CHAPTER 9: COORDINATION CHEMISTRY I: STRUCTURES AND ISOMERS

9.1

Hexagonal:	C_{2v}	C_{2v}	D_{2h}
Hexagonal pyramidal:	C_s	C_s	C_{2v}
Trigonal prismatic:	C_s	C_{2v}	C_2
Trigonal antiprismatic:	C_s	C_2	C_{2h}

The structures with C_2 symmetry would be optically active.

9.2 **a.** dicyanotetra(methylisocyano)iron(0) or dicyanotetra(methylisocyano)iron(0) Both methods of naming result in the same name in this case.

b. rubidium tetrafluoroargentate(III) or rubidium tetrafluoroargentate(1–)

c. *cis*- and *trans*-carbonylchlorobis(triphenylphosphine)iridium(I) or *cis*- and *trans*-carbonylchlorobis(triphenylphosphine)iridium(0)

d. pentaammineazidocobalt(III) sulfate or pentaammineazidocobalt(2+) sulfate

e. diamminesilver(I) tetrafluoroborate(III) or diamminesilver(1+) tetrafluoroborate(1–) (The BF_4^- ion is commonly called simply "tetrafluoroborate.")

9.3 **a.** tris(oxalato)vanadate(III) or tris(oxalato)vanadate(3–) (In the first printing, problem 9.2.d. was duplicated here.)

b. sodium tetrachloroaluminate(III) or sodium tetrachloroaluminate(1–)

c. carbonatobis(ethylenediamine)cobalt(III) chloride or carbonatobis(ethylenediamine)cobalt(1+) chloride

d. tris(2,2′-bipyridine)nickel(II) nitrate or tris(2,2′-bipyridine)nickel(2+) nitrate (The IUPAC name of the bidentate ligand, 2,2′-bipyridyl may also be used; this ligand is most familiarly called "bipy.")

e. hexacarbonylmolybdenum(0) (also commonly called "molybdenum hexacarbonyl") The (0) is often omitted. (In the first printing, problem 9.3.c. was duplicated here.)

9.4 **a.** tetraamminecopper(II) or tetraamminecopper(2+)

b. tetrachloroplatinate(II) or tetrachloroplatinate(2–)

c. tris(dimethyldithiocarbamato)iron(III) or tris(dimethyldithiocarbamato)iron(0)

d. hexacyanomanganate(II) or hexacyanomanganate(4–)

e. nonahydridorhenate(VII) or nonahydridorhenate(2–) (This ion is commonly called "enneahydridorhenate.")

9.5 **a.** triamminetrichloroplatinum(IV) or triamminetrichloroplatinum(1+)

b. diamminediaquadichlorocobalt(III) or diamminediaquadichlorocobalt(1+)

c. diamminediaquabromochlorocobalt(III) or diamminediaquabromochlorocobalt(1+)

d. triaquabromochloroiodochromium(III) or triaquabromochloroiodochromium(0)

e. dichlorobis(ethylenediamine)platinum(IV) or dichlorobis(ethylenediamine)platinum(2+) or dichlorobis(1,2-ethanediamine)platinum(IV) or dichlorobis(1,2-ethanediamine)platinum(2+)

f. diamminedichloro(*o*-phenanthroline)chromium(III) or diamminedichloro(*o*-phenanthroline)chromium(1+) or diamminedichloro(1,10-phenanthrolene)chromium(III) or diamminedichloro(1,10-phenanthrolene)chromium(1+)

g. bis(bipyridine)bromochloroplatinum(IV) or bis(bypyridine)bromochloroplatinum(2+) or bis(2,2′-bipyridyl)bromochloroplatinum(IV) or bis(2,2′-bipyridyl)bromochloroplatinum(2+)

h. dibromo[*o*-phenylene(dimethylarsine)(dimethylphosphine)]rhenium(II) or dibromo[*o*-phenylene(dimethylarsine)(dimethylphosphine)]rhenium(0) or dibromo[1,2-phenylene(dimethylarsine)(dimethylphosphine)]rhenium(II) or dibromo[1,2-phenylene(dimethylarsine)(dimethylphosphine)]rhenium(0)

i. dibromochlorodiethylenetriaminerhenium(III) or dibromochlorodiethylenetriaminerhenium(0) or dibromochloro(2,2′-diaminodiethylamine)rhenium(III) or dibromochloro(2,2′-diaminodiethylamine)rhenium(0)

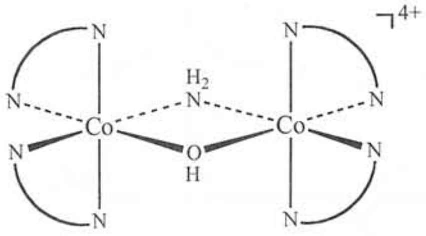
9.6 **a.** *cis*-dicarbonylbis(dimethyldithiocarbamato)ruthenium(III) or *cis*-dicarbonylbis(dimethyldithiocarbamato)ruthenium(0)

b. trisoxalatocobaltate(III) or trisoxalatocobaltate(3–)

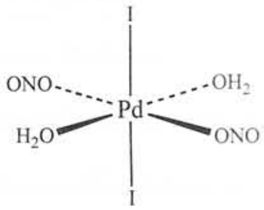
c. tris(ethylenediamine)ruthenium(II) or tris(ethylenediamine)ruthenium(2+)

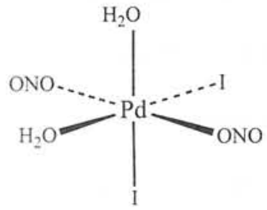
d. bis(2,2′-bipyridine)dichloronickel(II) or bis(2,2′-bipyridine)dichloronickel(2+)

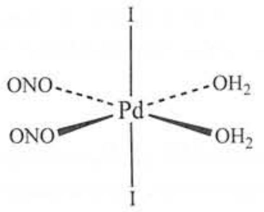
9.7 **a.** Bis(en)Co(III)-μ-amido-μ-hydroxobis(en)Co(III)

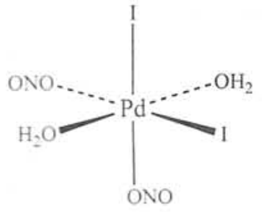


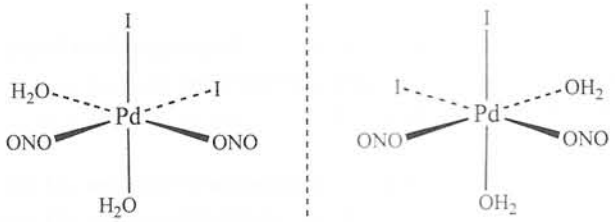
b. Diaquadiiododinitritopalladium(IV)





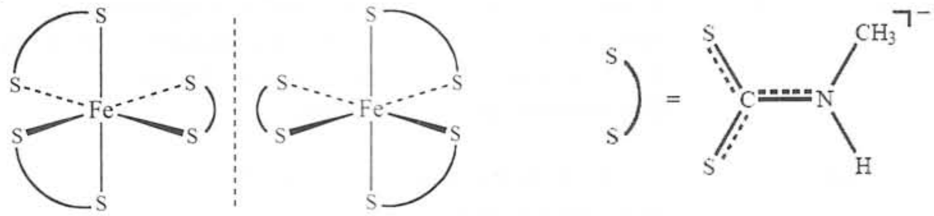






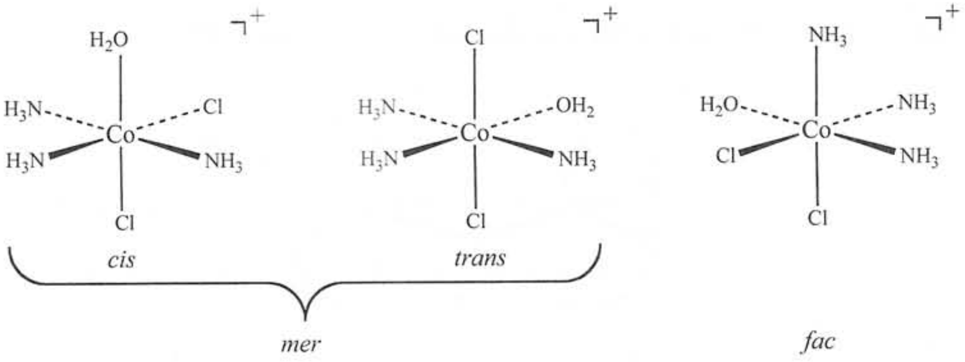
enantiomers

c. $Fe(dtc)_3$

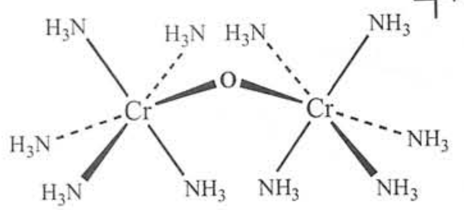


At low temperature, restricted rotation about the C–N bond can lead to additional isomers as a consequence of the different substituents on the nitrogen. These isomers, which are of the type in problem 9.11, can be observed by NMR.

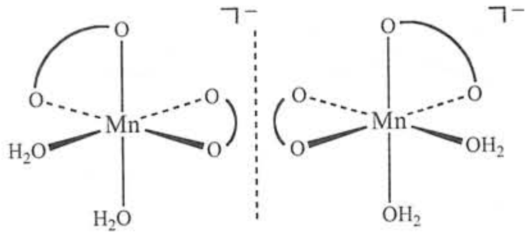
9.8 **a.** triamminequaqudichlorocobalt(III) chloride Isomers are of the cation:



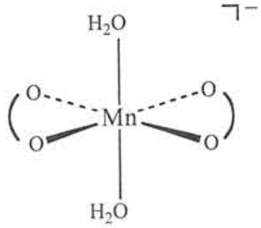
b. μ-oxo-bis(pentammine-chromium(III)) ion



c. potassium diaquabis(oxalato)manganate (III) Isomers are of the anion:

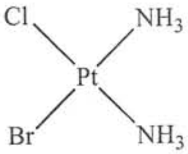


cis enantiomers

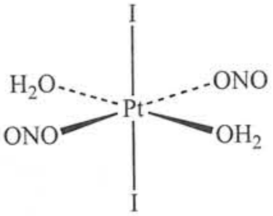


trans

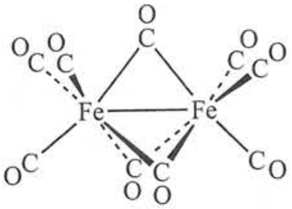
9.9 **a.** *cis*-diamminebromochloroplatinum(II)



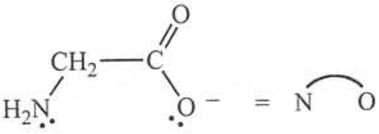
b. diaquadiiododinitritopalladium(IV)

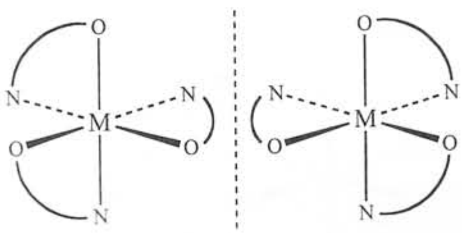


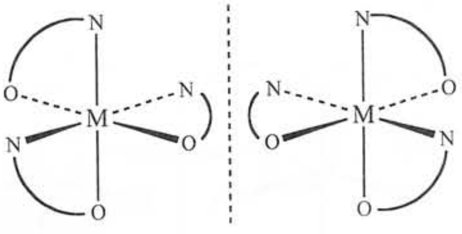
c. tri-μ-carbonylbis(tricarbonyliron(0))



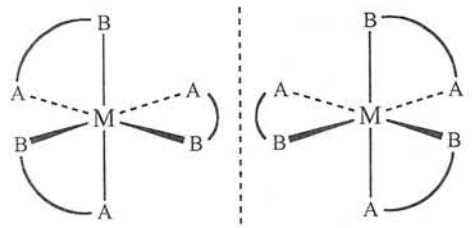
9.10



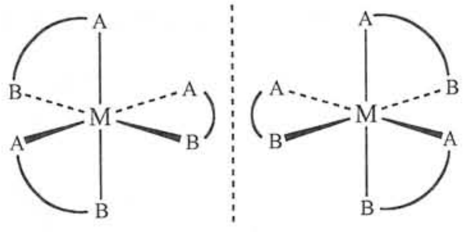




9.11 $M(AB)_3$ *fac* *mer*

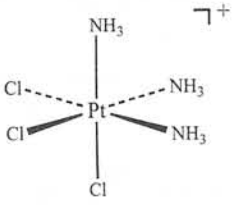


fac



mer

9.12 **a.** $[Pt(NH_3)_3Cl_3]^+$



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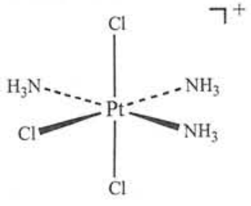
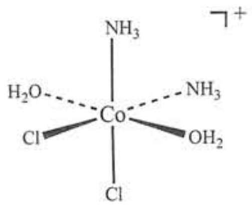
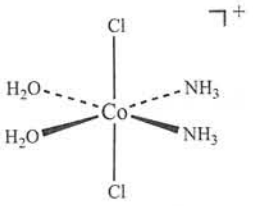
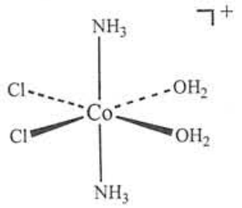


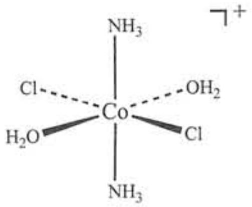
mer

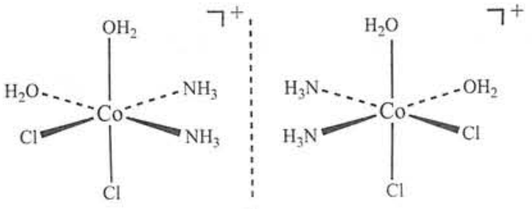
b. $[Co(NH_3)_2(H_2O)_2Cl_2]^+$





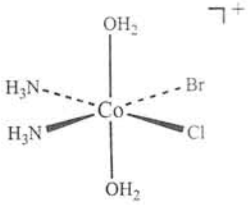


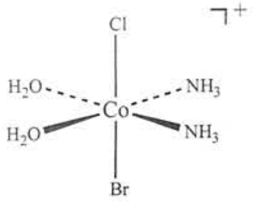


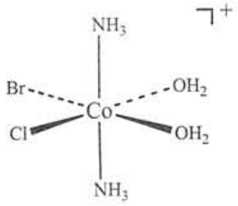


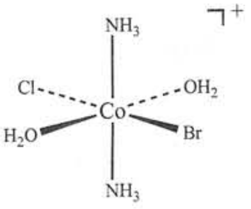
enantiomers

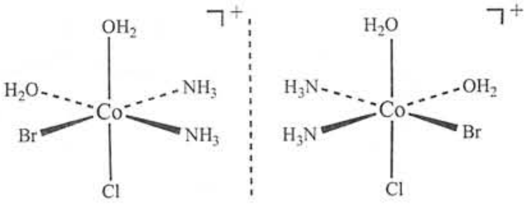
c. $[Co(NH_3)_2(H_2O)_2BrCl]^+$



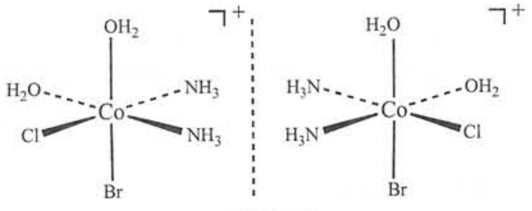






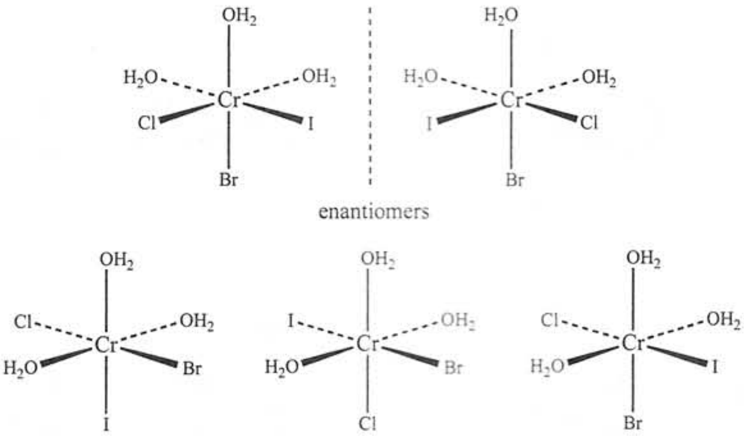


enantiomers

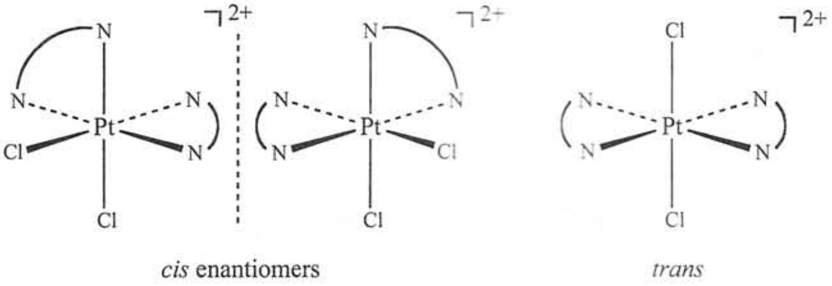


enantiomers

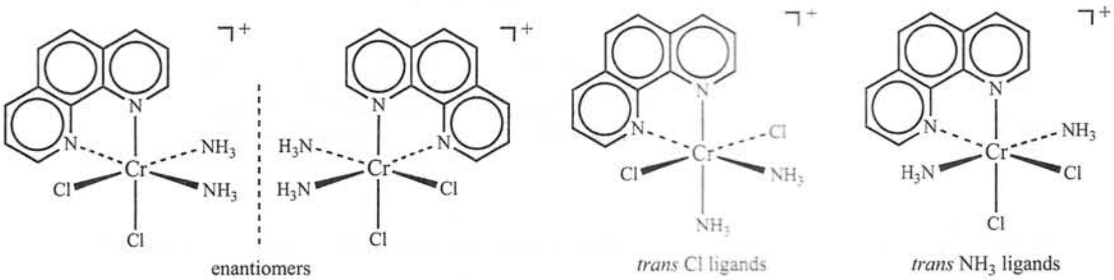
d. $Cr(H_2O)_3BrClI$



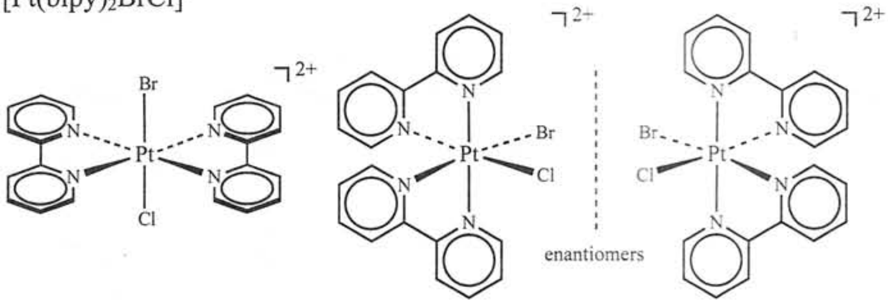
e. $[Pt(en)_2Cl_2]^{2+}$



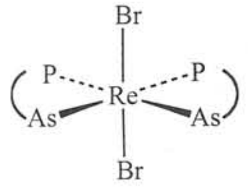
f. $[Cr(o\text{-phen})(NH_3)_2Cl_2]^+$

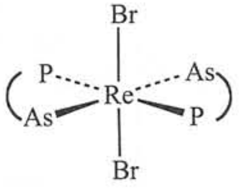


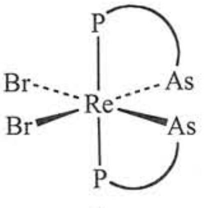
g. $[Pt(bipy)_2BrCl]^{2+}$



h. Re(arphos)$_2$Br$_2$ Abbreviating the bidentate ligands $\overset{\frown}{\text{As P}}$:







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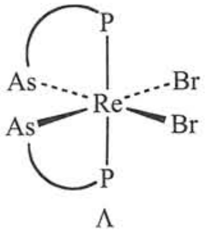

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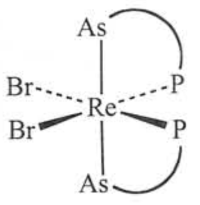

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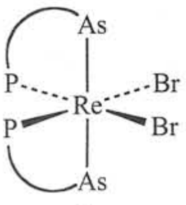

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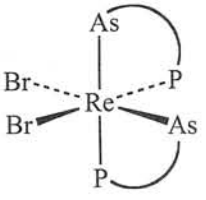

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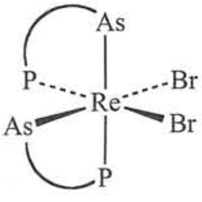

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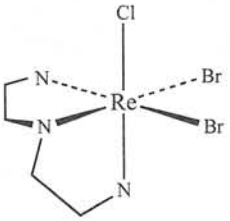
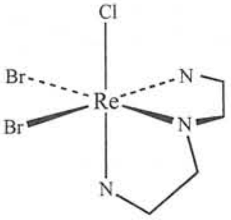
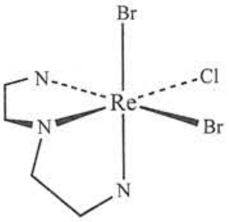
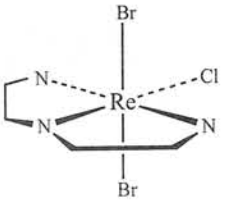
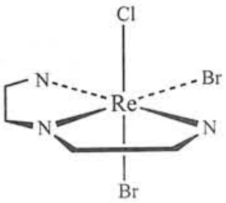
i. Re(dien)Br$_2$Cl





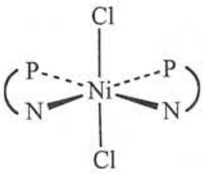


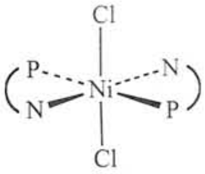


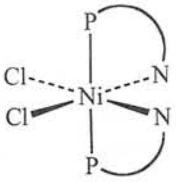


9.13 **a.** The "softer" phosphorus atom bonds preferentially to the soft metal Pd (see section 6.3.1).

b, c. Abbreviating the bidentate ligands $\overset{\frown}{\text{N P}}$:







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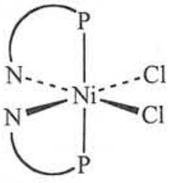

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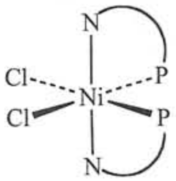

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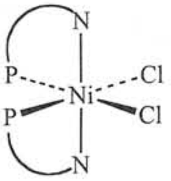

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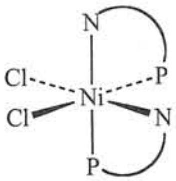

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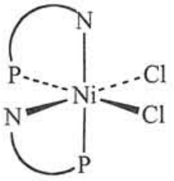
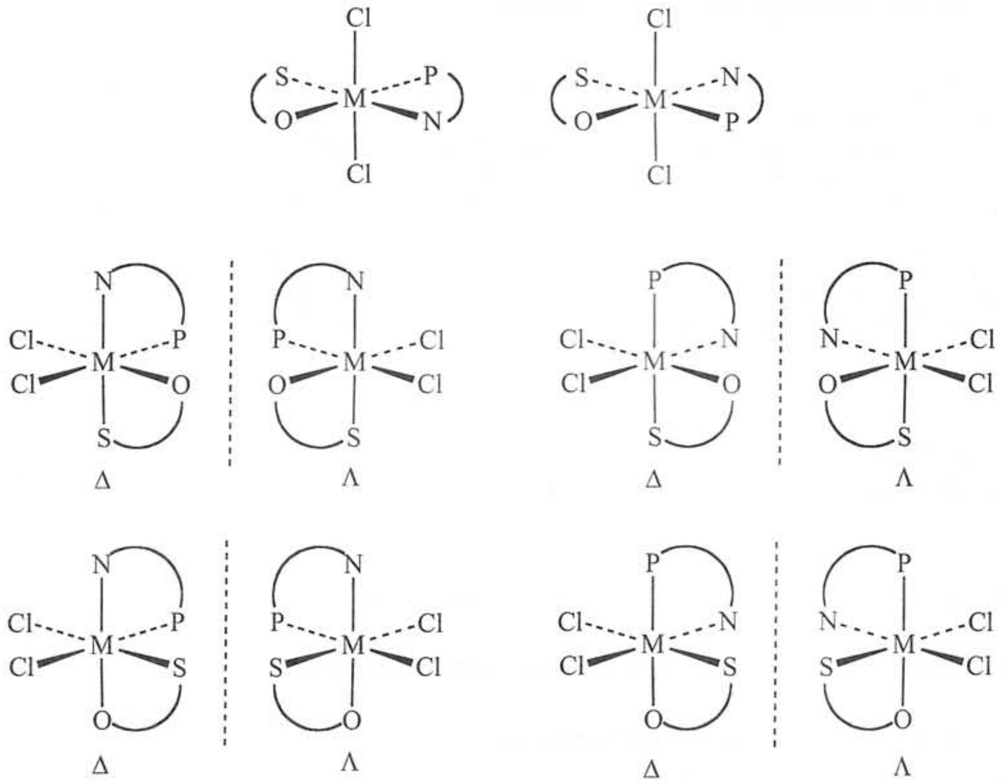
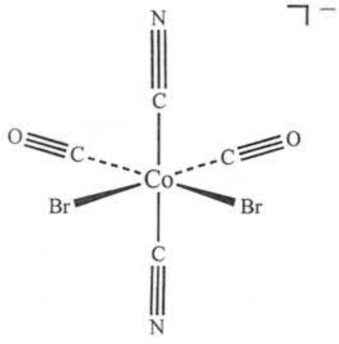


Λ

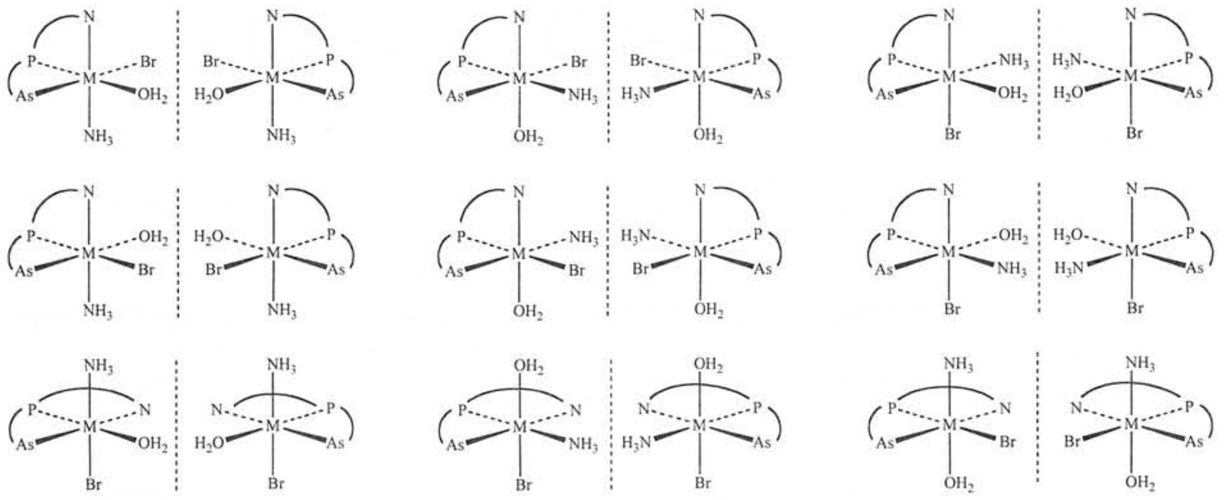
9.14 **a.** Abbreviating the bidentate ligands $\overset{\frown}{\mathrm{N\ P}}$ and $\overset{\frown}{\mathrm{O\ S}}$:



9.15 The single C–N stretching frequency indicates a *trans* structure for the cyanides (the symmetric stretch of the C–N bonds is not IR active), while the two C–O bands indicate a *cis* structure for the carbonyls (both the symmetric and antisymmetric C–O stretches are IR active). As a result, the bromo ligands are also *cis*.



9.16 There are 18 isomers overall, twelve with the chelating ligand in a *mer* geometry and six with the chelating ligand in a *fac* geometry. All are enantiomers. They are all shown below, with dashed lines separating the enantiomers.



9.17 **a.** Δ **b.** Δ **c.** Λ **d.** Δ

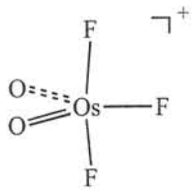
9.18 All are chiral if the ring in **b** does not switch conformations.

9.19 18b δ 18c top ring: δ, bottom ring: λ

9.20 The ^{19}F doublet is from the two axial fluorines (split by the equatorial fluorine).

The ^{19}F triplet is from the equatorial fluorine (split by the two axial fluorines).

The two doubly bonded oxygens are equatorial, as expected from VSEPR considerations.



9.21 Examples include both cations and anions:

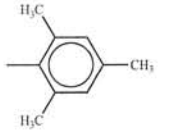
$[Cu(CN)_2]^-$, $[Cu_2(CN)_3]^-$, $[Cu_3(CN)_4]^-$, $[Cu_4(CN)_5]^-$, $[Cu_5(CN)_6]^-$
$[Cu_2(CN)]^+$, $[Cu_3(CN)_2]^+$, $[Cu_4(CN)_3]^+$, $[Cu_5(CN)_4]^+$, $[Cu_6(CN)_5]^+$

Based primarily on calculations (rather than experimental data), Dance et al. have proposed linear structures such as the following.:

$[Cu(CN)_2]^-$: NC—Cu—CN
$[Cu_2(CN)_3]^-$: NC—Cu—CN—Cu—CN
$[Cu_3(CN)_4]^-$: NC—Cu—CN—Cu—CN—Cu—CN
$[Cu_2(CN)]^+$: Cu—CN—Cu
$[Cu_3(CN)_2]^+$: Cu—CN—Cu—CN—Cu
$[Cu_4(CN)_3]^+$: Cu—CN—Cu—NC—Cu—CN—Cu

Where 2-coordinate copper appears in these ions, the geometry around the Cu is linear, as expected from VSEPR.

9.22 The bulky mesityl groups cause sufficient crowding that the phosphine ligands can show chirality (C_3 symmetry) and can be considered as similar to left handed (P_L) and right handed (P_R) propellers. If two P(mesityl)$_3$ phosphines are attached in a linear arrangement to a gold atom, three isomers are possible:

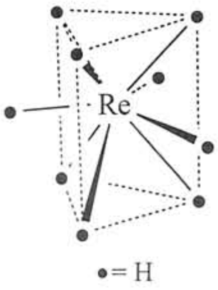


P_L—Au—P_L P_R—Au—P_R P_L—Au—P_R

mesityl

(P_R—Au—P_L is equivalent to P_L—Au—P_R, as can best be seen by making models.) NMR data at low temperature support the presence of these isomers, which interconvert at higher temperatures.

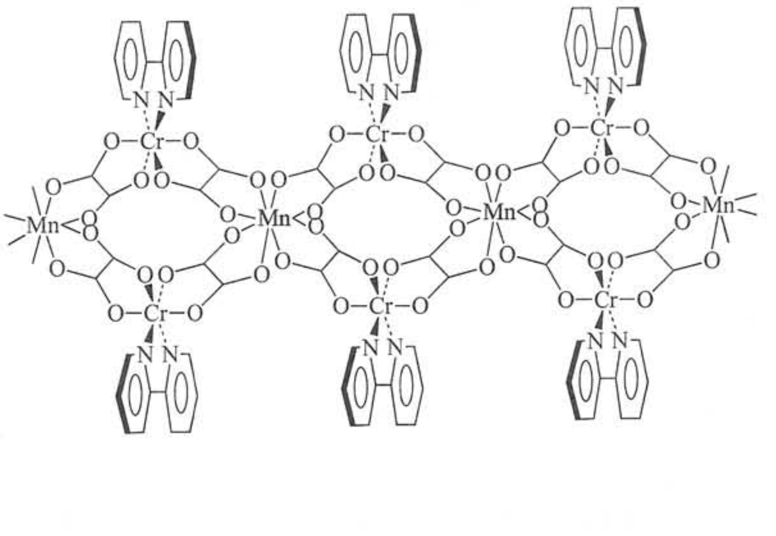
9.23 The point group is D_{3h}. A representation Γ based on the nine 1*s* orbitals of the hydride ligands is:



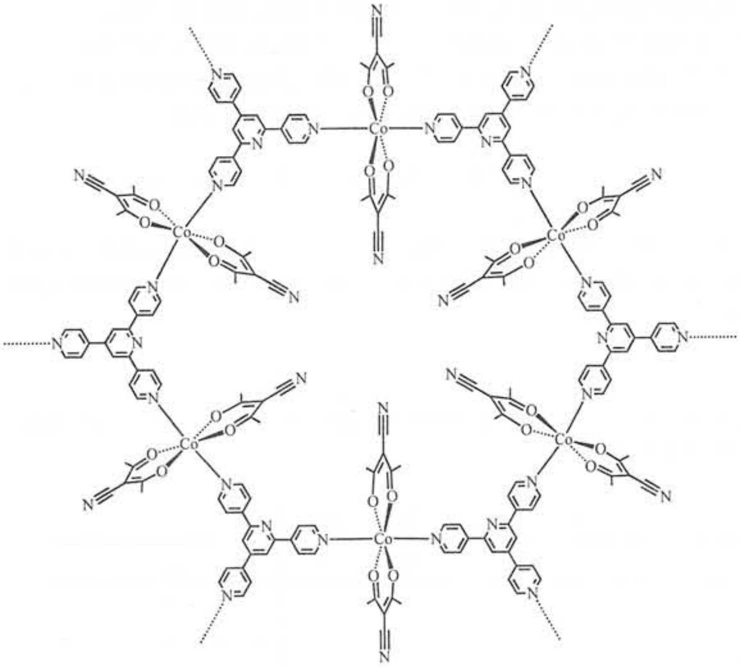
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
Γ	9	0	1	3	0	3	
A_1'	1	1	1	1	1	0	z^2
E'	2	−1	0	2	−1	0	$(x, y), (x^2-y^2, xy)$
A_2''	1	1	−1	−1	−1	1	z
E''	2	−1	0	−2	1	0	(xz, yz)

The representation Γ reduces to $2\,A_1' + 2\,E' + A_2'' + E''$. Collectively these representations match all the functions for *s* (totally symmetric, matching A_1'), *p*, and *d* orbitals of Re, so all the *s*, *p*, and *d* orbitals of the metal have suitable symmetry for interaction. (The strength of these interactions will also depend on the match in energies between the rhenium orbitals and the 1*s* orbital of hydrogen.)

9.24



9.25



9.26 **a.** Cu(acacCN)$_2$: D_{2h} tpt: C_{2v}

b. C_6