}p)Cl(PEt_3)_2$	Tri	$P\bar{1}$	2
427	$C_{22}H_{31}Cl_2N_3P_2Re^+.Br^-$	$[Re(HN_2Ph)Cl_2(NH_3)(PMe_2Ph)_2]Br$	M	$P2_1/n$	
426	$C_{52}H_{50}ClN_2P_2W^+.C_{24}H_{20}B^-$	$[W(N_2H_2)Cl(dppe)_2]BPh_4$	M	$P2_1/c$	4
429	$C_5H_{23}ClN_5Re^{2+}.2ClO_4^-$	$[Re(NMe)Cl(MeNH_2)_4](ClO_4)_2$	O	Pnam	4
142	$C_{54}H_{96}N_3O_3P_3Pd_3$	$[Pd(PhNO)(PBu^t_3)]_3$	M	$P2_1/c$	4

Unit cell constants						Data	R	R_w	Notes	Reference
a	b	c	α	β	γ					
14.918(1)	11.176(2)	28.162(3)		92.6(1)		3589	5.9			397
9.167(2)	16.983(3)	8.947(2)	91.46(1)	96.34(1)	77.04(1)	4292	5.2	6.6		398
9.561(1)	31.802(3)	11.004(1)		122.4(7)		2197	5.4			399
12.472(1)	19.658(2)	27.056(3)		92.53(1)		5599	6.4			400
16.908(4)	8.641(2)	12.759(5)				1066	4.1			401
15.33	14.64	26.75		97.8		4645	7.9			402

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TABLE 7 Crystal structure data: Binary metal-tertiary phosphine complexes.

Number	Formula	Structure	Crystal type	Space Group	Z
430	$C_{28}H_{46}P_2Pd$	$Pd(PBu^t_2Ph)_2$	M	Cc	4
			O	Fdd2	8
431	$C_{36}H_{66}P_2Pd$	$Pd(PCy_3)_2$	M	C2/c	4
432	$C_{54}H_{45}Au^+.B_9H_{12}S^-$	$[Au(PPh_3)_3]B_9H_{12}S$	Tri	$P\bar{1}$	

Unit cell constants						Data	R	R_w	Notes	Reference
a	b	c	α	β	γ					
10.070(2)	45.377(7)	8.075(1)		129.84(2)		2470	6.2			403
45.372	12.593	10.058				1264	10			404
16.858	9.616	22.382		92.11		2181	6.6			404
13.036(12)	19.635(32)	11.180(8)	103.60(16)	72.10(9)	94.76(15)	3094	7.7	8.9		405

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