RUTHENIUM AND OSMIUM: ANNUAL SURVEY FOR THE YEAR 1982

JEROME B. KEISTER
Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214 (U.S.A.)

CONTENTS

ABBREVIATIONS

Ac - acetyl

acac - acetylacetonate

bipy - 2,2'-bipyridine
Bu - *n*-butyl
i-Bu - *i*-butyl
t-Bu - *t*-butyl
Bz - benzyl
COD - 1,5-cyclo-octadiene
Cp - cyclopentadienyl
Cyc - cyclohexyl
das - *o*-phenylenebis(dimethylarsine)
DIOP - 2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DMSO - dimethyl sulfoxide
dpam - bis(diphenylarsino)methane
dppe - 1,2-bis(diphenylphosphino)ethane
dppm - bis(diphenylphosphino)methane
Et - ethyl
Me - methyl
OEP - octaethylporphyrin
Pc - phthalocyanine
Ph - phenyl
phen - 1,10-phenanthroline
Pr - *n*-propyl
i-Pr - *i*-propyl
TMED - N,N,N',N'-tetramethylethylenediamine
TPP - tetraphenylporphyrin
Ts - *p*-toluenesulfonyl

MONONUCLEAR COMPLEXES WITH CARBONYL, HYDRIDE, GROUP V, AND SULFUR LIGANDS

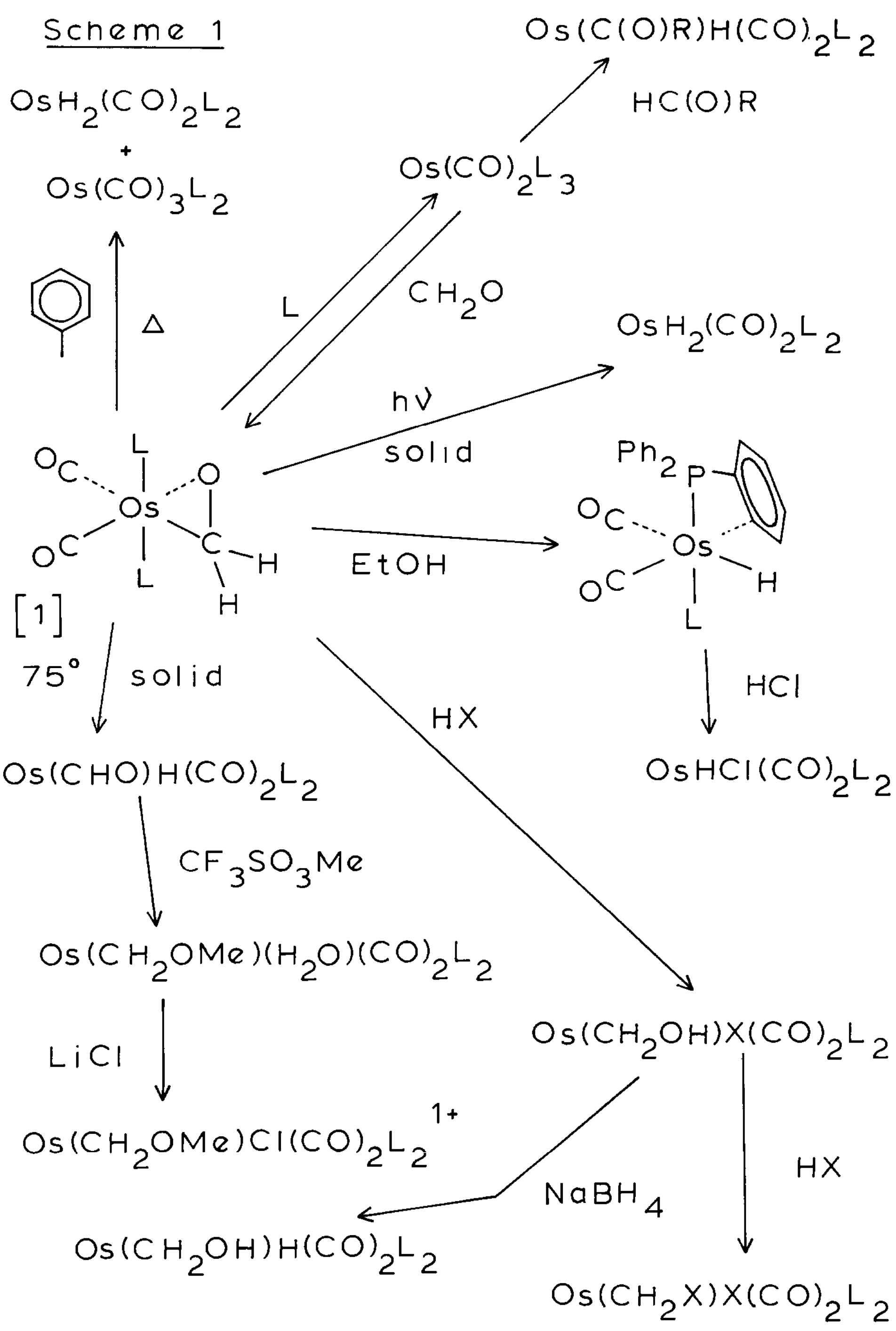
Simple Carbonyls and Substituted Derivatives in the Zero-valent State

The EPR spectrum of $Os(CO)_5^+$, prepared by gamma irradiation of $Os(CO)_5$ dissolved in crystals of $Cr(CO)_6$, was recorded at 100 K (1).

The IR spectra of $HRu(CO)_4^-$, $HOs(CO)_4^-$ and the deuterated analogs were examined to determine isotope effects upon the CO stretching frequencies. The study found evidence for significant interactions between M-H and C-O modes (2).

The reaction of $Os(CO)_2L_3$ (L=PPh_3) with aqueous formaldehyde was used to prepare one of the first formaldehyde complexes, $Os(CH_2O)(CO)_2L_2$ [1]. The product was characterized as an η^2-CH_2O complex by X-ray crystallography (3). Complex [1] decomposes in refluxing toluene to $Os(CO)_2L_3$ and $H_2Os(CO)_2L_2$, each in 50% yield. However, at 75° for several hours the complex in the solid state is transformed to the formyl complex $Os(CHO)H(CO)_2L_2$. Methylation of [1] with methyl trifluoromethanesulfonate gives the methoxymethyl derivative

Scheme 1


Os(C(O)R)H(CO)2L2
HC(O)R
OsH2(CO)2L2
+
Os(CO)3L2
Os(CO)2L3
L
CH2O
Δ
OsH2(CO)2L2
hν
solid
Ph2P
OC
OC
L
O
Os
C
H
H
L
[1]
EtOH
OC
OC
Os
H
L
75°
solid
HX
HCl
Os(CHO)H(CO)2L2
OsHCl(CO)2L2
CF3SO3Me
Os(CH2OMe)(H2O)(CO)2L2
Os(CH2OH)X(CO)2L2
LiCl
1+
Os(CH2OMe)Cl(CO)2L2
NaBH4
HX
Os(CH2OH)H(CO)2L2
Os(CH2X)X(CO)2L2

$Os(CH_2OMe)(H_2O)(CO)_2L_2^+$. Reaction of [1] with excess HX (X=Cl,Br,I) forms the corresponding $Os(CH_2X)X(CO)_2L_2$; the intermediate hydroxymethyl complex $Os(CH_2OH)X(CO)_2L_2$ can be isolated if only one equivalent of HX is used. Reactions of $Os(CO)_2L_3$ with other aldehydes HC(O)R yield $Os(\eta^1\text{-}C(O)R)H(CO)_2L_2$. These reactions are summarized in Scheme 1 (3). Syntheses for a number of zero-valent complexes of Os, including $Os(CO)_2L_3$, $Os(CO)_2(CS)L_2$, $Os(CO)(CS)L_3$, $Os(CO)(CNR)L_3$, $Os(CO)(CS)(CNR)L_2$, $Os(C_2H_4)(CO)(CNR)L_2$, $Os(C_2H_4)(CO)(CS)L_2$, $Os(CO)_2(CS_2)L_2$, $Os(CO)(CS)(CS_2)L_2$, $Os(CO)(CNR)(CS_2)L_2$, and $Os(CO)_2(C_2Ph_2)L_2$ (R=*p*-tolyl, L-PPh_3) were reported (Scheme 2) (4).

Resonance Raman spectra of $Ru(CO)_3(RN{=}CHCH{=}NR)$ (R=aryl or *i*-Pr), obtained by excitation into the lowest energy absorption band, were reported. The results were interpreted in terms of distortion of aryl groups on the diimine in the metal-to-ligand charge transfer excited state (5).

The coordination chemistry of α-diimines with Ru(0) was examined. These ligands may act as 2-,4-,6- or 8-electron donors. The mode of coordination is determined largely by the steric properties of the N-alkyl groups (6).

Photolysis of $Ru_3(CO)_{12}$ in the presence of excess $P(OMe)_3$ yields $Ru\{P(OMe)_3\}_5$, which is formed in a stepwise manner through $Ru(CO)_{5-n}\{P(OMe)_3\}_n$. Thermolysis of the product at 120° gives $Ru\{P(OMe)_3\}_4(Me)\{P(O)(OMe)_2\}$. Treatment of either $Ru\{P(OMe)_3\}_5$ or $Ru\{P(OMe)_3\}_4(Me)\{P(O)(OMe)_2\}$ with methyl iodide forms $[Ru\{P(OMe)_5\}(Me)]$ I. Photolysis of $Ru(CO)_2\{P(OMe)_3\}_3$ in the presence of $P(OPh)_3$ gives $HRu\{C_6H_4OP(OPh)_2\}\{P(OMe)_3\}_3$, containing an ortho-metallated phenyl ring (7).

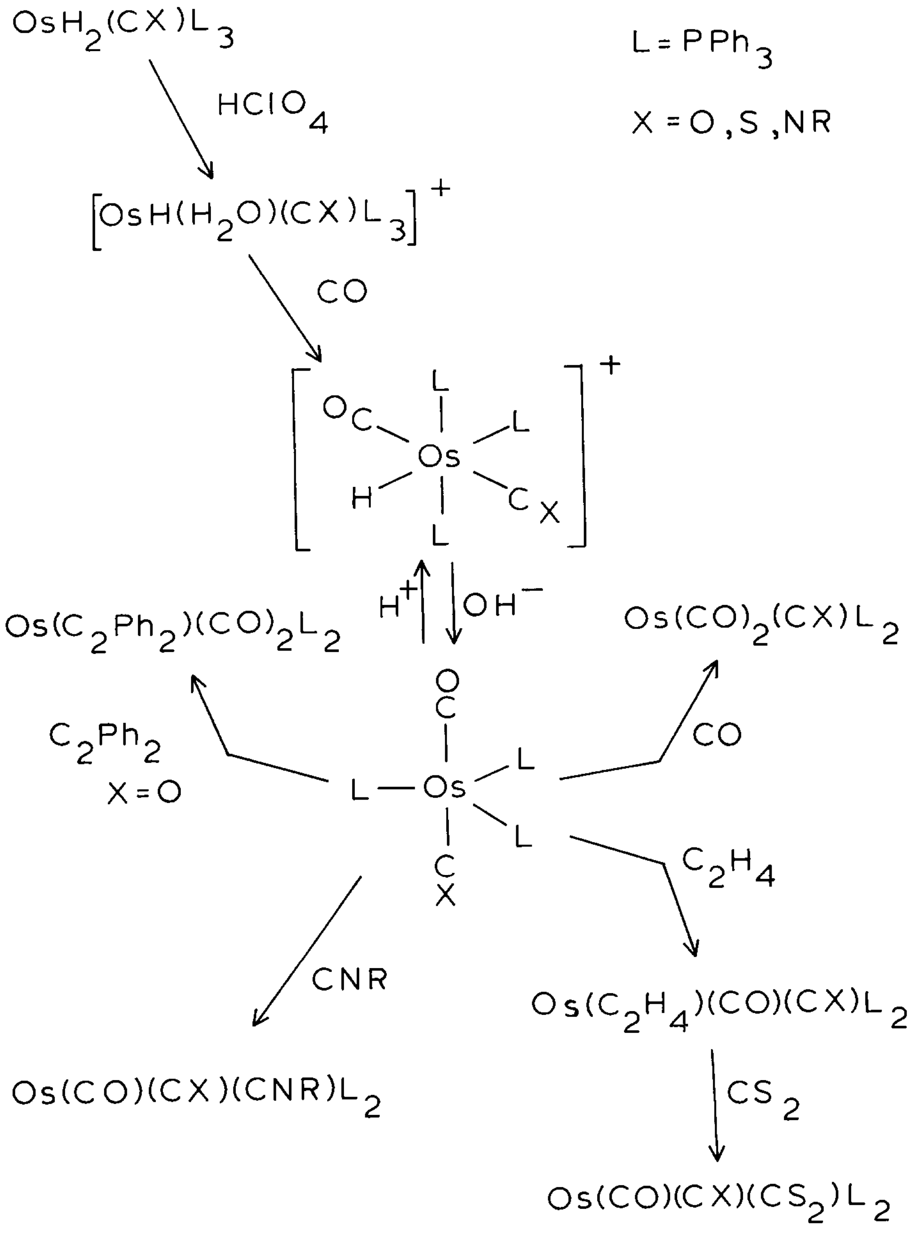
Carbonyls and Substituted Derivatives in the Divalent State

Bronsted acidities were measured for *cis*-$Os(CO)_4(E)(H)$ (E=H,Me, $Os(CO)_4H$) in acetonitrile, and rates of proton transfer were measured using NMR spectroscopy. The dinuclear complex $H_2Os_2(CO)_8$ is more acidic than $H_2Os(CO)_4$ by 0.4 pK_a units, while the latter is more acidic than $HOsMe(CO)_4$ by 2.2 pK_a units. The rate of proton transfer from a hydrido transition metal to its conjugate anion is much slower than to a nitrogen base of comparable strength (8).

The kinetic product from combination of $RuCl_3{\cdot}3H_2O$, CO, and PBz_nPh_{3-n} in refluxing 2-methoxyethanol is *trans*-$Ru(CO)_2(PBz_nPh_{3-n})_2Cl_2$. The kinetics of the thermal isomerization to the *cis*-form were examined. The isomerization is dissociative in nature, with the rate increasing as the cone angle of the phosphine increases. The crystal structures of *trans*-$Ru(CO)_2(PBz_3)_2Cl_2$ and *cis*-$Ru(CO)_2(PBzPh_2)_2Cl_2$ were reported (9).

The structure of $Ru(CO)Cl_2(PCyc_3)_2$ [2], determined by X-ray crystallography, is based on a distorted square pyramidal geometry around Ru with one cyclohexyl ring blocking the sixth coordination site, perhaps via a coordinated C-H (10). Syntheses for $RuHCl(CO)(PCyc_3)_2$ and $Ru(CO)_3(PCyc_3)_2$ were reported (335).

Scheme 2


$OsH_2(CX)L_3$
$HClO_4$
L = PPh_3
X = O, S, NR
$[OsH(H_2O)(CX)L_3]^+$
CO
OC
L
Os
H
CX
+
H^+
OH^-
$Os(C_2Ph_2)(CO)_2L_2$
C_2Ph_2
X = O
$Os(CO)_2(CX)L_2$
CO
C_2H_4
CNR
$Os(C_2H_4)(CO)(CX)L_2$
CS_2
$Os(CO)(CX)(CNR)L_2$
$Os(CO)(CX)(CS_2)L_2$

]

Reactions of $\mathrm{OsHCl(CO)(PCyc_3)_2}$ with deuterium gas and with EtOD lead to deuteriation of the cyclohexyl groups. The proposed mechanism involves both inter- and intramolecular C-H bond activation (Scheme 3) (11).

The carboxylate complexes $\mathrm{Ru(CO)_2(O_2CR)_2L}$ (R=Me,$\mathrm{CF_3}$; L=phen,bipy) can be prepared in 50-85% yield by treatment of $\mathrm{Ru(CO)_2Cl_2L}$ with $\mathrm{AgO_2CR}$ in refluxing $\mathrm{HO_2CR}$. Reactions of the acetate complexes with trifluoroacetic or trifluoromethanesulfonic acid can be used to prepare $\mathrm{Ru(CO)_2(O_2CCF_3)_2L}$; $\mathrm{Ru(CO)_2(OSO_2CF_3)_2}$(phen), or $\mathrm{[Ru(CO)_2(phen)(NCMe)_2][SO_3CF_3]_2}$. The last two complexes are starting materials for the preparation of $\mathrm{Ru(CO)_2L_2}^{2+}$, $\mathrm{Ru(CO)_2(phen)(bipy)}^{2+}$, and $\mathrm{Ru(CO)_2}$(phen)(3,4,7,8-tetramethyl-1,10-phenanthroline). Related chemistry from $\mathrm{Ru(CO)_2Cl_2py_2}$ is used to prepare $\mathrm{Ru(CO)_2(O_2CMe)_2py_2}$, $\mathrm{[Ru(CO)_2(NCMe)_2py_2][SO_3CF_3]_2}$, and other complexes (12).

At 25° the reaction of 2-formylpyridine with $\mathrm{RuHCl(CO)(PPh_3)_3}$ yields *cis*-$\mathrm{RuCl(OCH_2C_5H_4N\text{-}N,O)(CO)(PPh_3)_2}$. In refluxing benzene isomerization of the product to the thermodynamically favored *trans* form occurs. The analogous reactions of 2-acetyl- and 2-benzoylpyridine give rise to $\mathrm{RuCl(OCHRC_5H_4N\text{-}N,O)(CO)(PPh_3)_2}$ (13).

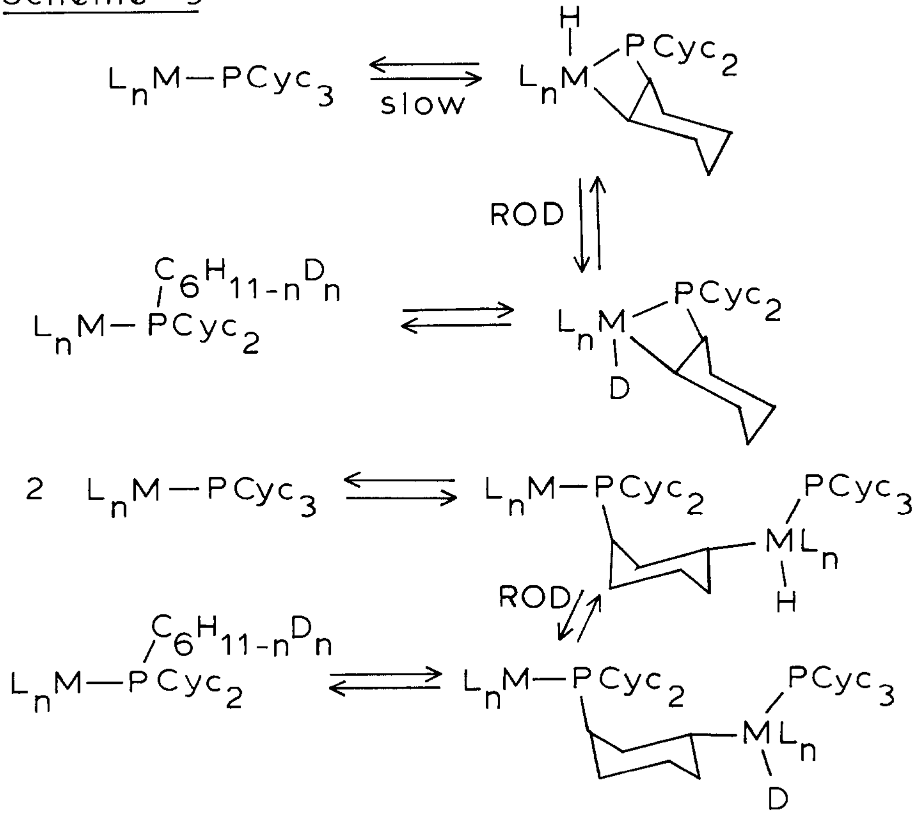
Co-condensation of Ru atoms and oxalyl chloride, followed by treatment of the product with $\mathrm{PMe_3}$, gives $\mathrm{Ru(PMe_3)_3(CO)Cl_2}$ in 70% yield (14).

The complexes $\mathrm{RuH_2(CO)(PPh_3)(L\text{-}L)}$ (L-L=$\mathrm{Ph_2P(CH_2)_nPPh_2}$ (n=1-4), $\mathrm{Ph_2PC_2H_4AsPh_2}$, and 1,2-$\mathrm{(Ph_2P)_2C_6H_4}$) were prepared. Reactions of these complexes with trifluoroacetic acid form the corresponding $\mathrm{Ru(O_2CCF_3)_2(CO)(PPh_3)_m(L\text{-}L)}$ (L-L= 1,2-$\mathrm{(Ph_2P)_2C_6H_4}$ (m=0,1), $\mathrm{Ph_2PC_2H_4AsPh_2}$ (m=1) and $\mathrm{Ph_2P(CH_2)_nPPh_2}$ (n=3,4; m=0). These complexes were characterized by ^{1}H, ^{31}P and ^{19}F NMR spectroscopy. Catalytic activities for alcohol dehydrogenation and ketone hydrogenation were determined. The new complexes are more active than $\mathrm{Ru(O_2CCF_3)_2(CO)(PPh_3)_2}$ for hydrogenation but all are deactivated during alcohol dehydrogenation, due to decarbonylation of the aldehyde product (15).

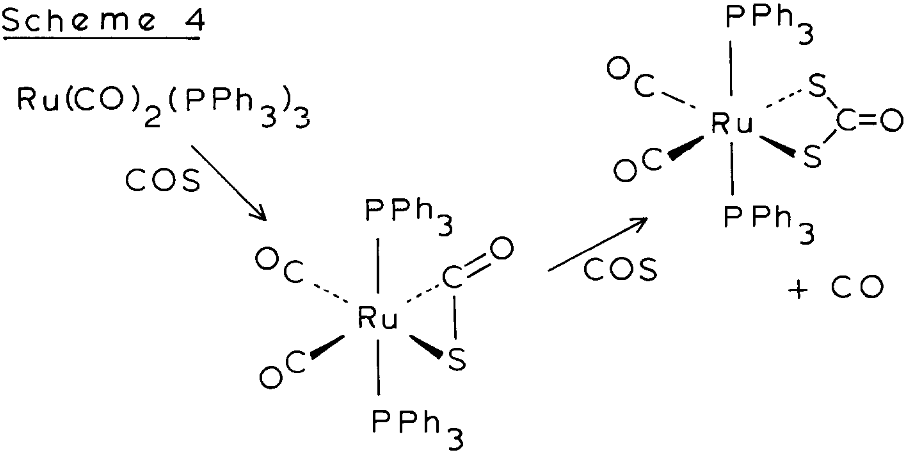
Cis- and *trans*-dichloro isomers of $\mathrm{RuCl_2(CO)_2}$(bidentate) were prepared from meso, racemic, and optically active forms of *o*-phenylenebis(methylphenylarsine) and the phosphine analog. In the case of the phosphine also isolated was $\mathrm{[RuCl(CO)_3}$(bidentate)]Cl, in which the CO ligands are meridional. Decarbonylation of these complexes forms the corresponding $\mathrm{\{RuCl_2(CO)(bidentate)\}_2}$. The DMSO derivative *cis*-$\mathrm{RuCl_2}$(CO)(bidentate)($\mathrm{Me_2SO\text{-}S}$) was prepared and epimerization of this complex at the metal site was examined (16).

Treatment of $\mathrm{RuCl_2(L\text{-}L)_2}$ with Ag(I) under CO yields $\mathrm{Ru(CO)_2(L\text{-}L)_2}^{2+}$ (L-L=dppm,dppe). For the dppm complex both *cis* and *trans* products are formed but only the trans isomer is isolated from the analogous reaction between *trans*-$\mathrm{RuCl_2(dppe)_2}$ and $\mathrm{AgSbF_6}$. However, the reaction of *cis*-$\mathrm{RuCl_2(dppm)_2}$ with $\mathrm{AgClO_4}$ or $\mathrm{AgAsF_6}$ under CO gives $\mathrm{[Ru(CO)_2(dppm)_2AgX]Y_2}$ (X=Cl, Y=$\mathrm{AsF_6}$ or

Scheme 3



Scheme 4



$X{=}Y{=}ClO_4$) [3]. The use of fresh $AgPF_6$ allows isolation of $[Ru(CO)_2(dppm)_2][PF_6]_2$ but aged samples give products such as $[Ru(CO)(O_2PF_2)(dppm)_2][PF_6]$ (17).

A new synthesis for $[Ru(bipy)_2(CO)_2][PF_6]_2$ from $RuCl_3{\cdot}3H_2O$ was reported. Two isomers, yellow [4] and purple [5], are formed (18).

Complexes $[RuCl(CO)(bipy)_2]Cl$ and $RuCl_2(CO)(trpy)$ were prepared from $RuCl_3{\cdot}nH_2O$ and the appropriate chelate. Carbonylation of $RuCl_2(bidentate)_2$ (bidentate=bipy, phen) in refluxing methanol gives $[RuCl(CO)(bipy)_2]Cl$ or $[RuCl(CO)(phen)_2]Cl$, while carbonylation of $RuCl_2(bidentate)_2$ in the presence of 2 equivalents of $AgSbF_6$ gives $[Ru(CO)_2(bidentate)_2][SbF_6]_2$ (19).

Treatment of cis-$Ru(bipy)_2(CO)Cl^+$ with sodium borohydride yields cis-$Ru(bipy)_2(CO)H^+$, which can be isolated as the PF_6 salt in 70% yield. In the presence of acid, this product decomposes rapidly to $Ru(bipy)_2(CO)(H_2O)^{2+}$ and hydrogen gas. The half-life of the hydride complex at 18° is 10 min. It was speculated that the complex might be an intermediate in photoproduction of hydrogen from water in some $Ru(bipy)_3^{2+}$ systems (20).

Removal of both CO ligands from $Ru(CO)_2Cl_2(L\text{-}L)$ can be achieved through the use of trimethylamine-N-oxide in the presence of a bidentate ligand such as phen, bipy, or 3,4,7,8-tetramethyl-1,10-phenanthroline to form $Ru(L\text{-}L)_3^{2+}$ or $Ru(L\text{-}L)(L'\text{-}L')_2^{2+}$ where $L\text{-}L \neq L'\text{-}L'$=bidentate ligand. Yields are reported to be 50-80% (21).

Treatment of $\{RuCl_2(CO)_3\}_2$ with the potentially bidentate ligand $Ph_2PCH_2CH_2SPh$ (L) forms first $RuCl_2(CO)_3L$ and then $RuCl_2(CO)_2L_2$ (45% yield); in both products only P is coordinated. The reaction of $RuCl_3{\cdot}3H_2O$ with L gives $RuCl_3L$ when only one equivalent of L is used, but $\{RuCl_2L_2\}_n$ is formed in 90% yield under reflux conditions. The complexes $RuCl_2(CO)L_2$ and $RuCl_2(CO)_2L_2$ are prepared when the reaction is conducted under a CO atmosphere (22).

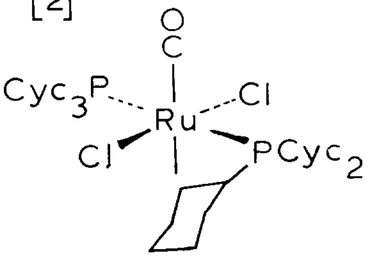
Complexes with Macrocyclic Nitrogen Donor Ligands

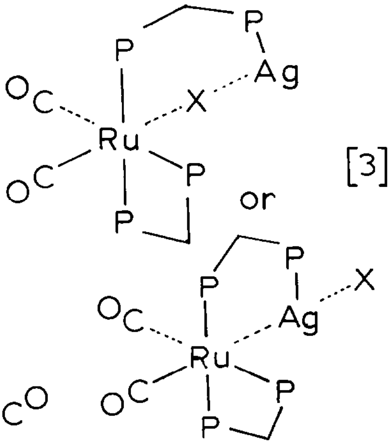
Oxidation of Ru(OEP)(CO) by t-butylhydroperoxide gives $O\{Ru(OEP)(OH)\}_2$. Oxidation of Os(OEP)(CO)(MeOH) with oxygen forms the related products $O\{Os(OEP)(OMe)\}_2$, $\{Os(OEP)OMe\}O\{Os(OEP)(OH)\}$ and $O\{Os(OEP)(OH)\}_2$ (23).

Cyclic voltammetric studies of Ru(CO){tetra(p-isopropylphenyl)porphinato}-(amine) were used to probe the effect of the axial ligands upon the oxidation potential of the macrocyclic ring. The redox potentials found cover a range of 0.09 V and depend upon the π-base and hydrogen bond donor strength of the amine. Values for all complexes of aliphatic amines are essentially the same (24).

Stability constants for the addition of nitrogen bases to Ru(TPP)(CO) and $Ru(TPP)(CO)^+$ were calculated from spectrophotometric and electrochemical measurements. Stability constants for the two species are similar and increase as the pK_a of the ligand increases (25).

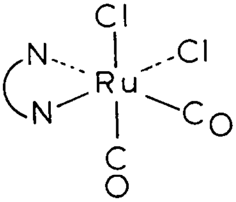
[2]


Cyc₃P
Ru
Cl
Cl
PCyc₂

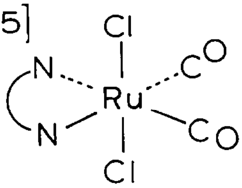

P
Ag
OC
X
Ru
OC
P
P
or
P
X
OC
Ag
Ru
OC
P
P

[3]

[4]


Cl
N
Cl
Ru
N
CO
CO

[5]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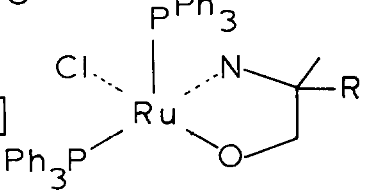
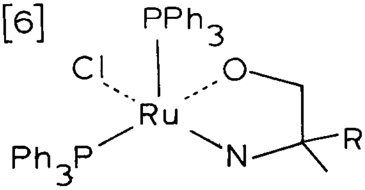
N
CO
Ru
N
CO
Cl

[7]


PPh₃
Cl
N
R
Ru
Ph₃P
O

[6]


PPh₃
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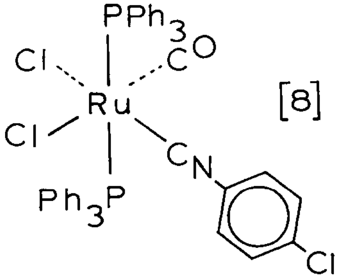
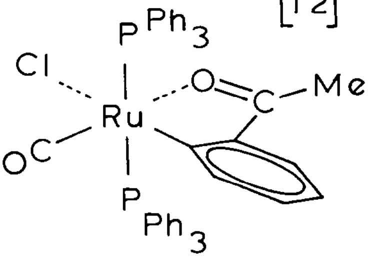
O
Ru
Ph₃P
N
R

[8]


PPh₃
Cl
CO
Ru
Cl
CN
Ph₃P
Cl

[12]


PPh₃
Cl
O
C
Me
Ru
OC
PPh₃

Electron transfer reactions of Ru(TPP)(CO) were studied by cyclic voltammetry and UV/visible spectrophotometry. In the ten solvents used, the complex Ru(TPP)(CO)(S) (S=solvent) is present in solution and can be reversibly oxidized or reduced by one electron. Potentials for the oxidation can be correlated with the Taft β parameter for Lewis basicity of the solvent. For the reduction a linear relation to the solvent's acceptor number is observed. Stability constants for Ru(TPP)(CO)(S) in dichloromethane are related to the Gutman donor number of the solvent (26).

Time-resolved excited state spectra were obtained from laser flash photolysis of Os(OEP)(L)(L') (L=L'=$P(OMe)_3$; L=CO, L'=py; L=NO, L'=OMe; L=L'=O). The initial excited state S_1 decays in $\leqslant$ 8, 50, 36, and 13 ps, respectively. The later excited state T_1 lives for times of 6.2, 16, 5.5, and 6 μs, respectively. The lowest E excited states for the first two complexes are (d,π^*) and for the second two, (π,π^*) states (27).

Flash photolysis, laser flash donors, and $n\pi^*$ photolysis were used to investigate the photochemistry of $Ru(Pc)(py)_2$ under CO to form Ru(Pc)(py)(CO). Substitution was suggested to proceed through a reduced Ru(II)(Pc) radical which is formed by hydride abstraction from donor solvents by the $n\pi^*$ excited state (28).

Phosphine Complexes of M(II)

Isomerization of cis- and trans-$Ru(dppm)_2Cl_2$ is induced by photolysis, heat, or oxidation to Ru(III). Trans to cis isomerization occurs thermally, while irradiation of the lowest-lying d-d transition causes cis to trans isomerization. Upon chemical or electrochemical oxidation of the cis isomer, quantitative conversion to the trans isomer of Ru(III) occurs (29).

The stereochemistry of cis- and trans-$RuCl_2(bidentate)_2$ containing diastereoisomers and enantiomers of o-phenylenebis(methylphenylarsine) and its P analog was studied. The optically active, racemic, meso, syn, and anti forms of the trans-dichloro complexes were isolated and then isomerized to the cis isomers by reaction with $AlEt_3$. Carbonyl derivatives were prepared by replacement of Cl (30).

Reduction of $[RuCl_2(ttp)]_x$ with sodium borohydride yields $RuH(\eta^2-BH_4)(ttp)$ ($ttp=PhP(CH_2CH_2CH_2PPh_2)_2$). Interchange of the hydrogens on B was investigated by ^1H NMR spectroscopy and the results interpreted in terms of a two-step intramolecular process. Reactions of $RuH(BH_4)(ttp)$ with acids and bases were also examined. With a base B(B=NEt_3, $P(OMe)_3$, or NaOMe) and a two-electron donor ligand L (L=CO, $P(OMe)_3$, or PPh_3), the products are $RuH_2L(ttp)$ and $B\cdot BH_3$. Protonation of $RuH(BH_4)(ttp)$ with HBF_4 and in the presence of L=CO,NCMe, or $P(OMe)_3$ generates $[RuHL_2(ttp)][BF_4]$, hydrogen, and $L\cdot BH_3$ or $THF\cdot BH_3$ (31,32).

Reactions of $RCO_2C_6H_4X$ (R=Me,Et; X=H, p-OMe) with $RuH_2(PPh_3)_4$ at 100° generate the corresponding RH, ethylene (R=Et), hydrogen, $RuH_2(CO)(PPh_3)_3$ and

$RuH(\eta^5-OC_6H_5)(PPh_3)_2$ (X=H). The reaction with $BuCO_2Ph$ (110°, 5h.) yields butane (15%), 1-butene (5%), *trans*-2-butene (5%), butadiene (4%), and hydrogen (39%) (33).

Complexes containing amino acid anions can be prepared through halide displacement from $RuCl_2(PPh_3)_3$. For example, RuCl(L-serinato)$(PPh_3)_2$ is prepared in 70% yield by reaction of the dihalide with L-serine and sodium bicarbonate in refluxing acetone. Other amino acids used were glycine, L-hydroxyproline, and L-allohydroxyproline. Proposed structures are [6] or [7]. Oxidative dehydrogenation of glycerin can be achieved using these complexes and N-methyl morpholine-N-oxide in acetone. A turnover number of 41 with 97% selectivity to glyceraldehyde over dihydroxyacetone is obtained. With the L-allohydroxyprolinato complex a 3% excess of the D-antepode is found (34).

Substitution reactions of green *trans*-RuX_2L_2 with phosphines and diphosphines yield $RuX(PR_3)L_2^+$, $Ru(PR_3)_2L_2^{2+}$, and $Ru(P-P)L_2^{2+}$ with $X(PR_3)$, $(PR_3)_2$, and (P-P) ligands in cis positions (X=Cl,Br,I; $PR_3=P(\textit{o}\text{-tolyl})_3$, PPh_3, PPh_2Me, $PPhMe_2$; P-P= dppe, $Ph_2P(CH_2)_3PPh_2$; L=2-(arylazo)pyridine). The UV/visible spectra of these complexes show shifts of the metal-to-ligand charge transfer (MLCT) band to higher energy in the order: $X_2 < (X)(PR_3) < (PR_3)_2 \sim (P-P)$. The MLCT energies for *cis*-RuX_2L_2, $RuX(PR_3)L_2^+$, $Ru(PR_3)_2L_2^{2+}$, and $Ru(P-P)L_2^+$ correlate linearly with the Ru(III)/Ru(II) redox potentials determined by cyclic voltammetry, while *trans*-RuX_2L_2 is far off this line. It was suggested that, during PR_3 substitution, geometrical isomerization of the RuL_2 fragment occurs. The kinetics of substitution by PMe_2Ph on *trans*-$RuCl_2\{2\text{-(phenylazo)pyridine}\}_2$ are second-order and the rate is found to decrease with the size of the phosphine ($PMe_2Ph > PMePh_2 \gg PPh_3$). An associative path involving nucleophilic trans attack or edge displacement was proposed (35).

Mononuclear Complexes of M(III) Containing Carbonyl or Group V Donor Ligands

Substitution by oxalate on $OsX_5(CO)^{2-}$ or *trans*-$OsX_4(CO)_2^-$ yields *mer*-$OsX_3(CO)(C_2O_4)^{2-}$ (X=Cl,Br,I). IR, Raman, and UV/visible spectroscopy were used to characterize these complexes (36).

An ESR study of $RuCl_5(CO)^{2-}$ found that the d_{xy} orbital lies higher in energy than the d_{xz} and d_{yz} orbitals. The relative order of these is determined by the π-donating and π-accepting abilities of the ligands (37).

The halide-bridged dimers $L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}^{Z/Z+1/Z+2}$ (L=PEt_2Ph, $As(C_6H_4Me-4)_3$; x=0, y=0, Z=+1; x=0, y=1, Z=0; x=0, y=2, Z=-1) were synthesized electrochemically in 0.50 M $[NBu_4][BF_4]$/dichloromethane at a Pt electrode. Measurements of the intervalence charge transfer bands and the magnetism at various temperatures for the Ru_2(III,III) complexes show that the degree of Ru-Ru interaction decreases as the molecular asymmetry y-x increases (38).

An XPS study of Ru complexes of the 0 to III oxidation state found a good correlation between the formal oxidation state and the binding energy of the $3d^{5/2}$

level for Ru(0) and Ru(III), but the distinction between Ru(I) and Ru(II) is less clear (39).

Reactions of nitrido complexes of Ru and Os have been studied. Attack by $PPh_2(OEt)$ on $OsNCl_3(AsPh_3)_2$ yields $Os\{NPPh_2(OEt)\}Cl_3\{PPh_2(OEt)\}_2$ but only $MCl_2\{P(OPh)_3\}_4$ (M=Ru,Os) can be isolated from the corresponding reactions with $P(OPh)_3$. The Lewis base adducts $MNCl_4 \cdot L^-$ or $\{MNCl_4\}_2L'^{2-}$ (L=py, ONC_5H_5, DMSO; L'=dioxane, pyrazine) react with PPh_3 to give the corresponding $M(NPPh_3)Cl_3(PPh_3)_2$. The new complex $Os(NPPh_3)(NCO)_3(PPh_3)_2$ was prepared in this way from $OsN(NCO)_5^{2-}$. Although no product can be isolated from reactions of $OsNI_4^{2-}$ with PPh_3 or $AsPh_3$, $SbPh_3$ yields $OsNI_3(SbPh_3)_2$. The oxo analog $OsOCl_4$ and PPh_3 form $Os(OPPh_3)_2Cl_4$ (40).

Complexes with Sulfur Ligands

The spin-lattice relaxation times (T_1) for the ^{31}P nuclei in the Ru(II) complexes cis-$Ru(S_2PMe_2)_2(PPh_2OEt)_2$, cis-$Ru(S_2PMe_2)_2(PPh_2H)_2$, cis-$Ru(S_2PMe_2)_2$-$(PPhCl_2)_2$, cis-$Ru(S_2PMe_2)_2(PCl_3)_2$, and $Ru(S_2PMe_2)(Ph_2POHOPPh_2OHOPPh_2)$ were determined (41).

The reaction between $Ru(CO)_2(PPh_3)_2$ and COS forms $Ru(CO)_2(\eta^2\text{-}COS)(PPh_3)_2$ in 99% yield after 5 min. In solution the product decomposes to $Ru(CO)_3(PPh_3)_2$ and $SPPh_3$. Further reaction of the COS complex with COS yields $Ru(S_2CO)(CO)_2(PPh_3)_2$ (61%). These reactions are shown in Scheme 4 (42).

Complexes of Ru with S donor ligands were prepared and their reactions with CO, PR_3, N_2H_4, and N_2 were examined. Chloride displacement from $Ru(CO)_3(THF)Cl_2$ by $LiSC_6H_4SMe$-2 gives cis-$Ru(CO)_2(MeSC_6H_4S)_2$, and the analogous reaction with 1,2-$(LiS)_2C_6H_4$ yields cis-$Ru(CO)_2(S_2C_6H_4)_2^{2-}$. The latter complex, upon treatment with 1,2-dibromoethane, forms cis-$Ru(CO)_2$(dttd) (H_2dttd=2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane). Although the CO ligands in these complexes are inert toward substitution, $Ru(CO)_2(S_2C_6H_4)_2^{2-}$ in refluxing ethanol reacts with PMe_3 and then 1,2-dibromoethane to yield $Ru(CO)(PMe_3)$(dttd). The disubstituted derivative $Ru(PMe_3)_2$(dttd) is prepared from $RuCl_2(PMe_3)_4$ and Li_2(dttd), and $Ru(PPh_3)_2$(dttd) from $RuCl_2(PPh_3)_3$ and H_2dttd. Reactions of $Ru(PPh_3)_2$(dttd) with CO and N_2H_4 give $Ru(CO)(PPh_3)$(dttd) and $Ru(N_2H_4)(PPh_3)$(dttd), respectively (43).

ISOCYANIDE, NITROSYL, DIAZO, AND DINITROGEN COMPLEXES

Isocyanide complexes

The kinetics of axial ligand substitution reactions of benzyl isocyanide and CO complexes of Ru(OEP), Ru(TPP) and Ru(Pc) were determined and compared with those of the Fe analogs. The relative lability of benzyl isocyanide complexes containing 1-methylimidazole (MeIm) and 4-t-butylpyridine (Bupy) is Ru(Pc) $<$ Ru(OEP) $\sim$ Ru(TPP) $\ll$ Fe(Pc). In complexes with two weak-field axial ligands, a spin change occurring along the reaction coordinate for dissociation of a ligand is proposed to account for the lower free energy of activation in Fe, but not Ru, systems. Dissociation of MeIm or Bupy trans to CO or CNBz is much faster than dissociation of these ligands trans to MeIm. Reactions examined were $Ru(OEP)(CNBz)_2$ + MeIm, Ru(OEP)L(CNBz) + CNBz (L=MeIm,Bupy), Ru(OEP)L(CO) + 2CNBz, and the analogous reactions of the TPP derivatives (44). Lineshape analysis of the temperature-dependent ^1H NMR spectra was used to determine the kinetics of axial ligand exchange for MeIm or Bupy complexes of Ru(TTP)(CNBz); the results were compared to the kinetics of ligand exchange for other Ru porphyrin systems and Ru(II) complexes with amine ligands (45).

The isocyanide complexes $Ru(NH_3)_5(CNR)^{2+}$ and trans-$Ru(NH_3)_4(CNR)_2{}^{2+}$ (R=Cyc,Bz) were prepared by substitution on $Ru(NH_3)_5(H_2O)^{2+}$. A study of the kinetics of aquation of $Ru(NH_3)_5(CNBz)^{2+}$ found the CNR ligand to be a trans labilizing ligand by a factor of 40 compared to ammonia. However, for replacement of water in $Ru(NH_3)_4(H_2O)(CNBz)^{2+}$ by isonicotinamide, the CNBz ligand is delabilizing. Cyclic voltammetry studies were also reported (46).

The crystal structure of the ethanol solvate of $RuCl_2(CO)(CNC_6H_4Cl\text{-}4)(PPh_3)_2$ [8] was reported (47). The Ru-Cl bond length trans to the isocyanide is 2.460 Å, while that trans to CO is 2.428 Å.

Nitrosyl Complexes

The nitrosyl complexes $[NH_4][Ru(NO)Cl_5]$ and $\{Ru(NO)Cl_2(PPh_3)\}_2$ can be prepared by treating $RuCl_3{\cdot}3H_2O$ with NOCl and PPh_3 in ethanol/dichloromethane. Refluxing $\{Ru(NO)Cl_2(PPh_3)\}_2$ and PPh_3 in dichloromethane gives $Ru(NO)Cl_2(PPh_3)_2$. The complex $Ru(NO)Cl_5$ is the first high-spin Ru(III) complex (48).

The treatment of $Ru(NO_2)_2(py)_4$ with HX yields $RuX(NO)(py)_4{}^{2+}$ (X=Cl,Br). Protonation with $HClO_4$ gives $Ru(OH)(py)_4(NO)^{2+}$. A reversible reaction between $[RuCl(py)_4(NO)][ClO_4]_2$ and hydroxide yields $RuCl(NO_2)(py)_4$ and water, while the reaction with azide forms a mixture of $RuCl(N_3)(py)_4$ and $RuCl(H_2O)(py)_4{}^+$ with evolution of nitrogen and nitrous oxide. The less soluble $[RuCl(py)_4(NO)][PF_6]_2$ reacts with azide to form $[RuCl(N_2)(py)_4][PF_6]$, which loses nitrogen in solution. Labeling experiments show that the reaction proceeds through a cyclic Ru-N=N-N=NO intermediate. Electrochemical reduction of $RuCl(py)_4(NO)^{2+}$ gives $Ru(H_2O)(py)_4(NO)^{2+}$ through a one-electron reduction and $RuCl(NH_3)(py)_4{}^+$ through a six-electron reduction involving two successive, reversible, one-electron steps and an irreversible four-electron reduction (49). A related complex trans-$Ru(bipy)_2(NO)(OH)^{2+}$ is prepared through the reaction of trans-$Ru(bipy)_2(H_2O)_2{}^{2+}$ with sodium nitrite (50).

Reduction of coordinated NO to coordinated NH_3 also occurs for polypyridyl complexes of Ru and Os. Cyclic voltammetry on $Ru(trpy)(bipy)(NO)^{3+}$ shows first a reversible, pH-independent reduction to $Ru(trpy)(bipy)(NO)^{2+}$ and then a second pH-independent reduction. The third wave is pH-dependent and coulometry past the third wave results in a quantitative six-electron reduction to

$Ru(trpy)(bipy)(NH_3)^{2+}$ and water. The proposed mechanism is shown in Scheme 5 (51).

Reactions of $K_2[M(NO)F_5]$ (M=Ru,Os) in aqueous solutions containing acids ($HClO_4$, HCl, HNO_3, H_2SO_4, or $H_2C_2O_4$) were studied by ^{19}F NMR spectroscopy. In each case substitution of an equatorial fluoride gives the corresponding $M(NO)F_{5-n}(H_2O)_n^{n-2}$ (n=1-4). For HNO_3, H_2SO_4, and $H_2C_2O_4$ coordination of the respective anion is also observed. Reactions of $M'_2[M(NO)X_5]$ (M'=Na,K,Rb,Cs; X=Cl,Br,I) with KHF_2 yield $M(NO)F_{5-n}X_n^{2-}$ and $Ru(NO)F_{4-n}X_n(H_2O)^-$ (n=1,2,3) (52). Substitution on $[NH_4]_2[Ru(NO)Cl_5]$ by ammonia in aqueous solution yields *trans*-$Ru(NO)(NH_3)_4(OH)^{2+}$; salts of this cation with various anions were characterized by electrical conductivity and spectroscopic methods. The thermal stabilities of these salts were also examined (53). Other compounds prepared were $[Ru(NO)(NH_3)_4(OH)][Ru(NO)(NO_2)_4(OH)]\cdot H_2O$, $[Ru(NO)(NH_3)_4Cl][Ru(NO)(NO_2)_4(OH)]$, $[Ru(NO)(NH_3)_5]_2[Ru(NO)Cl_5]_3\cdot 4H_2O$, and $[Ru(NO)(NH_3)_4L][Ru(NO)Cl_5]$ (L=OH,Cl); these compounds were studied by IR, X-ray powder pattern, thermal analysis, and electrical conductivity (54). The complex $Os(NO)(NO_2)_2(H_2O)_2(OH)$ was isolated as an intermediate in the hydrolysis of $Na_2[Os(NO)(NO_2)_4(OH)]$; the complex is a weak dibasic acid in aqueous solution (55).

The reaction of $Os(NO)_2(PPh_3)_2$ with trifluoroacetic acid gives a complex containing a trifluoroacetohydroxamate ligand in 90% yield after 30 min. in refluxing toluene. Analysis of the gas phase found water but no hydrogen. The crystal structure of $Os\{ON{=}C(O)CF_3\}(O_2CCF_3)(NO)(PPh_3)_2$ [9] was reported, and a signal in the ^{31}P NMR spectrum of the reaction mixture was attributed to the intermediate $Os(O_2CCF_3)_2(NHOH)(NO)(PPh_3)_2$. The reaction of the Ru analog gives $Ru(O_2CCF_3)_3(NO)(PPh_3)_2$ and $[NH_3OH][O_2CCF_3]$. The proposed mechanism is shown in Scheme 6 (56).

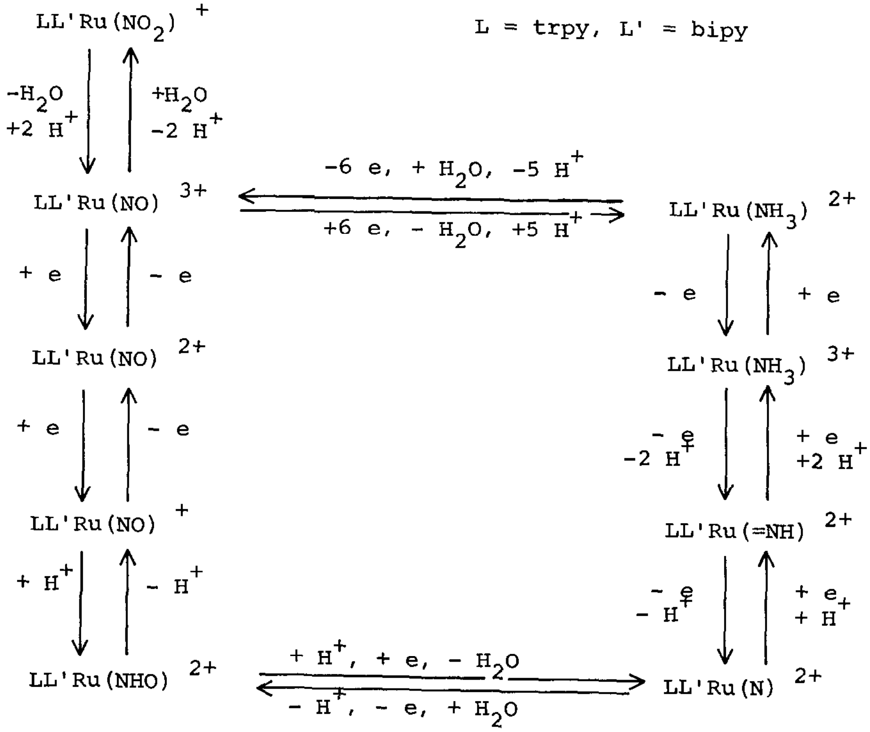
Irradiation of $RuCl(bipy)_2(NO)^{2+}$ in aqueous solution (pH 5) produces metastable $RuCl(bipy)_2\{N(O)OH\}^+$, which reverts to the starting complex in the dark. A reversible pH change is also produced (57).

The crystal structure of $\{Ru(acac)_2\}_2(\mu\text{-}NO)_2$ was reported. The Ru-Ru bond distance of 2.614 Å is the shortest distance reported for a "single" Ru-Ru bond (58).

Diazo Complexes

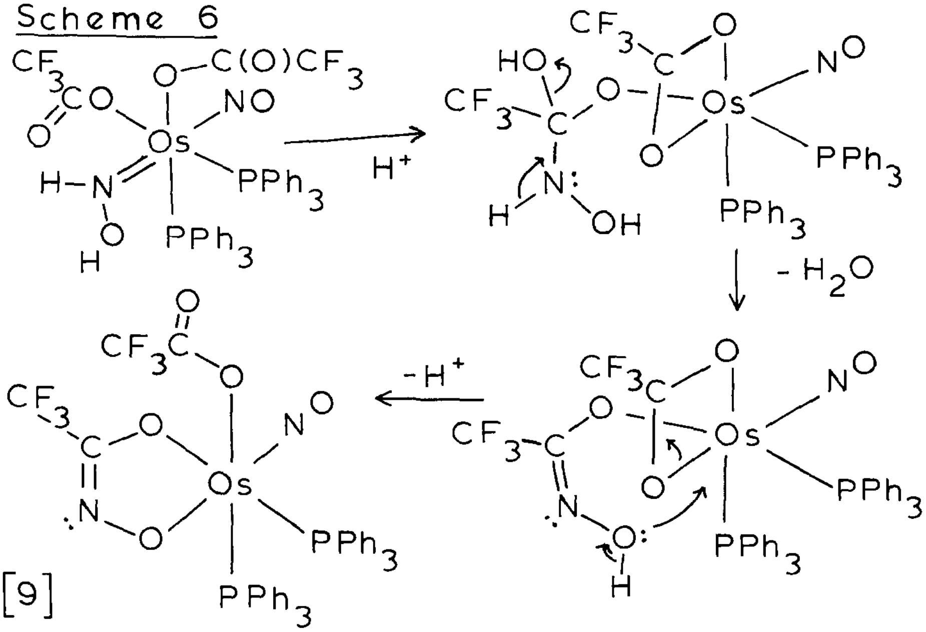
Metal and ligand core binding energies were determined for $[Ru(CO)_2(NO)(PPh_3)_2][PF_6]$, $RuCl_3(NO)(PEt_2Ph)_2$, $[RuCl(NO)(das)_2]Cl_2$, $Ru(NO)_2(PPh_3)_2$, $[Ru(N_2C_6H_4F\text{-}4)(CO)_2(PPh_3)_2][BF_4]$, $Ru(N_2C_6H_4Me\text{-}4)Cl_3(PPh_3)_2$, $RuCl(NO_2)(das)_2$, $Ru(CO)_3(PPh_3)_2$, $RuCl_2(das)_2$, $[RuCl(N_2)(das)_2][SbF_6]$, $[Ru(CO)Cl(das)_2][BPh_4]$, $OsBr_3(NO)(PPh_3)_2$, and $Os(N_2C_6H_4F\text{-}4)Br_3(PPh_3)_2$. To a first approximation the observed metal binding energy can be reproduced from a single set of ligand group shifts to the binding energy of the "bare metal atom"

Scheme 5



L = trpy, L' = bipy

Scheme 6



[9]

to within experimental error of ±0.2 eV (59).

Dinitrogen Complexes

The mechanisms of oxidation and reduction of $\{Ru(NH_3)_5\}_2(N_2)^{4+}$ by the hydroxyl radical and by the hydrated electron, respectively, were investigated by the use of pulse and ^{60}Co steady-state radiolysis. The reaction with hydroxyl radical forms an adduct $(NH_3)_5Ru^{II}N_2Ru^{II}(NH_3)_5(OH)^{4+}$, which decomposes to $\{Ru(NH_3)_5\}_2(N_2)^{5+}$. The latter product decomposes further to $Ru(NH_3)_5(N_2)^{2+}$ and $Ru(NH_3)_5(OH)^{2+}$. The hydrated electron reduces $\{Ru(NH_3)_5\}_2(N_2)^{4+}$ to $\{Ru(NH_3)_5\}_2(N_2)^{3+}$, which decomposes to $Ru(NH_3)_5(N_2)^{2+}$ and other products. Rate constants for all steps were determined (60).

The dinitrogen complex $Na_2[Ru(PDTA)(N_2)]\cdot 2H_2O$ (PDTA=propylenediaminetetraacetic acid) can be prepared in 90% yield by reaction of $Ru(HPDTA)(H_2O)$ with sodium azide in aqueous solution. The complex was characterized by elemental analysis, IR and UV/visible spectroscopy, magnetic measurements, and thermal decomposition (61)

METAL COMPLEXES WITH η^1-GROUP IV ATOM LIGANDS

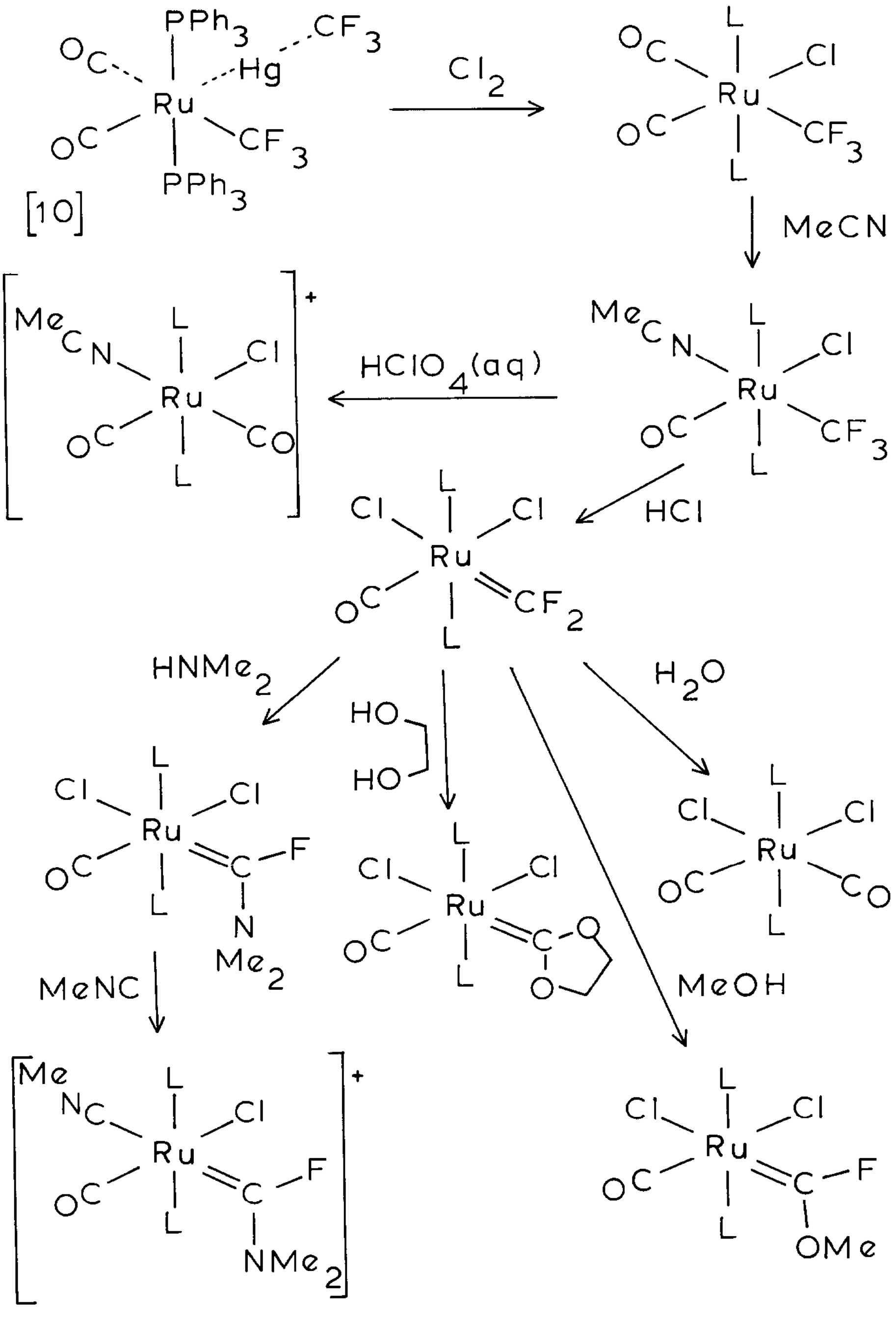
Reactions of $Hg(CF_3)_2$ with $Ru(CO)_3(PPh_3)_2$ or $Ru(CO)_2(PPh_3)_3$ yield $Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$ [10], the crystal structure of which was reported. Reactions of this trifluoromethyl complex, diagrammed in Scheme 7, were described (62).

Reactions of $RuCl_2(CCl_2)(CO)(PPh_3)_2$ with H_2X (X=O,S,Se) yield $RuCl_2(CX)(CO)(PPh_3)_2$, while substitutions at carbon with RXH (X=O,S), NH_3, and NH_2R form $RuCl_2\{C(XR)_2\}(CO)(PPh_3)_2$, $RuCl(CN)(CO)(NH_3)(PPh_3)_2$, and $RuCl_2(CNR)(CO)(PPh_3)_2$, respectively. The product with ethylenediamine is $RuCl_2(\overline{CNHC_2H_4NH})(PPh_3)_2$ (63). These reactions are summarized in Scheme 8.

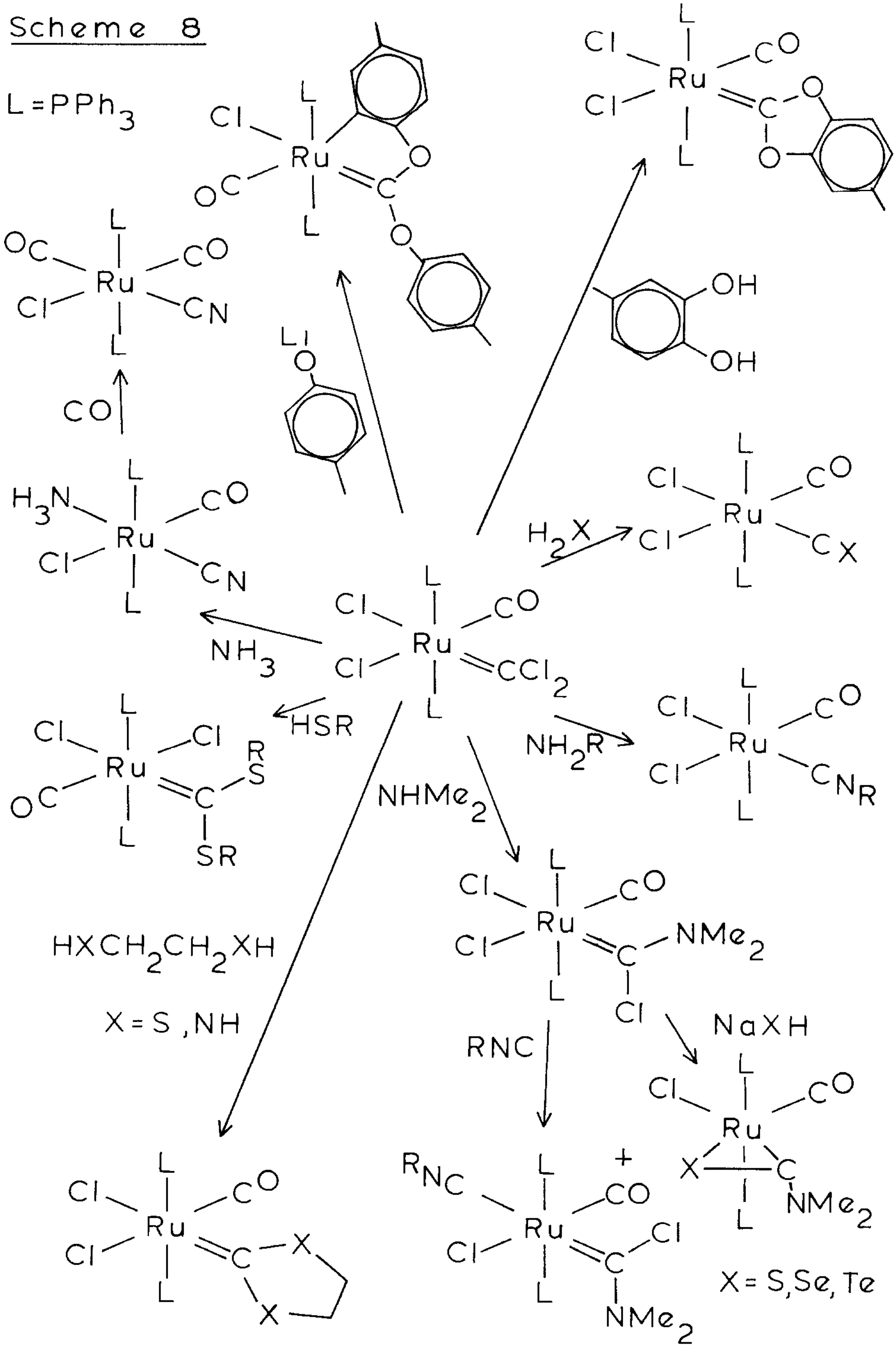
The metallobenzene complex [11] is prepared in 30% yield by reaction of $Os(CO)(CS)(PPh_3)_3$ with acetylene. The coordinated sulfur can be displaced by CO to give $\overline{Os\{C(S)CHCHCHCH}\}(CO)_2(PPh_3)_2$; the sulfur atom of the product reacts with H^+ or MeI to generate a new metallobenzene complex $\overline{Os\{C(SR)CHCHCHCH}\}(CO)_2(PPh_3)_2$ (R=H,Me). Complex [11] forms a similar product in direct reactions with HCl or MeI. These are summarized in Scheme 9 (64).

Sodium formate and $MRCl(CO)(PPh_3)_2$ react to form the corresponding formate complex $MR(O_2CH)(CO)(PPh_3)_2$ (M=Os,Ru; R=C_6H_4Me-4). Decarboxylation in the presence of PPh_3 yields $OsRH(CO)(PPh_3)_3$ from the Os complex; carbonylation of this product to $OsRH(CO)_2(PPh_3)_2$, followed by heating, gives $Os(C_6H_4PPh_2)H(CO)(PPh_3)_2$. On the other hand decarboxylation of $RuR(O_2CH)(CO)(PPh_3)_2$ in the presence of CO yields an equilibrium mixture of $Ru(CO)(PPh_3)_3$ and $Ru(C_6H_4PPh_2)H(CO)(PPh_3)_2$. The unsaturated complex $Ru(CO)(PPh_3)_3$ can be trapped with formaldehyde, hydrogen, HCl, or CO to form $\overline{Ru(OCH_2OCH_2})(CO)(PPh_3)_3$, $RuH_2(CO)(PPh_3)_3$, $RuHCl(CO)(PPh_3)_3$, or $Ru(CO)_3(PPh_3)_2$, respectively. These

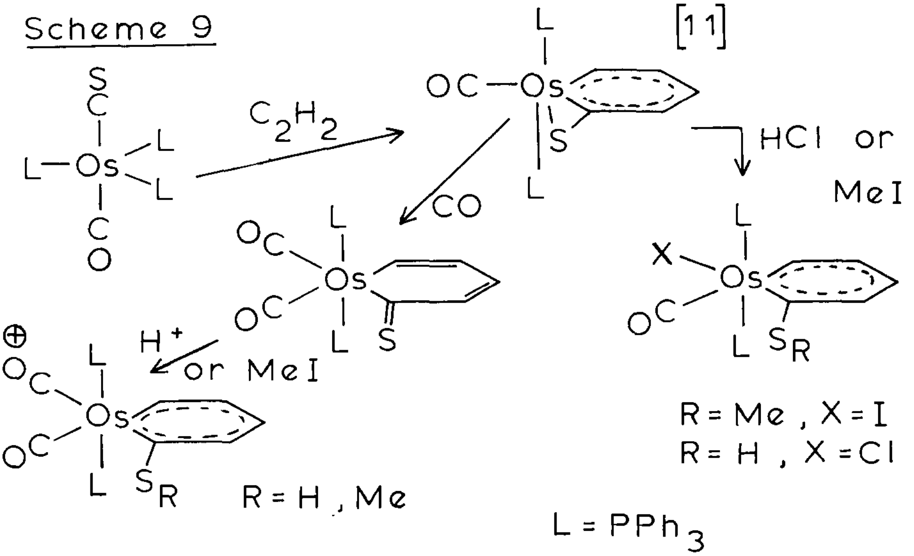
Scheme 7



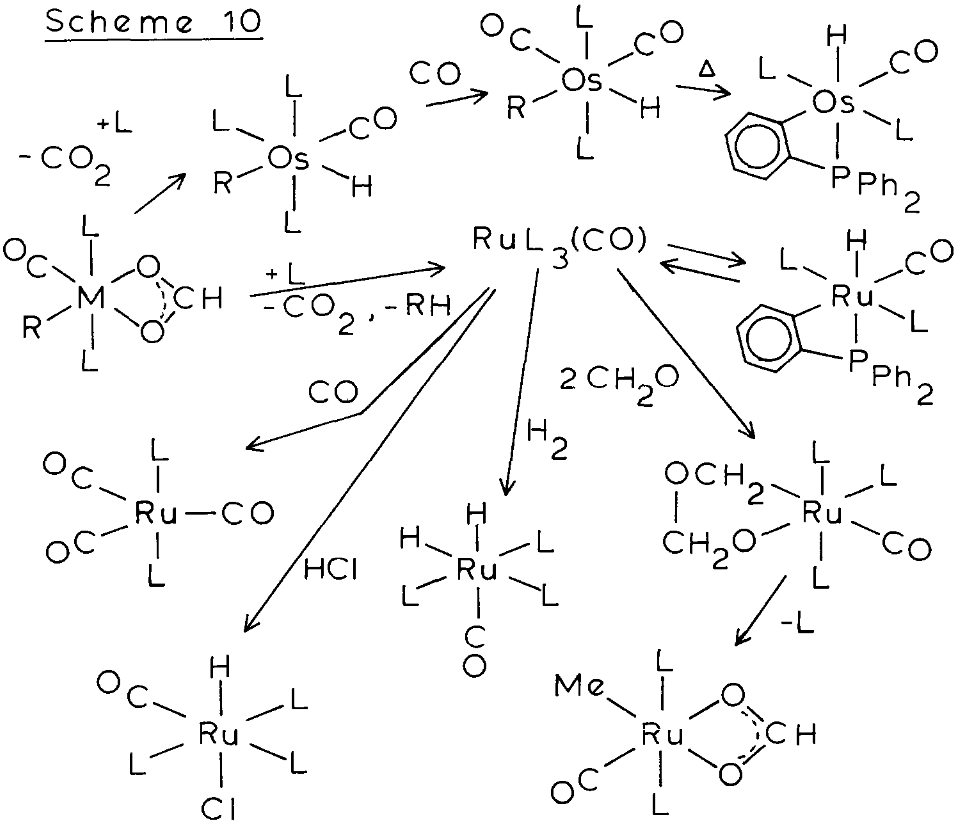
Scheme 8


L = PPh$_3$
CO
NH$_3$
HSR
H$_2$X
NH$_2$R
NHMe$_2$
HXCH$_2$CH$_2$XH
X = S, NH
RNC
NaXH
X = S, Se, Te
Li
OH
OH
+

Scheme 9



Scheme 10



reactions are summarized in Scheme 10 (65).

Methylation of $OsCl_6^{2-}$ with excess methyl lithium and in the presence of PPh_3 gives a mixture of trans-$OsMe_2(PPh_3)_4$ and $OsHMe(C_6H_4PPh_2)(PPh_3)_2$. Carbonylation of the former product forms the diacyl complex $Os(C(O)Me)_2(PPh_3)_4$. Other alkyls prepared by displacement of chloride were $OsH(CH_2SiMe_3)(C_6H_4PPh_2)$-$(PPh_3)$, $OsMe_4(PPh_3)_2$, $OsCl_3(CH_2SiMe_3)(PMe_3)_2$, $Os_2Cl(CHSiMe_3)_2(PMe_3)_5$, and $OsO(CH_2SiMe_3)_4$ (66).

Alkylation of $Na[Ru(CO)_2Cp]$ with chloromethyl methyl ether gives $Ru(CH_2OMe)$-$(CO)_2Cp$ in 90% yield. Treatment of the product with HCl gives $Ru(CH_2Cl)(CO)_2Cp$ in 15% yield (67).

The primary photoprocess following near-UV excitation of $RuR(CO)_2Cp$ (R=Me,Et, n-C_5H_{11}) is CO dissociation. The quantum yield for photosubstitution on $RuMe(CO)_2Cp$ is independent of the nature or concentration of the incoming ligand. For alkyl groups with β-hydrogens the major product is $RuH(CO)_2(C_5R'_5)$ (R'=H,Me) after near-UV irradiation at 298 K, but irradiation of $RuEt(CO)_2Cp$ at 77 K gives first $RuH(C_2H_4)(CO)Cp$, followed by formation of $RuH(CO)_2Cp$. In rigid paraffin media at 298 K evidence for $RuH(C_2H_4)(CO)Cp$ and $RuMe(CO)Cp$ was observed upon irradiation of $RuR(CO)_2Cp$, R=Et and Me, respectively (68).

The alkyl complexes $RuR(CO)_2Cp$ (R=Me,Bz) can be prepared in 30-40% yield by first treating $\{Ru(CO)_2Cp\}_2$ by triethylborohydride and then the appropriate alkyl iodide. Photochemically induced substitution by PPh_3 gives $RuR(CO)(PPh_3)Cp$. Electrochemical studies of these compounds were conducted. Oxidations of both $RuMe(CO)_2Cp$ and $RuMe(CO)(PPh_3)Cp$ are irreversible (69).

Insertion of acrylonitrile into the Ru-H bond of $RuHCl(CO)(PPh_3)_3$ gives $\{Ru(MeCHCN)Cl(CO)(PPh_3)_2\}_2$. Treatment of this product with 4-picoline, $NaBHPz_3$, $NaBPz_4$, or $Na[S_2CNEt_2]$ gives $\{Ru(MeCHCN)Cl(CO)(4\text{-picoline})(PPh_3)\}_2$, $Ru(MeCHCN)(BHPz_3)(CO)(PPh_3)$, $Ru_2(MeCHCN)_2Cl(BPz_4)(CO)_2(PPh_3)_2$, or $Na[Ru(MeCHCN)$-$Cl(S_2CNEt_2)(CO)(PPh_3)$, respectively (Pz=1-pyrazolyl). Reaction of $\{Ru(MeCHCN)Cl(CO)(4\text{-picoline})(PPh_3)\}_2$ with thallium(I) acetylacetonate yields $\{Ru(MeCHCN)(acac)(CO)(PPh_3)\}_2$. An analogous product $\{Ru(NCCH_2CHCN)Cl(CO)$-$(PPh_3)_2\}_2$ is prepared by reaction of fumaronitrile with $RuHCl(CO)(PPh_3)_3$ (70).

Alkylation of $OsH(CO)_4^-$ with RSO_3F (R=Me,Et) gives cis-$OsHR(CO)_4$ in 70% yield. Thermolysis yields $Os_2HR(CO)_8$ and $Os_3R_2(CO)_{12}$, in addition to ethylene when R=Et. The hydride complexes react with carbon tetrachloride to give the corresponding chlorides. Addition of phosphines to cis-$OsHMe(CO)_4$ causes reductive elimination of methane and formation of $Os(CO)_4(PR_3)$ (R=Et) but in the presence of a small amount of air, radical substitution by PPh_3 gives $OsHMe(CO)_3(PPh_3)$ (73).

Reduction of [trans-$Ru(CO)_2(dppe)_2][SbF_6]_2$ or [cis-$Ru(CO)_2(dppm)_2][SbF_6]_2$ with $Na[BH(OEt)_3]$ at -30° gives the corresponding formyl complex

$[Ru(CHO)(CO)(P-P)_2][SbF_6]$ (P-P=dppe or dppm). The product containing dppm is unstable and precipitates from nitromethane, but the dppe-substituted material can be crystallized. The labeled complex $[Ru(CDO)(CO)(dppe)_2][SbF_6]$ is similarly prepared. These formyl complexes decompose in solution to trans-$RuH(CO)(dppe)_2^+$ and $Ru(CO)(dppe)_2^{2+}$ (74).

The unexpected products from the reaction of cis-$Ru(bipy)_2(H_2O)Cl^+$ with phenylacetylene at 100° in water are cis-$Ru(bipy)_2(CO)Cl^+$ and toluene, in addition to a small amount of [cis-$Ru(bipy)_2(CO)(CH_2Ph)][PF_6]$. The alkyl complex and toluene are also formed in high yield by reaction of phenylacetylene with cis-$Ru(bipy)_2(H_2O)_2^{2+}$. Labeling studies were used to show that water is the source of the O atom of the CO ligand and the H atoms of the methyl group on toluene. The ^{31}P and ^{13}C NMR spectra and cyclic voltammetry of $Ru(bipy)_2(CO)(CH_2Ph)^+$ were reported. Other terminal acetylenes give similar products. Also prepared was $Ru(trpy)(PPh_3)(CO)(CH_2Ph)^+$ (71).

Aryl metallation occurs upon treatment of $Ru(O_2CMe)Cl(CO)(PPh_3)_2$ with acetophenone. The product $Ru\{C_6H_4C(O)Me\}Cl(CO)(PPh_3)_2$ [12] has been characterized by IR and NMR spectroscopy and by X-ray crystallography. The complex reacts with benzoic acid in refluxing toluene to give $Ru(O_2CPh)Cl(CO)(PPh_3)_2$ (72).

The synthesis of $Ru(SiRCl_2)X(CO)_3L$ and $\{Ru(SiRCl_2)X(CO)_3\}_2$ (L=CO,PR_3; R=Me,Cl; X=H,Cl,Br,I) were described. The reaction of $M_3(CO)_{12}$ (M=Ru,Os) with $SiHMeCl_2$ under CO forms $M(SiMeCl_2)_2(CO)_4$ in almost quantitative yield. Substitution by PPh_3 on cis-$Ru(SiMeCl_2)_2(CO)_4$ gives mer-$Ru(SiMeCl_2)_2(CO)_3(PPh_3)$. The trans effect of the $SiMeCl_2$ ligand is comparable to that of $SiCl_3$. Photolysis of $Ru_3(CO)_{12}$ and $SiHRCl_2$ under CO gives cis-$RuH(SiRCl_2)(CO)_4$ (R=Cl,Me) in 30% yield; the product reacts with phosphines to form mer-$RuH(SiRCl_2)(CO)_3PR_3$ and with carbon tetrachloride to give $\{Ru(SiRCl_2)Cl(CO)_3\}_2$ (75).

The ^{119}Sn NMR spectrum of $Ru(SnCl_3)_6^{4-}$ shows that the complex is stereochemically rigid on the NMR time scale. The coupling constant $^2J(^{119}Sn-^{117}Sn)$ between trans ligands is 12862 Hz. The reduced value of $^2K(Sn-Sn)_{trans}$ of 806.0×10^{21} cm^{-3} is the largest among analogous metal-tin complexes (76). The anions $M(SnCl_3)_5Cl^{4-}$ (M=Ru,Os) were also characterized by ^{119}Sn NMR and by ^{117}Sn and ^{115}Sn NMR for the Ru complex. The crystal structure of $[NEt_4][Ru(SnCl_3)_5Cl]\cdot$ 2 NCMe was reported; the Ru-Sn bond lengths were interpreted to indicate d_π-d_π interaction. The $Ru(SnCl_3)_5(NCMe)^{3-}$ complex was also prepared. The first observed coupling constant between ^{99}Ru and Sn was reported (77).

COMPLEXES WITH PI-BONDED HYDROCARBONS

Cyclopentadienyl Complexes

The series of complexes $MX(PPh_3)LCp$ (M=Ru; X=Cl,H,$S_2COC_{10}H_{19}$, S_2COMe; L=PPh_3, $PHPh_2$; M=Os, X=Cl,Br,I,H,D, xanthogenate, dithiocarbamate, BPh_4, L=PPh_3) was prepared. In methanol $OsCl(PPh_3)_2Cp$ partially ionizes to $Os(PPh_3)_2Cp^+$, which can be precipitated as the BPh_4 salt (78).

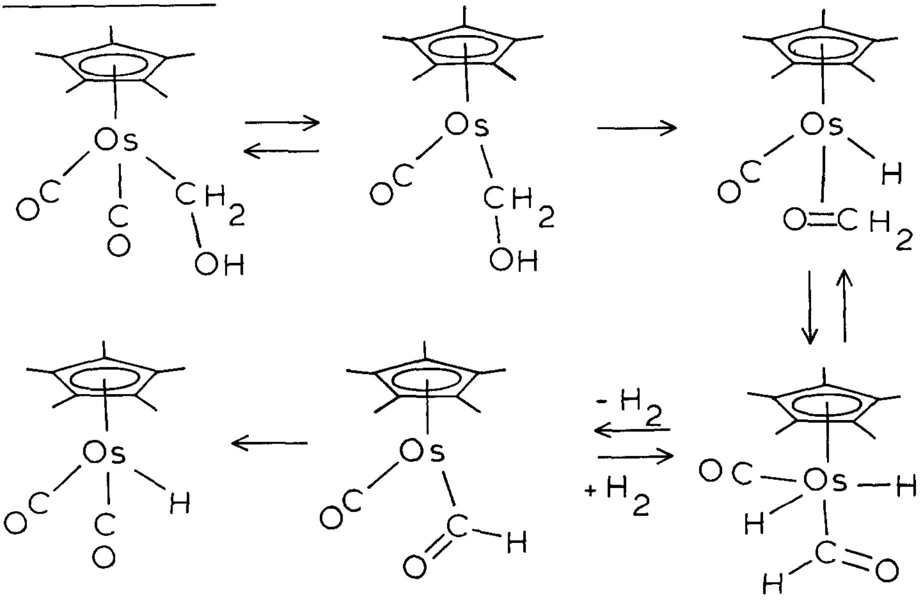
The first syntheses of Os compounds containing the pentamethylcyclopendadienyl ligand were described. The hydride complex $OsH(CO)_2(C_5Me_5)$ is prepared in 65% yield from $Os_3(CO)_{12}$ and HC_5Me_5 in heptane at 220°; reaction of TlC_5H_5 with $OsBr_2(CO)_4$ gives $OsH(CO)_2(C_5H_5)$ in 30% yield under the same conditions. The bromides $OsBr(CO)_2(C_5R_5)$ (R=H,Me) can be prepared in 40% and 57% yields through reactions with dicyclopentadiene and HC_5Me_5, respectively, in refluxing decane. Treatment of $OsH(CO)_2(C_5R_5)$ with iodine gives $OsI(CO)_2(C_5R_5)$; treatment of this product with sodium borohydride or LiR' (R'=Me,$SnMe_3$,$SnPh_3$) gives the corresponding $OsR'(CO)_2(C_5R_5)$. In the presence of donor ligands L (L=NCMe,THF,H_2O) oxidation of $OsH(CO)_2(C_5R_5)$ with trityl cation generates $OsL(CO)_2(C_5R_5)^+$; when L=H_2O, the product reacts with CO to give $[Os(CO)_3(C_5R_5)][BF_4]$. On the other hand, treatment of the hydrides with tropylium tetrafluoroborate generates first $Os(C_7H_8)(CO)_2(C_5R_5)^{1+}$, containing a 1,2-$\eta^2$-$C_7H_8$ ligand and which upon deprotonation by amines yields $Os(C_7H_7)(CO)_2(C_5R_5)$ (79). Reduction of $[Os(CO)_3(C_5Me_5)][BF_4]$ with sodium borohydride provides a facile synthesis of the hydroxymethyl complex $Os(CH_2OH)(CO)_2(C_5Me_5)$ (86% yield). Decarbonylation of this product to $OsH(CO)_2(C_5Me_5)$ (95% yield) occurs upon photolysis or upon heating at 174° for 20 h. The proposed mechanism (Scheme 11) is supported by labeling and by kinetic studies (80).

Photolysis of $OsH(CO)_2(C_5Me_5)$ under hydrogen can be used to prepare new hydride complexes. Photolysis under 1 atm of hydrogen gives $OsH_3(CO)(C_5Me_5)$, $\{OsH(CO)(C_5Me_5)\}_2$ [13], and $Os_2H_2(CO)(C_5Me_5)_2$ [14] in yields which can be optimized to 30-55% for each one. Irradiation of the same starting material under nitrogen gives low yields of the two dimeric species. The crystal structure of [13] is similar to that of $Os_3H_2(CO)_{10}$ in that it contains a short Os-Os bond, 2.677 Å. Irradiation of $\{OsH(CO)(C_5Me_5)\}_2$ [13] under hydrogen or nitrogen gives [14]. The suggested path for formation of these compounds is shown in Scheme 12 (81).

Alkene and alkyne complexes $Ru(Un)(PMe_3)_2Cp^+$ (Un=C_2H_4, (E)-CH(CN)=CHCN, CH_2=CHCH=CH_2, CH_2=C=CH_2, CH_2=C=CMe_2, C_2Ph_2, PhC_4Ph, PhC_2CO_2Et, $C_2(CO_2Me)_2$ and $C_2(CF_3)_2$) can be prepared by reacting the appropriate unsaturated hydrocarbon with $RuCl(PMe_3)_2Cp$ in the presence of NH_4PF_6. Crystal structures for the butadiene and allene complexes were determined (82).

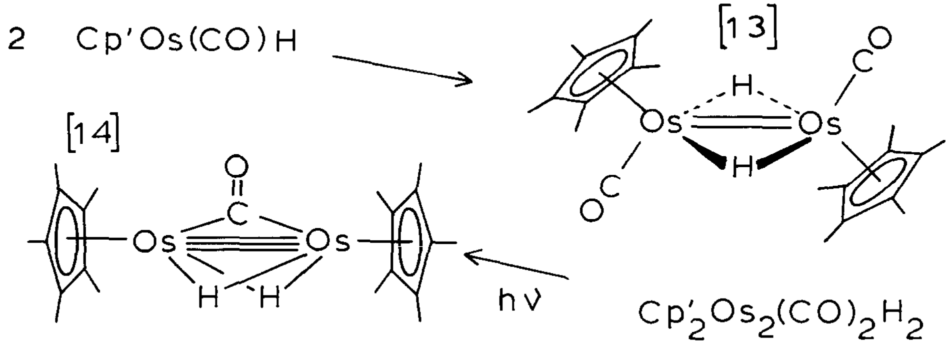
Some rare examples of Ru(IV) and Os(IV) phosphine complexes have been synthesized. Protonation of $MX(PR_3)_2Cp$ (M=Ru, X=Cl; M=Os, X=Br; R=Me,Ph) with HPF_6 gives $[MHX(PR_3)_2Cp][PF_6]$. Oxidation of $RuCl(PMe_3)_2Cp$ with chlorine gas and in the presence of NH_4PF_6 generates $[RuCl_2(PMe_3)_2Cp][PF_6]$, while oxidation with $NOPF_6$ gives the dications $M(NO)(PR_3)_2Cp^{2+}$. The crystal structure of $[Os(NO)(PMe_3)_2Cp][PF_6]_2$ was reported (83).

Scheme 11



Scheme 12

$$Cp'Os(CO)_2H \xrightarrow{h\nu} Cp'Os(CO)H + CO$$



[13]

[14]

$$Cp'Os(CO)H + H_2 \rightleftharpoons Cp'Os(CO)H_3$$

$$Cp'Os(CO)H + Cp'Os(CO)H_3 \longrightarrow$$

$$Cp'_2Os_2(CO)_2H_2 + H_2$$

Stereo- and regiospecific addition of $RuH(CO)_2Cp$, formed from $Ru_3(CO)_{12}$ and cyclopentadiene, to *endo*-dicyclopentadiene forms $Ru(C_{10}H_{13})(CO)_2Cp$. The product inserts CO to give $Ru\{C(O)C_{10}H_{13}\}(CO)_2Cp$ [15] in 20-60% yield; the crystal structure for the acyl complex was determined (84).

Reactions of $RuCl(PMe_3)_2Cp$ with terminal alkynes can be used to synthesize vinylidene compounds. In the presence of NH_4PF_6, HC_2R (R=H,Me,Ph) adds to form the appropriate $[Ru(C{=}CHR)(PMe_3)_2Cp][PF_6]$. The acetylide complex $Ru(C_2Me)(PMe_3)_2Cp$ is prepared by deprotonation of $[Ru(C{=}CHMe)(PMe_3)_2Cp][PF_6]$. The crystal structure of $[Ru(C{=}CHMe)(PMe_3)_2Cp][PF_6]$ [16] was reported (85). Also described was the crystal structure of $[Ru(C{=}C{=}CPh_2)(PMe_3)_2Cp][PF_6]$ [17], prepared in 76% yield from $RuCl(PMe_3)_2Cp$, $HC_2C(OH)Ph_2$, and NH_4PF_6 (86).

A study of the displacement of PPh_3 on $RuCl(PPh_3)_2Cp$ by optically active, chelating phosphines was described. Phosphines used were (+)-(R)-1,2-bis(diphenylphosphino)propane, (-)-(R)-1-phenyl-1,2-bis(diphenylphosphino)ethane, (-)-(S)-1-cyclohexyl-1,2-bis(diphenylphosphino)ethane, dppe, and (-)-(2S,3S)-2,3-bis(diphenylphosphino)butane (87).

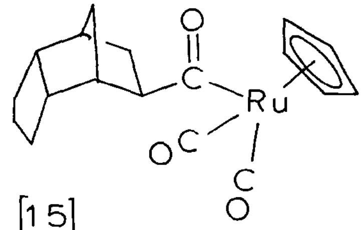
The UV-photoelectron spectra of conformational isomers of $Ru(CO)(\eta^3\text{-allyl})Cp$ and 2-methallyl analogs were reported and compared with those of $RuCl(CO)_2Cp$ and *exo*-$Fe(CO)(\eta^3\text{-allyl})Cp$. It was suggested that the HOMO of the coordinated allyl should be stabilized relative to the HOMO of the free allyl radical (88).

The crystal and molecular structure of biruthenocene shows that the mutual orientation of the cyclopentadienyl rings with a sandwich structure is not conformationally important and depends upon intermolecular interactions (89).

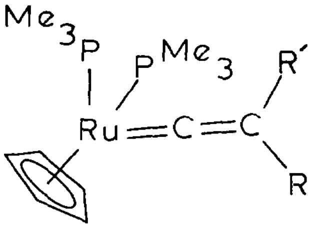
A phase transition for $RuCp_2$ in the solid state was observed at 392 K using proton spin-lattice relaxation time measurements and differential thermal analysis (90).

The synthesis and characterization of $Ru(C_5H_4SiCl_3)Cp$ were reported. This compound and also 1,1'-dicarboxyruthenocene were used to derivatize n-type silicon electrodes. These electrodes were then investigated using cyclic voltammetry (91).

The ruthenocene derivative $Ru(\eta^5\text{-}C_5H_4CH{=}C_5H_4)_2$ can be prepared in 60-70% yield through the reaction of $NaC_5H_4CH{=}C_5H_4$ with Ru^{2+} and in 40% yield from $Ru(C_5H_4Li)_2$ with $C_5H_4CHNMe_2$. This product is reduced with $LiBHEt_3$ to $Ru(C_5H_4CH_2C_5H_4)_2^{2-}$ and then treatment with ferrous chloride forms $Ru(C_5H_4CH_2C_5H_4)_2Fe$ in 20-25% yield; this bimetallic product can also be obtained from $Fe(C_5H_4CH\text{-}C_5H_4)_2$ and $RuCl_2(DMSO)_4$. The homometallic complex $Ru(C_5H_4CH_2C_5H_4)_2Ru$ has also been prepared (92). The electrochemistry of these compounds has been studied. A reversible one-electron oxidation of Fe and an irreversible two-electron oxidation on Ru for $Ru(C_5H_4CH_2C_5H_4)_2Fe$ were taken to indicate non-interacting metal centers. However, the two metal centers of $Ru(C_5H_4CH_2C_5H_4)_2Ru$ do interact strongly; in this case a quasi-reversible, two-electron oxidation is found at



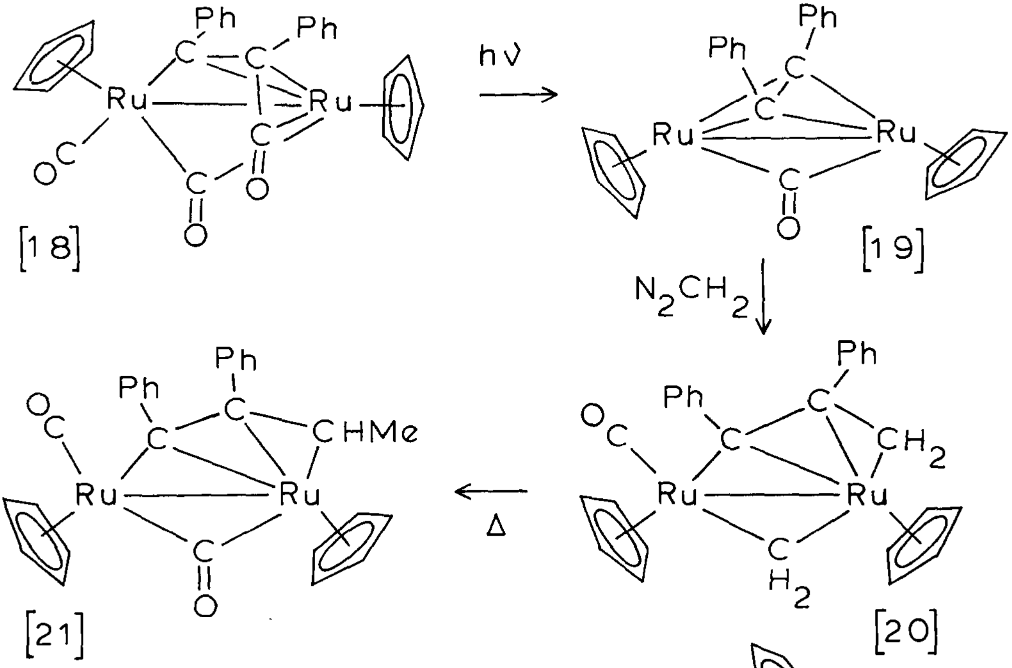
[15]



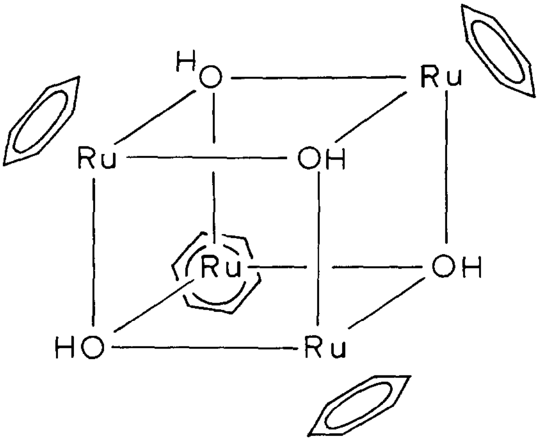
[16] R = H
R′ = Me

[17] R = Ph
R′ = Ph

Scheme 13



[18] [19] [20] [21]



[22]

low potential. A mixed valence species consisting of $RuCp_2$ and $RuCp_2^{2+}$ units was proposed, based upon NMR and UV/visible spectra (93).

Photolysis of $RuCp(C_6H_6)^+$ in acetonitrile affords $RuCp(NCMe)_3^+$ quantitatively with a quantum yield at 315 nm of 0.4. By varying the temperature and solvent, one, two, or three acetonitrile ligands can be selectively replaced. For example, $[RuCp(NCMe)_2\{P(OMe)_3\}][PF_6]$ can be prepared quantitatively using excess $P(OMe)_3$ in acetonitrile at 25°, but further treatment with $P(OMe)_3$ for several days leads to $[RuCp(NCMe)\{P(OMe)_3\}_2][PF_6]$ quantitatively and refluxing the latter in dichloroethane for several hours with excess $P(OMe)_3$ yields $[RuCp\{P(OMe)_3\}_3][PF_6]$. Other compounds synthesized are $[RuCp(\eta^6\text{-}C_6Me_6)][PF_6]$, $[RuCp(\eta^6\text{-}[2.2]\text{-}\underline{p}\text{-cyclophane})][PF_6]$, $[RuCp(\eta^6\text{-}\underline{p}\text{-}Cl_2C_6H_4)][PF_6]$, and $[RuCp(\eta^6\text{-}C_8H_8)][PF_6]$. Photolysis of $RuCp(\eta^6\text{-}C_6H_6)^+$ in dichloromethane and in the absence of other ligands gives no net reaction, but addition of $P(OMe)_3$ or $P(OEt)_3$ yields the tris phosphite product (94).

The preparation and fluxional behavior of $Ru(CO)_2Cp(\eta^1\text{-}C_7H_7)$ were described. The compound can be prepared in 20% yield from $Na[Ru(CO)_2Cp]$ and $[C_7H_7][BF_4]$. Spin saturation labeling experiments provided evidence for both 1,2- and 1,4-metal shifts (95).

Thermogravimetric analysis was used to examine the fate of $Ru_2(CO)_4Cp_2$ and $Ru_4(CO)_4Cp_4$ upon heating. The range of decomposition is dependent upon the rate of heating. The tetramer is stable to prolonged heating at 350°C and decomposes to Ru metal at 400-450°C (96).

Photolysis of $Ru_2(CO)_4Cp_2$ and diphenylacetylene forms $Ru_2(CO)_2\{C(O)C_2Ph_2\}Cp_2$ [18]; the crystal structure of the product was reported. This compound undergoes alkyne exchange with C_2H_2, C_2Me_2, HC_2Me, HC_2Ph, and MeC_2Ph in near quantitative yield in refluxing toluene (97).

Photolysis of [18] gives a 50% yield of the unsaturated dimer $Ru_2(CO)(C_2Ph_2)Cp_2$ [19]. This product reacts at 0° with diazomethane to form $Ru_2(CO)(CH_2)(CPhCPhCH_2)Cp_2$ [20] in 25% yield. The crystal structures of both [19] and [20] were reported. When [20] is heated in refluxing xylene, the product $Ru_2(CO)_2(CPhCPhCHMe)Cp_2$ [21] is formed in 25% yield. This sequence, shown in Scheme 13, is another example of C-C bond formation on a multimetallic system (98). A related compound $Ru_2(CO)_2(CHCHCH_2)Cp_2$ can be prepared in 65% yield by passing an acetone-hexane solution of $Ru(CO)(\eta^3\text{-}C_3H_5)Cp$ over deactivated silica gel; the derivative $Ru_2(CO)_2(CHCMeCH_2)Cp_2$ can be prepared in the same manner from the methallyl analog. Based upon NMR data the structures are proposed to be analogous to [20] (99).

Arene Complexes

The methyl complexes $RuMe_2(PR_3)(C_6Me_6)$ (R_3=Me_3,$MePh_2$,Ph_3) are prepared from $RuCl_2(PR_3)(C_6Me_6)$ and methyl lithium. Upon treatment of the methyl complexes with trifluoroacetic acid, methane elimination and formation of $RuMe(O_2CCF_3)(PR_3)(C_6Me_6)$ and $Ru(O_2CCF_3)_2(PR_3)(C_6Me_6)$ occurs. The latter complexes react with

$Na[AlH_2(OC_2H_4OMe)_2]$ to form $RuH_2(PR_3)(C_6Me_6)$, which are inert to CO, ethylene, or PMe_3 up to 60°C. Displacement of trifluoroacetate from $Ru(O_2CCF_3)_2(PMe_3)(C_6Me_6)$ by excess PMe_3 and in the presence of NH_4PF_6 generates $[Ru(O_2CCF_3)(PMe_3)_2(C_6Me_6)][PF_6]$ (100).

Symmetrical and unsymmetrical $Ru(arene)_2^+$ cations were prepared and their reactions with sodium borohydride were examined. Reduction gives the corresponding Ru(arene)(cyclohexadiene) complex in ca. 70% yield. Hydride addition occurs preferentially at the less alkylated ring (101).

Reduction of $\{RuCl_2(C_6Me_6)\}_2$ with aqueous sodium carbonate in 2-propanol or with hydrogen in the presence of triethylamine gives $[Ru_2(\mu\text{-}H)(\mu\text{-}Cl)_2(C_6Me_6)_2][Cl]$. Reduction of the product with sodium borohydride yields $[Ru_2(\mu\text{-}H)_3(C_6Me_6)_2][PF_6]$. Related complexes such as $[Ru_2(\mu\text{-}H)(\mu\text{-}O_2CMe)(\mu\text{-}X)(C_6Me_6)_2][PF_6]$ ($X=O_2CMe,Cl$) are isolated from reactions of $Ru(O_2CMe)X(arene)$ ($X=Cl,O_2CMe$) with 2-propanol (102). Reduction of $\{RuCl_2(C_6H_6)\}_2$ with aqueous sodium carbonate and in the presence of excess sodium sulfate yields a cubane-type complex $[\{Ru(OH)(C_6H_6)\}_4][SO_4]_2\cdot 12\ H_2O$ [22], whose structure was crystallographically determined. Reactions of this product with sodium hydroxide, lithium bromide, and pyridine/water give $[Ru_2(OH)_3(C_6H_6)_2][BPh_4]$, $\{RuBr_2(C_6H_6)\}_2$, and $[\{Ru(OH)(py)(C_6H_6)\}_2][PF_6]_2$, respectively (103).

The reaction of $\{MCl_2(arene)\}_2$ with TlCp generates the corresponding $MCp(arene)^+$ cation (M=Ru, arene=C_6H_6, *p*-$MeC_6H_4CHMe_2$, C_6H_5OMe, C_6Me_6; M=Os, arene=C_6H_6, *p*-MeC_6H_4-$CHMe_2$) in high yields (50-80% for Ru, 20-40% for Os). The electrochemistry and reaction chemistry of these cations were described. Treatment of these cations with some nucleophiles Y yield no reaction (M=Ru, Y=PR_3; M=Os, Y=PR_3, H^-, CN^-, OH^-) while others cause decomposition (M=Ru, Y=CN^-, OH^-). No electrochemical reduction of these cations is observed up to the potential for reduction of acetonitrile, but irreversible oxidation occurs at moderate potentials (104).

An X-ray crystal structure determination for $Ru(CO)(SiCl_3)_2$(*p*-*t*-$Bu_2C_6H_4$)$\cdot$1/2 C_6H_5Me was undertaken to establish the conformation. The arene ring is roughly 10° from the staggered conformation with respect to the $Ru(CO)(SiCl_3)_2$ moiety. The carbon atoms of the ring which are attached to the *t*-Bu groups are slightly out of the plane made by the other ring carbons (105).

Fifteen complexes of the general formula $Ru(cyclophane)(arene)^{2+}$ (arene=C_6H_6, *p*-cumene, mesitylene, C_6Me_6; cyclophane=[2.2]paracyclophane, *anti*-[2.2]metacyclophane, $[2_3]$(1,3,5)cyclophane, $[2_3]$(1,2,4)cyclophane, $[2_4]$(1,2,3,4)cyclophane, $[2_4]$(1,2,3,5)-cyclophane, $[2_4]$(1,2,4,5)cyclophane, $[2_5]$(1,2,3,4,5)cyclophane, and $[2_6]$(1,2,3,4,5,6)-cyclophane) were synthesized. The triple-layed complexes (η^6,η^6-cyclophane)bis-(η^6-arene)diruthenium(II) were also prepared (arene=*p*-cumene, mesitylene, C_6Me_6; cyclophane=[2.2]paracyclophane or $[2_4]$(1,2,4,5)cyclophane). The cyclic voltammetry and electronic spectra of these complexes were discussed in relation to the molecular geometry. The general synthetic procedure involves reaction of $\{RuCl_2(arene)\}_2$ with Ag^+ in acetone to form $Ru(acetone)_3(arene)^{2+}$, followed by reaction of the cation with cyclophane and trifluoroacetic acid to yield $Ru(arene)(cyclophane)^{2+}$ (106).

The structure of (η^6-hexamethylbenzene)(η^6-4,12-dimethyl-7,15-dimethoxy[2.2]-metacyclophane)ruthenium(II) bis(tetrafluoroborate) [23] was reported (107).

Deprotonation of $[Ru(C_6Me_6)_2][PF_6]_2$ by potassium t-butoxide in THF gives $Ru(C_6Me_6)\{C_6Me_4(CH_2)_2\}$ [24] in 87% yield. The complex, characterized by X-ray crystallography, contains an o-xylylene ligand. The reaction is reversed with acid. The intermediate $[Ru(C_6Me_6)\{C_6Me_5(CH_2)\}][BPh_4]$ can also be isolated. Methylation of [24] with methyl trifluoromethylsulfonate yields $[Ru(C_6Me_6)(C_6Me_4Et_2)][SO_3CF_3]_2$ (108).

Hydrogenation of Ru(η^4-cycloocta-1,5-diene)(η^6-cycloocta-1,3,5-triene) in the presence of an arene forms Ru(η^4-cycloocta-1,5-diene)(η^6-arene) (35-95% yield) and cyclooctene. These products react with HCl to give $\{RuCl_2(arene)\}_2$. Arenes examined were benzene, toluene, p-xylene, mesitylene, ethylbenzene, isopropylbenzene, Et_2CHPh, $Ph(CH_2)_3Ph$, $Me_2CHCHMePh$, $NH_2CHMePh$, anisole, and acetophenone (109).

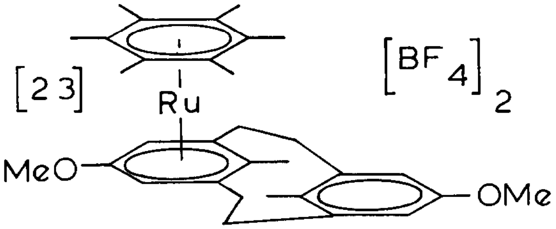
The structure of di-μ-chlorobis[chloro(η^6-p-cymene)osmium(II)] [25] was reported (110).

The crystal structures of $Ru(\eta^3\text{-}C_3H_5)(\eta^6\text{-}C_6H_6)I$ and $Ru(\eta^3\text{-}C_3H_5)(\eta^6\text{-}C_6H_6)CN$ were described (111).

Other Pi Complexes

The o-xylylene complexes $\overline{Ru(CH_2C_6H_4C}H_2)L_3$ (L=PMe_2Ph, $PMePh_2$, PEt_3) can be prepared in 30-60% yield by treatment of $RuCl_2L_4$ with o-$MeC_6H_4CH_2MgBr$. Although $RuCl_2(PMe_3)_4$ does not react under similar conditions, $\overline{Ru(CH_2C_6H_4C}H_2)(PMe_3)_3$ can be prepared through reaction of the chloride with o-$MeC_6H_4CH_2LiTMED$ in toluene. The crystal structure of $\overline{Ru(CH_2C_6H_4C}H_2)(PMe_2Ph)_3$ was reported; bonding of the xylylene ligand is similar to that in [24] (112). Another route to related complexes $\overline{Ru(CH_2C_6Me_4C}H_2)L_2L'$ is deprotonation of $[Ru(\eta^6\text{-}C_6Me_6)L_2(NO_3)][NO_3]$ by potassium t-butoxide in the presence of L' (L=L'=$P(OMe)_3$; L=L'=$P(OCH_2)_3CMe$; L=L'=PMe_2Ph; L_2=dppe, L'=PMe_2Ph). The reaction is reversed by protonation with HBF_4. However, protonation of $\overline{Ru(CH_2C_6Me_4C}H_2)(dppe)(PMe_2Ph)$ with HPF_6 yields [26], which is a fluxional η^3-benzyl complex in which the proton bridges to Ru. Exchange of the methyl protons is rapid on the NMR timescale (113).

In refluxing aqueous ethanol cis-$OsCl_2(bipy)_2$ and alkynes react to form [cis-$Os(bipy)_2(alkyne)Cl][PF_6]$ (alkyne=3-hexyne, dimethyl acetylenedicarboxylate) in 70% yield. Analogous alkene complexes can be prepared in the same way. The complex $Os(bipy)_2(norbornadiene)^{2+}$ can be prepared through the reaction of $Os(bipy)_2(CO_3)$ with aqueous acid and norbornadiene. In all cases the unsaturated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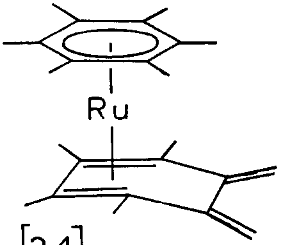
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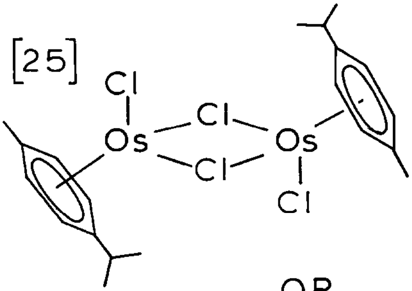
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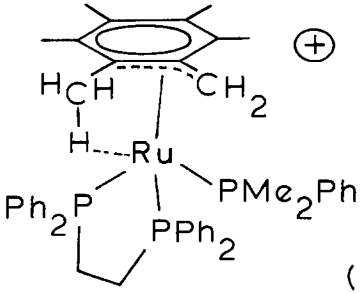
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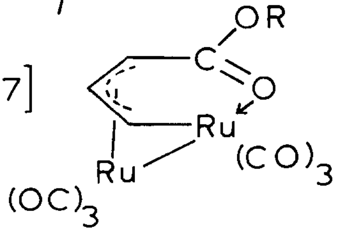
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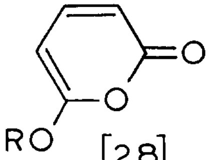
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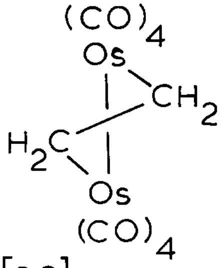
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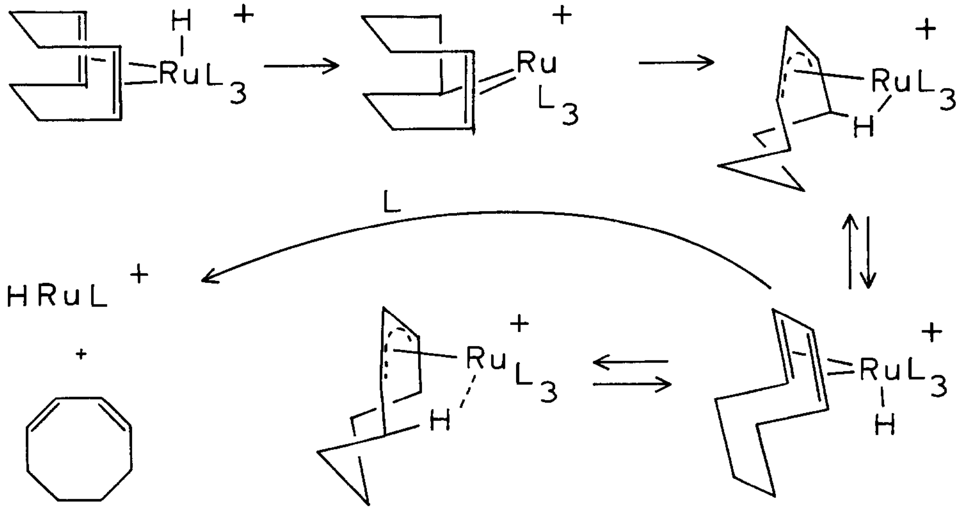
Scheme 14



hydrocarbon is proposed to exchange with coordinated water. Ligand exchange with NCMe or other unsaturated hydrocarbons can occur. Cyclic voltammetry and controlled potential electrolysis show evidence for stable Os(III) species derived from *cis*-$Os(bipy)_2(Et_2C_2)Cl^+$ and *cis*-$Os(bipy)_2(C_2H_3Ph)Cl^+$. The relative order of the Os(II)/Os(III) potentials suggests that the order of π-acceptor ability is: $NO^+ > CO > C_2(CO_2Me)_2 >$ alkenes $>$ CNMe $> PPh_3 > C_2Et_2 >$ MeCN (114).

The σ,π-metalloallyl complex [27] can be prepared in 55% yield through reactions of 2-alkoxyfurans with $Ru_3(CO)_{12}$ at 120° for 3 h. At a higher temperature and under CO (65 atm) the organic product [28] can be isolated in 50% yield in addition to [27] (67%). A mechanism for formation of these products was proposed (115).

The formation of $[Ru(\eta^3\text{-}C_8H_{13})L_3][PF_6]$ as an intermediate in the conversion of $[RuH(COD)L_3][PF_6]$ ($L=PMe_3$, $P(OMe)_2Ph$, PMe_2Ph, $P(OMe)Ph_2$, and $P(OCH_2CMe_3)_3$) into $[RuHL_4(solvent)][PF_6]$ ($L=P(OMe)Ph_2$ and $P(OCH_2CMe_3)_3$) and $[RuHL_5][PF_6]$ and cycloocta-1,3-diene is dependent upon the size of L. Small ligands give rise to stable $RuH(COD)L_3^+$ ions but larger ligands favor the η^3-cyclooctenyl complexes. At -20° when $L=P(OMe)_2Ph$, PMe_2Ph, or $P(OMe)Ph_2$, $RuH(COD)L_3^+$ is formed, but at 30° rapid conversion to $Ru(\eta^3\text{-}C_8H_{13})L_3^+$ occurs; this process is not reversed upon cooling. With isocyanides, $[Ru(1{:}4\text{-}5\text{-}\eta\text{-}C_8H_{13})(CNR)_4][PF_6]$ (R=*t*-Bu,xylyl) can be isolated, but this cannot be converted to the η^3-allyl. The reaction pathway proposed is shown in Scheme 14 (116).

Reactions of Ru(COD)(COT) (COT=η^6-cycloocta-1,3,5-triene) with phosphines have been used to prepare new phosphine complexes, which differ in composition, depending upon the size of the phosphine. For $L=PMe_3$ or $P(OMe)_3$, Ru(COD)(COT)L can be isolated in quantitative yield, but the product from $L=P(\textit{i}\text{-}Pr)_3$ or $P(\textit{t}\text{-}Bu)_3$ is $Ru_2H_8L_4$ (60 and 30%, respectively). The monomer RuH_6L_2 can be isolated in high yield from the reaction with $PCyc_3$. Other complexes thus prepared were $RuH_2(dppe)$, $Ru(COD)(dppm)_2$ and $Ru_2(COD)_2(COT)(dppm)_2$. Under hydrogen Ru(COD)(COT) and dppm form $RuH_2(dppm)_2$ in 100% yield (117).

The borapentadienyl complex $Ru(\eta^5\text{-}CH_2CHB(Cl)CHCH_2)(CO)_3$ (30% yield) can be prepared by reaction of $BCl(C_2H_3)_2$ with $Ru_3(CO)_{12}$. The reagent $BCl(C_2H_3)_2$ is prepared from BCl_3 and $Me_2Sn(C_2H_3)_2$ (118).

CLUSTER COMPOUNDS

Dinuclear Species (Excluding η^5-Cp Complexes)

All-electron ab initio self-consistent field and configuration interaction calculations have been done for 112 electronic states resulting from interactions of two Ru atoms. The equilibrium distance (5.13 au), bond dissociation energy (0.64 eV) and vibrational frequency (116 cm^{-1}) indicate a weaker bond than expected. Inadequacies in the calculations are suggested to cause underestimation of the bond distance and dissociation energy (119).

The paramagnetic dimers $Os_2(O_2CR)_4Cl_2$ ($R=Pr,Et,CH_2Cl$) are synthesized from

$\{Os(O_2CMe)_2Cl\}_n$ and the appropriate acid at 140° for 8 h. The derivative from butyric acid is prepared in 60% yield; the Os-Os bond distance in this product, determined by X-ray crystallography, is 2.301 Å. The magnetic moment for $Os_2(O_2CPr)_4Cl_2$ is 1.15 μ_B per Os at 300 K and 1.02 μ_B per Os at 188 K, indicating considerable antiferromagnetic interaction (120).

The dianion $Os_2(CO)_8^{2-}$, prepared by reduction of $\overline{Os_2(CO)_8}I_2$ with sodium-mercury amalgam, reacts with $X(CH_2)_nX$ to give $(OC)_4\overline{Os(CH_2)_nOs}(CO)_4$ (n=1 (35% yield), n=2 (10%), n=3; X=I, OTs). The crystal structure of $(OC)_4\overline{Os(CH_2)_2Os}(CO)_4$ [29] was determined. Ethylene and $(OC)_4\overline{OsCH_2Os}(CO)_4$ at 100° form $(OC)_4\overline{Os(CH_2)_3\text{-}Os}(CO)_4$ (85% yield); the reaction can be reversed at 130° but some methane and propene are also formed. Thermolysis of $Os_2(CO)_8Me_2$ at 120° also gives $(OC)_4\overline{Os(CH_2)Os}(CO)_4$ and methane (0.73 equiv) (121).

Trinuclear Species

Xα calculations were done for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. Centrally directed M-M sigma and pi bonding orbitals and antibonding counterparts are occupied and stability of the antibonding orbitals is due to M-CO pi bonding. The two lowest energy electronic transitions are dipole-allowed (strongly M-M antibonding) and dipole-forbidden (M-CO antibonding) HOMO-LUMO transitions. Raman spectra of $Ru_3(CO)_{12}$ show resonance enhancement of both the 185 and 130 cm^{-1} Ru-Ru stretching vibrations, confirming the antibonding nature of the lowest allowed transition and suggesting a Jahn-Teller distortion in the excited state. Spectrophotometric titrations show $Os_3(CO)_{12}$ to be 5 times more basic toward the proton than $Ru_3(CO)_{12}$ (122).

Single-crystal IR reflectance with polarized light has been used to examine the carbonyl region of the spectrum of $Ru_3(CO)_{12}$. In conjunction with Raman and low temperature IR spectra, essentially complete assignments of bands were made. Seven ν(CO) modes were located and ν(M-C) modes were analyzed in the spectra of $Os_3(CO)_{12}$ in KBr and Nujol matrices (123).

Photolysis of $Ru_3(CO)_{12}$ has been re-examined (124,125). The primary product under CO, even in carbon tetrachloride solvent, is $Ru(CO)_5$. The kinetics of photochemical fragmentation under CO show a dependence of the quantum yield upon the concentration of CO. The proposed mechanism is:

$$Ru_3(CO)_{12} \underset{k_r}{\overset{h\nu}{\rightleftarrows}} Ru_3(CO)_{12}^{*} \xrightarrow[k_f]{CO} \text{intermediate} \xrightarrow{\text{fast}} 3\ Ru(CO)_5$$

A diradical intermediate can be excluded because the reaction of the intermediate with CO is much faster than its reaction with carbon tetrachloride. A thermal reaction between $Ru(CO)_5$ and carbon tetrachloride does produce Ru-Cl species. Weak Lewis bases such as THF inhibit fragmentation; this is attributed to trapping of the intermediate by THF, followed by collapse of this adduct back to $Ru_3(CO)_{12}$ upon THF dissociation. A possible structure for the intermediate which contains a bridging carbonyl has been suggested.

Photolysis of $Ru_3(CO)_9L_3$ (L=CO,PPh_3,$P(OMe)_3$, $P(\underline{o}\text{-tolyl})_3$) at 355 nm generates a catalyst for the isomerization of 1-pentene. Steric effects of L are responsible for the variation in the initial trans/cis ratio of the alkene product, with larger L giving a smaller ratio. The primary photoprocess is proposed to be Ru-Ru bond rupture (126).

The plastic metal cluster model introduced by Quicksall and Spiro for the vibrational spectra of metal clusters was used to obtain a good optimized fit between calculated and observed M-M stretching frequencies for C_{2v} Os_3 clusters. The stretching force constants of unbridged Os-Os bonds correlate with the bond lengths obtained from crystallographic studies. The frequency data may be used to obtain Os-Os-Os bond angles. Clusters thus treated were $Os_3(OEt)_2(CO)_{10}$, $HOs_3(C_2H_3)(CO)_{10}$, $HOs_3(SMe)(CO)_{10}$, and $H_2Os_3(CO)_{10}$ (127).

Reactions of hydroxide and methoxide with $Ru_3(CO)_{12}$ and $Ru(CO)_5$ have been examined. Methoxide reacts reversibly with $Ru_3(CO)_{12}$ to form $Ru_3(CO)_{11}(CO_2Me)^-$. Hydroxide also reacts reversibly to give $Ru_3(CO)_{11}(CO_2H)^-$, but this anion decarboxylates to $HRu_3(CO)_{11}^-$. The analogous process with $Ru(CO)_5$ forms $Ru(CO)_4(CO_2H)^-$, which decarboxylates to $HRu(CO)_4^-$. The kinetics of initial nucleophilic addition were determined using stopped flow methods. The rate law is of the form $(k_1[OR^-]+k_{-1})$[complex]. The order of reactivity is $Os(CO)_5 > Ru(CO)_5 >> Fe(CO)_5$ but $Fe_3(CO)_{12} > Ru_3(CO)_{12} > Os_3(CO)_{12}$ (128). These reactions are summarized in Scheme 15.

Nucleophilic attack by $LiNMe_2$ on $Os_3(CO)_{12}$ at 0° forms the amide derivative $Os_3(CO)_{11}\{C(O)NMe_2\}^-$, but at 25° loss of CO from this product generates $Os_3(\mu\text{-}O{=}CNMe_2)(CO)_{10}^-$. The latter can be protonated to $HOs_3(\mu\text{-}O{=}CNMe_2)(CO)_{10}$. In a similar fashion, attack by methyl lithium on $Os_3(CO)_{12}$ forms the acyl $Os_3(CO)_{11}\{C(O)Me\}^-$, which decarbonylates at 25° to $Os_3(\mu\text{-}O{=}CMe)(CO)_{10}^-$; protonation of the latter gives $HOs_3(\mu\text{-}O{=}CMe)(CO)_{10}$ in 50% yield. Attack by alkoxide and then protonation can be used to prepare $HOs_3(\mu\text{-}O{=}COR)(CO)_{10}$ (10% yield) and $HOs_3(\mu\text{-}OR)(CO)_{10}$ (10%); the remainder of the product mixture is unreacted $Os_3(CO)_{12}$. One Ru cluster, $Ru_3(\mu\text{-}O{=}CNMe_2)(CO)_{10}^-$, has been prepared by reaction of $Ru_3(CO)_{12}$ with $C(NMe_2)_4$ (129). These reactions are summarized in Scheme 15.

The acyl derivative $HOs_3(\mu\text{-}O{=}CMe)(CO)_{10}$ reacts further with methyl lithium to give initially a second acyl ligand; methylation of this intermediate with methyl fluorosulfonate forms $HOs_3(\mu\text{-}O{=}CMe)\{C(OMe)Me\}(CO)_9$ [30] in 68% yield. The crystal structure of [30] was reported (130). This reaction sequence is shown in Scheme 15.

A minor product from the reaction of methyl lithium (in the presence of

22.5% lithium bromide) with $Ru_3(CO)_{12}$ is $HRu_3(\mu\text{-}Br)(CO)_{10}$ (optimized yield 30%), of which the crystal structure was determined. The chloride and iodide derivatives can be prepared in 15% and 6% yields, respectively, by treatment of $Ru_3(CO)_{12}$ with the appropriate LiX and two equiv of trimethylamine-N-oxide in THF for 1 h, followed by acidification. From the reaction with iodide, $HRu_3(\mu_3\text{-}I)(CO)_9$ (40%) is also formed; this product and $HRu_3(\mu\text{-}I)(CO)_{10}$ are in equilibrium and a CO atmosphere converts the former to the latter. Treatment of $HRu_3(\mu\text{-}Br)(CO)_{10}$ with $LiPPh_2$ gives $HRu_3(\mu\text{-}PPh_2)(CO)_{10}$ in 35% yield. Reactions of $HRu_3(\mu\text{-}Br)(CO)_{10}$ with ethylene and with diphenyl acetylene give $HRu_3Br(CO)_9(C_2H_4)$ and a vinyl derivative, respectively (131). These reactions are summarized in Scheme 15.

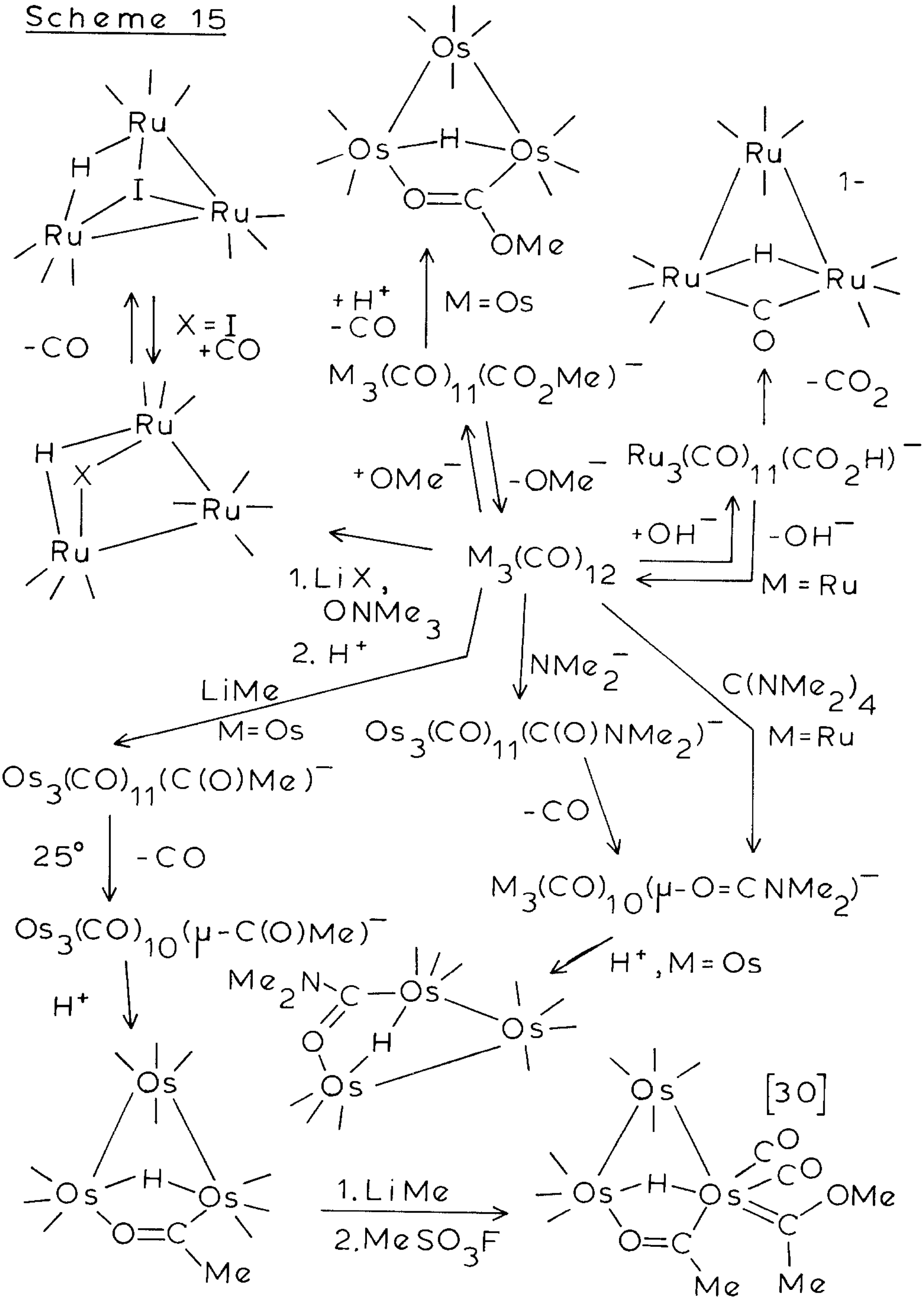
Interpretation of the IR spectrum of $HDOs_3(CO)_{10}$ (ca. 5%) in a matrix of $D_2Os_3(CO)_{10}$ led to the conclusions that (i) the two hydrides of $H_2Os_3(CO)_{10}$ are symmetrically disposed with respect to the Os-H bond length and Os-H-Os bond angle but are inequivalent as evidenced by the dissimilarity of the Os_2H rocking frequencies, and (ii) the symmetric Os-H stretching mode in $HDOs_3(CO)_{10}$ is at a higher energy than the antisymmetric mode. The latter point allows assessment of the error associated with the relation between M-H stretching frequencies and the interbond angles; the M-H-M angles determined by that method will be underestimated by at least 4 to 5 degrees (132).

MO calculations and photoelectron spectra for $H_2Os_3(CO)_{10}$ were reported. Bonding in the H_2Os_2 system is described as two 3-center-2-electron Os-H-Os bonds; there is an additional bonding interaction due to "t_{2g}-t_{2g}" bonding because the CO ligands preferentially back-bond to anti-bonding combinations of the pseudo-t_{2g} orbitals (133).

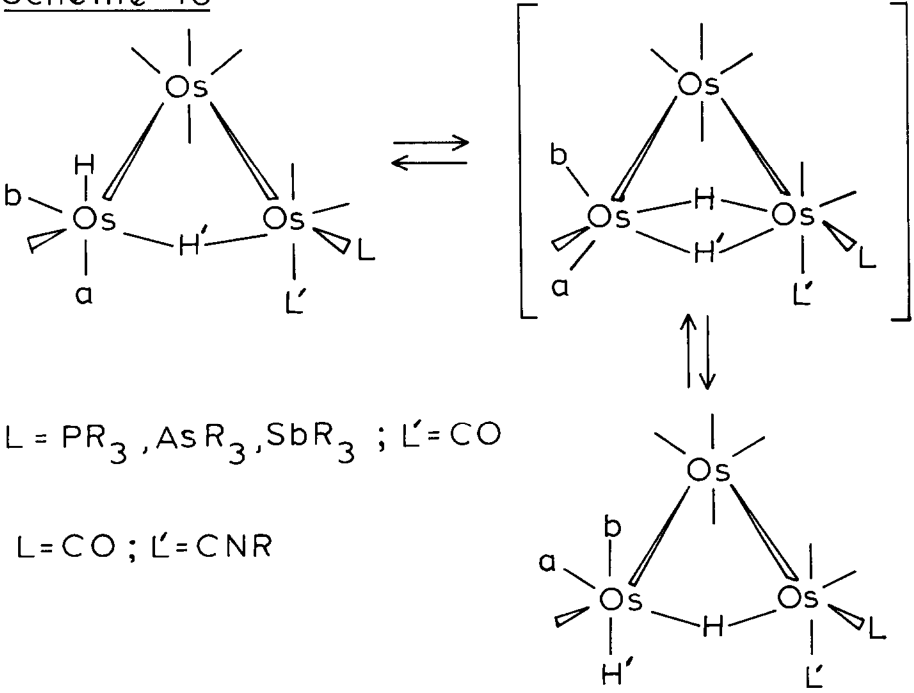
Adducts of the unsaturated cluster $H_2Os_3(CO)_{10}$ with Lewis bases, L=CO, PR_3, $P(OR)_3$, AsR_3, $SbPh_3$, amines, nitriles, isocyanides, halides, and pseudohalides, have been prepared. Each of these adducts $H_2Os_3(CO)_{10}L$ contains one axial, terminal hydride and one bridging hydride. These molecules are fluxional, and variable temperature ^1H and ^{13}C NMR studies reveal that the two hydride ligands and two of the carbonyls undergo simultaneous exchange. The free energy of activation for the exchange process varies between 13.5 and 11.0 kcal/mol, depending upon the steric and electronic properties of L, increasing as the size of L increases and decreasing as the polarizability of the donor atom of L increases. The proposed mechanism, Scheme 16, involves a turnstile-like movement of the two hydrides and an axial and an equatorial CO ligand on a single Os atom through a transition state with two equivalent hydrides bridging the same Os-Os vector (134).

The hydride anion $HRu_3(CO)_{11}^-$ functions as an apparent hydride donor in the presence of CO and at 25°. The potassium salt is stable in THF at 25° but under CO (1 atm) is converted to $Ru_3(CO)_{12}$. Removal of the CO atmosphere results

Scheme 15


Ru
H
I
Ru
Ru
-CO
X = I
+CO
H
X
Ru
Ru
Ru
Os
Os
H
Os
O=C
OMe
+H⁺
-CO
M = Os
M₃(CO)₁₁(CO₂Me)⁻
+OMe⁻
-OMe⁻
Ru
1-
H
Ru
Ru
C
O
-CO₂
Ru₃(CO)₁₁(CO₂H)⁻
+OH⁻
-OH⁻
M = Ru
M₃(CO)₁₂
1. LiX, ONMe₃
2. H⁺
LiMe
M=Os
NMe₂⁻
Os₃(CO)₁₁(C(O)NMe₂)⁻
C(NMe₂)₄
M=Ru
Os₃(CO)₁₁(C(O)Me)⁻
25°
-CO
-CO
M₃(CO)₁₀(μ-O=CNMe₂)⁻
Os₃(CO)₁₀(μ-C(O)Me)⁻
H⁺, M = Os
H⁺
Me₂N
C
Os
O
H
Os
Os
Os
Os
H
Os
O=C
Me
1. LiMe
2. MeSO₃F
[30]
Os
Os
H
Os
CO
CO
OMe
O=C
C
Me
Me

Scheme 16



$L = PR_3, AsR_3, SbR_3$; $L' = CO$

$L = CO$; $L' = CNR$

Scheme 17

$$Ru_3(CO)_{12} + Ph_2CO^{\overset{\cdot}{-}} \longrightarrow Ru_3(CO)_{12}^{\overset{\cdot}{-}} + Ph_2CO$$

$$Ru_3(CO)_{12}^{\overset{\cdot}{-}} + L \longrightarrow Ru_3(CO)_{11}L^{\overset{\cdot}{-}} + CO$$

$$Ru_3(CO)_{11}L^{\overset{\cdot}{-}} + Ru_3(CO)_{12} \longrightarrow Ru_3(CO)_{11}L + Ru_3(CO)_{12}^{\overset{\cdot}{-}}$$

in a rapid back reaction to $HRu_3(CO)_{11}^-$. Potassium hydride and $Ru_3(CO)_{12}$ in THF are converted to $K[HRu_3(CO)_{11}]$. Although very slow in the absence of CO, $K[HRu_3(CO)_{11}]$ and $[Ph_3C][BF_4]$ react rapidly under CO to give $K[BF_4]$, $Ru_3(CO)_{12}$, and Ph_3CH. Similarly, $K[DRu_3(CO)_{11}]$ and H_2O under CO form HD, $Ru_3(CO)_{12}$ and potassium hydroxide, but in the absence of CO only a trace of HD is formed. The $HRu_3(CO)_{11}^-$ ion is suggested to play a major role in water gas shift catalysis by Ru carbonyls (135).

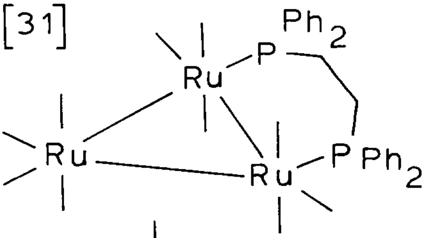
Catalytic amounts of the radical anion formed by reduction of benzophenone effect substitution of $M_3(CO)_{12}$ (M=Ru,Os) and $H_4Ru_4(CO)_{12}$ in greatly improved yields by stoichiometric quantities of Lewis bases in THF. The reactive intermediate in each case in proposed to be a cluster radical anion in which the added electron is in an antibonding orbital. The proposed mechanism is shown in Scheme 17. Complexes prepared by this method include $Ru_3(CO)_{12-n}L_n$ (L=CN-*t*-Bu, n=1,2; L=PPh_3, n=1,2,3; L=dppe,n=2; L=$AsPh_3$,$SbPh_3$,n=1), $H_4Ru_4(CO)_{12-n}L_n$ (L=CN-*t*-Bu, n=2; L=PPh_3, n=1; L=$P(OPh)_3$, n=1,3) and $Os_3(CO)_{12-n}L_n$ (L=CN-*t*-Bu,PPh_3; n=1) (136,259).

Substitution reactions of $Ru_3(CO)_{11}$(CN-*t*-Bu) were conducted. Products prepared were $Ru_3(CO)_{11}L$ and $Ru_3(CO)_{10}$(CN-*t*-Bu)L (L=CN-*t*-Bu,PPh_3, $P(C_6H_4Me\text{-}4)_3$, $PCyc_3$, $AsPh_3$, $SbPh_3$). Monosubstituted derivatives are not commonly major products from substitutions of $Ru_3(CO)_{12}$ (137,259).

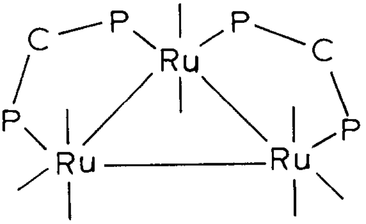
An explanation for the observed disorder in the solid-state structures of $M_3(CO)_{12-n}L_n$ (M=Fe,Ru,n=1-3) is provided by a model in which peripheral atoms (O for CO, N for CNR, P for PR_3) occupy the same sites while the M_3 triangle takes up one of two orientations, related by a 60° rotation about a vector normal to the M_3 plane (138). This model may be related to fluxionality in these systems.

The resonance Raman spectra of $Ru_3(CO)_9L_3$ (L=PPh_3, PBu_3, $P(OPh)_3$) and $H_4Ru_4(CO)_8(PPh_3)_4$ were studied. Identifications of Ru-Ru, Ru-C, and Ru-P modes were made. Information about the origin of the lowest energy electron transition was obtained (139).

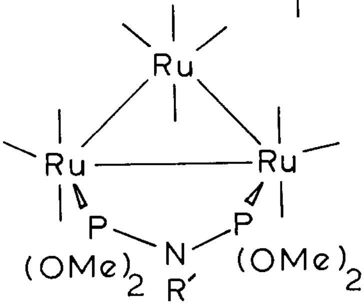
Derivatives of $Ru_3(CO)_{12}$ with chelating phosphine ligands have been prepared and characterized. The crystal structures of $Ru_3(CO)_{10}$(dppe) [31] (140) and $Ru_3(CO)_8(dppm)_2$ [32] (141) were reported. Substitution catalyzed by sodium/benzophenone was used to synthesize $Ru_3(CO)_{11}$(dppe), $\{Ru_3(CO)_{11}\}_2$dppe, $Ru_3(CO)_{10}$(dppe), and $Ru_3(CO)_8(dppe)_2$ (260). The thermal reaction of $Ru_3(CO)_{12}$ with $(RO)_2PNR'P(OR)_2$ (R'=Et, R=Me or Ph; R'=Me, R=Et) forms $Ru_3(CO)_{10}\{\mu\text{-}(RO)_2PNR'P(OR)_2\}$ [33]; photolysis in the presence of excess ligand gives $Ru_2(\mu\text{-}CO)\{\mu\text{-}(RO)_2PNR'P(OR)_2\}(CO)_4$ [34], which is very susceptible to electrophilic attack (142). The tridentate ligand $HC(PPh_2)_3$ reacts with $Ru_3(CO)_{12}$ to give a wide variety of products, including $Ru_3(CO)_9\{HC(PPh_2)_3\}$ [35] and



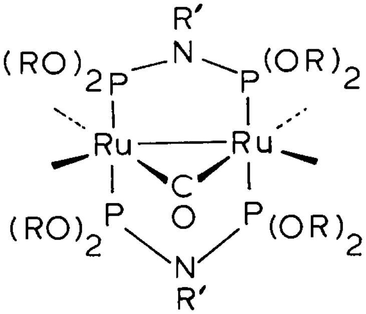
[31]



[32]



[33]



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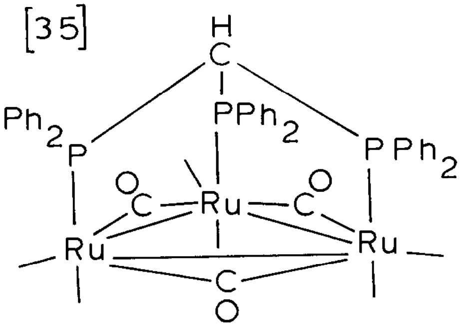

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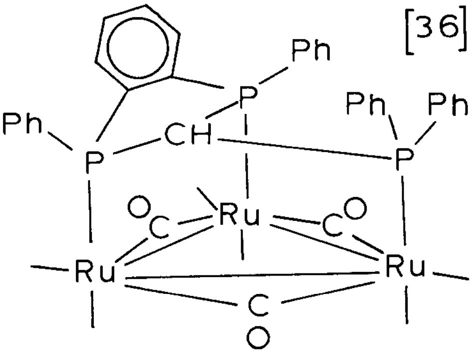

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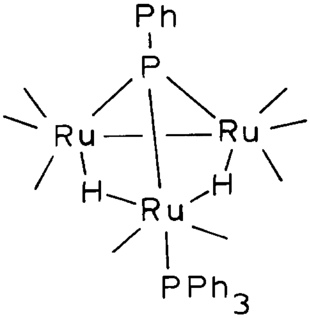
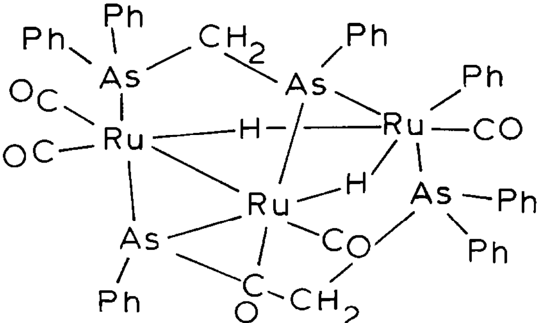


[37]



[38]

$Ru_3(CO)_9\{HC(PPh_2)(PhPC_6H_4PPh)\}$ [36], which was characterized by X-ray crystallography (143).

The crystal structure of $H_2Ru_3(CO)_8(PPh_3)(\mu_3\text{-}PPh)$ [37] was reported (144). The Ru-H-Ru angle is 109° and the Ru-Ru vectors bridged by hydrides are longer than the unbridged Ru-Ru bond length. The PPh_3 ligand is axially coordinated.

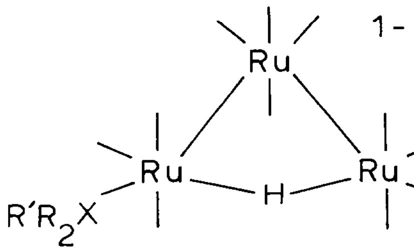
Hydrogenation of $Ru_3(CO)_8(dppm)_2$ [32] at 85° for 1.5 h gives CO, benzene, and $H_2Ru_3(CO)_6(\mu\text{-}PhPCH_2PPh_2)_2$ [38] in 77% yield; the crystal structure of the product has been determined. Hydrogenation of $Ru_3(CO)_8(dpam)_2$ at 85° yields $HRu_3(CO)_7(\mu\text{-}PhAsCH_2AsPh_2)(dpam)$, which reacts further at 120° under hydrogen to $H_2Ru_3(CO)_6(\mu\text{-}PhAsCH_2AsPh_2)_2$. Protonation of the latter with trifluoroacetic acid forms $H_3Ru_3(CO)_6(\mu\text{-}PhAsCH_2AsPh_2)_2^+$ with all three Ru-Ru vectors bridged by hydrides. The dppm cluster is a catalyst precursor for hydrogenation of cyclohexanone (145).

Oxidative additions of HXR_3 (X=Si,Ge,Sn) by $HRu_3(CO)_{11}^-$ have been reported. Oxidative addition of $HSiEt_3$ by $HRu_3(CO)_{11}^-$ yields $HRu_3(CO)_{10}(SiEt_3)_2^-$, CO, and hydrogen in nearly quantitative yield. The reaction can be reversed under a CO/hydrogen atmosphere. Only $HRu_3(CO)_{10}(SiEt_3)_2^-$ is formed from $DRu_3(CO)_{11}^-$ and $HSiEt_3$. In THF both cluster anions are catalyst precursors for hydrosilylation of ethylene (146). In a similar fashion, $Na[HRu_3(CO)_{11}]$ reacts reversibly with HXR_2R' (X=Si,Ge,Sn; R,R'=Ph,Et,Me) to give the corresponding $HRu_3(CO)_{10}(XR_2R')_2^-$ [39], isolated as NEt_4 or PPN salts (147).

Methylation of $[PPN][Ru_3(CO)_{10}(NO)]$ with methyl trifluoromethanesulfonate forms $Ru_3(CO)_{10}(NOMe)$ [40] in 66% yield; the crystal structure of the product was determined. The ^{15}N NMR spectrum consists of a single resonance at 285.8 ppm downfield from ammonia (vs. 529 ppm upfield from ammonia for $Ru_3(CO)_{10}(NO)^-$). Hydrogenation of $Ru_3(CO)_{10}(NOMe)$ forms $H_2Ru_3(CO)_9(NOMe)$. Protonation of $[PPN][Ru_3(CO)_{10}(NO)]$ with trifluoroacetic acid gives $HRu_3(CO)_{10}(NO)$ but protonation with the stronger acid trifluoromethanesulfonic acid yields $Ru_3(CO)_{10}(NOH)$ (ν_{O-H} 3494 cm^{-1}; ν_{N-O} 1110 cm^{-1}; δ_{O-H} 8.90; ^{15}N NMR 250.6 ppm). Unlike the isoelectronic $HRu_3(CO)_{10}(COH)$, this product is stable at 25°, but treatment with $[PPN][O_2CCF_3]$ or nitrate instantaneously converts it to $HRu_3(CO)_{10}(NO)$ (148). These reactions are summarized in Scheme 18.

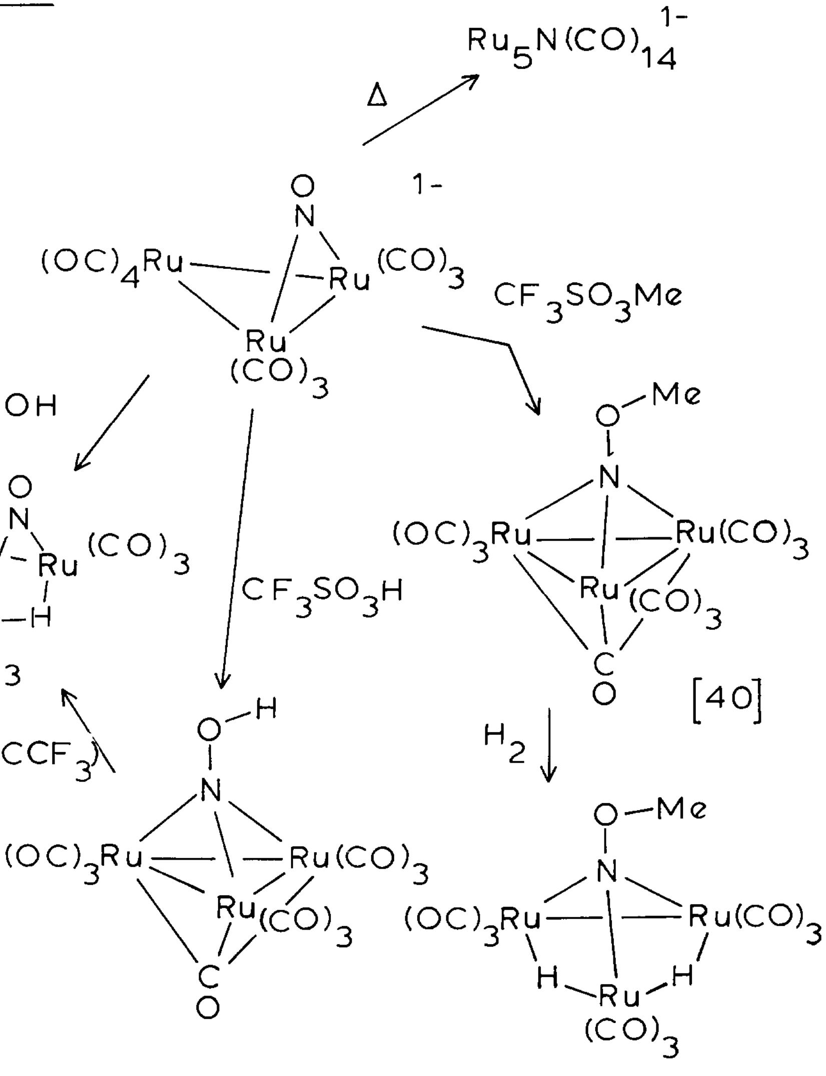
Reactions of $Os_3(CO)_{11}(NH_3)$ with ketones OCR_2 form imide complexes $Os_3(CO)_{11}(NHCR_2)$. The crystal structure of one product, $Os_3(CO)_{11}\text{-}\{NH\overline{C(CH_2)_4C}H_2\}$, contains an axially coordinated imine. Upon heating these complexes undergo decarbonylation and oxidative addition of N-H to form $HOs_3(\mu\text{-}NCR_2)(CO)_{10}$ (149).

The "lightly stabilized" cluster $Os_3(CO)_{10}(C_8H_{14})_2$ adds formic acid ($H^{12}CO_2H$, DCO_2H, or $H^{13}CO_2H$) to give labeled formate complexes $HOs_3(\mu\text{-}O_2{}^{12}CH)(CO)_{10}$, $HOs_3(\mu\text{-}O_2CD)(CO)_{10}$, and $HOs_3(\mu\text{-}O_2{}^{13}CH)(CO)_{10}$. From the spectra


1-
Ru
Ru
Ru
H
R′R$_2$X
XR$_2$R′

[39]

Scheme 18


Δ
Ru$_5$N(CO)$_{14}$ 1-
O
N
1-
(OC)$_4$Ru
Ru(CO)$_3$
Ru
(CO)$_3$
CF$_3$SO$_3$Me
CF$_3$COOH
(CO)$_4$
Ru
O
N
Ru (CO)$_3$
Ru—H
(CO)$_3$
CF$_3$SO$_3$H
(PPN)(OOCCF$_3$)
O—Me
N
(OC)$_3$Ru
Ru(CO)$_3$
Ru
(CO)$_3$
C
O
[40]
H$_2$
O—H
N
(OC)$_3$Ru
Ru(CO)$_3$
Ru(CO)$_3$
C
O
O—Me
N
(OC)$_3$Ru
Ru(CO)$_3$
H
Ru
H
(CO)$_3$

of these complexes the vibrational modes of the formate ligand were assigned. The structure, determined by X-ray crystallography, contains a diaxially bridging formate ligand; the Os_3-CO_2 plane angle is 99.5°. The C-H stretching frequency (2978 cm^{-1}) is considerably higher than in most other formate complexes, implying a high covalency in the formate-Os bond. Good overall agreement was found between the formate vibrational modes of this complex and the modes for formate chemisorbed on Cu(100) and Ag(110) surfaces (150).

In an analogous reaction to that described above with formic acid, $Os_3(CO)_{12}$ or $Os_3(CO)_{10}(C_8H_{14})_2$ and BzNHCH=NBz form $HOs_3(\mu\text{-}BzNCHNBz)(CO)_{10}$; this product, upon thermolysis, yields $H_2Os_3(\mu\text{-}\overline{BzNCHNCH_2C_6H_4})(CO)_{10}$. In the same reaction with *i*-PrNHCH=N-*i*-Pr, loss of CO from $HOs_3(\mu\text{-}i\text{-}PrNCHN\text{-}i\text{-}Pr)(CO)_{10}$ gives $HOs_3(\mu_3\text{-}i\text{-}Pr\text{-}NCHN\text{-}i\text{-}Pr)(CO)_9$ and this product adds PMe_2Ph to yield $HOs_3(\mu\text{-}i\text{-}PrNCHN\text{-}i\text{-}Pr)(CO)_9$-$(PMe_2Ph)$. These structures are shown in Scheme 19. Also formed in these processes are dinuclear complexes $Os_2(\mu\text{-}RNCHNR)_2(CO)_6$ (151).

Hydrogenation of $Ru_3(CO)_{11}(CN\text{-}t\text{-}Bu)$ in refluxing cyclohexane forms $HRu_3(\mu_3\text{-}CHN\text{-}t\text{-}Bu)(CO)_9$ [41] (52% yield), $HRu_3(\mu_3\text{-}CHN\text{-}t\text{-}Bu)(CO)_8(CN\text{-}t\text{-}Bu)$ (15%) and $H_4Ru_4(CO)_{12-n}(CN\text{-}t\text{-}Bu)_n$ (n=0(12%), 1(13%), 2(5%)) (152).

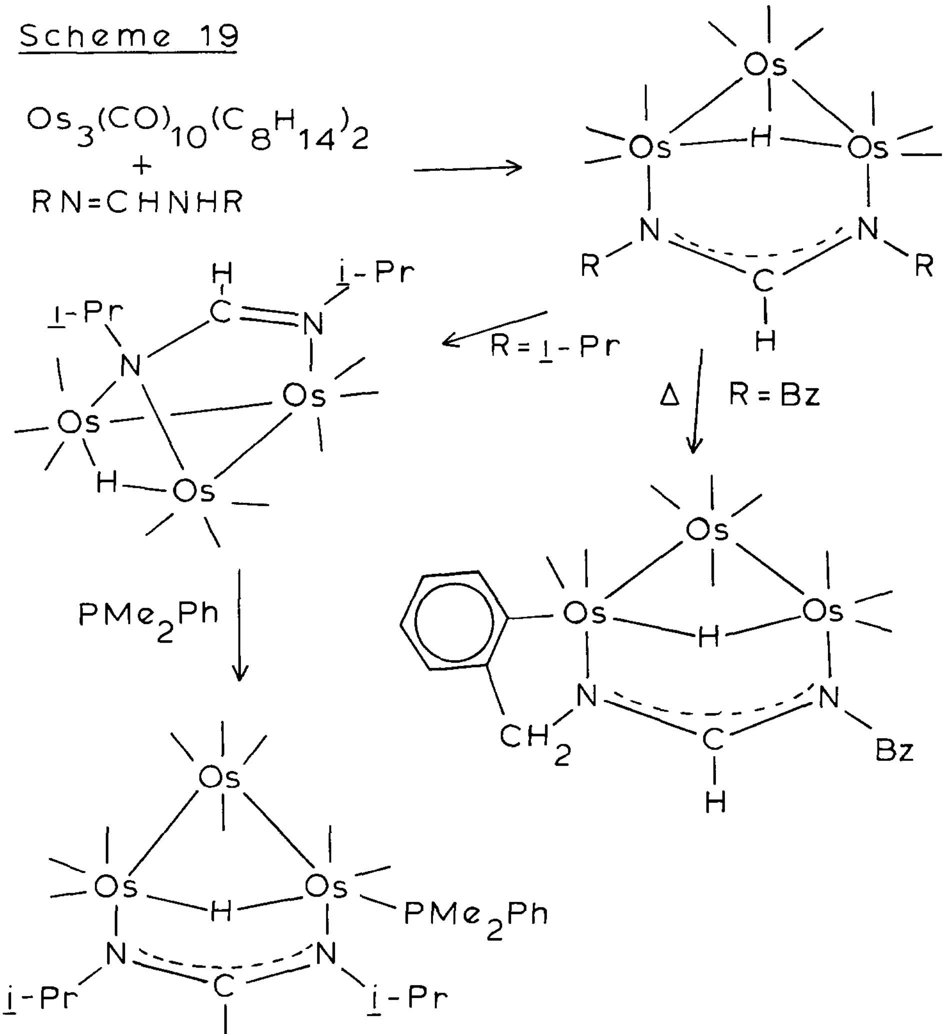
Reactions between $H_2Os_3(CO)_{10}$ and CF_3CN produce $HOs_3(\mu\text{-}NCHCF_3)(CO)_{10}$ [42] (69%) and $HOs_3(\mu\text{-}HNCCF_3)(CO)_{10}$ [43] (14%). Hydrogenation of [42] (49 atm, 140°, 16 h) gives $HOs_3(\mu\text{-}HNCH_2CF_3)(CO)_{10}$ [44], $H_2Os_3(\mu_3\text{-}NCH_2CF_3)(CO)_9$ [45], and $H_4Os_3(\mu_3\text{-}NCH_2CF_3)(CO)_8$ [46] in approximately equivalent yields of 25%. The structures of [44], [45], and [46] were determined by X-ray crystallography. The hydrogenation of [45] to [46] is reversible. These reactions are summarized in Scheme 20 (153).

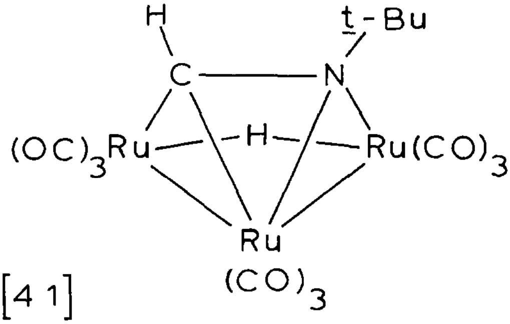
The ammonia complex $H_2Os_3(CO)_{10}(NH_3)$ is quantitatively and reversibly produced from $H_2Os_3(CO)_{10}$ and ammonia, but $Os_3(CO)_{12}$ in liquid ammonia forms $HOs_3(CO)_{10}(NH_2CO)$. Reactions of $Os_3(CO)_{12}$, $Os_3(CO)_{10}(NCMe)_2$, or $Os_3(CO)_{11}(NCMe)$ with hydrazine or NH_2NMe_2 produce $HOs_3(\mu\text{-}NHC(O)NHNR_2)(CO)_{10}$ [47] (R=H,Me), characterized by X-ray crystallography. A minor product from the hydrazine reaction, $HOs_3(\mu\text{-}NCO)(CO)_{10}$, can be prepared in 87% yield from $Os_3(CO)_{10}(NCMe)_2$ and HNCO; this cluster is susceptible to nucleophilic addition of hydrazine or NH_2NMe_2 to give [47] and generally reacts with HX (X=OR,NR_2) to form the corresponding $HOs_3(\mu\text{-}NHC(O)X)(CO)_{10}$. These reactions are shown in Scheme 21 (154).

Treatment of $Os_3(CO)_{11}L$ (L=NCMe,py) with N_3R forms $Os_3(CON_3R)(CO)_9L$ [48]. Both complexes where R=Ph were characterized by X-ray crystallography (155,156).

Different products are obtained from reactions of N_3R (R=Ph,Bu,Bz,Cyc, $CPhCH_2$) with $H_2Os_3(CO)_{10}$. In these cases the products are $HOs_3(HN_3R)(CO)_{10}$ [49]. The structure of the derivative where R=Ph was established by X-ray crystallography. Thermolysis of $HOs_3(HN_3CPhCH_2)(CO)_{10}$ forms $HOs_3(\mu\text{-}NCMePh)(CO)_{10}$. Other clusters

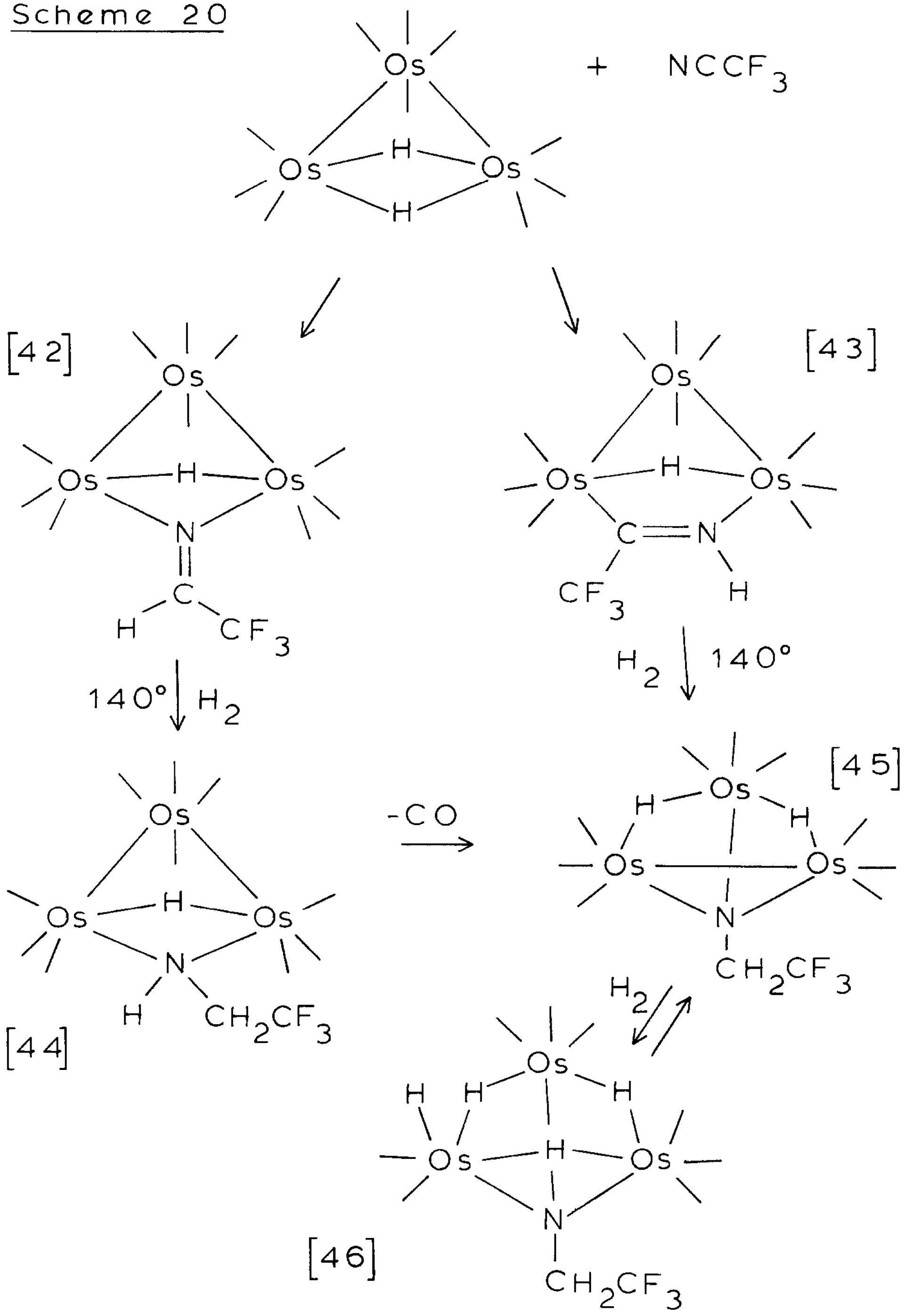
Scheme 19


Os3(CO)10(C8H14)2
+
RN=CHNHR
Os
Os
H
Os
N
N
R
R
C
H
R = i-Pr
Δ
R = Bz
H
i-Pr
i-Pr
C
N
N
Os
Os
H
Os
Os
Os
H
Os
N
N
CH2
C
Bz
H
PMe2Ph
Os
Os
H
Os
PMe2Ph
N
N
i-Pr
C
i-Pr
H

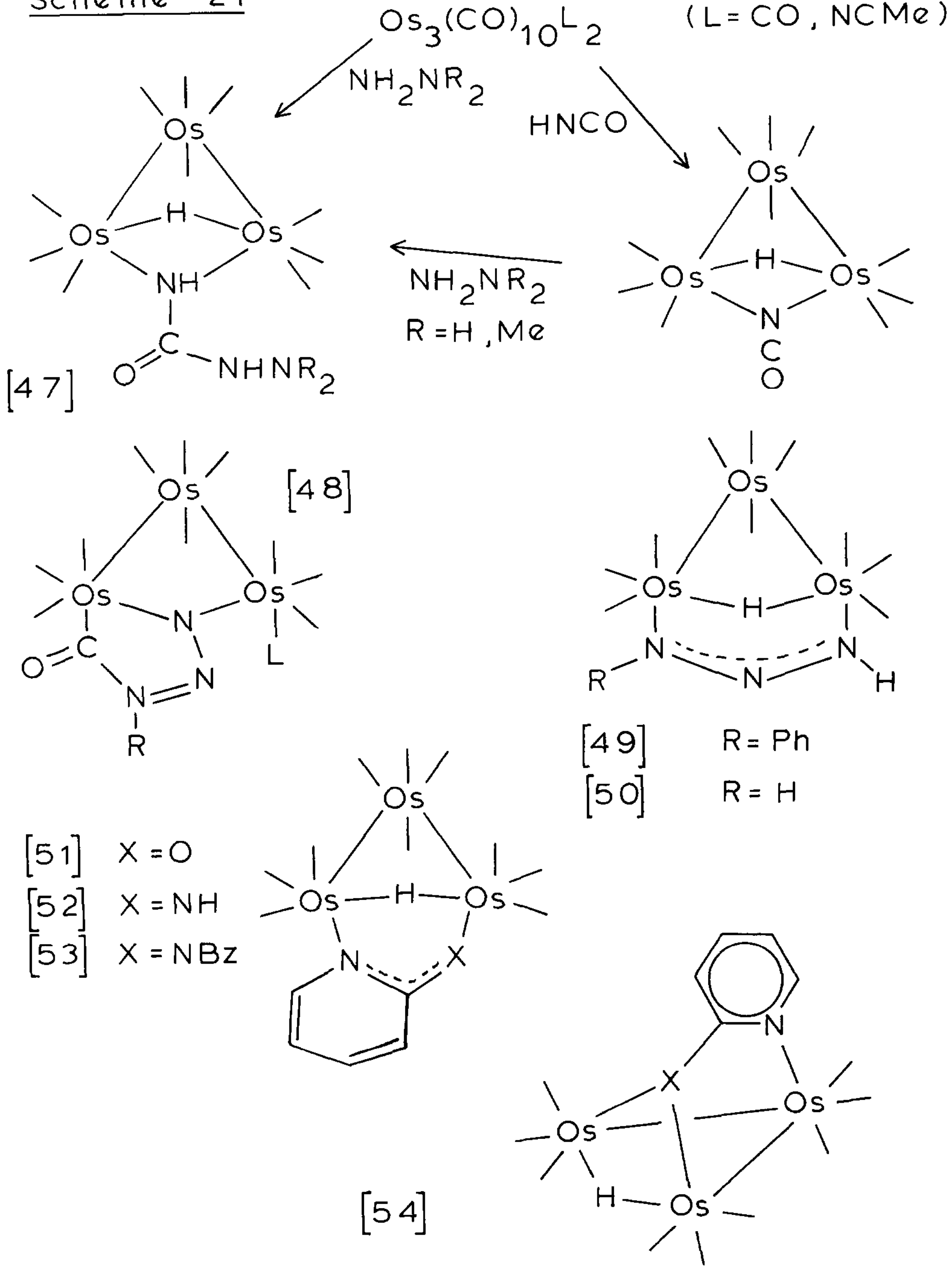

H
t-Bu
C
N
(OC)3Ru
H
Ru(CO)3
Ru
(CO)3

[41]

Scheme 20



Scheme 21


Os3(CO)10L2
(L = CO, NCMe)
NH2NR2
HNCO
NH2NR2
R = H, Me
[47]
[48]
[49] R = Ph
[50] R = H
[51] X = O
[52] X = NH
[53] X = NBz
[54]

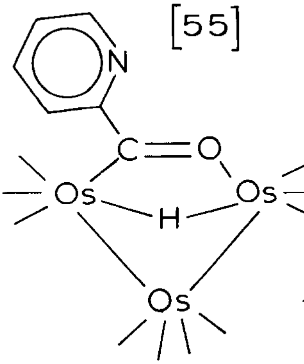
synthesized are $HOs_3(\mu\text{-}NHR)(CO)_{10}$ ($R=PO(OPh)_2$ or $2\text{-}(6\text{-}ClNC_5H_3)$) using phenacyl azides and $HOs_3(2\text{-}NHCN_2HC_6H_4)(CO)_{10}$ using 2-azidobenzimidazole (156,157). Treatment of $H_2Os_3(CO)_{10}$ with N_3SiMe_3 yields $HOs_3(N_3H_2)(CO)_{10}$ (25% yield); thermolysis of this product forms $HOs_3(\mu\text{-}NH_2)(CO)_{10}$ in quantitative yield. The Ph derivative $HOs_3(NHPh)(CO)_{10}$, prepared from $Os_3(CO)_{11}(NCMe)$ and aniline, yields $H_2Os_3(\mu_3\text{-}NPh)(CO)_9$ upon thermolysis. The reaction of $HOs_3(CO)_{11}^-$ with N_3SiMe_3 gives $HOs_3(\mu\text{-}NHSiMe_3)(CO)_{10}$. The crystal structures of $HOs_3(N_3H_2)(CO)_{10}$ [50] and $HOs_3(\mu\text{-}NHSiMe_3)(CO)_{10}$ were reported (158).

Reactions of $Os_3(CO)_{10}L_2$ ($L=CO,NCMe,C_8H_{14}$) with pyridines have been examined. From $Os_3(CO)_{12}$ or $Os_3(CO)_{10}(C_8H_{14})_2$ and 2-pyridine, 2-aminopyridine, or 2-(benzylamino)pyridine, complexes [51]-[53] are produced. Further heating causes loss of CO and formation of a triply bridged cluster as in [54] (X=NH), for which the structure was determined crystallography (159). From $2\text{-}NC_5H_4X$ (X=Cl,CN,Me) and $Os_3(CO)_{10}(NCMe)_2$ the product is $HOs_3(NC_5H_3X)(CO)_{10}$ [56], but products from $2\text{-}NC_5H_4X$ ($X=OH,SH,NH_2$), although of the same formulation, have structures as found for [51]-[53]. Pyrolysis of $HOs_3(NC_5H_4Y)(CO)_{10}$ (Y=O,S,NH) forms $HOs_3(NC_5H_4Y)(CO)_9$ of structure [54]. The reaction of $2\text{-}NC_5H_4CHO$ at 40° with $Os_3(CO)_{11}(NCMe)$ gives $HOs_3(OCC_5H_4N)(CO)_{10}$ [55]; pyrolysis of the product at 90° for 1 h gives $HOs_3(NC_5H_4)(CO)_{10}$ [56] (160). Products from reactions of $Os_3(CO)_{10}(C_8H_{14})_2$ with LH (LH=2-methyl- or 2-benzylpyridine or 1,2-, 1,3- or 1,4-diazines) are $HOs_3(L)(CO)_{10}$ ([56] (R=Me,Bz) or [57a and b]). The ^1H NMR spectrum of the product from 2-benzylpyridine shows a rigid structure on the NMR timescale. The product derived from $Os_3(CO)_{12}$ and 2,2'-bipyridyl is $HOs_3(C_{10}H_7N_2)(CO)_9$ [58], which was crystallography characterized (161).

Diazoalkanes $N_2CR^1R^2$ ($R^1=R^2=Ph$; $R^1=Ph,R^2=Me$; $R^1=Ph,R^2=H$; $R^1=R^2=Me$) and $H_2Os_3(CO)_{10}$ react to form $HOs_3(NHNCR^1R^2)(CO)_{10}$ [59]. Crystal structures of two of these products were described. Insertion of N_2CMe_2 is reversible, as $HOs_3(NHNCMe_2)(CO)_{10}$ reverts to $H_2Os_3(CO)_{10}$ in solution (162). The crystal structure of $HOs_3(NHNCPh_2)(CO)_{10}$ has been previously reported by others.

Clusters $Os_3(\mu\text{-}ER)_2(CO)_{10}$ (E=S,R=Me,Ph, or Bz; E=Se,R=Ph) are prepared in 20-50% yield from $Os_3(CO)_{11}(NCMe)$ and R_2E_2. Although three isomeric forms differing in the stereochemistry at the two ER ligands are possible, only one, which has inequivalent R groups, is initially formed. The SMe derivative isomerizes to a second form with equivalent Me groups (163).

Upon heating, $Os_3(CO)_{12}$ and RSPh (R=Me,i-Pr) go to $HOs_3(\mu\text{-}SR)(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ [60]; the crystal structure of the Me derivative was reported. The compounds exist in solution as two rapidly equilibrating isomers at 25°. Two dynamical processes were demonstrated by variable temperature NMR experiments. The lower energy, degenerate process involves migration of the hydride ligand between two Os-Os bonds. The higher energy process is an isomerization involving



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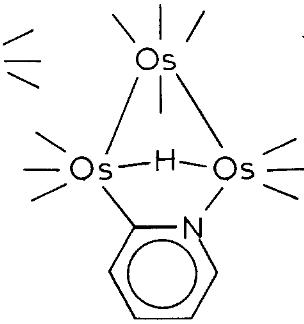

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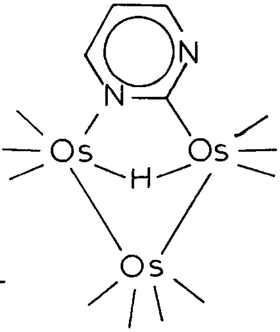

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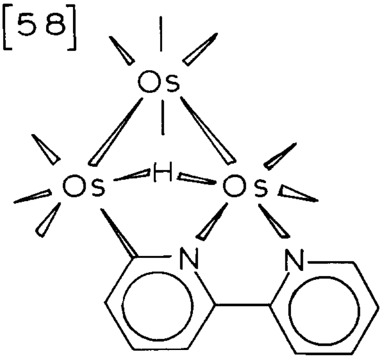

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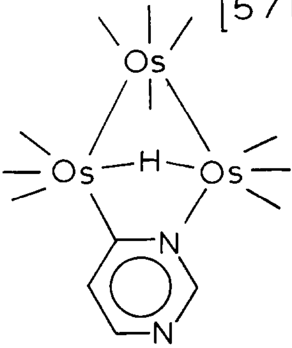
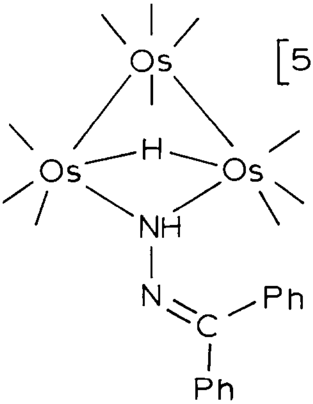
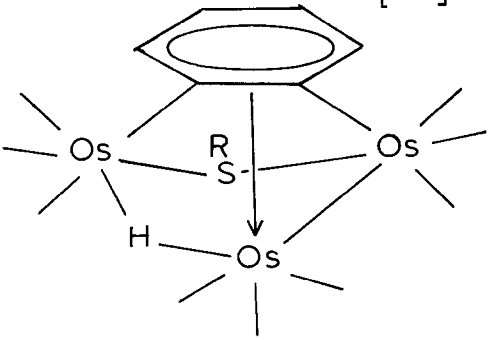


[57b]



[59]



[60]

inversion of configuration at the S atom (164).

The reaction between $SnCl_4$ and $H_2Ru_3(\mu_3\text{-}S)(CO)_9$ [61] yields $HRu_3(\mu_3\text{-}S)(\mu\text{-}Cl)(CO)_8(SnCl_3)$ [62]. Molecular structures of both reactant and product were determined by X-ray crystallography (165).

Reactions of $Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_8(PMe_2Ph)$ with HCl, $P(OMe)_3$ or $HSnMe_3$ were examined. The product from HCl is $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_8(PMe_2Ph)Cl$ [63]. With $P(OMe)_3$ the product is $Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)\{P(OMe)_3\}$ [64] (166). From $HSnMe_3$ the two products obtained are $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)$ [65] and $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)$ [66] (167). The structures of all these products were crystallographically determined.

In refluxing octane $S(NSiMe_3)_2$ and $Os_3(CO)_{12}$ form $Os_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}NSiMe_3)$ [67] (13% yield); the crystal structure of the product was determined. The temperature dependence of the ^{13}C NMR spectrum of this product suggests that two different structures are present at elevated temperatures. Reversible opening and closing of Os-Os bonds is suggested to account for this behavior (168).

The crystal structure of $Os_3(\mu\text{-}Cl)_2(CO)_{10}$ was reported. The chlorides bridge the same Os-Os vector, and the Os-Os distance of 3.233 Å is consistent with a zero bond order (169).

The crystal structure of $HOs_3(\mu\text{-}CH{=}CHPh)(CO)_{10}$ [68] was determined. The hydride was not located (170).

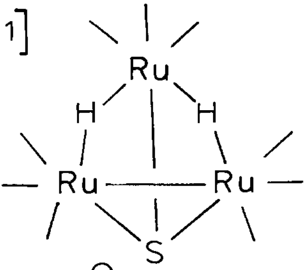
Vibrational spectra were recorded and assignments made for $HOs_3(\mu\text{-}CH{=}CH_2)(CO)_{10}$, $H_2Os_3(\mu_3\text{-}C{=}CH_2)(CO)_9$, $H_2Os_3(CO)_{10}$, and $D_2Os_3(CO)_{10}$ (also see ref. 127 and 132). These clusters are possible models for the hydrocarbon moieties bound to metal surfaces (171).

Measurement and assignment of the IR spectra of $H_2Os_3(\mu\text{-}CH_2)(CO)_{10}$ and $Os_3(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_{10}$ were also done. The vibrational modes were compared to methylene adsorbed on W(110) and Ni(111) surfaces (172).

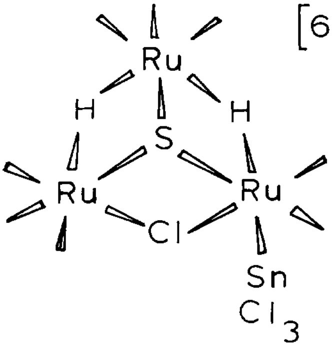
The He(I) photoelectron spectra of $HOs_3(\mu\text{-}CH{=}CH_2)(CO)_{10}$, $HOs_3(\mu_3\text{-}\eta^3\text{-}CMeCHCMe)(CO)_9$, and $HOs_3(\mu_3\text{-}\eta^3\text{-}CMeCCMe_2)(CO)_9$ were recorded. Comparisons of these spectra with those of $Os_3(CO)_{12}$ and $HOs_3(\mu_3\text{-}C{\equiv}CR)(CO)_9$ allowed assignment of Os-Os and Os-H-Os ionizations (173).

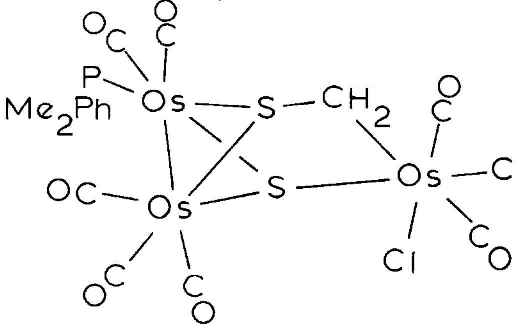
Adducts between the unsaturated clusters $H_2Os_3(CO)_9L$ ($L{=}PPh_2Et, PPh_3, P(OMe)_3$) and acetylene, ethylene, and CNMe have been synthesized and characterized by spectroscopic methods. The insertion product from acetylene is $HOs_3(CO)_9L(\mu\text{-}CH{=}CH_2)$ with the two isomers in a 4/1 ratio for $L{=}PPh_2Et$. Pyrolysis of the PPh_2Et derivative gives $H_2Os_3(CO)_8(PPh_2Et)(\mu_3\text{-}C{=}CH_2)$. Under ethylene (2.4 atm) the adduct $H_2Os_3(CO)_9(PPh_2Et)(C_2H_4)$ can be formed reversibly; eventual formation of $HOs_3(CO)_9L(\mu\text{-}CH{=}CH_2)$ and ethane occurs. Only the vinyl product is obtained from ethylene and $H_2Os_3(CO)_{10}$. Pi acceptor ligands preferentially bind to the phosphine-substituted metal atom. Pyrolysis of $HOs_3(CO)_9(PPh_2Et)(\mu\text{-}CH{=}CH_2)$ gives

[61]

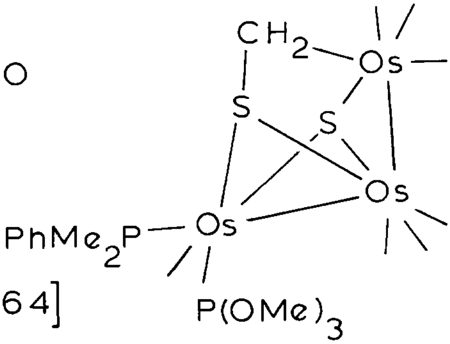


[62]





[63]



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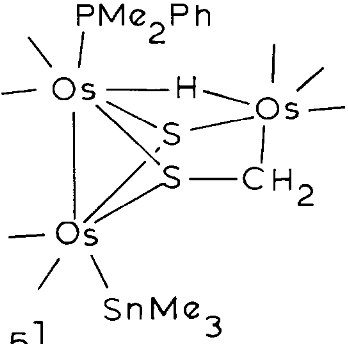

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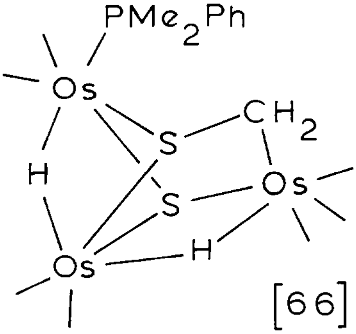

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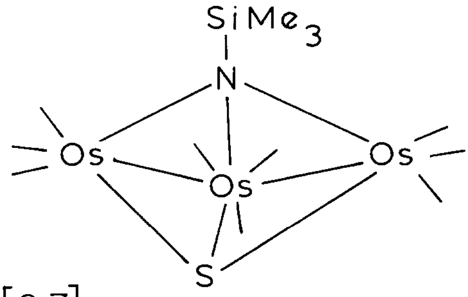

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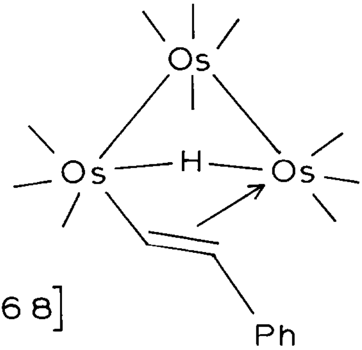


[68]

$H_2Os_3(CO)_9(PPh_2Et)(\mu_3\text{-}C{=}CH_2)$, which can be hydrogenated at 125° to $H_3Os_3(CO)_8(PPh_2Et)(\mu_3\text{-}CMe)$. These reactions are summarized in Scheme 22 (174).

The acetylide cluster $HRu_3(CO)_9(C_2\text{-}\underline{t}\text{-}Bu)$ reacts with C_2Ph_2 or $Ni_2(C_2Ph_2)Cp_2$ to give $Ru_3(CO)_7(\underline{t}\text{-}BuC_2C(Ph)CHPh)(C_2Ph_2)$ [69] in 5-10% yield after 10 h in refluxing heptane. The complex was characterized by X-ray crystallography (175).

Zwitterionic 1:1 adducts are formed by addition of PMe_2Ph to a carbon of $HOs_3(CO)_9(C_2R)$ (R=H,Me,Ph,CMe_2OH), $HOs_3(CO)_{10}(C_2Ph)$, or $HOs_3(CO)_9(MeC{=}C{=}CH_2)$. The crystal structures of $HOs_3(CO)_9(MeC{=}CCH_2PMe_2Ph)$ [70], $HOs_3(CO)_{10}(C{=}CPhPMe_2Ph)$ [71] and $HOs_3(CO)_9(CH{=}CPMe_2Ph)$ [72] were determined. The complexes $HOs_3(CO)_9(CR{=}CPMe_2Ph)$ (R=H,Me) are fluxional due to flipping of the alkyne moiety as it rotates around Os_3 face (176).

The temperature dependence of the ^1H and ^{13}C NMR spectra of $HM_3(CO)_9(MeC{=}C{=}CMe_2)$ (M=Ru,Os) were examined. For the Ru cluster a dynamic process averages the inequivalent methyl groups and also generates a two-fold symmetry plane with respect to the CO ligands. The proposed mechanism (Scheme 23) is edge-hopping of the hydride ligand and a simultaneous wagging motion of the organic ligand. For the Os cluster the activation energy for the fluxional process involving the organic ligand is higher, but it could not be established whether this motion is coupled with hydride mobility. The ^{13}C NMR spectrum of $HRu_3(CO)_9(MeCCHCMe)$ was also investigated. No motion of the organic ligand can be detected but opening of the hydride bridge is evidenced by the different barriers to axial-radial CO exchange at different Ru atoms. For $HRu_3(CO)_8(PPh_3)(CMeCHCMe)$, which has the phosphine ligand on a Ru bonded to the hydride, a higher barrier to axial-radial CO exchange at the bridged Ru atoms is observed (177).

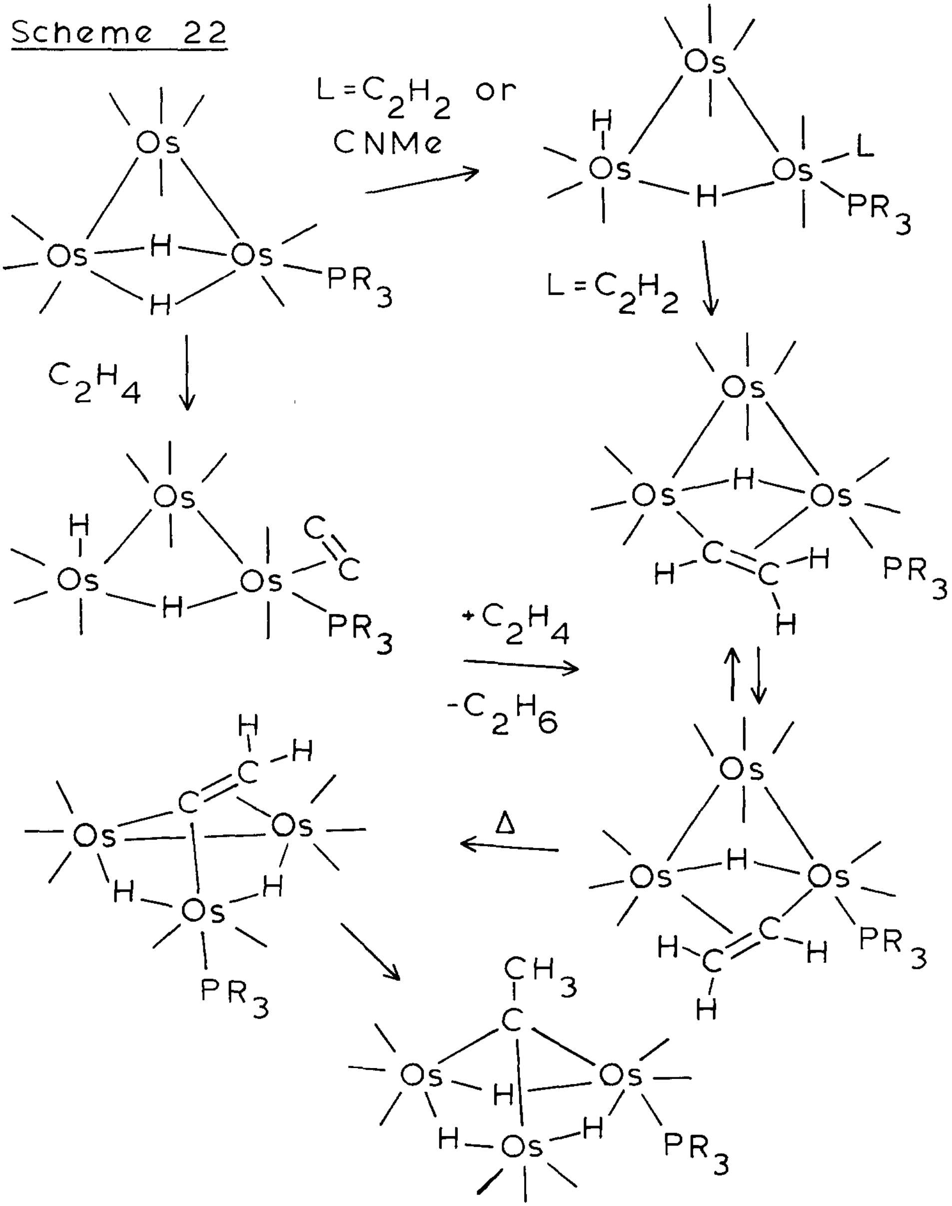
The acetylide clusters $HM_3(CO)_9(\mu_3\text{-}C{\equiv}CCPh_2OH)$ (M=Ru,Os) are synthesized by heating $C_2(CPh_2OH)_2$ and $M_3(CO)_{12}$. In the presence of trifluoroacetic acid these products rearrange to $HM_3(\mu\text{-}OH)(CO)_9(\mu_3\text{-}C{=}C{=}CPh_2)$ [73]; the crystal structure of the Os cluster was reported (178).

Hydrogenation of $Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ (R=$\underline{t}$-Bu,$\underline{i}$-Pr) at 25° and 1 atm very rapidly forms the corresponding $CH_2{=}CHR$ and $HRu_3(CO)_9(\mu\text{-}PPh_2)$ [74] (40%) and $H_2Ru_3(CO)_9(\mu\text{-}PPh)$ (10%). The crystal structure of the former cluster product was determined. The unsaturated cluster [74] is stabilized by a weak Ru-Ph interaction. This weak stabilization allows rapid addition of CO or PR_3 to $HRu_3(CO)_9(\mu\text{-}PPh_2)$. At 80° hydrogenation of [74] gives $H_2Ru_3(CO)_9(\mu_3\text{-}PPh)$ in 80% yield. Pyrolysis of [74] at 80° in the absence of hydrogen forms $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ [75] in 40% yield; the structure of [75] was determined by X-ray crystallography (179).

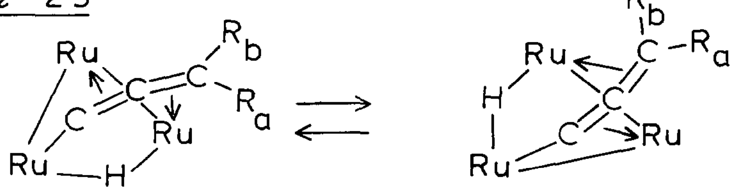
The crystal structure of the methylidyne cluster $H_3Ru_3(\mu_3\text{-}CCl)(CO)_9$ [76] was determined at 160 K. The Ru-H bond distance is 1.79 Å and the Ru-H-Ru angle is 105° (180).

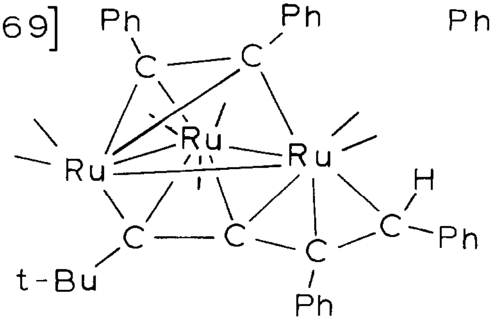
The vibrational spectra of $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X=H,Cl) have been recorded and

Scheme 22



Scheme 23





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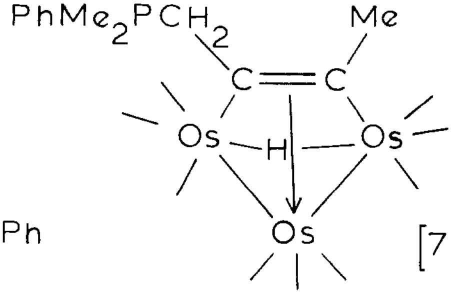

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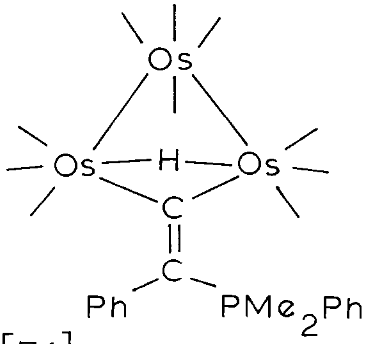

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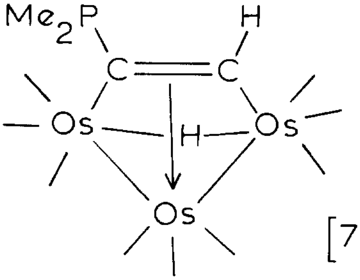

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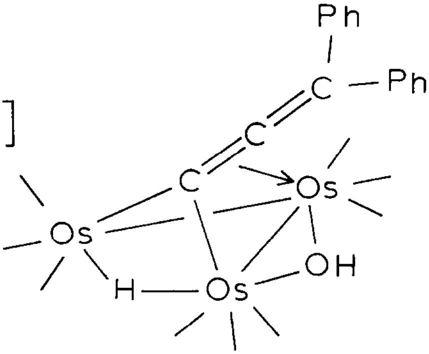

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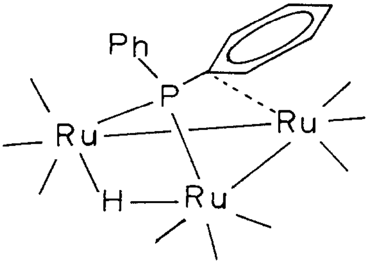

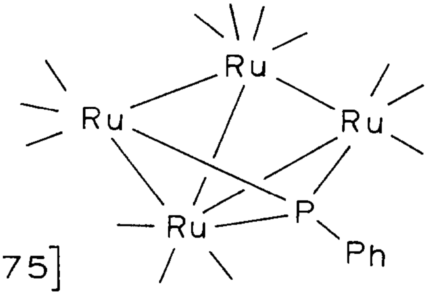

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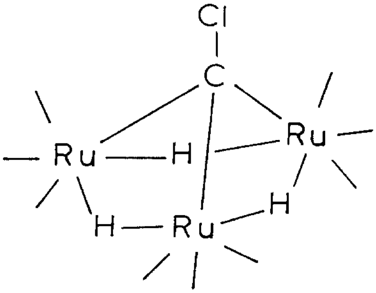


[76]

assignments made for the H_3Ru_3CX core. Normal coordinate analysis was used to derive the force constants for comparison with those of the Co analogs (181).

Gas-phase UV photoelectron spectra and Fenske-Hall MO calculations of $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X=H,Cl,Br) were reported. Comparison of these results to similar studies of $Ru_3(CO)_{12}$ suggests that the Ru-H-Ru interaction is a 3-center, 2-electron bridge with no direct Ru-Ru bond. The Ru-C bond is best described in terms of a sp-hybridized C which forms delocalized Ru-C bonds with the remaining C 2p orbitals. The sp "lone pair" is not delocalized onto the cluster and retains considerable C character. The HOMO is mainly Ru-C in character, unlike the analogs $Co_3(\mu_3\text{-}CX)(CO)_9$, which have a HOMO involving mainly Co-Co bonding. Another difference between these Ru and Co clusters is that the orbital which is $(C\ 2p_\pi\text{-}\{e_g^*\})$ bonding in the Co clusters is a bent bond outside the Co_3C tetrahedron, while in the Ru clusters this orbital is directed along the edge of the Ru_3C tetrahedron (182).

Pyrolysis of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ in refluxing benzene forms what was suggested from the ^1H and ^{13}C NMR spectra to be $H_2Os_3(CO)_9(\mu_3\text{-}1,2\text{-}\eta^2\text{-}CCO)$ [77] in 80% yield (183). A crystal structure determination (184) later showed this to contain a $\mu_3\text{-}\eta^1\text{-}CCO$ ligand [78]. The cluster adds methanol to form $H_3Os_3(\mu_3\text{-}CCO_2Me)(CO)_9$.

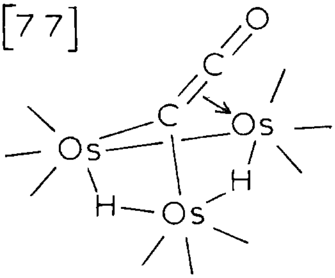
Carbonylation of $HOs_3(CO)_{10}(CF_3C{=}CHCF_3)$ yields first cis- and trans-isomers of $Os_3(CO)_{11}(CF_3CH{=}CHCF_3)$ and then the free alkene and $Os_3(CO)_{12}$. The crystal structure determination for $Os_3(CO)_{11}$(cis-$CF_3CH{=}CHCF_3$) [79] is the first for a monosubstituted alkene derivative of a binary metal carbonyl cluster (185). The C=C bond is in the same plane as the Os_3 triangle.

Keten and $Os_3(CO)_{10}(NCMe)_2$ yield $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ (49%), but diketen produces $Os_3(CO)_{11}(C_3H_4)$ [80] (18%), a μ-allene cluster (186). The allene complex was prepared by other workers in quantitative yield from $Os_3(CO)_{11}(NCMe)$ and allene, and the structure was determined by X-ray crystallography (187). Pyrolysis of $Os_3(CO)_{11}(C_3H_4)$ at 125° gives $Os_4(CO)_{12}(CHCMe)$ in 50% yield. Diazomethane reacts with $Os_3(CO)_{11}(NCMe)$ to give $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$, as well (187). Vinylene carbonate and $Os_3(CO)_{10}(NCMe)_2$ form $Os_3(CO)_{10}(CHCHO)$ [81] in 65% yield (186).

In refluxing decalin, pyrrole and $Os_3(CO)_{12}$ give $H_2Os_3(\mu_3\text{-}C_4H_2NH)(CO)_9$ [82] in 54% yield. The N-methyl analog is similarly prepared in 46% yield. The amino hydrogen does not exchange with D_2O. Hydride fluxionality is found in both complexes (188).

Pyrolysis of $Os_3(CO)_{11}\{AsMe_2(C_6H_4Me\text{-}2)\}$ at 125° yields $HOs_3(CO)_9(\mu\text{-}AsMe_2)$-$(\mu_3\text{-}C_6H_3Me\text{-}4)$ [83]. From 2- or $4\text{-}MeOC_6H_4AsMe_2$, the $3\text{-}MeOC_6H_3$ complex is formed. These complexes exist in solution as rapidly interconverting isomers differing in the relative positions of the hydride and R substituents (189).

The conversion of $H_2Os_3(CO)_{10}\{CN(CH_2)_3Si(OEt)_3\}$ to $HOs_3(CO)_{10}\{\mu\text{-}CNH(CH_2)_3\text{-}$



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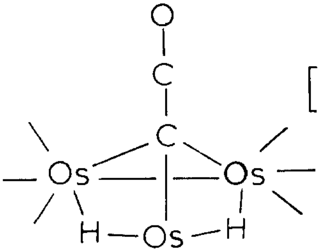

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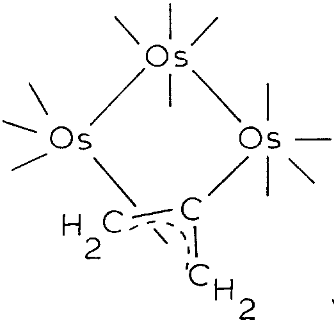

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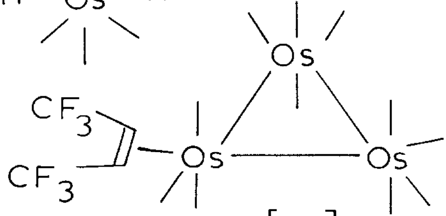

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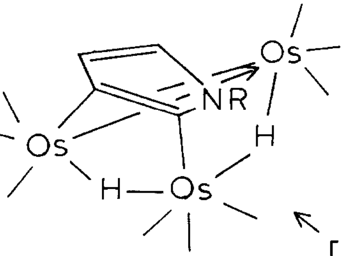

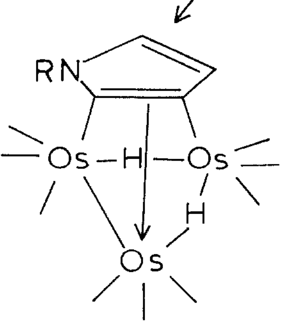

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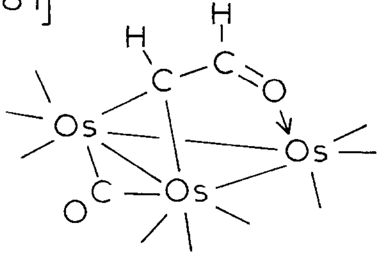

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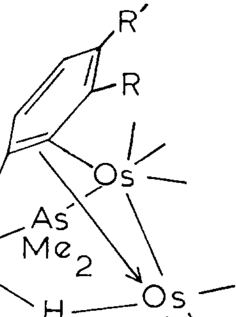
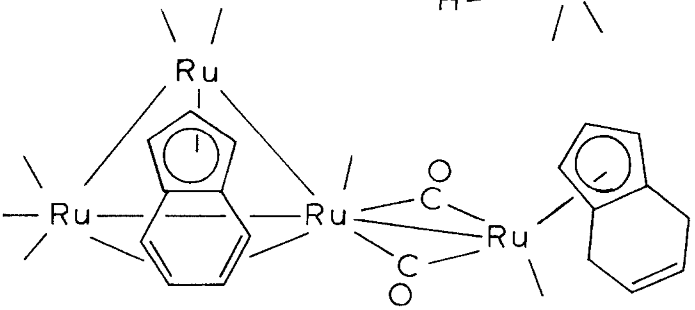


[83]

R = OMe, R′ = H

R = H , R′ = Me



[84]

$Si(OEt)_3\}$ is accelerated by interaction of the cluster with some metal oxides (Al_2O_3, TiO_2, SiO_2, ZnO, MgO). The ultimate product is the oxide-supported cluster $HOs_3(CO)_{10}\{\mu\text{-}CNH(CH_2)_3Si(OEt)_{3-x}(O\equiv)_x\}$, where $O\equiv$ indicates the oxide support (190).

Tetranuclear and Larger Clusters

Protonation of a number of metal carbonyls, including $Ru_4(CO)_{13}^{2-}$, $Ru_6(CO)_{18}^{2-}$, and $Ru_3Co(CO)_{13}^{-}$, with trifluoromethanesulfonic acid yields methane via reduction of coordinated CO. Protonation of $HRu_3(CO)_{11}^{-}$ yields only a trace of methane and protonation of $Ru_3(CO)_{12}$, none. The order of reactivity is: $Co_4(CO)_{12} < FeCo_3(CO)_{12}^{-} < Ru_3Co(CO)_{13}^{-} < Fe_3Co(CO)_{13}^{-} < Ru_4(CO)_{13}^{2-} < Fe_4(CO)_{13}^{2-}$ (191).

A kinetic study of catalytic hydrogenation of ethylene using $H_4Ru_4(CO)_{12}$ was described. At 70° the stoichiometric reaction forms two moles of ethane per mole of cluster. The rate of the catalytic reaction is inhibited by CO and is first-order in cluster concentration. The rate law is:

$$-\frac{d[C_2H_4]}{dt} = \frac{k_4' K_3' \,[P_{C_2H_4}][P_{H_2}][Ru_4]_{Total}}{1 + K_2' \,[P_{H_2}] + K_3' \,[P_{C_2H_4}] + P_{CO}/K_1'}$$

The proposed mechanism is:

$$H_4Ru_4(CO)_{12} \overset{K_1}{\rightleftarrows} H_4Ru_4(CO)_{11} + CO$$

$$H_2 + H_4Ru_4(CO)_{11} \overset{K_2}{\rightleftarrows} H_6Ru_4(CO)_{11}$$

$$C_2H_4 + H_4Ru_4(CO)_{11} \overset{K_3}{\rightleftarrows} H_3Ru_4(CO)_{11}(C_2H_5)$$

$$H_2 + H_3Ru_4(CO)_{11}(C_2H_5) \xrightarrow{k_4} H_4Ru_4(CO)_{11} + C_2H_6$$

The value for k_H/k_D is 1.22. H-D exchange with unreacted ethylene was also noted (192).

Photolysis of $H_4Ru_4(CO)_{12}$ causes CO dissociation. In the presence of $L=P(OMe)_3$ or PPh_3 the substitution product $H_4Ru_4(CO)_{11}L$ is formed. In the presence of alkenes $H_2Ru_4(CO)_{13}$ is the principal Ru-containing product, and irradiation of $H_2Ru_4(CO)_{13}$ in the presence of an alkene accelerates catalysis of alkene isomerization and causes stoichiometric alkene hydrogenation. No alkene reduction occurs at 25° in the absence of light (193). Another group found that photolysis at wavelengths $\geqslant$310 nm causes hydrogenation. Induction periods are noted and catalytis activity gradually decreases after the light is off. Neither carbon tetrachloride nor oxygen affects the activity but CO suppresses hydrogenation. Recovery of the cluster is 100% within experimental error (194).

In refluxing methylcyclohexane $Ru_4(CO)_9(\mu_3\text{-}\eta^2,\eta^5,\eta^2\text{-indenyl})(\eta^5\text{-dihydroindenyl})$ [84] (9.6%) and $Ru_2(CO)_4(\eta^5\text{-indenyl})_2$ (9.4%) are products from the reaction of $Ru_3(CO)_{12}$ and indene. The X-ray crystal structure determination for [84] was reported. The Ru_4 frame is planar (195).

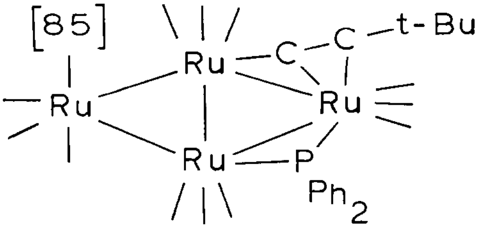
Pyrolysis of $Ru_3(CO)_{11}(Ph_2PC_2\text{-}\underline{t}\text{-Bu})$ and $Ru_3(CO)_9(Ph_2PC_2\text{-}\underline{t}\text{-Bu})_3$ form $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2\text{-}\underline{t}\text{-Bu})$ [85] (10%) and $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(C_2\text{-}\underline{t}\text{-Bu})_2$-$(Ph_2PC_2\text{-}\underline{t}\text{-Bu})$ [86] (10%), respectively. Pyrolysis of $HRu_3(CO)_9(PPh_2)$ yields $Ru_4(CO)_{13}(PPh)$ (50%). All products were characterized crystallography. The skeletal geometry of each of these can be correlated with the electronic structure. Clusters having 62-electron counts have butterfly structures, while those having 64 electrons have almost planar frameworks (196).

Pyrolysis of $Ru_3(CO)_{12}$ in the presence of excess styrene yields $Ru_4(CO)_{12}$-(PhC_2H) [87] and $Ru_4(CO)_9(PhC_2H)(PhEt)$ [88], characterized by ^1H and ^{13}C NMR spectroscopy and by mass spectrometry. Upon further heating binuclear complexes are formed (97).

Reactions between $H_3M_4(CO)_{12}^-$ and NO^+ give rise to several different products. From $H_3Os_4(CO)_{12}^-$ and $[NO][BF_4]$ the nitrosyl-substituted cluster $H_3Os_4(CO)_{12}(\mu\text{-}NO)$ [89] is isolated in 30% yield; the structure was determined by X-ray methods. The analogous reaction involving $H_3Ru_4(CO)_{12}^-$ forms $HRu_4N(CO)_{12}$ in low yield; the $P(OMe)_3$-substituted derivative [90] was prepared and its crystal structure determined (198). However, in acetonitrile oxidation of $H_3Os_4(CO)_{12}^-$ by [NO][X] ($X{=}BF_4,PF_6$) forms $[H_3Os_4(CO)_{12}(NCMe)_2][X]$ [91] in 35% yield; this product was also characterized crystallographically. The cationic cluster can also be formed by cyclic voltammetry on $H_3Os_4(CO)_{12}^-$ in acetonitrile (199).

In refluxing toluene $Ru_3(CO)_{12}$ and phenylphosphine react to produce a variety of clusters including $HRu_3(\mu\text{-}PHPh)(CO)_{10}$, $H_2Ru_3(\mu_3\text{-}PPh)(CO)_9$, $Ru_5(\mu_4\text{-}PPh)(CO)_{12}$, and $Ru_4(\mu_4\text{-}PPh)_2(CO)_{11}$ [92], the last of which was characterized by X-ray crystallography (200). Carbon monoxide reversibly adds to [92] to give $Ru_4(\mu_3\text{-}PPh)_2(CO)_{13}$ [93]. Carbonylation is accompanied by cleavage of Ru-Ru and Ru-P bonds. Crystal structures for $Ru_4(\mu_3\text{-}EPh)_2(CO)_{13}$ (E=P or As) were reported (201).

At 165° and under a CO atmosphere, $Os_6(CO)_{18}$ and excess CS_2 generate $Os_3(CO)_8(CS)(S)_2$, $Os_3(CO)_9(S)_2$, and $Os_4(CO)_{12}(CS)S$ [94]. The tetranuclear cluster was characterized by X-ray methods (202).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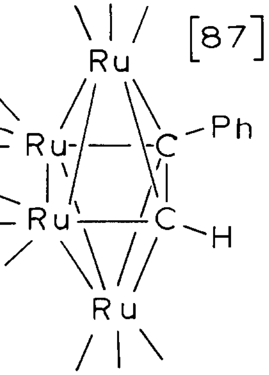
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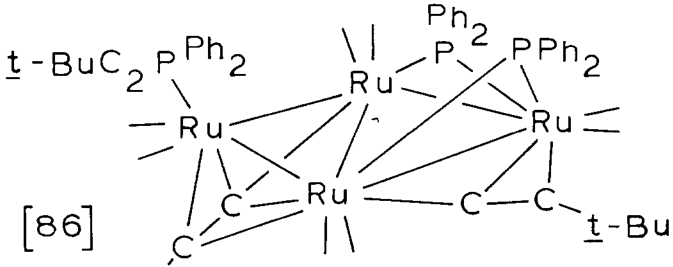
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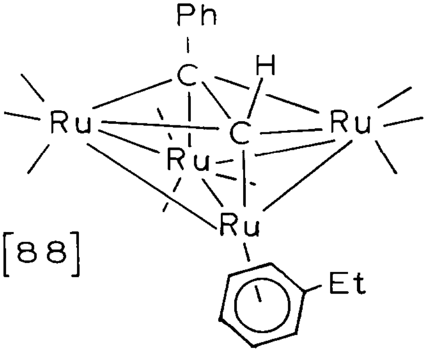
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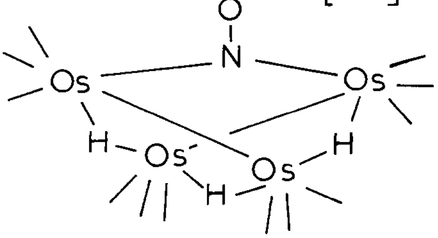
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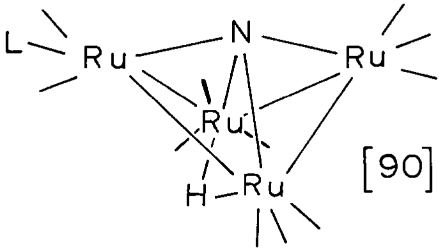
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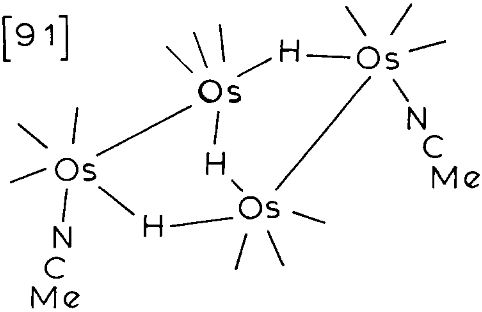
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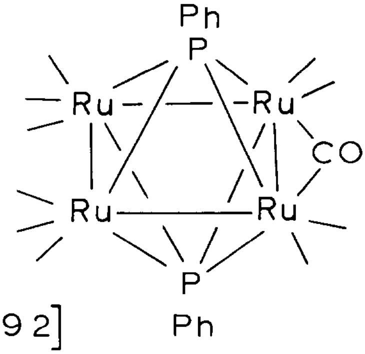
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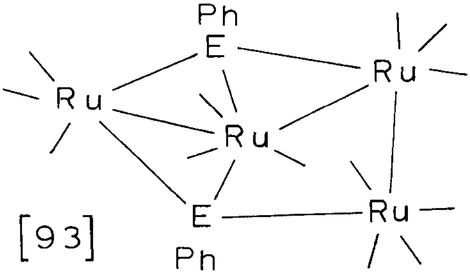

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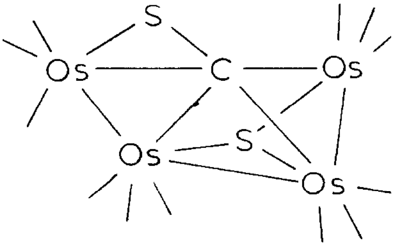

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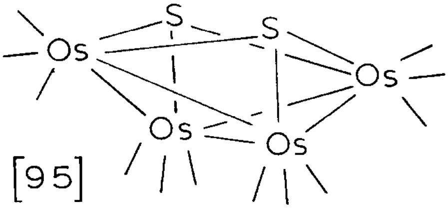

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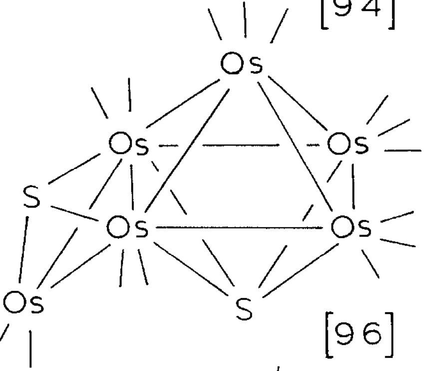

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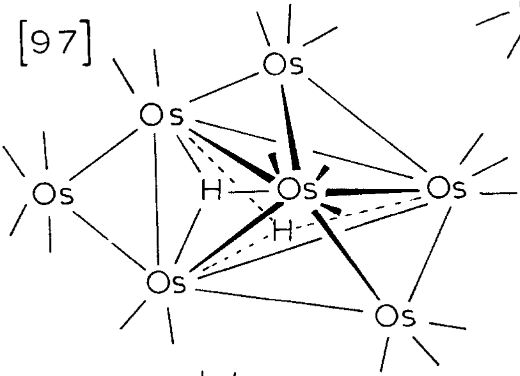

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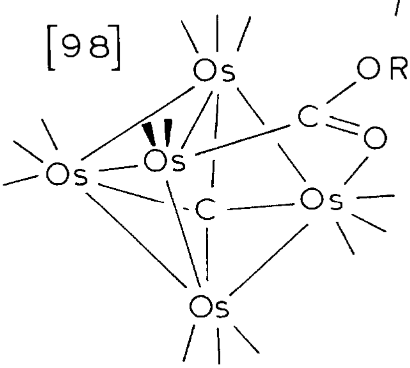

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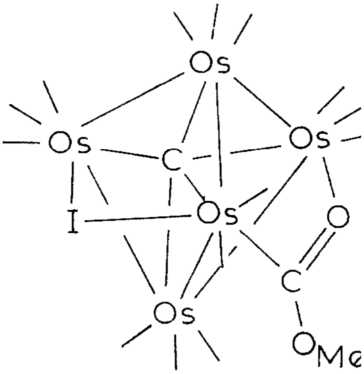

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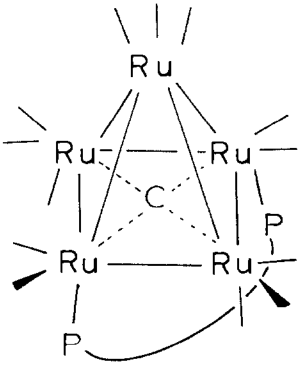


[100]

Larger Clusters

A "cluster cone angle" has been defined and computed from $M(CO)_3$, $M(CO)_2$, and M(CO) fragments (203). The cluster cone angle is similar to the Tolman cone angle for ligands bound to a single metal atom, but the tip of the cone is defined as the center of the metal polyhedron and the cone encloses the ligand bound to the metal atoms on the cluster surface. The cluster cone angle is useful in evaluating steric effects due to ligand packing on the cluster. The maximum number of ligands that can fit around a given metal polydedron, n_{max}, is established by the formula:

$$n_{max} = \text{ideal polyhedral cone angle} \times \text{no. of metal atoms/M(CO) cone angle}$$

The IR vibrational frequencies associated with the carbonyl ligands of $Ru_6C(\mu\text{-}CO)(CO)_{16}$ were recorded and analyzed (204).

Pyrolysis of $HOs_3(CO)_{10}(\mu\text{-}SPh)$ in refluxing nonane yields $H_2Os_3(\mu_3\text{-}S)(CO)_9$ (trace), $Os_3(\mu_3\text{-}S)_2(CO)_9$ (10%), $Os_4(\mu_3\text{-}S)(CO)_{12}$ (10%), $Os_4(\mu_3\text{-}S)_2(CO)_{12}$ [95] (2%) and $Os_6(\mu_3\text{-}S)(\mu_4\text{-}S)(CO)_{16}$ [96] (15%). The structures of the last two products were determined by X-ray crystallography (205).

The stepwise buildup of Os_4 and Os_7 clusters is achieved via reactions of "lightly stabilized" clusters. Syntheses thus achieved are:

$$H_2Os(CO)_4 + Os_3(CO)_{11}(NCMe) \rightarrow H_2Os_4(CO)_{15} \qquad (70\%)$$

$$H_2Os(CO)_4 + Os_3(CO)_{10}(NCMe)_2 \rightarrow H_2Os_4(CO)_{14}(NCMe) \qquad (75\%)$$

$$Os(CO)_4^{2-} + Os_3(CO)_{10}(NCMe)_2 \xrightarrow{H+} H_2Os_4(CO)_{13} \qquad (80\%)$$

$$H_2Os(CO)_4 + Os_6(CO)_{17}(NCMe) \rightarrow H_2Os_7(CO)_{21} \qquad (28\%)$$

$$H_2Os_7(CO)_{21} \xrightarrow{\Delta} H_2Os_7(CO)_{20}$$

The crystal structure of $H_2Os_7(CO)_{20}$ [97] was reported; the hydride positions were proposed, based upon potential energy calculations. A second cluster of the same formulation is prepared by protonation of $Os_7(CO)_{20}^{2-}$ (206).

Reactions of pentanuclear clusters with alcohols have been investigated. Attack on the carbonyl ligand leads to carboalkoxy-containing products $HOs_5C(CO)_{14}(CO_2R)$ [98] and $Os_5IC(CO)_{14}(CO_2R)$ [99] from $Os_5C(CO)_{15}$ and $Os_5I_2C(CO)_{15}$, respectively. The structures of the products were determined by X-ray crystallography (207).

An analysis of the IR spectra of $M_5C(CO)_{15}$ (M=Fe,Ru,Os) found "extra" bands due to M-C stretches for M=Ru or Os, apparently due to multiple-size occupancy displayed in the crystal, rather than intermolecular vibrational coupling. Values between 811 and 730 cm^{-1} are found, with three bands expected. The frequencies of the M-C vibrations decrease in the order Fe>Os>Ru (208).

The effect of chain length upon coordination of $Ph_2P(CH_2)_nPPh_2$ (n=1,2,3,4) in $Ru_5C(CO)_{13}(P-P)$ was examined. With dppb (n=4) the thermodynamic product is $Ru_5C(CO)_{13}(dppb)$ [100]; the structure was determined by X-ray methods. The kinetic products are isomers [101] and [102]. With dppp (n=3) structure [100] is the kinetic product, while [101] and [102] are the thermodynamic products. Two products from dppm (n=1) are $Ru_5C(CO)_{11}(dppm)_2$ and $Ru_5C(CO)_{13}(dppm)$, which exists as an equilibrium mixture of [101] and [102]. Finally, dppe gives $Ru_5C(CO)_{13}(dppe)$, which exists as structure [102] (209).

Improved syntheses for a number of larger Ru and Os clusters have been developed. Reduction of $Ru_3(CO)_{12}$ with sodium in refluxing THF gives a 78% yield of $Ru_6(CO)_{18}^{2-}$; in refluxing diglyme this anion is converted to $Ru_6C(CO)_{16}^{2-}$ (93% yield). Reduction of $Os_3(CO)_{12}$ with sodium in refluxing diglyme yields $Os_6(CO)_{18}^{2-}$ (65%) but in triglyme the major product is $Os_{10}C(CO)_{24}^{2-}$ and in tetraglyme (230-260°C) the latter anion is formed in 63% yield. Oxidation of $Ru_6C(CO)_{16}^{2-}$ with ferric ion under CO yields $Ru_6C(CO)_{17}$ (68%); the analogous reaction with $Os_6(CO)_{18}^{2-}$ gives $Os_6(CO)_{18}$ (88%) (210).

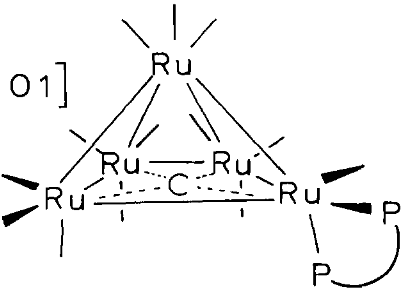
Thermolysis of $HOs_3(\mu_3\text{-}S)(\mu\text{-}HCNR)(CO)_9$ (R=Ph, C_6H_4F-4) causes CO loss and condensation to $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)_2(CO)_{17}$ [103] and $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)\text{-}(\mu\text{-}HC{=}NR)_2(CO)_{16}$ [104]. The former product is believed to be the precursor to the latter. Crystal structures of both products were reported (211).

Ru and Os clusters under high pressures of CO and hydrogen were examined using IR spectroscopy. Under 90 atm of CO and at 160° $Os_6(CO)_{18}$ in solution is converted in one hour to $Os_5(CO)_{19}$ and $Os(CO)_5$; however, in the solid state $Os_6(CO)_{18}$ is carbonylated to $Os_6(CO)_{20}$. Carbonylation of $Os_5(CO)_{19}$ yields $Os_3(CO)_{12}$ and $Os_2(CO)_9$. Combination of $Os_2(CO)_9$ and $Os_5(CO)_{19}$ gives $Os_7(CO)_{21}$. Thermolysis of $Os_5(CO)_{19}$ generates $Os_5(CO)_{16}$ but the reaction is reversed under CO. Hydrogenation of $Os_5(CO)_{16}$, $H_2Os_5(CO)_{16}$, $Os_6(CO)_{18}$ or $H_2Os_6(CO)_{18}$ gives $H_4Os_4(CO)_{12}$ and $H_2Os(CO)_4$. Other reactions investigated were carbonylation of $Ru_3(CO)_{12}$ to $Ru(CO)_5$, carbonylation of $Ru_6C(CO)_{17}$ to $Ru_5C(CO)_{15}$ and $Ru(CO)_5$, and thermolysis of $H_2Ru_6(CO)_{18}$ under argon to $Ru_6C(CO)_{17}$ (212).

Reactions of pentanuclear Os carbonyls were studied. Carbonylation of $Os_6(CO)_{18}$ at 160° and 90 atm allows the synthesis of $Os_5(CO)_{19}$ [105] in 80% yield; the crystal structure of the product was reported. This cluster reacts with $L{=}P(OMe)_3$ (1 h) or PEt_3 (20 h) at 40° to give $Os_5(CO)_{16-n}L_n$ (n=1 or 2). Decarbonylation of $Os_5(CO)_{19}$ at 120° for 15 min gives $Os_5(CO)_{16}$, which can be recarbonylated at 155° and 50 atm for 1 h. Addition of $L{=}P(OMe)_3$ or PEt_3 to $Os_5(CO)_{16}$ forms $Os_5(CO)_{16}L_3$; the structure of the $P(OMe)_3$ derivative [106] was reported (213).

Upon dissolution in acetonitrile, $Ru_5C(CO)_{15}$ forms $Ru_5C(CO)_{15}(NCMe)$ [107], the structure of which was determined by X-ray crystallography. The Ru-C(carbide)

[101]



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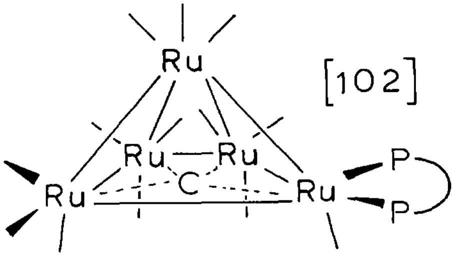

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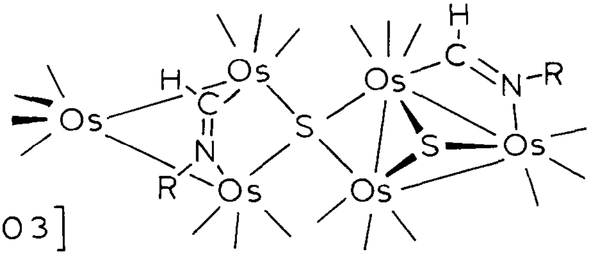

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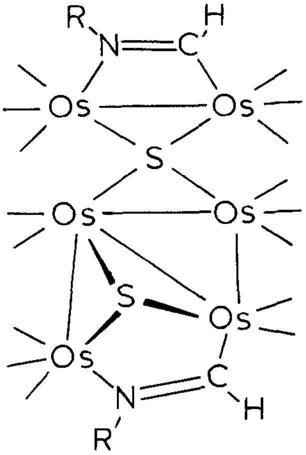

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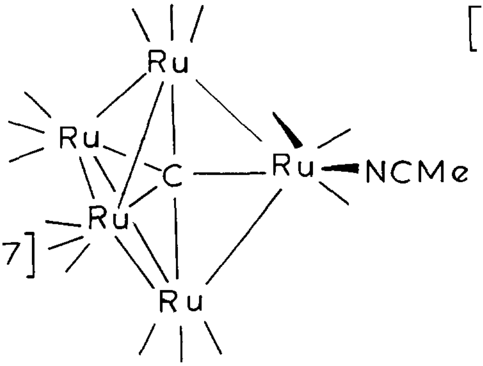

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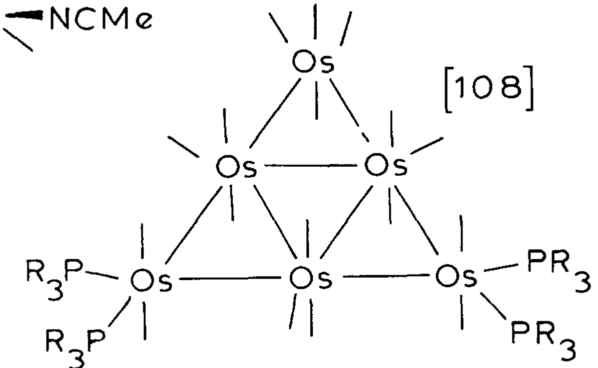

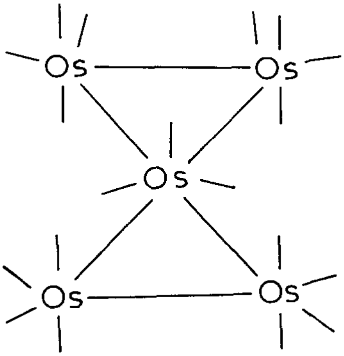

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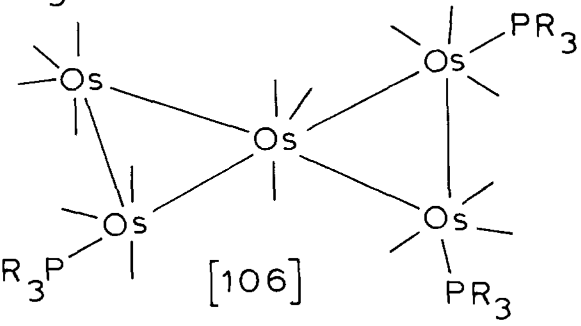


[106]

stretches occurs at 817 and 674 cm^{-1} (214).

Substitution on $Os_6(CO)_{20}$ by $P(OMe)_3$ produces $Os_6(CO)_{21-n}\{P(OMe)_3\}_n$ (n=1-6). The structure of the tetrasubstituted cluster [108] was determined by X-ray diffraction. The parent carbonyl is still unknown (215).

The first cluster containing more than six Ru atoms, $Ru_{10}C_2(CO)_{24}^{2-}$ [109], has been prepared in 35% yield through pyrolysis of $[NEt_4]_2[Ru_6C(CO)_{16}]$ in tetraglyme at 220° for 8 h. The counterion influences the reaction; NEt_3R^+ (R=Et,Bz) or NBu_4^+ as counterions are successful, while Na^+, NMe_3Bz^+, or PPN^+ are not. The structure of the product was established by X-ray crystallography. The ^{13}C resonance for the carbides is at 457 ppm (216).

Pyrolysis of $Os_3(CO)_{11}(py)$ at 250° under vacuum produces $Os_{10}C(CO)_{24}^{2-}$, isolated after treatment with [PPN]Cl in 13-65% yield, and $HOs_5C(CO)_{14}(NC_5H_4)$ (4%). Other products formed are $H_4Os_4(CO)_{12}$, $HOs_3(NC_5H_4)(CO)_{10}$, and $[PPN][HOs_5(CO)_{15}]$. Crystal structures for $Os_{10}C(CO)_{24}^{2-}$ [110] and $HOs_5C(CO)_{14}(NC_5H_4)$ [111] were reported (217).

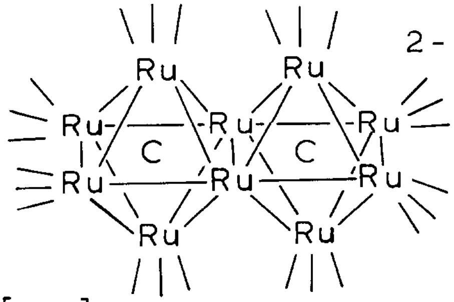
Protonation of $Os_{10}C(CO)_{24}^{2-}$ with concentrated sulfuric acid yields $HOs_{10}C(CO)_{24}^-$ and $H_2Os_{10}C(CO)_{24}$. An X-ray study of the $AsPh_4$ and $PMePh_3$ salts of the monoanion showed a close-packed carbonyl distribution, essentially the same as found for the dianion [110]. It was suggested that the hydride ligand is in a tetrahedral site. The hydride resonance is at -15.25 ppm (218).

Proton NMR spectra for $HOs_3(\mu\text{-}Cl)(CO)_{10}$, $HOs_3Cl(CO)_{11}$, $K[H_3Os_4(CO)_{12}]$ (two isomers), $[PPN][HOs_{10}C(CO)_{24}]$ and $H_4Os_4(CO)_{12}$ were recorded and ^{187}Os-^{1}H coupling constants determined. Based upon these values, the hydride ligand of $HOs_{10}C(CO)_{24}^-$ is proposed to occupy an interstitial tetrahedral hole (219).

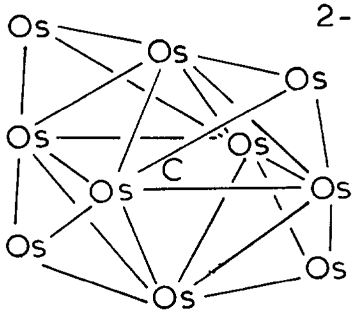
Below 70 K, $H_2Os_{10}C(CO)_{24}$, an even-electron cluster, is paramagnetic. This is a direct verification that this cluster, corresponding to an Os metal particle with a diameter of 10 Å, has magnetic properties similar to those of small metal particles and displays quantum-size effects. Magnetic susceptibility measurements from 4.7 to 300 K for $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$, as well as $H_2Os_{10}C(CO)_{24}$, were reported. At the high temperature limit the diamagnetic susceptibilities are in the order $Os_3<Os_6<Os_{20}$ (220).

Treatment of $Os_{10}C(CO)_{24}^{2-}$ with $[NO][BF_4]$ gives $Os_{10}C(CO)_{24}(\mu\text{-}NO)^-$ [112] in 85% yield. After 10 days, CO loss generates $Os_{10}C(CO)_{23}(NO)^-$. Crystal structures of both anions were reported (221).

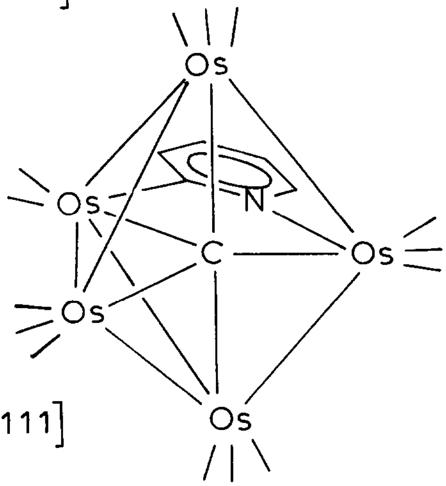
Prolonged heating of $Os_3(CO)_{12}$ and potassium hydroxide in isobutanol produces a mixture of larger clusters, including $HOs_3(CO)_{11}^-$, $HOs_3(O\text{-}\underline{i}\text{-}Bu)(CO)_{10}$, $H_3Os_4(CO)_{12}^-$, $Os_6(CO)_{18}$, $HOs_6(CO)_{18}^-$, and $HOs_{10}C(CO)_{24}^-$. The major product formed from $Os_6(CO)_{18}$ in refluxing isobutanol is $HOs_8(CO)_{22}^-$ [113]; the crystal structure of this product was reported. The last anion is the first example of a high nuclearity Os cluster with only CO and hydride ligands whose structure cannot be explained by extended electron-counting procedures. Protonation of [113] by



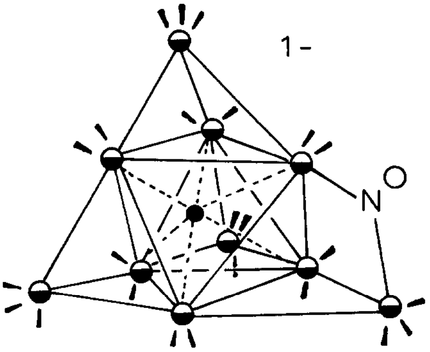
[109]



[110]



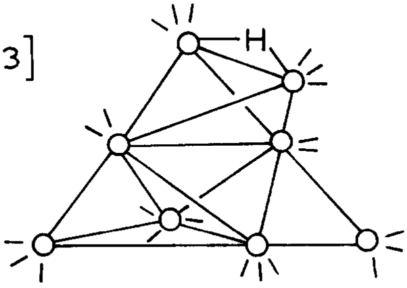
[111]



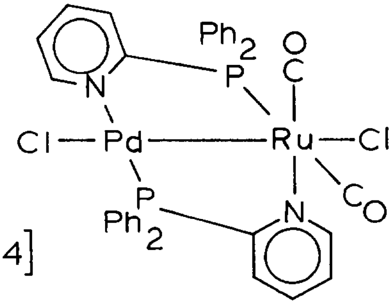
[112]

◒ = Os
● = C

[113]



O = Os



[114]

concentrated sulfuric acid in acetonitrile forms $H_2Os_8(CO)_{22}$, while deprotonation gives the previously known $Os_8(CO)_{22}^-$ (222).

Mixed Metal Clusters

A study of the vibrational spectra of $Os_{3-n}Ru_n(CO)_{12}$ (n=0-3) in the 150-30 cm^{-1} region was reported. A model based upon local C_{2v} symmetry at each metal atom explains the simpler than expected spectra of the mixed metal clusters (223).

Syntheses of mixed metal clusters of Ru and Pd were attempted through reactions of $Ru(Ph_2Ppy)_2(CO)_3$ with $PdCl_2(COD)$ and of $Ru(Ph_2Ppy)_2(CO)_2Cl_2$ with Pd(dibenzylideneacetone)$_3$ (Ph_2Ppy = Ph_2P(2-pyridyl)). In the first case the products are $Ru(Ph_2Ppy)_2(CO)_2Cl_2$, $Ru(Ph_2Ppy)(CO)_2Cl_2$, $Pd_2(Ph_2Ppy)_2Cl_2$ and two isomers of the mixed complex $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$. One of the isomers, [114], was characterized by X-ray methods. The two isomers interconvert upon heating. Combination of the second pair of reactants forms predominantly the two mixed metal species. Other compounds prepared were $Ru_3(CO)_9(Ph_2Ppy)_3$, $Ru(Ph_2Ppy)_2(CO)_3$, $Pd(Ph_2Ppy)_2Cl_2$ and $Pd_2(Ph_2Ppy)_2Cl_2$ (224).

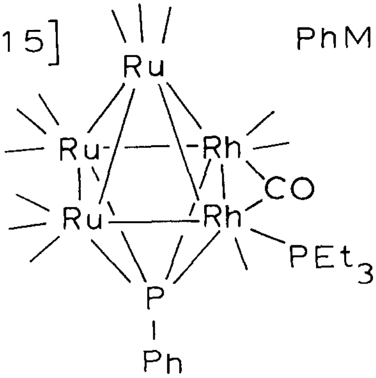
The mixed metal clusters $Ru_3Rh_2(CO)_{13}(PEt_3)(\mu_4\text{-}PPh)$ [115] and $HRu_3Au(CO)_9(PMe_2Ph)(\mu_3\text{-}PPh)$ [116] have been synthesized and their crystal structures determined. Deprotonation of $H_2Ru_3(CO)_9(\mu_3\text{-}PPh)$ with methanolic potassium hydroxide, followed by treatment with $[Rh(CO)_3(PEt_3)_2][BF_4]$ gives a 50% yield of $HRu_3Rh(CO)_{10}(PEt_3)(\mu_3\text{-}PPh)$ and a 5% yield of [115]. Treatment of $HRu_3(CO)_9(\mu_3\text{-}PPh)^-$ with $\{M(PEt_3)I\}_4$ or $[Au(PR_2R')_2][PF_6]$ gives the corresponding $HRu_3M(CO)_9(PEt_3)(\mu_3\text{-}PPh)$ (M=Cu or Ag) or $HRu_3Au(CO)_9(PR_2R')(\mu_3\text{-}PPh)$ (R=R'=Et; R=Me,R'=Ph) (225).

Treatment of $[NEt_4]_2[Ru_6C(CO)_{16}]$ with $[Cu(NCMe)_4][BF_4]$ in acetone generates $(MeCN)_2Cu_2Ru_6C(CO)_{16}$ [117] in 72% yield. The structure of this cluster, determined by X-ray crystallography, is a distorted octahedral Ru_6C core, capped by two directly bonded Cu atoms, one of which caps a trigonal Ru_3 face, a second a $CuRu_2$ face. The Cu-Cu bond distance is 2.693 Å (226).

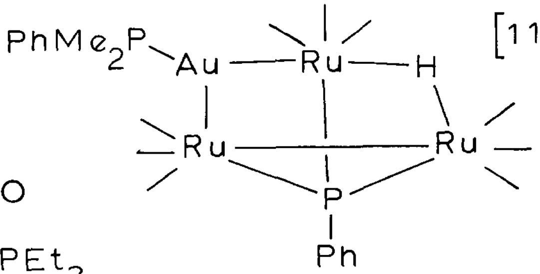
The Au/Co/Ru cluster $Au_3CoRu_3(CO)_{12}(PPh_3)_3$ [118] is prepared in 55% yield from $[PPN][CoRu_3(CO)_{13}]$ and $[\{Au(PPh_3)\}_3O][BF_4]$; the crystal structure of [118] was reported. Unlike $H_3CoRu_3(CO)_{12}$, which has edge-bridging hydride ligands, the Au atoms of [118] are bonded to one another and are face-capping. Also prepared were $AuCoRu_3(CO)_{13}(PPh_3)$ and $HAu_2CoRu_3(CO)_{12}(PPh_3)_2$ (227).

Mixed metal clusters of Os and Au can be prepared through reactions of Os cluster anions with $AuCl(PPh_3)$. Clusters that may be prepared in this manner include $Os_4AuH(CO)_{13}(PR_3)$ [119] (60%), $Os_4AuH_3(CO)_{12}(PR_3)$ [120] (50%), $Os_3FeAuH(CO)_{13}(PEt_3)$ (60%), $Ru_4AuH_3(CO)_{12}(PEt_3)$ (80%), and $Os_5AuH(CO)_{15}(PR_3)$ (50%) (R=Ph,Et). Structures [119] and [120] were determined by X-ray methods (227). The reaction of [120] with $AuCl(PR_3)$, $Tl[BF_4]$, and NEt_3 generates two isomers of the formula $Os_4H_2(CO)_{12}(AuPR_3)_2$. The structure of one isomer, [121],

[115]



[116]



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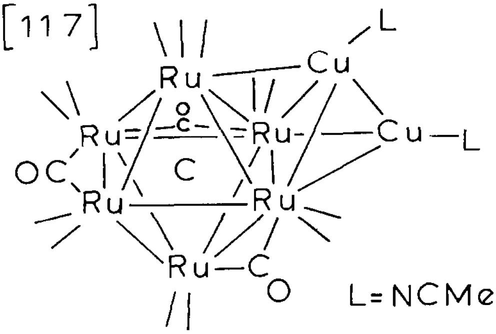
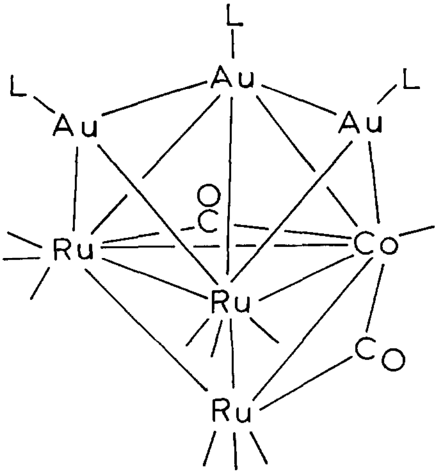
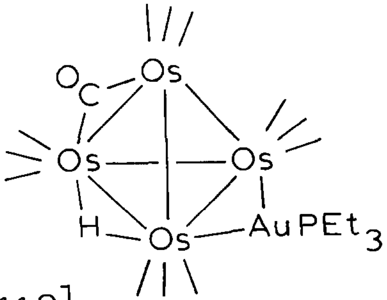


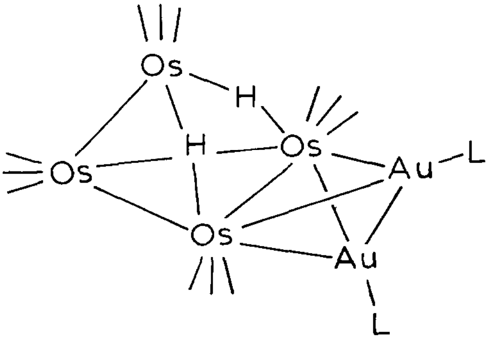
L = NCMe



[118] L = PPh$_3$

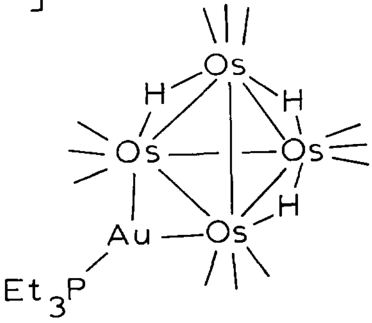


[119]



[121]

L = PPh$_3$



[120]

was determined by X-ray methods. Treatment of $H_4Os_4(CO)_{12}$ with Pt R_2(dppe) (R=Me,Ph) gives $Os_4H_2(CO)_{12}\{Pt(dppe)\}$ (228).

Reactions of methylidyne clusters $HM_3(\mu\text{-}COMe)(CO)_{10}$ (M=Fe,Ru) and $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ with Au and Pt reagents can be used to prepare mixed metal clusters. Treatment of $HM_3(\mu\text{-}COMe)(CO)_{10}$ with $MeAuPPh_3$ leads to $Ph_3PAuM_3(\mu\text{-}COMe)(CO)_{10}$ in 60% yield; the crystal structure of the Ru cluster [122] was reported. Addition of $Pt(C_2H_4)_2PPh_3$ to $HFe_3(\mu\text{-}COMe)(CO)_{10}$ forms $Fe_3PtH(\mu_3\text{-}COMe)(CO)_{10}(PPh_3)$ [123] (50% yield), the structure of which was determined by X-ray crystallography (229). Treatment of $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ with $MeAuPPh_3$ gives methane and mixed metal clusters $AuRu_3H_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)$ [124] (27%), $Au_2Ru_3H(\mu_3\text{-}COMe)(CO)_9(PPh_3)_2$ (21%), and $Ru_3Au_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3$ [125] (12%); the crystal structures of [124] and [125] were reported. A similar reaction yields $Ru_4Au_3H(CO)_{12}(PPh_3)_3$ [126], also crystallographically characterized (230).

In a related synthesis, deprotonation of $HRu_3(C_2\text{-}t\text{-}Bu)(CO)_9$ with sodium hydride, followed by treatment of the cluster anion with $ClAuPPh_3$, yields $Ph_3PAuRu_3(C_2\text{-}t\text{-}Bu)(CO)_9$ [127], the structure of which was determined by X-ray crystallography (231).

Mixed Ru/Pt clusters have been prepared (232). The reaction between $Ru_3(CO)_{11}(CN\text{-}t\text{-}Bu)$ and $Pt(C_2H_4)(PPh_3)_2$ at -30°C forms an intermediate X. Upon warming to 25°C, X forms a mixture of products including $Ru_2Pt(CO)_7(PPh_3)_3$, $RuPt_2(CO)_5(PPh_3)_3$ [128] (structurally characterized), $RuPt_2(CO)_7(CN\text{-}t\text{-}Bu)(PPh_3)$, and $Ru_2Pt_2(CO)_9(CN\text{-}t\text{-}Bu)(PPh_3)$. At 80° $Ru_2Pt_4(CO)_{5-n}(CN\text{-}t\text{-}Bu)(PPh_3)_{4+n}$ (n=0,1) and $Ru_2Pt(CO)_5(CN\text{-}t\text{-}Bu)(PPh_3)_4$ are formed. Reactions of X with CO, CN-t-Bu, PMe_3, $P(C_6H_4Me\text{-}4)_3$ or $P(OMe)_3$ produce substituted Ru_2Pt and $RuPt_2$ clusters.

MO calculations on clusters containing $Pt(PR_3)_2$ fragments have been used to rationalize the structures adopted in terms of the polyhedral skeletal electron pair theory. Clusters thus treated include $Os_3PtH_2(CO)_{10}(PR_3)$ and $Os_2Pt_2H_2(CO)_8(PR_3)_2$ (233).

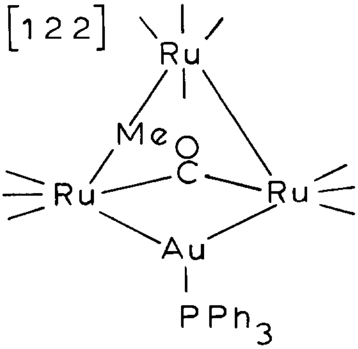
After 6 h at 70°, $H_2IrOs_3(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_9(PPh_3)$ [129] is formed in 15% yield from $Ir(N_2)(PPh_3)_2Cl$ and $H_2Os_3(CO)_{10}$. The structure of the product was determined by X-ray crystallography, although the hydrides were not located (234).

Condensation of $Fe_2(CO)_4Cp_2$ with $HRu_3(CO)_9(C_5H_7)$ forms $CpFeRu_3(CO)_9(C_5H_7)$ [130], characterized by spectroscopic methods. A low yield of $Ru_4(CO)_{12}(C_5H_8)$ [131] is produced from $Ru_3(CO)_{12}$ and $HRu_3(CO)_9(C_5H_7)$. The product structures are interpreted in terms of Wade's rules as cluster expansion from a nido pentagonal bipyramidal cluster to a closo structure (235).

Products from the reaction between $Ru_3(CO)_{12}$ and $Mn(CO)_2(PH_2R)Cp$ are $Cp(CO)_2MnRu_2(CO)_6(\mu_3\text{-}PR)$ [132] and $H_2Ru_3(CO)_9(\mu_3\text{-}PR)$ (R=Cyc,Ph). Crystal structures were determined for both (R=Cyc) (236).

Treatment of $RuCl_2(PPh_2Cl)$(*p*-cumene) with $Co_2(CO)_8$ in THF forms

[122]



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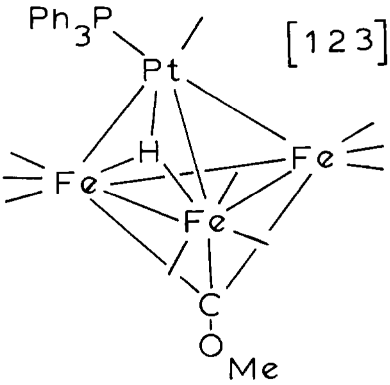

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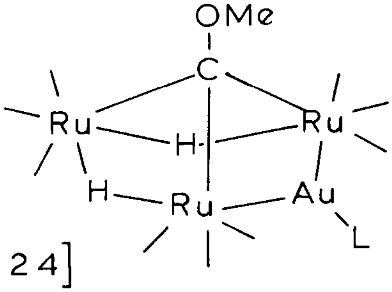

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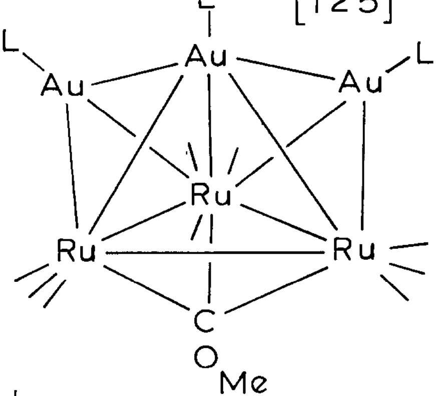

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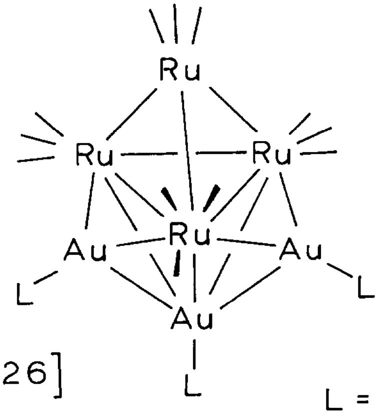

L = PPh$_3$

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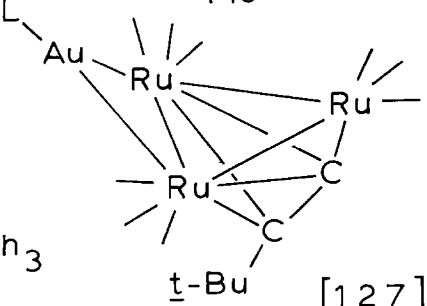

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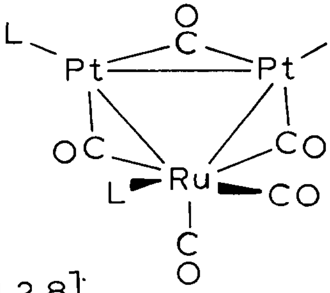

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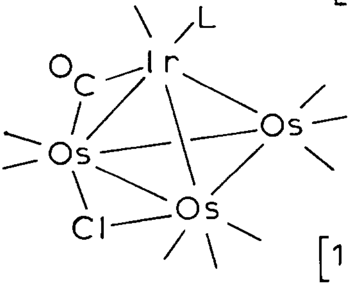

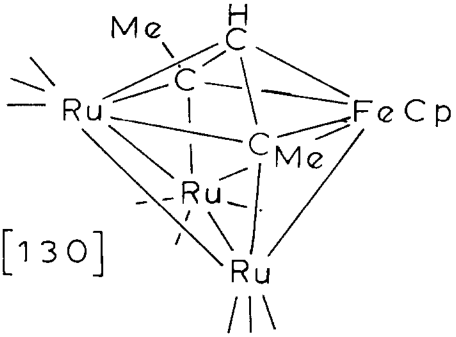

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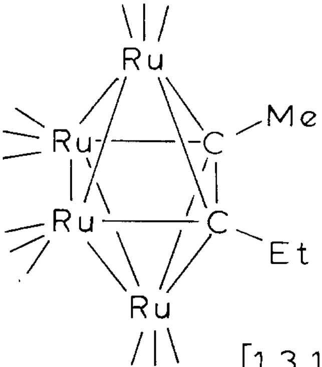

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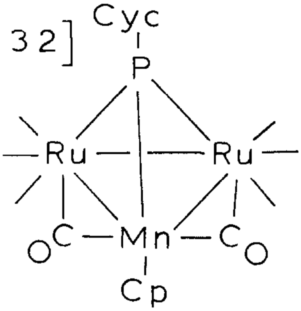

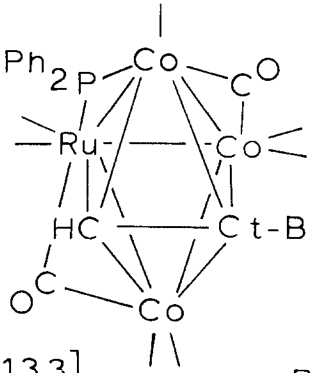

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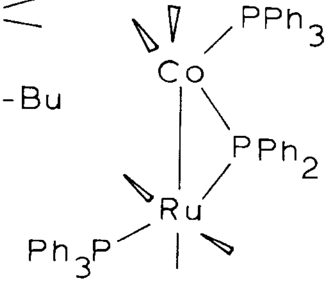

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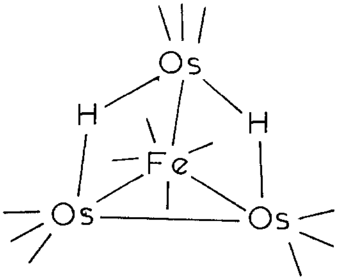

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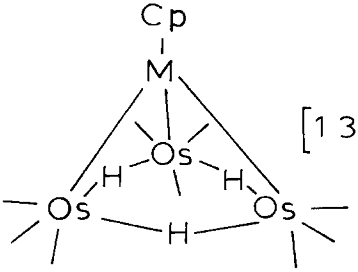

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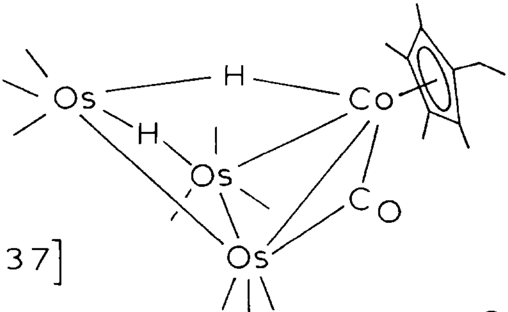

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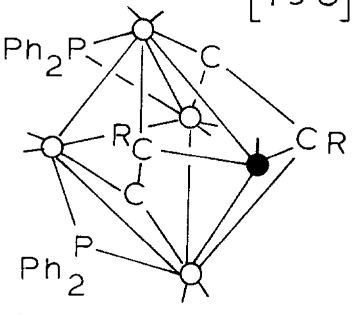


● = Ni , O = Ru , R = i-Pr

RuCo(μ-PPh$_2$)(CO)$_7$ and (*p*-cumene)RuCo(μ-PPh$_2$)(CO)$_4$ (237). However, RuCl$_2$(Ph$_2$PC≡C-*t*-Bu)(*p*-cumene) and Co$_2$(CO)$_8$ form RuCo$_3$(μ-PPh$_2$)(μ_4-η^2-HC≡C-*t*-Bu)(μ-CO)$_2$(CO)$_7$ [133] in 30% yield. The latter product was characterized by X-ray methods (238).

Condensation of Na[Co(CO)$_4$] and RuHCl(CO)(PPh$_3$)$_3$ at 40° for 12 h yields RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$ [134] (28%); the crystal structure of the product was reported. Benzene is a by-product in the reaction. Isomers of the composition RuCoHCl(μ-PPh$_2$)(CO)$_4$(PPh$_3$)$_2$ are formed by treatment of [134] with HCl (239).

A number of mixed metal clusters have been prepared by addition of metal fragments to H$_2$Os$_3$(CO)$_{10}$. Combination of Fe$_2$(CO)$_9$ and H$_2$Os$_3$(CO)$_{10}$ gives an 80% yield of H$_2$Os$_3$Fe(CO)$_{13}$ [135]. The structure, including hydride positions, was determined by X-ray crystallography. The Fe atom has two terminal and two semi-bridging CO ligands. The ^{13}C NMR spectrum of this cluster at -63°C is consistent with the solid state structure, and the temperature dependence of the spectrum is similar to the behavior reported for H$_2$Ru$_3$Fe(CO)$_{13}$ (240). Treatment of H$_2$Os$_3$(CO)$_{10}$ with CpCo(CO)$_2$ and hydrogen at 90°C for 53 h produces H$_3$CoOs$_3$(CO)$_9$Cp [136] (33%), a cluster with one unpaired electron, and H$_4$CoOs$_3$(CO)$_9$Cp (32%); the crystal structure of [136] was reported. Treatment of H$_2$Os$_3$(CO)$_{10}$ with {CpNi(CO)}$_2$ and hydrogen at 90°C for 10 h gives H$_3$NiOs$_3$(CO)$_9$Cp (93%), which was characterized by X-ray crystallography and which is isomorphous with [136]. Other new compounds prepared are H$_2$RhOs$_3$(CO)$_{10}$Cp (42%) and H$_2$IrOs$_3$(CO)$_{10}$Cp (21%) (241). Pyrolysis of Co(η^5-C$_5$Me$_4$Et)(C$_2$H$_4$)Me$_2$ in the presence of H$_2$Os$_3$(CO)$_{10}$ generates H$_2$Os$_3$Co(CO)$_{10}$(η^5-C$_5$Me$_4$Et) [137] (40%), which was characterized by X-ray crystallography; this cluster product is hydrogenated at 80° to give H$_4$Os$_3$Co(CO)$_9$(η^5-C$_5$Me$_4$Et) (85%). Both mixed metal clusters fragment under CO to Os$_3$(CO)$_{12}$ and Co(η^5-C$_5$Me$_4$Et)(CO)$_2$ (242).

Reactions between Co(CO)$_4^-$ and RuCl$_3$·nH$_2$O or RuCl$_3$L$_3$ (L=*o*-MeC$_6$H$_4$CN, PhSMe) form RuCo$_3$(CO)$_{12}^-$. This cluster anion reacts with H$^+$ or Me$_3$CCl to form HRuCo$_3$(CO)$_{12}$ and with Ph$_3$PAuCl to give Ph$_3$PAuRuCo$_3$(CO)$_{12}$. The structure of the latter cluster was determined crystallographically (243).

The ^{13}C NMR spectrum of [PPN][CoRu$_3$(CO)$_{13}$] has been measured as a function of temperature. The lowest energy fluxional process observed involves concerted motion of twelve of the thirteen CO ligands and interconverts the two enantiomers of the cluster. All thirteen CO ligands exchange at higher temperature. Two possible mechanisms have been suggested (244).

Mixed metal clusters of Ru and Ni have been prepared. In refluxing heptane Ru$_3$(CO)$_9$(μ-PPh$_2$)(μ_3-η^2-C≡C-*i*-Pr) and {Ni(CO)Cp}$_2$ (2 mol) form four products, one of which was characterized by X-ray crystallography as NiRu$_4$(CO)$_9$(μ-PPh$_2$)$_2$(μ_4-C$_2$-*i*-Pr)$_2$ [138] (245). On the other hand, treatment of {Ni(CO)Cp}$_2$ with HC$_2$-*i*-Pr in refluxing heptane for 3 h, followed by addition of Ru$_3$(CO)$_{12}$ and refluxing for 20 min gives $Cp_2Ni_2Ru_2(CO)_6\{HC_2C(CH_2)CH_3\}$ [139] (48%), which was characterized by X-ray crystallography (246).

Catalysis by Clusters or Supported Clusters

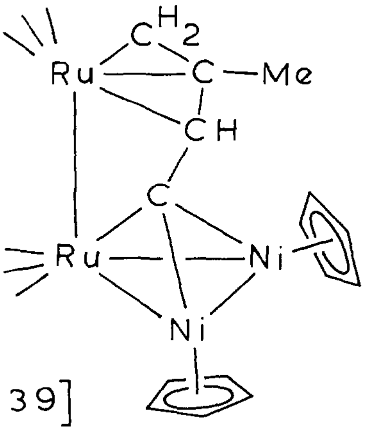
Hydroformylation, hydrogenation, silacarbonylation and hydrosilylation of alkenes are catalyzed by $HRu_3(CO)_{11}^-$. Aldehydes are obtained from ethylene or propylene under CO and hydrogen at 100°. After 5 h, 74% conversion of ethylene is obtained. From propylene the ratio of linear to branched aldehyde is 21. The cluster anion is in equilibrium with $H_3Ru_4(CO)_{12}^-$, which is also a catalyst. Hydrogenation of ethylene or propylene at 20 bar of hydrogen pressure and 100° occurs with a turnover number of 300 after 15 h. The product from $HSiEt_3$, ethylene, and CO at 100° is $MeCH{=}CHOSiEt_3$ (turnover 280); $HRu_3(CO)_{10}(SiEt_3)_2^-$ can be isolated from the reaction. In the absence of CO, the products from ethylene and $HSiEt_3$ are $CH_2{=}CHSiEt_3$ (52%) and $SiEt_4$ (22%) (247).

A kinetic study of catalytic hydrogenation of ethylene using $H_4Ru_4(CO)_{12}$ was described (192). The results are summarized in the subsection of this review on Tetranuclear and Larger Clusters.

Treatment of diphenylphosphino-functionalized polystyrene with $H_2Os_3(CO)_{10}$ or $H_2Os_3(CO)_9(PPh_3)$ gives polymer-supported trinuclear clusters. These supported clusters, characterized by IR spectroscopy, are catalysts for isomerization of 1-hexene but not for hydrogenation of ethylene at 1 atm (248).

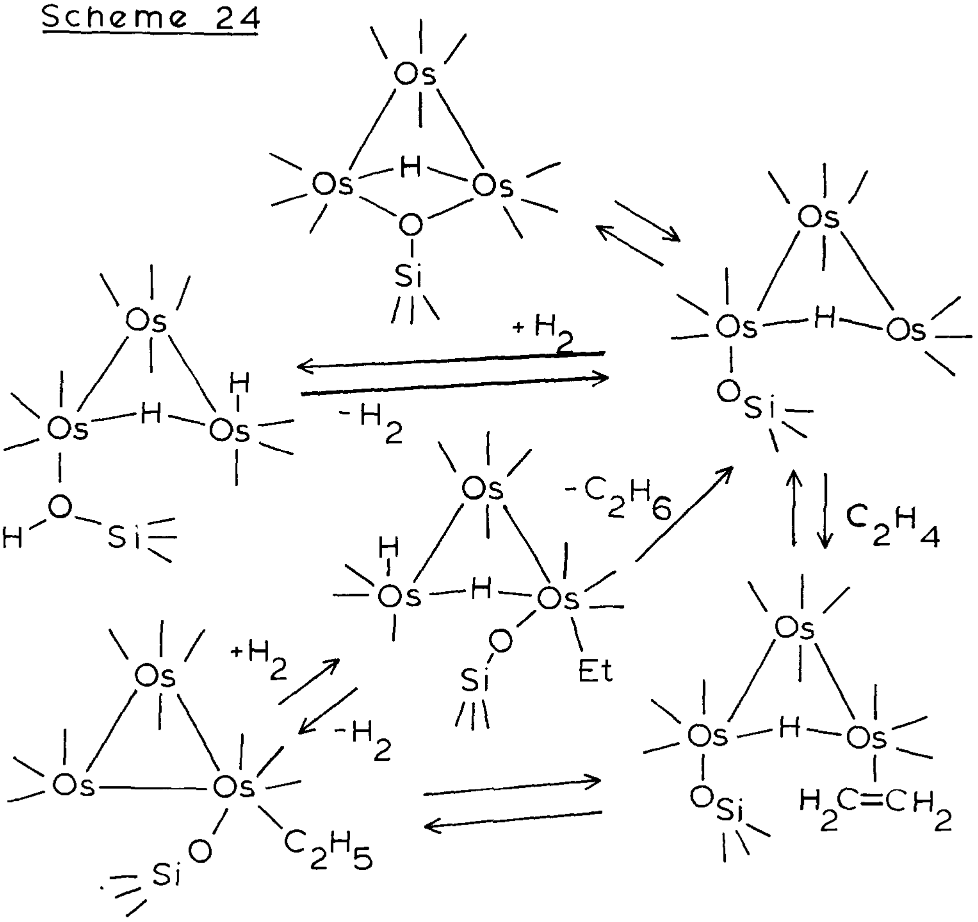
The structure and decomposition of $Ru_3(CO)_{12}$ on oxide supports were examined by IR spectroscopy. Weak interactions exist between the cluster and support for SiO_2 and ZnO, but strong binding to γ-Al_2O_3 gives rise to a stable species presumed to be a mononuclear Ru carbonyl. Thermal decomposition on γ-Al_2O_3, followed by reduction at 450°, produces a highly dispersed catalyst. Adsorption of CO and of hydrogen were examined. Both linear and twin-type CO on Ru were observed on metal derived from $Ru_3(CO)_{12}$ and multiple- and twin-type CO on Ru derived from $RuCl_3$. The twin-type CO is not very reactive toward reduction. The IR bands for CO on Ru/MgO or $Ru/K_2CO_3/Al_2O_3$ are shifted to lower frequencies (249).

Adsorption of $Ru_3(CO)_{12}$ on hydrated Al_2O_3 under oxygen forms an anchored mononuclear dicarbonyl species Ru_B. In the absence of oxygen, hydroxyl groups on the surface act as oxidizing agents at >383 K, and a variety of oxidized Ru species are formed. In vacuo at 423-673 K, dicarbonyl species Ru_A, Ru_B, and Ru_C are formed (IR spectra 2138-2075, 2072-2005, and 2054-1977 cm^{-1}, respectively). At higher temperatures decarbonylation generates an oxidized form of Ru. Decarbonylation under hydrogen favors Ru_C at intermediate temperatures and Ru metal at higher temperatures (250). These supported species were studied under $^{13}CO/^{12}CO$. Species Ru_A, Ru_B, and Ru_C all contain two coupled CO oscillators per Ru atom. The local structure is tetrahedral for Ru_A and octahedral for Ru_B and Ru_C. Ru_B and Ru_C are interconverted under reducing and oxidizing atmospheres



[139]

Scheme 24



and the proposed oxidation states are III for Ru_A, II for Ru_B, and 0 for Ru_C (251). Samples decarbonylated in vacuo are apparently oxidized. The major products are Ru(III), which can act as nucleation centers for formation of very small Ru particles. These particles are broken up by CO at 473 K to low nuclearity, anchored carbonyl species. Samples decarbonylated under hydrogen give rise to larger particles which resist CO attack (252).

A vapor impregnation technique was used to support $Ru_3(CO)_{12}$ on Na-Y zeolite, silica, and alumina. The IR spectra of the supported carbonyl species were reported and depend greatly upon the support. The interaction with the support is directly responsible for the presence of weak, high frequency bands which are characteristic of the support used. There was no experimental evidence to indicate cluster disruption but the supported cluster is unstable in oxygen or air (253).

Catalysts for hydrogenation of carbon dioxide or carbon monoxide have been prepared from $Ru_3(CO)_{12}$, $H_2Ru_4(CO)_{13}$, $H_2FeRu_3(CO)_{13}$, or $[PPN][CoRu_3(CO)_{13}]$ on γ-alumina, silica, or Na-Y zeolite. The catalysts were activated at 200°C under hydrogen. Activities were highest for catalysts on alumina and lowest for catalysts on silica. The most active catalyst was prepared from $Ru_3(CO)_{12}$ (254).

The silica-supported cluster $HOs_3(CO)_{10}(OSi{\equiv})$ is a catalyst for ethylene hydrogenation at up to 373 K. A mechanistic study indicated reversible coordination of ethylene at 253 K. The adduct was suggested to be $Os_3(C_2H_5)(CO)_{10}$-$(OSi{\equiv})$. Hydrogen does not coordinate to $HOs_3(CO)_{10}(OSi{\equiv})$ at 353 K, but at 373 K a species suggested to be $H_2Os_3(CO)_{10}(HOSi{\equiv})$ is formed reversibly. The reaction sequence proposed is shown in Scheme 24 (255).

Catalysts prepared by impregnation of $Os_3(CO)_{12}$, $Os_6(CO)_{18}$, or $Ru_3(CO)_{12}$ on alumina, silica, or titania are active for alkene hydrogenation and alkane hydrogenolysis but are distinguished from conventional supported catalysts by stability in air (256).

Thermal and photochemical anchoring of $H_4Ru_4(CO)_{12}$ to phosphinated silica or alumina forms mixtures of mono- and disubstituted products. The combination of $HOs_3(CO)_{10}\{S(CH_2)_3Si(OMe)_3\}$ with an oxide $M'O_n$ ($M'O_n$=SiO_2,Al_2O_3,TiO_2,SnO_2,ZnO,MgO) forms $HOs_3(CO)_{10}\{S(CH_2)_3Si(OMe)_{3-x}(OM'O_n)_x\}$; this species can also be prepared from $Os_3(CO)_{12}$ and $HS(CH_2)_3Si(OMe)_{3-x}(OM'O_n)_x$. Reactions between $M_3(CO)_{12}$ (M=Ru,Os) and $M'O_n$ form $HM_3(CO)_{10}(OM'O_n)$ and/or oxidized metal carbonyl species. These surface-bound complexes were characterized by IR spectroscopy and were compared with model compounds (257).

In situ Mössbauer studies and simultaneous catalytic reactions of CO and hydrogen to form alkenes were conducted on catalysts prepared from $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ on Cab-O-Sil. The spectrum of the mixed metal system was similar to that of a catalyst derived from $Fe_3(CO)_{12}$ alone, but a large χ-carbide signal was not detected. It was concluded that a reactive surface carbon layer is formed and a stable carbide, also formed, accumulates. A third form of carbon which cannot migrate to form chains but which can be converted to methane was also proposed (258).

A homogeneous catalyst system derived from $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ was used as a model for studying several aspects of heterogeneously catalyzed hydrodenitrogenation (HDN). $Os_3(CO)_{12}$ is a catalyst precursor for catalytic cleavage of C-N bonds in NEt_3 to form $NHEt_2$, NEt_2Bu, and EtOH. Similar products are formed over a common heterogeneous catalyst comprised of Co and Mo on alumina (261).

CATALYSIS AND ORGANIC SYNTHESIS

Reductions and Hydrogen Transfers

Reduction of the prochiral ketones acetophenone and $PhC(O)CH_2CH_2CHMe_2$ by optically active hydrogen donors, such as (-)(S)-2-methylbutan-1-ol, (-)-2-*exo*, 3-*exo*-camphandiol, (-)-1,2-*O*-isopropyliden-α-D-glucofuranose, and (-)-menthol, can be catalyzed by $H_4Ru_4(CO)_8(PBu_3)_4$. Optically active product mixtures are obtained in the case of reduction of acetophenone by 2-*exo*,3-*exo*-camphandiol (0.4% enantioface discrimination) or by 1,2-*O*-isopropyliden-α-D-glucofuranose (1.0% enantioface discrimination) (262).

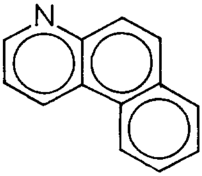
Reduction of polynuclear heteroaromatic compounds [140]-[144] by hydrogen is catalyzed by $RuCl_2(CO)_2(PPh_3)_2$ and by $H_4Ru_4(CO)_{12}$. Using the latter catalyst at a 10/1 substrate:catalyst ratio, reduction under 350 psi of hydrogen and at 150° for 2 h in cyclohexane gives as products 1,2,3,4-tetrahydro-5,6-benzoquinoline (75%), 1,2,3,4-tetrahydro-7,8-benzoquinoline (8%), 9,10-dihydropenantridine (15%), 9,10-dihydroacridine (100%), and 1,2,3,4-tetrahydroquinoline (100%), respectively. Using $RuCl_2(CO)_2(PPh_3)_2$ at 180° in THF, [141] is reduced to 1,2,3,4-tetrahydro-7,8-benzoquinoline (72% yield) (263).

Reduction of aldehydes and ketones to alcohols using formic acid as the hydrogen source is catalyzed by Ru complexes. Catalytic activity decreases in the order: $RuCl_2(PPh_3)_3 > RuHCl(PPh_3)_3 > RuHCl(CO)(PPh_3)_3 > RuH_2(PPh_3)_4$. In a typical example, acetophenone is reduced by formic acid to 1-phenylethanol (84% yield, 90% selectivity) using $RuCl_2(PPh_3)_3$ at 125° for 3 h. Bulky substituents on the ketone reduce the rate. Decomposition of formic acid to hydrogen and CO is very rapid (264).

Reduction of 4-*t*-butylcyclohexanone using di- and trialkylsilanes as the hydrogen source is catalyzed by $RuCl_2(PPh_3)_3$. Best results are obtained at 110° in toluene and with the combination of 1 mol of AgO_2CCF_3 per mol of Ru; in this case the silyl ether product is obtained in 96% yield with an equatorial/axial preference of 5/95 (265).

Nitroalkanes, CO, and water react to form amides (primary), ketones (secondary), or amines (tertiary) using $[Ru(COD)(py)_4][BPh_4]_2$ as a catalyst. Nitrosobenzene and picoline N-oxide are reduced to amines. Oximes are presumed

[140]



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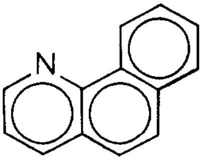

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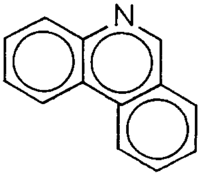

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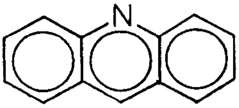

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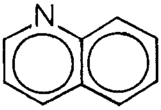
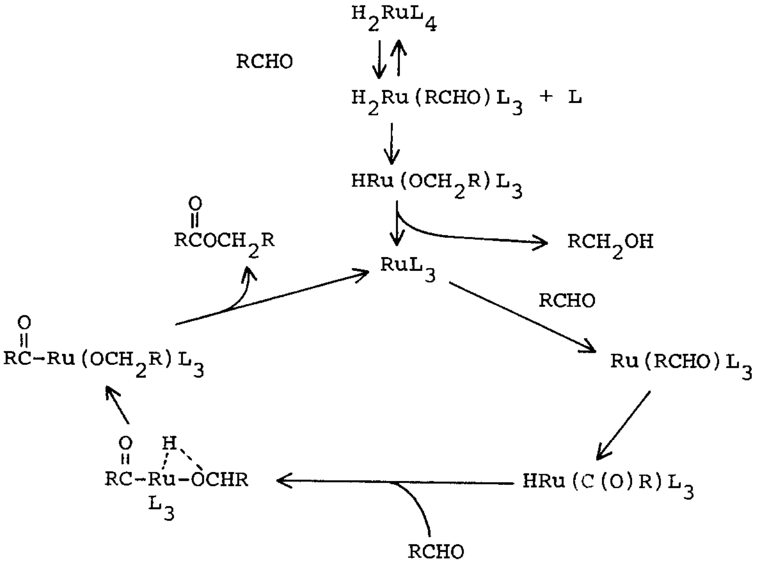


Scheme 25



intermediates in the formation of ketones. Typical conditions are 0.1 mmol catalyst, 20 mmol nitroalkane, and 40 mmol of water in THF at 140° and under 10-80 atm CO for 20 h. Yields of reduced products vary from 54% for $EtC(O)NH_2$ to 100% for picoline (from picoline-N-oxide) (266).

Hydrogen transfer from racemic alcohols to prochiral ketones is achieved using $H_4Ru_4(CO)_8\{(-)\text{-DIOP}\}_2$ as the catalyst precursor. The enantiomeric excess is affected by the structures of the reactants, temperature, and the amount of excess DIOP present. Hydrogen transfer from 1-phenylethanol to 1-phenyl-3-methylbutan-1-one at 100° for 592 h occurs to the extent of 16% and the optical purity of the residual 1-phenylethanol is 1.34% (R configuration) and of the 1-phenyl-3-methylbutan-1-ol is 13.9% (S configuration). Higher temperatures produce higher conversions but lower optical purity (267).

Hydrogen transfer from alcohols to α-trichloromethyl- and α-tribromomethylcarbinols to give dihalomethyl compounds is catalyzed by $RuCl_2(PPh_3)_3$:

$$R^1R^2CHOH + RCH(OH)CX_3 \rightarrow R^1R^2CO + RCH(OH)CHX_2 + HX$$

Benzyl alcohols are very efficient hydrogen donors and aliphatic secondary carbinols are more reactive than primary carbinols. Yield of 16-80% for the dihalides are obtained. Neither radical initiators nor inhibitors affect the rate of the reaction. The addition of the trihalomethyl compound to $RuHCl(PPh_3)_3$ is suggested to be the rate determining step (268).

Hydrogen transfer between natural product alcohols and cyclohexanone is catalyzed by $RuCl_2(PPh_3)_3$ in diphenyl ether at 140°. The trend for decreasing reactivity for hydrogen transfer is: menthol>cholesterol>β-citronellol and D-sorbitol>mannitol>L-arabinose>D-xylose>D-glucose∿sucrose>D-mannose∿D-galactose (269).

Hydrogen transfers from alcohols to hydrogen acceptors A (A=tolane, chalcone, or maleic anhydride), catalyzed by $Ru_3(CO)_{12}$ at 145°, generate esters derived from the alcohols:

$$2RCH_2OH + 2A \rightarrow RCO_2CH_2R + 2AH_2$$

Mononuclear metal complexes appear to be inactive. Carboxylic acids are not intermediates, but a Tishchenko type reaction ($2RCHO \rightarrow RCO_2CH_2R$) is ruled out. Participants in the intermolecular coupling stage are alcohols and aldehydes. Polymerization and lactonization of α,ω-diols is noted, but 1,4-butanediol gives only the lactone, while 1,2-ethanediol and 1,3-propanediol give polymers (277).

Dehydrogenation of prochiral diols using benzalacetone as the hydrogen acceptor is catalyzed by $Ru_2Cl_4\{(-)\text{-DIOP}\}_3$ in the presence of triethylamine.

The products are optically active δ- and γ-lactones in yields of up to 90% and enantiomeric excesses from 2.0 to 15.2%. For example, 1,5-pentanediol (5 mmol), benzalacetone (10 mmol), triethylamine (0.12 mL), and $Ru_2Cl_4\{(-)\text{-DIOP}\}_3$ (0.1 mmol) in refluxing toluene for 10 h forms 3-methylvalerolactone (1.9 mmol, 10.8% e.e., R configuration) (270).

Addition of trichloroacetyl chloride to alkenes is catalyzed by $RuCl_2(PPh_3)_3$. Hydrolysis of the products yield α,α,γ-trichloroalkanoic acids. In a typical example, 1-decene (150 mmol), trichloroacetyl chloride (297 mmol), and $RuCl_2(PPh_3)_3$ (0.87 mmol) were reacted in refluxing toluene for 12 h to give a 90% yield of 2,2,4-trichlorododecanoyl chloride (271).

Conversion of an alkene, CO, and an alcohol (as a hydrogen source) to a ketone is catalyzed by Ru complexes. From ethylene (5 bar), CO (10 bar), and isopropanol (40 mL) at 160° for 24 h the products are acetone, diethyl ketone, isopropyl propionate, ethane, hydrogen, carbon dioxide, C_1-C_4 hydrocarbons, propionaldehyde, _n_-propanol, and isopropyl formate. The effects of the metal catalyst, hydrogen donor, the presence of base, CO pressure, CO/ethylene ratio, temperature, and the presence of water were examined (272).

Diethyl ketone can be prepared in low yield from propionaldehyde and ethylene at 180-220° in the presence of $RuCl_2(PPh_3)_3$. Most of the aldehyde is converted to 2-methyl-2-penten-1-al. Other aldehydes and alkenes can also be used. Reactions of propionaldehyde with $RuH_2(PPh_3)_4$ or $RuHCl(PPh_3)_3$ generate propyl propionate; from the latter reaction $RuH(O_2CEt)(PPh_3)_3$ can also be isolated (273).

Conversions of aldehydes to esters are catalyzed by hydrides of Ru, including $RuH_2(PPh_3)_4$. Aldehyde decarbonylation converts $RuH_2(PPh_3)_4$ to $Ru(CO)_3(PPh_3)_2$. Addition of water causes formation of $Ru(O_2CR)_2(CO)_m(PPh_3)_2$ (m=1 or 2). The order of reactivity for aldehydes RCHO is: R=Et>Me>_n_-Pr>_i_-Pr>>Ph. Carboxylic acids inhibit the reaction. Two mechanisms were proposed. One of these is shown in Scheme 25 (274).

Disproportionation of an aldehyde to the acid and alcohol is catalyzed by Ru complexes in dioxane/water solvent at 120°. Catalysts include $H_4Ru_4(CO)_8(PBu_3)_4$, $H_4Ru_4(CO)_8\{(-)\text{-DIOP}\}_2$, and $Ru_2(CO)_4(OAc)_2(PBu_3)_2$. Enantiomeric selection with the DIOP-substituted catalyst for the disproportionation of (R)(S)-2-methylbutanal forms (-)(S)-2-methylbutanoic acid of 1.7% optical purity. Racemization of the substrate occurs during the reaction (275).

Five-membered cyclic anhydrides can be converted stoichiometrically to γ-lactones using $RuH_2(PPh_3)_4$. Treatment of phthalic anhydride or succinic anhydride with $RuH_2(PPh_3)_4$ at 40° for 5 h gives a 20-70% yield of RuH{_o_-OC(O)-$C_6H_4CHO\}(PPh_3)_3$ or $RuH(O_2CCH_2CH_2CHO)(PPh_3)_3$, respectively. With methyl- or ethylsuccinic anhydride mixtures of isomers $RuH(O_2CCHRCH_2CHO)(PPh_3)_3$ and $RuH(O_2CCH_2CHRCHO)(PPh_3)_3$ are formed in a 3:1 ratio. Also prepared were

$RuH\{\underline{o}-O_2CC_6H_4C(O)Me\}(PPh_3)_3$ and $RuH\{O_2CCH_2CH_2C(O)R\}(PPh_3)_3$ (R=Me,Ph). The corresponding γ-lactones can be released from the metal complex by treatment with hydrogen (150°, 5 kg/cm^2), HCl, or CO. Hydrogenation of 3-acyl propionic acids using Ru(II) catalysts at 10 kg/cm^2 of hydrogen and 180° for 24 h gives γ-substituted γ-lactones in 30-99% yield (276).

Reactions Involving Synthesis Gas

In carboxylic acid solvents, Ru compounds catalyze the formation of glycol esters, in addition to methyl and ethyl esters. Quaternary Group VB salts are promoters. The highest glycol yields are obtained using $[PR_4][OAc]$ (R=alkyl or alkyl and aryl) as the promoter. Turnover frequencies of 10^{-2} S^{-1} are obtained with $RuCl_3/[PBu_4][OAc]$ at 220° and 430 atm; the glycol/MeOAc ratio under these conditions is 1/8.7. The highest glycol selectivity is obtained with a $RuCl_3/Cs[OAc]$ catalyst. Labeling studies show that the glycol carbons are not derived from the solvent. The order of promoter activity is: $Na^+ < Ba^{2+} < Cs^+$ and $[PPN]^+ < [NBu_4]^+ < [NMe_4]^+ < [PBu_4]^+ < [PPh_3(heptyl)]^+ > [PPh_4]^+ > [AsPh_4]^+$. The optimum $Ru/[PR_4]^+$ ratio for glycol is 1/8. The proposed intermediate responsible for the observed products is an acetoxymethylene complex (Scheme 26) (278).

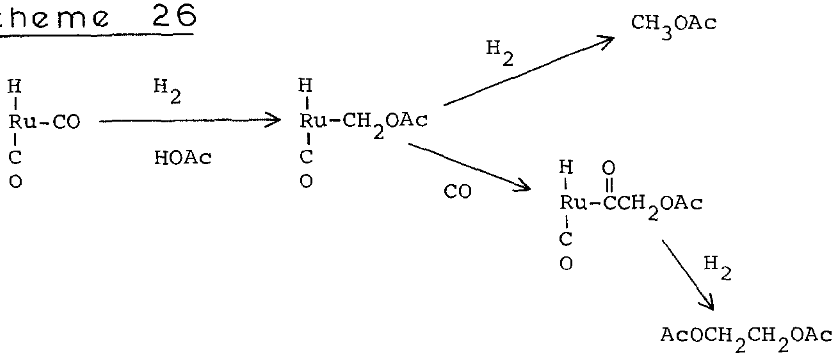
Acceleration by hydrosilanes of metal-catalyzed CO reduction has been noted. From $HSi(\underline{n}-C_6H_{13})_3$ and either CO or CO/hydrogen (1:1, 1000-8000 psi), derivatives of methanol, ethylene glycol, and $\underline{n}-C_6H_{13}CH_2OH$ can be obtained using $Ru_3(CO)_{12}$ as the catalyst in sulfolane, dibutyl ether, or $SiEt_4$ as solvent. The nature of the accelerating influence is unknown but may involve silylation of coordinated CO (279).

The complexes $[RuCl(CO)(N-N)_2]Cl$ (N-N=bipy or phen) are catalysts for the water gas shift reaction at 1-3 atm CO and 100-160° under photolytic conditions. Turnover numbers of up to 20 h^{-1} are achieved. Stoichiometric reactions and labeling studies show that the carbon dioxide is produced thermally, while the hydrogen is produced photochemically. The rate determining step is photochemical loss of hydrogen from $^-RuClH_2(bipy)_2{}^+$. The proposed mechanism is shown in Scheme 27 (280).

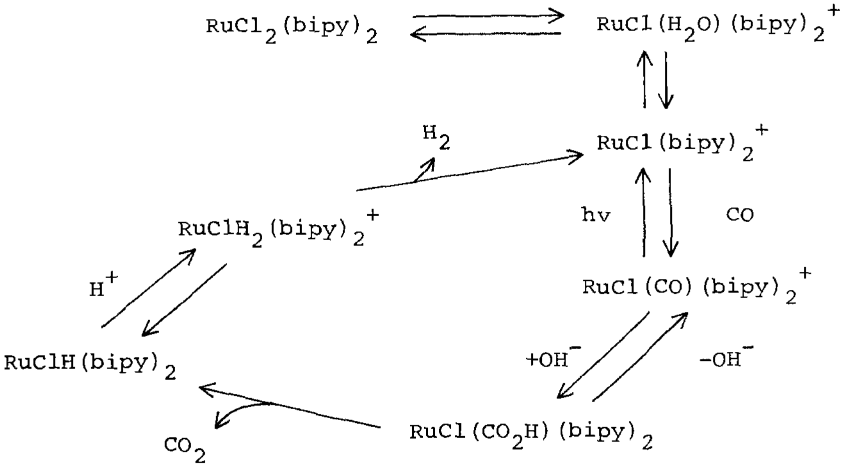
The role of iodide promoters in Ru-catalyzed homologation of methyl acetate has been investigated. A significant cation effect upon the distribution of products is noted. Carbonylation is favored by Na^+, Li^+, ammonium, or $NR_4{}^+$, thus improving selectivity to acetic acid. Water is removed by the water gas shift reaction, which is favored by Na^+, Li^+, or ammonium cations. Other iodide promoters investigated were CsI, CuI, and SnI_2 (281).

Homologation of methanol to ethanol in methanol/amine solutions is catalyzed by $Ru_3(CO)_{12}$ or $Fe(CO)_5/Ru_3(CO)_{12}$. Typical conditions are 300 atm of CO and hydrogen and at 200° in the presence of N-methyl piperidine. The cluster $HRu_3(CO)_{11}{}^-$ was identified in solution. Methyl formate is a presumed intermediate (282).

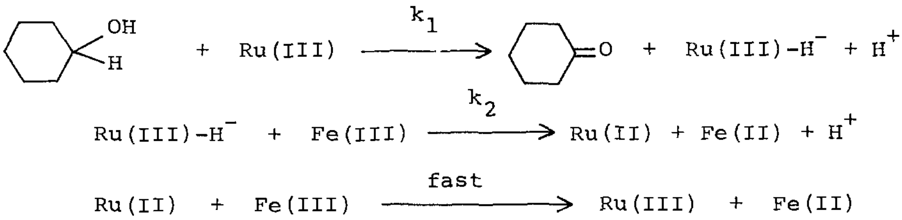
Scheme 26



Scheme 27



Scheme 28



Homologation of methanol with CO and hydrogen and using a mixed Co/Ru catalyst system was investigated. The effects of the Ru/Co ratio, pressure, temperature, added iodide, and solvent upon the percent conversion and selectivity toward ethanol were determined. The maximum yield of ethanol is obtained at $RuCl_3 \cdot nH_2O/Co_2(CO)_8$ ratios of 0.2 to 0.4. Ethers give both higher yield and higher selectivity to ethanol (60% yield, 80% selectivity (283)).

Homologation of methyl esters using CO and hydrogen is catalyzed by Ru/Co catalysts with methyl iodide as a promoter. Catalysts examined were $[NEt_4][RuCo_3(CO)_{12}]$, $[NEt_4][Ru_3Co(CO)_{13}]$, and $Ru(acac)_3/Co_2(CO)_8$. Using these catalysts, yields of ethyl acetate from methyl acetate are twice as great as with $Ru(acac)_3$ alone and three times as great as with $Co_2(CO)_8$ alone (284).

Oxidations

Oxidation of cyclohexanol by ferricyanide in alkaline aqueous solution is catalyzed by K_3RuCl_6. The value of k_H/k_D is 4 for d_0-cyclohexanol/d_{12}-cyclohexanol. The rate law has the form:

$$-\frac{d\ Fe(III)}{dt} = [Ru]\ (2\ k_1k_2[alcohol][Fe(III)])/(2\ k_1[alcohol] + k_2[Fe(III)])$$

The mechanism proposed is shown in Scheme 28 (285).

The kinetics of $RuCl_3$-catalyzed oxidation of di- and triethylene glycols by ferricyanide in aqueous alkaline solution were determined. A mechanism involving hydrogen transfer from the α-carbon of the glycol to Ru(III) was suggested (286).

The rate law for Ru(III)-catalyzed oxidation of aqueous 2,4,6-RR'(O_2N)-C_6H_2OH (R=R'=H; R=R'=NO_2; R=NO_2,R'=H) by periodate is zero-order in periodate and first-order in substrate. The rate law varies with pH (287).

The kinetics of oxidation of 2-propanol to acetone by $Ru(trpy)(bipy)O^{2+}$ in aqueous solution and by $Ru(bipy)_2(py)O^{2+}$ in acetonitrile have been determined. Oxygen transfer from Ru to the substrate does not occur. The most likely mechanism involves a concerted two-electron hydride transfer from the α-carbon to Ru(IV)=O with the oxygen acting as a lead-in atom to Ru(IV). Slower oxidations by Ru(III) products are also observed (288).

The kinetics of oxidation of *p*-*i*-$PrC_6H_4CO_2^-$, *p*-$EtC_6H_4CO_2^-$, and *p*-$MeC_6H_4CO_2^-$ by $Ru(trpy)(bipy)O^{2+}$ to α-alcohols in water and of *i*-PrC_6H_5 and MeC_6H_5 by $Ru(bipy)_2(py)O^{2+}$ in acetonitrile have been determined. The redox step involves a two-electron, hydride transfer step. The oxygen atom in the product comes from the solvent, not the Ru complex, and solvent or added nucleophile is directly involved in the redox step, possibly assisting in the loss of hydride ion (289).

Ruthenate, RuO_4^{2-}, is a catalyst for homogeneous oxidation of primary and secondary alcohols by peroxodisulfate ($S_2O_8^{2-}$) (290).

Molecular oxygen, activated by Ru complexes, can oxygenate catechols. Catechols are oxygenated to two kinds of intermediates, an intradiol type [145] and 2H-pyran-2-ones [146]. Typical conditions are: 3,5-di-t-butylcatechol (2 mmol) and $RuCl_2(PPh_3)_3$ (0.7 mmol) in tetrachloroethane at 25° for 15 h under oxygen (1 atm) to give muconic acid anhydride (26%) and 2H-pyran-2-one (64%) (Scheme 29) (291).

Oxidation of benzylamine to benzonitrile by oxygen is catalyzed by $Ru(NH_2CH_2Ph)_2Cl_2(PPh_3)_2$ at 80°. ESR evidence was obtained for an intermediate Ru(III) species. Other amine complexes prepared were $Ru(NH_2R)_2Cl_2(PPh_3)_2$ (R=H, C_5H_{11}, p-$MeOC_6H_4$) and Ru(chelate)$Cl_2(PPh_3)_2$ (chelate=5-methyl-1,2-phenylenediamine, ethylenediamine, benzoylhydroxylamine, and benzoylhydrazine) (292).

Oxidation of alkynyl ethers and amines by iodosylbenzene to give α-ketoesters and α-ketoamides is catalyzed by Ru compounds. Yields of 44 to 84% are obtained. In a typical example, dimethyl(phenylethynyl)amine (10 mmol), iodosylbenzene (26 mmol) and $RuCl_2(PPh_3)_3$ (96 mg) in dichloromethane are reacted at 25° for 1.5 h to form N,N-dimethyl 2-oxo-benzylamide (84%). Catalysts used were $RuCl_2(PPh_3)_3$, $Ru_3(CO)_{12}$, $RuCl_2(CO)_2(PPh_3)_2$, $RuCp_2$, $RuCl_3 \cdot 3H_2O$, and RuO_4 (293).

The kinetics of $RuCl_3$-catalyzed oxidation of Me_2CO, EtC(O)Me, $Me_2CHCH_2C(O)Me$, $MeC(O)CH_2CH_2Me$, cyclopentanone, and cyclohexanone by $NaIO_4$ in alkaline aqueous solution were reported (294).

The activity of $[Ru_3O(OAc)_6(H_2O)_3][OAc]$ as a catalyst for oxidation of 1-acetoxycyclohexene was determined (295).

The kinetics of Os(VIII) catalysis of oxidations of unsaturated carboxylic acids by Ce(IV) have been determined. Oxidation of maleic, fumaric, cinnamic, and acrylic acids and styrene in aqueous acetic acid and sulfuric acid have rate laws of the form:

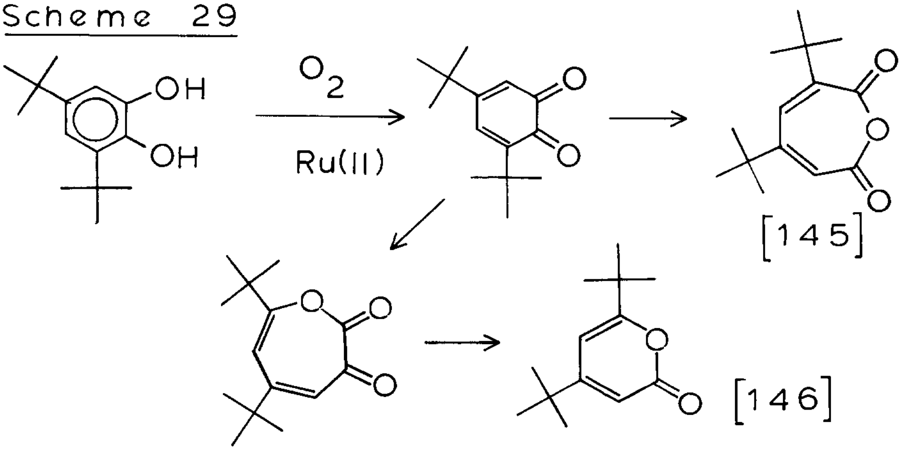
$$\text{rate} = k[\text{substrate}][\text{Os}]$$

The acid dependence is of a fractional order. Complex formation between substrate and Os is involved in the rate-determing electron transfer. An Os(VI) intermediate is then coverted to Os(VIII) in a fast step (296). Oxidation of acrylic, methacrylic, and crotonic acids by $Ce(SO_4)_2$ in aqueous sulfuric acid has a rate law zero-order in Ce(IV) and first-order in substrate and in catalyst (297).

Other Reactions

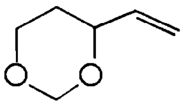
Alkylations of aliphatic amines by alcohols are catalyzed by Ru complexes. One group used $RuCl_2(PPh_3)_3$ as the catalyst and the general procedure involving a primary alkylamine (6 mmol), methanol (15-180 mmol), and 0.06 mmol of catalyst

Scheme 29

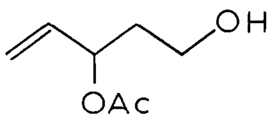


[145]

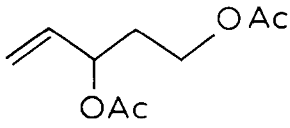
[146]



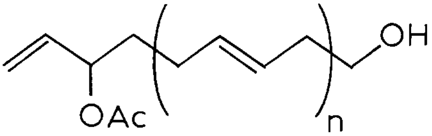
[147]



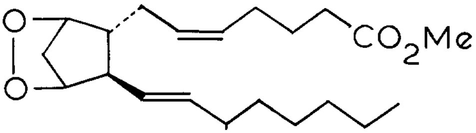
[148]



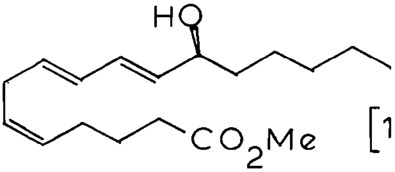
[149]



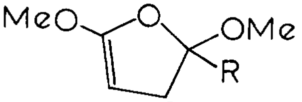
[150]



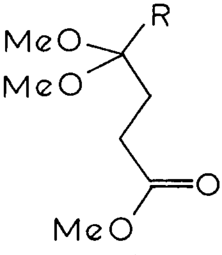
[151]



[152]

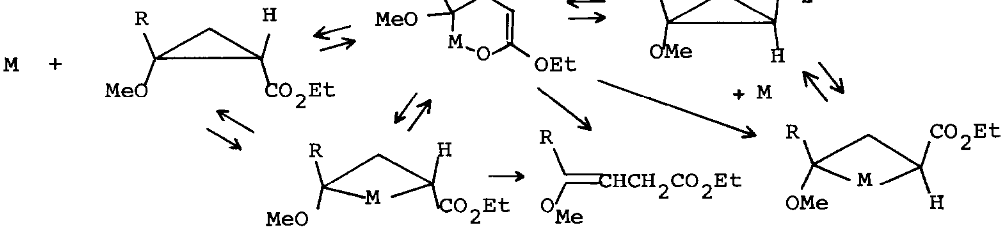


[153]



[154]

Scheme 30



in a sealed tube at 180° for 7 h; in this way $NBuMe_2$ can be obtained in 75% yield from NH_2Bu (298). Another group found $RuH_2(PPh_3)_4$ to be a catalyst for the preparation of unsymmetrical secondary and tertiary amines from aliphatic alcohols and primary amines. Cyclic amines can be prepared from aminoalcohols, e.g. 4-amino-1-butanol yields pyrrolidine (79%). Indole derivatives can also be prepared (299).

The mechanism of polymerization of norbornene catalyzed by Ru initiators has been discussed. The reaction order (between 0 and 1 or between 1 and 2), the role of the solvent, and the effect of catalyst pretreatment have been interpreted by one group in terms of a dissociative mechanism (300). However, a second group interpreted the same data in terms of a reaction second order in norbornene (301).

Treatment of $PhCH_2X$ ($X=OH,OCH_2Ph,OMe,OAc$) with HI(aq) and CO/hydrogen (9-10 MPa, 220°) and in the presence of $\{Ru(CO)_3I_2\}_2$ yields toluene, HX, and $H(C_7H_6)_nH$ (n=2-6). The mechanism involves dehydration of benzyl alcohol to dibenzyl ether and then disproportionation of the latter to toluene and benzaldehyde. The Ru component catalyzes reduction of benzaldehyde to benzyl alcohol or catalyzes polymer formation. In a typical run at 220° for 2 h, benzyl alcohol and methyl iodide at 99.8% conversion form toluene (17.3%), benzaldehyde (0.3%), dibenzyl ether (0.03%), benzyl iodide (0.1%), methyl benzyl ether (0.04%), diphenylmethane (0.3%), phenyltolylmethane (12.3%), and polytolyls (67.0%) (302).

Mono- or dienes react with aldehydes and carboxylic acids in the presence of $RuCl_3 \cdot 3H_2O$ to form derivatives of 1,3-diols. For example, butadiene (400 mmol), paraformaldehyde (400 mmol), and acetic acid (400 mmol), and $RuCl_3 \cdot 3H_2O$ (1 mmol) after 3 h are converted (51%) to [147] (5.5%), [148] (66%), [149] (6%), [150] (12%), acetoxybutenes (8%) and oligomers (25%) (303).

Radical decompositions of 1,4-epiperoxides are catalyzed by $RuCl_2(PPh_3)_3$. For example, with 3 mol % of catalyst at 19° [151] is converted to [152] (304).

Conversion of 2-butyne-1,4-diol to butyrolactone is catalyzed by Ru compounds, particularly $RuH_2(PPh_3)_3$ and $RuH_2(PPh_3)_4$, in yields of up to 49%. Butyrolactone can also be prepared in 40% yield from <u>cis</u>-1,4-butenediol using $Ru_3(CO)_{12}$. Best results (49% yield of butyrolactone) are obtained with $RuH_2(PPh_3)_4$ (0.27 mmol) and diol (0.7 mmol) in diglyme at 145° for 12 h (305).

Isomerizations of 2,5-dimethoxy-2,5-dihydrofurans to precursors for γ-ketoesters are catalyzed by $RuHCl(PPh_3)_3 \cdot (C_6H_5Me)$ or $RuHCl(CO)(PPh_3)_3$. For example, in methanol at 150° [153] is converted to [154] in 90% yield after 12 h (306).

Conversions of 2-alkoxycyclopropanecarboxylate esters to vinyl ethers are catalyzed by $\{Ru(CO)_3Cl_2\}_2$. Epimerization of the reactant is also observed. The proposed mechanism is shown in Scheme 30 (307).

Mixed etherification of allyl alcohols is catalyzed by $RuCl_3$. For example, 4-phenylbut-3-en-2-ol (3.7 mmol) and $RuCl_3 \cdot 3H_2O$ (0.4 mmol) at 60° for 3 h in methanol give a 93% yield of the methyl ether. Allylic rearrangement to the thermodynamically favored product is observed. The Lewis acid character of $RuCl_3$ is claimed important (308).

REVIEWS AND OTHER WORKS

The following reviews and other works have appeared which contain material of relevance to ruthenium and osmium organometallic chemistry.

"Multinuclear NMR studies of transition metal carbonyl clusters", by S. Aime (309).

"Structure and reactivity in organometallic chemistry. An applied molecular orbital approach", by T. A. Albright (310).

"Advances in homologation", by H. Bahrman, W. Lipps, and G. Cornils (311).

"Associative substitution reactions of 18-electron transition metal organometallic complexes", by F. Basolo (312).

"Homogeneous hydrogenation of carbon monoxide", by J. R. Blackborrow, R. J. Daroda, and G. Wilkinson (313).

"Phosphido-bridged iron group clusters", by A. J. Carty (314).

"Structural chemistry and reactivity of cluster-bound acetylides: close relatives of carbides?" by A. J. Carty (315).

"A discussion of the different kinds of solute-solute and solute-solvent interactions acting in homogeneous catalysis by transition metal complexes", by E. Cesarotti, R. Ugo, and L. Kaplan (316).

"The preparation and properties of metallacyclic compounds of the transition elements", by S. D. Chappell and D. J. Cole-Hamilton (317).

"Ligand effects", by J. Chatt (318).

"The reactions of dinitrogen in its metal complexes", by J. Chatt and R. L. Richards (319).

"Liquid-phase conversion of carbon monoxide in the presence of transition metal coordination compounds", by E. G. Chepaikin and M. L. Khidekel (320).

"Polymer-supported transition metal catalysts: established results, limitations, and potential developments", by F. Ciardelli, G. Braca, C. Carlini, G. Sbrana, and G. Valentini (321).

"The coordination chemistry of hydrogen cyanide, cyanogen, and cyanogen halides", by B. Corain (322).

"Unsupported small metal particles: preparation, reactivity, and characterization", by S. C. Davis and K. J. Klabunde (323).

"Mechanism of the decomposition of organometallic compounds of the transition metals and the role of intermediate products in catalysis", by B. A. Dolgoplosk, I. A. Oreshkin, E. I. Tinyakova, and V. A. Yakovlev (324).

"Catalytic aspects of industrial Fischer-Tropsch synthesis", by M. E. Dry (325).
"The raw materials future: critical examination of the role played by catalysis", by J. Falbe and C. D. Frohning (326).
"Chemistry of cluster compounds - new trends in inorganic chemistry", by S. P. Gubin (327).
"The chemistry of ruthenium, osmium, rhodium, iridium, palladium, and platinum in the higher oxidation states", by D. J. Gulliver and W. Levason (328)
"Determination and significance of transition metal-alkyl band dissociation energies", by J. Halpern (329).
"Formation of carbon-hydrogen bonds by reductive elimination", by J. Halpern (330).
"The methylene bridge: a challenge to synthetic, mechanistic and structural organometallic chemistry", by W. A. Herrman (331).
"Organometallic aspects of the Fischer-Tropsch synthesis", by W. A. Herrmann (332).
"Reactivities of carbon disulphide, carbon dioxide, and carbonyl sulphide towards some transition-metal systems", by J. A. Ibers (333).
"Cluster-derived supported catalysts and their uses", by M. Ichikawa (334).
"Criteria for identifying transition metal cluster-catalyzed reactions", by R. M. Laine (336).
"Clusters: stoichiometry, structure, and valence electrons", by D. A. Lemenovskii (337).
"Electrochemistry of transition metal clusters", by P. Lemoine (338).
"Structure and chemistry of some carbonyl cluster compounds of osmium and ruthenium", by J. Lewis and B. F. G. Johnson (339).
"Synthesis and chemical properties of clusters with intercavity atoms", by V. E. Lopatin and S. P. Gubin (340).
"Organometallic pi-complexes of silacycles", by R. J. McMahon (341).
"Osmium alkyl complexes", by D. S. Moore (342).
"Hydrocarbon reactions at metal centers", by E. L. Muetterties (343).
"The organometallic chemistry of metal surfaces", by E. L. Muetterties (344).
"Structural, stereochemical, and electronic features of arene-metal complexes", by E. L. Muetterties, J. R. Bleeke, E. J. Wucherer, and T. A. Albright (345).
"Disulfur complexes", by A. Muller, W. Jaegermann, and J. H. Enemark (346).
"Coordination chemistry of metal alkynyl compounds", by R. Nast (347).
"Organometallic intramolecular coordination compounds containing a cyclopentadienyl donor ligand", by I. Omae (348).
"Organometallic intramolecular coordination compounds containing an arsine donor ligand", by I. Omae (349).
"Organometallic intramolecular pi-olefin-metal coordination compounds", by I. Omae (350).
"A ligand's eye view of coordination", by R. V. Parish (351).

"The Bronsted acidity of transition metal hydrides", by R. G. Pearson and P. C. Ford (352).

"Ruthenium", by K. R. Seddon (353).

"Osmium", by K. R. Seddon (354).

"Homogeneous and heterogeneous catalytic reactions of CO_2", by R. P. A. Sneeden (355).

"Monometallic hydride complexes of transition metals", by G. L. Soloveichik and B. M. Bulychev (356).

"New X-ray diffraction studies of metal catalysts and polynuclear complexes", by Yu. T. Struchkov and Yu. L. Slovokhotov (357).

"Transition metal complexes with bridging hydride ligands", by L. M. Venanzi (358).

"Novel coordination compounds formed from CS_2 and heteroallenes", by H. Werner (359).

"Metal basicity as a synthetic tool in organometallic chemistry", by H. Werner (360).

"Photogeneration of reactive organometallic species", by M. S. Wrighton, J. L. Graff, R. J. Kazlauskas, J. C. Mitchener, and C. L. Reichel (361).

"Structure of organometallic compounds with metal chains, metal rings, and metal frameworks", by L. N. Zakharov and Yu. T. Struchkov (362).

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