RUTHENIUM AND OSMIUM: ANNUAL SURVEY FOR THE YEAR 1981

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CONTENTS

ABBREVIATIONS

acac - acetylacetonate
bipy - 2,2'-bipyridine
Bu - n-butyl
t-Bu - t-butyl
COD - cyclo-octa-1,5-diene
Cp - η^5-cyclopentadienyl
dppe - 1,2-bis(diphenylphosphino)ethane
dppm - bis(diphenylphosphino)methane
Et - ethyl
Me - methyl
OEP - octaethylporphyrin
Ph - phenyl
phen - 1,10-phenanthroline
PPN - bis(triphenylphosphine)iminium
Pr - n-propyl
i-Pr - i-propyl
py - pyridine
TPP - tetraphenylporphyrin
trpy - 2,2',2"-terpyridine

This year for the first time the Annual Survey for ruthenium and osmium is separate from that for iron. While we have tried to maintain the same organization of topics as in previous surveys, it is obvious that the distribution of papers among these topics is quite different. In particular, papers concerning cluster compounds account for roughly one third of the literature surveyed. The primary literature was covered directly and a computer literature search was accomplished to insure a comprehensive review.

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

Simple Carbonyls, Carbonyl Hydrides, and Carbonylate Anions

Effective syntheses for $[PPN][HM(CO)_4]$, M=Ru or Os, were reported. Treatment of the appropriate $Na_2M(CO)_4$ salt in methanol with [PPN]Cl at -78°C afforded the product in 60% yield (1).

Kinetic studies have found unusual lability for the carbonyl hydride complex $H_2Ru(CO)_4$ and its iron analog (2). In acetone at -70°C a rapid reaction with $P(OMe)_3$ gave $H_2Ru(CO)_3[P(OMe)_3]$ in which the phosphite ligand is cis to the two hydrides. At 25°C in methanol, rapid decomposition of $[HRu(CO)_4]^-$ formed $[HRu_3(CO)_{11}]^-$ and the rate of decomposition was slowed by added sodium methoxide. It was proposed that this clusterification proceeds by protonation of $[HRu(CO)_4]^-$, followed by rapid attack of $[HRu(CO)_4]^-$ on $H_2Ru(CO)_4$. The lability of $H_2Ru(CO)_4$ was suggested to be due to rapid, reversible hydride migration to form the unsaturated formyl $HRu(CHO)(CO)_3$. Another possible explanation is that the hydride ligands labilize the molecule toward CO dissociation.

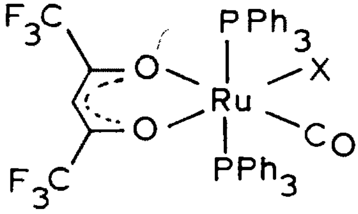
The cationic hydrides $[HRu(CO)_5]^+$ and $[HRu(CO)_4(PPh_3)]^+$ were prepared in situ by extraction of hexane solutions of $Ru(CO)_5$ and $Ru(CO)_4(PPh_3)$ with concentrated sulfuric acid. The cations were characterized by ^{13}C NMR spectroscopy. Both are rigid on the NMR timescale at 25°C. The cation $[HRu(CO)_4(PPh_3)]^+$ has a cis configuration (3).

M(II) Phosphine Complexes Containing Hydride, Halo, and Other Ligands

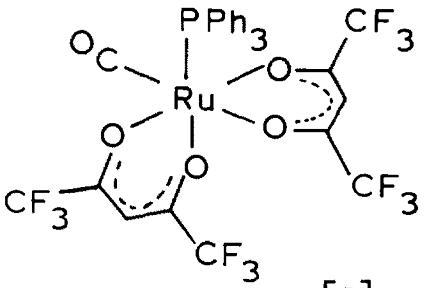
The ^1H NMR spectra of a series of EPh_3 complexes (E=P, As, Sb), including $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ and $RuH(O_2CCF_3)(CO)(PPh_3)_2$ in d_6-benzene, were found to be sensitive to the relative orientation of the EPh_3 ligands. Although the spectra in d_2-dichloromethane or d-chloroform were not particularly sensitive to geometry, in benzene the aryl protons for a given complex were clearly resolved into ortho- and meta-/para- signals with the former to lower field. The magnitude of the separation between these signals for trans-oriented EPh_3 ligands was greater than 0.5 ppm (usually 0.6-1.0 ppm) and for cis-oriented ligands was less than 0.5 ppm (usually 0.2-0.4 ppm) (4). Substitution of a variety of ligands L (L=CN-t-Bu, $PF_2(NMe_2)$, $P(OCH_2)_3CMe$, $P(OMe)_3$, dppe) for one, two, or all three PPh_3 ligands of $RuH(O_2CCH_3)(PPh_3)_3$ caused conversion of the acetate coordination from bidentate to unidentate. With fluorinated phosphine ligands, elimination of acetic acid gave RuL'_5 (L'=$PF_2(NMe_2)$, $PF_2(NC_4H_8)$), $RL'_4(PPh_3)$ (L'=PF_3), or $RuL'_3(PPh_3)_2$ (L'=PF_3) (5).

Treatment of $RuH_2(CO)(PPh_3)_3$ with HBF_4 and water afforded $[RuH(H_2O)(CO)(PPh_3)_3][BF_4]$. Reaction of this product with CO gave $[RuH(H_2O)(CO)_2(PPh_3)_2][BF_4]$. A crystal structure determination of the latter found that the BF_4 anion is hydrogen bonded to the coordinated water molecule and to an ethanol molecule in the crystal lattice (6).

Reaction of $RuH_2(CO)(PPh_3)_3$ with $Pd(hfacac)_2$ (hfacac=hexafluoroacetylacetonate) yielded $RuH(CO)(hfacac)(PPh_3)_2$ [1] and $Ru(hfacac)_2(CO)(PPh_3)$ [2]. The products were characterized by ^{19}F, ^1H, and ^{31}P NMR spectroscopy. The chloro derivative $RuCl(hfacac)(CO)(PPh_3)_2$ [3] was prepared from the same reaction with $RuHCl(CO)(PPh_3)_3$ (7).



[1] X = H
[3] X = Cl



[2]

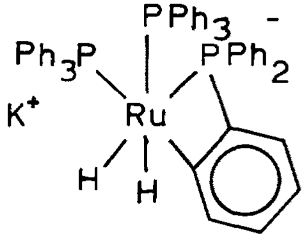
Complexes of ruthenium anchored onto polymers via carboxylate groups were prepared. The carboxylate groups of alternating co-polymers of maleic acid and alkyl and aryl vinyl ethers were used to heterogenize $RuH_2(CO)(PPh_3)_3$. The physical and chemical properties of the polymer depend upon the nature of the ether co-units. Heterogenized $RuCl_2(PPh_3)_3$ was achieved using the sodium salts of poly(acrylic acid) or of ethylene/maleic acid alternating co-polymer (8).

Reduction of $MHCl(CO)(PPh_3)_3$ (M=Ru,Os) by 1,8-diazobicyclo-[5.4.0]-undec-7-ene (DBU) in the presence of CO is a high yield route to the corresponding $M(CO)_3(PPh_3)_2$. For Os an 83% yield was obtained after 5-6 h at 150-160° and under 80 psi of CO. For Ru a 97% yield was obtained after only 3.5 h at 80°. The isocyanide-substituted derivatives $Ru(CO)(CNR)(PPh_3)_3$ were obtained in 78% yield by reduction of $RuHCl(CO)(CNR)(PPh_3)_2$ with DBU in the presence of excess PPh_3 (9).

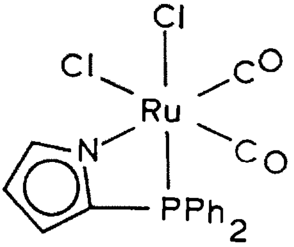
The molecular structure and absolute configuration of trans-$RuHCl(diop)_2$ (diop = (+)-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane) has been determined crystallographically. This compound is a catalyst for asymmetric hydrogenations; the active catalyst species may have only one diop ligand (10).

The crystal structure of $OsHCl(CO)[P(C_6H_{11})_3]_2$ was determined (11). The molecule has a square pyramidal coordination geometry with trans phosphines and the hydride ligand (not located) occupying the apical position. Although the compound is coordinately unsaturated, no unusual interactions between the metal and the cyclohexyl rings were detected.

New anionic hydride complexes of ruthenium were prepared. Reduction of $RuHCl(PPh_3)_3 \cdot C_6H_5Me$ with potassium naphthalene (1:2) at -80° in THF gave $K[H_2RuC_6H_4PPh_2(PPh_3)_2] \cdot C_{10}H_8 \cdot Et_2O$ [4]. The structure of this compound was crystallographically determined. Reduction of $[RuHCl(PPh_3)_2]_2 \cdot 2\ C_6H_5Me$ under the same conditions gave $K_2[Ru_2H_2(PPh_2)(PPh_3)_3] \cdot 2\ C_6H_{14}O_3$, which was characterized by ^1H and ^{31}P NMR spectroscopy and by chemical degradation with HCl (12). Both new complexes are hydrogenation catalysts. Aldehydes and ketones were reduced at 85° and 620 kPa of hydrogen to alcohols. Hydrogenation of acrolein gave either propionaldehyde or mixtures of propionaldehyde and allyl alcohol. Activated esters such as CF_3CO_2Me, $CF_3CO_2CH_2CF_3$, or dimethyl oxalate were hydrogenated to CF_3CH_2OH and methanol, CF_3CH_2OH, and $HOCH_2CO_2Me$, respectively. The complex $K_2[Ru_2H_2(PPh_2)(PPh_3)_3]$ is a catalyst for the hydrogenation of methyl acetate to methanol, ethanol and ethyl acetate at 90° and 620 kPa of hydrogen. This is the first example of a homogeneous catalytic hydrogenation of a simple aliphatic ester. Nitriles were hydrogenated to amines (13).



[4]



[5]

Aquation of trans-$[Ru(NH_3)_4\{P(OR)_3\}_2]^{2+}$ and trans-$[Ru(NH_3)_4\{P(OMe)_3\}\{P(OR)_3\}]^{2+}$ (R=Me, i-Pr, and n-Bu) was studied. For all complexes a common mechanism leads to the most stable monophosphite complex. The formation constants for trans-$[Ru(NH_3)_4\{P(OR)_3\}(pyrazine)]^{2+}$ were suggested to indicate the importance of Ru-to-P π-backbonding, which decreases in the order $P(OMe)_3 > P(OEt)_3 > P(O\text{-}n\text{-}Bu)_3 > P(O\text{-}i\text{-}Pr)_3$ (14).

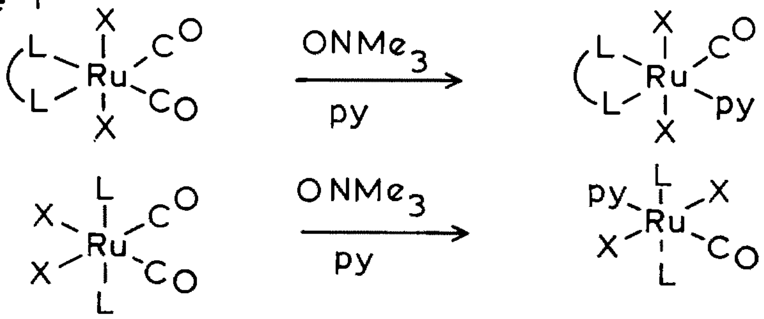
The oxidations of $RuCl_2(PPh_3)_3$ and $[Ru_2(PEt_2Ph)_6Cl_3]Cl$ in the solid phase were studied using thermogravimetry, IR spectroscopy and elemental analysis. Inner-sphere oxidation of the phosphines to the phosphine oxides occurred at 140-2°. The product was isolated and characterized as $Ru(OPPh_3)_3Cl_2$ (15).

The product from the reaction of $[Ru(CO)_3(2\text{-}Ph_2Ppy)]_3$ with chlorine is $Ru(CO)_2Cl_2(2\text{-}Ph_2Ppy)$ [5]. The complex was characterized crystallographically. Further reaction with 2-Ph_2Ppy gave $Ru(2\text{-}Ph_2Ppy)_2(CO)_2Cl_2$ with displacement of the N-donor end of the chelate (16).

Carbonyl Halide and Related Complexes

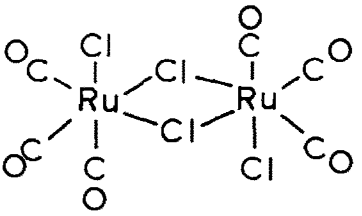
Decarbonylation of $Ru(CO)_2X_2L_2$ (L_2=1,10-phenanthroline, X=Cl, Br, CF_3CO_2; L_2=bipy, X=Cl or CF_3CO_2; $L_2=(PPh_3)_2$, X=Cl,Br) using trimethylamine-N-oxide in pyridine afforded $Ru(CO)X_2L_2(py)$. The reaction proceeds with retention of stereochemistry at the metal when L_2 is a chelate, but the bis(PPh_3) complexes undergo isomerization (Scheme 1) (17).

Scheme 1

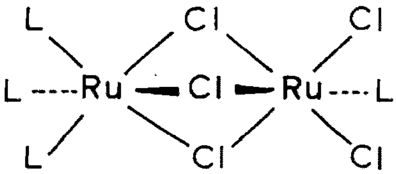


Isomerization of $OsX_2^*(py)_2(CO)_2$ (X=Cl, Br, I, * indicates trans ligands) to the thermodynamically favored $OsX_2(py)_2^*(CO)_2$ occurred upon heating under high vacuum. The new isomers were separated by chromatography (18). The new complexes trans-$[OsX_4(py)(CO)]^-$ (X=Cl, Br, I) were prepared by treatment of trans-$[OsX_4(CO)_2]^-$ or $[OsX_5(CO)]^{2-}$ with pyridine in the presence of bentonite. These new complexes were studied by IR, Raman, and UV/visible spectroscopy. The shifts of the positions of the Os-C and C-O modes in the IR and Raman spectra indicate that metal-to-ligand π-backdonation is stronger with pyridine than with the halides but significantly weaker compared to CO. In the UV/visible spectra, intense π-π* transitions of the pyridine ligand and the charge-transfer transitions from ligand levels split by spin-orbit coupling were assigned. The vibrational fine structure observed for trans-$[OsCl_4(py)(CO)]^-$ originates from coupling with the centrosymmetric mode of pyridine or with the Os-Cl mode. Treatment of trans-$[OsX_4(CO)_2]^-$ with aqueous pyridine gave $OsX_2^*py_3(CO)$. Oxidative ligand exchange yielded the mixed halide derivatives $Os(XY)^*(py)_3(CO)$ (X, Y=Cl, Br, I). The corresponding complexes of Os(III) were easily reduced and could be isolated. The new complexes were characterized by their electronic and vibrational spectra (19).

The complex $[Ru(CO)_3Cl_2]_2 \cdot SbCl_3$ [6] was prepared by reaction of $SbCl_5$ with $Ru_3(CO)_{12}$. The crystal structure of the product was determined (20).



[6]

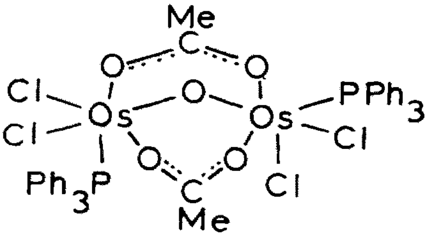


[7] L = PEt_2Ph

Several isomers of the dimers $M_2Cl_5L_4$ (M=Ru, L=$AsPh_3$, As(p-tolyl)$_3$, As(p-$C_6H_4Cl)_3$, PEt_2Ph, PMe_2Ph; $L_2=Ph_2AsC_2H_4AsPh_2$; M=Os, L=PPh_3, $AsPh_3$) were synthesized and characterized by magnetic, ESR, and electrochemical measurements. The crystal structure of $[(PEt_2Ph)Cl_2RuCl_3Ru(PEt_2Ph)_3]$ [7] was determined (21).

The carboxylate-bridged complexes $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR_3)_2$ were prepared by refluxing $OsO_2X_2(PR_3)_2$ (X=Cl, Br) in carboxylic acids. The structure of $Os_2(\mu\text{-}O)(\mu\text{-}O_2C\ CH_3)_2Cl_4(PPh_3)_2$ [8] was crystallographically determined (22). The Os-O-Os angle is 140° and the Os-O distances are 1.829 Å, compared with 1.778 Å previously found for $[Os_2OCl_{10}]^{4-}$ with a linear Os-O-Os arrangement. The electrochemistry of these complexes was examined by cyclic voltammetry.

[8]



The complexes $OsCl(O_2CMe)_2(CO)(py)_2$, $Os_2(O_2CMe)_4(PPh_3)_2$, $Os(O_2CMe)_3$-$(PMe_3)_3Cl$, and others were prepared from reactions of the new starting material $[OsCl(O_2CMe)_2]_n$. This material was prepared by treatment of Na_2OsCl_6 with acetic anhydride and HCl in acetic acid. A number of other coordination compounds were prepared from this material (23).

A variety of phosphine complexes were prepared from ruthenium carboxylates. Reaction of $[Ru_2O(O_2CH)_6(H_2O)_3][O_2CH]$ with pyridine gave $Ru(O_2CH)_2(py)_2$ and $Ru(O_2CH)_2(py)_4$ and with CO gave $Ru_3O(O_2CH)_6(H_2O)_2(CO)$ and $Na[Ru(O_2CH)_3(H_2O)]$. The complexes $[Ru_2(O_2CMe)_4L_2][ClO_4]$ were prepared from $[RuO(O_2CMe)_6(MeOH)_3]^{0,1+}$ and dppm or dppe. Also synthesized were $[Ru_2(O_2CMe)_4(dppm)_2]$, $Ru(O_2CMe)_2(dppm)_2$ and $Ru_6O_2(O_2CMe)_{12}(dppe)_3$ (24).

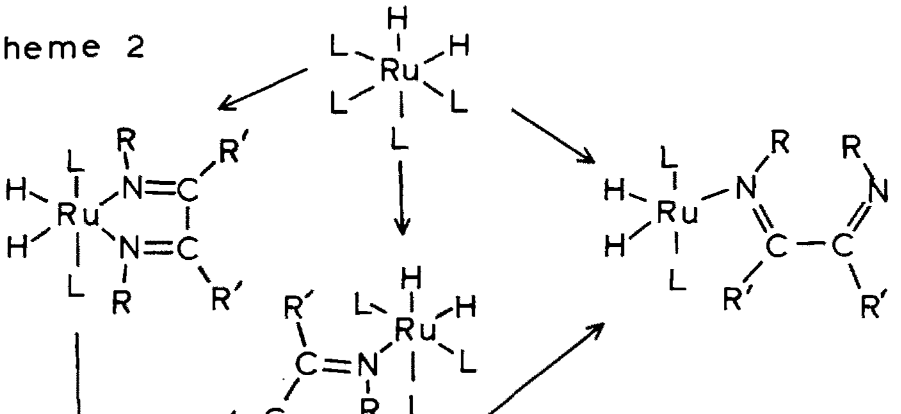
Complexes with Nitrogen Donor Ligands

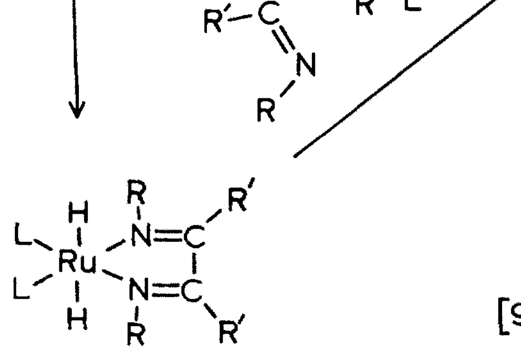
The synthesis of the green complexes RuX_2L_2 and the red complexes

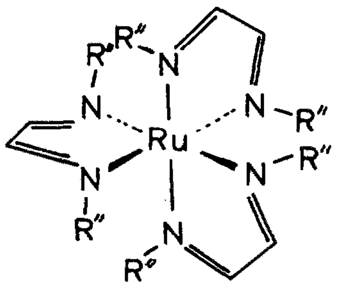
$[Ru(bipy)_2L][ClO_4]_2 \cdot H_2O$ (X=Cl, Br, I; L=2-(phenylazo)pyridine or 2-(*m*-tolylazo)pyridine) were reported. The former complexes were unreactive to Ag^+ or nitrogen bases but did react with phosphines L' to give $[RuClL_2L']^+$. The electrochemistry of these species was also investigated (25).

Reduction of $RuCl_3 \cdot 3H_2O$ in the presence of *i*-PrN=CHCH=N-*i*-Pr (DAD-A) afforded *cis*-$Ru(DAD\text{-}A)_2Cl_2$ in moderate yield; the X-ray structure determination and spectroscopic characterizations were reported (26). Reactions of $H_2Ru(PPh_3)_n$ (n=3 or 4) with DAD-A, 2,3-di(phenylimino)butane (DAD-C), and 1,2-di(p-methoxyphenylimino)ethane (DAD-D) produced symmetrical *trans*-dihydride complexes. However, the product from DAD-C could not be isolated; instead the *cis*-dihydride hexacoordinate and pentacoordinate complexes were isolated (Scheme 2) (27). A field desorption mass spectrometric study of compounds of α-diimines, including $Ru(CO)_3$(Mes N=CHCH=NMes), $M_2(CO)_6$(RN=CHCH=NR) (M=Ru, Os; Ru=*t*-Bu, *i*-Pr, C_6H_{11}), $FeRu(CO)_6$(*t*-BuN=CHCH=N*t*Bu), $Ru_4(CO)_8$-$(RN{=}CHCH{=}NR)_2$, and $Ru_2(CO)_4(RN{=}CHCH{=}NR)_2$, found that the technique was very useful for characterization of thermally labile and involitile complexes (28). The formally 20-electron complex Ru(*p*-$MeOC_6H_4$N=CHCH=N-*p*-$C_6H_4OMe)_3$ [9] was prepared by reaction of $RuH_2(PPh_3)_4$ or $RuH(C_6H_4PPh_2)(PPh_3)_2(C_2H_4)$ with the α-diimine; the structure was confirmed by X-ray crystallography (29).

Scheme 2



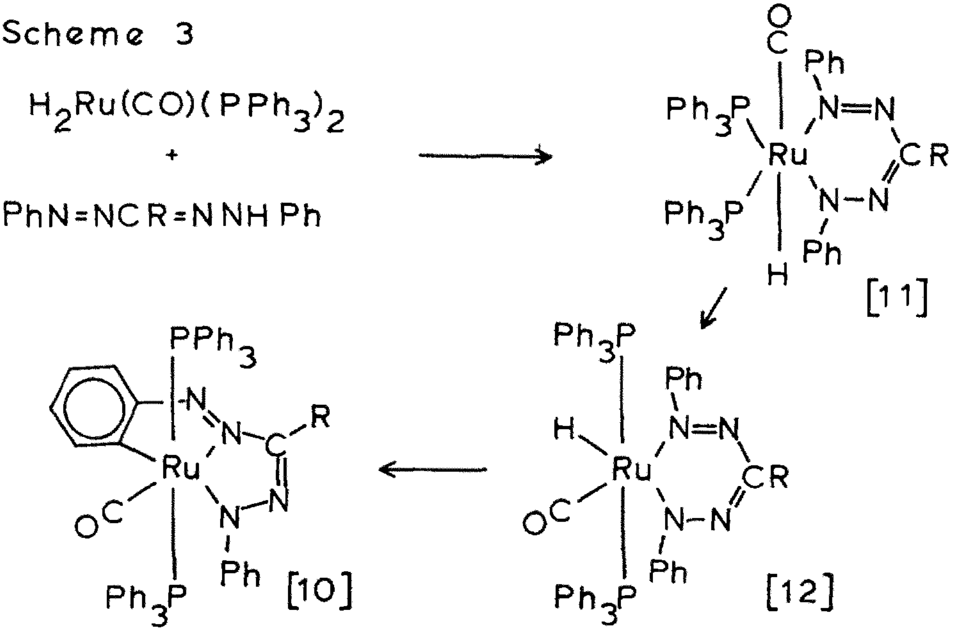




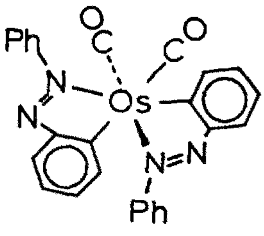
[9] R'' = p-C_6H_4OMe

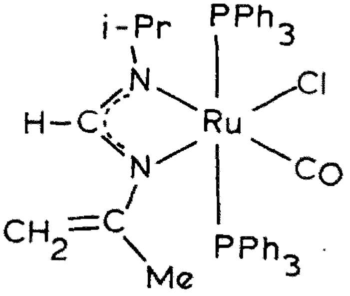
The o-metallated complexes $M[(o\text{-}C_6H_4)N{=}NCR{=}NNPh](CO)(EPh_3)_2$ [10] (M=Ru, E=P, R=H, Me, or Ph; M=Ru, E=As, R=Ph; M=Os, E=P, R=H, Me, or Ph), isolated as green air-stable solids, were prepared by reactions of the appropriate 1,5-diphenylformazan PhN=NCR=NNHPh (R=H, Me, Ph) with $RuH_2(CO)(PPh_3)_3$, $RuH_2(CO)(AsPh_3)_3$, $RuHCl(CO)(PPh_3)_3$, $Os(O_2CCF_3)_2(CO)(PPh_3)_2$ and $OsH(O_2CCF_3)(CO)(PPh_3)_2$ in boiling 2-methoxyethanol or DMF. However, the initial products of these reactions were N^1,N^5-chelates which subsequently rearrange and undergo cyclometalation. The isomeric intermediates $Ru(PhN{=}NCH{=}NNPh)H(CO)(PPh_3)_2$ with cis [11] and trans [12] PPh_3 ligands were isolated from $RuH_2(CO)(PPh_3)_3$ and were shown to convert to $Ru[(o\text{-}C_6H_4)N{=}NCH{=}NNPh)(CO)(PPh_3)_2$ upon heating. The crystal structure of the Ph analog [10] was reported. The reaction is summarized in Scheme 3 (30).

Scheme 3



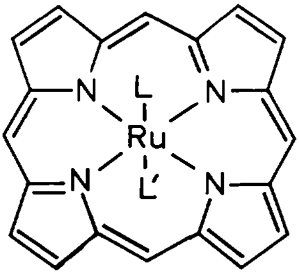
Bis(azobenzenido)dicarbonylosmium(II) [13] was prepared by reaction of $Os_3(CO)_{12}$ with azobenzene in refluxing octane. The crystal structure was determined (31).


[13]


[14]

Reactions of $C(N\text{-}\underline{i}\text{-}Pr)_2$ with ruthenium and osmium complexes were studied. In refluxing benzene, $RuX(CH_2{=}CMeNCHCN\text{-}\underline{i}\text{-}Pr)(CO)(PPh_3)_2$ (X=Cl, Br) were prepared from $RuHX(CO)(PPh_3)_3$; the crystal structure of the complex where X=Cl [14] was reported. Reaction with $OsH_2(CO)(PPh_3)_3$ gave $OsH(\underline{i}\text{-}PrNCHN\text{-}\underline{i}\text{-}Pr)(CO)(PPh_3)_2$, which upon heating is transferred into $OsH(CH_2{=}CMeNCHN\text{-}\underline{i}\text{-}Pr)(CO)(PPh_3)_2$ (322).

An ^1H NMR study of $Ru(OEP)L_2$ (OEP=octaethylporphyrin, L=L'= $P(\underline{n}\text{-}Bu)_3$ [15]; L=PBu_3, L'=CO [16]; L=$P(\underline{t}\text{-}Bu)_3$, L'=CO [17]) found that the metal lies out of the plane of the porphyrin ring in [17] but not in [16]. Calculations using models for ring current shifts of protons of axially coordinated ligands suggested that in [17] the metal atom is ca. 0.4 Å out of the plane on the side toward the $P(\underline{t}\text{-}Bu)_3$ ligand. Other complexes studied were $Ru(OEP)(np)_2$, $Ru(OEP)(dppe)_2$, $Ru(TPP)(np)_2$, Ru(OEP)(CO)(np), and Ru(OEP)(CO)-(dppe) where np=diethyl(diphenylphosphinoethyl)amine and TPP=tetraphenylporphyrin. The ^{31}P and ^1H NMR spectra of Ru(OEP)(CO)(dppe) suggested equilibrium amounts of $[Ru(OEP)(CO)]_2(dppe)$ and of seven-coordinate Ru(OEP)-(CO)(dppe), in addition to six-coordinate Ru(OEP)(CO)(dppe) (32).



[15] L = L = $P(\underline{n}\text{-}Bu)_3$

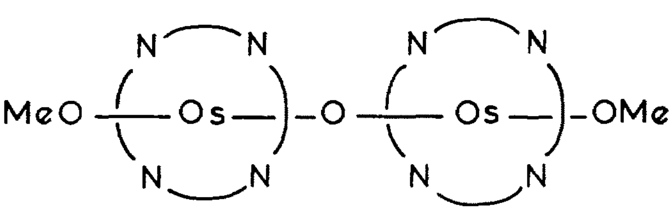
[16] L = $P(\underline{n}\text{-}Bu)_3$, L′ = CO

[17] L = $P(\underline{t}\text{-}Bu)_3$, L′ = CO

Chemical oxidation of Ru(OEP)(CO)(py) with bromine in the presence of excess cyanide ion afforded $[Ru(OEP)(CN)_2]^-$. This product was converted to Ru(OEP)(CN)(py). Reduction of the latter in the presence of thiophosgene gave the thiocarbonyl Ru(OEP)(CS)(py). The spectroscopic and electrochemical properties of the series M(OEP)(CX)(py) (M=Fe, Ru, Os; X=O,S) were examined; the M-CS bond was suggested to be stronger than the M-CO bond. These studies provide further evidence that CS is a stronger π-acid than CO. The ions $[Ru(OEP)(CN)(L)]^-$ (L=CO, py) were identified in solution (33).

Oxidation of Os(OEP)(CO) with oxygen in the presence of 2,3-dimethylindole produced $[Os(OEP)(OMe)]_2O$ [18], a diamagnetic oxo-bridged dimer (34). The product was characterized by ^1H NMR, IR and UV/visible spectroscopy, elemental analysis, and a molecular weight determination.

[18]



The first example of intense charge-transfer (CT) emission from a series of complexes $[Os(trpy)(diphosp)L]^{+n}$ (trpy=2,2',2"-terpyridine; (diphosp,L)=($Ph_2PCH=CHPPh_2$,Cl), ($Ph_2PCH=CHPPh_2$,py), ($Ph_2PCH=CHPPh_2$,MeCN), ($Ph_2PCH_2PPh_2$,$Ph_2PCH_2PPh_2$), ($Ph_2PCH=CHPPh_2$,CO)) at room temperature in fluid solution was reported. These complexes can have relatively long CT excited-state lifetimes while also exhibiting photo-substitution. Although metal-ligand CT-based luminescence for complexes of bipy and 1,10-phenanthroline is common, trpy complexes had until this work exhibited weak or no luminescence under these conditions. It was suggested that extremely rapid non-radiative processes were responsible for this difference. With the exception of the chloride complexes, all molecules examined were photolabile; the corresponding bipy or 1,10-phenanthroline complexes do not exhibit significant photo-substitution (35).

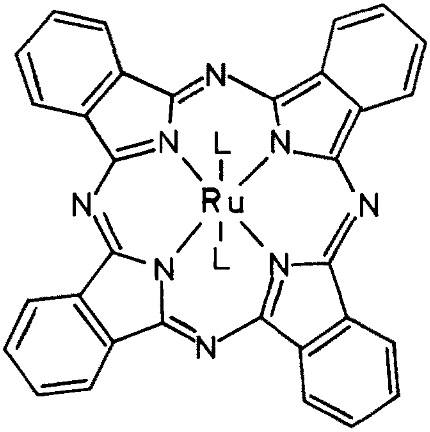
The excited-state and redox properties of Ru(p-XTPP)(CO) (X=MeO, Me, H, F, Cl, Br;TPP=tetraphenylporphyrin) have been defined using flash photolysis and cyclic voltammetry. Two one-electron oxidations were found in dichloromethane solution with the first step occurring at a potential of 0.74 to 0.87 V and the second from 1.18 to 1.27 V. A one-electron reduction in DMSO was found between -1.35 and -1.24 V. The first oxidation and the reduction steps were respectively assigned to π-electron removal or acceptance by the porphyrin ring; the second oxidation was of the metal center. Photochemical studies formed emission bands centered at 730 nm with excited-state lifetimes on the order of 30 μs. The redox potentials of these compounds increase as the electronegativity of X increases but the excited-state lifetimes decrease (36).

Photolysis of $Os(OEP)[P(OMe)_3]_2$ in chlorinated solvents at 365 and 405 nm gave $Os(OEP)Cl_2$. The rate of product formation depended upon the solvent, with relative rates CH_2Cl_2,1<$CHCl_3$,8<CCl_4,120. The quantum yield for product formation was 0.004 in CH_2Cl_2 and 1.4 in CCl_4. A radical mechanism was proposed (37).

Reactions of Ru(OEP)(CO)(EtOH) and Ru(TPP)(CO)(EtOH) with diphosphines (diphosp=$Ph_2P(CH_2)_nPPh_2$ (n=1,2) or $Ph_2PC_2H_4N(Et)C_2H_4PPh_2$) produced complexes $Ru(OEP)(diphosp)_2$ and $Ru(TPP)(diphosp)_2$. The crystal structure of

Ru(TPP)($Ph_2PCH_2PPh_2$)$_2$ was reported (38). Each diphosphine ligand is coordinated in a monodentate fashion trans to the other.

The syntheses and characterizations of complexes Ru(Pc)L_2 (Pc=phthalocyanine or monochlorophthalocyanine, L=N-methyl imidazole, pyridine, P(n-Bu)$_3$, and P(O-n-Bu)$_3$) [19] and the kinetics and thermodynamics of axial ligand substitution were reported. The mechanism of substitution is dissociative and the five-coordinate intermediate Ru(Pc)L shows little or no discrimination between nucleophiles. These Ru(Pc)L_2 complexes are more labile than the iron analogs but metal-to-ligand π-backbonding was suggested to be more important for Ru. Trans-group and leaving group effects were examined. The order of decreasing rate with leaving group was py>N-methyl imidazole>P(O-n-Bu)$_3$ and the trans group effect showed decreasing rate in the order P(O-n-Bu)$_3$>P(n-Bu)$_3$>py,N-methyl imidazole (39).



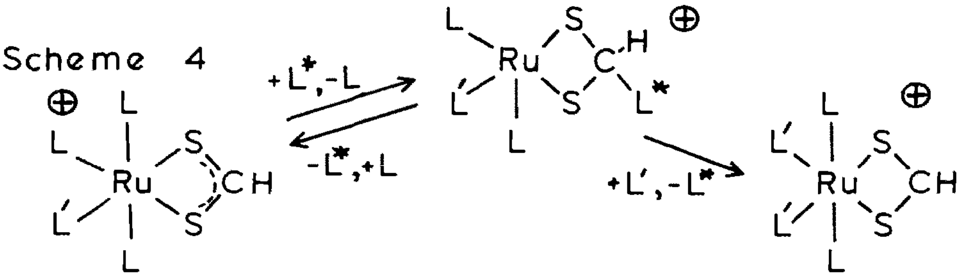
[19]

The Ru^{II}(myoglobin)(CO) complex was examined by UV/visible spectroscopy. Protonation of the distal histidine or the presence of low concentrations of guanidine hydrochloride caused a decrease in the separation between the two α bands (534 and 546.5 nm). This separation is very sensitive to the tertiary structure of the protein and is interpreted in terms of lowering of the square-planar symmetry of the metal porphyrin as a result of the constraint of the distal histidine on the linear Ru-CO grouping which forces the carbonyl off the axis normal to the prophyrin plane (40).

Complexes with Sulfur Ligands

The tetrahydrothiophene complex Os(OEP)(SC_4H_{10})$_2$ was prepared by reaction of Os(OEP)(N_2) with tetrahydrothiophene. This product reacted readily with L=1-methylimidazole or py at 50° to give Os(OEP)(SC_4H_{10})L. These unsymmetrical complexes did not react with CO but did undergo one-

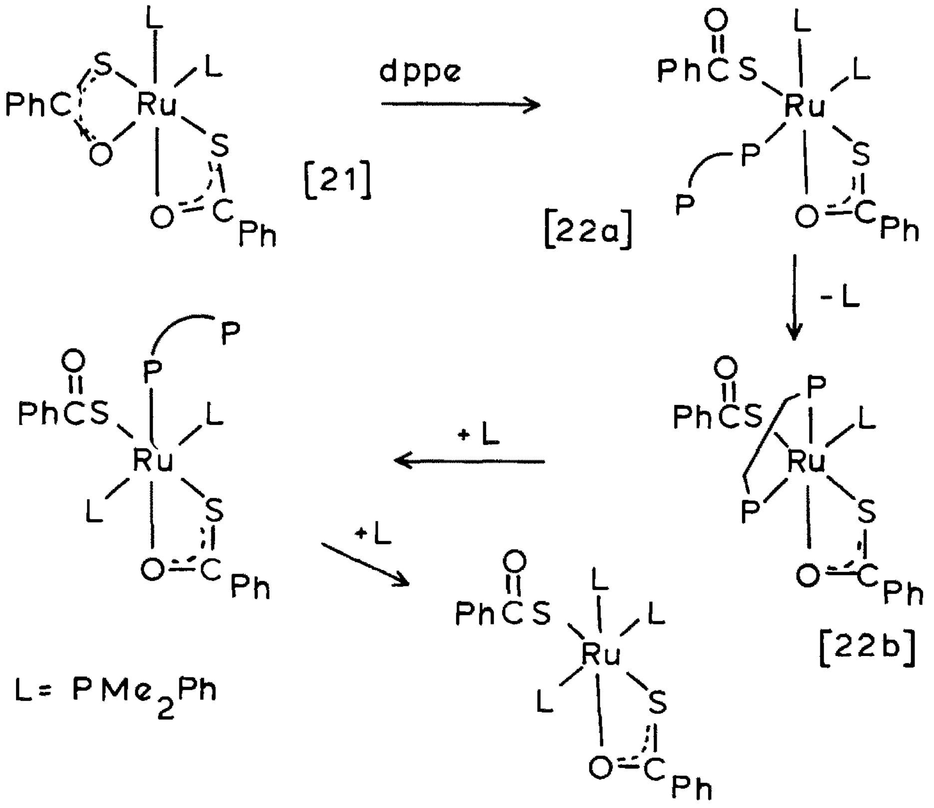
Scheme 4



electron redox reactions. The electrochemistry and UV/visible spectra of these compounds were reported (64).

The cation $[Ru(S_2CH)(PMe_2Ph)_3\{P(OMe)_3\}]^+$ reacted with $P(OMe)_3$ to afford $[Ru(S_2CH)(PMe_2Ph)_2\{P(OMe)_3\}_2]^+$. A kinetic study of the substitution produced evidence that nucleophilic attack by PMe_2Ph on the carbon of the dithioformate

Scheme 5



ligand catalyzes the substitution. The PF_6 salt of $[Ru\{S_2CHPMe_2Ph\}(PMe_2Ph)_2\{P(OMe)_2Ph\}]^+$ was isolated and was suggested to be structurally analogous to the intermediate in the substitution (65). The proposed mechanism is shown in Scheme 4.

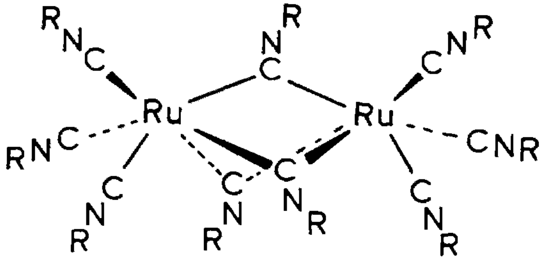
The monothiobenzoate complex $Ru(SOCPh)_2(PMe_2Ph)_2$ [21] reacted with dppm in ethanol to form mer-$[Ru(SOCPh)_2(PMe_2Ph)_3]$-dppm with only one end of the dppm ligand coordinated, and the corresponding reaction with dppe produced $[Ru(SOCPh)_2(PMe_2Ph)(dppe)]$ [22]. The latter consists of two isomers containing bidentate [23a] and S-bonded [22b] monothiobenzoate ligands; the crystal structure of [22b] was determined. The reaction of [21] with PMe_2Ph gave an isomeric mixture of mer-$[Ru(SOCPh)_2(PMe_2Ph)_3]$. Treatment of cis-$[RuCl_2(PMe_2Ph)_4]$ with ammonium monothiobenzoate in methanol for a brief period gave the fac isomer but after several hours $[Ru(SOCPh)(PMe_2Ph)_4]^+$ was formed (Scheme 5) (66).

ISOCYANIDE, NITROSYL, DIAZENATO, AND DINITROGEN COMPLEXES

Isocyanide Complexes

The new homoleptic isocyanide complex $Ru_2(CN\text{-}i\text{-}Pr)_9$ was prepared by reduction of $RuCl_2(CN\text{-}i\text{-}Pr)_4$ with sodium amalgam in the presence of excess isopropyl isocyanide. The structure [20] is presumably the same as that found by X-ray crystallography for $Fe_2(CNEt)_9$. The Ru complex undergoes fluxional exchange of bridging and terminal isocyanide ligands (41).

[20]



Cleavage of the metal-metal multiple bond of $Ru_2(O_2CMe)_4Cl$ with t-butyl isocyanide gave trans-$Ru(CN\text{-}t\text{-}Bu)_4(O_2CMe)_2$ in 87% yield (42). Another Ru(II) isocyanide complex $RuH_2(PMe_3)_2(CN\text{-}t\text{-}Bu)_2$ was prepared by reaction of $RuMe_2(PMe_3)_4$ with t-butyl isocyanide (43); this product was characterized by IR and ^{31}P and ^1H NMR spectroscopy.

The new complex $Ru_2Cp_2(CO)_2(CN\text{-}i\text{-}Pr)_2$ exists as a mixture of isomers differing in orientation of the Cp rings and in the location of the isocyanide ligands in bridging and terminal positions. From studies of this compound and a large number of iron analogs, it was found that the isocyanide ligands with bulkier substituents favored terminal coordination but those with electron-withdrawing substituents preferred bridging positions (44).

The syntheses of RuCl(CNR)(PPh_3)Cp (R=t-Bu,c-C_6H_{11}, $CH_2SO_2C_6H_4$Me, and 4-C_6H_4OMe) and RuCl(CN-t-Bu)$_2$Cp were achieved by substitution of CNR for PPh_3 on RuCl$(PPh_3)_2$Cp in refluxing solvents. Only with CN-t-Bu under forcing conditions (180°/12 h) was the disubstituted product RuCl(CNR)$_2$Cp isolated as an unstable solid. In the presence of NH_4PF_6 in methanol, [Ru(CNR)$(PPh_3)_2$Cp]PF_6 was formed. Reactions of Ru(CN)$(PPh_3)_2$Cp with electrophiles HPF_6 or trialkyloxonium salts gave [Ru(CNR)$(PPh_3)_2$Cp][PF_6] (R=H, Me, Et) (45).

Nitrosyl Complexes

Oxygen atom transfer from a nitrite ligand to a carbonyl ligand on $Ru(NO_2)_2(CO)_2(PPh_3)_2$ in the presence of excess PPh_3 first gave Ru(ONO)(CO)(NO)$(PPh_3)_2$ and carbon dioxide. This intermediate O-nitrito complex was then reduced by PPh_3 to form $Ru(NO)_2(PPh_3)_2$ and $OPPh_3$. The intermediate was independently synthesized and characterized. Thermolysis of labeled $Ru(N^{18}O_2)_2(CO)_2(PPh_3)_2$ verfied the nitrite as the source of oxygen in the carbon dioxide formed; scrambling of O between N and C prior to carbon dioxide loss led to a statistical distribution in all possible sites. Double labeling studies using $Ru(N^{18}O_2)_2(CO)_2(PPh_3)_2$ and $Ru(NO_2)_2(^{13}CO)_2(PPh_3)_2$ were consistent with an intermolecular mechanism for O atom transfer from nitrite to carbon monoxide (46).

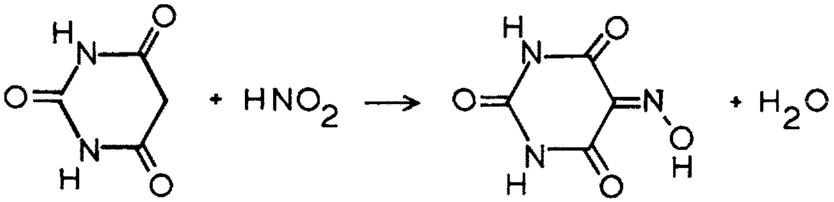
A kinetic study of the rates of substitution by PPh_3 on polymer-supported $RuCl_3(NO)(SbPh_3)_2$ was made. Three resins with different Sb and Ru contents were employed. Comparisons were to the homogeneous reaction for $RuCl_3(NO)(Ph_2Sb(CH_2)_3SbPh_2)$. The reaction involves two different pathways from a common intermediate, the rate law being: rate = $(k_1+k_2[PPh_3])$-[complex] (47).

Nitrosyl complexes of the types $Os(NO)X_3(EPh_3)_2$ (X=halogen, E=P, As), $Os(NO)(NO_2)(PPh_3)_3$, and $Os(NO)Cl(AsPh_3)_3$ were prepared through reactions of $OsCl_3$ with NOX (X=Cl, Br, Br_3) or N_2O_3 in the presence of PPh_3 or $AsPh_3$. Products were characterized by their elemental analyses, IR spectra, and electrical conductivity (48).

The electrochemical behavior of $[Os(NO)(dppe)_2]^+$ and its Fe analog were examined. The reduction of the complex proceeded in two reversible one-electron steps to give the monoanion. Comparisons were made to the Ru analog (49).

Photolysis of acetonitrile solutions of cis-$[Ru(bipy)_2(NO)X]^{+n}$ ($X=Cl^-$, Br^-, NO_2^-, n=2; X=MeCN, py, n=3), cis-$[Ru(bipy)(phen)(NO)X]^{2+}$ and cis-$[Ru(phen)_2(NO)X]^{2+}$ (X=Cl, Br, NO_2) was studied using spectrophotometry. Photosolvation of NO and X ligands was achieved using UV irradiation and quantum yields were determined (50).

Complexes of the general formula $Ru(VR_2)_2X(NO)$ and $[Ru(VR_2)_2Y(NO)][ClO_4]$ (VR_2=violurate, R=H or Me; $X=Cl^-$, NO_3^-, or OH^-, Y=MeCN, Me_2SO, py, $N_2C_3H_4$ or H_2O) have heen synthesized by acidification of $[Ru(NO_2)_4(OH)(NO)]^{2-}$ in the presence of HVR_2 and $NaVR_2$. Some properties were reported (51). These complexes where R=H and $X=OH^-$ were prepared, in addition to $[Ru(VR_2)(NO_2)_2(NO)(OH)]^-$, by reaction with barbituric acid. The stoichiometry of the latter reaction and kinetic experiments have allowed determination of the mechanism of N-C bond formation:



The HNO_2 is generated by acidic aquation of the starting ruthenium complex (52).

The cation $[(trpy)(bipy)Ru(NO)]^{3+}$ was the initial product upon oxidation of $[(trpy)(bipy)Ru(NH_3)]^{2+}$ at a potential of 0.8 V (vs. saturated NaCl calomel) in aqueous solution at a pH of 4.9. However, this nitrosyl complex is in equilibrium with the nitrito complex $[(trpy)(bipy)Ru(NO_2)]^+$ (53).

Refluxing $OsCl_5$ and Cl_3CNO_2 afforded $(NO)_2[OsCl_5(NO)]$. Thermolysis of the product at 170° under vacuum formed $OsCl_3(NO)$. The nitrosyl complexes were characterized by their IR spectra (54).

Oxidation of the $[Ru(NH_3)_6]^{3+}$ cation, exchanged into X- and Y-type zeolites, produced a variety of intermediates which were characterized by IR and X-ray photoelectron spectroscopy. After heating at 450 K in flowing oxygen, the predominant complex in both zeolites was $[Ru(O_{zeolite})_3(NH_3)_X(NO)]$ (X=1 or 2). Further decomposition of this species at 530 K gave RuO_2 in flowing oxygen or a reduced Ru species under vacuum (55). Reactions of $[Ru(NH_3)_6]^{2+}$ in these zeolites with nitrous oxide gave $[Ru(NH_3)_5(N_2)]^{2+}$, $[Ru(NH_3)_5(NO)]^{3+}$ and NH_4^+ in the zeolite (56).

Other studies have examined nitrosyl complexes by physical or other techniques. Nine nitrosyl complexes of Ru in aqueous nitric acid were separated by chromatography and identified (57). The catalytic activity of

$Ru(NO)(NO_3)_3 \cdot 2H_2O$, $Na_2[Ru(NO)(NO_2)_4(OH)] \cdot 2H_2O$, and $[Ru(NO)(NH_3)_5][SO_4]$ for Hg^+ oxidation by Ce(IV) or Mn(III) and for p-benzoquinone oxidation by Mn(III) was examined (58). The chromatographic separation of $Na_2[Ru(NO_2)_4(NO)(OH)]$ in 3 M nitric acid/3-methyl-2-butanone was re-investigated (59). A nitrosyl complex was one of the products formed by electrochemical oxidation of $[Ru(bipy)_2(i\text{-}nic)(NO_2)]^+$ (i-nic=isonicotinic acid) attached to alkylamine silanized platinum oxide electrode surfaces by amide coupling (60).

Diazoalkane and Dinitrogen Complexes

A series of $M\text{-}N_2R$ complexes, where M=Ru(0) and others and N_2R is either a tetrahalo derivative of diazocyclopentadiene or is 9-diazofluorene, was prepared. Reactions of these complexes with COS were studied (61).

Discrete variation method Hartree-Fock-Slater calculations on $[Ru(NH_3)_6]^{+2,+3}$ and $[Ru(N_2)(NH_3)_5]^{2+}$ showed significant σ-covalency and strong π-backbonding in the dinitrogen complex. In this ion the directly bonded N atom is considerably more negatively charged than the other, in agreement with simple electrostatic and bonding arguments (62).

Complexes of $Ru^{II}(H_n edta)L_n$ ($n=1, 2$; $L=N_2$, CO, NO, RCN) were prepared through reactions of $[Ru^{II}(Hedta)(H_2O)]^-$ with L. For the dinitrogen reaction both terminal and bridging N_2 species were observed in solution and isolated as solids. At 25°C $[\{Ru(edta)\}_2N_2]^{4-}$ dissociates with $\Delta H^{\neq}$ of 4.4 kJ/mole and $\Delta S^{\neq}$ of -140 J K^{-1} (63).

Reduction of $Os^{VI}O_2(OEP)$ with hydrazine afforded $Os^{II}(N_2)(OEP)$. Other ligands L, such as tetrahydrothiophene, displace N_2 to form adducts $Os^{II}(OEP)L_2$ (64).

METAL-GROUP IV ATOM σ-BONDED SPECIES

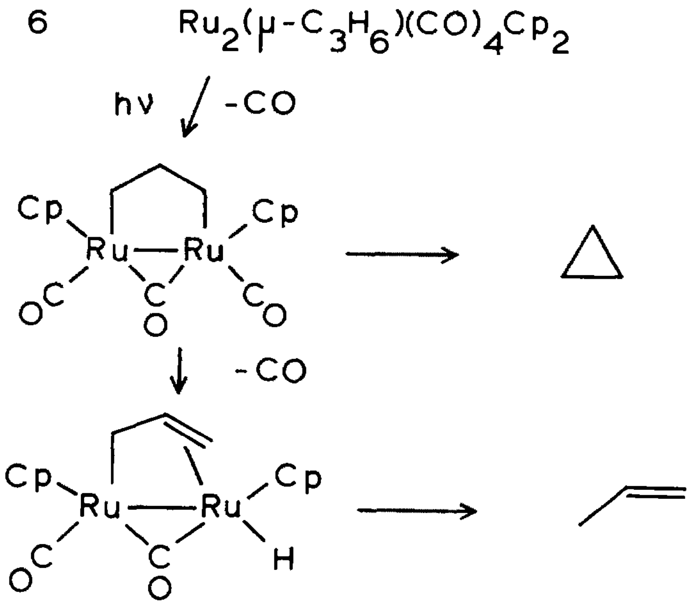
The alkyl complexes $OsEtX(CO)_2(PPh_3)_2$ (X=Cl, I, O_2CCF_3, $OClO_3$) were prepared by treatment of $Os(C_2H_4)(CO)_2(PPh_3)_2$ with the appropriate acid HX. In the presence of excess HCl, migratory insertion, followed by protonation, gave $OsCl_2[C(OH)Et](CO)(PPh_3)_2$. Migration in $OsEt(OClO_3)(CO)_2(PPh_3)_2$ was induced by CO, CNR or $S_2CNEt_2^-$ to give, respectively, $[Os\{C(O)Et\}(CO)_3(PPh_3)_2][ClO_4]$, $[Os\{C(O)Et\}(CO)(CNR)_2(PPh_3)_2][ClO_4]$, and $Os\{C(O)Et\}(S_2CNEt_2)(CO)(PPh_3)_2$ (67).

Photolysis of Cp_2TiMe_2 in the presence of $RuCl_2(CO)_2L_2$ afforded $RuMeCl(CO)_2L_2$. Methyl transfer was also observed with other metal-halide and metal-metal bonded dimers. Radical intermediates were proposed (68).

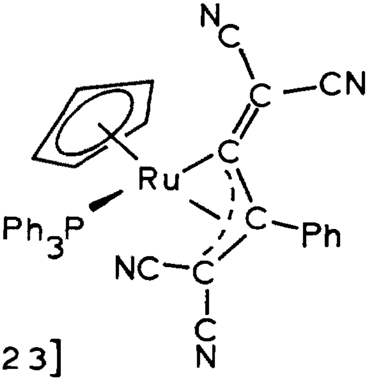
The crystal structure of $(-)_{436}\text{-}(\eta^6\text{-}C_6H_6)Ru(SnCl_3)Me[PPh_2(NHCHMePh)]$ was determined; the complex was found to have the R configuration (69).

Photochemical decomposition of $[Cp(CO)_2Ru\{\mu\text{-}(CH_2)_3\}Ru(CO)_2Cp]$ resulted in evolution of propene and cyclopropane in a 50:1 ratio (70). The results were interpreted in terms of a transient dimetallocycle which decomposes via β-elimination and reductive elimination and were suggested to be related to the mechanism of Fischer-Tropsch catalysis. The proposed mechanism is illustrated in Scheme 6.

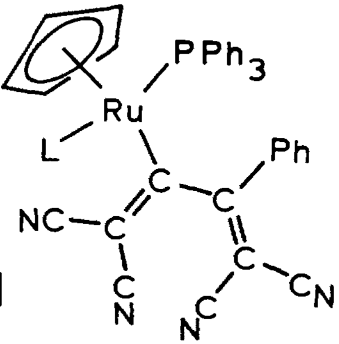
Scheme 6



The reaction of $Ru(C_2Ph)(PPh_3)_2Cp$ with tetracyanoethylene afforded $Ru[\eta^3\text{-}C(CN)_2C(Ph)C{=}C(CN)_2](PPh_3)Cp$ [23]. Treatment of this product with L=CO or CN-t-Bu yielded $Ru[\eta^1\text{-}C({=}C(CN)_2)C(Ph){=}C(CN)_2]L(PPh_3)Cp$ [24]. The structures of [23] and [24] (L=CN-t-Bu) were crystallographically determined (71).



[23]



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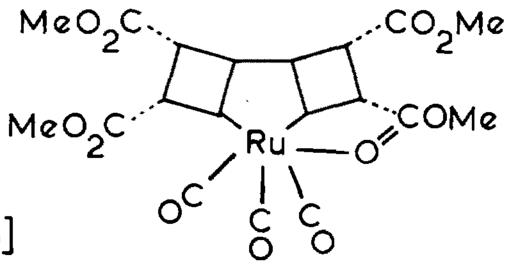
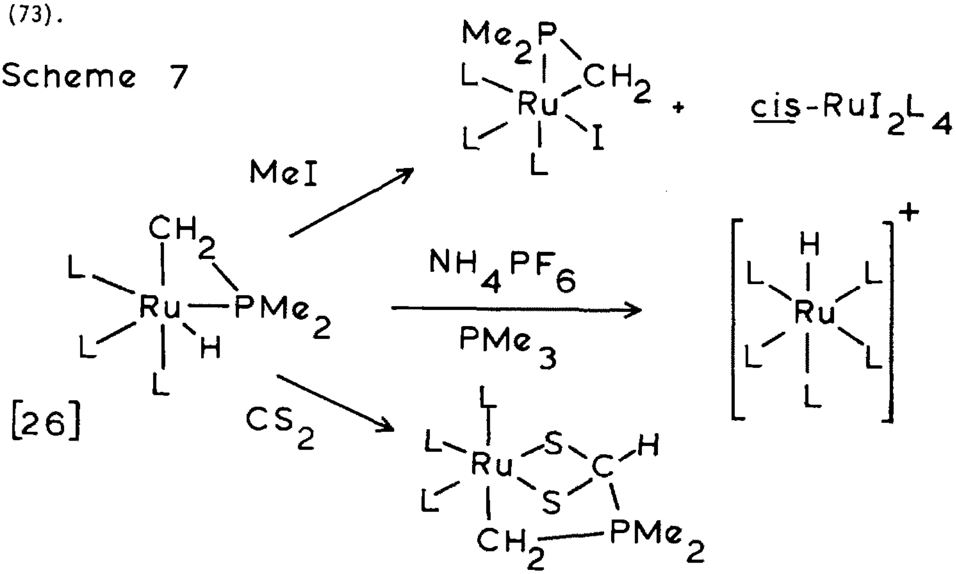


[25]

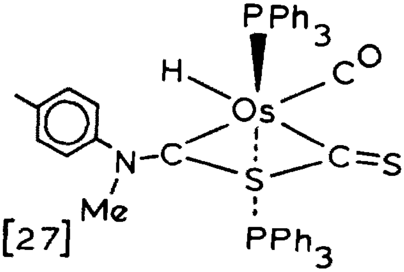
The metallocyclopentane complex [25] was prepared by treatment of $Ru(CO)_3(CH_2{=}CHCO_2Me)_2$ with dimethyl *cis*-cyclobutene-3,4-dicarboxylate (72).

Metallation of a PMe_3 ligand after reduction of *trans*-$RuCl_2(PMe_3)_4$ with sodium amalgam gave $RuH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3$ [26]. This product did not react with either CO or PMe_3, unlike the Fe analog, which gives $Fe(PMe_3)_{5-n}L_n$ (n=2 or 3). However, the complex did react with a number of other reagents (Scheme 7). Products were characterized by ^1H and ^{31}P NMR spectroscopy (73).

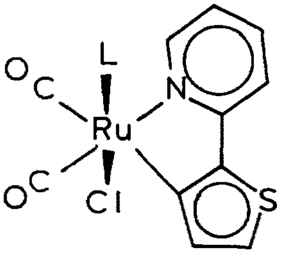
Scheme 7



The crystal structure of $Os[CS_2CN(p\text{-tolyl})Me]H(CO)(PPh_3)_2$ [27] was reported (74).



[27]



[28]

The ligand 2-(2-thienyl)pyridine (H(2-tp)) reacted with $[Ru(CO)_3Cl_2]_2$ to give the metallated adduct $[Ru(2\text{-}tp)(CO)_2Cl]_2$. This complex then was reacted with py or $P(\underline{n}\text{-}Bu)_3$ to give a complex [28] in which the 2-tp ligand is chelated through N and the C atom at the 2-position of the thiophene moiety. These complexes are analogous to complexes of cyclometallated 2-phenylpyridine (75).

The crystal structure determination and ^{119}Sn NMR spectrum of $[NEt_4]_4$-$[Ru(SnCl_3)_5Cl]$ were reported. The ^{99}Ru-^{119}Sn coupling constants were 847 and 810 Hz (76). Reaction of $[M(SnCl_5)Cl]^{4-}$ (M=Ru, Os) with PPh_3 and $OPPh_3$ in ethanolic HCl gave $[HPPh_3]_n[M(SnCl_3)_5Cl]$ and $[M\{SnCl_2(OPPh_3)\}_5Cl]Cl$, respectively. Oxidation of $[HPPh_3]_n[M(SnCl_3)_5Cl]$ gave $M\{SnCl_2(OPPh_3)\}_n$-$(SnCl_3)_{5-n}Cl$. The structures of the products were elucidated by IR spectroscopy and electrical conductivity (77).

The complex *cis*-$Os(CO)_4(SiXCl_2)H$ was the major product formed by photolysis of $Os_3H_3(CO)_9(SiXCl_2)_3$ (X=Me, Cl) in hexane under CO (2 atm). These products, in addition to $[Os(CO)_4(SiXCl_2)]_2$, were also formed by heating the cluster with CO at high temperatures and pressures. At 75°C *cis*-$[Os(CO)_4(SiXCl_2)H]$ reacted with PPh_3 to give *mer*-$[Os(CO)_3(PPh_3)(SiXCl_2)H]$. Pyrolysis of $Os(CO)_4(SiXCl_2)H$ in solution gave mainly $[Os(CO)_4(SiXCl_2)]_2$ under vacuum but $Os(CO)_5$ under CO (78).

The complex, reported in *Chem. Abst.* to be $Ru(PPh_3)(SnCl_3)Cl$, but more likely $Ru(PPh_3)_3(SnCl_3)Cl$, was prepared and characterized by IR spectroscopy and electrical conductivity. This compound was an extremely active catalyst for homogeneous hydrogenations of 1-hexene, penta-1,3-diene, and, less actively, 1-hexyne. No isomerization was observed. This catalyst is reported to be superior in activity and selectivity to $RuCl_2(PPh_3)_3$ (79).

Photolysis of $M_2(CO)_8(SiMe_3)_2$ (M=Ru, Os) in dichloromethane or toluene and in the presence of the radical spin trap nitrosodurene RNO (R=2,3,5,6-tetramethylphenyl) in the cavity of an ESR spectrometer gave evidence for the generation of metal-based radicals. The radicals $M(CO)_4(SiMe_3)\{N(\dot{O})R\}$ were characterized by their ESR spectra (80).

COMPLEXES WITH π-BONDED HYDROCARBONS

Monoalkene Species

Photolysis of $Ru_3(CO)_{12}$ in the presence of excess olefin (methyl acrylate, dimethyl fumarate, dimethyl maleate, allyl acetate, methyl vinyl ketone, or acrylonitrile) afforded $Ru(CO)_4$(olefin) complexes quantitatively. Quantum yields of 0.003 to 0.12 were found to depend upon the olefin, concentration, and wavelength. The moderately stable $Ru(CO)_4$(methyl acrylate) could be used as a convenient source of $Ru(CO)_4$ (81). Irradiation of

$Ru_3(CO)_{12}$ with UV light in the presence of excess olefin gave $Ru(CO)_3(olefin)_2$; for example, $Ru(CO)_3$(methyl acrylate)$_2$ was prepared in 61% yield. The fluxional ^1H NMR spectral behavior of these complexes was studied. The reaction of $Ru(CO)_3$(methyl acrylate)$_2$ with dimethyl cis-cyclobutene-3,4-dicarboxylate gave tricarbonyl-6-ruthenatricyclo[5.2.0.0]nonane [25] (82).

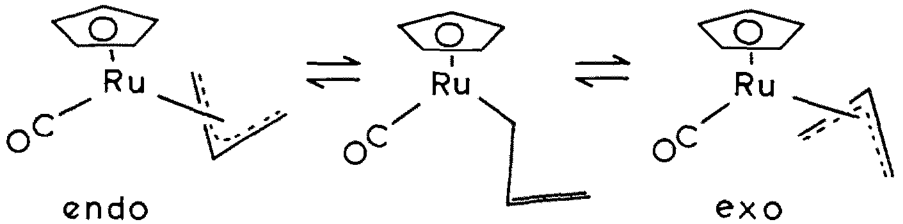
The ethylene complex $Os(C_2H_4)(CO)_2(PPh_3)_2$ was prepared from $Os(CO)_2(PPh_3)_3$ and ethylene. This complex was protonated with one equiv of acid HX to give the ethyl complex $Os(C_2H_5)X(CO)_2(PPh_3)_2$ (X=Cl, I, O_2CCF_3, ClO_4) (67).

Reactions of $[Ru(CO)(C_2H_4)Cl_2(PMe_2Ph)_2]^+$ salts with nucleophiles have been examined. At 308 K, PMe_2Ph substituted for ethylene but at low temperatures the kinetically favored product was $[Ru(CO)(\sigma\text{-}CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3]^+$ by attack at the olefin to form a β-phosphoniumethyl group. The complexes $Ru(CO)(C_2H_4)X_2(AsMe_2Ph)_2$ (X=Cl, Br) reacted with PMe_2Ph to give $[Ru(CO)(\sigma\text{-}CH_2CH_2PMe_2Ph)X(AsMe_2Ph)_2(PMe_3Ph)]^+$, and $Ru(CO)(C_2H_4)Cl_2(PMe_2Ph)_2$ with $PMePh_2$ formed $[Ru(CO)(\sigma\text{-}CH_2CH_2PMePh_2)Cl(PMe_2Ph)_2(PMePh_2)]^+$. Nucleophiles $AsMe_2Ph$, NH_2CH_2Ph, $P(OMe)_2Ph$, 4-picoline, and SMe_2 showed no evidence for attack at the ethylene ligand (83).

Allyl Complexes

Phase transfer catalysis was utilized in a high yield route to endo- and exo- Cp(η^3-allyl)Ru(CO) and the corresponding η^3-2-methallyl complex. In both cases the endo isomer thermally rearranged to the more stable exo isomer. Activation parameters for the isomerizations were substantially greater than those for the corresponding Fe compounds but a similar $\eta^3\rightarrow\eta^1\rightarrow\eta^3$ transformation was suggested (Scheme 8). A typical synthesis took $CpRu(CO)_2Br$ and allyl bromide in a mixture of methylene chloride, 5 N sodium hydroxide and benzyltriethylammonium chloride and yielded 89% Cp(η^3-C_3H_5)Ru(CO) as a 1:1 mixture of exo and endo isomers (84).

Scheme 8

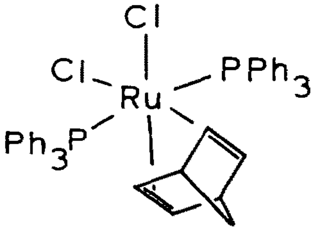


The complexes (η^6-C_6H_6)Ru(η^3-C_3H_5)X (X=I, Br, OCN, CN, O_2CF_3, SCN, ONO_2) were prepared in 26-70% yield by metathesis between (η^6-C_6H_6)(η^3-C_3H_5)RuX and MX (M=Li, K, Ag). The influence of the ligand X upon the ^1H and ^{13}C NMR spectra of these complexes was reported (85).

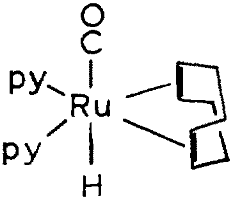
Cyclobutadiene, Diolefin, Polyolefin Complexes

The tetraphenylcyclobutadiene complexes $Ru(CO)_{3-n}[P(OMe)_3]_n(\eta^4-C_4Ph_4)$ (n=2 or 3) underwent reversible one-electron oxidation at a Pt electrode in dichloromethane to give radical cations $[Ru(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4-C_4Ph_4)]^+$. The Fe analogs were also investigated. The halide salts $[RuX(CO)\{P(OMe)_3\}_2(\eta^4-C_4Ph_4)]^+$ (X=Cl, Br) reacted with PPh_3 to displace the halotetraphenylcyclobutenyl radicals C_4Ph_4X (86).

The norbornadiene complex $RuCl_2(PPh_3)_2(C_7H_8)$ [29] was prepared by treatment of $RuCl_2(PPh_3)_4$ with the diene. The structure was determined by X-ray crystallography (87). The 1,5-cyclooctadiene complexes $RuHCl(COD)(amine)_2$ underwent amine exchange with pyridine, α-picoline, and 4-(dimethylamine)-pyridine. The structure of $RuClH(COD)(py)_2$ [30] was determined crystallographically (88).

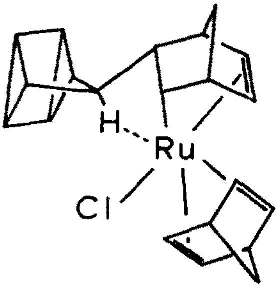


[29]

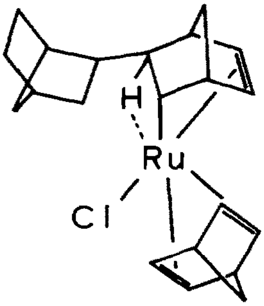


[30]

Reduction of $[RuCl_2(diene)]_n$ (diene=norbornadiene or 1,5-cyclooctadiene) by zinc in the presence of norbornadiene in refluxing acetonitrile gave two new compounds of the formula $RuClC_{21}H_{25}$. X-ray crystallographic studies of both compounds found structures [31] and [32]. Complex [31] reacted with silver triflate in acetonitrile-diethyl ether to give in 85% yield the cation resulting from replacement of chloride by acetonitrile. In both complexes the C-H---Ru interactions were viewed as incipient 3-center-2-electron bonds (89).

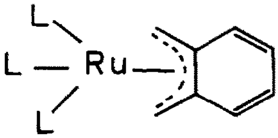


[31]

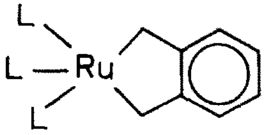


[32]

The *o*-xylylene complexes $Ru(CH_2C_6H_4CH_2)L_3$ (L=PMe_2Ph, $PMePh_2$) were prepared by reaction of $RuCl_2L_4$ with *o*-$MeC_6H_4CH_2MgBr$. Characterization by spectroscopic and chemical methods suggested that the complexes should be considered to have a 1-4-η-bonded *o*-xylylene ligand [33] rather than a σ-bonded dialkyl [34] (90).



[33]

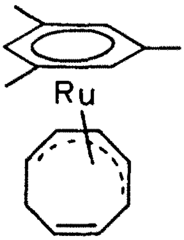


[34]

Vinyl ethers containing $Ru(CO)_3$(1-4-η^4-1,3-pentadiene) were prepared by selective dienylation with pentadienyl potassium. This material was polymerized using cationic initiators to give high molecular weight polymers containing diene complexes of Ru. Protonation with HCl gave polymer-bound $Ru(CO)_3$(1-3-η^3-allyl) species (91).

Protonation of Ru(η^6-arene)(η^4-COT) (arene=mesitylene, hexamethylbenzene, *t*-butylbenzene; COT=cyclooctatetraene) with HPF_6, HBF_4 or CF_3CO_2H gave the corresponding $[Ru(1\text{-}5\text{-}\eta^5\text{-}C_8H_9)(arene)]^+$ cation isolated as the PF_6 or BF_4 salts. Mesitylene and hexamethylbenzene complexes isomerized upon warming in solution to give $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(arene)]^+$, but in the presence of CF_3CO_2H isomerization was incomplete. Unlike the protonation of $Fe(CO)_3$-(COT), protonation of either Ru(arene)(COT) or $Ru(CO)_3$(COT) did not lead to a 2-6-η-bicyclo[5.1.0]octadienyl species. Protonation with CF_3CO_2D gave $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_8D)(arene)]^+$ (arene=C_6Me_6, C_6H_5-*t*-Bu) with the deuterium atom exo to the metal and the label did not shift during the subsequent isomerization. The crystal structure of $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6H_3Me_3)][PF_6]$ [35] was determined (92).

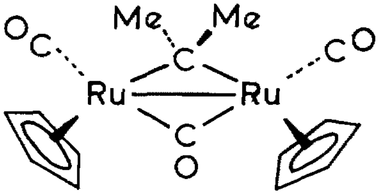
[35]



Cyclopentadienyl Complexes

Carbon-carbon bond cleavage was observed in reactions of ligands L with $Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}Cp_2$ to give $Ru_2(CO)\{P(OMe)_3\}_2(\mu\text{-}CO)_2Cp_2$

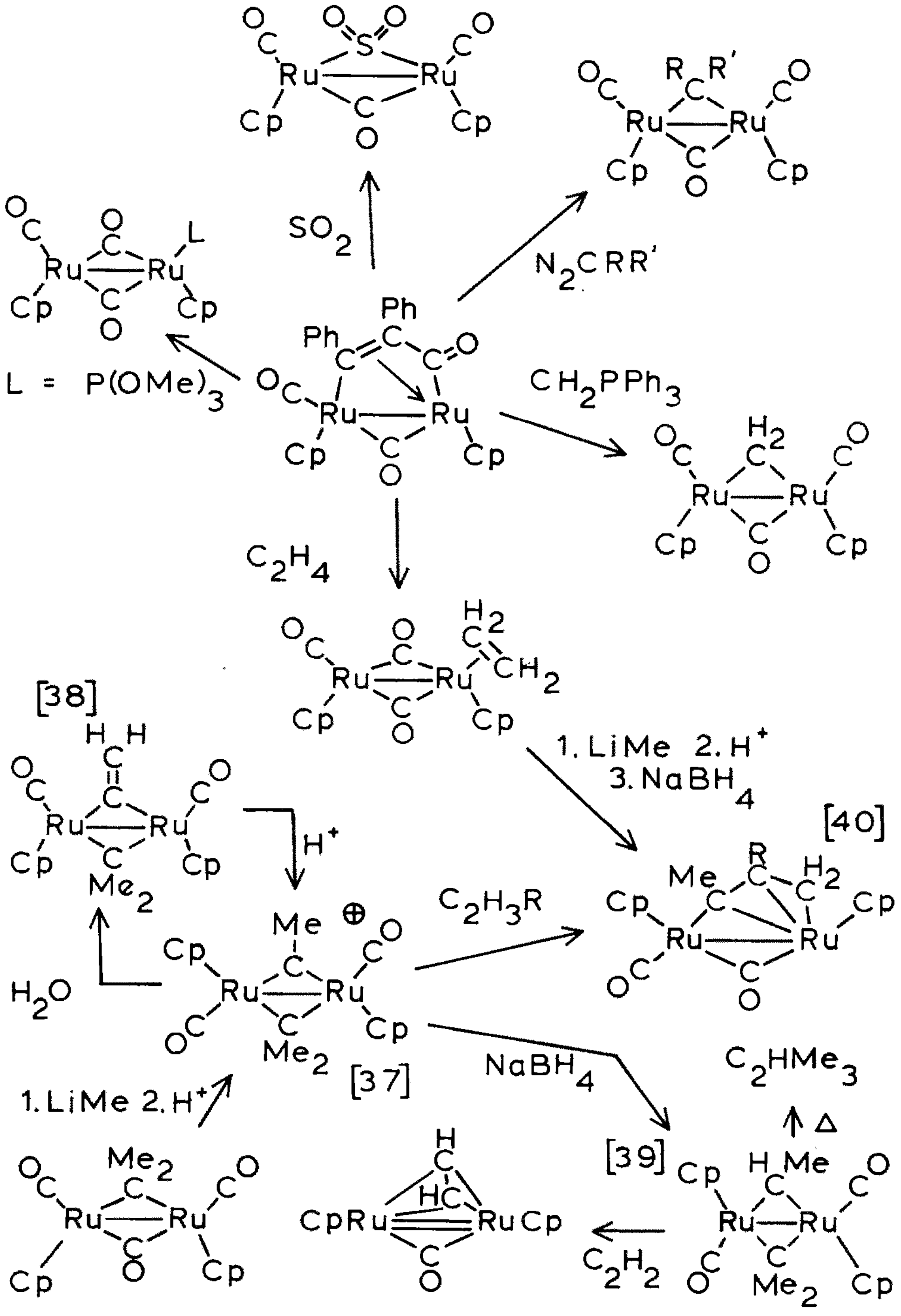
(L=P(OMe$_3$)) or Ru$_2$(CO)$_2$(μ-CO)(μ-L)Cp$_2$ (L=SO$_2$, CR$_2$, CH$_2$). The carbene derivatives were prepared using the appropriate diazoalkane (Scheme 9) (122). The μ-dimethylcarbene complex Ru$_2$(CO)$_2$(μ-CO)(μ-CMe$_2$)Cp$_2$ [36] was shown by X-ray crystallography to adopt the cis configuration in the solid state. However, ^{1}H NMR studies showed that both cis and trans isomers were present in solution in a ca. 1:1 ratio at 39°C. Interconversion between these isomers occurs at 140° at a rate which is rapid on the NMR timescale.



[36]

The mechanism for this process was suggested to involve bridge opening to give an intermediate with a terminal carbene (93). Treatment of this carbene complex with methyl lithium, followed by protonation with HBF$_4$ at -78°C, quantitatively afforded the carbyne-carbene complex [Ru$_2$(CO)$_2$(μ-CMe)(μ-CMe$_2$)Cp$_2$][BF$_4$] [37]. Deprotonation of the cation by shaking in dichloromethane-water gave Ru$_2$(CO)$_2$(μ-CCH$_2$)(μ-CMe$_2$)Cp$_2$ [38] in 66% yield. The dicarbene complex Ru$_2$(CO)$_2$(μ-CHMe)(μ-CMe$_2$)Cp$_2$ [39] was prepared in 75% yield by treatment of [37] with NaBH$_4$; the crystal structure of was reported. Compounds [37-39] all adopt a trans arrangement of C$_5$H$_5$ ligands and unlike [36] do not undergo fluxional cis-trans isomerization in solution on the NMR timescale. Pyrolysis of [39] at 200°C afforded Me$_2$C=CHMe (70%) in addition to small amounts of ethylene and propene; the lack of 2-butenes or Me$_2$C=CMe$_2$ indicate that this is an intramolecular process (94). Irradiation of [37] with ethylene or propylene afforded Ru$_2$(CO)(μ-CO){μ-η^1,η^3-C(Me)C(R)CH$_2$}-Cp$_2$ (R=H, Me) [40] in 40% yield; the molecular structure was determined by X-ray diffraction. The product may be formed either by (a) initial electrophile attack of the carbyne cation upon the olefin, followed by coordination, or (b) by substitution of the olefin for a carbonyl, followed by intramolecular electrophilic attack of the carbyne upon the coordinated olefin. Since [40] (R=H) can be formed in 50% yield by treatment of Ru$_2$(CO)(C$_2$H$_4$)(μ-CO)$_2$Cp$_2$ with, sequentially, methyl lithium, HBF$_4$, and NaBH$_4$, the path (b) is favored (95). These reactions are summarized in Scheme 9.

Scheme 9


SO$_2$
N$_2$CRR'
L = P(OMe)$_3$
CH$_2$PPh$_3$
C$_2$H$_4$
1. LiMe 2. H$^+$
3. NaBH$_4$
[38]
[40]
H$^+$
C$_2$H$_3$R
H$_2$O
[37]
NaBH$_4$
C$_2$HMe$_3$
Δ
1. LiMe 2. H$^+$
[39]
C$_2$H$_2$

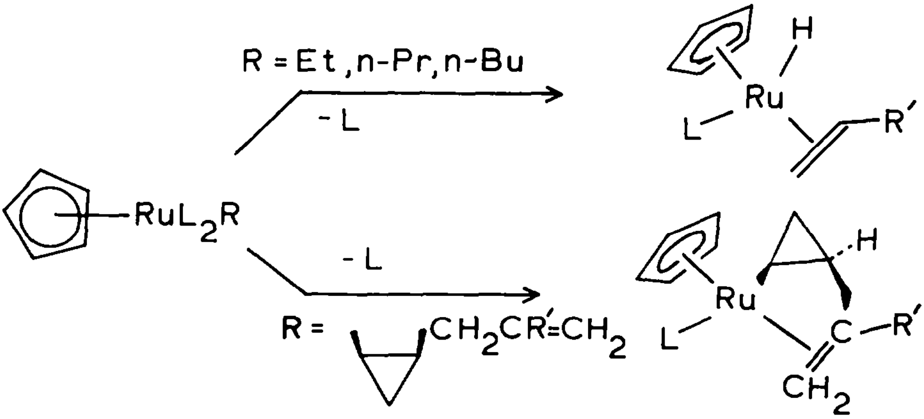
The dimer $Ru_2(CO)_2(CN\text{-}\underline{i}\text{-}Pr)_2Cp_2$ has been prepared. The molecule exists in solution as a rapidly interconverting mixture of isomers (44).

The halides $CpRu(CO)_2X$ (X=Cl, Br) were prepared in excellent yields by reaction of $[CpRu(CO)_2]_2$ with CX_4 upon exposure to room light or in the dark. These products were also obtained by treatment of $CpRu(CO)_2H$ with CX_4. The mechanism presumably involves the $CpRu(CO)_2$ radical (96).

Substitutions of L=$P(OPh)_3$, $P(OMe)_3$, or PPh_3 on $Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2Br$ to give $Ru(\eta^5\text{-}C_5Me_4Et)(CO)LBr$ were studied in diglyme solution. The kinetics indicated a dissociative mechanism. A dissociative mechanism was also observed for substitution of $RuCp(CO)_2Br$ with PPh_3 or $P(OPh)_3$, but the rate was slower than that observed for $Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2Br$. The C_5Me_4Et ligand was suggested to labilize the complex through stabilization of the transition state. However, in dibutyl ether substitution of $RuCp(CO)_2Br$ with $P(OPh)_3$ or PPh_3 apparently proceeded through a free radical mechanism (97).

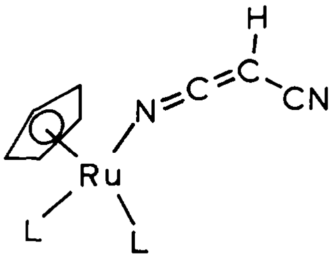
The main product from alkylation of $Na[Ru(CO)_2Cp]$ with chloromethyl methyl ether at -78°C was $RuCp(CO)_2(CH_2OMe)$. Smaller amounts of $RuCp(CO)_2(CH_2Cl)$ were also formed. The latter could be prepared from $RuCp(CO)_2(CH_2OMe)$ by treatment with HCl (98). Other $RuCpL_2$(alkyl) complexes (L=PPh_3, R=Me, Et, n-Pr, n-Bu, CH_2CHMe_2, $CH_2CH_2CH_2CMe{=}CH_2$) were prepared from $RuCpL_2Cl$ and the corresponding Grignard reagent. With secondary or tertiary alkyls the ultimate product was $RuCpL_2H$ after olefin elimination. At 80°C the complexes $RuCpL_2R$ (R=Et, n-Pr, n-Bu) underwent dissociation of L to give the hydrido olefin complexes RuCpLH(olefin) (olefin=C_2H_4, $CH_2{=}CHMe$, $CH_2{=}CHEt$). Stable $RuCpL(\eta^1,\eta^2\text{-}4\text{-alkenyl})$ complexes were obtained if β-hydride elimination was prevented by maintaining an unfavorable relationship between Ru and H in a cyclopropenyl system (Scheme 10) (99).

Scheme 10

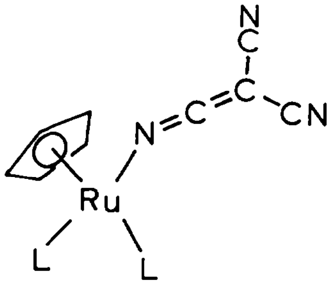


Quaternary ammonium salts of tetrahydroborate were used to prepare a number of metal hydrides, including $CpRu(CO)_2H$. This complex was prepared in 83% yield from $CpRu(CO)_2Br$ and tetraethylammonium borohydride in dichloromethane at 45°C for 2 hr. The product could also be prepared in 74% yield using sodium borohydride in aqueous solution and $CpRu(CO)_2Br$ in dichloromethane in the presence of tetraethylammonium bromide, but the reaction took 17 hr. (100). The substituted derivative $CpRu(PPh_3)_2H$ was prepared by treatment of $CpRu(PPh_3)_2Cl$ with MOR (M=alkali metal, R=alkyl with α-hydrogens). Other complexes of the type $CpRu(PPh_3)_2X$ (X=Br, I, NCS, NCO, CN, BH_4) were prepared by ligand exchange of Cl or H with MX salts or HX, respectively. Reaction of either $CpRu(PPh_3)_2Cl$ or $CpRu(PPh_3)_2H$ with cyclopentadiene afforded ruthenocene. The same reaction with pyrrole gave azaruthenocene. Other complexes prepared were $CpRu(S_2CZ)(PPh_3)$ ($Z=NR_2$, OR) (101). Reaction of the related complex $CpRu(PMe_3)_2Cl$ with L (L=olefin, allene, diene, alkyne, CS_2) in the presence of NH_4PF_6 gave the $[CpRu(PMe_3)_2L]^+$. Treatment of $CpRu(PMe_3)_2Cl$ with HCl or Cl_2 afforded $[CpRu(PMe_3)_2ClX]^+$ (X=H or Cl); related reactions with the Os analog gave $[CpOs(PR_3)_2HBr]^+$ (R=Me, Ph). Ligands used were ethylene, fumaronitrile, 1,3-butadiene, allene, 1,1-dimethyl allene, diphenyl acetylene, ethyl phenylpropiolate, dimethyl acetylene dicarboxylate, and hexafluoro-2-butyne (102).

A series of cyanocarbon and cyanonitrogen derivatives $CpRu(PPh_3)_2R$ ($R=CH(CN)_2$ [41], $C(CN)_3$ [42], $N(CN)_2$ [43], $C_3(CN)_5$ [44], and $N[C_2(CN)_3]_2$ [45])) were prepared by treatment of $CpRu(PPh_3)_2Cl$ with the appropriate anion. The X-ray structure of $CpRu\{N{=}C{=}C(CN)C(CN){=}C(CN)_2\}\{P(OMe)_3\}(PPh_3)$ established that the ligand was bonded through the N atom. The structures of the other complexes were also believed to be keteniminato complexes (103). Reaction between CF_3CN and $CpRu(PPh_3)_2Cl$ afforded $CpRu\{NH{=}C(CF_3)N{=}C(CF_3)NH\}(PPh_3)$; exchange with $P(OMe)_3$ gave the corresponding $P(OMe)_3$ derivative, whose structure was determined [46] (104).

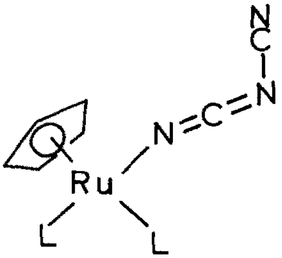


[41]

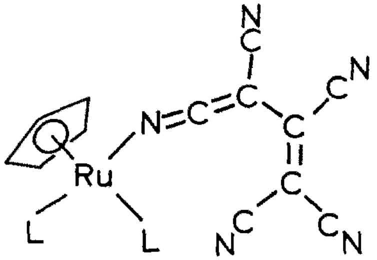


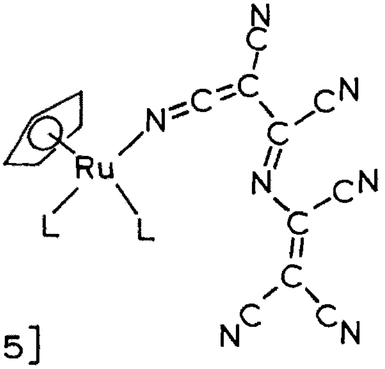
[42]

[43]



[44]





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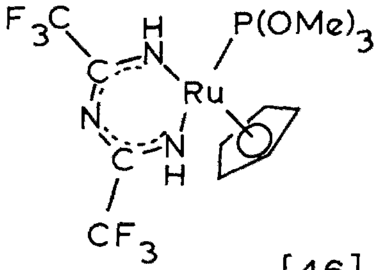
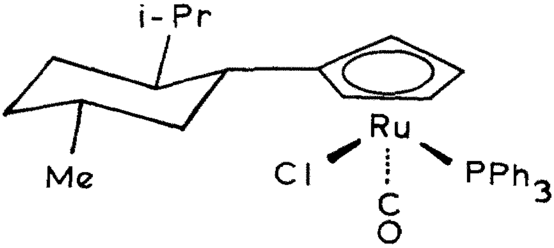


[46]

The syntheses of $CpRu(PMe_3)_2Cl$ and $[CpRu(PMe_3)_2L]^+$ (L=MeCN, CO, CN-*t*-Bu, or PMe_3) were reported. The crystal structures of $CpRu(PPh_3)_2Cl$ and $CpRu(PMe_3)_2Cl$ were determined (105). Reduction of $[CpRu(L_3)][PF_6]$ (L_3=$PPh_2CH_2CH_2PPhCH_2CH_2PPh_2$ (triphos) or $(PPh_2CH_2)_3CMe$ (tripod)) with $LiAlH_4$ afforded $Ru(\eta^4-C_5H_6)(L_3)$ via exo hydride attack; this differed from results with the Fe analog, which gave the metal-hydride (106). The synthesis of the diastereoisomeric pair $(+)_{578}$- and $(-)_{578}$- $[Ru(\eta^5-Mcp)(CO)(PPh_3)Cl]$ (Mcp=(R)-(-)-menthylcyclopentadienyl) was carried out by refluxing $Ru(\eta^5-Mcp)(CO)_2Cl$ with PPh_3 in xylene and the isomers were separated by preparative thin layer chromatography. The structure of the $(+)_{578}$ isomer was determined to be S (based upon the Stanley and Baird sequencing rules) by a crystallographic determination [47] (107).

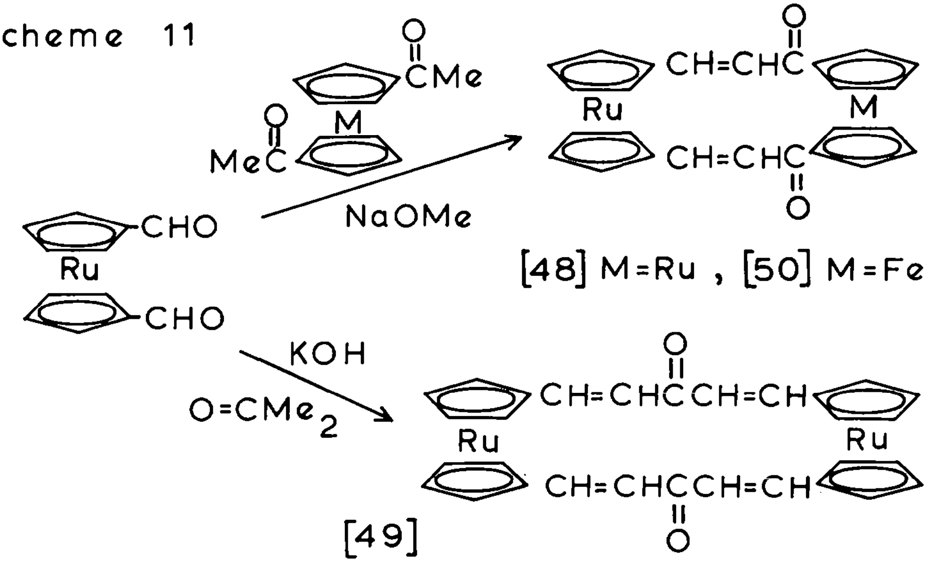


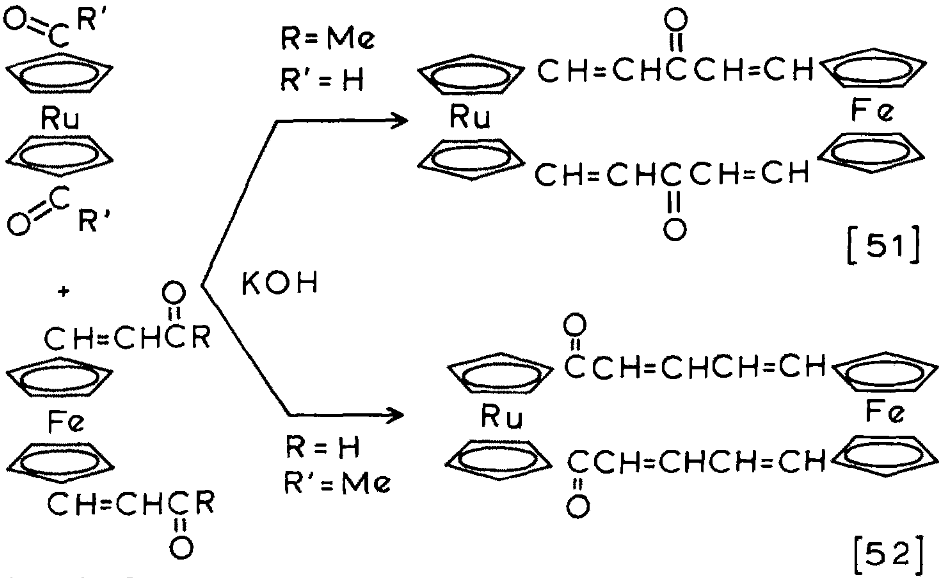
[47]

The ruthenocene derivative $CpRu\{\eta^5-C_5(CO_2Me)_5\}$ has been prepared and its crystal structure determined. Reaction of $CpM(PPh_3)_2Cl$ with $Tl\{C_5(CO_2Me)_5\}$ in acetonitrile afforded $[CpM(PPh_3)_2(NCMe)][C_5(CO_2Me)_5]$ (M=Ru, Os), in which the $[C_5(CO_2Me)_5]$ anion is not coordinated. However, the same reaction in methanol and in the presence of oxygen gave $CpRu\{\eta^5-C_5(CO_2Me)_5\}$. The structure of this complex showed a symmetrical $C_5(CO_2Me)_5$ ring (108).

Chemical shielding parameters for ruthenocene and a number of other cyclopentadienyl complexes were reported (109). Proton affinities for a number of organometallic complexes, including ruthenocene, were determined in the gas phase using ion cyclotron resonance spectroscopy; for ruthenocene the proton affinity was 220 ± 3 kcal/mole, the adiabatic ionization potential was 7.5 ± 0.2 eV, and the homolytic $(B-H)^+$ bond energy was 79 ± 5 kcal/mol (110). Voltammetry of ruthenocene at a vitreous carbon electrode in an aluminum chloride-n-butylpyridinium chloride melt (0.8:1 molar ratio) showed an irreversible one-electron oxidation ($E_{p/2}$=+0.68 V, 100 mV s^{-1}); in acidic melts (excess aluminum chloride) ruthenocene was oxidized by multistep pathways which were sensitive to the melt conditions (111). The synthesis of [3.3] (1,1')-ruthenocenophane-2,14-diene-1,16-dione [48], [5.5] (1,1')-ruthenocenophane-2,14,17,29-tetraene-1,16-dione [49], and some mixed Fe-Ru analogs [50-52] were reported (Scheme 11) (112). Reaction of ^{14}C-labeled glucosamine hydrochloride with ^{103}Ru-labeled ruthenocenecarbaldehyde gave 2-amino-N-(ruthenocenemethyl)-2-deoxysorbitol-1-^{14}C (113); the rate of excretion from and organ distribution in tumor-bearing mice of these labelled materials was investigated (114).

Scheme 11





[51]

[52]

Arene Complexes

The complexes $[M(\eta^6\text{-arene})X(py)_2][PF_6]$(M=Ru; X=Cl, Br, I; M=Os, X=Cl) were prepared by reaction of the corresponding $[M(\eta^6\text{-arene})X_2]_2$ with pyridine in methanol, followed by addition of NH_4PF_6. Treatment of an equimolar mixture of $[M(\eta^6\text{-arene})X(py)_2][PF_6]$ and the corresponding $M(\eta^6\text{-arene})X_2py$ with HBF_4 in methanol gave the triple halide-bridged complexes $[M_2(\eta^6\text{-arene})_2X_3][BF_4]$ in high yield. Spectroscopic evidence was obtained for formation of hetero-bridged, heteroarene and heteronuclear triple halide-bridged complexes of Ru(II) and Os(II) (115). Reactions of $[M(\eta^6\text{-}C_6H_6)Cl_2]_2$ (M=Ru, Os) with excess sodium hydroxide or sodium carbonate in aqueous solution, followed by addition of $NaBPh_4$, formed as the major product $[(\eta^6\text{-}C_6H_6)(OH)M(OH)_2M(H_2O)(\eta^6\text{-}C_6H_6)][BPh_4]$ with $[M_2(\eta^6\text{-}C_6H_6)_2(OH)_3]$-$[BPh_4]$ as minor product. Some other Ru-arene complexes under the same conditions gave only $[Ru_2(\eta^6\text{-arene})_2(OH)_3]^+$ salts (arene=p-MeC_6H_4-i-Pr, $C_6H_3Me_3$, C_6Me_6). The salts $[M_2(\eta^6\text{-arene})_2(OR)_3][BPh_4]$ (M=Ru, R=Me, Et, Ph; arene=C_6H_6; M=Ru, R=Me, arene=$C_6H_3Me_3$, C_6Me_6; M=Os, R=Me, arene=C_6H_6) were prepared by reaction of the appropriate $[M(\eta^6\text{-arene})Cl_2]_2$ compound with NaOR in ROH (116). The chloride bridges of $[Ru(\eta^6\text{-}C_6Me_6)Cl_2]_2$ were cleaved by PMe_3 to give $Ru(\eta^6\text{-}C_6Me_6)Cl_2(PMe_3)$. Treatment of the product with AgO_2CMe afforded $Ru(\eta^6\text{-}C_6Me_6)(O_2CMe)_2(PMe_3)$, in which one acetate undergoes rapid exchange with excess acetate in aqueous solution. The mechanism of acetate exchange was shown to involve the intermediate cation $[Ru(\eta^6\text{-}C_6Me_6)(O_2CMe)(PMe_3)]^+$, which was isolated as its PF_6^- salt. Reduction of

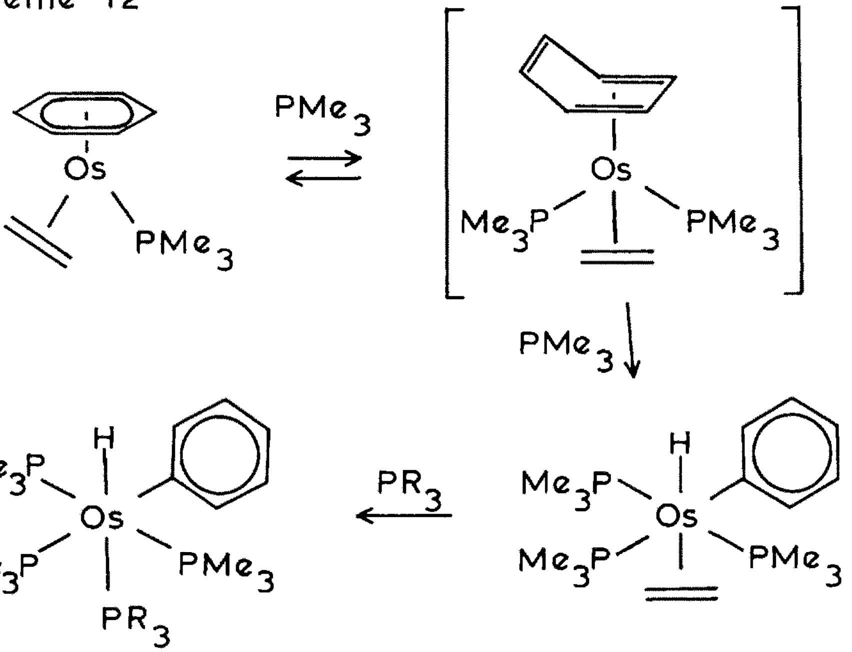
$Ru(\eta^6-C_6Me_6)Cl_2(PMe_3)$ with either $NaBH_4$ or $Na[AlH_2(OC_2H_4OMe)_2]$ gave $Ru(\eta^6-C_6Me_6)H_2(PMe_3)$ (117).

Nucleophilic attack by PR_3 on the arene ring of $[Ru(\eta^6-C_6H_6)L_2Cl][PF_6]$, $Ru(\eta^6-C_6H_6)LCl_2$, or $[Ru(\eta^6-C_6H_6)(NCMe)_3][PF_6]_2$ afforded the η^5-cyclohexadienylphosphonium complexes $[Ru(\eta^5-C_6H_6PR_3)L_3]^{2+}$ (PR_3=PMe_3, PMe_2Ph; L_3=$(PMe_3)_3$, $(PMe_3)_2PPh_3$, $(PMe_3)(PPh_3)(PMe_2Ph)$, $(PMe_3)_2\{P(NMe_2)_3\}$, $(PMe_3)_2(NCMe)$). The ^1H and ^{31}P NMR spectra of these complexes at low temperatures revealed that rotation around the metal-to-ring bond was restricted. The PR_3 ligand of $[Ru(\eta^5-C_6H_6PR_3)L_3]^{2+}$ could be removed by treatment with CF_3CO_2H to give $[Ru(\eta^6-C_6H_6)L_3]^{2+}$ (L_3=$(PMe_3)_3$, $(PMe_3)_2(PPh_3)$, $(PMe_3)_2(NCMe)$) (118).

The cations $[Os(\eta^6-C_6H_6)(NH_3)_3]^{2+}$, $[Os(\eta^6-C_6H_6)(NH_3)_2Cl]^+$, and $[Os(\eta^6-C_6H_6)(NH_2CH_2CH_2NH_2)Cl]^+$, and other Os(II)-$C_6H_6$ complexes were prepared and their coordination chemistry investigated (119). In acidic solution $Os(\eta^6-C_6H_6)Cl_2$ reacted with Ag^+ to form a dication believed to be $[Os(\eta^6-C_6H_6)(H_2O)_3]^{2+}$. The pKa's of $[Os(\eta^6-C_6H_6)(NH_2C_2H_4NH_2)(H_2O)]^{2+}$, $[Os(\eta^6-C_6H_6)(NH_3)_2(H_2O)]^{2+}$, and $[Ru(\eta^6-C_6H_6)(NH_2C_2H_4NH_2)(H_2O)]^{2+}$ were found to be 6.3, 6.4, and 7.9, respectively, at 20°C. The association constant for $[Os(\eta^6-C_6H_6)(NH_2C_2H_4NH_2)(H_2O)]^{2+}$ and chloride ion was measured to be 1.1×10^2. The stability of the chloride complex and the acidity of the aquo ion suggested that the arene ring is electron-withdrawing.

The unstable complexes $Os(\eta^6-C_6H_6)L_2$ (L=PPh_3, $P(OMe)_3$) were prepared by reduction of $[Os(\eta^6-C_6H_6)L_2I][PF_6]$ with sodium naphthalide. The olefin complexes $Os(\eta^6-C_6H_6)(PMe_3)(C_2H_3R)$ (R=H, Me) were more stable. Reactions of these complexes with excess PMe_3 gave, instead of the expected $Os(\eta^6-C_6H_6)(PMe_3)_2$, the phenyl hydride cis-$Os(PMe_3)_4(C_6H_5)H$ by intramolecular insertion into the aryl C-H bond. An intermediate $Os(PMe_3)_3(C_2H_4)(C_6H_5)H$ was observed by ^1H NMR spectroscopy and was isolated; subsequent reaction of this olefin complex with PMe_3 gave the final product. The proposed reaction path is summarized in Scheme 12 (120).

Scheme 12



The kinetics of substitution of dimethyl sulfoxide (dmso) in $RuX_2(\eta^6\text{-}C_6H_6)$(dmso) by PPh_3 in either dmso or 1,2-dichloroethane was studied (121). In dmso the slow formation of $Ru(\eta^6\text{-}C_6H_6)X_2(PPh_3)$ has a rate law

$$\text{rate} = k[\text{complex}][PPh_3]$$

but in 1,2-dichloroethane, stopped flow techniques were required to establish the more complex rate expression

$$\text{rate} = k_1k_2[\text{complex}][PPh_3]/(k_{-1}[\text{dmso}] + k_2[PPh_3])$$

In either solvent the proposed mechanism (Scheme 13) involves initial dissociation of dmso (k_1) to generate the unsaturated intermediate $Ru(\eta^6\text{-}C_6H_6)X_2$. The intermediate then either recombines with dmso (k_{-1}) or adds PPh_3 irreversibly (k_2). The value for k_1 was twice as great when X=Cl (10 s^{-1}) than for X=Br (5 s^{-1}) at 19.0°C and the competition ratio k_{-1}/k_2 varied between 2.2 and 8.4, depending upon the complex.

Scheme 13

$$(\eta^6\text{-}C_6H_6)RuX_2(\text{dmso}) \underset{k\text{-}1,+\text{dmso}}{\overset{k_1,-\text{dmso}}{\rightleftharpoons}} (\eta^6\text{-}C_6H_6)RuX_2 \xrightarrow[+PPh_3]{k_2} (\eta^6\text{-}C_6H_6)RuX_2(PPh_3)$$

CLUSTER COMPOUNDS

Metal Cluster Bonding

A new classification scheme for clusters was proposed. Class I clusters were defined as those using all available Cluster Valence Molecular Orbitals (CVMO's), Class II compounds have vacant s and p CVMO's, and Class III clusters have vacant d CVMO's. In general, the early transition elements form Class III clusters and the late transition elements Class II clusters. Class I is favored by the central Group VIII elements (including Fe, Ru and Os) and only Class I follows the Polyhedral Skeletal Electron Pair analogy to main group elements (123).

He I and He II gas phase photoelectron spectra of $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Os_6(CO)_{18}$, $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$ were recorded and fragment MO analysis was used to assign these spectra. The results for hydride-containing clusters supported the many-center, two-electron bond picture with a high degree of hydrogen localization. The first ionization energies for these clusters were compared with the work function of the corresponding metal surface (124).

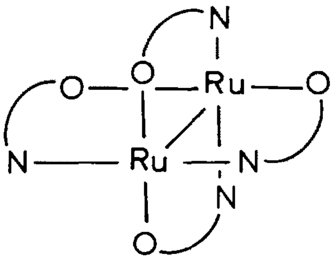
Metal-metal and metal-ligand bond energies have been determined for a number of cluster systems. Microcalorimetric measurements at 520-550 K for the heats of thermal decomposition of $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$ and $Ru_3(CO)_{12}$ were used to calculate ΔH_f° for the clusters and the enthalpy for disruption of the clusters to the metal vapor and CO. Values obtained were $Fe_2Ru(CO)_{12}$, 1820 ± 14 kJ mol^{-1}; $FeRu_2(CO)_{12}$, 1891 ± 16 kJ mol^{-1}, and $Ru_3(CO)_{12}$, 1903 ± 18 kJ/mol^{-1}. Enthalpies of sublimation were estimated and the Fe-Ru bond enthalpy contribution was derived as 95 ± 20 kJ mol^{-1}, which was significantly greater than the mean of the Ru-Ru and Fe-Fe bond enthalpies (125).

Bond length (d)-enthalpy (E) relationships of the form $E=Ad^{-4.6}$ were used to assign metal-metal bond enthalpies for metal carbonyl clusters, including some Ru and Os clusters (126). The M-M bond enthalpies are: $Ru_3(CO)_{12}$, 78 kJ mol^{-1}; $Os_3(CO)_{12}$, 94 kJ mol^{-1}; $Os_5(CO)_{15}$, 116 and 94 kJ mol^{-1}; $Os_6(CO)_{18}$, 120, 110, 107 and 102 kJ mol^{-1}; and $Os_7(CO)_{21}$, 103, 98, and 94 kJ mol^{-1}. The metal-carbonyl bonds become stronger as the cluster nuclearity increases, as shown by the average metal-carbonyl bond dissociation enthalpies: $Os_3(CO)_{12}$, 201 kJ mol^{-1}; $Os_5(CO)_{16}$, 205 kJ mol^{-1}; $Os_6(CO)_{18}$, 208 kJ mol^{-1}; $Os_7(CO)_{21}$, 209 kJ/mol^{-1}. The metal-metal bond strengths obtained were lower than those found in previous treatments.

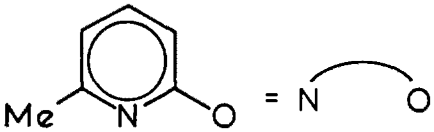
Binuclear Species (excluding (η^5-C_5H_5) Complexes)

Metal-metal bonding in ligand-bridged dimers has been examined using spectroscopic and crystallographic techniques. The complex $Ru_2(mhp)_4$ [53]

(mhp=the anion of 6-methyl-2-hydroxypyridine), prepared in 8% yield by reaction of $Ru_2(O_2CMe)_4Cl$ with Na(mhp), was characterized by X-ray crystallography. Pertinent bond distances are Ru-Ru, 2.238 (1)Å, Ru-N, 2.089(5)Å and Ru-O, 2.044(10)Å. Magnetic susceptibility measurements at 308 K found a μ_{eff} of 2.9 μ_B. The He I photoelectron spectrum of this complex was interpreted to indicate a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1(\pi^*)^3$ configuration with a δ-π splitting of 1.4 eV and a Ru-Ru bond order of 2. The Ru-Ru stretching frequency was 281 cm^{-1} (127). The Resonance Raman spectra of the related compounds $Ru_2(O_2CMe)_4Cl$, $[Ru_2(O_2CMe)_4(H_2O)_2][BF_4]$, $Ru_2(O_2CH)_4Cl$, $Ru_2(O_2CEt)_4Cl$, and $Ru_2(O_2CPr)_4Cl$ at 298 and 80 K were reported (128). The Raman band which was most resonance enhanced was 326-340 cm^{-1} and was assigned to the ν_1 (a_{1g}) fundamental, the Ru-Ru stretching mode. The next most enhanced, between 369 and 432 cm^{-1}, was assigned to the ν_2 (a_{1g}) fundamental, the symmetric Ru-O stretch. The electronic band excited was at about 21000 cm^{-1} (128).



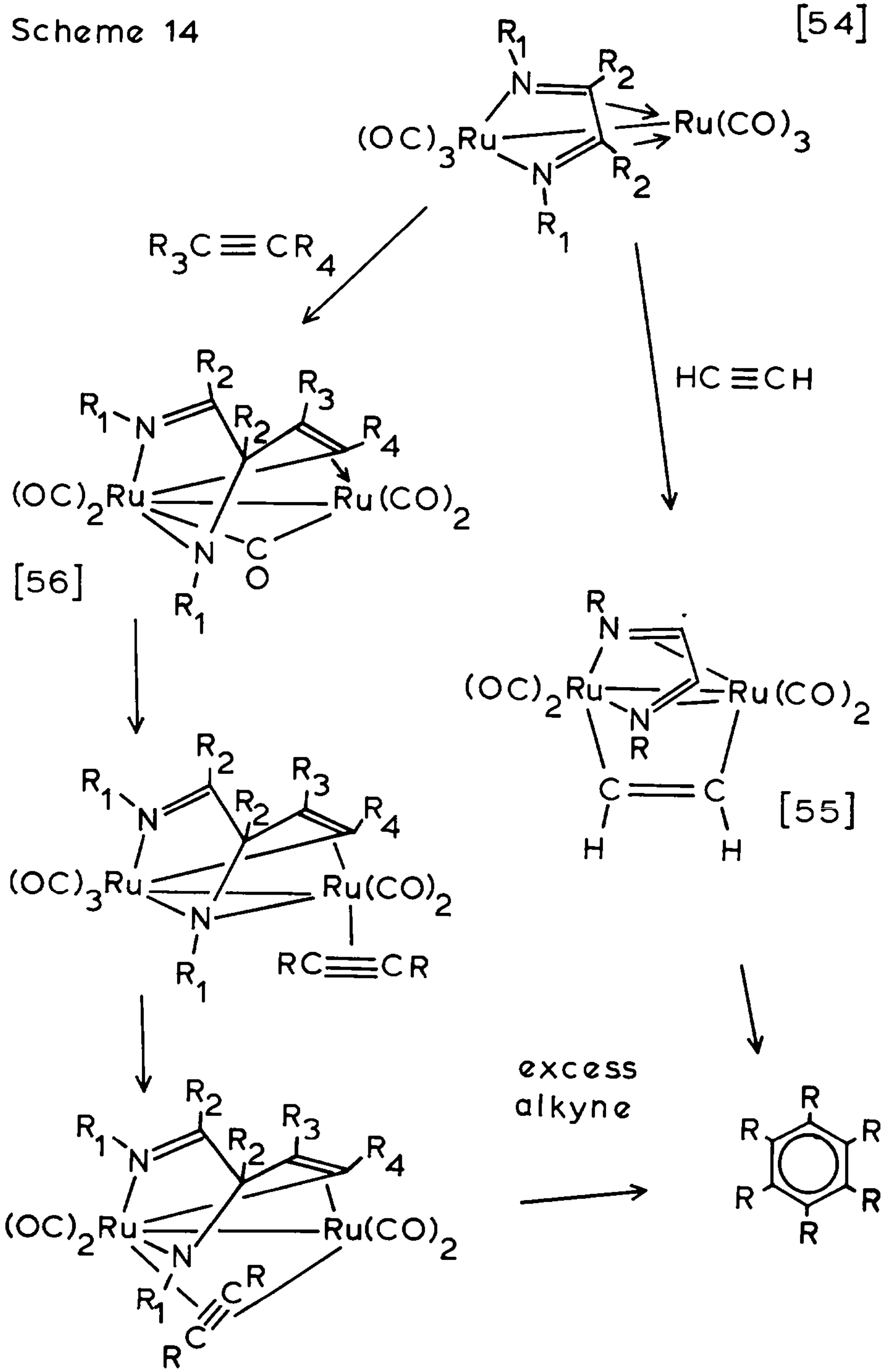
[53]



Pyrolysis of porphyrin complexes $Ru(P)(py)_2$ (P-octaethylporphyrin, meso-tetratolylporphyrin, or meso-tetraphenylporphyrin) under vacuum afforded the dimers $[Ru(P)]_2$ which contain a metal-metal double bond. These dimers are paramagnetic with two unpaired spins (μ_{eff}=2.8 μ_B). In each case, exposure to oxygen irreversibly formed a single diamagnetic product which was proposed to be $(HORuP)_2O$ (129).

A number of complexes containing 1,4-diazabutadiene ligands have been prepared and characterized. Reactions of 1,4-diazabutadienes (DAB) with $Ru_3(CO)_{12}$ gave $Ru(CO)_3(DAB)$, $Ru_2(CO)_6(DAB)$, $Ru_3(CO)_8(DAB)$ and $Ru_4(CO)_8(DAB)_2$, depending upon reaction conditions and the degree of branching at the α carbon (130). The ^{13}C NMR spectra of $M_2(CO)_6(DAB)$ [54] (M=Fe, Ru, DAB=1,4-diazabutadiene) were recorded. Chemical shifts of ca. 175 ppm were observed for the σ-coordinated imine fragment and 60-80 ppm for the η^2-C=N fragment. For both Ru and Fe complexes local scrambling of carbonyls on the NMR timescale was observed (131). Reactions of these complexes have also been investigated. Acetylene reacted with $Ru_2(CO)_6$[glyoxal bis(isopropylimine)] or $Ru_2(CO)_6$[glyoxal bis(cyclohexylimine)] to give $Ru_2(CO)_4(DAB)(C_2H_2)$ [55].

Scheme 14


[54]
(OC)$_3$Ru
Ru(CO)$_3$
R$_1$
R$_2$
$R_3C\equiv CR_4$
$HC\equiv CH$
[56]
(OC)$_2$Ru
Ru(CO)$_2$
R$_3$
R$_4$
(OC)$_3$Ru
$RC\equiv CR$
[55]
excess
alkyne
R

The crystal structure of the isopropyl derivative was determined; the acetylene is bound in 1,2-σ fashion parallel to the Ru-Ru bond. This is the first example of a σ-N, σ-N', η^2-C=N, η^2-C=N'-coordinated 1,4-diazabutadiene ligand (132). On the other hand, C-C coupling between the acetylene and the DAB ligand was observed, as well. Refluxing $Ru_2(CO)_6$(DAB) complexes with acetylenes in heptane gave $Ru_2(CO)_5$(AIB) complexes (AIB=3-amino-4-imino-1-buten-1-yl). The molecular structure of [2-phenyl-3-(t-butylamino)-4-(t-butylimino)-1-buten-1-yl]$Ru_2(CO)_5$ [56] was determined. The AIB ligand donates 8 electrons to the Ru_2 system. These complexes $Ru_2(CO)_5$(AIB) reacted further with acetylenes to give first $Ru_2(CO)_5$(AIB)(alkyne) and then $Ru_2(CO)_4$(AIB)(alkyne). All these complexes were catalysts for alkyne cyclotrimerization at 110° for a maximum of 380 cycles, but the actual catalyst seemed to be formed from $Ru_2(CO)_4$(AIB)(alkyne). However, deuterium labelling was used to show that the coordinated alkyne was not cyclotrimerized. The reaction sequence for the reaction of $Ru_2(CO)_6$(DAB) with alkynes is shown in Scheme 14 (133). Reversed-phase hplc was used to monitor the exchange of coordinated DAB with free DAB in solutions of $Ru_2(CO)_6$(DAB) (DAB=i-PrDAB and t-BuDAB) (134).

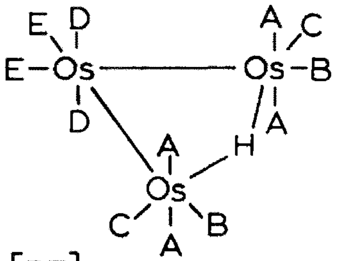
The synthesis of Ru_2(CN-i-Pr)$_9$ [20] by reduction of $RuCl_2$(CN-i-Pr)$_4$ with sodium amalgam in the presence of excess CN-i-Pr was reported. The complex is presumed to be iso structural with $Fe_2(CNEt)_9$, which was crystallographically characterized. The bridging and terminal isocyanides undergo fluxional exchange (41).

Trinuclear Species

The cluster dianions $[Os_3(CO)_{11}]^{2-}$ and $[Ru_3(CO)_{11}]^{2-}$ were prepared by reduction of the corresponding $M_3(CO)_{12}$ with K and Ca, respectively, in the presence of benzophenone. The salt $Ca[Ru_3(CO)_{11}]\cdot 2\ C_4H_{10}O_2$ was prepared in 71% yield. Characterization of $K_2[Os_3(CO)_{11}]$, prepared in 79% yield, by IR and ^{13}C NMR spectroscopy suggested a structure with one bridging carbonyl (135).

Laser Raman spectra of $M_3(CO)_{12}$ (M=Ru, Os) were recorded at 295, 200, 100, and 15 K using a surface-scanning technique to prevent sample decomposition. Analysis of the data showed that neither compound underwent a phase change within the temperature range examined. Contrary to earlier measurements at room temperature, site-symmetry and correlation effects were more widespread than previously suspected (136).

The temperature-dependent ^{13}C NMR spectra for $^{187}Os_3(CO)_{12}$ (99.8% ^{187}Os) and $[H\ ^{187}Os_3(CO)_{12}]^+$ were recorded and the ^1J (^{187}Os-^{13}C) couplings were determined (137). At 150°C the ^{13}C NMR spectrum of $^{187}Os_3(CO)_{12}$ was a 1:3:3:1 quadruplet with $^1J(^{187}Os-^{13}C)$ of 33±1 Hz. At 25°C the spectrum consisted of two doublets at 182.3 and 170.4 ppm with ^1J equal to 90±2 and 115±2 Hz, respectively. The spectrum of $[H\ ^{187}Os(CO)_{12}]^+$ [57] was interpreted shown:

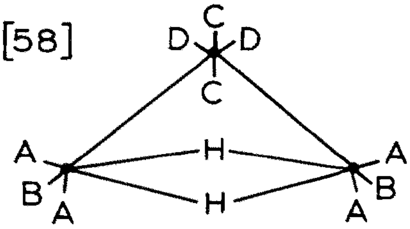


[57]

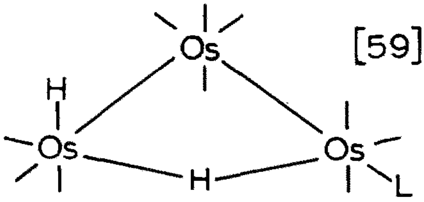
chemical shift	assignment	$^1J(^{187}Os-^{13}C)$	$^2J(^{13}C-^1H)$
177.6 (2c)	D	85±1	broad
171.1 (4c)	A	84±1	
166.7 (2c)	E	121±2	
161.4 (2c)	B	120±2	3.3
160.8 (2c)	C	116±2	6.7

The ^{13}C NMR spectra of $H_2Os_3(CO)_{10}$ [58] were also examined. The cis $^2J\ (^{13}C-^{13}C)$ value was 3.2 Hz for carbonyls C and D, while the coupling constant between the trans-carbonyls was ca. 40 Hz (138).

[58]



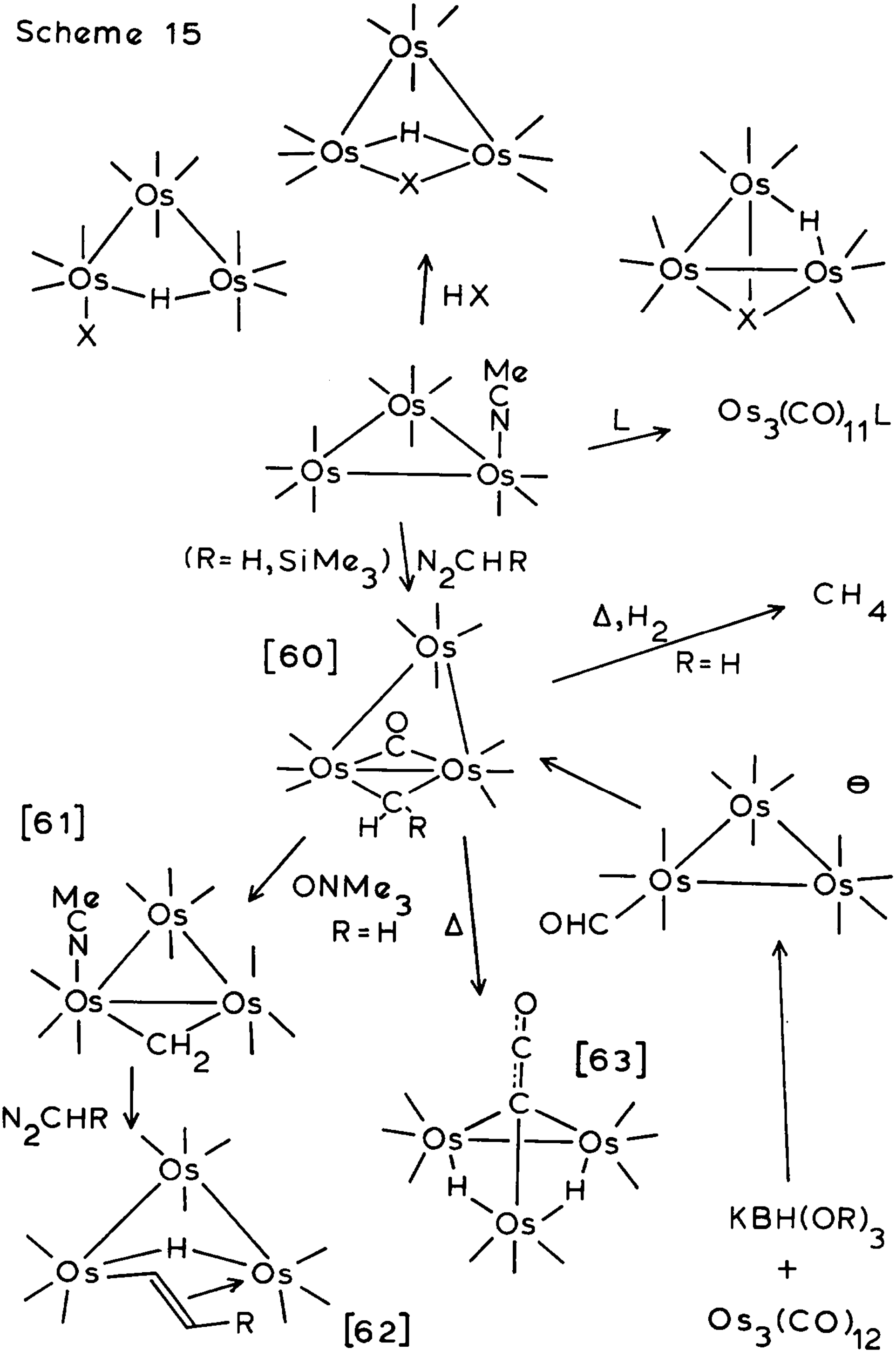
[59]



Variable-temperature ^{13}C NMR spectra of $H_2Os_3(CO)_{10}$ and $H_2Os_3(CO)_{10}L$ (L=PPh_3, $P(O\text{-}\underline{i}\text{-}Pr)_3$, and $P(\underline{i}\text{-}Pr)_3$) [59] were used to show that fluxional exchange of only two carbonyl ligands of the latter cluster was associated with the previously reported exchange of the terminal and bridging hydrides. A concerted motion of the two carbonyls and the two hydrides on a single Os atom was proposed to explain the spectra (139).

The "lightly stabilized" cluster $Os_3(CO)_{11}(NCMe)$, prepared by treatment of $Os_3(CO)_{12}$ with trimethylamine-N-oxide in acetonitrile, has been used to prepare a number of triosmium clusters. When L=CO, PPh_3, $CNCH_2OSO_2C_6H_4$-4-Me, C_2H_4, or py, reaction with this cluster under mild conditions gave the corresponding $Os_3(CO)_{11}L$ in good yield. With HX (X=Cl, Br, I) $Os_3(CO)_{11}HX$, $Os_3(CO)_{10}HX$, and $Os_3(CO)_9HX$ were isolated; in these clusters X is terminal, μ_2-bridging, or μ_3-bridging, respectively (140). Treatment of $Os_3(CO)_{11}(NCMe)$ with diazomethane gave $Os_3(CO)_{11}(CH_2)$ in 50% yield; $Os_3(CO)_{11}(CHSiMe_3)$ [60] was prepared in the same way and its crystal structure was determined (141). Reaction of $Os_3(CO)_{11}(CH_2)$ with trimethylamine-N-oxide in acetonitrile

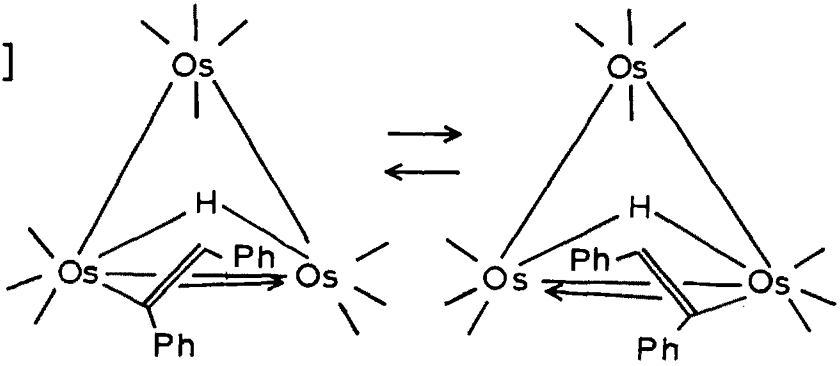
Scheme 15


HX
Me
C
N
L
$Os_3(CO)_{11}L$
(R= H, SiMe$_3$)
N_2CHR
[60]
Δ, H_2
R= H
CH_4
[61]
$ONMe_3$
R = H
Δ
OHC
⊖
Me
C
N
CH_2
N_2CHR
R
[62]
[63]
$KBH(OR)_3$
+
$Os_3(CO)_{12}$

formed $Os_3(CO)_{10}(NCMe)(CH_2)$ [61]; addition of PMe_2Ph to this product gave $Os_3(CO)_{10}(PMe_2Ph)(CH_2)$. Reaction of [61] with N_2CHR (R=H, Me, $SiMe_3$) gave the vinyl complex $HOs_3(\mu_2\text{-}CH{=}CHR)(CO)_{10}$ [62]; the reaction of N_2CH_2 with $Os_3(CO)_{10}(NCMe)(^{13}CH_2)$ demonstrated that there was complete scrambling of the label between the two vinyl carbons in the product (141). Others synthesized $Os_3(CO)_{11}(CH_2)$ by acidification with phosphoric acid of $[Os_3(CO)_{11}(CHO)]^-$, which was prepared by reduction of $Os_3(CO)_{12}$ with KBH(O-i-Pr)$_3$ at 0° (142). Acidification of the formyl cluster anion with CF_3CO_2D gave only d_0-$Os_3(CO)_{11}(CH_2)$, but acidification of $[Os_3(CO)_{11}(CDO)]^-$ with d_0-phosphoric acid formed d_2-$Os_3(CO)_{11}(CH_2)$. Pyrolysis of $Os_3(CO)_{11}(CH_2)$ at 70-80°C under hydrogen produced 20% methane; under deuterium only d_2-methane was found. However, pyrolysis under a nitrogen atmosphere generated the new cluster $H_2Os_3(CO)_{10}C$ [63] in 80% yield (142); complex [63] contains no carbon-hydrogen linkages and is proposed to contain a 1,1-dimetalloketene ligand. Recent results have shown this to involve an μ_3-η^1-CCO ligand (143). These reactions are summarized in Scheme 15.

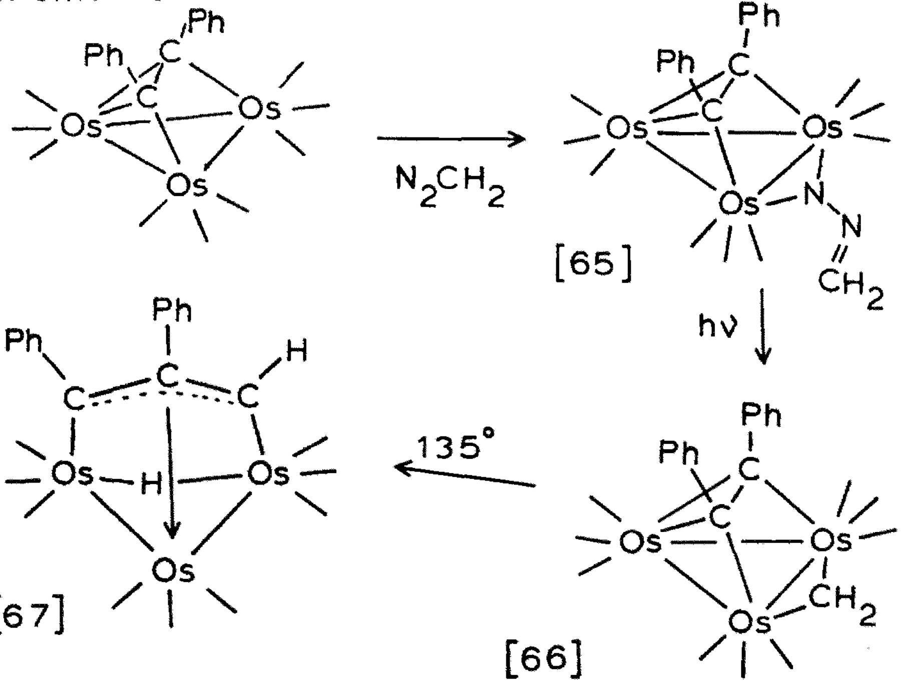
The crystal structure of $HOs_3(CO)_{10}(\mu\text{-}CPh{=}CHPh)$ [64] was determined (144). This compound, formed by insertion of diphenylacetylene into an Os-H bond of $H_2Os_3(CO)_{10}$, differs from other vinyl clusters in the orientation of the vinyl group relative to the Os_3 triangle. Variable-temperature ^{13}C NMR spectra revealed fluxional interchange of the π-vinyl bond between the bridged Os atoms with a free energy of activation of 11.3 kcal/mol at the coalescence temperature, compared with 10.3 kcal/mol for $HOs_3(\mu\text{-}CHCH_2)(CO)_{10}$ [62].

[64]

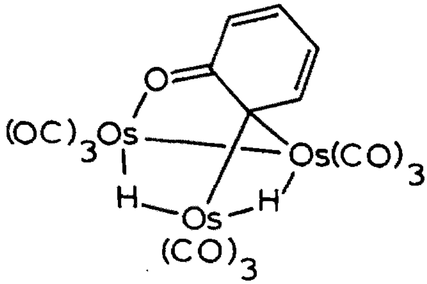


Diazomethane reacted with $Os_3(CO)_9(C_2Ph_2)$ to give $Os_3(CO)_9(C_2Ph_2)(N_2CH_2)$ (39%) [65] and $Os_3(CO)_9(C_2Ph_2)(CH_2)$ (32%) [66]. Product [65] was stable to 80°C but did not give [66] upon decomposition. However, photolysis of [65] did give [66], for which the crystal structure was determined. Thermolysis of [66] at 135°C gave $HOs_3(CO)_9(\mu_3-\eta^3-C_3Ph_2H)$ [67], which could also be prepared by treatment of $Os_3(CO)_{10}(NCMe)_2$ with 1,2-diphenylcyclopropene in refluxing cyclohexane. The rate-determining step in conversion of [66] to [67] was suggested to be C-C bond formation (Scheme 16) (145).

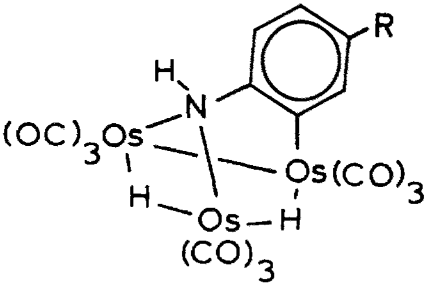
Scheme 16



The clusters $H_2Os_3(CO)_9(C_6H_4X)$ (X=O, NH) were prepared through reactions of $Os_3(CO)_{12}$ with phenol or aniline. A study of the ^1H and ^{13}C NMR spectra of these and substituted derivatives was made. Based upon the spectral characteristics of these compounds, the phenol derivatives form complexes best described as cyclohexadienones [68], while the aniline derivatives are suggested to maintain an aromatic C_6 ring [69]. The crystal structure of $H_2Os_3(CO)_9$-(NHC_6H_3F) [69, R=F] was determined by X-ray methods (154).

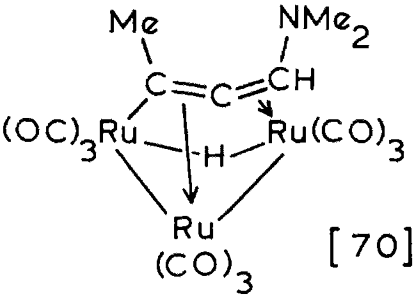


[68]

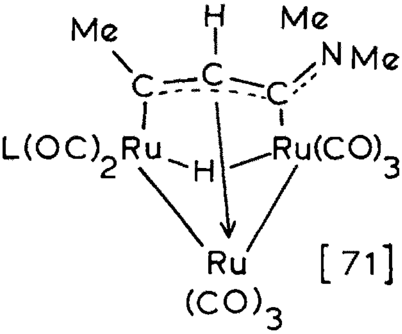


[69]

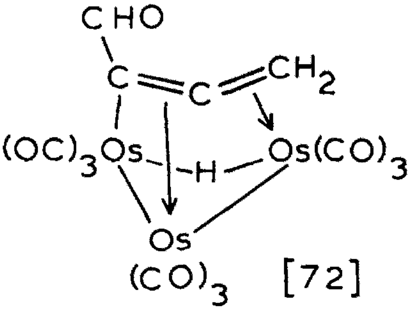
The isomeric clusters $HRu_3(CO)_9(MeC{=}C{=}CHNMe_2)$ [70] and $HRu_3(CO)_9$-$(MeCCHCNMe_2)$ [71, L=CO] were prepared by reaction of $Ru_3(CO)_{12}$ with $MeC{\equiv}CCH_2NMe_2$. The energy barrier to rotation about the $C{-}NMe_2$ bond of [71] was sensitive to the nature of L for the substituted derivatives $HRu_3(CO)_8L$-$(MeCCHCNMe_2)$ [71, L=P-(iPr)$_3$, PPh_3, $P(OPh)_3$] even though L is located at the Ru remote from the hydrocarbon ligand. This energy barrier was also affected by protonation at the cluster. Both effects are consistent with lower energy barriers to rotation with increasing electron availability at the cluster (146).



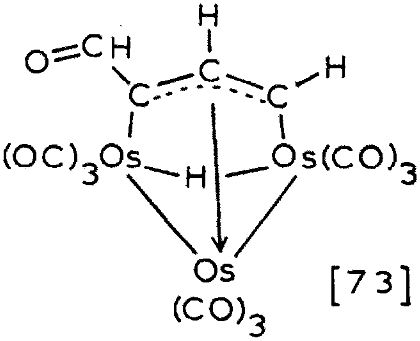
[70]



[71]



[72]

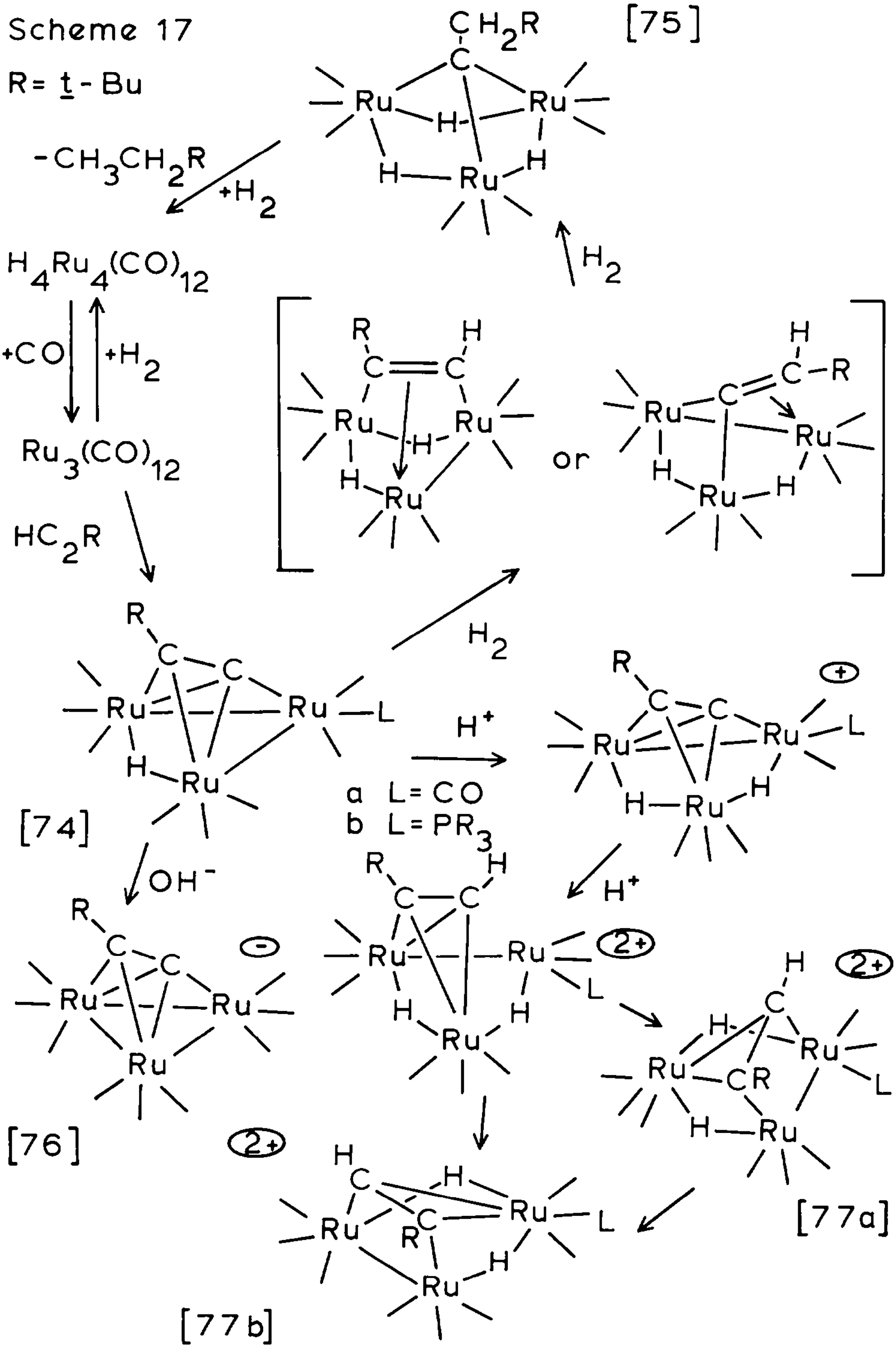


[73]

Reactions of 1,4-dihydroxybut-2-yne with either $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ in refluxing cyclohexane gave a mixture of $Ru_2(CO)_6[C_4(CH_2OH)_4]$, $HRu_3(CO)_9$-[CHCHCCHO] and $HRu_3(CO)_9(CHCHCCH_2OH)$, all in low yield. The same reaction with $H_2Os_3(CO)_{10}$ afforded $Os_3(CO)_{10}(HOCH_2C{\equiv}CCH_2OH)$. Pyrolysis of the latter at 96°C gave $HOs_3(CO)_9(CH_2CCCHO)$ [72] by decarbonylation, dehydration of the diol, and hydrogen transfer from carbon to Os. Finally, at 132°C a 1,2-hydrogen atom shift in [72] formed $HOs_3(CO)_9(CHCHCCHO)$ [73], which was characterized by X-ray crystallography (147).

The chemistry of $HRu_3(C_2\text{-}\underline{t}\text{-Bu})(CO)_9$ [74a] is proving to be extensive. Hydrogenation of this cluster in refluxing octane gave the alkylidyne cluster $H_3Ru_3(CO)_9(\mu_3\text{-}CCH_2\text{-}\underline{t}\text{-Bu})$ [75], which was crystallographically characterized. Further hydrogenation of [75] gave neohexane and $H_4Ru_4(CO)_{12}$. The proposed reaction path is shown in Scheme 17 (148). Deprotonation of [74a] under CO with hydroxide gave the monoanion, isolated as $[AsPh_4][Ru_3(CO)_9$-$(C_2\text{-}\underline{t}\text{-Bu})]$ [76] and for which an X-ray structural determination was conducted. The variable-temperature ^{13}C NMR spectra of this anion indicated axial-radial carbonyl exchange with the barrier to exchange at metal atoms formerly bridged by the hydride 5 kcal/mol lower than on the same positions in [74a] (149). Protonation of [74a] and its mono- and bis(phosphine)-substituted derivatives with CF_3SO_3H was studied by variable-temperature NMR spectroscopy. Initial protonation took place at the metal core, but differences in relative basicities and rates of inter- and intramolecular hydrogen exchange were observed. In neat sulfuric acid a second protonation occurred at the acetylide ligand to give $[H_2Ru_3(CO)_9(CH{=}C\text{-}\underline{t}\text{-Bu})]^{2+}$ from [74a]. For $HRu_3(CO)_8$-$(PR_3)(C_2\text{-}\underline{t}\text{-Bu})$ (R=Ph, OMe) [74b] two isomeric dications [77a and b] were initially formed in a 1.5:1 ratio, but over a period of 6 days this ratio increased to >16 by rearrangement to the thermodynamically preferred product. In d_2-sulfuric acid only the final product was observed, but $DRu_3(CO)_8(PR_3)$-$(C_2{=}\underline{t}\text{-Bu})$ in sulfuric acid gave a different ratio of the initially formed isomers than for the d_0- [74b]. This was attributed to a deuterium isotope effect on hydride migration (150). These reactions are summarized in Scheme 17. The X-ray crystal structure determination of $HRu_3(CO)_8\{PPh_2(OEt)\}$-$(C_2\text{-}\underline{t}\text{-Bu})$ [74b, L=$PPh_2(OEt)$], including direct location of the hydride ligand, was reported; the Ru-H distances were 1.76 and 1.73 Å and the Ru-H-Ru angle was 106.6° (151).

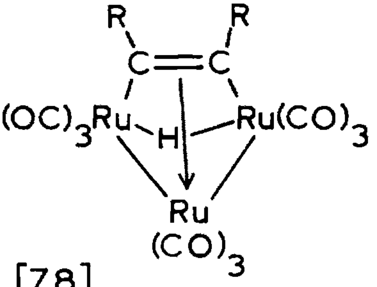
The reaction of ethylene with $Ru_3(CO)_{12}$ has been studied. A rapid process initially formed $Ru(CO)_4(C_2H_4)$ but continued heating produced a complex mixture of products, including $H_2Ru_3(CO)_9(C_2R_2)$ [78] (R=H, Me, or Et), $HRu_3(CO)_9(RCCHCEt)$ [79] (R=Me, Et) and $Ru_4(CO)_{12}(MeC{\equiv}CMe)$ [80]. The fluxionality of the three products [78] was studied by variable-temperature



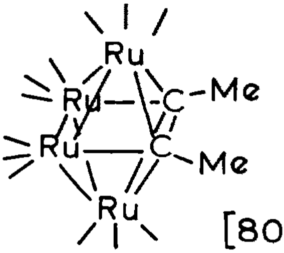
Scheme 17

R= t-Bu
[75]
CH_2R
$-CH_3CH_2R$
$+H_2$
$H_4Ru_4(CO)_{12}$
+CO
$+H_2$
$Ru_3(CO)_{12}$
HC_2R
H_2
or
H_2
[74]
H^+
a L= CO
b L= PR_3
OH^-
H^+
[76]
2+
[77a]
[77b]
Ru
H
C
R
L

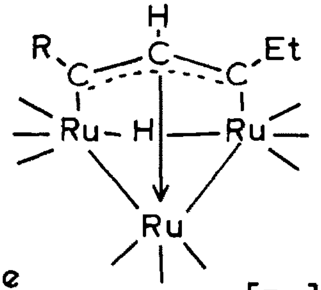
^1H NMR spectroscopy.



[78]

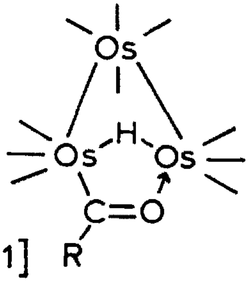


[80]

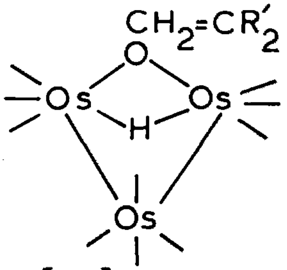


[79]

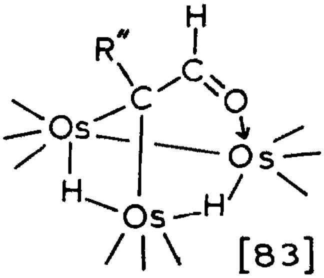
Insertion of ketene or substituted ketenes into an Os-H bond of $H_2Os_3(CO)_{10}$ gave acyl complexes $HOs_3(\mu\text{-}OCR)(CO)_{10}$ [81] (R=Me, C_5H_{11}, C_6H_{12}, $PhCH_2$, Me_2CH, or Ph) or enolato complexes $HOs_3(CO)_{10}(\mu\text{-}OCH{=}CR'_2)$ [82] (R'=H, Me, Ph) (152). These complexes could also be prepared by oxidative addition of aldehyldes by $Os_3(CO)_{12}$ (152), or by reaction of $Os_3(CO)_{10}(NCMe)_2$ with aldehydes RCHO (R=Me, Ph, CH_2Ph, C_6H_{13}) (153). The structure of [81], where R=CH_2Ph, was determined by X-ray crystallography (153). The complexes [81] (R=Me, Ph, or Ph_2CH) decarbonylated upon heating to give products derived from the alkyls thus formed. When R=Me, C_5H_{11}, C_6H_{13} or $PhCH_2$, decarbonylation at the metal, followed by hydrogen transfer, gave $H_2Os_3(CO)_9(\mu_3\text{-}R''CCHO)$ [83] with a coordinated formyl group (152).



[81]



[82]

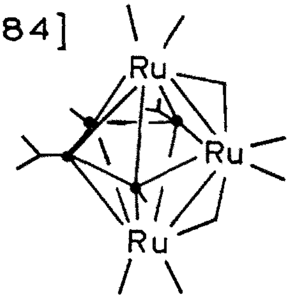


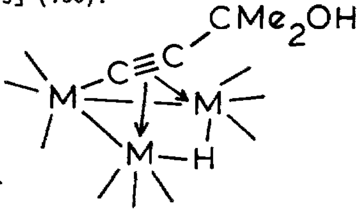
[83]

Reactions of acetylenes with clusters continue to produce many unusual complexes. The open cluster $Ru_3(CO)_8(C_{12}H_{18})$ [84] was formed by dimerization and dehydrogenation of 4-methylpent-2-yne on $Ru_3(CO)_{12}$; an X-ray crystal structure determination found an Ru_3C_4 pentagonal bipyramidal core (155). Reaction of $HC{\equiv}CCMe_2OH$ with $Ru_3(CO)_{12}$ gave $HRu_3(CO)_9(C{\equiv}CCMe_2OH)$ [85, M=Ru] in low yield and isomers of the formula $Ru_2(CO)_6(alkyne)_2$, containing the ruthenacyclopentadiene moiety, as the major products; higher yields of the Os analog were obtained (156). The unsaturated cluster $H_2Os_3(CO)_{10}$ and

$HC{\equiv}CCMe_2OH$ afforded $Os_3(CO)_{10}(HC_2CMe_2OH)$ [86] and $HOs_3(CO)_{10}(CH{=}CHCMe_2OH)$ [87]; the dynamic NMR behavior of [86] was examined (156). Pyrolysis of [85, M=Os] at 120°C gave $HOs_3(C{\equiv}CCMe{=}CH_2)(CO)_9$ [88] by dehydration; pyrolysis of [86] produced [85, M=Os] (156).

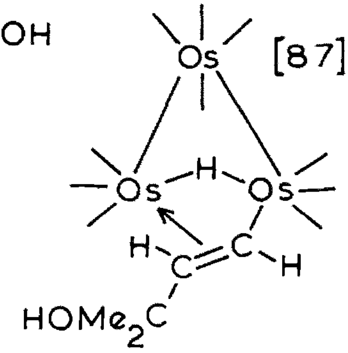
[84]



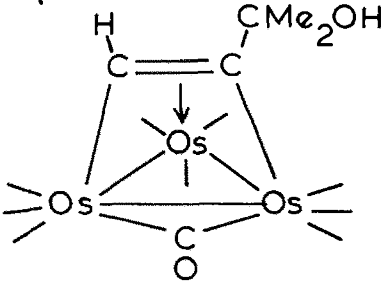


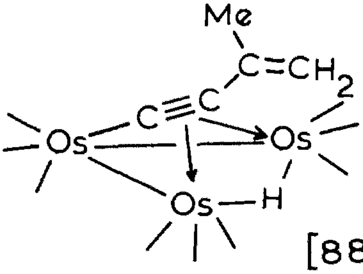
[85]

[87]



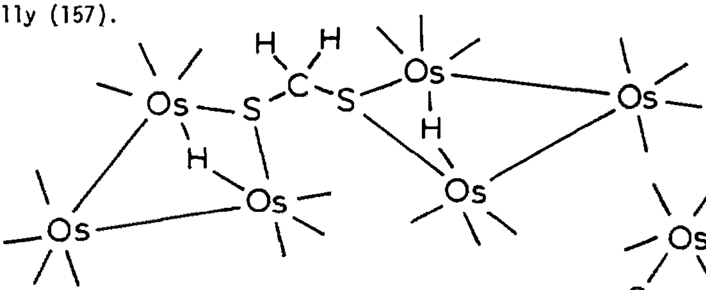
[86]





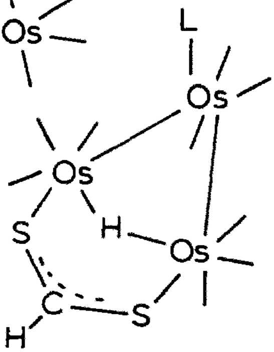
[88]

Treatment of the unsaturated clusters $H_2Os_3(CO)_{10}$ and $H_2Os_3(CO)_9$-(PMe_2Ph) with carbon disulfide gave $(\mu\text{-}S_2CH_2)[HOs_3(CO)_9L]_2$ [89] (L=CO or PMe_2Ph); the crystal structure of the CO derivative was determined. Other products from these reactions were $(\mu\text{-}S_2CH)HOs_3(CO)_9(PMe_2Ph)$ [90] and $(\mu\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_9(PMe_2Ph)$ [91], the structure of which was also determined crystallographically. Both [90] and [91] thermally decarbonylate to $(\mu_3\text{-}\eta^2\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_8(PMe_2Ph)$ [92], also characterized crystallographically (157).

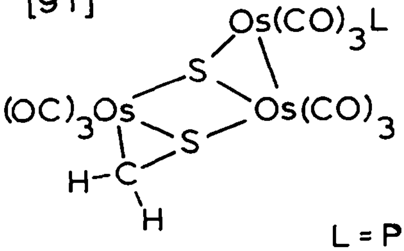


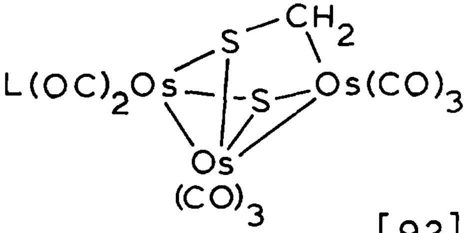
[89]

[90]



[91]

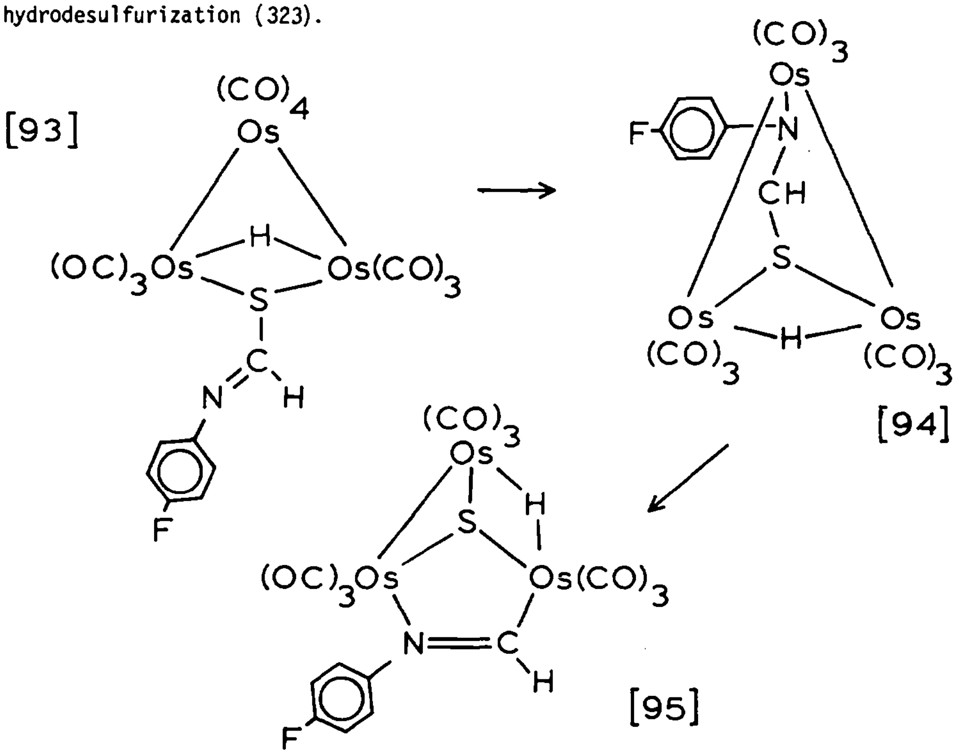




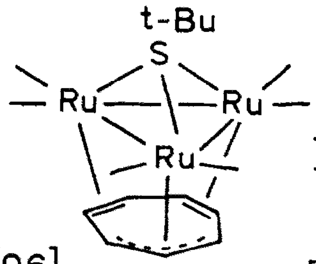
[92]

$L = PMe_2Ph$

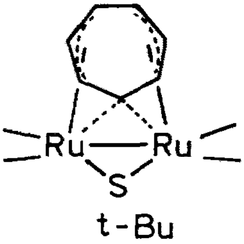
Another S-containing cluster $HOs_3(\mu\text{-}\eta^1\text{-SCHN-}p\text{-}C_6H_4F)(CO)_{10}$ [93] was obtained in 86% yield by treatment of $H_2Os_3(CO)_{10}$ with $p\text{-}FC_6H_4NCS$, and its crystal structure was determined. This product loses CO at 25° over 5 days to give the red cluster $HOs_3(\mu_3\text{-}\eta^2\text{-SC(H)N-p-}C_6H_4F)(CO)_9$ [94] in 45% yield; the crystal structure of [94] was also determined. Pyrolysis of [94] for 15 min in refluxing octane gave yellow $HOs_3(\mu_3\text{-S})(\mu\text{-}\eta^2\text{-HC=N-p-}C_6H_4F)(CO)_9$ [95] in 62% yield; the product was characterized crystallographically. The overall transformation of [93] to [95] effects desulfurization of the thioformamide ligand by a metal cluster and may model metal-surface-catalyzed hydrodesulfurization (323).



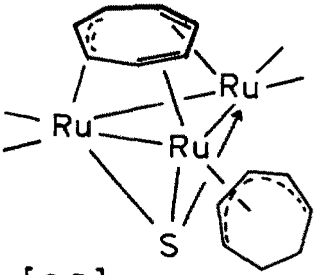
Although bicyclo-octatetraenyl was formed by reaction of C_8H_7SMe with $Ru_3(CO)_{12}$, $C_7H_7S\text{-}\underline{t}\text{-Bu-7}$ gave $Ru_3(CO)_6(\mu_3\text{-S-}\underline{t}\text{-Bu})\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}$ [96] and $Ru_2(CO)_4(\mu\text{-S-}\underline{t}\text{-Bu})\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}$ [97]. Similar products were formed with $C_7H_7\text{-7-SMe}$ (158). The same products could be prepared by reaction of $HRu_3(CO)_9(\mu_3\text{-S-}\underline{t}\text{-Bu})$ with cycloheptatriene in refluxing heptane. The crystal structure of [96] (R=$\underline{t}$-Bu) was determined. Treatment of [96] with CO gave [97]. Similar reactions with cyclooctatetraene, cyclooctatriene and cyclopentadiene gave $Ru_2(CO)_6(\mu\text{-S-}\underline{t}\text{-Bu})\{\mu\text{-}(\eta^7\text{-}C_8H_9)\}$ or $Ru_2(\mu\text{-H})(CO)_2(\mu\text{-S-}\underline{t}\text{-Bu})(\eta^5\text{-}C_5H_5)_2$. The reaction of $H_2Ru_3(\mu_3\text{-S})(CO)_9$ with cyclooctatetraene afforded $Ru_3(CO)_6(\mu_3\text{-S})\{\mu_3\text{-}(\eta^8\text{-}C_8H_8)\}$ with a face-bridging, fluxional C_8H_8 ring; the corresponding reaction with C_7H_8 gave $Ru_3(CO)_4(\mu_3\text{-S})(\eta^5\text{-}C_7H_9)\text{-}\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}$ [98], $Ru_4(CO)_6(\mu_3\text{-S})(\eta^5\text{-}C_7H_9)\{\mu_3\text{-}(\eta^7\text{-}C_7H_7)\}$ [99], and $Ru_4(CO)_8(\mu_4\text{-S})\{\mu\text{-}(\eta^7\text{-}C_7H_7)\}_2$ [100] (159).



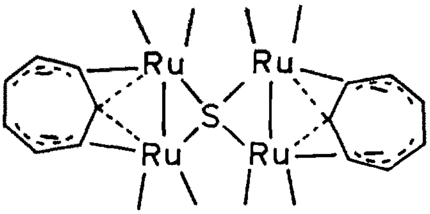
[96]



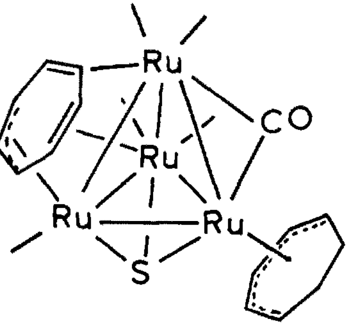
[97]



[98]



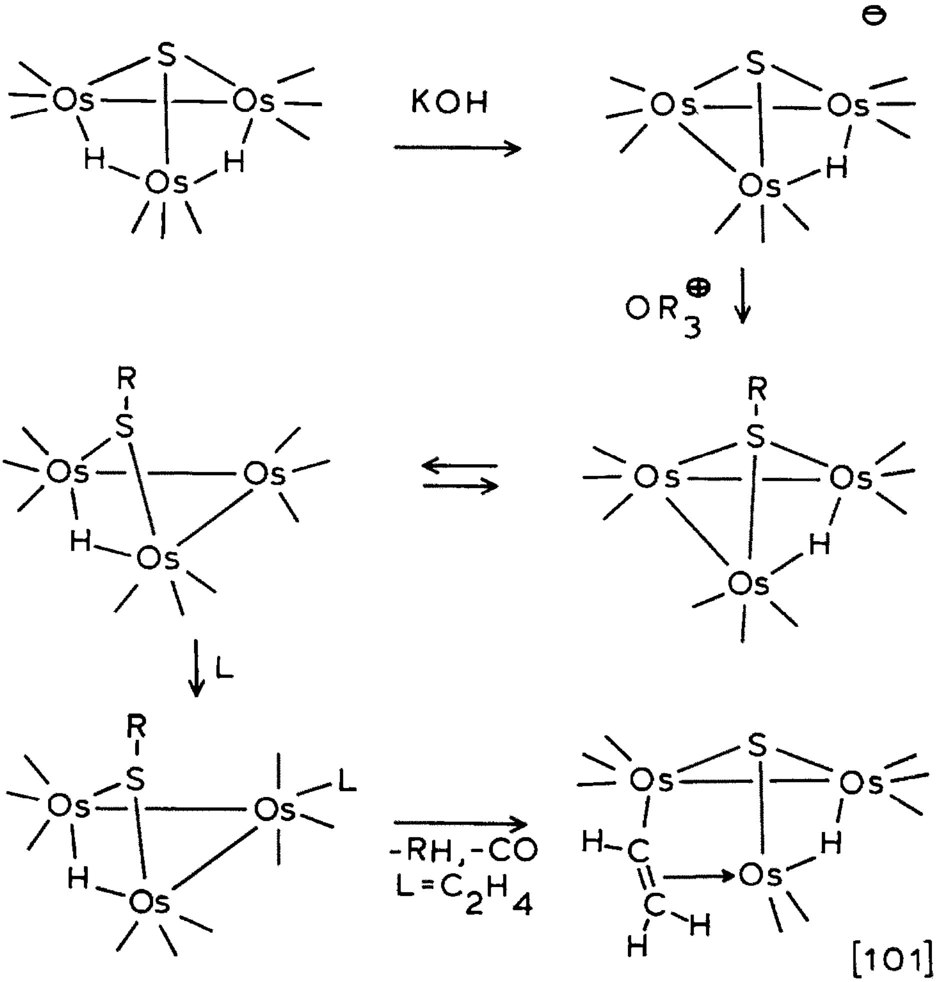
[100]



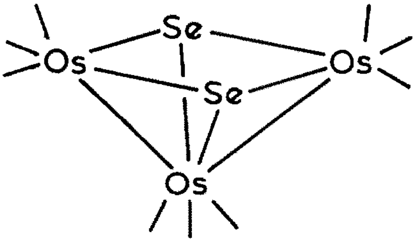
[99]

Deprotonation of $H_2Os_3(CO)_9(\mu_3\text{-S})$ with potassium hydroxide in methanol, followed by reaction with trimethyl- or triethyloxonium salts, gave $HOs_3(CO)_9\text{-}(\mu_3\text{-SR})$ (R=Me, Et); this product reacted with a number of ligands L (L=C_2H_4, CO, PR_3, or NCMe) to give $HOs_3(CO)_9L(\mu_2\text{-SR})$. In these reactions conversion of the SR group from a 5-electron donor, μ_3-ligand to a 3-electron donor, μ_2-ligand generates an unsaturated cluster capable of adding L. At 125°C $HOs_3(CO)_9(C_2H_4)(\mu_3\text{-SR})$ eliminated RH and one carbonyl to give $HOs_3(CO)_8(\mu\text{-}CH{=}CH_2)(\mu_3\text{-S})$ [101]. These reactions are summarized in Scheme 18 (160).

Scheme 18



The structure of $Os_3(CO)_9(\mu_3\text{-}Se)_2$ [102] was determined by X-ray crystallography. The molecule is isostructural with the Fe analog (161).



[102]

Formyl-containing clusters have been identified by ^1H, ^2H, and ^{13}C NMR spectroscopy in the products resulting from reduction of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ with $LiBHEt_3$ and $LiBDEt_3$. The proposed formyl $Os_3(CO)_{11}(CHO)^-$ (^1H NMR: δ(CHO) 14.9 ppm) decomposed to $HOs_3(CO)_{11}^-$ at ca. -10°C, but for Ru only $HRu_3(CO)_{11}^-$ was observed even below -40°C. However, reduction of $Ru_3(CO)_{12}$ with $LiBDEt_3$ at -50°C produced a signal attributed to $Ru_3(CO)_{11}(CDO)^-$ (^2H NMR: δ(CDO) 12.8). The authors suggested that the formyl was kinetically stabilized by the deuterium isotope effect (162).

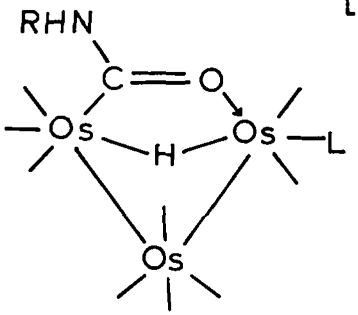
A large number of new trimeric clusters containing N-donor ligands have been prepared. Treatment of $H_2Os_3(CO)_{10}$ with methyl isocyanate afforded $HOs_3(CO)_{10}(\mu\text{-CHONMe})$ [103a] in 80% yield and two other products $HOs_3(CO)_{10}(COHNMe)$ [104] and $HOs_3(CO)_{10}$ (MeNCOCONHMe) [105] in 6 and 10% yield, respectively. Complex [104] exists as a tautomeric mixture of forms a and b; however, this complex is unstable, decomposing to $HOs_3(CO)_{10}(CHONMe)$ [106a]. Complexes [106a] and [103a] were not interconvertible, but at 125° the former was decarbonylated to $HOs_3(CO)_{10}(\mu\text{-NHMe})$ [107]. On the other hand, [103a] was decarbonylated at 150°C to $H_2Os_3(CO)_9(\mu_3\text{-NMe})$ [108] (163); a crystal structure determination of [108] has appeared (164).

Reactions of $H_2Os_3(CO)_9L$ (L=CO or PMe_2Ph) with aryl isocyanates were also examined. Reaction of $H_2Os_3(CO)_{10}$ with OCNR gave $HOs_3(CO)_{10}(CHONR)$ [106b], (R=aryl); the X-ray structure of [106b] (R=p-MeC_6H_4) was determined. This complex reacted with PMe_2Ph to give $HOs_3(CO)_9(PMe_2Ph)$(p-MeC_6H_4NCHO) [106c], for which the structure was determined by X-ray crystallography. On the other hand, $H_2Os_3(CO)_9(PMe_2Ph)$ and ONC-p-C_6H_4Me gave, instead of [106c], an isomeric compound [103c], also characterized by X-ray crystallography. A minor product from the reaction of $H_2Os_3(CO)_{10}$ with OCN-p-C_6H_4Me was $HOs_3(CO)_{10}$(p-MeC_6H_4NHCO) [103d]; [103d] and [106b] were not interconvertible (165).

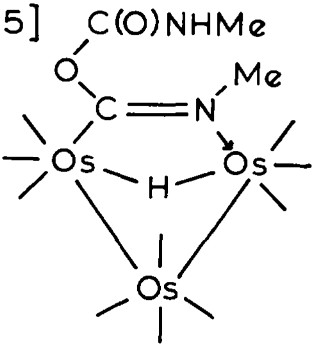
Another route to clusters $HOs_3(CO)_{10}(\mu\text{-NHCOR}^1)(CO)_{10}$ [106] is through reactions of $Os_3(CO)_{10}(NCMe)_2$ with amides NH_2COR^1 (R^1=H, Me, Et, Ph, Pr). These complexes were prepared in yields of 50 to 70% after refluxing in cyclohexane. When R=H, pyrolysis gave $HOs_3(NHCHO)(CO)_9$ (153).

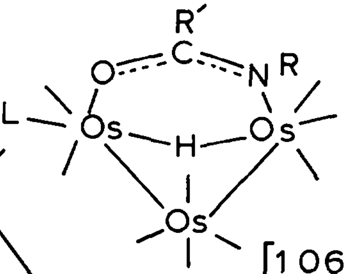
Clusters containing μ-η^2-formamide groups have also been prepared from $H_2Os_3(CO)_{10}$ and diisopropylcarbodiimine. Both $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-i-PrNHCN-i-Pr})$ [109] and $HOs_3(CO)_9$(CN-i-Pr)(μ-η^2-CONH-i-Pr) [103b] were isolated and characterized by crystallography. Pyrolysis of [109] gave $HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{-i-}$PrNH(N-iPr), but [103b], was not formed (166).

[103]



[105]





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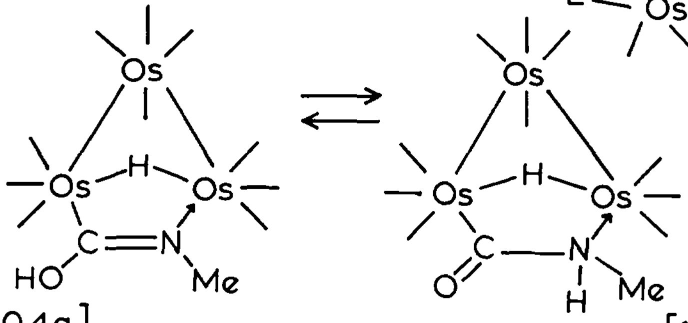
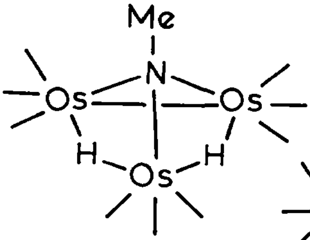
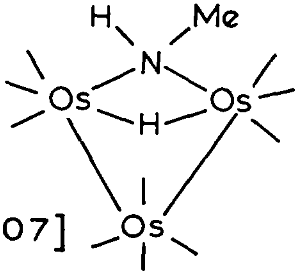


[104a]

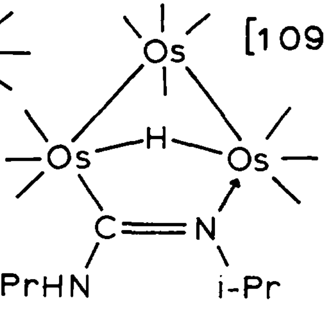
[104b]



[108]

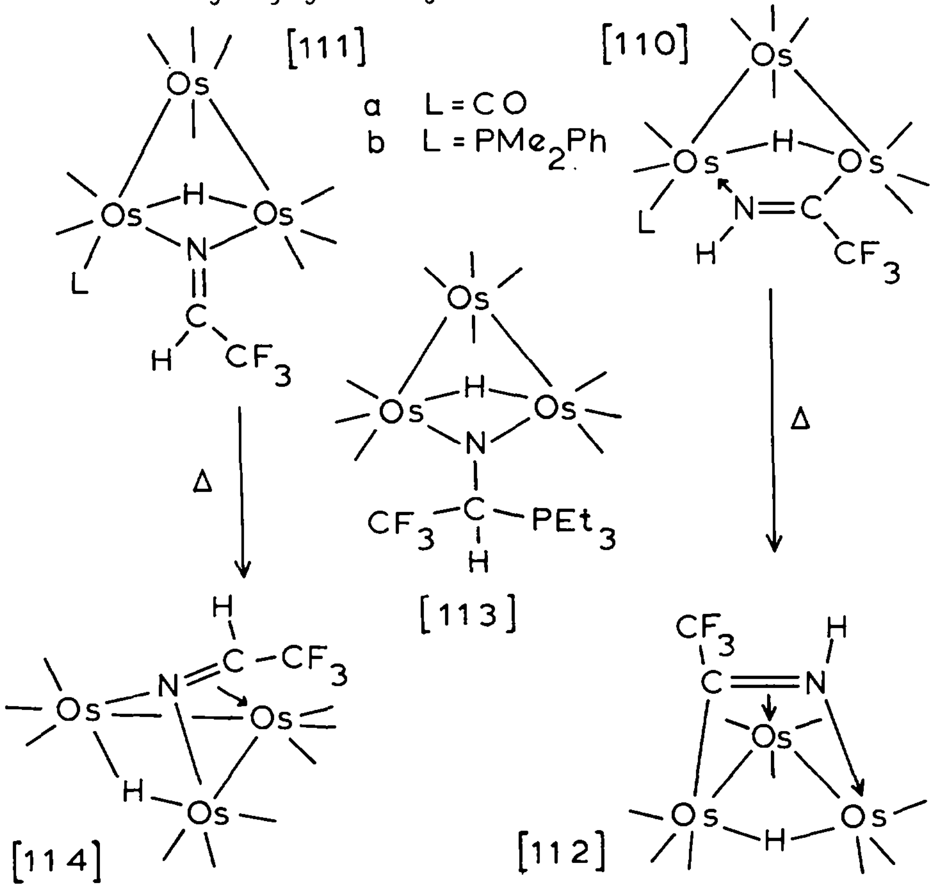


[107]



[109]

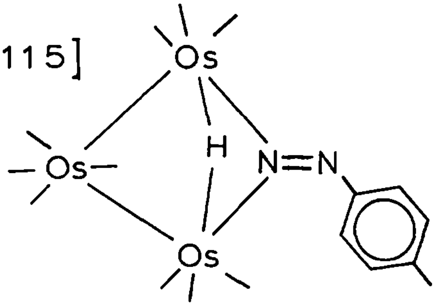
The clusters $HOs_3(\mu\text{-}\eta^2\text{-}CF_3C{=}NH)(CO)_9L$ [110, a, L=CO; b, $L{=}PMe_2Ph$] and $HOs_3(\mu\text{-}\eta^1\text{-}N{=}CHCF_3)(CO)_9L$ [111, a, L=CO; b, $L{=}PMe_2Ph$] were prepared by treatment of the appropriate $H_2Os_3(CO)_9L$ with trifluoroacetonitrile (167,168). The structures of [110b] and [111b] were determined by X-ray crystallography (167,169) and of [111a] by neutron diffraction (170). The complex [111b] exists as two isomers differing in the orientation of the CF_3 group with respect to the PMe$_2$Ph ligand (169). Formation of [111a] occurs by an intramolecular process. Pyrolysis of [110a] gave HOs$_3$(CO)$_9$(μ_3-η^2-CF$_3$C=NH)(CO)$_9$ [112] (167,168). Substitution of [111a] with PMe$_2$Ph gave two mono-substituted isomers, one of which was [111b] (167). However, reaction [111a] with PEt$_3$ gave the addition product HOs$_3$(CO)$_{10}$(μ-NCHCF$_3$PEt$_3$) [113] (168). Pyrolysis of [111a] gave HOs$_3$(CO)$_9$(μ_3-η^2-NHCCF$_3$) [114] (168).



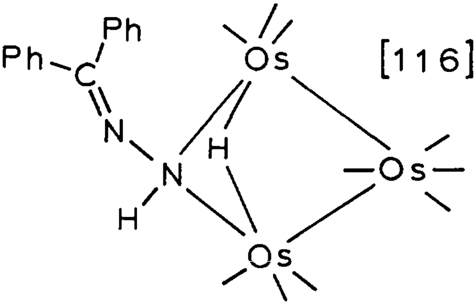
Other N-bridged triosmium clusters which have been structurally characterized include HOs$_3$(μ-η^1-N$_2$C$_6$H$_4$-p-Me)(CO)$_{10}$ [115] (171), for which the hydride was located from the X-ray diffraction data, and HOs$_3$(CO)$_{10}$(μ-NHNCPh$_2$) [116] (172). The latter was prepared by reaction of H$_2$Os$_3$(CO)$_{10}$ with diphenyldiazomethane. Structural parameters were compared with other HOs$_3$X(CO)$_{10}$ clusters in which both X and H bridge the same Os-Os vector. The qualitative trends which were noted were (a) a decrease in the Os-X-Os angle with increasing Os-X distance, (b) an increase in the dibridged Os-Os distance with increasing size of X, (c) a slight increase in the non-bridged

Os-Os distance with decreasing electronegativity of X, and (d) the parameter Δ (the bridged Os-Os distance - the non-bridged Os-Os distance) is negative for small bridgehead atoms, such as H, C, N, or O, and zero or positive for larger bridgehead atoms, such as S, Cl, and Br.

[115]



[116]



Reactions of 1,4-diazabutadienes with trinuclear clusters have been examined. Glyoxalbis(alkylimine) (DAB,alkyl=i-Pr, t-Bu) reacted with $Os_3(CO)_{12}$ to give predominantly $Os_2(CO)_6(DAB)$ but $Os_3(CO)_9$(i-PrN=CH-CH=N-i-Pr) was also isolated (173). Reversed-phase hplc was used to monitor the reactions of $Ru_3(CO)_{12}$ with DAB. Formation of an intermediate was the rate-determining step and was first-order in both $Ru_3(CO)_{12}$ and DAB. The rate was found to depend strongly upon the substituents on DAB (134).

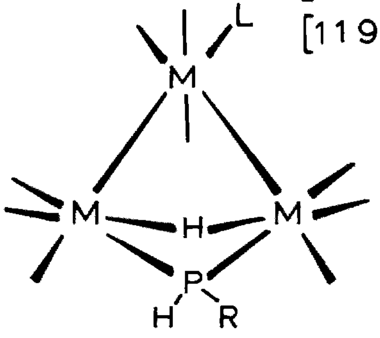
A new reagent, bis(triphenylphosphine)imminium nitrite, [PPN][NO_2], has been exploited for the synthesis of nitrosyl-containing metal clusters. For example, $Ru_3(CO)_{12}$ was treated with [PPN][NO_2] in THF to afford the new cluster [PPN][$Ru_3(CO)_{10}(NO)$] in 78% yield; protonation of this product with trifluoroacetic acid gave the known $HRu_3(CO)_{10}(NO)$. The analogous reaction with $Os_3(CO)_{12}$ produced [PPN][$Os_3(CO)_{10}(NO)$] in 55% yield, and protonation of the product gave the known $HOs_3(CO)_{10}(NO)$ (174).

A number of complexes containing bridging phosphorus ligands have been prepared through reactions of trimetallic clusters with primary and secondary phosphines. Treatment of $Os_3(CO)_{12}$ with trimethylamine-N-oxide in the presence of PH_2R gave $Os_3(CO)_{11}(PH_2R)$ and $HOs_3(CO)_{10}(\mu_2\text{-}PHR)$ [117, M=Os, R=Ph, p-$MeOC_6H_4$, C_6H_{11}]. Thermolysis of $Os_3(CO)_{11}(PH_2R)$ gave [117] and also $H_2Os_3(CO)_9(\mu_3\text{-}PR)$ [118, M=Os, R=Ph, C_6H_{11}]. These complexes were characterized by ^{31}P and ^1H NMR spectroscopy and mass spectrometry, and crystal structures were determined for [117, M=Os, R=Ph] and [118, M=Os, R=Ph] (175,176). Analogous products were obtained from $Ru_3(CO)_{12}$ and PH_2R (R=Ph, p-$MeOC_6H_4$, p-BrC_6H_4) and also AsH_2Ph (176,177); X-ray structural determinations were made for [117, M=Ru, R=Ph], [118, M=Ru, R=Ph] (176), and [118, M=Ru, R=p-$MeOC_6H_4$] (177). Also isolated from these reactions were $Ru_3(CO)_{11}(PH_2Ph)$, $HM_3(CO)_9(\mu_2\text{-}PHPh)(PH_2Ph)$ [119, M=Ru, Os] (176) and

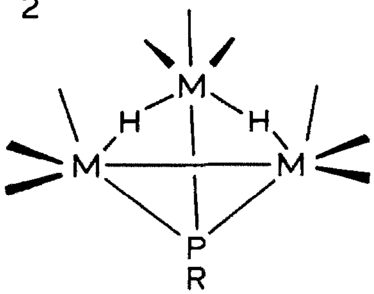
$Ru_3(CO)_9(\mu_3\text{-}PR)_2$ (177).

[117] L=CO

[119] L=PH_2Ph

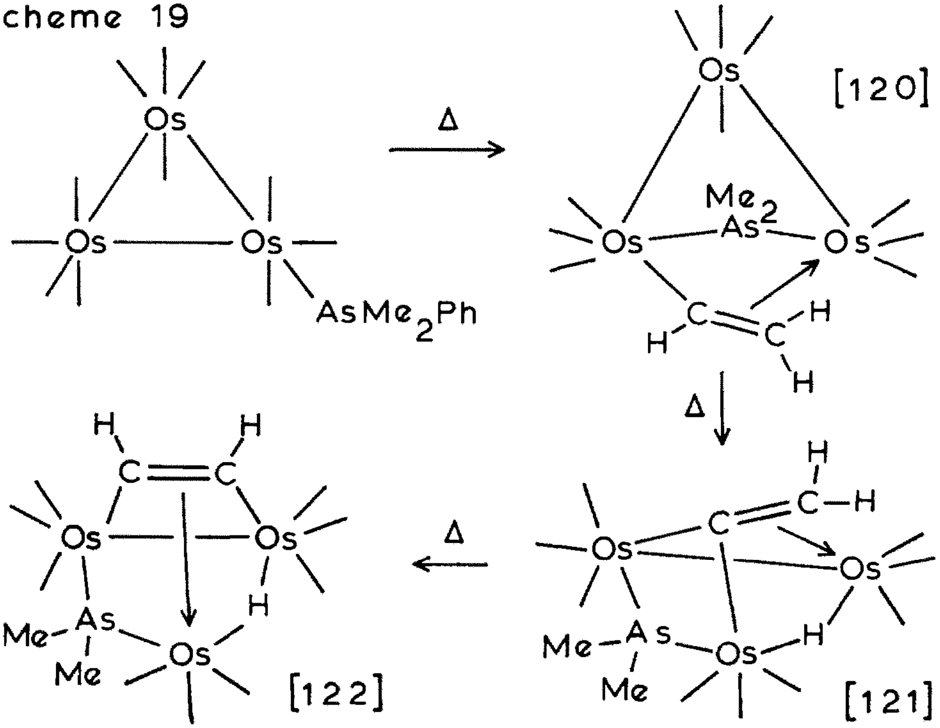


[118]

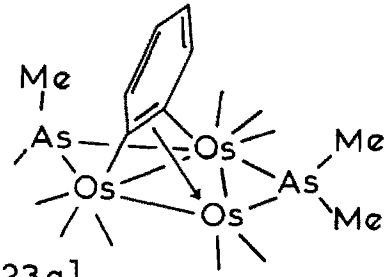


In a related reaction, thermal decarbonylation of $Os_3(CO)_{11}\{AsMe_2(CH{=}CH_2)\}$ gave the new cluster products $Os_3(CO)_{10}(AsMe_2)(CH{=}CH_2)$ [120], $HOs_3(CO)_9(C{=}CH_2)\text{-}(AsMe_2)$ [121], and $HOs_3(CO)_9(CH{=}CH)(AsMe_2)$ [122], which were shown to be formed successively (Scheme 19) (178).

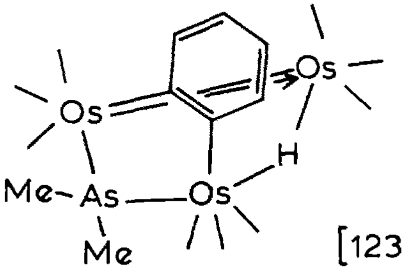
Scheme 19



Variable-temperature ^1H and ^{13}C NMR spectra of $Os_3(C_6H_4)(AsMe_2)_2(CO)_7$ [123a] and the C_6H_3-i-Pr analog showed both carbonyl mobility and mobility of the benzyne moiety. One carbonyl ligand rapidly transfers between two metal atoms and interchange of the opposite faces of the benzyne ligand occurs during two distinct fast intramolecular processes. The crystal structure of $HOs_3(AsMe_2)(C_6H_4)(CO)_9$ [123b] was determined (179).

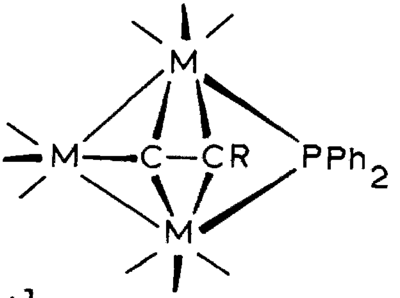


[123a]

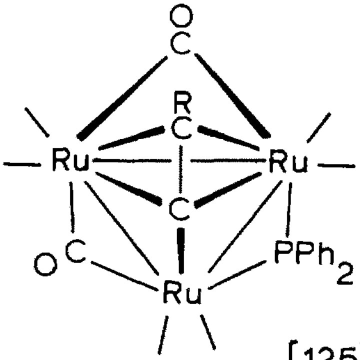


[123b]

The clusters $M_3(CO)_9(CCR)(PPh_2)$ (M=Ru, Os; R=*i*-Pr, *t*-Bu) [124] were prepared in ca. 70% yield by reactions of $M_3(CO)_{12}$ with Ph_2PC_2R in heptane at 25° for 12 h (M=Ru) or at 75° for 4 h in the presence of 2 equiv of trimethylamine-N-oxide (M=Os). The crystal structure determinations on these compounds found "open" structures with only two metal-metal bonds. However, upon standing in solution the Ru cluster lost one CO ligand to give $Ru_3(CO)_8(CCR)(PPh_2)$ [125], which was shown by X-ray crystallography to have a "closed" structure. Rapid conversion of [125] to [124] (M=Ru) was achieved under 1 atm of CO. This is the first example of facile, reversible metal-metal bond formation in a triruthenium cluster (180).



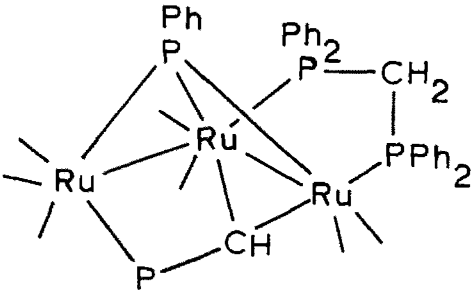
[124]



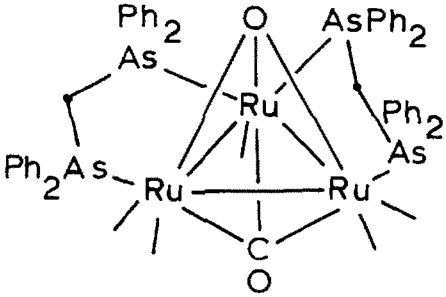
[125]

Bridging phosphide ligands were also produced in the pyrolysis of $Ru_3(CO)_8(dppm)_2$. After 2 h at 80° the complex $Ru_3(CO)_7(\mu_3\text{-}PPh)(\mu\text{-}CHPPh_2)(dppme)$ [126] was isolated in 42% yield and characterized by X-ray crystallography

(181). The clusters $Ru_3(CO)_8(L_2)_2$ (L_2 = dppm, $(AsPh_2)_2CH_2$) also reacted with oxygen in xylene solution at 80° to give $Ru_3O(CO)_6(L_2)_2$ [127], which were characterized by IR and NMR spectroscopy and by X-ray crystallography for the arsine derivative (182).

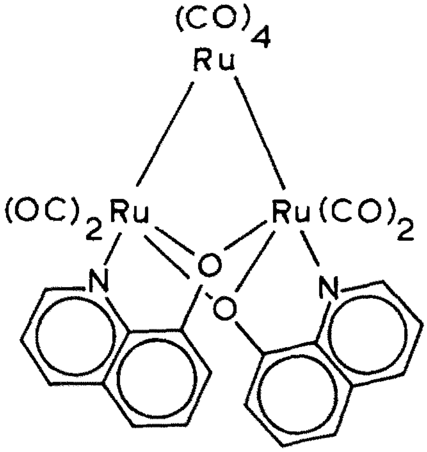


[126]

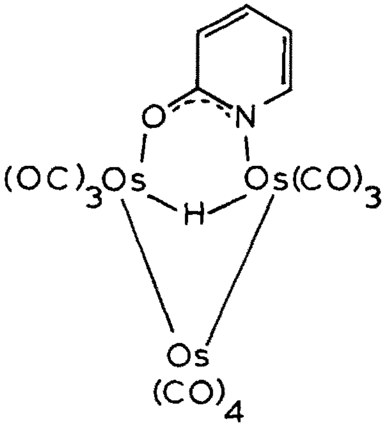


[127]

Reaction of 8-quinolinol with $Ru_3(CO)_{12}$ gave $Ru_3(CO)_8(C_9H_6NO)_2$ [128] and $Ru(CO)_2(C_9H_6NO)_2$; an X-ray crystallographic study showed [128] to be an open, 50-electron cluster with only two metal-metal bonds. Other hydroxyhydrocarbylpyridines gave complexes of similar composition (183). In a related reaction $HOs_3(CO)_{10}(NOC_5H_4)$ [129] was prepared in 75% yield from 2-hydroxypyridine and $Os_3(CO)_{10}(NCMe)_2$ (153).



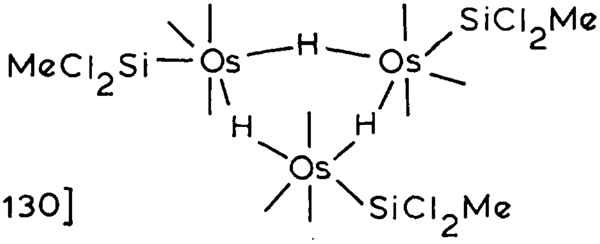
[128]



[129]

The kinetics of oxidation of $Ru_3(CO)_9(PPh_3)_3$ with I_2, Br_2, and ICl in cyclohexane and also of $Ru_3(CO)_9(PBu_3)_3$ and $Ru_3(CO)_9\{P(OPh)_3\}_3$ with I_2 and Br_2 were studied. Except for ICl, all reactions proceeded in two kinetically observable stages to give $Ru(CO)_3LX_2$. Spectroscopic titration studies suggested that the second stage involved a reaction of $Ru_2(CO)_6L_2X_2$. Kinetic and spectroscopic evidence was obtained for the formation of adducts between the complex and one or more halogen molecules. In some cases, the kinetics showed a complex rate dependence upon the concentration of halogen (184).

Clusters containing metal-silicon bonds have been prepared. Reaction of $M_3(CO)_{12}$ (M=Ru, Os) with $HSiCl_2X$ (X=Me, Cl) gave $M(CO)_4(SiXCl_2)_2$ and $H_3M_3(CO)_9(SiXCl_2)_3$ [130] in yields of 20 to 60%. The crystal structure of the $H_3Os_3(CO)_9(SiMeCl_2)_3$ was determined; in the crystal there are two conformational isomers with differing orientations of the $SiMeCl_2$ group about the Os-Si bond (185). Ultraviolet irradiation of [130] (M=Os; X=Me, Cl) in hexane under CO (2 atm) gave *cis*-$Os(CO)_4H(SiXCl_2)$ as the major product. The same product, along with $[Os(CO)_4(SiXCl_2)]_2$, could be isolated after thermolysis under CO (186). The silyl-containing cluster anion $[HRu_3(CO)_{10}(SiEt_3)_2]^-$ was isolated from a catalytic system for production of silyl formates from CO_2 and $HSiEt_3$; the catalyst system involved $[HRu_3(CO)_{11}]^-$ at 60° and 50 atm of CO_2 for 24 h (187).

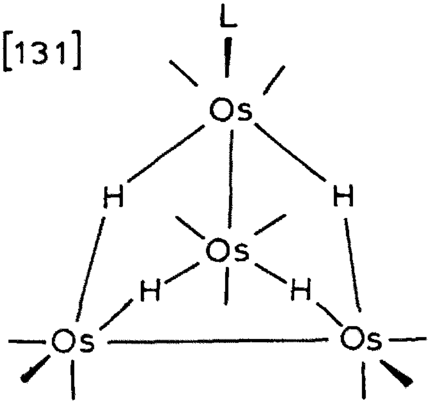


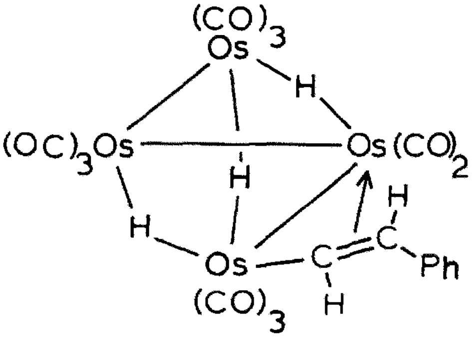
[130]

Tetranuclear and Larger Clusters

An X-ray and neutron diffraction study of $H_4Os_4(CO)_{11}\{P(OMe)_3\}$ [131, L=$P(OMe)_3$] was performed. The average Os-H distance was 1.787 Å and the Os-H-Os angle was 112.2(4)° (188). An X-ray diffraction study of $H_4Os_4(CO)_{12}$ [131, L=CO] was also reported (189).

[131]

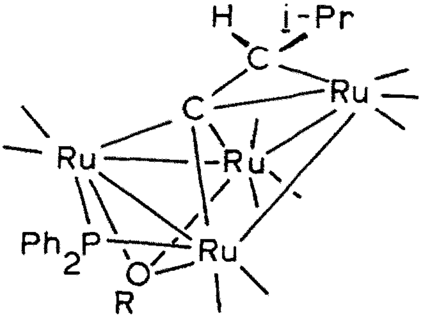


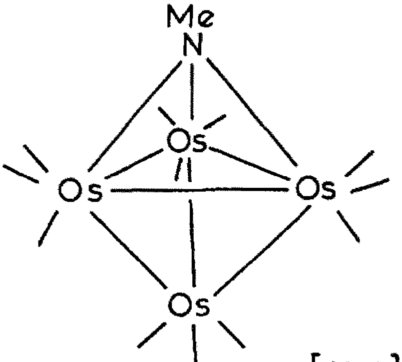


[132]

Photolysis of $H_4Os_4(CO)_{12}$ in the presence of styrene gave the vinyl complex $H_3Os_4(CO)_{11}(CHCHPh)$ [132]. Both X-ray and neutron diffraction studies were done on the product. As for $HOs_3(\mu\text{-}CHCHR)(CO)_{10}$, the vinyl group is μ-σ,π-coordinated (190).

The "butterfly" clusters $Ru_4(CO)_{10}(C{=}CH\text{-}\underline{i}\text{-}Pr)(OR)(PPh_2)$ (R=H, Et) [133] were prepared in 30% yield by pyrolysis of $Ru_3(CO)_{11}(Ph_2PC_2\text{-}\underline{i}\text{-}Pr)$ in wet THF or THF-EtOH, respectively. The compounds were characterized crystallographically (191).



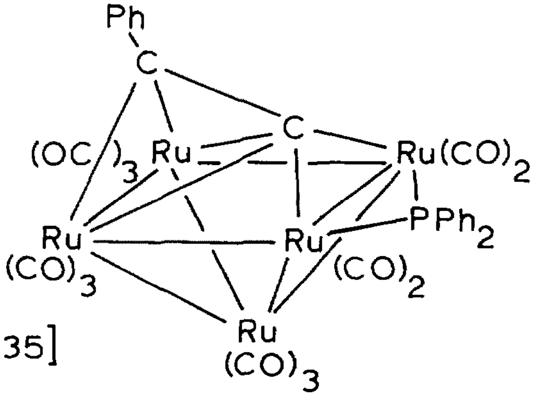


[133]

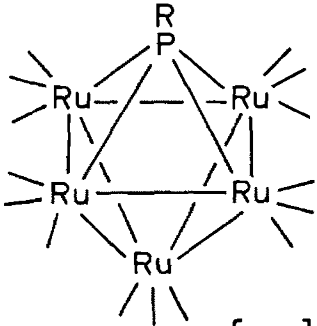
[134]

The structure of $Os_4(\mu_3\text{-}NMe)(CO)_{12}$ [134], found in 35% yield by pyrolysis of $H_2Os_3(\mu_3\text{-}NMe)(CO)_9$ at 198°C, was determined by X-ray crystallography (164).

Pyrolysis of $Ru_3(CO)_{11}(Ph_2PC_2Ph)$ in heptane at 70° for 8 h gave predominantly $Ru_2(CO)_6(C{\equiv}CPh)(PPh_2)$, a hexanuclear product which was not characterized, and $Ru_5(CO)_{13}(C_2Ph)(PPh_2)$ [135] in 30% yield. The crystal structure of [135] revealed a square pyramid of metal atoms bridged on the square base by a μ_4-η^2-C_2Ph ligand (192). This is one of the few examples of coordination of a hydrocarbon moiety to a square cluster face.



[135]

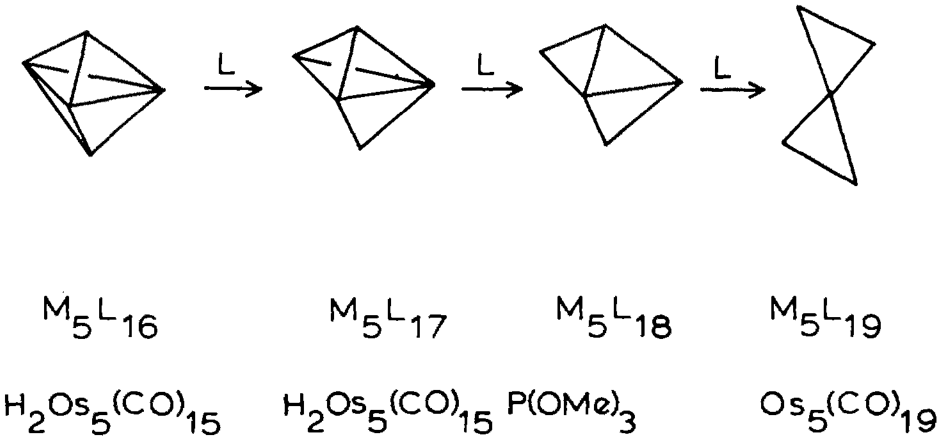


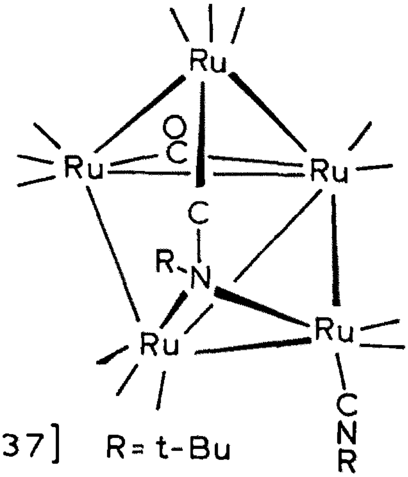
[136]

Other face-bridged clusters $Ru_5(CO)_{15}(PR)$ [136] (R=Ph, Et, Me, Ch_2Ph) were prepared in 5-10% yield by reaction of $Ru_3(CO)_{12}$ and $CpMn(CO)_2(PRCl_2)$ at 100°C for 8 h. The crystal structures of the products with R=Ph and Et were determined (193).

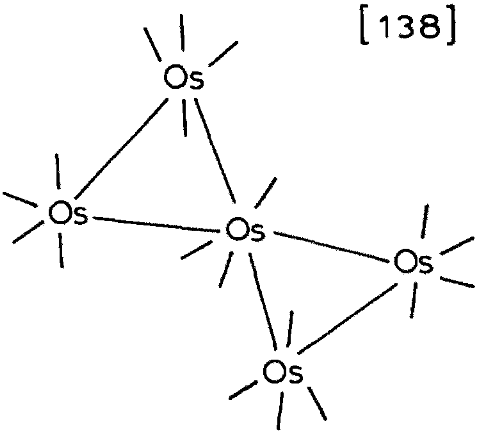
Pyrolysis of $Ru_3(CO)_{11}$(CN-t-Bu) for 16 h at 120°C gave $Ru_5(CO)_{14}$(CN-t-Bu)$_2$ [137] in moderate yields. The crystal structure of this compound showed a six-electron donor CN-t-Bu ligand on a closo polyhedron which is related to the structures of $Os_5(CO)_{16}$ and $H_2Os_5(CO)_{15}$. The changes in the metal framework upon the addition of two-electron donor ligands are illustrated in Scheme 20 (194).

Scheme 20





[137] R = t-Bu

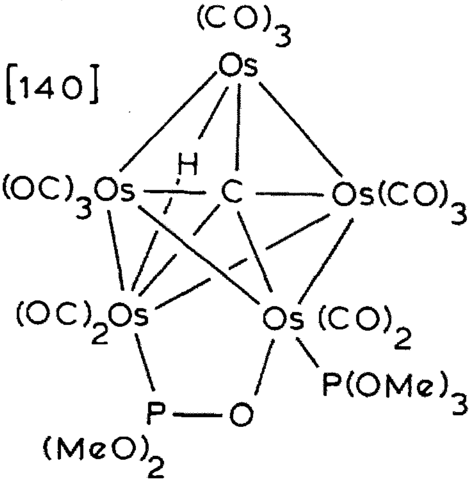


[138]

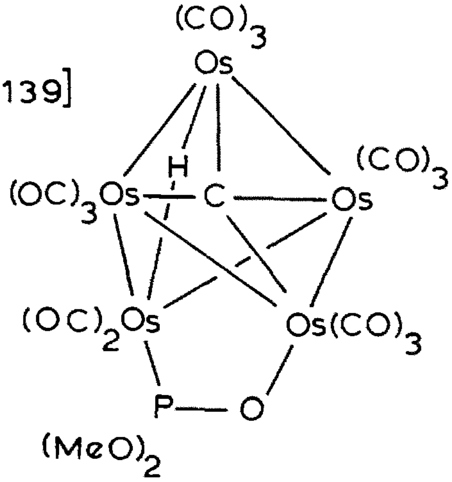
The last member of the series in Scheme 20, Os$_5$(CO)$_{19}$ [138], was prepared by carbonylation of Os$_6$(CO)$_{18}$ at 90 atm and 160° for one hour. The structure was determined using X-ray crystallography. The other product in the reaction was Os(CO)$_5$. Over longer times, other products, including Os$_3$(CO)$_{12}$, Os$_5$(CO)$_{16}$, Os$_5$(CO)$_{19}$, Os$_6$(CO)$_{20}$, and Os$_7$(CO)$_{21}$, were formed. In the solid state Os$_6$(CO)$_{18}$ reacted quantitatively with CO to give Os$_6$(CO)$_{20}$, which regenerated Os$_6$(CO)$_{18}$ upon heating (195).

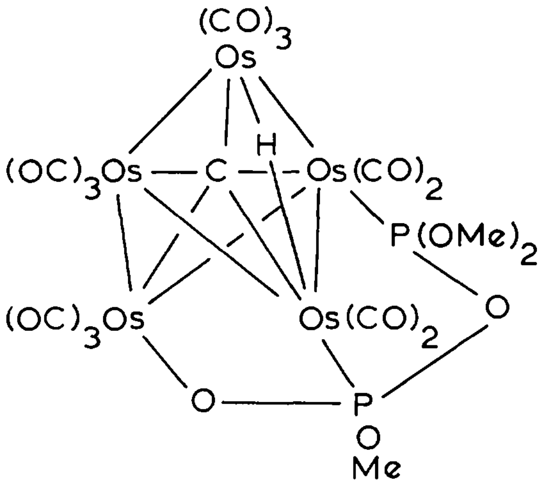
Pyrolysis of Os$_3$(CO)$_{11}${P(OMe)$_3$} gave four complexes: Os$_5$C(CO)$_{14}$H{OP(OMe)$_2$} [139], Os$_5$C(CO)$_{13}$H{OP(OMe)$_2$}{P(OMe)$_3$} [140], Os$_5$C(CO)$_{13}$H{OP(OMe)OP(OMe)$_2$} [141], and Os$_5$(CO)$_{15}${P(OMe) } [142]. The structure of [140] was crystallography determined; the other products were previously reported (196).

[140]

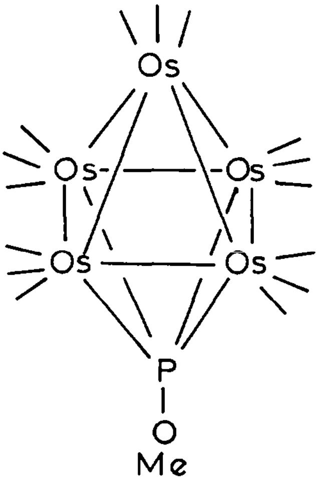


[139]





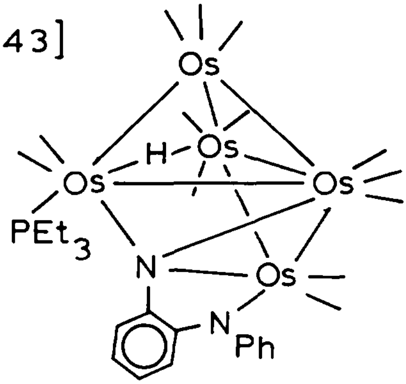
[141]



[142]

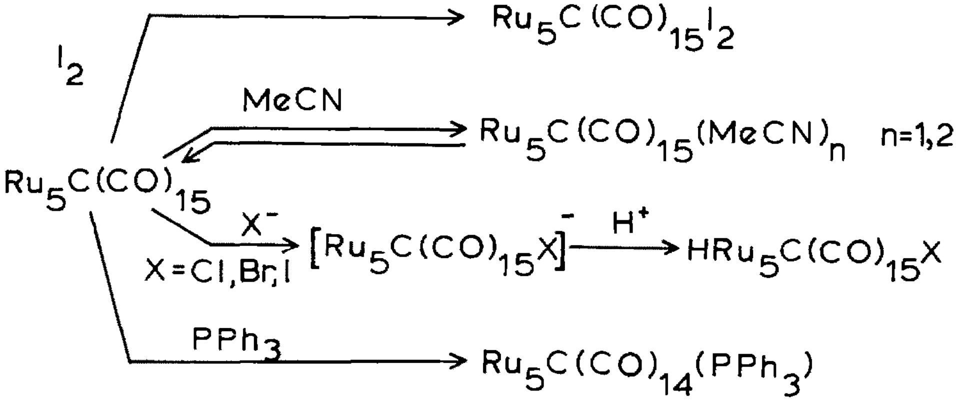
The 1:1 addition products $Os_5(CO)_{13}H(PhNC_6H_4N)L$ (L=PEt_3, CN-t-Bu, and CO) [143] were formed by treatment of $Os_5(CO)_{13}H(PhNC_6H_4N)$ with L. The crystal structure was determined for the PEt_3 adduct. When L=CO, the reaction was reversible (197).

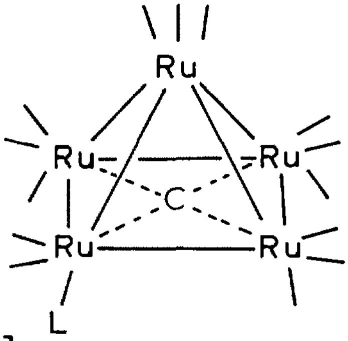
[143]



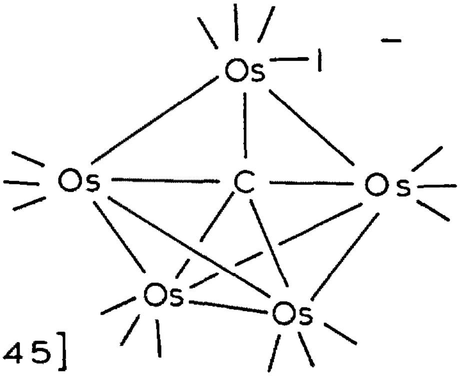
Carbonylation of $Ru_6C(CO)_{17}$ at 70° and 80 atm afforded a quantitative yield of $Ru(CO)_5$ and $Ru_5C(CO)_{15}$ [144, L=CO]; X-ray structural details were reported for this pentanuclear cluster and for its PPh_3-substituted derivative [144, L=PPh_3]. The reactions in Scheme 21 were reported (198). The solid state IR spectra of $HRu_5C(CO)_{15}Cl$ and $HRu_5C(CO)_{15}Br$ were interpreted to indicate structures of the bridged butterfly type, analogous to $[Os_5C(CO)_{15}I]^-$ [145] (321).

Scheme 21



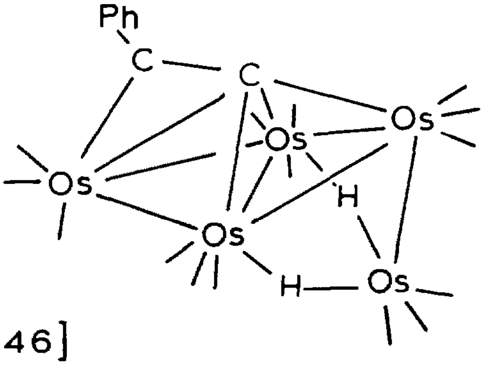


[144]



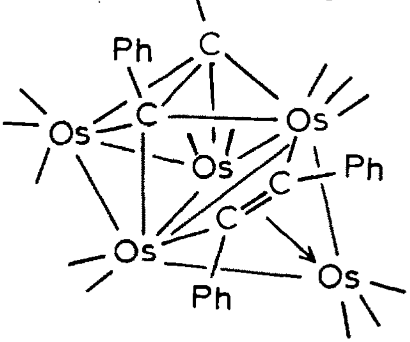
[145]

The reactions of acetylenes $R^1C{\equiv}CR^2$ (R^1=H, R^2=Ph; R^1=R^2=Ph) with $H_2Os_5(CO)_{15}$ produced a number of acetylene-containing Os_5 clusters. The structures of two of these, $H_2Os_5(CO)_{15}(C{\equiv}CPh)$ [146] and $Os_5(CO)_{13}$-$(PhC{\equiv}CPh)_2$ [147], were determined by X-ray crystallography (199).

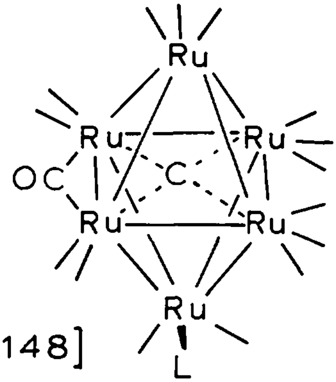


[146]

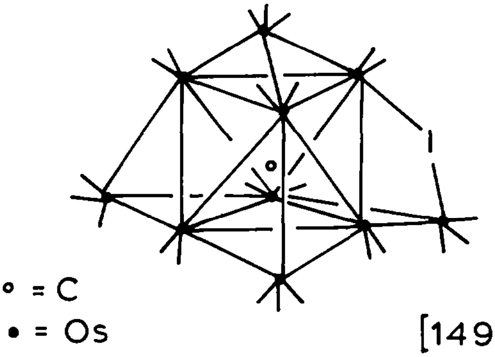
[147]



Substitution reactions of $Ru_6C(CO)_{17}$ gave $Ru_6C(CO)_{17-n}L_n$ (L=PPh_2Et, n=1, 2; L=$P(OMe)_3$, n=1-4). The crystal structure of $Ru_6C(CO)_{16}(PPh_2Et)$ [148] was determined and used as a basis for NMR studies of the other complexes. Silica-bound $Ru_6C(CO)_{16}\{PPh_2C_2H_4Si(OEt)_x(OSi-)_{3-x}\}$ was also prepared and was characterized by analogy to the soluble derivatives (200).

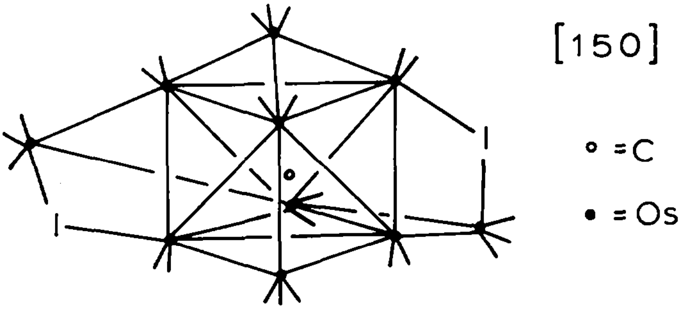


[148]



[149]

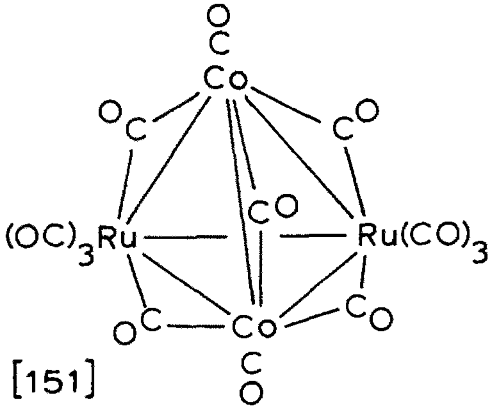
Reactions of $[Os_{10}C(CO)_{24}]^{2-}$ with halogens X_2 gave first $[Os_{10}C(CO)_{24}X]^-$ and then $[Os_{10}C(CO)_{24}X_2]$ (X=Cl, Br, I). The dianion could be regenerated from these products by treatment with nucleophiles such as X^-, PR_3, or pyridine. The X-ray crystal structure determinations for $[PPN][Os_{10}C(CO)_{24}I]$ [149] and $Os_{10}C(CO)_{24}I_2$ [150] were reported (201).



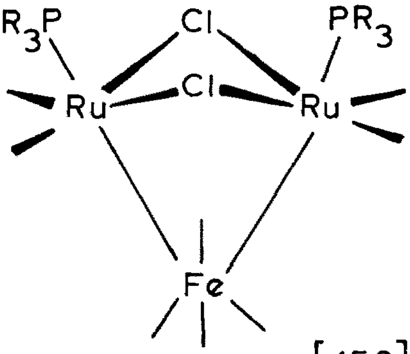
[150]

Mixed Metal Clusters

Halide-displacement from $[Ru(CO)_3Cl_2]_2$ by $KCo(CO)_4$ was used to prepare $RuCo_2(CO)_{11}$ in 76% yield. This complex showed high reactivity toward donor reagents and disproportionated in solution to $Co_4(CO)_{12}$ and $Ru_2Co_2(CO)_{13}$ [151] (46%). The crystal structure of the latter molecule was reported (202). The cluster anion $[RuCo_3(CO)_{12}]^-$ was isolated in 68% yield as its Na salt after reaction of $NaCo(CO)_4$ with $RuCl_3$; cation exchange was used to prepare the Cs^+ and NEt_4^+ salts (203).



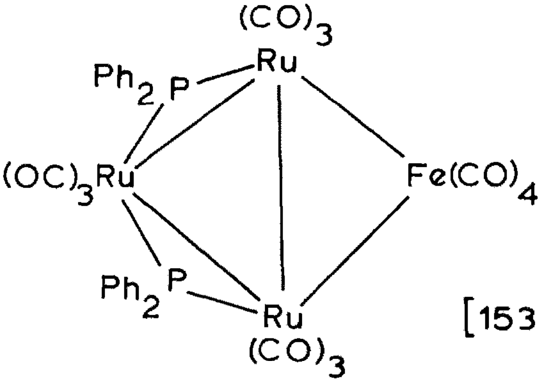
[151]



[152]

A mixture of products, including $Ru_3(CO)_{10}L_2$, $FeRu_2(CO)_{10}L_2$, $RuFe_2(CO)_{11}L$, and the major product $Ru_2Fe(\mu\text{-}Cl)_2(CO)_8L_2$, was prepared by reaction of $RuCl_2L(\eta^6\text{-}C_6H_6)$ (L=$P(OMe)_3$, PPh_3, PMe_2Ph, PMe_3, $PPh_2(C_2\text{-}\underline{t}\text{-}Bu)$) with $Fe_2(CO)_9$. The crystal structure of $Ru_2Fe(\mu\text{-}Cl)_2(CO)_8\{PPh_2(C_2\text{-}\underline{t}\text{-}Bu)\}$ [152] was determined (204). In all cases, PR_3 was coordinated to Ru rather than Fe. Reactions of $FeRu_2(\mu\text{-}Cl)_2(CO)_8L_2$ (L=PPh_3, PMe_3) with bases were examined. In acetone the product was $FeRu_2(\mu\text{-}OH)_2(CO)_8(PR_3)_2$ but sodium carbonate in isopropanol gave $FeRu_2(\mu\text{-}H)(\mu\text{-}OH)(CO)_8(PR_3)_2$ (205).

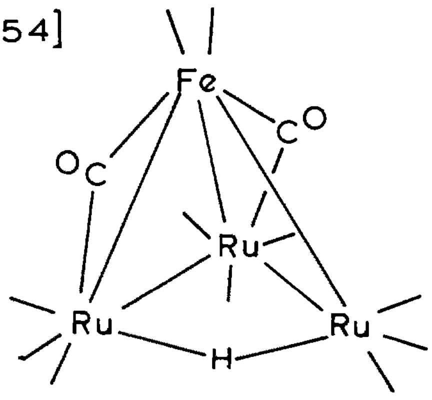
The X-ray structure determination for $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$ [153] was performed. This cluster was prepared by reaction of $Ru_3(CO)_{12}$ and $Fe(CO)_4\text{-}(PPh_2PPh_2)$. The metals form a triangulated rhombus (206).



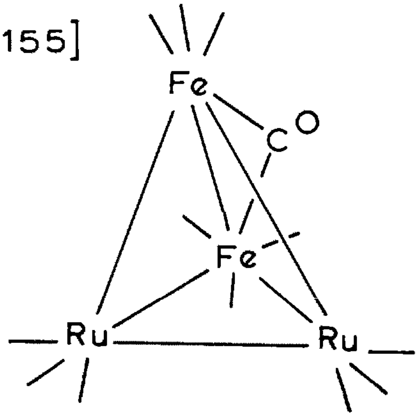
[153]

The combination of $[PPN][HFe(CO)_4]$ and $Ru_3(CO)_{12}$ in refluxing THF gave $[PPN][HFeRu_3(CO)_{13}]$ in 47% yield; under the same conditions $FeRu_2(CO)_{12}$ and the $HFe(CO)_4^-$ salt gave $[PPN][HFe_2Ru_2(CO)_{13}]$ in 4% yield. The former product was characterized by both X-ray and neutron diffraction and the latter by X-ray data alone. The $[HFeRu_3(CO)_{13}]^-$ cluster [154] has two semi-bridging carbonyls between the Fe and two Ru atoms, while $[HFe_2Ru_2(CO)_{13}]^-$ [155] has a single, fully bridging carbonyl between the two Fe atoms (207). The protonated product from [154], $H_2FeRu_3(CO)_{13}$, reacted with a large number of phosphine ligands to give $H_2FeRu_3(CO)_{13-n}L_n$ (n=1, 2; L=PPh_3, $PMePh_2$, PMe_2Ph, PEt_2Ph, $P(OMe)_3$, $P(OEt)_3$, $P(OEt)_2Ph$, PMe_3, P(*i*-Pr)$_3$) in yields of 20-30%. NMR studies showed that for n=1, two isomeric forms of C_S [156] and C_1 [157] symmetry were present. The ratio of these two isomers depended both upon the ligand's size and basicity, with large ligands giving only the C_S isomer and more basic ligands favoring the C_1 isomer. The kinetics of substitution by PPh_3 was found to be first-order in cluster and independent of the concentration of PPh_3 with $\Delta H^{\ddagger}$ of 25.3 ± 0.9 kcal/mol and $\Delta S^{\ddagger}$ of 4.9 ± 3.1 eu. The structure of the C_S isomer was determined by X-ray crystallography (208). The fluxionality of these clusters was also examined by ^1H, ^{31}P and ^{13}C NMR spectroscopy for n=1, L=PMe_2Ph, PMe_3 and n=2, L=PMe_3, PPh_3, $P(OMe)_3$, and $P(OEt)_3$. Processes involving bridge-terminal carbonyl exchange localized on Fe, cyclic exchange of carbonyls about the cluster face which is bridged by carbonyls, and rearrangement of the metal framework with shifts of carbonyls and hydrides were observed (209). Finally, reactions of $H_2FeRu_3(CO)_{13}$ with acetylenes RC_2R' (R=R'=Ph; R=R'=Me; R=Ph, R'=Me) gave $FeRu_3(CO)_{12}(RC{\equiv}CR')$. For the symmetrical acetylenes, two isomers of the product were formed, but three isomers were obtained for $FeRu_3(CO)_{12}(PhC{\equiv}CMe)$. The two isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ [158a and b] were characterized crystallographically. Isomer [158b] rearranged rapidly to [158a] and alkyne dissociation did not take place during the isomerization (210).

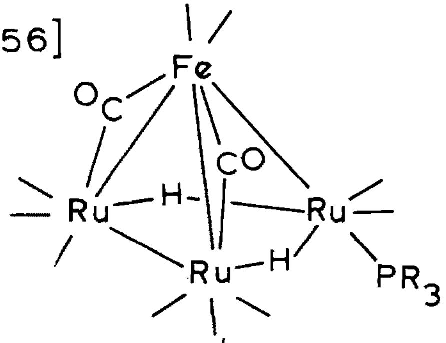
[154]



[155]



[156]



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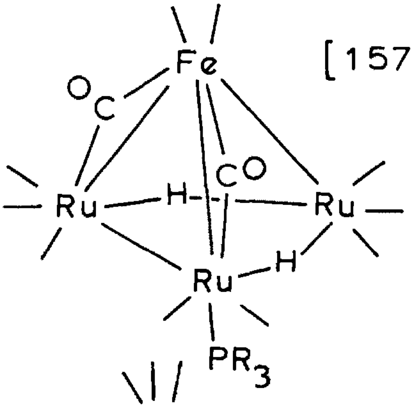
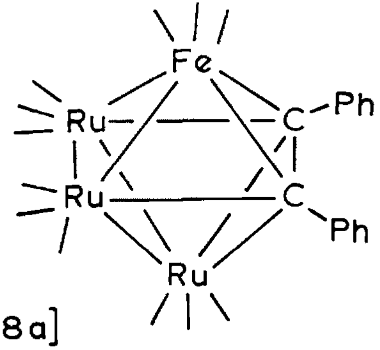
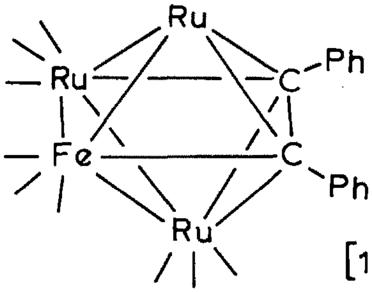




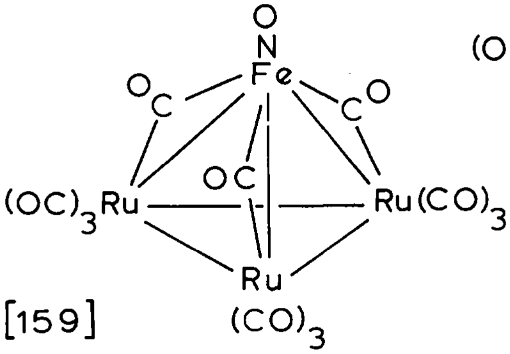
[158a]



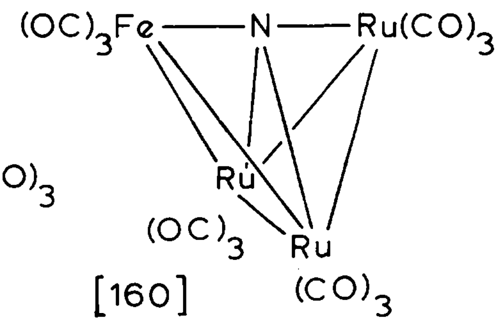
[158b]

Photolysis of $H_2FeRu_3(CO)_{13}$, $H_2Ru_4(CO)_{13}$, and $H_2FeOs_3(CO)_{13}$ in the presence of PPh_3 and hydrogen gave the corresponding $H_2M_4(CO)_{12}(PPh_3)$ and $H_4M_4(CO)_{12}$. Irradiation at 366 nm in the presence of PPh_3 resulted in quantum yields of 0.030, 0.016, and 0.057, respectively; photolysis under CO caused cluster fragmentation but with a quantum yield of less than 10^{-5}. For $H_2FeRu_3(CO)_{13}$ the quantum yield for PPh_3 substitution was independent of PPh_3 concentration but was decreased under a CO atmosphere; this was interpreted to indicate competition between CO and PPh_3 for the same photogenerated intermediate. The primary photochemical event was proposed to be carbonyl dissociation, rather than metal-metal bond cleavage (211).

A mixed-metal, nitrosyl-containing cluster $[PPN][FeRu_3(CO)_{12}(NO)]$ [159] was prepared in 80% yield by condensation of $[PPN][Fe(CO)_3(NO)]$ with $Ru_3(CO)_{12}$. The crystal structure of the product was determined and was found to contain a terminal nitrosyl bound to Fe. Protonation of this product with CF_3CO_2H unexpectedly caused CO_2 elimination to afford $HFeRu_3N(CO)_{12}$ [160] in 75% yield; the structure of this molecule was proposed to be of the butterfly type with the N atom bridging the wing tips (212).



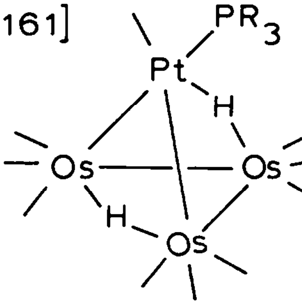
[159]



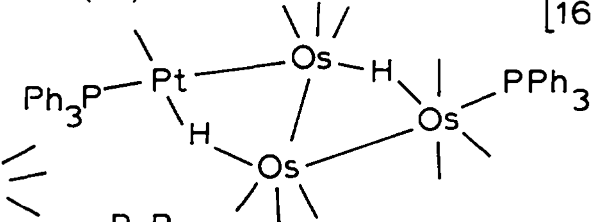
[160]

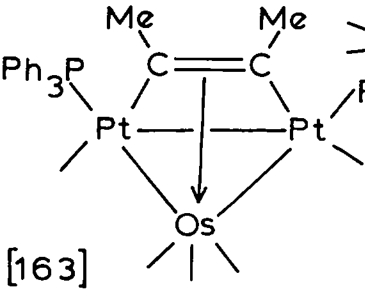
From the neutral complexes $Pt(C_2H_4)_2(PR_3)$ (PR_3=$P(C_6H_{11})_3$, PPh_3, or $PMe(\underline{t}\text{-}Bu)_2$) and $H_2Os_3(CO)_{12}$, the mixed-metal clusters $Os_3PtH_2(CO)_{10}(PR_3)$ [161] were prepared. Fluxional exchange of the hydride ligands was noted. The crystal structure of the $P(C_6H_{11})_3$ complex was determined (213). These clusters reacted with donor ligands L, such as CO, PPh_3, or $AsPh_3$, to give $Os_3PtH_2(CO)_{10}(PR_3)L$; the X-ray structure determination of $Os_3PtH_2(CO)_{10}(PPh_3)_2$ [162] was reported. The corresponding reaction with 2-butyne gave a mixture of five compounds, one of which, $OsPt_2(CO)_5(PPh_3)_2(\mu_3\text{-}MeC_2Me)$ [163], was structurally characterized (214). Treatment of $Os_3PtH_2(CO)_{10}\{P(C_6H_{11})_3\}$ with diazomethane gave as the kinetically controlled product one isomer of $Os_3PtH_2(\mu\text{-}CH_2)(CO)_{10}\{P(C_6H_{11})_3\}$ [164]; however, this isomer rearranges over several days in solution to a second isomer [165]. The crystal structures of both isomers were determined (215).

[161]

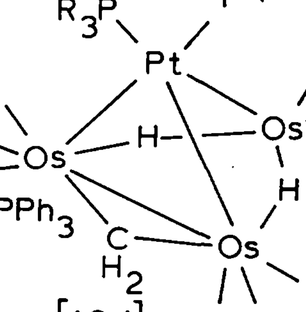


[162]

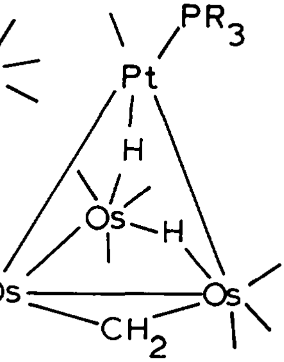




[163]

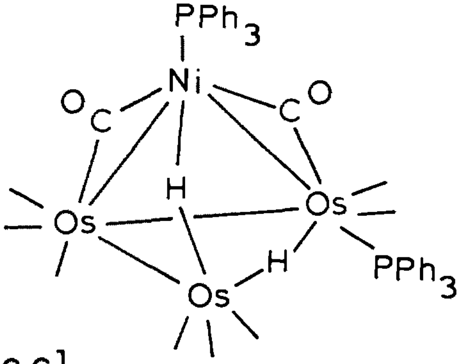


[164]

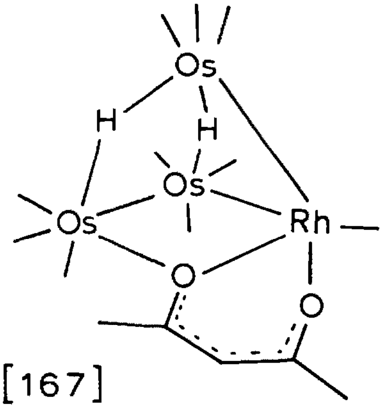


[165]

Other mixed-metal clusters containing three Os atoms were prepared through similar reactions of $H_2Os_3(CO)_{10}$. The reaction with $Ni(C_2H_4)(PPh_3)_2$ gave $NiOs_3H_2(CO)_{10}(PPh_3)_2$ [166] and with $Rh(acac)(C_2H_4)_2$ gave $RhOs_3H_2(acac)(CO)_{10}$ [167]; the structures of both products were determined by X-ray crystallography. The latter cluster, being coordinatively unsaturated, added PPh_3 at Rh (216). Combination of $[PPN][HFe(CO)_4]$ with $H_2Os_3(CO)_{10}$, followed by acidification with HBr, formed $H_2Fe_2Os_3(CO)_{15}$ (217).

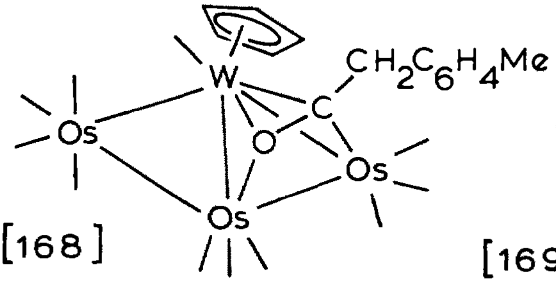


[166]

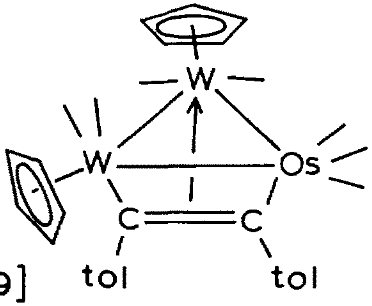


[167]

Another method for synthesis of mixed-metal clusters is combination of a coordinatively unsaturated metal cluster with an electron-rich metal carbene or carbyne complex. For example, $H_2Os_3(CO)_{10}$ reacted with $Cp(CO)_2W(CC_6H_4Me)$ to give $CpWOs_3(CO)_{12}(CH_2\ C_6H_4Me)$ [168] in 21% yield and $Cp_2W_2Os(CO)_7(CC_6H_4Me)_2$ [169] in 33% yield. Crystal structure determinations of both products were reported. NMR studies in situ showed that [169] appeared rapidly with formation of a molar equivalent of $H_2Os_2(CO)_8$, followed by slower formation of [168]. The cluster [169] was fluxional in solution and the crystal contained two isomers related by rotation of the acetylene ligand about the triangular W_2Os face (218). Only product [168] was formed by reaction of $Os_3(CO)_{10}(C_8H_{14})_2$ with $Cp(CO)_2W(CC_6H_4Me)$, but $Cp(CO)_2W(CC_6H_4Me)$ with $H_2Os_3(CH_2)(CO)_{10}$ afforded [169]. The Ru analogs of [169] were formed using $Ru_3(CO)_{12}$ (219).

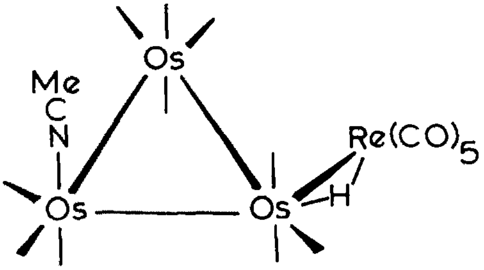


[168]

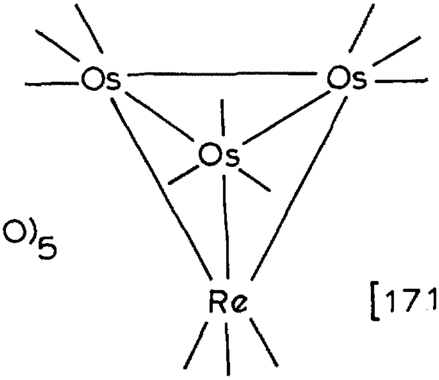


[169]

Heating an acetonitrile solution of $H_2Os_3Re_2(CO)_{20}$ produced $HOs_3Re(CO)_{15}$(NCMe) [170] in quantitative yield. This reaction could be reversed by treatment of the product with $HRe(CO)_5$ in a hydrocarbon solvent. When $HOs_3Re(CO)_{15}$(NCMe) was treated with trimethylamine-N-oxide in refluxing acetonitrile under a hydrogen atmosphere, the new cluster $H_5Os_3Re(CO)_{12}$ [171] was obtained in 70% yield. X-ray structural determinations of both products were reported. The proposed positions of the hydride ligands, which were not located, were bridging five of the six edges of the metal tetrahedron. The hydride ^1H NMR resonance appeared as a broad singlet (220,221).



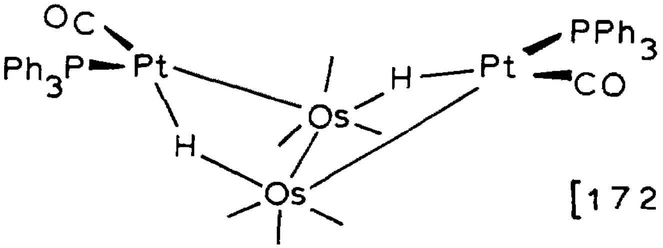
[170]



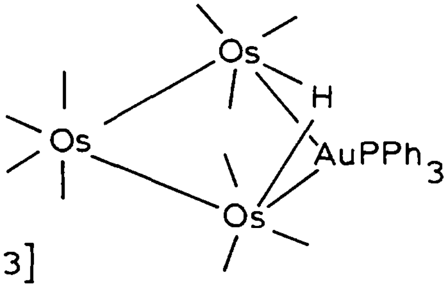
[171]

The clusters $Os_2Pt_2H_2(CO)_8(PR_3)_2$ (R=Ph, C_6H_{11}, or Me) were prepared by reaction of $Pt(C_2H_4)_2(PR_3)$ with $H_2Os(CO)_4$. The molecular structure, determined for R=Ph [172] was shown to be a butterfly type with Pt atoms at the wing-tips (222).

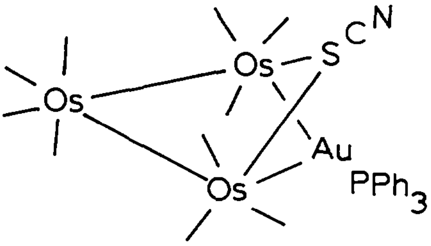
Gold-osmium clusters were also prepared from triosmium clusters. Reactions of salts of $[HOs_3(CO)_{11}]^-$ with $AuCl(PR_3)$ (R=Et, Ph) gave $HOs_3Au(CO)_{10}(PR_3)$ [173]. The crystal structures of this product and also $Os_3Au(CO)_{10}(PPh_3)$(SCN) [174] were determined. The bridged Os-Os bond in [173] was short, compared with that of [174], and this difference was attributed to unsaturation in the former (223). Treatment of [173] with [PPN]Cl gave $[PPN][Os_6Au(CO)_{20}H_2]$ [175], which was characterized by X-ray crystallography (224).



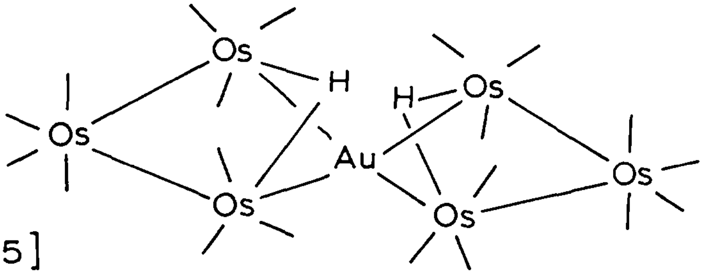
[172]



[173]

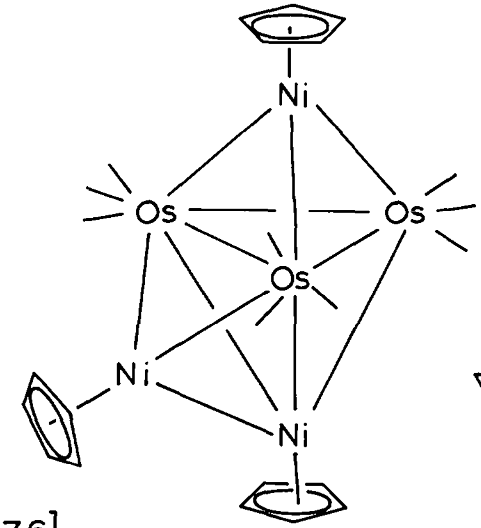


[174]

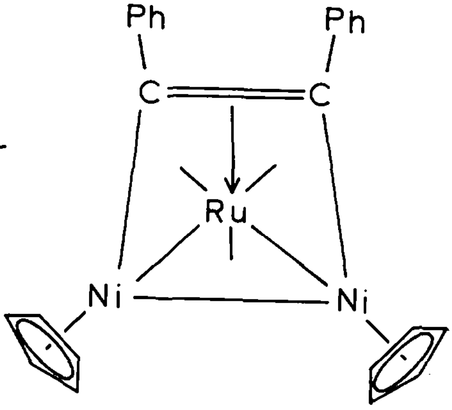


[175]

Pyrolysis of $Os_3(CO)_{12}$ in the presence of $[CpNi(CO)]_2$ in refluxing octane produced a 40% yield of $Cp_3Ni_3Os_3(CO)_9$ [176], the crystal structure of which was determined. In solution only one cyclopentadienyl resonance was observed in the ^1H NMR spectrum even though all three groups were non-equivalent in the crystal (225).

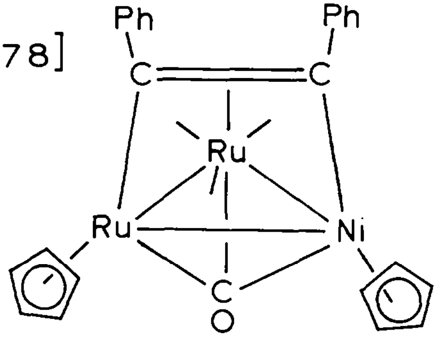


[176]

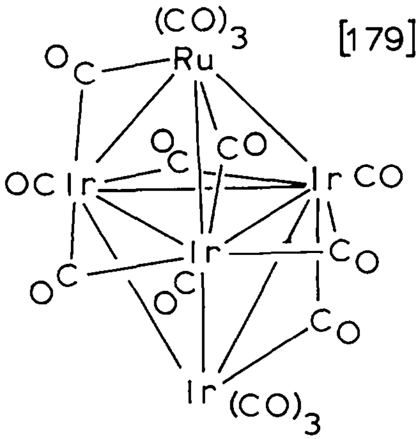


[177]

[178]



[179]



Reactions of nickelocene, $[CpNi(CO)]_2$, and $Cp_2Ni_2(RC_2R')$ (R=H, R'=t-Bu; R=R'=Et, Ph) with $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $HRu_3(CO)_9(C_2$-t-Bu) and $HRu_3(CO)_9(C_6H_9)$ were conducted. The dark-green cluster $Cp_2Ni_2Ru(CO)_3(PhC_2Ph)$ [177] was prepared in 10% yield through reaction of $Cp_2Ni_2(PhC_2Ph)$ with $Ru_3(CO)_{12}$; isolated from the same reaction in 15% yield was $CpNiRu_3(CO)_9(PhC_2Ph)$ (226). Pyrolysis of the same starting materials in refluxing octane for 20 min gave a 10% yield of $Cp_2Ru_2Ni(CO)_4(PhC_2Ph)$ [178]. X-ray crystal structure determinations were made for both [177] and [178].

The X-ray structural determination for $[PPN]_2[RuIr_4(CO)_{15}]$ [179] was described. This compound was prepared in 18% yield from $Ir_4(CO)_{12}$ and $RuCl_3$ in the presence of NaOH and CO in methanol (228).

The carbonyl fluxionality of $Os_3(CO)_{12}$, $RuOs_2(CO)_{12}$ and $Ru_2Os(CO)_{12}$ was examined by ^{13}C NMR spectroscopy. The free energy of activation for carbonyl fluxionality increased in the order $Ru_2Os(CO)_{12} < RuOs_2(CO)_{12} < Os_3(CO)_{12}$. For $Ru_2Os(CO)_{12}$ rapid intramolecular CO exchange at 30°C gave rise to one signal at 191.5 ppm and for $RuOs_2(CO)_{12}$ at 145° a signal at 183.9 ppm; at 30° the spectrum of $RuOs_2(CO)_{12}$ consisted of signals at 186.4 (10 CO's) and 170.3 ppm (2 CO's). A process involving two bridging carbonyls only between Ru and Os atoms was proposed (229).

Catalysis by Clusters or Supported Clusters

The formation of silyl formates from carbon dioxide and hydrosilanes was catalyzed by salts of $[HRu_3(CO)_{11}]^-$. For example, 63% conversion of $HSiEt_3$ to Et_3SiO_2CH (81% yield) was achieved after 24 h at 60° and 50 bar CO_2 pressure. This represented a turnover of 235. The cluster anion $[HRu_3(CO)_{10}(SiEt_3)_2]^-$ was isolated from the reaction mixture (230).

The cluster anion $[HRu_3(CO)_{11}]^-$ has been suggested to be an important species in a ruthenium/iodide catalyst system for conversion of CO and hydrogen to alcohols, including ethylene glycol. The other important metal species in this system is $[Ru(CO)_3I_3]^-$ (231).

Catalytic activation of C-H bonds in trialkylamines was achieved with homogeneous solutions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. Only α- and β-hydrogen exchange was observed. The patterns of substitution using D_2O were compared with results obtained using Pd black catalysts. In these homogeneous systems, clusters were proposed to be the catalytically active species (232).

A previous report of enhancement of $Os_3(CO)_{12}$-catalyzed conversion of CO and hydrogen to methane in the presence of excess $P(OMe)_3$ has been shown to be incorrect through ^{13}C and ^2H labeling studies. When ^{13}CO was used, only $^{12}CH_4$ was produced, but in the presence of ^{13}C-enriched $P(OMe)_3$, similarly enriched $^{13}CH_4$ was formed. The P-containing product $MePO(OMe)_2$ was characterized after conducting the reaction for 100 h at 180°C. No other products were detected (233). Catalytic hydrogenation of CO at 180°C and 2 atm in boron tribromide and using $Os_3(CO)_{12}$ as the catalyst precursor gave CH_4, C_2H_6, C_3H_9, isobutane, neopentane, MeBr, EtBr, propyl bromides and butyl bromides, with the major products being MeBr and EtBr. The primary metal product was $Os_2(CO)_6Br_4$, which also served as a catalyst precursor. With BCl_3, $Os_3(CO)_{10}Cl_2$ and $Os_2(CO)_6Cl_4$ were formed, but no alkyl chlorides, only hydrocarbons were formed (234).

Catalytic activities of $H_2Os_3(CO)_9(PPh_2C_2H_4SIL)$ and $Os_3(CO)_{11}(PPh_2C_2H_4SIL)$, where SIL indicates bonding to silica gel through exchange with an $Si(OEt)_3$ group, were determined for hydrogenation of ethylene. These heterogeneous catalysts were compared with the homogeneous analogs $H_2Os_3(CO)_9(PPh_2Et)$ and $Os_3(CO)_{11}(PPh_2Et)$. Lower turnovers were obtained with the anchored catalysts. One deactivation process was the formation of $H_3Os_3(CO)_8(\mu_3\text{-CMe})$-$(PPh_2C_2H_4SIL)$. Both heterogeneous catalysts were effective for cyclohexene hydrogenation. Above 100 atm of hydrogen, isomerization of 1-heptene predominated over hydrogenation when $Os_3(CO)_{11}(PPh_2C_2H_4SIL)$ was used as the catalyst (235).

Surface-bound $Ru_6C(CO)_{16}(PPh_2C_2H_4SIL)$ was prepared by anchoring $Ru_6C(CO)_{16}(PPh_2C_2H_4Si(OEt)_3)$ to hydroxyl groups on a silica surface. The surface-bound complex was characterized by comparison to $Ru_6C(CO)_{16}(PPh_2Et)$. At 100° the silica-bound catalyst fragmented to what was probably cis-$Ru(CO)_2(OSi\equiv)_2(PPh_2C_2H_4SIL)_2$ (236). At 150° this material was an active catalyst for olefin hydrogenation, but Ru metal was formed under these conditions (236).

Supported metal clusters were also prepared by phosphine ligand exchange between molecular metal clusters and diphenylphosphine-functionalized poly(styrene divinylbenzene). Supported clusters which were prepared included $ClAuOs_3(CO)_{10}(PPh_2\text{-polymer})$, $H_2PtOs_3(CO)_{10}(PPh_2\text{-polymer})_2$, and $HAuOs_3(CO)_{10}(PPh_2\text{-polymer})$. Only the first was catalytically active for ethylene hydrogenation at 1 atm and less than 100°C (237).

Dispersions of colloidal metal particles of 10-200 Å dimensions were prepared by thermal decomposition of $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ bound to styrene-p-styryldiphenylphosphine copolymer. These dispersions were useful as catalysts or as ablative optical recording media (238).

Catalysts prepared by reactions of metal carbonyls with silica or alumina surfaces were also studied. Catalysts were prepared by thermal degradation of $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$, $Os_6(CO)_{18}$, and $Os_3(CO)_{10}(NCMe)_2$ at 150°C. Oxidative addition of surface hydroxyl groups by the triosmium clusters gave a species identified as $HOs_3(CO)_{10}(OM)$ ($M=Al(O-)_3$ or $Si(O-)_3$), by comparison with molecular $HOs_3(CO)_{10}(OSiPh_3)$. On silica, treatment of the surface-bound cluster with CO and H_2O regenerated $Os_3(CO)_{12}$. At 200°C the clusters broke down to $[Os(CO)_3X_2]_2$ and $[Os(CO)_2X_2]_n$ (X=oxide) on the surface. The same species could be formed by decomposition of $[Os(CO)_3X_2]$ (X=Br, Cl) on silica or alumina or by treatment of surface-adsorbed OsX_3 (X=Br, Cl) at 200°C under CO. These surface-bound species were reduced to Os metal by hydrogen only above 400°C. These materials were catalysts for selective methane formation from CO and hydrogen (239). Other workers found that these species could be reversibly interconverted. A detailed analysis of the IR spectra in the carbonyl region provided an estimate of the geometry of the Os complexes (240). Methane formation from $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ was observed during temperature-programmed desorption in flowing hydrogen; also studied were a number of other supported mononuclear and polynuclear complexes. The Os cluster was one of two complexes giving the largest amount of methane per metal atom, ca. 4 moles of methane per mole of Os (241).

Adsorption of $Os_3(CO)_{12}$ on MgO gave a material whose IR spectrum suggested it to be $HOs_3(CO)_{10}\{OMg(O-)_n\}$. Oxidation of this product in air gave what was believed to be a mononuclear Os carbonyl adsorbed on the surface. Either of these two materials was an active catalyst for conversion of CO and hydrogen to C_1-C_4 hydrocarbons at low conversion. After this catalytic process, the IR spectrum of the catalyst suggested the presence of a trinuclear Os carbonyl cluster chemisorbed on the surface (242).

Temperature-programmed decompositions of $H_2FeRu_3(CO)_{12}$ and $Fe_2Ru(CO)_{12}$ supported on Cab-O-Sil HS-5 (a silica support) and also in the crystalline state were studied. Differences in interaction between the support and the complexes were observed. Carbon monoxide evolution occurred in several steps under either hydrogen or helium flow; hydrocarbons were formed at higher temperatures. Under helium, 20-40% of the carbon remained associated with the supported metal (243). Activities of the supported materials for Fischer-Tropsch catalysis and for butane hydrogenolysis were determined. The active catalysts were prepared by partial decarbonylation of the clusters at 370 K in hydrogen and helium. Interaction with the support at higher temperatures was demonstrated by XPS and DSC. The activity of the catalysts formed in helium was higher than that of catalysts formed in hydrogen, as well as conventional catalysts formed from inorganic salts. Changes in selectivity indicated that a bimetallic interaction was occurring in catalysts prepared from mixed-metal clusters (244).

Thermal decomposition of $Ru_3(CO)_{12}$ on silica produced a supported carbonyl species A and metallic Ru. These materials were compared with homogeneous solutions of $Ru_3(CO)_{12}$ for catalytic hydrogenation and isomerization of 1-hexene. The order of decreasing activity for isomerization was $Ru_3(CO)_{12}$>A>Ru metal, but the reverse order was observed for hydrogenation activity. Effects of solvents, Lewis bases, and hydrogen pressure on these systems were also examined (245). Inelastic electron tunneling spectroscopy was used to characterize metallic particles on alumina supports and $Ru_3(CO)_{12}$ on alumina (246). The activity of silica-supported Ru cluster catalysts for hydrogenation of hydrocarbons was also examined. The cluster-derived catalysts showed higher activity for hydrogenolysis of aliphatic hydrocarbons to methane and at lower temperatures than the conventionally prepared Ru metal catalysts. The increased activity was apparently correlated with smaller metal particle sizes obtained using the clusters. Higher activity for conversion of ethylbenzene to toluene and methane was also observed; conversions of up to 30% at 225°C and 1 atm of hydrogen were obtained using $Ru_3(CO)_{12}$ on silica. Relative rates for ethylbenzene and xylene isomers were determined (247).

Catalytic behavior of clusters supported on zeolites was examined. At high temperatures, $Os_3(CO)_{12}$ deposited on an acid zeolite reacted with hydroxyl groups of the support to give a catalyst which was active for the water gas shift reaction (248). Deposition of $Ru_3(CO)_{12}$ on Y-zeolites produced a Fischer-Tropsch catalyst which was selective for C_1-C_9 hydrocarbons. The chain length selectivity was attributed to the formation of small metal particles in the zeolite super cage (249).

A highly active reforming catalyst was prepared from $Ru_3(CO)_{12}$, Pt, Re and Cl dispersed on alumina. Interaction of the Pt group metal with the Ru compound was suggested to be important (250).

SYNTHETIC AND CATALYTIC REACTIONS INVOLVING ORGANORUTHENIUM AND -OSMIUM COMPOUNDS

Hydrogenations

The complexes $RuCl_2(AsPh_3)_3$, $RuCl_2(SbPh_3)_3$, $RuCl_2(dmso)_4$, $RuCl_2(dmso)(SbPh_3)_3$, $RuCl_2(dppe)_2$, $RuCl_2(Ph_2AsC_2H_4AsPh_2)_2$, $RuCl(SnCl_3)(PPh_3)_3$, and $RuCl(SnCl_3)(AsPh_3)_3$ were examined as catalysts for reduction of cyclohexane at 30°C and 1 atm of hydrogen. The dependencies of the rates upon catalyst concentration, substrate concentration, and ligand were examined (251).

A polymer-bound analog of $RuHClL_3$ was used to hydrogenate olefins. The rate of hydrogenation of 1-hexene with this catalyst was proportional to the concentration of Ru, the concentration of hydrogen and the ratio of [olefin]/(1+[olefin]). Under the same conditions, short-chain, terminal olefins could be hydrogenated more rapidly than longer-chain olefins, presumably because of diffusion effects. The catalyst was attached to phosphinated polystyrene crosslinked with 2% divinylbenzene (252).

Another polymer-bound hydrogenation catalyst was prepared from (η^6-cycloocta-1,3,5-triene)(η^4-cycloocta-1,5-diene)Ru by exchange with polystyrene under hydrogen to give a phenyl-coordinated Ru complex. An analog was prepared by reacting the Ru precursor with 1,3-diphenylpropane, forming soluble (η^6-diphenylpropane)(η^4-C_8H_{12})Ru and insoluble (diphenylpropane)Ru_2. The latter was similar to the polystyrene complex. Both diphenylpropane and polystyrene complexes hydrogenated olefins, aromatic hydrocarbons, ketones, oximes, and nitro derivatives at 25-80°C and 50 atm of hydrogen (253).

A new class of anionic Ru hydrides containing Group V donor ligands was prepared and the compounds were used as catalysts for reduction of aldehydes, ketones, olefins, or alkynes (254). Syntheses and structures of $K_2[Ru_2H_2(PPh_2)(PPh_3)]$ and $K[H_2RuC_6H_4PPh_2)(PPh_3)]$ [4] have appeared in the open literature (12,13).

Hydrogenations of aldehydes using $RuHCl(CO)(PPh_3)_3$ and other complexes as catalysts were examined. Turnovers of up to 32000 were achieved. The rate of hydrogenation was first order in aldehyde, catalyst, and the hydrogen pressure. Acid or base additives were also found to affect the rate. Other compounds examined as catalysts were $RuHCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$, $H_4Ru(PPh_3)_3$, $RuCl_2(CO)_2(PPh_3)_2$, $H_2Ru(PPh_3)_4$, $HRu(NO)(PPh_3)_3$, and $Ru_3(CO)_{12}$ (255). Another study concerned hydrogenation of aldehydes and ketones using as the catalyst $RuCl_2(CO)_2(PPh_3)_2$ both in solution and in supported liquid phases. Substrates included methyl ethyl ketone, cyclohexanone, butanal, 2-methylpentanal, and 2-ethyl butanal. The supported liquid phases were the reactant and Carbowax 1500 (256).

Liquid-phase hydrogenation of benzene to cyclohexane was achieved at 40-80°C and 20-60 atm of hydrogen using as a catalyst an aqueous solution of an Ru salt (257).

Hydrogen Transfer Reactions

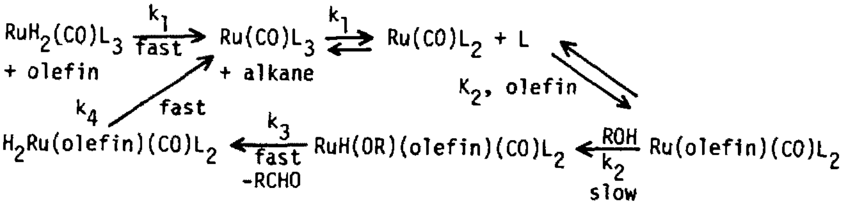
Sodium formate was used as the reductant in the conversion of 1,3-diphenyl-1-propen-3-one (chalcone) to 1,3-diphenylpropan-3-one with $RuCl_2(PPh_3)_3$ as a catalyst and in the presence of phase-transfer catalysts such as tetrahexylammonium hydrogen sulfate, tetradecylammonium bromide, tetrabutylphosphonium bromide, benzyltriethylammonium chloride, and tricaprylmethylammonium chloride. Typically, o-dichlorobenzene (19 ml) was used as solvent and the components were chalcone (5 mmol), $RuCl_2L_3$ (0.05 mmol), sodium formate (50 mmol), tetrahexylammonium hydrogen sulfate (0.1 mmol) and water (20 ml). Selectivity of 100% at 99% conversion was obtained after 10 min at 109°C (258).

Hydrogen transfer from alcohols to olefins was catalyzed by $RuCl_2(PPh_3)_3$. Kinetic studies at 170-190°C using benzyl alcohol, diphenylcarbinol, phenylmethylcarbinol, and benzoin as hydrogen donors and benzylidene acetone as the hydrogen acceptor in diphenyl ether solvent were used to elucidate the mechanism (259). The rate of the reaction was found to be first order each in Ru, olefin and alcohol. Added PPh_3 had no effect upon the rate. The kinetic isotope effect (k_H/k_D) of 2.5 was found using $PhCH_2OD$. The proposed mechanism (Scheme 22) involved initial conversion of $RuCl_2(PPh_3)_3$ to $H_2Ru(CO)(PPh_3)_3$, which was identified in solution. This product then hydrogenates the benzylidene acetone. The slow step was considered to be oxidative addition of HOR to Ru. Then, if $K_1K_2[\text{olefin}] \ll k_1$ and $[L] \ll K_1$, the observed rate law is

$$\text{rate} = k_2K_2[\text{Ru}][\text{olefin}][\text{ROH}]$$

Another study of reduction of ketones with secondary alcohols as hydrogen sources used $Ru(CO)(PPh_3)_3(O_2CCF_3)_2$ as the catalyst. The reaction was reversible, with equilibrium constants ranging between 0.1 and 21. The rate-determining step was proposed to be dehydrogenation of the alcohol (260).

Scheme 22



In a related reaction, an aldehyde RCHO, a primary alcohol RCH_2OH, and diphenylacetylene were converted to <u>cis</u>-stilbene and the ester RCO_2CH_2R using $Ru_3(CO)_{12}$ as the catalyst (261). The reactions were run using equimolar quantitites of aldehyde, alcohol, and acetylene with 0.3 mol % $Ru_3(CO)_{12}$. For example, using benzaldehyde, benzyl alcohol, and diphenyl acetylene for 2 h at 147°C, a 72% yield of benzyl benzoate was isolated with a turnover number of 54 mol of ester formed per mol of catalyst per hour. The alcohol was converted to aldehyde during the reaction, so that the alcohol alone could be used. The proposed reaction sequence was:

$$RCH_2OH + Ru \rightarrow RCHO + RuH_2$$
$$RCH_2OH + RCHO \rightleftarrows RCH(OH)OCH_2R$$
$$RCH(OH)OCH_2R + Ru \rightarrow RCO_2CH_2R + RuH_2$$
$$2RuH_2 + 2Ph_2C_2 \rightarrow 2\ PhCH{=}CHPh + 2Ru$$

Isomerizations

Isomerization of allyl benzenes and allyl alcohols by $RuCl_2(PPh_3)_3$ and by the same material anchored to diphenylphosphinated styrene-divinylbenzene was compared. Activity was reduced upon anchoring, but the catalyst could be easily recycled. Solvent-dependent catalytic activity was attributed to polymer swelling, and leaching of the catalyst from the polymer was also found to depend upon the solvent (262).

Synthesis Gas Reactions

Hydroformylation of 1-octene was catalyzed by $(\eta^5\text{-}C_5R_5)Ru(CO)_2X$ and $[(\eta^5\text{-}C_5R_5)Ru(CO)_2]_2$ (R=H, Me, C_6H_5; X=Cl, Br, I) at 135° and 80 atm (263). The monomeric complexes were found to be more active than the dimers, but selectivity for hydrogenated products was greater for the monomers, as well. The suggested catalyst in either type of system was $(\eta^5\text{-}C_5R_5)Ru(CO)_2H$. Methyl or phenyl substituents on the cyclopentadienyl ring decreased activity. On the other hand, addition of triethylamine decreased the hydrogenation of 1-octene and reduced the amount of acid-catalyzed condensation of the aldehyde products. Best results were obtained with $(\eta^5\text{-}C_5H_5)Ru(CO)_2Br$ at 135° for 40 h in toluene, which resulted in 99.6% conversion to mainly C_9 alcohols (39%, normal-to-iso ratio 0.7) and <u>n</u>-octane (37%). Condensation products accounted for 23% of the mixture.

A polymer-bound hydroformylation catalyst was prepared by reacting $Ru(CO)_3(PPh_3)_2$ with diphenylphosphinated styrene-divinylbenzene. Resins with 29% and 5% PPh_2 groups were used and polymers with P/Ru ratios of 3.1, 6.7, and 11.3 were prepared from the higher phosphinated material. These polymer-anchored metal catalysts were active for hydroformylation of 1-pentene; no olefin isomerization was observed. Comparisons were made to unbound Ru $(CO)_3(PPh_3)_2$. Catalysts with P/Ru ratios of 3.1 and 6.7 gave higher linear-to-branched selectivities (3.5-3.8) than the homogeneous analog with P/Ru of 20 but not as high as for $Ru(CO)_3(PPh_3)_2$ in molten PPh_3 (n/i of 5.1). The ligand 1,1'-bis(diphenylphosphino) ferrocene induced a higher n/i ratio than the homogeneous catalyst containing PPh_3, but the catalyst was less active (264).

Methanol homologation to ethanol was achieved using Cs^+ and $NEt_4{}^+$ salts of the $[RuCo_3(CO)_{12}]^-$ cluster anion. The latter salt gave a selectivity increase to 51% ethanol at 40% conversion, compared to <2% for $Co_2(CO)_8$ at 46% conversion and 10% for $Ru_3(CO)_{12}$ at 18% conversion. Typical conditions were 0.13 mmol catalyst, 500 mmol methanol, 5 mmol methyl iodide as promoter, 120 atm CO/H_2 (1:2) for 3 hr at 180°C (203).

Homologation of p-$MeC_6H_4CH_2OH$ to 2-p-tolylethanol was achieved using a mixture of $Co(OAc)_2$ and $RuCl_3$ at 100-200°C and $\geq$50 atm of CO/H_2. Typical conditions were 0.1 mol p-$MeC_6H_4CH_2OH$, 2.5 mmol $Co(OAc)_2 \cdot 4H_2O$, 0.38 mmol $RuCl_3$, 0.75 mmol NaI, 47 mmol water, and 100 atm CO/H_2 (1:1) at 140° for 4 h. The products consisted of 2-p-tolylethanol (75%) and p-xylene (15%) at 36% conversion (265).

The carbonylation of methyl alcohols, ethers, and esters to acetate derivatives was achieved using soluble Ru catalysts with iodide-containing promoters at 200°C and 150-200 atm CO. Using CO/H_2 mixtures, dimethyl ether was converted to ethyl acetate with a selectivity of 70%. The effects of promoters, proton suppliers, and Ru species upon the rate and selectivity were examined (266). A related study found that trivalent phosphorus compounds were promoters for homologation of methyl formate to ethanol and ethyl formate in the presence of iodide-containing compounds at 220° and 270 atm of CO/H_2 (1:1). Although the phosphorus ligands were rapidly quaternized during the reaction, decomposition of phosphonium salts also occurred. Methyltriphenylphosphonium bromide and triphenylphosphine sulfide were promoters, but benzyltrimethylammonium bromide, triphenylarsine, and triphenylantimony were not. Under these conditions the major Ru species was $[Ru(CO)_3I_3]^-$, but in the presence of $SbPh_3$, $Ru(CO)_2(SbMe_3)_2I_2$ was isolated in 70% yield after the catalytic run (267).

Considerable progress was made in the area of homogeneous catalysis of conversion of CO and hydrogen to alcohol products. A comprehensive mechanism for reduction of CO was proposed with formaldehyde as the key organic intermediate. This mechanism was based upon work performed in a number of laboratories and, although mainly based upon catalysis by Co or Rh compounds, is also applicable to Ru-catalyzed synthesis gas conversion (Scheme 23) (268).

Scheme 23

$$Ru(CO)_5 + H_2 \rightleftarrows H_2Ru(CO)_4 + CO$$

$$H_2Ru(CO)_4 \rightleftarrows (OCH)RuH(CO)_3$$

$$(OCH)RuH(CO)_3 + H_2 \longrightarrow H_2Ru(CO)_3 + CH_2O$$

$$H_2Ru(CO)_3 + CH_2O \xrightarrow{CO} CH_3ORuH(CO)_4$$

$$CH_3ORuH(CO)_4 + CO \longrightarrow CH_3OH + Ru(CO)_5$$

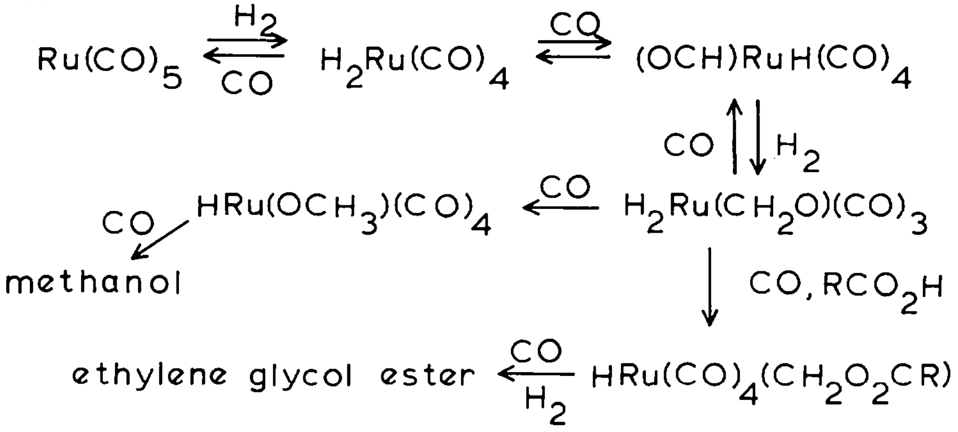
Although soluble Ru compounds were originally only observed to give conversion to methanol, modifiers have been found to allow ethylene glycol formation, as well. A careful study found that ionic iodide promoters enhanced the activity and selectivity for Ru-catalyzed synthesis gas conversion to C_2 products, primarily ethanol and ethylene glycol. Ethanol was formed in a secondary reaction through homologation of methanol. The optimum I/Ru ratio was found to be 0.5, and the predominant Ru species were $[HRu_3(CO)_{11}]^-$ and $[Ru(CO)_3I_3]^-$, presumably formed by the reaction:

$$7/3\ Ru_3(CO)_{12} + 3\ I^- + H_2 \rightarrow 2\ [HRu_3(CO)_{11}]^- + [Ru(CO)_3I_3]^- + 3\ CO$$

This latter process was demonstrated even at 25°C and 1 atm hydrogen. Neither $[PPN][HRu_3(CO)_{11}]$ nor $[PPN][Ru(CO)_3I_3]$ was especially active in the presence or absence of iodide, but optimum activity for the mixture was achieved at a 2:1 ratio of $[HRu_3(CO)_{11}]^-$ to $[Ru(CO)_3I_3]^-$ (231). A related system developed by other workers used $Ru(acac)_3$ or RuO_2 dispersed in a molten quaternary phosphonium or ammonium salt. In this system the $[HRu_3(CO)_{11}]^-$ ion was also identified. Quaternary arsonium and stibonium salts were not effective, while ammonium salts degraded under the reaction conditions (269).

A different mechanism (Scheme 24) for promotion of ethylene glycol esters from synthesis gas was proposed for Ru catalysts in carboxylic acid solvents at 260° and 640 atm. Other polar solvents were not effective (270).

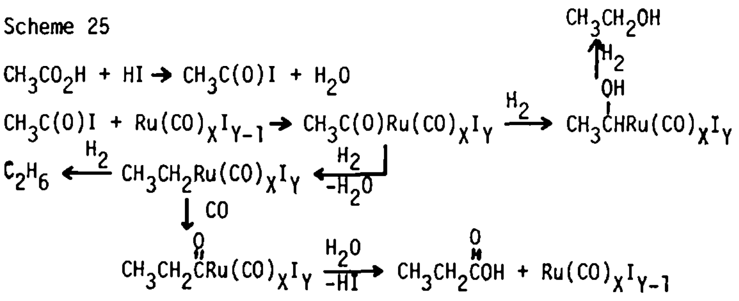
Scheme 24



A mixed-metal catalyst system consisting of $Ru(acac)_3$ and $Rh_2(O_2CMe)_4 \cdot 2MeOH$ in the presence of 2,2'-bipyridyl was claimed to give selective conversion of synthesis gas to ethylene glycol. The products from one run were methyl acetate (94 mmol), ethyl acetate (21 mmol), ethylene glycol diacetate (82 mmol), ethylene glycol monoacetate (52 mmol) and ethylene glycol (134 mmol) (271).

Homologation of carboxylic acids with CO/H_2 was achieved using a soluble Ru catalyst and an iodide-containing promoter at 220°C and 270 atm of synthesis gas (1:1). Although $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and RuO_2 were all active, the major species present was $[Ru(CO)_3I_3]^-$. ^{13}C-labelled acetic acid was used to show that the methylene in the propionic acid product originated from the carboxylate group of the reactant, although the use of d_4-acetic acid demonstrated extensive H-D scrambling. Considerable hydrogenation of acetic acid to ethane occurred at higher H_2/CO ratios. The proposed mechanism (Scheme 25) involved initial conversion of the acid to the acid iodide. However, it has been shown that Ru compounds can catalyze reduction of acids to alcohols, and the mechanism may involve homologation of this product (272).

Scheme 25



Homologation of formaldehyde by CO/H_2 at 75-250°C using a Ru catalyst and a halide promoter was claimed in a patent. Acetaldehyde was the initial product, but reduction to ethanol occurred in a second stage. Among the catalysts tested were $[Ru(CO)_3Cl_2]_2$ and a mixture of $Ru_3(CO)_{12}$ and HBr (273).

Other Reactions

Polymer-anchored derivatives of $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ were used to dehydrogenate alcohols. The reaction characteristics seemed similar to those using the unsupported catalyst. Polymers used were phosphine-functionalized polystyrene, carboxylate-functionalized polystyrene, and a polymer containing both functionalities (274).

Oxidations of allyl alcohols to carbonyl compounds were catalyzed by Ru(II) complexes. For example, (E)-2,7-dimethylocta-2,6-dien-1-ol (geraniol) was oxidized to the corresponding aldehyde (67%) using $RuCl_2(PPh_3)_3$ as the catalyst in dichloroethane under 1 atm oxygen at 25°C for 48 h. Yields ranged from 46 to 100%. The reaction was found to proceed with retention of stereochemistry and did not affect other functional groups, including sulfides. The PPh_3 ligands were oxidized to $OPPh_3$ within 5 min (275). The same catalyst in benzene was used to oxidize 1,10-undecanediol to 10-hydroxyundecanal in 89% yield after 2 h. Selectivity for terminal alcohols was demonstrated by a 50-fold faster rate for oxidation of 1-dodecanol than for 4-dodecanol (276).

At higher temperatures Ru catalysts were used to decarbonylate aldehydes. The catalysts used were $Ru(TPP)(PPh_3)_2$ and $Ru(TPP)(PBu_3)_2$ at temperatures of ca. 60°C. Turnover numbers of up to 50000 hr^{-1} were obtained. A combination of ESR, IR, and UV/vis spectroscopy and cyclic voltammetry was used to investigate the reaction. Organic radicals were detected during the decarbonylation of cyclohexen-4-al, and hydroquinone completely inhibited the decarbonylation of phenylacetaldehyde. Eventual loss of the porphyrin ligand was indicated by the final, visible absorption spectrum (277).

Oxidations of alkanes by Cr(VI), HNO_3, $HClO_4$, and others were reported to be catalyzed by Ru(IV) in aqueous solution. The mechanism was proposed to involve activation of the oxidant through complexation to Ru(IV) and then hydrogen atom abstraction from the alkane by the activated oxidant (278).

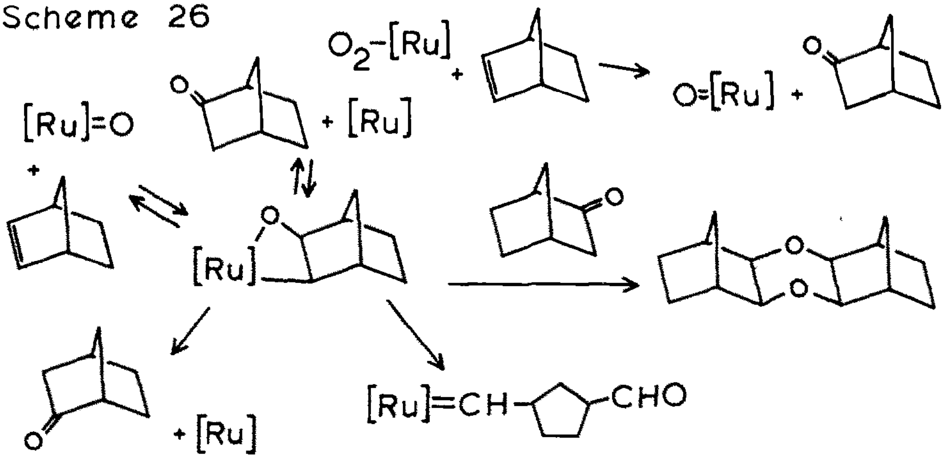
The kinetics of Ru(III)-catalyzed oxidation of primary and secondary alcohols by bromate has been studied. These oxidations were first-order in both substrate and Ru(III), but zero-order in BrO_3^-. A rate-limiting outer sphere hydride abstraction step was proposed (279). Other workers examined Ru(III)-catalyzed oxidations of alcohols using bis(tellurato)cuprate(III).

As with BrO_3^-, the kinetics were first-order in Ru(III) and alcohol and zero-order in Cu(III). The rate was found to increase with increasing $[OH^-]$. The proposed mechanism involved complexation of the alcohol to Ru(III), followed by slow disproportionation to Ru(I) and alcohol oxidation products by hydride abstraction. The Taft plot for the reaction was linear with a slope of $\rho^* = -1.2$ (280). The mechanism of Ru(III)-catalyzed oxidations of α-hydroxycarboxylate ions by $[Fe(CN)_6]^{3-}$ in alkaline solution was also examined. The kinetics were zero-order in oxidant and first-order in Ru(III). In these systems the rate decreased with increasing $[OH^-]$ and was first-order in [α-hydroxycarboxylate] at low concentrations but approached zero-order at higher concentrations. The suggested mechanism had an intermediate complex between this substrate and Ru(III) which disproportionates to a Ru(III) hydride and a carbocation. Rapid reaction of the carbocation with hydroxide gives the α-ketocarboxylate. Finally, the Ru(III)-hydride is oxidized by $[Fe(CN)_6]^{3-}$ (281).

Dimerization and trimerization of isobutene to 2,2,6,6,-tetramethylheptane and 2,2,4,5,6-pentamethylhept-3-ene was achieved using a Ru-stannous chloride catalyst. The catalyst system was comprised of stannous chloride (8 mmol) and $RuCl_3 \cdot nH_2O$ (1 mmol) in nitromethane, and the reaction was conducted over 7 h at 20°C (283).

Ring-opening polymerization of norbornene was catalyzed by $RuCl_2(PPh_3)_4$ and $RuCl_2(py)_2(PPh_3)_2$. The reaction was enhanced as much as 100 times by the presence of oxygen. Oxidation of norbornene to the epoxide was also observed. Catalyst pretreatment with oxygen at 100°C in chlorobenzene also enhanced activity, and the epoxide in the absence of oxygen had a similar effect. In the absence of olefin the epoxide was isomerized to the ketone (45% after 12 h at 100°C). The suggested explanation is shown in Scheme 26 (283).

Scheme 26



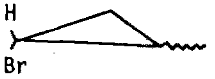
Linear co-dimerization of terminal acetylenes and 1,3-butadiene was catalyzed by $H_2Ru(PR_3)_4$ (R=Bu, Et) (284):

$$RC{\equiv}CH + CH_2{=}CHCH{=}CH_2 \rightarrow \underline{trans}\text{-}RC{\equiv}CCH{=}CHCH_2CH_3$$

Carbenoid transformations were catalyzed by Ru compounds, including $Ru_3(CO)_{12}$, $[Ru(CO)_3Cl_2]_2$, and $RuCl_3(NO)(PPh_3)_2$ (285). Exceptional selectivity for ylide generation was noted for $Ru_3(CO)_{12}$. The two reactions investigated were of ethyl diazoacetate with allyl methyl sulfide (A) and with n-butyl vinyl ether (B) and the ratio of A/B, determined from the products, was used as a measure of selectivity toward ylide generation:

(A) $CH_2{=}CHCH_2SMe + N_2CHCO_2Et \rightarrow CH_2{=}CHCH_2CH(SMe)CO_2Et + N_2$

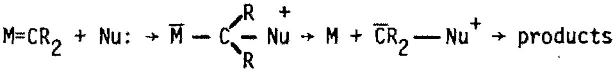
(B) n-$BuOCH{=}CH_2 + N_2CHCO_2Et \rightarrow$



$Co_2Et + N_2$

With $Ru_3(CO)_{12}$ (0.5 mol %) and a 5-fold molar excess of each olefin at 60°C for 8 h, 96% A and 65% B were obtained. The same reaction with $Os_3(CO)_{12}$ gave only 4% A and 13% B. Competition experiments showed that cyclopropanation and ylide generation occurred through the same reaction intermediates. Plots of %A/%B vs. the molar ratio of reactants were linear and intercepted at the origin. The proposed mechanism is shown in Scheme 27.

Scheme 27



$$M{=}CR_2 + Nu\!: \rightarrow \bar{M} - \overset{R}{\underset{R}{C}} \overset{+}{-} Nu \rightarrow M + \bar{C}R_2 - Nu^+ \rightarrow \text{products}$$

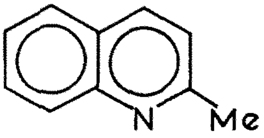
Ketones and aldehydes were hydrosilylated by $HSi(OR)_3$ (R=Me, Et) using $RuCl_2(PPh_3)_3$ as the catalyst and were then reduced by alcoholysis. For example, acetophenone was reduced to the alcohol in 84% yield after 10 h at 120°C (286).

Silyl esters of formic acid were prepared from carbon dioxide and hydrosilanes using Ru-phosphine complexes as catalysts. In a typical reaction $HSiMeEt_2$ (20 mmol) and $RuCl_2(PPh_3)_3$ (0.2 mmol) were stirred at 100°C under CO_2 (30 atm) for 20 h; distillation yielded $Et_2SiMeOCHO$ as the major product (287).

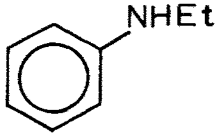
Nitrosobenzene was converted to azoxybenzene using $Ru(CO)_3(PPh_3)_2$ as the catalyst under an inert atmosphere. However, under CO, nitrosobenzene was converted to azobenzene and aniline, while azoxybenzene gave azobenzene (288).

Several studies of Ru-catalyzed conversion of nitroarenes to aniline and aniline derivatives were reported. Reduction and carbonylation of nitroarenes by a mixture of sodium methoxide, α-methoxyethanol, and $Ru_3(CO)_{12}$ in THF or benzene gave the corresponding formamide as the major product, but using 1:1 CO/H_2 in the absence of α-methoxyethanol gave both the formamide and the amine. On the other hand, using $Fe_3(CO)_{12}$ as the catalyst gave mainly carbamate esters and smaller amounts of the urea derivatives. General conditions were 0.3 mmol catalyst, sodium methoxide (6 mmol), CO (1 atm), 3 h at 25°C to form the active solution, and then stirring with the nitro arene overnight at 60°C under CO/H_2 (1:1, 1 atm) (289). A more active catalyst system, derived from $[Ru(1,5\text{-cyclooctadiene})(py)_4][BF_4]$ with CO and water, was reported to give anilines selectively. The water could not be replaced with hydrogen. The yield of the aniline product was strongly dependent upon the CO pressure. For example, at 100° for 20 h nitrobenzene was reduced to 36% aniline at 15 atm but 90% at 60 atm. Other effective catalysts were $RuCl_2(CO)_2(py)_2$, $RuCl_2(py)_4$ and $Ru_3(CO)_{12}$ (290).

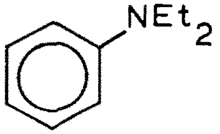
Alkyl-substituted quinolines and N-alkyl anilines were prepared by reaction of nitrobenzene with primary and secondary alcohols and using Ru catalysts. A typical procedure took nitrobenzene (40 mmol), aniline (0 or 10 mmol), an alcohol (20 ml) and $RuCl_2(PPh_3)_3$ (0.4 mmol) and stirred under argon at 180° for 4 h. Using ethanol, a 99% conversion was obtained to 43% [180], 11% [181], and 5% [182]. The probable mechanism was suggested to involve alcohol dehydrogenation to the aldehyde, followed by hydrogen transfer to nitrobenzene to form aniline. Then condensation of aniline with the aldehyde and Ru-catalyzed reduction gives the observed products (291,292). A similar process effected the alkylation of primary and secondary amines by primary and secondary alcohols in the presence of $H_2Ru(PPh_3)_4$. N-methylation of pyrrolidine by methanol with 5 mol % catalyst over 48 h at reflux gave 15% N-methyl pyrrolidine (293). A related process converted primary amines to symmetrical secondary amines by heating at 185° for 5 h in the presence of $RuCl_2(PPh_3)_3$ (294). With α,ω-aliphatic diamines this reaction gave heterocyclic amines, e.g. $NH_2(CH_2)_5NH_2$ at 180°C for 5 h in the presence of $RuCl_2(PPh_3)_3$ (2 mol %) in diphenyl ether gave 90% piperidine (295).



[180]



[181]



[182]

REVIEWS AND DISSERTATION ABSTRACTS

Reviews: The following reviews have appeared which contain material of relevance to ruthenium and osmium organometallic chemistry:

"Effect of the nature of ligands on redox potentials of coordination compounds," by Yu. N. Kukushkin (296).

"Developments and future of C_1 chemistry industry," by Y. Murado (297).

"Transition metal chemistry review.2. Ruthenium and osmium," by K. R. Seddon (298).

"Annual surveys of iron, ruthenium, and osmium for 1977," by J. A. McCleverty (299).

"Annual Surveys of iron, ruthenium, and osmium for 1979," by D. L. Reger (300).

"Liquid fuels from coal. Developments in the use of ruthenium catalysts for the Fischer-Tropsch reaction," by R. C. Everson and D. T. Thompson (301).

"Review on asymmetric homogeneous catalysis by ruthenium complexes," by U. Matteoli, P. Frediani, M. Bianchi, C. Botteghi, and S. Gladiali (302).

"Thermal and photochemical reactivity of $H_2FeRu_3(CO)_{13}$ and related mixed metal clusters," by G. L. Geoffroy, H. C. Foley, J. R. Fox, and W. L. Gladfelter (303).

"Ruthenium carbonyl catalysis of water gas shift in acidic solutions," by P. C. Ford, P. Yarrow, and H. Cohen (304).

"Transition-metal molecular clusters," by B. F. G. Johnson and J. Lewis (305).

"Heterolytic activation of hydrogen by transition metal complexes," by P. J. Brothers (306).

"Metal carbide clusters," by M. Tachikawa and E. L. Muetterties (307).

"Phase-transfer catalysis in organometallic chemistry," by H. Alper (308).

"Novel types of metal-metal bonded complexes containing allyl and cyclopentadienyl bridging ligands," by H. Werner (309).

"The application of ^{13}C-NMR spectroscopy to organo-transition metal complexes," by P. W. Jolly and R. Mynott (310).

"The coordination chemistry of sulfoxides with transition metals," by J. A. Davies (311).

"Structures and fluxional behavior of transition metal cluster carbonyls," by R. E. Benfield and B. F. G. Johnson (312).

"Nuclear magnetic resonance spectroscopy," by B. E. Mann (313).

"Vibrational spectra of transition-element compounds," by J. S. Ogden (314).

"Organometallic, co-ordination, and inorganic compounds investigated by mass spectrometry," by R. H. Cragg (315).

"Electronic structures of transition metal cluster complexes," by M. C. Manning and W. C. Trogler (316).

Dissertation Abstracts

"The characterization and catalytic activity of ruthenium-exchanged zeolites," by B. L. Gustafson (317).

"Physical and chemical characterizations of catalyst model systems, (1) ruthenium compounds supported on a Y-type zeolite; and (2) an unsupported iron-ruthenium bimetallic," by M. D. Patil (318).

"Preparation and characterization of some new anionic ruthenium clusters; the reactivity of tri- and tetranuclear ruthenium clusters," by C. C. Nagel (319).

"Catalytic behavior of supported ruthenium cluster compounds," by V. L. Payne (320).

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