

RUTHENIUM AND OSMIUM: ANNUAL SURVEY FOR THE YEAR 1983

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CONTENTS

Spectroscopic Methods	298
Mononuclear Complexes	
Zero-Valent Metal Complexes with Carbonyl, Group 15 Donor, or Hydride Ligands	298
Divalent Metal Complexes with Carbonyl, Group 15 Donor, or Hydride Ligands	299
Complexes of Metals in Higher Oxidation States	305
Nitrosyl, Thionitrosyl, and Dinitrogen Complexes	306
η^1 -Hydrocarbon Complexes	309
Cyclopentadienyl Complexes	317
Arene Complexes	321
Other Pi Hydrocarbon Complexes	325
Cluster Compounds	330
Dinuclear Clusters	330
Trinuclear Clusters	334
Tetranuclear and Larger Clusters	351
Mixed Metal Clusters	364
Catalysis by Clusters and Supported Clusters	378
Miscellaneous Studies of Clusters	381
Catalysis	
Reduction	382
Reactions Involving Synthesis Gas	384
Oxidation	386
Other Reactions	387
Reviews and Other Works	390
References	392

ABBREVIATIONS

Ac - acetyl
 acac - acetylacetonate
 bipy - 2,2'-bipyridine
 Bu - n-butyl
i-Bu - i-butyl
 Bz - benzyl
 COD - 1,5-cyclooctadiene
 Cp - cyclopentadienyl

*Previous review see J.Organomet.Chem., 274(1984)457-553.

Cyc - cyclohexyl
 diars - *o*-phenylenebis(dimethylarsine)
 dmpe - 1,2-bis(dimethylphosphino)ethane
 DMSO - dimethyl sulfoxide
 dpam - bis(diphenylarsino)methane
 dpae - 1,2-bis(diphenylarsino)ethane
 dppe - 1,2-bis(diphenylphosphino)ethane
 dppm - bis(diphenylphosphino)methane
 en - ethylenediamine
 Et - ethyl
 Me - methyl
 nbd - norbornadiene
 OEP - octaethylporphyrin
 Ph - phenyl
 phen - 1,10-phenanthroline
 PPN - bis(triphenylphosphine)iminium
 Pr - propyl
i-Pr - *i*-propyl
 py - pyridine
 Tol - tolyl
 TPP - tetraphenylporphyrin
 Ts - *p*-toluenesulfonyl

SPECTROSCOPIC METHODS

FAB mass spectra were reported for $[\text{RuCl}_2(\text{PPh}_3)_3]$ and $[\text{Os}_4\text{H}_2(\text{CO})_{12}^-(\text{NCMe})_2][\text{PF}_6]$. The former complex displayed the $(\text{M}+\text{H}-\text{PPh}_3)^+$ ion. The positive ion spectrum of the cluster consisted of the cation (m/e 1189) and the cation-two NCMe (m/e 1107), while the negative ion spectrum contained the $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$ ion (m/e 1107) (1).

^{99}Ru NMR studies were described for $[\text{RuCp}_2]$, $[\text{Ru}_3(\text{CO})_{12}]$, $\text{K}_4[\text{Ru}(\text{CN})_6]$, $[\text{Ru}_2(\text{CO})_6\text{Cl}_4]$, $\text{Cs}[\text{RuCl}_3(\text{CO})_3]$, $[\text{NEt}_4]_4[\text{Ru}(\text{SnCl}_3)_5\text{Cl}]$, $\text{Cs}_2[\text{Ru}(\text{CO})_2\text{Cl}_4]$, $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$, $[\text{Ru}(1-(2\text{-pyridyl})-3,5\text{-dimethylpyrazole})_3][\text{PF}_6]_2$, and $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$. Using $[\text{Ru}(\text{CN})_6]^{4-}$ as the reference, a chemical shift range from -1270 to +7821 ppm was observed. The zero oxidation state is at the low frequency end and the resonances shift to higher frequency with increasing oxidation number. Large ligand effects are noted, e.g. a 4500 ppm difference between the shifts of $[\text{Ru}(\text{bipy})_3]^{2+}$ and $[\text{Ru}(\text{CN})_6]^{4-}$ (2).

MONONUCLEAR COMPLEXES

Zero-Valent Metal Complexes with Carbonyl, Group 15 Donor, or Hydride

Ligands

Carbonylation of solid $[\text{Ru}_3(\text{CO})_{12}]$ at 200 atm and 160° forms $[\text{Ru}(\text{CO})_5]$ nearly quantitatively. At 200 atm and 280° $[\text{Os}(\text{CO})_5]$ is formed in 60% yield from $[\text{Os}_3(\text{CO})_{12}]$ but in hexane solution some $[\text{OsH}_2(\text{CO})_4]$ is formed due to hydrogen released by hexane dehydrogenation. The ^{13}C NMR spectrum of either $[\text{M}(\text{CO})_5]$ is a singlet down to -40° . At -78° , chlorine and $[\text{Os}(\text{CO})_5]$ go to $[\text{Os}(\text{CO})_5\text{Cl}]\text{Cl}$, which dimerizes to $[\{\text{Os}(\text{CO})_3\text{Cl}_2\}_2]$ in refluxing hexane. UV irradiation of $[\text{Os}(\text{CO})_5]$ in the presence of diethyl fumarate and CO forms $[\text{Os}(\text{CO})_4(\text{diethylfumarate})]$; the ^{13}C NMR spectrum of the product consists of two CO resonances at 25° which broaden at higher temperatures (3).

Substitution on $[\text{M}(\text{CO})_5]$ was used to prepare $[\text{Ru}(\text{CO})_4(\text{AsPh}_3)]$, $[\text{Os}(\text{CO})_4(\text{AsPh}_3)]$, and $[\text{Os}(\text{CO})_4(\text{SbPh}_3)]$, all of which were crystallographically characterized; these structures were compared with other complexes $[\text{M}(\text{CO})_4(\text{EPh}_3)]$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$; $\text{E}=\text{P}, \text{As}, \text{Sb}$). In the solid state, axial coordination of EPh_3 is observed for $[\text{M}(\text{CO})_4(\text{EPh}_3)]$. Both isomers exist in solution for $\text{M}=\text{Ru}$ or Os and $\text{E}=\text{As}$ or Sb . The tendency for equatorial coordination decreases in the order $\text{E}=\text{Sb} > \text{As} > \text{P}$. This observation could be explained by the tendency of weaker sigma donors to favor equatorial coordination and the order of sigma donor ability: $\text{PPh}_3 > \text{AsPh}_3 > \text{CO} > \text{SbPh}_3$. However, steric effects may contribute, since the equatorial position is more sterically hindered (4).

The di-imine complex $[\text{Ru}(4\text{-MeOC}_6\text{H}_4\text{N}=\text{CHCH}=\text{NC}_6\text{H}_4\text{OMe-4})_3]$ was prepared in 70% yield by reaction of 3 equiv of the di-imine with $[\text{RuH}_2(\text{PPh}_3)_4]$ or $[\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$. The product was characterized by X-ray crystallography. The complex is diamagnetic below -10° and paramagnetic above this temperature (5).

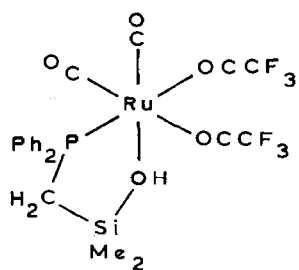
The reaction of $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ with diphenylphosphonylazide in refluxing THF produces $[\text{Ru}(\text{CO})_3(\text{RN}=\text{PPh}_3)_2]$ ($\text{R}=\text{P}(\text{O})(\text{OPh})_2$) in 50% yield (6).

Divalent Metal Complexes with Carbonyl, Group 15 Donor, or Hydride Ligands

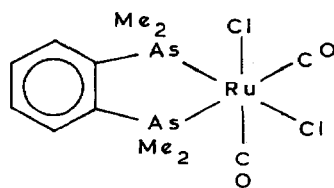
Zeolite-encapsulated $[\text{Ru}(\text{NH}_3)_5(\text{CO})]^{2+}$ is formed by thermal activation of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ in X- or Y-zeolites under a CO and/or water atmosphere at temperatures less than 400 K. At higher temperatures the predominant species is a $[\text{Ru}(\text{CO})_3]^{+}$ complex, while in the presence of water a $[\text{Ru}(\text{CO})_2]^{+}$ complex dominates (7).

The oxidation of $[\text{Ru}_2(\text{CO})_6(\text{Ph}_2\text{PCH}_2\text{SiMe}_2)_2]$ with trifluoroacetic acid yields $[\text{Ru}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{SiMe}_2\text{OH})(\text{O}_2\text{CCF}_3)_2]$ [1], characterized by X-ray crystallography. A molecule of diethyl ether is hydrogen-bonded to the hydroxyl group (8).

Photophysical properties of low-lying, emissive metal-to-ligand charge transfer excited states of a series of complexes including $[\text{Ru}(\text{bipy})_2(\text{dmpe})]^{2+}$, $[\text{Ru}(\text{bipy})_2(\text{diars})]^{2+}$, trans- $[\text{Ru}(\text{bipy})_2(\text{PPh}_2\text{Me})_2]^{2+}$, and

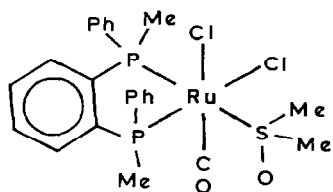


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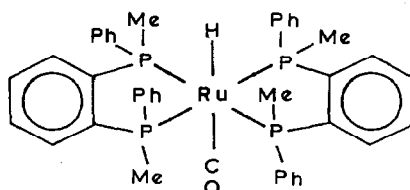


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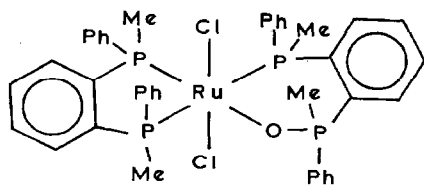
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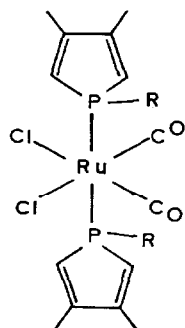
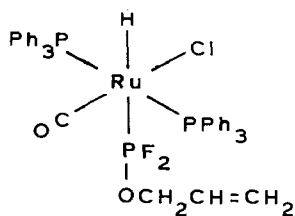
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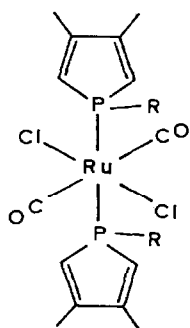
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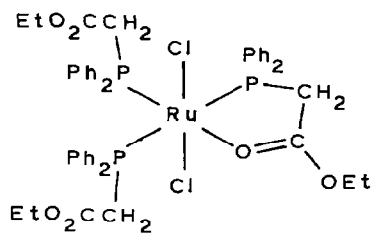
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$[\text{Ru}(\text{bipy})_2(\text{dppene})]^{2+}$ (dppene = *cis*-1,2-bis(diphenylphosphino)ethylene) were investigated by luminescence measurements and redox potentials for excited- and ground-state redox couples. The MLCT state(s) lifetime(s) are dictated by (a) a radiative decay pathway relatively insensitive to the ligands, (b) a nonradiative transition to the ground state, the rate constant varying as predicted by the energy gap law for radiationless transitions, and (c) the rate of a thermally activated transition between the MLCT state and a low-lying, metal-centered dd excited state. It is the last transition and the role that the ligands play in stabilizing the MLCT state relative to the dd state that provide an explanation for the absence of room temperature emission and/or the appearance of ligand-loss photochemistry in the cases where phosphines, arsines, or CO ligands are present (9).

The crystal structures of *cis*- $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{opmpa})]$ [2] (245), *cis*- $[\text{Ru}(\text{CO})\text{Cl}_2(\text{DMSO})(\text{opmpp})]$ [3] (245), and *trans*- $[\text{RuH}(\text{CO})(\text{opmpp})_2][\text{PF}_6] \cdot 2 \text{Me}_2\text{CO}$ [4] (10) (opmpa and opmpp = (\pm)-*o*-phenylenebis(methylphenylarsine) and - (methylphenylphosphine), respectively), were reported. Also reported was the structure of *trans*- $[\text{RuCl}_2(\text{opmpp})(\text{omppo})]$ [5] (omppo = (\pm)-*o*-phenylene-(methylphenylphosphine)(methylphenylphosphine-P-oxide)), isolated as a minor product from reaction of RuCl_3 with opmpp and formaldehyde (11).

The preparation and chemistry of $[\text{RuCl}_2(\text{ttp})]_x$ and $[\text{RuCl}_2(\text{Cytttp})]$ (ttp=PhP(CH₂CH₂CH₂PPh₂)₂, Cytttp=PhP(CH₂PCyc₂)₂) were described. New complexes reported were $[\text{Ru}(\text{ttp})(\text{NCMe})_2][\text{AsF}_6]_2$, $[\text{Ru}(\text{ttp})(\text{CO})_2][\text{BF}_4]_2$, $[\text{RuCl}_2(\text{Cytttp})(\text{SO}_2)]$, $[\text{RuI}(\text{CO})_2(\text{Cytttp})]$, $[\text{RuH}(\text{CO})_2(\text{Cytttp})][\text{BF}_4]$, $[\text{RuH}(\text{NCMe})(\text{PF}_3)(\text{ttp})][\text{BF}_4]$, *trans*- $[\text{RuH}(\text{P}(\text{OMe})_3)_2(\text{ttp})][\text{BF}_4]$, *cis*- $[\text{RuH}_2(\text{P}(\text{OMe})_3)(\text{ttp})]$, and $[\text{RuH}(\text{CO})(\text{P}(\text{OMe})_3)(\text{ttp})][\text{BF}_4]$. The reaction of $[\text{Ru}(\text{CO})_2(\text{Cytttp})]$ with oxygen in benzene yields $[\text{Ru}(\text{CO}_3)(\text{CO})(\text{Cytttp})]$ and the reaction with bromine or iodine yields the corresponding *cis*- $[\text{RuX}(\text{CO})_2(\text{Cytttp})]\text{X}$ (12).

Ligand substitution reactions were used to prepare $[\text{RuCl}(\text{CO})\text{H}(\text{PPh}_3)_2\text{-}\{\text{PF}_2\text{-}(\text{OCH}_2\text{CH}=\text{CH}_2)\}]$ (6) and $[\text{RuCl}_2(\text{PPh}_3)_2\{\text{PF}_2(\text{OCH}_2\text{CH}=\text{CH}_2)\}]$. The products were characterized spectroscopically and for [6] by X-ray crystallography (13).

A number of Ru and Os complexes containing bipy or phen ligands were prepared and characterized by spectroscopic and electrochemical methods. In refluxing ethylene glycol, *cis*- $[\text{Os}(\text{bipy})_2(\text{CO})\text{Cl}]^+$ is reduced by excess PPh₃ to *cis*- $[\text{Os}(\text{bipy})_2(\text{CO})\text{H}]^+$ (50%). The Ru analog was reported in 45% yield by thermolysis of *cis*- $[\text{Ru}(\text{bipy})_2(\text{CO})(\text{O}_2\text{CH})]^+$ in 2-methoxyethanol. Substitution on *mer*- $[\text{Os}(\text{PPh}_3)_3(\text{CO})\text{ClH}]$ by bipy generates *trans*- $[\text{Os}(\text{bipy})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$. Complexes were characterized by ¹H and ³¹P NMR spectroscopy and by IR spectroscopy. Cyclic voltammetry indicated irreversible oxidation of these complexes, followed by rapid chemical reactions. The hydride complexes react with HPF₆ to generate hydrogen gas and, in acetonitrile, solvato

complexes. Also prepared was the phosphine chelate complex $[\text{Os}(\text{phen})(\text{PPh}_3)-(\text{o-phenylenebis}(\text{diphenylphosphine})\text{H})]^+$. The Os complexes are rare examples of metal hydrides which luminesce at room temperature in solution. However, the excited state decay by non-radiative processes is rapid (14).

A new synthesis for $[\text{Ru}(\text{bipy})_2(\text{CO})\text{Cl}]^+$ was reported; the complex was found to be a catalyst for the water gas shift reaction. In refluxing ethylene glycol $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$ is converted in the presence of a catalytic amount of $[(\text{bipy})_2\text{Ru}(\mu\text{-O})_2\text{MoO}_2]$ into the desired product, precipitated as the PF_6 salt in 70% yield. The complex catalyzes the conversion of CO and water (1-3 atm, 100-160°) to hydrogen with a turnover number of 112 over a 20 h period. The proposed mechanism (Scheme 1) involves $[\text{Ru}(\text{bipy})_2(\text{CO})_2]^{2+}$ and $[\text{Ru}(\text{bipy})_2(\text{CO})(\text{CO}_2\text{H})]^+$, both of which were isolated (15).

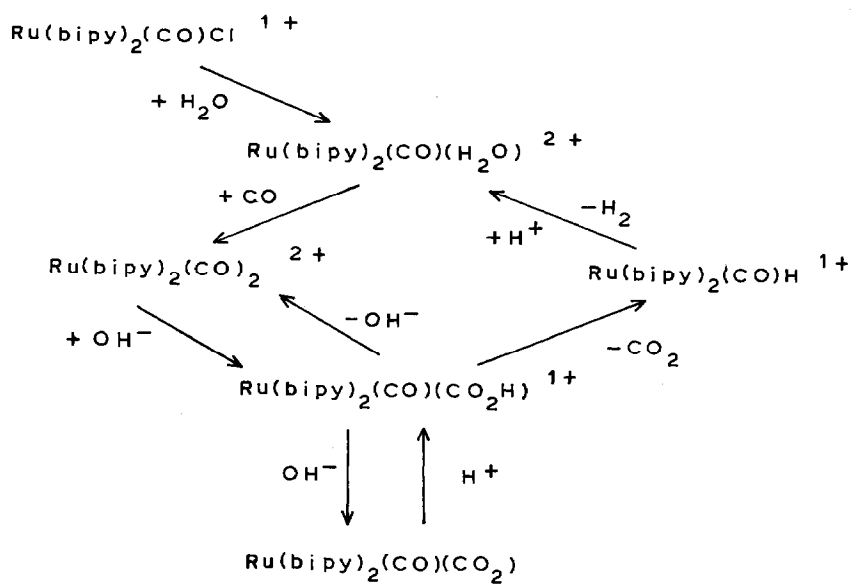
Ligand substitution on $[\text{RuCl}_2(\text{PPh}_3)_3]$ and $[\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})]$ was used to prepare cis- and trans- $[\text{RuCl}_2\text{L}_4]$ (L=AsMePh₂, AsMe₂Ph) and mer- $[\text{RuCl}_3\text{L}_3]$ (L=PPh₃, PMePh₂, PMe₂Ph, PEtPh₂), respectively. Other products were polymeric $[\text{RuCl}_2(\text{AsPh}_3)_2]_n$ and $[\text{RuCl}_2(\text{PPh}_3)(\text{AsPh}_3)]_n$ (16).

Ruthenium complexes of 1-substituted 3,4-dimethylphospholes (RDMP, R=Me, Bu, CMe₃, Ph, Bz) were prepared and characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy. The complexes $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{RDMP})_2]$ were prepared by reaction of RDMP with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and CO in ethanol or 2-methoxyethanol. The cis isomers [7] are the kinetic products but these rearrange to the trans isomers [8]. The phosphole ligands will displace PPh₃ from $[\text{RuCl}_2(\text{PPh}_3)_4]$. The crystal structure of trans- $[\text{RuCl}_2(\text{CO})(\text{PhDMP})_3]$ was reported. Some of these complexes are catalysts for alkene hydrogenation (17).

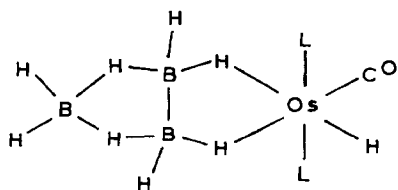
Photolysis of cis or trans- $[\text{Ru}(\text{dmpe})_2\text{Cl}_2]$ in a number of solvents gives the trans photolysis product regardless of the geometry of the reactant. In methanol or ethanol the product is trans- $[\text{Ru}(\text{dmpe})_2\text{Cl}_2]$, in H₂O/HOR or H₂O, trans- $[\text{Ru}(\text{dmpe})_2(\text{H}_2\text{O})\text{Cl}]^+$, and in DMSO, trans- $[\text{Ru}(\text{dmpe})_2(\text{DMSO})\text{Cl}]^+$. Quantum yields vary with the solvent, but the nature of ligand loss and the product geometry is the same in all solvents. The primary photoprocess is suggested to be formation of a 5-coordinate excited state and this intermediate has a thermodynamic preference to rearrange to the isomer in which chloride is in an apical position (18).

Ligand displacement from $[\text{RuCl}_3(2\text{-MeC}_6\text{H}_4\text{CN})_3]$ by Ph₂PCH₂CO₂Et (P-O) produces trans, trans, trans- $[\text{RuCl}_2(2\text{-MeC}_6\text{H}_4\text{CN})_2(\text{P-O})_2]$ with monodentate P-O ligands. However, the reaction between RuCl_3 and P-O generates trans- $[\text{RuCl}_2(\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt})(\text{P-O})_2]$ [9], characterized by X-ray crystallography. The Ru-O bond of [9] is labile and CO substitution produces trans, trans, trans- $[\text{RuCl}_2(\text{CO})_2(\text{P-O})_2]$ with monodentate P-O ligands. Bubbling nitrogen through a solution of the latter reversibly generates chelated $[\text{RuCl}_2(\text{CO})(\text{Ph}_2\text{-PCH}_2\text{C}(\text{O})\text{OEt})(\text{P-O})]$ (19).

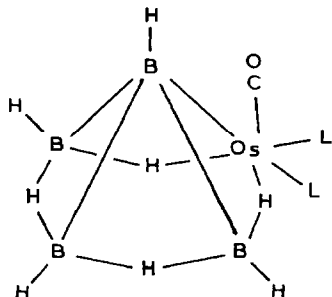
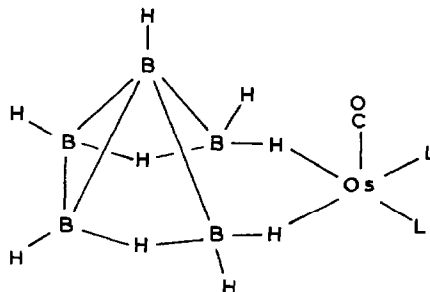
Scheme 1



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11



12

A variety of phosphine, arsine, and stibine complexes have been prepared by ligand substitution on $[\text{RuCl}_2(\text{DMSO})_4]$ in acidic ethanol. Complexes thus prepared were $[\text{RuCl}_2(\text{DMSO})_2(\text{AsPh}_3)_2]$, $[\text{RuCl}_2(\text{DMSO})\text{L}_2]$ ($\text{L}=\text{AsMePh}_2$, AsMe_2Ph , SbPh_3), and $[\text{RuCl}_2\text{L}_2]$ ($\text{L}=\text{dpam}$, dppe , dppm , dpae). Also prepared were $[\text{RuCl}_2\text{L}_3]$ ($\text{L}=\text{AsMePh}_2$, AsMe_2Ph , SbPh_3) from Ru(II) generated by reduction of RuCl_3 with zinc/mercury amalgam. Reactions of these complexes with CO, hydrogen, nitrogen, and nitric oxide were examined (20).

An easy and convenient preparation of cis- $[\text{Os}(\text{CO})_4\text{Cl}_2]$ involves reacting solid, anhydrous OsCl_3 with CO (65 atm) at 155° for 22 h; sublimation yields pure material (60%). In refluxing chloroform, cis- $[\text{Os}(\text{CO})_4\text{Cl}_2]$ is converted to $[\{\text{Os}(\text{CO})_3\text{Cl}_2\}_2]$ (90-97%) (21).

Ligand substitution on $[\text{MHCl}(\text{CO})\text{L}_3]$ ($\text{M}=\text{Ru}, \text{Os}$; $\text{L}=\text{PPh}_3$) by $\text{L}'=\text{P}(\text{OR})\text{Ph}_2$, $\text{P}(\text{OR})_2\text{Ph}$, or $\text{P}(\text{OR})_3$ ($\text{R}=\text{Me}, \text{Et}$) occurs trans to the hydride, forming $[\text{MHCl}(\text{CO})\text{L}_2\text{L}']$. The Ru complex substitutes further to $[\text{RuH}(\text{CO})\text{L}_2\text{L}']^+$, $[\text{RuH}(\text{CO})\text{LL}'_3]^+$ and $[\text{RuH}(\text{CO})\text{L}'_4]^+$ (22).

Treatment of $[\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}]$ ($\text{L}=\text{bipy}$ or phen) with trifluoromethanesulfonic acid produces $[\text{Ru}(\text{CO})_2(\text{SO}_3\text{CF}_3)_2\text{L}]$ (40-60%) and HCl. Reactions of these products with $\text{L}'=\text{bipy}$, phen , or other chelates yield $[\text{Ru}(\text{CO})_2\text{LL}']^{2+}$. The trifluoromethanesulfonate complexes are as reactive as acetonitrile complexes and more readily prepared (23).

Reactions of borohydride anions arachno- $[\text{B}_3\text{H}_8]^-$ and nido- $[\text{B}_5\text{H}_8]^-$ with $[\text{Os}(\text{CO})\text{HCl}(\text{PPh}_3)_3]$ produce arachno- $[(\text{HOsB}_3\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ [10] (65%) and nido- $[(\text{OsB}_5\text{H}_9)(\text{CO})(\text{PPh}_3)_2]$ [11] (80%), respectively. These are the first air-stable polyhedral osmaborane complexes. Thermolysis of [11] yields nido- $[(\text{OsB}_4\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ [12] (40%). Characterization was accomplished by spectroscopic methods (24).

The syntheses, characterizations, and electrochemistry of $[\text{Ru}(\text{OEP})-(\text{PBu}_3)_2]$, $[\text{Ru}(\text{OEP})(\text{CO})\text{L}]$ ($\text{L}=\text{PPh}_3, \text{PBu}_3$), $[\text{Ru}(\text{OEP})(\text{PBu}_3)_2]\text{Br}$, $[\text{Ru}(\text{OEP})(\text{PBu}_3)-\text{Br}]$, and $[\text{Ru}(\text{OEP})(\text{CO})(\text{EtOH})]$ were reported. $[\text{Ru}(\text{OEP})(\text{CO})(\text{EtOH})]$ reversibly dissociates EtOH in dichloromethane and undergoes a one-electron oxidation of the OEP ligand, forming $[\text{Ru}(\text{OEP}^+)(\text{CO})]^+$. This product can coordinate bromide or py, and these same two species can be formed by oxidation of $[\text{Ru}(\text{OEP})(\text{CO})(\text{EtOH})]$ with bromine or by oxidation of $[\text{Ru}(\text{OEP})(\text{CO})(\text{py})]$, respectively. Oxidation of $[\text{Ru}(\text{OEP})(\text{PBu}_3)_2]^+$ at 1.2 V yields $[\text{Ru}(\text{OEP}^+)-(\text{PBu}_3)_2]^{2+}$; the bromide salt decomposes to $[\text{Ru}(\text{OEP})(\text{PBu}_3)\text{Br}]$, PPh_3 , $[\text{Ru}(\text{OEP})(\text{PBu}_3)_2]$ and $[\text{PBu}_3\text{Br}]\text{Br}$ (25).

An improved procedure for insertion of Os into porphyrin ring systems was reported. The procedure uses K_2OsCl_6 in diethyleneglycol monomethyl ether as the source of metal ion. Complexes prepared by this route were $[\text{Os}(\text{TTP})(\text{CO})(\text{py})]$ (72%), $[\text{Os}(\text{TTP})(\text{CO})(\text{MeOH})]$ (45%), $[\text{Os}(\text{TTP})(\text{CO})(\text{MeOH})]$

(68%), [Os(mesoporphyrinato-IX-dimethyl ester)(CO)(py)] (47%), and [Os(mesoporphyrinato-IX)(CO)(py)] (86%) (26).

[Os(TTP)(CO)(py)] was also prepared in 80% yield from [$\{\text{Os}(\text{CO})_3\text{Cl}_2\}_2$], H_2 [TTP], and CO in 2-(2'-methoxyethoxy)ethanol. Pyrolysis of [Os(TTP)(py) $_2$] at 320° gave [$\{\text{Os}(\text{TTP})\}_2$] (95%) having a formal Os=Os double bond. The OEP analogs were also prepared (27).

Picosecond laser spectroscopy of [Os(OEP)(NO) $_2$] and [Os(OEP)(py) $_2$] was reported. The initial excited states S_1 decay in ≤ 9 ps and the second excited states T_1 live for 9 and 1 ns, respectively. The results support prior assignments of these states for T_1 as π, π^* and d, π^* , respectively (28).

Thiocarbonyl complexes have been prepared from trans-[RuCl $_2$ (CS)(H $_2$ O)-(PPh $_3$) $_2$], formed in 78% yield by refluxing [RuCl $_2$ (PPh $_3$) $_3$], carbon disulfide and excess PPh $_3$ in xylene for 24 h. This complex reacts with CNR to form sequentially trans-[RuCl $_2$ (CS)(CNR)(PPh $_3$) $_2$] and then cis-[RuCl $_2$ (CS)(CNR)-(PPh $_3$) $_2$]. The cationic complexes [RuCl(CS)(CNR)L'(PPh $_3$) $_2$] $^+$ (L=CO, CNR) can be prepared by halide abstraction from cis-[RuCl $_2$ (CS)(CNR)(PPh $_3$) $_2$] with Ag $^+$, giving cis-[RuCl(CS)(H $_2$ O)(CNR)(PPh $_3$) $_2$] $^+$, and then adding L. Similarly, addition of sodium formate to [RuCl $_2$ (CS)(H $_2$ O)(PPh $_3$) $_2$] produces [Ru(η^2 -O $_2$ CH)Cl(CS)(PPh $_3$) $_2$], which is transformed by PPh $_3$ in refluxing MeOH to an equilibrium mixture of [RuHCl(CS)(PPh $_3$) $_3$] and [RuHCl(CS)(PPh $_3$) $_2$]. The latter 16-electron complex reacts with carboxylates Na[O $_2$ CR] to produce [RuH(CS)(η^2 -O $_2$ CR)(PPh $_3$) $_2$] (29).

Complexes of Metals in Higher Oxidation States

The electronic structure of the intervalence transfer (IT) absorption band of the weakly coupled mixed-valence dimer [(bipy) $_2$ ClOs(II)(PPh $_2$ CH $_2$ PPh $_2$)-Os(III)Cl(bipy) $_2$] $^{3+}$ is attributed to the large spin-orbit (SO) coupling constant for Os, which leads to well-separated SO states for the Os(III) $d-\pi^5$ electronic configuration. The Ru analog is proposed to have a similar IT spectrum but because of the smaller SO coupling the three closely spaced components are not resolvable (30).

The complexes [OsO $_2$ X $_2$ L $_2$] (L=PPh $_3$, PMePh $_2$, PEtPh $_2$, PET $_2$ Ph; X=Cl, Br) are prepared by reaction of [OsO $_4$], concentrated HX, and L in ethanol. These complexes are intermediates in the formation of trans-[OsX $_4$ L $_2$] and mer-[OsX $_3$ L $_3$]. In refluxing ethanol [OsO $_2$ X $_2$ L $_2$] reacts with HB (HB=2-hydroxypyridine, 2-hydroxy-6-methylpyridine, picolinic acid) to give [OsX $_2$ BL $_2$]. Treatment of [OsO $_2$ X $_2$ (PPh $_3$) $_2$] with 1,3-diphenyltriazine and butyl lithium forms [OsX $_2$ (PhN $_3$ Ph)(PPh $_3$) $_2$]. In ethanol [OsO $_2$ Cl $_2$ (PET $_2$ Ph) $_2$] and 2-hydroxy-6-methylpyridine (HB) give [OsCl $_3$ (CO)(PET $_2$ Ph) $_2$], but trans-[OsX $_4$ (PPh $_3$) $_2$] and the same reagents give [OsXB(CO)(PPh $_3$) $_2$]. X-ray photoelectron spectra,

ESR spectra, and cyclic voltammograms were reported (31).

In refluxing carboxylic acids RCO_2H ($\text{R}=\text{Me}, \text{Et}$) $\text{trans-}[\text{OsO}_2\text{X}_2\text{L}_2]$ ($\text{X}=\text{Cl}, \text{Br}; \text{L}=\text{PPh}_3, \text{PEt}_2\text{Ph}$) is converted to $[\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2\text{X}_4\text{L}_2]$ in 30-80% yield. cyclic voltammetric studies were described. Chemical reduction with sodium produces $[\text{Os}_2(\text{O})(\text{O}_2\text{CMe})_2\text{Cl}_4\text{L}_2]^-$, isolated as the AsPh_4 salt. The products were characterized by NMR, IR, and UV/visible spectroscopy, magnetic moment measurements, and X-ray photoelectron spectroscopy. The crystal structure for $[\text{Os}_2(\text{O})(\text{O}_2\text{CMe})_2\text{Cl}_4(\text{PPh}_3)_2]$ [13] was reported; the Os-O-Os angle is 140.2° (32).

Aromatic nitriles or N-aryolphosphinimines react with $[\text{OsCl}_4(\text{PPh}_3)_2]$ in refluxing xylene to produce $[\text{OsCl}_3(\text{NCR})(\text{PPh}_3)_2]$, while $[\text{OsO}_2\text{Cl}_2(\text{PPh}_3)_2]$ forms $[\text{OsCl}_2(\text{NCR})_2(\text{PPh}_3)_2]$ and $[\text{OsCl}_2(\text{RC}(\text{O})\text{NPPH}_3)(\text{PPh}_3)_2]$, respectively. Thermal decomposition of N-aryolphosphinimines $\text{RC}(\text{O})\text{NPPH}_3$ gives the corresponding RCN and triphenylphosphine oxide. Triphenylphosphine reacts with $[\text{OsO}_2\text{Cl}_2(\text{PPh}_3)_2]$, yielding either $[\text{OsCl}_4(\text{PPh}_3)_2]$ or $[\text{OsCl}_2(\text{PPh}_3)_3]$, depending upon reaction conditions. These products were used to prepare a variety of carbonyl, nitrile, and hydride complexes (33).

Coordination complexes with phosphine or isocyanide ligands were prepared from $[\text{Os}_2(\mu\text{-O}_2\text{CMe})_4\text{Cl}_2]$ (Scheme 2) (34).

The new complex $[\text{RuCl}_3(\text{AsTol}_3)_2(\text{MeOH})]$ ($\text{Tol}=\text{C}_6\text{H}_4\text{Me}-4$) was prepared and used as a starting material for the preparation of other complexes. Reactions with excess nitriles NCR produce $[\text{RuCl}_3(\text{AsTol}_3)_2(\text{NCR})]$ ($\text{R}=\text{Me}, \text{Ph}, \text{Bz}$), with py form $[\text{RuCl}_3(\text{AsTol}_3)(\text{py})_2]$ in hexane or $[\text{RuCl}_2(\text{py})_4]$ in dichloromethane, and with bipy or phen produce $[\text{RuCl}_3(\text{AsTol}_3)(\text{chelate})]$. The complex is transformed to $[\text{RuCl}_3(\text{AsTol})_2]$ in dichloromethane or benzene and to $[\text{RuCl}_3(\text{AsTol}_3)(\text{OCMe}_2)]$ in acetone (35).

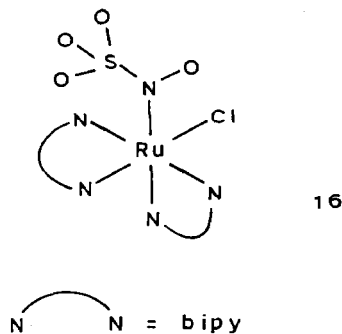
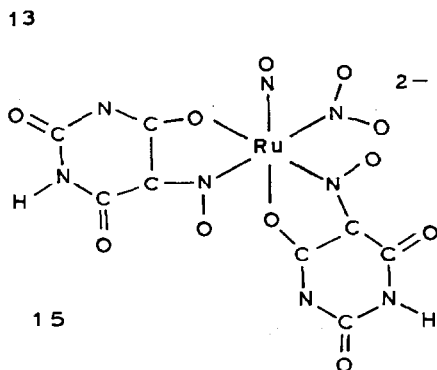
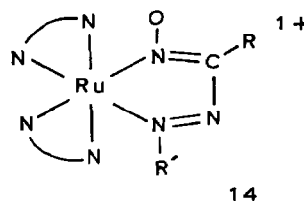
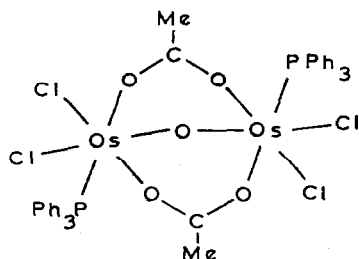
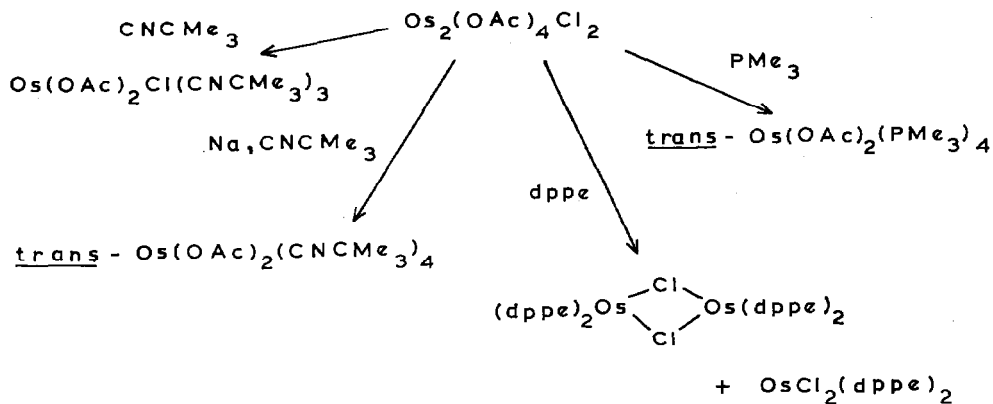
Nitrosyl, Thionitrosyl, and Dinitrogen Complexes

The syntheses of $[\text{PPh}_4][\text{Os}(\text{NO})(\text{N}_3)_5]$ (30%) and $[\text{Os}(\text{NO})(\text{N}_3)_3(\text{phen})]$ (50%) were achieved through reactions of OsO_4 with hydroxylamine hydrochloride and then sodium azide, followed by phenanthroline in the latter case (36). The X-ray crystal structure of $[\text{PMePh}_3][\text{Os}(\text{NO})\text{Cl}_4]$ was reported; the nitrosyl ligand is coordinated in a linear fashion and in the axial coordination site of the square pyramidal $[\text{Os}(\text{NO})\text{Cl}_4]$ anion (37).

The synthesis and structure of $[\text{PPh}_4]_2[\text{OsCl}_3(\text{NO})(\text{SnCl}_3)_2]$ was reported. The compound was prepared from $[\text{OsCl}_3(\text{NO})]$ and $[\text{PPh}_4][\text{SnCl}_3]$ in dichloromethane. The SnCl_3 ligands are trans (38).

A new synthesis of $[\text{NH}_4][\text{Ru}(\text{NO})\text{Cl}_5]$ was achieved by reaction of NO Cl with $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ in ethanol and in the presence of PPh_3 . The iodide and bromide analogs were also prepared (39).

Scheme 2



Oxidation addition reactions of $[\text{Ru}(\text{NO})\text{ClL}_2]$ ($\text{L}=\text{AsPh}_3$) with AcCl , MeI , PhCl , O_2 , Cl_2 , Br_2 , and I_2 produce $[\text{Ru}(\text{NO})\text{Cl}_2(\text{Ac})\text{L}_2]$, $[\text{Ru}(\text{NO})\text{ClIME}\text{L}_2]$, $[\text{Ru}(\text{NO})\text{Cl}_2(\text{Ph})\text{L}_2]$, $[\text{Ru}(\text{NO})\text{ClO}_2\text{L}_2]$, and $[\text{Ru}(\text{NO})\text{ClX}_2\text{L}_2]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$), respectively. The high reactivity was attributed to the presence of the NO ligand (375).

Condensation of the nitrosyl ligand of $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}]^{2+}$ with $\text{RCH}=\text{NNHR}'$ in the presence of sodium methoxide forms [14] ($\text{R}=\text{Me}, \text{Ph}, \text{C}_6\text{H}_4\text{Me}$; $\text{R}'=\text{Ph}, \text{C}_6\text{H}_4\text{Me}$). Protonation of [14] with perchloric acid gives $[\text{Ru}(\text{bipy})_2(\text{HA})][\text{ClO}_4]$ ($\text{A}=\text{RC}(\text{NO})\text{NNR}'$). The electrochemistry and UV/visible spectroscopy were discussed (40).

The structure of $\text{Na}_2[\text{Ru}(\text{C}_4\text{HN}_3\text{O}_4)_2(\text{NO})(\text{NO}_2)] \cdot 7\text{H}_2\text{O}$ [15] was reported. The compound was prepared by treatment of $[\text{Ru}(\text{H}_2\text{Vi})_3(\text{NO})]$ (H_2Vi =monoanion of 2,4,5,6-(1H,3H)-pyrimidinetetrone-5-oxime) with sodium hydroxide and sodium nitrite (41).

Reactions of SO_3^{2-} with trans- $[\text{RuCl}(\text{py})_4(\text{NO})]^{2+}$ or with cis- $[\text{RuX}(\text{bipy})_2(\text{NO})]^{2+}$ ($\text{X}=\text{Cl}, \text{Br}$) form $[\text{RuCl}(\text{py})_4(\text{N}(\text{O})\text{SO}_3)]$ or cis- $[\text{RuX}(\text{bipy})_2(\text{N}(\text{O})\text{SO}_3)]$ [16], respectively. These products are considered to be Ru(II) complexes of N-ONSO_3^- . Adduct formation is reversed upon refluxing in aqueous acid. The structure of [16] was reported (42).

Sulfur and $[\text{Ru}(\text{NO})\text{X}_3\text{L}_2]$ ($\text{X}=\text{Cl}, \text{Br}; \text{L}=\text{PPh}_3, \text{AsPh}_3$) react to form $[\{\text{Ru}(\text{NO})\text{-X}_2\text{L}\}_2\text{S}]$. Oxidation of the products with perbenzoic acid yields $[\{\text{Ru}(\text{NO})\text{-X}_2\text{L}\}_2\text{SO}]$. Characterization was achieved by IR spectroscopy and elemental analysis (43).

The electrochemistry of $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2]$ was examined. Oxidation in acetonitrile at a platinum electrode is an irreversible 2-electron process. The slow oxidation was attributed to a rearrangement from the C_{2v} isomer to the planar (D_{2h}) isomer prior to oxidation. The dication can be reversibly reduced to the monocation but the dication is decomposed by reaction with $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2]$. In the presence of chloride, $[\text{RuCl}_2(\text{NO})_2(\text{PPh}_3)_2]$ is formed and this product can be electrochemically converted to $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2]$ (44).

The ^{15}N NMR spectra of Ru and Os nitrosyl complexes have been recorded. For $[\text{RuCl}_3(^{15}\text{NO})(\text{PMe}_2\text{Ph})_2]$ and $[\text{RuCl}(^{15}\text{NO})(\text{NO})(\text{PPh}_3)_2][\text{BF}_4]$ the nitrogen is deshielded by up to 450 ppm in the bent form as compared with linear NO. The deshielding is correlated with the presence of low-energy $n_{\text{N}} \rightarrow \pi^*$ transitions. The nitrogen of the adjacent linear nitrosyl is deshielded by 100 to 150 ppm, when compared with the mononitrosyl complex. ^{15}N and ^{31}P NMR spectra of $[\text{RuCl}(^{15}\text{NO})(\text{NO})(\text{PPh}_3)_2]^+$ indicate that the complex exists in solution as an equilibrium mixture of two isomers, one trigonal bipyramidal with equivalent nitrosyls and one square pyramidal with linear and bent nitrosyls (45). The explanation for the deshielding of bent nitrosyl ^{15}N signals was supported by studies of $[\text{Os}(\text{NO})_2(\text{PPh}_3)_2]$, $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2]$, $[\text{Os}(\text{NH}_3)_5(\text{NO})\text{Cl}_3]$ and trans- $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$ (46).

An NMR study of $[\text{Ru}(\text{NO})\text{X}_3\text{L}_2]$ ($\text{X}=\text{Cl}, \text{Br}; \text{L}=\text{SEt}_2, \text{SEtPh}, \text{SPr}_2, \text{SBz}_2, \text{SeEt}_2, \text{SeEtPh}$) at 200-375 K investigated the fluxionality of the ER_2 ligands.

Inversion at S or Se was proposed to account for averaging of the methylene protons. Higher barriers to exchange were found for SeR_2 complexes (47).

Reactions of $[\text{OsCl}_5]^-$ with trithiazyltrichloride form $[\text{OsCl}_4(\text{NSCl})_2]$ and $[\text{OsCl}_4(\text{NS})_2]$. The reaction of $[\text{AsPh}_4]\text{Cl}$ with $[\text{OsCl}_4(\text{NSCl})_2]$ yields $[\text{AsPh}_4][\text{OsCl}_4(\text{NS})_2\text{Cl}]$, which can be converted to $[\text{OsCl}_4(\text{NS})_2]$ by treatment with GaCl_3 . The X-ray structure of $[\text{AsPh}_4][\text{OsCl}_4(\text{NS})_2\text{Cl}]$ [17] was reported (48).

Reactions of trithiazyltrichloride in THF with $[\text{RuCl}_2(\text{PPh}_3)_3]$, $[\text{RuBr}_2(\text{PPh}_3)_3]$, $[\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})]$ and $[\text{RuBr}_3(\text{AsPh}_3)_2(\text{MeOH})]$ give $[\text{Ru}(\text{NS})\text{Br}_2\text{Cl}(\text{PPh}_3)_2]$, $[\text{Ru}(\text{NS})\text{Cl}_3(\text{AsPh}_3)_2]$, $[\text{Ru}(\text{NS})\text{Br}_2\text{Cl}(\text{AsPh}_3)_2]$, $[\text{Ru}(\text{NS})\text{Cl}_3(\text{PPh}_3)(\text{AsPh}_3)]$ and $[\text{Ru}(\text{NS})\text{Cl}_3(\text{SbPh}_3)(\text{AsPh}_3)]$, the last two formed by ligand substitution. Irradiation in the presence of air was used to form $[\text{Ru}(\text{NS})\text{X}_3\text{L}]$ and the corresponding OEPPh_3 . Reaction of $[\text{Ru}(\text{NS})\text{X}_3\text{L}]$ with excess L' gives $[\text{Ru}(\text{NS})\text{X}_3\text{LL}']$ and with NOX ($\text{X}=\text{Cl}, \text{Br}, \text{Br}_3$) give mixed nitrosyls $[\text{Ru}(\text{NO})\text{X}_3\text{L}_2]$. Reactions of $[\text{Ru}(\text{NS})\text{Cl}_3\text{L}_2]$ or $[\text{Ru}(\text{NS})\text{Br}_2\text{ClL}_2]$ with N_2O_3 in the presence of excess L give $[\text{Ru}(\text{NO})\text{Cl}_2(\text{NO}_3)\text{L}_2]$ and $[\text{Ru}(\text{NO})\text{ClBr}(\text{NO}_3)\text{L}_2]$ (49). Treatment of $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ with $(\text{NSCl})_3$ gives only *cis*- $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$ (50).

Substitution on *mer*- $[\text{OsX}_2(\text{N}_2)(\text{PR}_3)_3]$ by MS_2CNR_2 was used to prepare *mer*- $[\text{OsCl}(\text{S}_2\text{CNR}_2)(\text{PR}_3)_2]$ when $\text{M}=\text{Tl}$ and *cis*- $[\text{Os}(\text{S}_2\text{CNR}_2)_2(\text{PR}_3)_2]$ when $\text{M}=\text{Na}$. Reaction of the N_2 complex with $\text{Pb}(\text{SC}_6\text{F}_5)_2$ gives *mer*- $[\text{OsCl}(\text{SC}_6\text{F}_5)(\text{N}_2)(\text{PMe}_2\text{Ph})_3]$, [18], crystallographically characterized, and *mer*- $[\text{Os}(\text{SC}_6\text{F}_5)_2(\text{N}_2)(\text{PMe}_2\text{Ph})_3]$ (51).

η^1 -Hydrocarbon Complexes

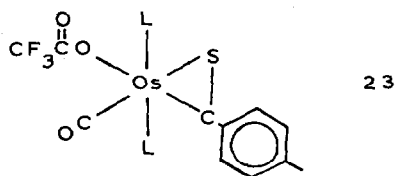
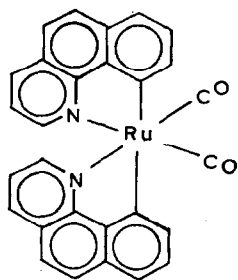
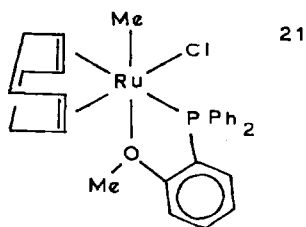
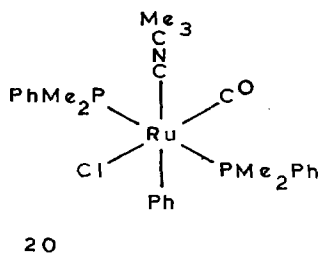
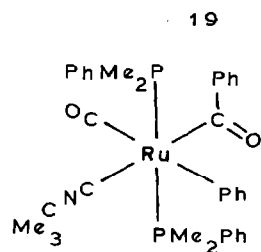
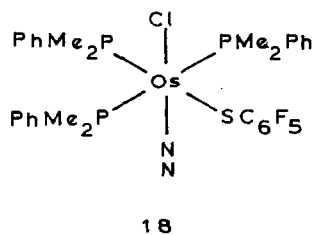
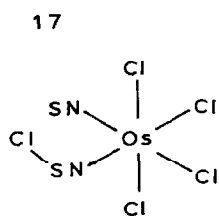
The structures of $[\text{RuPh}(\text{C}(\text{O})\text{Ph})(\text{PMe}_2\text{Ph})_2(\text{CO})(\text{CNCMe}_3)]$ [19] (52) and $[\text{RuPh}(\text{CO})\text{Cl}(\text{PMe}_2\text{Ph})_2(\text{CNCMe}_3)]$ [20] (53) were described.

The crystal structure of $[\text{RuMeCl}(\text{COD})\{\text{PPh}_2(\text{C}_6\text{H}_4\text{OMe}-2)\}]$ [21] was reported. The coordinated methoxy group is easily displaced by small ligands such as CO (54).

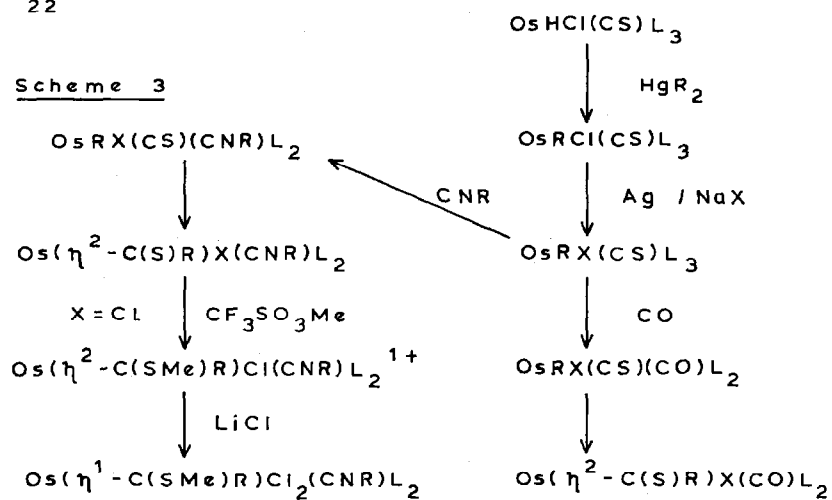
The chelated aryl complex *cis*- $[\text{Ru}(\text{CO})_2(\text{benzo}[\text{h}]\text{quinolin-10-yl})_2]$ [22] was characterized by X-ray crystallography (55).

Carbonylation of $[\text{RuXMe}(\text{CO})_2(\text{PMe}_3)_2]$ ($\text{X}=\text{I}, \text{Me}$) produces $[\text{RuX}(\text{C}(\text{O})\text{Me})(\text{CO})_2(\text{PMe}_3)_2]$ by *cis* insertion of CO , rather than by methyl migration (56).

Treatment of $[\text{OsHCl}(\text{CS})\text{L}_3]$ ($\text{L}=\text{PPh}_3$) with HgR_2 ($\text{R}=\text{C}_6\text{H}_4\text{Me}-4$) provides a route to $[\text{OsRCl}(\text{CS})\text{L}_2]$ in 90% yield. The product reacts with nucleophiles Y^- ($\text{Y}=\text{S}_2\text{CNET}_2, \text{O}_2\text{CMe}, \text{O}_2\text{CCF}_3$) to give $[\text{OsR}(\eta^2\text{-Y})(\text{CS})\text{L}_2]$, but the conjugate acid $\text{CF}_3\text{CO}_2\text{H}$ forms $[\text{Os}(\eta^1\text{-O}_2\text{CCF}_3)(\text{EtOH})(\text{CS})\text{L}_2]$ in ethanol. Addition of $\text{L}'=\text{CO}$, CNR , or NCR to $[\text{OsRX}(\text{CS})\text{L}_3]$ produces $[\text{OsRX}(\text{CS})\text{L}'\text{L}_2]$, which undergoes aryl migration, forming $[\text{Os}(\eta^2\text{-C}(\text{S})\text{R})\text{XL}'\text{L}_2]$. Similarly, $[\text{OsR}(\eta^1\text{-O}_2\text{CCF}_3)(\text{CS})\text{L}'\text{L}_2]$ ($\text{L}'=\text{CO}, \text{CNC}_6\text{H}_4\text{Cl}-4$) rearranges to $[\text{Os}(\eta^2\text{-C}(\text{S})\text{R})(\eta^1\text{-O}_2\text{CCF}_3)\text{L}'\text{L}_2]$ [23], characterized by X-ray crystallography for $\text{L}'=\text{CO}$. These reactions



Scheme 3



and others are summarized in Scheme 3 (57).

Methylation with methylmagnesium bromide of $(S)_{Ru}$, $(R)_c$ -[CpRuCl(prophos)] or $(R)_{Ru}$, $(R)_c$ -[CpRuCl(prophos)] (prophos=propylene bis(diphenylphosphine)) occurs stereospecifically with retention of configuration at Ru to produce $(S)_{Ru}$, $(R)_c$ -[CpRuMe(prophos)] or $(R)_{Ru}$, $(R)_c$ -[CpRuMe(prophos)]. The crystal structure of the former product proves the configuration. However, the analogous reactions with *s*-butylmagnesium bromide give [CpRuH(prophos)], stereospecific within NMR detection limits (58).

Reactions of [CpRuCl(PPh₃)₂] with RMgX (R=Et, Pr, Bu, *i*-Bu) produce [CpRuR(PPh₃)₂]. Above 50° phosphine dissociation and β-hydrogen elimination yields the appropriate [CpRuH(PPh₃)(η²-alkene)]. When R=*i*-Bu, the intermediate [CpRuR(PPh₃)] can be reacted with ethylene to produce [CpRu(*i*-Bu)-(PPh₃)(C₂H₄)]. Hydrogen-deuterium scrambling in [CpRu(CH₂CD₃)(PPh₃)₂] indicates that β-hydrogen elimination is reversible (59).

Reduction of [CpRu(CO)₃][PF₆] with methanolic sodium cyanoborohydride produces [CpRu(CO)₂(CH₂OH)] in 50% yield. The compound is stable to 60° but is decomposed by potassium *t*-butoxide in THF to [CpRu(CO)₂H] and (CH₂O)_x. Acylation of the hydroxymethyl ligand with acetyl chloride/pyridine or acetic anhydride produces [CpRu(CO)₂(CH₂O₂CMe)]. In methanol the hydroxymethyl complex slowly forms [CpRu(CO)₂(CH₂OMe)], and silylation with chlorotrimethylsilane/pyridine gives the analogous [CpRu(CO)₂(CH₂OSiMe₃)]. No reaction of [CpRu(CO)₂(CH₂OH)] with CO was observed even under 4000 psi of CO and at 80° (60).

Alkylation of Na[CpRu(CO)₂] with 0.5 mol dichloromethane at -35° in THF produces [{CpRu(CO)₂}]₂CH₂, characterized by X-ray crystallography; the Ru-Ru distance of 3.8 Å and the Ru-C-Ru angle of 123° indicated the absence of a metal-metal bond. Photolysis of this product forms *cis*- and *trans*-[{CpRu(CO)₂}]₂(μ-CO)(μ-CH₂) in 80% yield. Carbon monoxide insertion (40 psig, 25°) produces [{CpRu(CO)₂}]₂(μ-CH₂C(O)) [24] (80%), also produced in low yield from Na[CpRu(CO)₂] and CH₂ClC(O)Cl. Carbonylation of [{CpRu(CO)₂}]₂CH₂ in methanol forms methyl acetate and [{CpRu(CO)₂}]₂, and photolysis of [{CpRu(CO)₂}]₂(μ-CH₂C(O)) in methanol also produces methyl acetate. Reactions of other α,γ-dihalocarbons X(CH₂)_nX (n=2, X=Cl; n=3, X=Br; n=4, X=Br) with Na[CpRu(CO)₂] produce the corresponding [CpRu(CO)₂(CH₂)_nRu(CO)₂Cp]. For n=2 thermal decomposition at 70° gives ethylene. For n=3, irradiation yields equimolar quantities of [CpRu(CO)₂H] and [CpRu(CO)(η-C₃H₅)] (61).

Some of these hydrocarbon-linked Ru₂ complexes and mixed Fe-Ru analogs were prepared by others. Reactions between Na[CpRu(CO)₂] and I(CH₂)_nI (n=3 or 4) form [CpRu(CO)₂(CH₂)_nRu(CO)₂Cp]; the mixed-metal analog [CpFe(CO)₂(CH₂)₃Ru(CO)₂Cp] is prepared in 87% yield by halide displacement

from $[\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_3\text{I}\}]$ by $[\text{CpRu}(\text{CO})_2]^-$. Photolysis of $[\{\text{CpRu}(\text{CO})_2\}_2(\text{CH}_2)_3]$ forms $[\{\text{CpRu}(\text{CO})_2\}_2]$ (27%), $[\{\text{CpRu}(\text{CO})\}_4]$ (25%), $[\text{Ru}_4(\text{CO})_6(\mu-\sigma:\eta^5-\text{C}_5\text{H}_4)_2\text{Cp}_2]$ (20%), $[\text{Ru}_2(\text{CO})_4\text{Cp}(\eta-\text{C}_5\text{H}_4\text{Ru}(\text{CO})_2\text{Cp})]$ (4%), and $[\text{Ru}_2(\text{CO})_3(\text{C}_2\text{H}_3\text{Me})-\text{Cp}_2]$ (2%); $[\{\text{CpRu}(\text{CO})_2\}_2]$ is believed to be the primary photoproduct, and the organic products are propene, cyclopropane, and traces of methane, ethylene, and ethane. Photolysis of $[\text{CpRu}(\text{CO})_2(\text{CH}_2)_3\text{Ru}(\text{CO})_2\text{Cp}]$ gives propene (100%), and thermolysis, propene and cyclopropane in a 84:1 ratio. Thermolysis of the Fe-Ru analog produces a 1:1.3 ratio of propene to cyclopropane. Thermolysis of $[\text{CpRu}(\text{CO})_2(\text{CH}_2)_4\text{Ru}(\text{CO})_2\text{Cp}]$ produces 1-butene and cis- and trans-2-butene. The mechanism for these reactions is shown in Scheme 4 (62).

Vinyl complexes $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{R})=\text{C}(\text{CO}_2\text{R})\text{Cl}\}\text{ClL}_2]$ [25] ($\text{R}=\text{Me}, \text{Et}; \text{L}=\text{PMe}_2-\text{Ph}, \text{AsMe}_2\text{Ph}$) are produced by the reaction of trans- $[\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}_2]$ with an equimolar quantity of $\text{C}_2(\text{CO}_2\text{R})_2$ in acetone. The products have been characterized by spectroscopic methods and by X-ray crystallography for $\text{R}=\text{Me}$ and $\text{L}=\text{PMe}_2\text{Ph}$. The proposed mechanism involves intramolecular addition of the Ru-Cl unit across the coordinated alkyne. These products react with PMe_2Ph by substitution for CO, rather than CO insertion into the Ru-C bond, and no further reaction with additional alkyne can be induced (63).

The acyl complex $[\text{Ru}(\text{CO})_2\text{Cl}(\text{PPh}_3)_2\{\text{C}(\text{O})\text{C}_7\text{H}_9\}]$ [26] is formed by treatment of $[\text{RuHCl}(\text{PPh}_3)_2(\text{norbornadiene})]$ with CO (64).

Alkylation of cis- or trans- $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PMe}_2\text{Ph})_2]$ with alkyllithium reagents produces $[\text{Ru}(\text{CO})_2\text{R}_2(\text{PMe}_2\text{Ph})_2]$, but initial attack is believed to occur at a CO ligand. During these reactions trans to cis isomerization is catalyzed. Dialkylmercury reagents react only with the trans dichloride. The mixed alkyl-aryl complex $[\text{Ru}(\text{CO})_2\text{MePh}(\text{PMe}_2\text{Ph})_2]$ was also prepared and the mixed aryl complex $[\text{Ru}(\text{CO})_2\text{Ph}(\text{C}_6\text{H}_4\text{OMe}-4)(\text{PMe}_2\text{Ph})_2]$ was prepared using $\text{Hg}(\text{C}_6\text{H}_4\text{OMe}-4)_2$ for the first arylation and phenyllithium for the second. Carbon monoxide insertion on $[\text{Ru}(\text{CO})_2\text{Me}_2(\text{PMe}_2\text{Ph})_2]$ occurs at 25° under CO to give $[\text{Ru}(\text{CO})_2(\text{C}(\text{O})\text{Me})\text{Me}(\text{PMe}_2\text{Ph})_2]$. The aryl complexes do not undergo CO insertion reactions (65).

Formyl complexes of Ru and Os have been prepared. Attack on trans- $[\text{Os}(\text{CO})_2(\text{dppe})_2]^{2+}$ by $\text{KBH}(\text{O}-i\text{-Pr})_3$ forms $[\text{Os}(\text{CHO})(\text{CO})(\text{dppe})_2][\text{SbF}_6]$ [27], characterized by X-ray crystallography. The complex is thermally stable; only 60% conversion to $[\text{OsCl}(\text{CO})(\text{dppe})_2]^+$ was observed after refluxing in chloroform under nitrogen for 5 days (66). Treatment of cis- $[\text{Ru}(\text{CO})_2(\text{dppm})_2][\text{SbF}_6]_2$ and trans- $[\text{Ru}(\text{CO})_2(\text{dppe})_2][\text{SbF}_6]_2$ with $\text{NaBH}(\text{OEt})_3$ or $\text{KBH}(\text{O}-i\text{-Pr})_3$ form $[\text{Ru}(\text{CHO})(\text{CO})(\text{dppm})_2][\text{SbF}_6]$ and $[\text{Ru}(\text{CHO})(\text{CO})(\text{dppe})_2][\text{SbF}_6]$, respectively, in high yield. The deuterium labeled materials were prepared

using LiBDEt_3 . The compounds were characterized by ^1H , ^{13}C , and ^{31}P NMR and IR spectroscopy and by X-ray crystallography for trans- $[\text{Ru}(\text{CDO})(\text{CO})(\text{dppe})_2]\text{-}[\text{SbF}_6]$ [27]. The Ru formyls are stable at -30° (67).

A Ru formyl complex is formed by treatment of $[\text{RuI}_2(\text{CO})_4]$ with LiBDEt_3 (evidenced by ^2H NMR signal at 13.65 ppm), but no formyls were observed after reactions of $[\text{RuI}_2(\text{CO})_4]$ with $[\text{PPN}][\text{Ru}_3\text{H}(\text{CO})_{11}]$ or $[\text{PPN}][\text{RuH}(\text{CO})_4]$ at -60° . It was thought that reactions with these metal hydrides might generate formyl intermediates in the catalytic conversion of CO and hydrogen to methanol and ethylene glycol, catalyzed by Ru carbonyls with iodide promoters. Some support for this was obtained from the production of $[\text{CpRe}(\text{CO})(\text{NO})\text{D}]$ (-8.44 ppm), $[\text{Ru}_3\text{D}(\text{CO})_{11}]^-$ (-12.70 ppm) and $[\text{CpRe}(\text{CO})(\text{NO})(\text{CDO})]$ (16.18 ppm, 20–30%) from $[\text{CpRe}(\text{CO})_2(\text{NO})]^+$ and $[\text{RuD}(\text{CO})_4]^-$. The reaction of $[\text{CpRe}(\text{CO})_2(\text{NO})]^+$ with $[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$ produces $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{CpRe}(\text{CO})(\text{NO})\text{H}]$, possibly by an electron transfer pathway (68).

The formaldehyde complex $[\text{Os}(\eta^2\text{-CH}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]$ reacts with carbon disulfide to form $[\text{Os}(\overline{\text{CH}_2\text{OC}(\text{Se})\text{Se}})(\text{CO})_2(\text{PPh}_3)_2]$. Reactions of these complexes were investigated and the results are summarized in Scheme 5 (69).

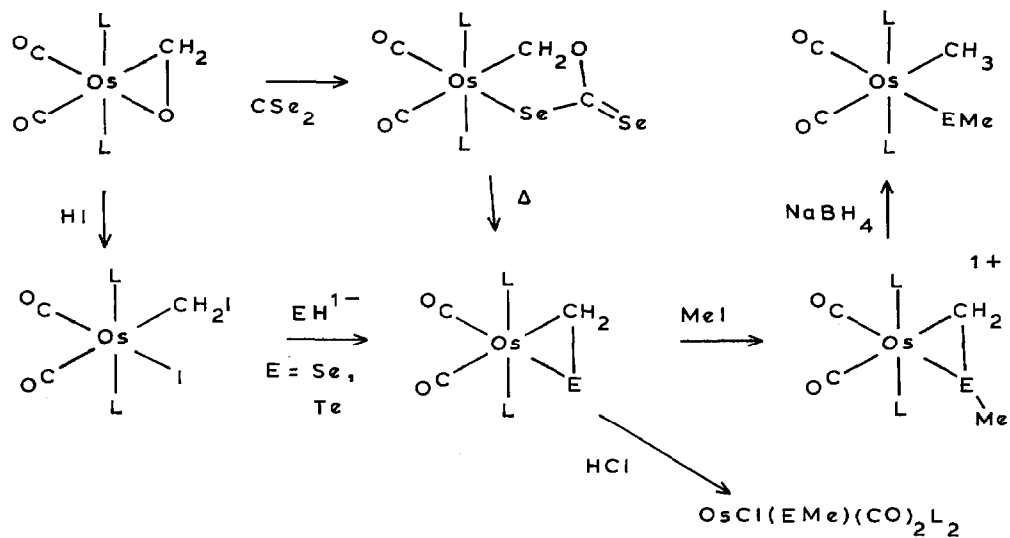
Reduction of trans- $[\text{OsCl}_2(\text{PMe}_3)_4]$ with $\text{NaC}_{10}\text{H}_8$ at 25° in THF forms $[\text{Os}(\overline{\text{PMe}_2\text{CH}_2})(\text{PMe}_3)_4\text{H}]$ [28], but at -78° the product is cis- $[\text{OsH}_2(\text{PMe}_3)_4]$. Complex [28] is configurationally stable on the NMR timescale, unlike the Fe analog, and does not react with CO or $\text{P}(\text{OMe})_3$. However, reactions of [28] with methyl iodide, HX, ($\text{X}=\text{Cl}, \text{O}_2\text{CCF}_3$, and C_2Ph), and methanol were investigated (Scheme 6). Treatment of trans- $[\text{OsCl}_2(\text{PMe}_3)_4]$ with AgPF_6 forms $[\text{OsCl}_2(\text{PMe}_3)_4][\text{PF}_6]$, which reacts with CO, forming $[\text{OsCl}_2(\text{CO})(\text{PMe}_3)_3]$. Protonation of cis- $[\text{OsH}_2(\text{PMe}_3)_4]$ with NH_4PF_6 produces $[\text{OsH}_3(\text{PMe}_3)_4][\text{PF}_6]$; carbonylation of the product yields $[\text{OsH}(\text{CO})(\text{PMe}_3)_4][\text{PF}_6]$ (70).

The carbene complex $[\text{Os}(\text{CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ [29] was prepared in 82% yield from $[\text{OsCl}(\text{NO})(\text{PPh}_3)_3]$ and diazomethane. The product was characterized by X-ray crystallography and its reactions with electrophiles were studied (Scheme 7). Rearrangement of $[\text{OsCl}_2(\text{NO})(\text{CH}_2\text{Cl})(\text{PPh}_3)_2]$ [30] to $[\text{OsCl}_2(\text{NO})(\text{CH}_2\text{PPh}_3)(\text{PPh}_3)]$ [31] was proposed to occur through the intermediate $[\text{OsCl}_2(\text{NO})(\text{CH}_2)(\text{PPh}_3)_2]^+$. The crystal structure of $[\text{OsCl}(\text{NO})(\text{CH}_2\text{AuI})(\text{PPh}_3)_2]$ [32] was also reported (71).

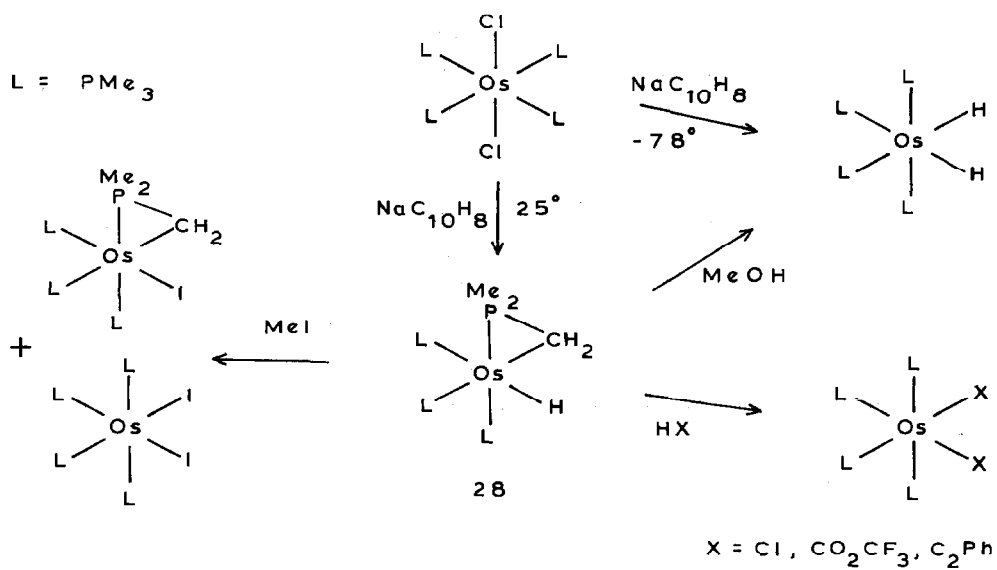
Carbene ligands containing heteroatom substituents are prepared from reactions of epoxides or aziridine with $[\text{CpRu}(\text{CO})_3][\text{PF}_6]$. Using NHC_2H_4 and 2-bromoethylammonium bromide at 25° for 10 min., $[\text{CpRu}(\text{CO})_2(\overline{=\text{COC}_2\text{H}_4\text{NH}})]\text{-}[\text{PF}_6]$ is obtained in 87% yield. $[\text{CpRu}(\text{CO})_2(\overline{=\text{COC}_2\text{H}_4\text{O}})]\text{-}[\text{PF}_6]$ is obtained in 73% yield from ethylene oxide and bromide ion in 2-bromoethanol solvent (72).

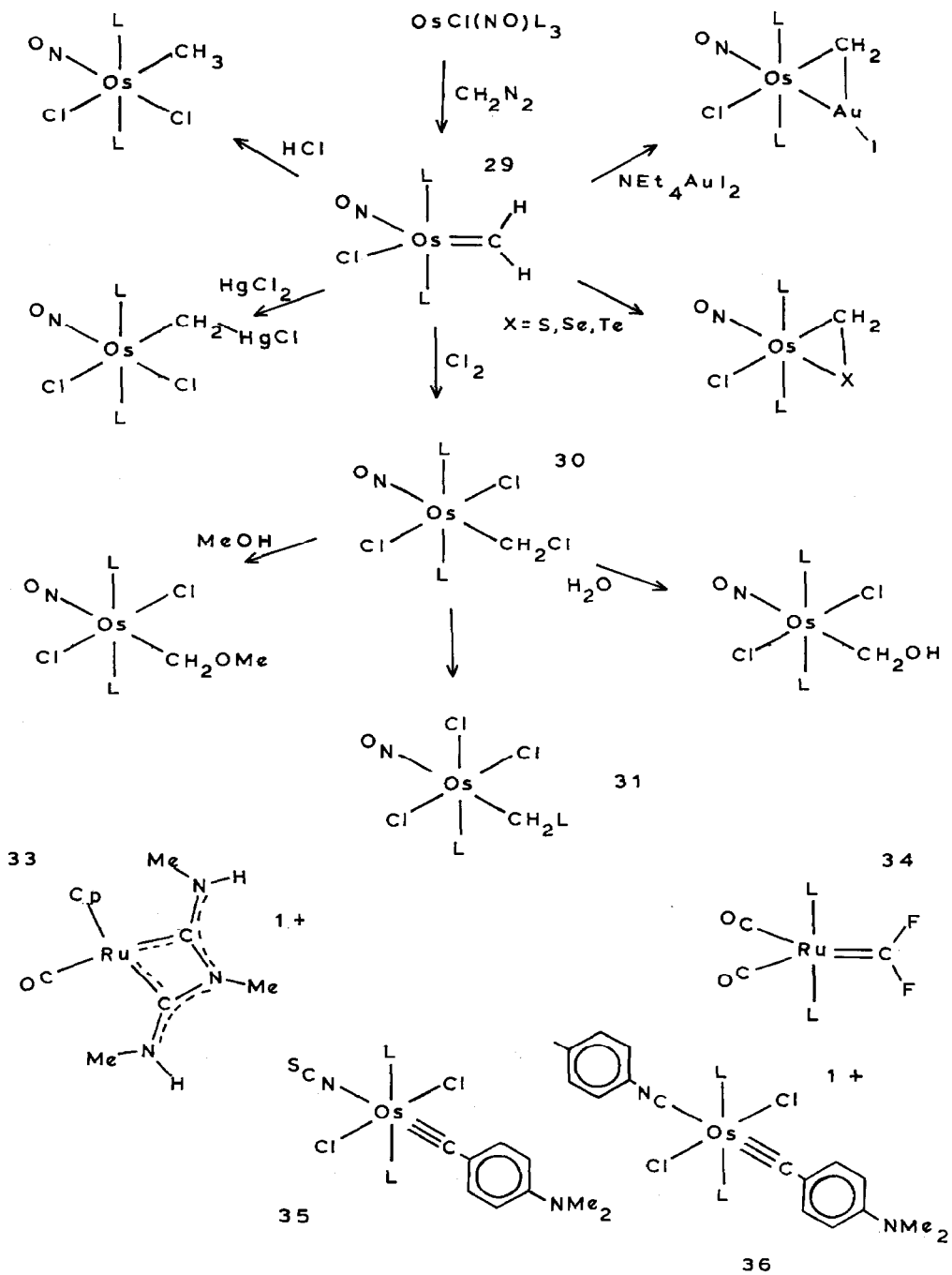
Diaminocarbene complexes $[\text{CpRu}(\text{CO})(\text{CN})\{\text{C}(\text{NHMe})\text{NHR}\}]$ and $[\text{CpRu}(\text{CO})(\text{CN})\{\text{C}(\text{NHMe})\text{NR}_2\}]$ are prepared by reactions of primary and secondary amines

Scheme 5

L = PPh₃

Scheme 6





with $[\text{CpRu}(\text{CO})(\text{CN})(\text{CNMe})]$. The cationic carbene complexes $[\text{CpRu}(\text{CO})(\text{CNMe})-\{\text{C}(\text{NHMe})_2\}]^+$ and $[\text{CpRu}(\text{CO})\{\text{C}(\text{NHMe})_2\}_2]^+$ are prepared from $[\text{CpRu}(\text{CNMe})_2(\text{CO})]^+$ and methylamine. Methylamine and $[\text{CpRu}(\text{CNMe})_3]^+$ give $[\text{CpRu}(\text{CNMe})_2\{\text{C}(\text{NHMe})_2\}]^+$ and $[\text{CpRu}(\text{CNMe})\{\text{C}(\text{NHMe})_2\}_2]^+$ and at low temperature $[\text{CpRu}(\text{CO})-\{\text{C}(\text{NHMe})\text{N}(\text{Me})\text{CNHMe}\}]^+$ [33]. Dimethylamine forms similar products, and the deprotonated chelate $[\text{CpRu}(\text{CO})\{\text{C}(\text{NMe})\text{N}(\text{Me})\text{CNMe}_2\}]$ was detected spectroscopically (73).

Difluorocarbene complexes have been prepared and their reaction chemistry investigated. Treatment of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ with $\text{Hg}(\text{CF}_3)_2$ or with $[\text{Cd}(\text{CF}_3)_2(\text{MeOC}_2\text{H}_4\text{OMe})]$ yields $[\text{Ru}(\text{CF}_3)(\text{HgCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$ and $[\text{Ru}(\text{CF}_2)(\text{CO})_2-(\text{PPh}_3)_2]$ [34]. The latter product was characterized by X-ray crystallography. Although [34] does not react with alcohols or with phenyllithium, a slow reaction with methylamine forms $[\text{Ru}(\text{CNMe})(\text{CO})_2(\text{PPh}_3)_2]$. Reactions of [34] with $\text{Ag}[\text{SbF}_6]$, $[\text{NEt}_4][\text{AuI}_2]$, and HCl yield $[\text{Ru}(\text{CF}_2\text{Ag}(\text{H}_2\text{O}))(\text{CO})_2-(\text{PPh}_3)_2][\text{SbF}_6]$, $[\text{Ru}(\text{CF}_2\text{AuI})(\text{CO})_2(\text{PPh}_3)_2]$, and $[\text{Ru}(\text{CF}_2\text{H})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$, respectively. Treatment of [34] with HCl or SiClMe_3 , followed by methanol, forms $[\text{RuCl}_2(\text{CHOMe})(\text{CO})(\text{PPh}_3)_2]$ through the intermediacy of $[\text{RuCl}_2(\text{CHF})(\text{CO})-(\text{PPh}_3)_2]$ (74).

Reactions of carbyne complexes were investigated. Oxygen reacts with $[\text{OsCl}(\text{CPh})(\text{CO})(\text{PPh}_3)_2]$ and $[\text{OsCl}(\text{CC}_6\text{H}_4\text{NMe}_2-4)(\text{CO})(\text{PPh}_3)_2]$ to $[\text{OsClPh}(\text{CO})_2-(\text{PPh}_3)_2]$ and $[\text{Os}(\text{O}_2\text{CO})\text{Cl}(\text{CC}_6\text{H}_4\text{NMe}_2-4)(\text{PPh}_3)_2]$, respectively. The latter product loses CO_2 upon treatment with HCl , forming $[\text{OsCl}_2(\text{CC}_6\text{H}_4\text{NMe}_2-4)-(\text{H}_2\text{O})(\text{PPh}_3)_2]^+$. Although this product was not isolated in a pure form, derivatization to $[\text{OsCl}_2(\text{NCS})(\text{CC}_6\text{H}_4\text{NMe}_2-4)(\text{PPh}_3)_2]$ [35] and $[\text{OsCl}_2(\text{CC}_6\text{H}_4\text{NMe}_2-4)(\text{CNC}_6\text{H}_4\text{Me}-4)(\text{PPh}_3)_2][\text{ClO}_4]$ [36] was achieved and both of these were characterized by X-ray crystallography (75).

The photochemistry of carbyne complexes $[\text{OsCl}(\text{CPh})(\text{CO})(\text{PPh}_3)_2]$ and $[\text{Os}(\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]^+$ was examined. Excitation in the Os-to-CPh charge transfer band converts these complexes to $[\text{OsCl}_2(=\text{CPh})(\text{CO})(\text{PPh}_3)_2]$ in solutions containing HCl . The relaxed charge transfer state is considered to be a square pyramidal Os(II) complex with a bent Os-CPh linkage (76).

Vinylidene complexes $[\text{CpRu}(=\text{C}=\text{CRR}')\text{L}_2]^+$ ($\text{R}=\text{Me, Et, Bz}$; $\text{R}'=\text{Me, Et, Bu, Ph}$) are synthesized in yields of 60 to 90% from reactions of electrophiles MeI , EtI , or BzBr with $[\text{CpRu}(\text{C}_2\text{R}')\text{L}_2]$ ($\text{R}=\text{Me, Et, Bu, Ph}$; $\text{L}_2=(\text{PPh}_3)_2, \text{dppe}$) (77).

Cyclopentadienyl Complexes

The crystal structures of $[\text{CpRu}(\text{CO})_2\text{Br}]$ and $[(\text{C}_5\text{Me}_4\text{Et})\text{Ru}(\text{CO})_2\text{Br}]$ were determined. No evidence for weaker Ru-CO bonds in the latter was obtained from the structures. This suggests that the enhanced rate of CO dissociation from the latter is due to transition state stabilization (78).

Diamine or dialkene complexes $[\text{CpRu}(\text{L}_2)(\text{PPh}_3)][\text{ClO}_4]$ ($\text{L}_2 = \text{en}, \text{bipy}, \text{phen}, \text{propylenediamine}, \text{bi-imidazole} (\text{H}_2\text{bim}), \text{bibenzimidazole} (\text{H}_2\text{bdzim}), 2-(2'\text{-pyridylbenzimidazole} (\text{Hpybzim}), \text{norbornadiene} (\text{nbid}), \text{tetrafluorobenzobarra-lene} (\text{tfb}))$ were prepared from $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ and the diamine or dialkene in the presence of NaClO_4 . The crystal structure of $[\text{CpRu}(\text{nbid})(\text{PPh}_3)][\text{ClO}_4]$ was reported. Oxygen and $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ in the presence of NaClO_4 yield $[\text{CpRu}(\eta^6\text{-C}_6\text{H}_5\text{P}(\text{O})\text{Ph}_2)][\text{ClO}_4]$, also characterized by X-ray crystallography. The bimetallic complexes $[\text{Cp}(\text{PPh}_3)\text{Ru}(\mu\text{-bim})\text{RhL}_2]_x$ ($x=2, \text{L}_2 = (\text{CO})_2, \text{nbid}; x=1, \text{L}_2 = \text{tfb}$) were prepared from $[\text{CpRu}(\text{Hbim})(\text{PPh}_3)]$ and $[\text{Rh}(\text{acac})\text{L}_2]$, and the analogous $[\text{Cp}(\text{PPh}_3)\text{Ru}(\mu\text{-bbzim})\text{RhL}_2]$ ($\text{L}_2 = (\text{CO})_2, \text{COD}, \text{nbid}, \text{tfb}$) from $[\text{CpRu}(\text{Hbbim})(\text{PPh}_3)]$ (79). Proposed structures for the mixed metal complexes with $\text{L}_2 = (\text{CO})_2$ are [37] and [38].

Ligand substitution on $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ by dppm in refluxing benzene gives first $[\text{CpRu}(\text{PPh}_3)(\eta^1\text{-dppm})\text{Cl}]$, characterized by X-ray crystallography, and then at longer times $[\text{CpRu}(\text{dppm})_2]^+$. Methylation of $[\text{CpRu}(\text{PPh}_3)(\text{dppm})\text{-Cl}]$ with methyl iodide forms $[\text{CpRu}(\text{PPh}_3)(\text{PPh}_2\text{CH}_2\text{PPh}_2\text{Me})\text{I}]$. Also prepared were $[\text{CpRu}(\text{dppm})\text{Cl}]$ and $[\text{CpRu}(\text{dppm})_2]\text{Cl}$ (80).

The synthesis and crystal structure of $[\text{CpOs}(\text{PPh}_3)_2\text{Cl}]$ were reported. The product was formed in 75% yield by reaction of $[\text{CpOs}(\text{PPh}_3)_2\text{H}]$ with chloroform. The structure of the dichloromethane solvate was compared with that of the unsolvated Ru analog (81).

Substitution on $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ by $\text{PPh}_2(\text{CHRCH}_2\text{PPh}_2)$ ($\text{R} = \text{Me}, \text{Cyc}, \text{Ph}$) produces equimolar amounts of diastereomers $[\text{CpRu}(\text{PPh}_2\text{CHRCH}_2\text{PPh}_2)\text{Cl}]$, which can be separated by fractional crystallization. The diastereomeric composition at equilibrium shows a low asymmetric induction (ca. 35%) by the optically active ligand on the chiral Ru center. The crystal structure of (S)- $[\text{CpRu}\{(\text{R})\text{-PPh}_2\text{CHMeCH}_2\text{PPh}_2\}\text{Cl}]$ was reported. The chiroptical properties of these complexes are dominated by the conformation of the chelate and are little influenced by the configuration of the metal (82).

Reactions of each of the two diastereomers of $[\text{CpRu}\{(\text{R})\text{-PPh}_2\text{CHMeCH}_2\text{-PPh}_2\}\text{Cl}]$ with SnCl_2 proceed stereospecifically with retention of configuration at Ru to $[\text{CpRu}\{(\text{R})\text{-PPh}_2\text{CHMeCH}_2\text{PPh}_2\}(\text{SnCl}_3)]$. The stereochemistry was established by X-ray analysis of one of the products (83).

The tridentate chelate complexes $[\text{CpRu}(\text{tripod})][\text{PF}_6]$ and $[\text{CpRu}(\text{triphos})][\text{PF}_6]$ ($\text{tripod} = (\text{PPh}_2\text{CH}_2)_3\text{CMe}$; $\text{triphos} = (\text{PPh}_2\text{CH}_2\text{CH}_2)_2\text{PPh}_3$) were prepared in 73% and 77% yields, respectively, by refluxing $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$, NH_4PF_6 , and the appropriate ligand in decalin for 4 h. Reduction of $[\text{CpRu}(\text{tripod})][\text{PF}_6]$ with LiAlD_4 occurred on the Cp ring, producing $[(\eta^4\text{-C}_5\text{H}_5\text{D})\text{Ru}(\text{tripod})]$ (70%), in which the deuterium is exo; the triphos analog was produced in the same manner in 65% yield (84).

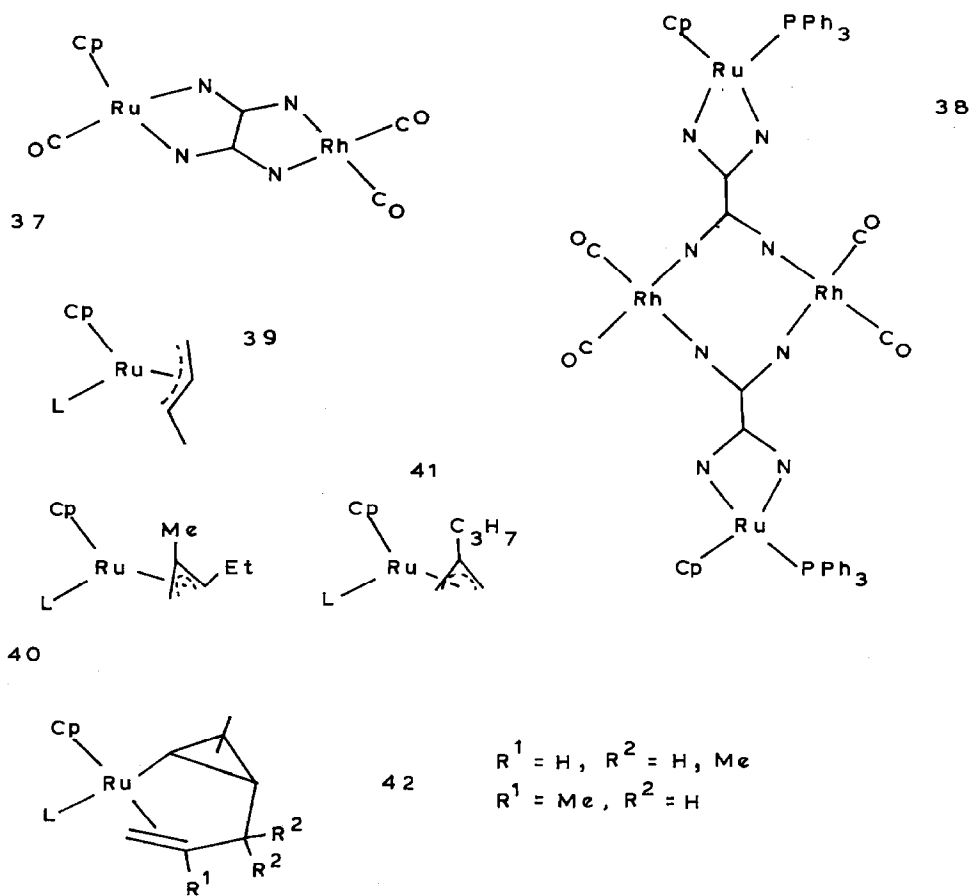
In air the product from the reaction of $\text{Ti}[\text{C}_5(\text{CO}_2\text{Me})_5]$ with $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ or $[\text{CpRu}(\text{CO})_2\text{Cl}]$ is $[\text{CpRu}\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}]$ (85%), characterized by X-ray crystallography; however, under a nitrogen atmosphere in acetonitrile solution the product from $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ is $[\text{CpRu}(\text{PPh}_3)_2(\text{NCMe})][\text{C}_5(\text{CO}_2\text{Me})_5]$ (90%), which can also be prepared by addition of PPh_3 to $[\text{CpRu}\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\} \text{Me}_5]$ in refluxing acetonitrile. The product from $\text{HC}_5(\text{CO}_2\text{Me})_5$ and $[\text{CpRu}(\text{PPh}_3)_2\text{H}]$ is $[\text{CpRu}(\text{PPh}_3)_2\text{H}_2][\text{C}_5(\text{CO}_2\text{Me})_5]$ (94%) (85).

A hydroxymethyl complex of pentamethylcyclopentadienyldicarbonylruthenium has been synthesized and its chemistry investigated. $[(\text{C}_5\text{Me}_5)\text{-Ru}(\text{CO})_2\text{I}]$ is prepared in 95% yield by oxidation of $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{CO})_2]$ with iodine, and then carbonylation (60 psi) by treatment with Ag^+ yields $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{CO})_3][\text{BF}_4]$ (82%). Reduction of the latter with $\text{NaBH}_4/\text{THF}/\text{H}_2\text{O}$ or $\text{NaAlH}_2\text{Et}_2$ or excess $\text{NaBH}_3\text{CN}/\text{MeOH}$ forms $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{CO})_2(\text{CH}_2\text{OME})]$. The hydroxymethyl complex does not undergo CO insertion even under 5000 psi of CO at 80° for 5 h. Silylation of $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{CO})_2(\text{CH}_2\text{OH})]$ with N,N-bis(trimethylsilyl) trifluoroacetamide gives $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{CO})_2(\text{CH}_2\text{OSiMe}_3)]$, which reacts with NBu_4F or $[\text{NH}_4][\text{H}_2\text{F}]$ to form $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{CO})_2\text{H}]$ (86).

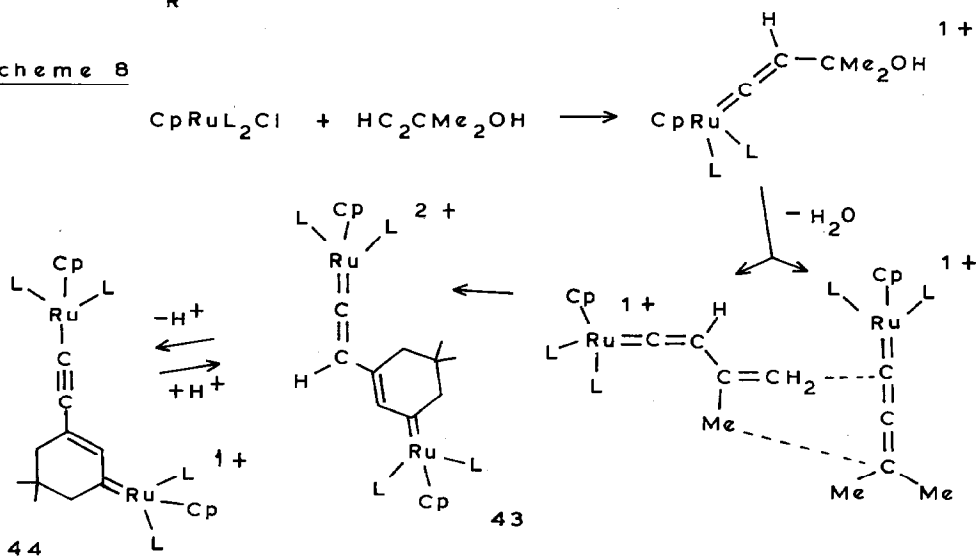
Treatment of $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ with LiAlH_4 in THF produces $[\text{CpRu}(\text{PPh}_3)_3]$ and $[\text{CpRu}(\text{PPh}_3)_2\text{H}]$ in a 4:1 ratio. The analogous reaction for $[\text{CpRu}(\text{dppe})\text{-Cl}]$ forms only $[\text{CpRu}(\text{dppe})\text{H}]$. Reduction of $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ with sodium methoxide/methanol produces $[\text{CpRu}(\text{PPh}_3)_2\text{H}]$ (78%). The reaction scheme involves phosphine dissociation, giving $[\text{CpRu}(\text{PPh}_3)\text{Cl}]$, and the hydride addition to form an intermediate $[\text{CpRu}(\text{PPh}_3)\text{ClH}]^-$. This intermediate may lose chloride, add hydride and then deprotonate water to form $[\text{CpRu}(\text{PPh}_3)_3]$ or may lose chloride and add PPh_3 to form $[\text{CpRu}(\text{PPh}_3)_2\text{H}]$ (372).

Cyanide complexes have been prepared and their reaction chemistry investigated. The dicyanide complex $\text{K}[\text{CpRu}(\text{CO})(\text{CN})_2]$ was prepared in 48% yield by the reaction of $[\text{CpRu}(\text{CO})_2\text{Br}]$ with KCN in refluxing methanol. This product reacts with methyl iodide at 50° in acetonitrile, forming $[\text{CpRu}(\text{CO})(\text{CNMe})(\text{CN})]$ (36%), and at reflux temperature to give $[\text{CpRu}(\text{CO})(\text{CNMe})_2]^+$. Photolysis of $[\text{CpRu}(\text{CO})(\text{CNMe})_2]\text{I}$ in dichloromethane yields $[\text{CpRu}(\text{CNMe})_2\text{I}]$ (48%) and treatment of the product with Ag^+ in THF forms $[\text{CpRu}(\text{CNMe})_3]^+$, isolated as the PF_6 salt in 39% yield. An 81% yield of $[\text{CpRu}(\text{CO})(\text{PPh}_3)(\text{CN})]$ was obtained by treating $[\text{CpRu}(\text{CO})(\text{PPh}_3)\text{Br}]$ with first Ag^+ in THF and then NaCN in DMF; the product can be methylated by methyl iodide in refluxing acetonitrile to $[\text{CpRu}(\text{CO})(\text{PPh}_3)(\text{CNMe})][\text{BPh}_4]$ (70%) (87).

Alkylations of $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ with RMgX ($\text{R}=(\text{CH}_2)_n\text{CR}'=\text{CH}_2$, $n=0, 2$, $\text{R}'=\text{H}$; $n=3$, $\text{R}'=\text{Me}$) form the corresponding $[\text{CpRu}(\text{PPh}_3)_2\text{R}]$, which undergo further reactions. The vinyl complex dissociated PPh_3 at temperatures above 100° , forming in the presence of ethylene $[\text{CpRu}(\text{PPh}_3)(\eta^3\text{-1-methallyl})]$.



Scheme 8



After PPh_3 dissociation the 3- and 4-alkenyl complexes isomerize at 80-100° via η^2 -alkadiene intermediates to η^3 -allyls [39], [40] and [41], respectively. Stable η^1, η^2 -alkenyl complexes [42] are formed from the appropriate cyclopropyl Grignard reagent if β -hydrogen elimination is prevented (88).

The reaction between $\text{HC}_2\text{Me}_2\text{OH}$ and $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ in the presence of NH_4PF_6 forms $[\text{Ru}_2(\mu\text{-C}_{10}\text{H}_{12})(\text{PPh}_3)_4\text{Cp}_2][\text{PF}_6]_2$ [43] in 97% yield. The product was characterized by X-ray crystallography. Deprotonation with base or water forms $[\text{Ru}_2(\mu\text{-C}_{10}\text{H}_{11})(\text{PPh}_3)_4\text{Cp}_2][\text{PF}_6]$ [44]; the reaction can be reversed by treatment with trifluoroacetic acid. The proposed reaction sequence is shown in Scheme 8 (89).

The electrochemical oxidation of $[\text{Ru}(\text{C}_5\text{Me}_5)_2]$ was reported. Cyclic voltammetry in dichloromethane and in acetonitrile solution was used to characterize the oxidation process and ESR spectroscopy the reaction products (90).

$^{13}\text{C}\{^{57}\text{Fe}\}$ double resonance NMR spectroscopy was reported for $[\text{CpFe}(\text{C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{RuCp}][\text{BF}_4]$. The ^{57}Fe resonance is at 405.0 ppm relative to that for ferrocene. The ^{13}C NMR spectra are temperature dependent due to rotation about the $\text{C}(1)\text{-C}_\alpha$ exocyclic bond (91).

The effective polarizability anisotropy, the electric quadrupole moment, and the magnetic anisotropy of ruthenocene were determined. The molecule is more polarizable in directions parallel to the Cp-Ru-Cp axis, suggesting that bonding results in transfer of electronic charge from the metal to the cyclopentadienyl rings. A new synthesis for $[\text{RuCp}_2]$ in 87% yield from NaCp and $[\text{RuCl}_2(\text{DMSO})_4]$ was reported (92).

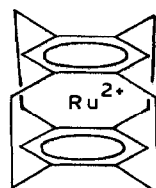
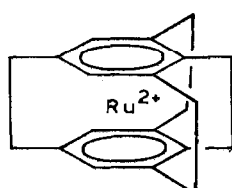
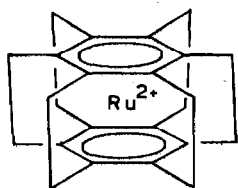
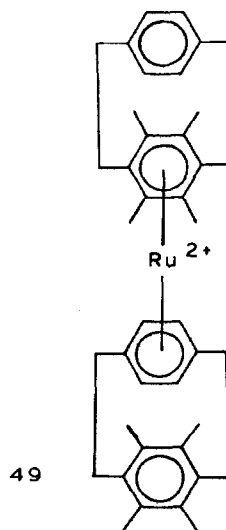
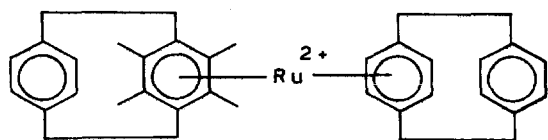
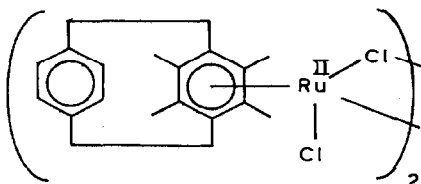
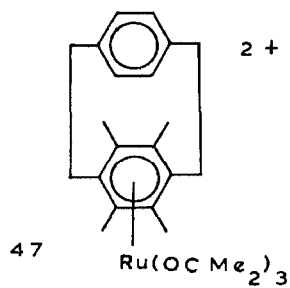
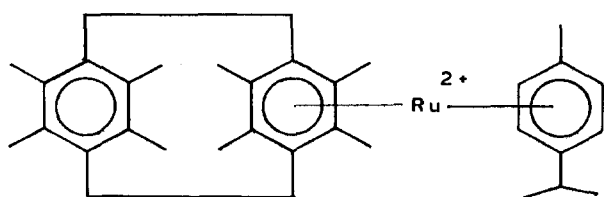
The *p*-nitrophenyl ester of (E)-ruthenocene acrylic acid reacts in a complex to acylate β -cyclodextrin but with poorer binding and rate constants than for the iron analog (93).

^{19}F NMR data for *p*-fluorophenylcyclopentadienyl complexes of Fe, Ru, Os, Rh, Pd, Li, Na, K, Cu, Mg, Tl, Mn, and Re were used to estimate the net charges on the Cp rings (94).

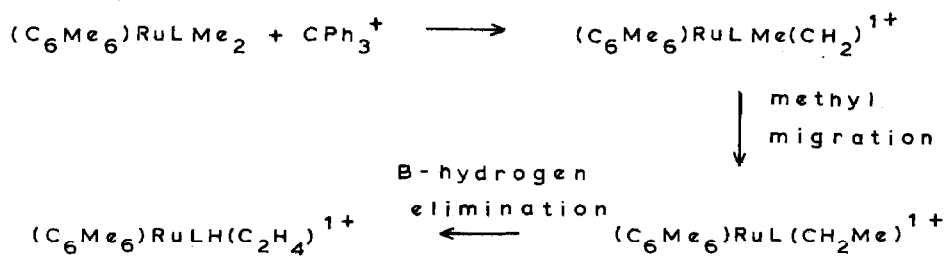
Arene Complexes

$[(p\text{-cymene})(\text{octamethyl}[2.2]\text{paracyclophane})\text{Ru}][\text{BF}_4]_2$ [45] was prepared in 66% yield from the reaction of $[(p\text{-cymene})\text{Ru}(\text{acetone})_3]^{2+}$ with $[(\text{octamethyl}[2.2]\text{paracyclophane})_2\text{Fe}][\text{PF}_6]_2$ (95).

Cyclophane complexes [46], [47], [48], and [49] were prepared. Reaction of 12,15-dihydro-4,5,7,8-tetramethyl[2₂](1,4)cyclophane with RuCl_3 in ethanol gave the dimeric chloride [46] (41%). In acetone solution [46] reacts with AgBF_4 to form [47], which in turn is reacted with [2₂](1,4) cyclophane in the presence of trifluoroacetic acid to yield [48]. Alternatively, [47] and 4,5,7,8-tetramethyl[2₂](1,4) cyclophane give [49].



Scheme 9



These are the first $[\text{Ru}(\eta^2\text{cyclophane})_2]$ complexes to be prepared (96).

An electrochemical study was made of the two-electron reductions of $[(\text{C}_6\text{Me}_6)_2\text{Ru}]^{2+}$ and $[(\text{C}_6\text{Me}_6)\text{Ru}(\eta^2\text{cyclophane})]^{2+}$ ($\eta^2\text{cyclophane} = [\eta^2_6](1,2,3,4,5,6)\text{cyclophane}$ [50], $[\eta^2_4](1,2,3,5)\text{cyclophane}$ [51], and $[\eta^2_4](1,2,4,5)\text{cyclophane}$ [52]). A two-electron, partially reversible reduction wave converts $[(\text{C}_6\text{Me}_6)_2\text{Ru}]^{2+}$ to $[(\eta^6\text{-C}_6\text{Me}_6)(\eta^4\text{-C}_6\text{Me}_6)\text{Ru}]$. The ease of reduction of the cyclophane complexes is in the order $[50] < [51] < [52]$ in two closely spaced, overlapping one-electron waves; this order parallels the order of closeness of the cyclophane geometry to η^4 -coordination. Changing from acetonitrile solution to dichloromethane allows further separation of these two waves. The mechanism for reductions of $[(\text{C}_6\text{Me}_6)_2\text{Ru}]^{2+}$ and of [50] is proposed to be EE_C , where the geometry of the radical cation intermediate is closer to that of the starting Ru(II) complex than to that of the product Ru(0) complex. For [52] the mechanism is $\text{E}_\text{C}\text{E}$ or ECE with the radical cation intermediate resembling the product (97).

A new synthesis for $[(\eta^6\text{-arene})(\eta^6\text{-arene}')\text{Ru}]_2\text{Y}_2$ complexes involves direct exchange of arenes for chlorides on $[\{\text{Ru}(\eta^6\text{-arene})\text{Cl}_2\}_2]$ in refluxing trifluoroacetic acid. In a typical procedure $[\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]$ (0.25 mmol) and the arene (0.5 mL) are refluxed in the acid (3 mL) until the color of the solution is yellow and then the solution is evaporated to dryness; the residue is then dissolved in aqueous NH_4PF_6 solution. If no arene is added, the product is $[\text{Ru}_2(\eta^6\text{-C}_6\text{H}_6)_2\text{Cl}_3][\text{PF}_6]$ (98).

Hydride abstraction from $[(\text{C}_6\text{Me}_6)\text{RuMe}_2(\text{PPh}_3)]$ by trityl cation at -78° gives $[(\text{C}_6\text{Me}_6)\text{RuH}(\text{C}_2\text{H}_4)(\text{PPh}_3)][\text{PF}_6]$ (71%); the product was characterized by X-ray crystallography. The PMePh_2 analog was also prepared. The proposed mechanism for this transformation is shown in Scheme 9 (99).

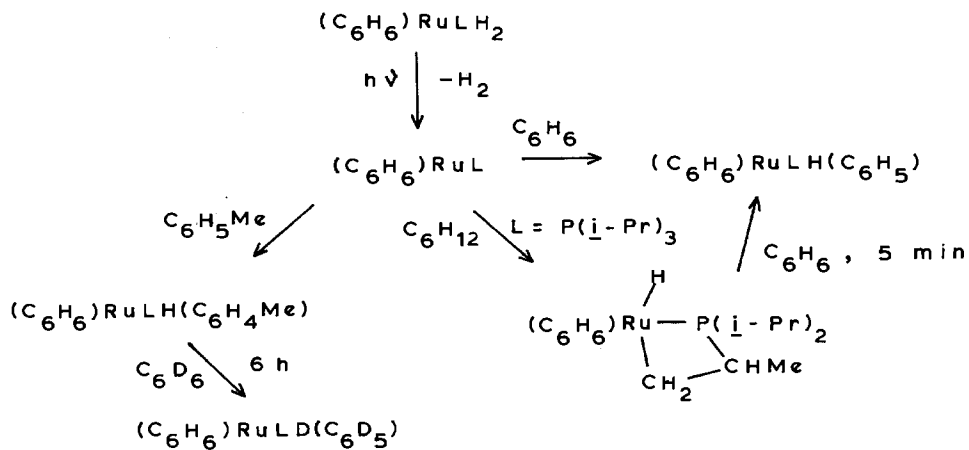
Photolysis of $[(\text{C}_6\text{H}_6)\text{Ru}(\text{P}(i\text{-Pr})_3)_2\text{H}_2]$ or $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{PMe}_3)_2\text{H}_2]$ causes hydrogen elimination and oxidative addition of C-H bonds by the resulting unsaturated metal complex. These reactions are summarized in Scheme 10 (100).

Sodium naphthalide reduces $[(\text{C}_6\text{H}_6)\text{OsI}(\text{PMe}_3)(\text{CNR})][\text{PF}_6]$ to $[(\text{C}_6\text{H}_6)\text{Os}(\text{PMe}_3)(\text{CNR})]$ [$\text{R}=\text{Me}, \text{CMe}_3, \text{Ph}, \text{C}_6\text{H}_4\text{Me}-4$]. These products are very good nucleophiles, reacting with NH_4PF_6 , MeI , and $[\text{ClAuPPh}_3]$ to give $[(\text{C}_6\text{H}_6)\text{OsX}(\text{PMe}_3)(\text{CNR})]^+$, where $\text{X}=\text{H}, \text{Me},$ and AuPPh_3 , respectively. These products react in turn with excess PMe_3 , displacing benzene and forming trans- $[\text{OsX}(\text{CNR})(\text{PMe}_3)_4]^-[\text{PF}_6]$ (101).

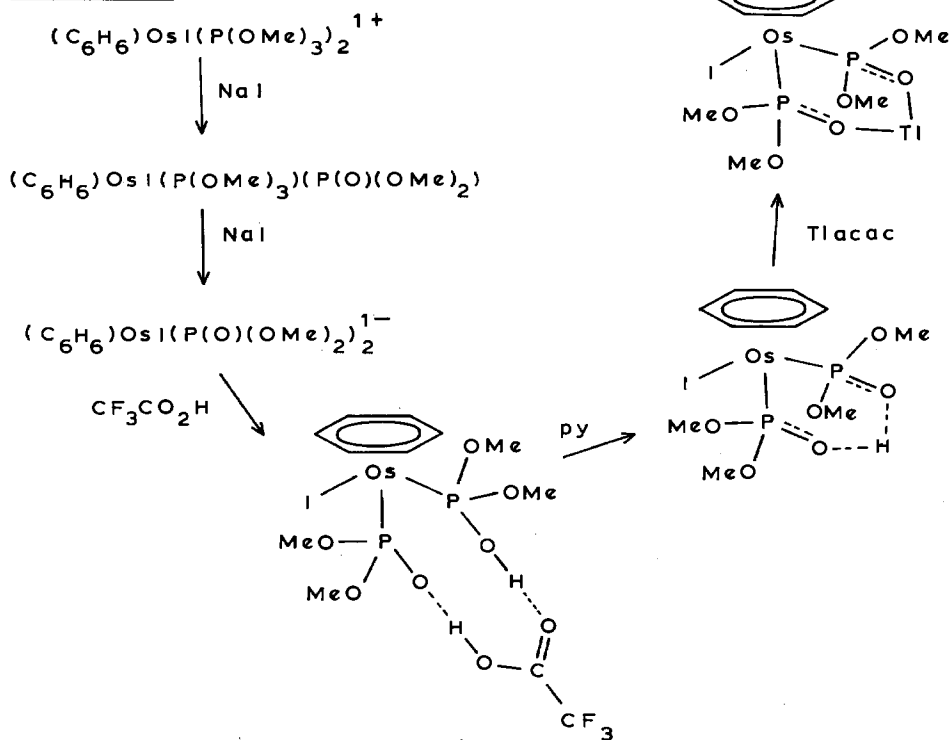
Treatment of $[(\text{C}_6\text{H}_6)\text{OsI}\{\text{P}(\text{OMe})_2\}_2][\text{PF}_6]$ with sodium iodide in acetone gives $[(\text{C}_6\text{H}_6)\text{OsI}\{\text{P}(\text{O})(\text{OMe})_2\}_2]^-$, which can be protonated with trifluoroacetic acid to $[(\text{C}_6\text{H}_6)\text{OsI}\{\text{P}(\text{O})(\text{OMe})_2\}_2\text{H}]\cdot\text{CF}_3\text{CO}_2\text{H}$. Treatment with $\text{Tl}(\text{acac})$ yields $[(\text{C}_6\text{H}_6)\text{OsI}\{\text{P}(\text{O})(\text{OMe})_2\}_2\text{Tl}]$. Crystal structures of $[(\text{C}_6\text{H}_6)\text{OsI}\{\text{P}(\text{O})(\text{OMe})_2\}_2]^-[\text{PF}_6]$ and $[(\text{C}_6\text{H}_6)\text{OsI}\{\text{P}(\text{O})(\text{OMe})_2\}_2\text{H}]$ were reported. These reactions are summarized in Scheme 11 (102).

Protonation of $[(\text{C}_6\text{Me}_6)\text{RuH}_2(\text{PR}_3)]$ with trifluoroacetic acid and

Scheme 10



Scheme 11



NH_4PF_6 at -78° gives $[(\text{C}_6\text{Me}_6)\text{RuH}_3(\text{PR}_3)][\text{PF}_6]$ ($\text{R}_3=\text{Me}_3, \text{MePh}_2, \text{Ph}_3$) in yields of 20-43%. Also prepared were $[(\text{C}_6\text{H}_6)\text{RuH}_2\{\text{P}(\underline{i}\text{-Pr})_3\}]$ and $[(\text{C}_6\text{H}_6)\text{RuH}_3\{\text{P}(\underline{i}\text{-Pr})_3\}][\text{PF}_6]$ (103).

The arene complexes $[(\eta^6\text{-arene})\text{RuX}(\text{O}_2\text{CR})]$ and $[(\eta^6\text{-arene})\text{Ru}(\text{O}_2\text{CR})_2]$ ($\text{X}=\text{Cl}, \text{Br}$; $\text{R}=\text{Me}, \text{CF}_3$; arene= C_6H_6 , 4-Me $\text{C}_6\text{H}_4\text{CHMe}_2$, 1,3,5-Me $_3\text{C}_6\text{H}_3$, 1,2,4,5-Me $_4\text{-C}_6\text{H}_2$, or C_6Me_6) were prepared from $[(\eta^6\text{-arene})\text{RuX}_2]_2$. Bidentate carboxylates are present in $[(\eta^6\text{-arene})\text{RuX}(\text{O}_2\text{CR})]$, while $[(\eta^6\text{-arene})\text{Ru}(\text{O}_2\text{CR})_2]$ contain one unidentate and one bidentate carboxylate and are fluxional on the NMR time-scale. Trifluoroacetic acid reacts with $[(\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$ to give a complex proposed to be $[(\text{C}_6\text{Me}_6)\text{Ru}(\mu\text{-Cl})_2(\mu\text{-O}_2\text{CCF}_3)\text{Ru}(\text{C}_6\text{Me}_6)][\text{H}(\text{O}_2\text{CCF}_3)_2]\cdot\text{CF}_3\text{CO}_2\text{H}$. Phosphine addition to $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{O}_2\text{CR})_2]$ gives $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{O}_2\text{CR})_2(\text{PR}_3)]$ with unidentate carboxylates. Ligand substitution by $\text{L}=\text{py}$ or PEtPh_2 on $[(\text{C}_6\text{H}_6)\text{-RuCl}(\text{O}_2\text{CCF}_3)]$ yields $[(\text{C}_6\text{H}_6)\text{RuClL}_2]^+$. Reactions of pyrazine, 4,4'-bipy, or 1,3-dithiane with $[(\text{arene})\text{RuCl}_2]_2$ or $[(\text{C}_6\text{H}_6)\text{RuCl}(\text{O}_2\text{CCF}_3)]$ form $[(\text{arene})\text{-RuClL}_2]^+$ with only one donor atom coordinated but pyrazine reacts with $[(4\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ yielding $[(4\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2(\mu\text{-pyrazine})$. The crystal structure of $[(4\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{pyrazine})_2][\text{PF}_6]$ was reported (104).

The kinetics of nucleophilic addition by $\text{P}(\text{OBu})_3$ to $[(\text{C}_6\text{H}_6)_2\text{M}]^{2+}$, yielding $[(\eta^6\text{-C}_6\text{H}_6)\text{M}(\eta^5\text{-C}_6\text{H}_6\text{PR}_3)]^{2+}$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$) were determined. In acetonitrile at 25° the forward rate constants were $70 \text{ M}^{-1} \text{ s}^{-1}$ and $24 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{M}=\text{Ru}$ and Os , respectively; the reverse rate constants were 0.08 s^{-1} and 0.06 s^{-1} . The order of rates $\text{Fe} \gg \text{Ru}, \text{Os}$ for attack on the ring is explained by the pi backbonding abilities, which fall in the order: $\text{Ru(II)}, \text{Os(II)} \gg \text{Fe(II)}$ (105).

Other Pi Hydrocarbon Complexes

Coupling of diphenylacetylene with the thiocarbonyl ligand of $[\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3]$ in refluxing benzene gives $[\text{Os}\{\text{C}(\text{S})\text{CPhCPh}\}(\text{CO})_2(\text{PPh}_3)_2]$, in addition to $[\text{Os}(\text{C}_2\text{Ph}_2)(\text{CS})(\text{PPh}_3)_2]$. Carbonylation of the latter yields the former product. S-alkylation to $[\text{Os}\{\text{C}(\text{SMe})\text{CPhCPh}\}(\text{CO})_2(\text{PPh}_3)_2]$ is achieved with methyl iodide but HCl and $[\text{Os}(\text{C}_2\text{Ph}_2)(\text{CS})(\text{PPh}_3)_2]$ give $[\text{Os}(\eta^1\text{-CPh=CHPh})\text{Cl}(\text{CS})(\text{PPh}_3)_3]$. These reactions are summarized in Scheme 12 (106).

Ruthenium complexes containing the $\eta^5\text{-C}_4\text{H}_4\text{BPh}^+$ ligand were prepared. Reactions of $\text{CH}_2\text{CH=CHCH}_2\text{BPh}$ with $[\text{Ru}_3(\text{CO})_{12}]$ and with $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_8)]$ form $[\text{Ru}(\eta^5\text{-C}_4\text{H}_4\text{BPh})(\text{CO})_3]$ (35%) and $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\eta^5\text{-C}_4\text{H}_4\text{BPh})]$ (22%), respectively (107).

The reaction between $[\text{Ru}(\text{CO})\text{Cl}_2(\text{PMe}_2\text{Ph})_2]_2$ and $\text{SnBu}_3(\text{C}_5\text{H}_7)$ gives $[\text{Ru}(\text{CO})\text{Cl}(\eta^3\text{-C}_5\text{H}_7)(\text{PMe}_2\text{Ph})_2]$ (41%). Two possible structures are [53] and [54], with the latter considered more likely (108).

Under a CO atmosphere and at 150°, 2-methoxyfuran and $[\text{Ru}_3(\text{CO})_{12}]$ form $[\text{Ru}_2(\text{C}_3\text{H}_3\text{CO}_2\text{Me})(\text{CO})_6]$ [55] (67%), $\text{C}_6\text{H}_6\text{O}_3$ [56] (50%), and $\text{MeO}_2\text{CCH}_2\text{CH}=\text{CHCO}_2\text{Me}$ (74%). The proposed mechanism is shown in Scheme 13 (109).

The formal $[\pi 6s + \pi 2s]$ cycloaddition of acetylene to $[\text{Ru}(1-6-\eta\text{-cyclo-octa-triene})(1-2:5-6-\eta\text{-cyclo-octadiene})]$ gives $[\text{Ru}(\eta^4, \eta^2\text{-bicyclo-[4.2.2]deca-2,4,6-triene})(1-2:5-6-\eta\text{-cyclo-octadiene})]$ [57]. Propyne and 1-butyne react similarly. The chemical reactivity of these complexes (Scheme 14) was investigated (110).

Co-condensation of Ru atoms and 1,3-butadiene at -196°C, followed by addition of $\text{L}=\text{PF}_3$, CO, or CNCMe_3 at 25°C yields $[\text{RuL}(\eta^4\text{-C}_4\text{H}_6)_2]$ (111).

Treatment of $[\text{RuCl}_2(\text{py})_2(\text{nbid})]$ with first isopropylmagnesium bromide at -78°C and then cycloheptatriene at -40°C forms $[\text{Ru}(\eta^4\text{-nbid})(\eta^6\text{-cycloheptatriene})]$ (80-90%). Acetylene adds to this product at 0°, giving $[\text{Ru}(\eta^4\text{-nbid})(\text{bicyclo-[4.2.1]nona-2,4,7-triene})]$ [58] (67%) (112).

Addition of PPh_3 to $[\text{Ru}(1-3:5-6-\eta\text{-cyclooctadienyl})(\text{CO})_3]^+$ forms initially a phosphonium ion, which slowly isomerizes to $[\text{Ru}(4-6-\eta,1-\sigma\text{-cyclo-octadienyl})(\text{CO})_2(\text{PPh}_3)]^+$. Attack on $[\text{Ru}(1-3:5-6-\eta\text{-cyclo-octadienyl})(\text{CO})_3]^+$ by iodide gives $[\text{Ru}(4-6-\eta,1-\sigma\text{-cyclo-octadienyl})(\text{CO})_2\text{I}]$, and iodide abstraction by Ag^+ yields an intermediate $[\text{Ru}(1-3:5,6-\eta\text{-cyclo-octadienyl})(\text{CO})_2]^+$, which reacts with hydride donors and with PPh_3 to form $[\text{Ru}(4-6-\eta,1-\sigma\text{-cyclo-octadienyl})(\text{CO})_2\text{H}]$ and $[\text{Ru}(1-3:5-6-\eta\text{-cyclo-octadienyl})(\text{CO})_2(\text{PPh}_3)]^+$, respectively. These reactions are summarized in Scheme 15 (113).

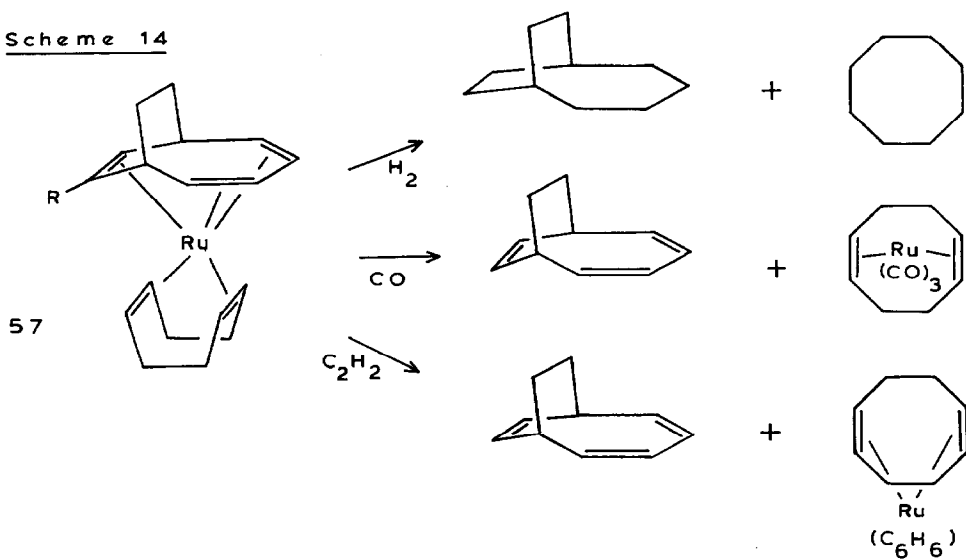
Iodide-bridged diene complexes $[\{\text{Ru}(\text{diene})\text{L}(\mu\text{-I})\}_2]$ [59] ($\text{HL}=\text{2(1H)-pyrimidinethione}$, $\text{diene}=\text{1,5-cyclo-octadiene}$, $\text{HL}=\text{2-pyrimidinethiol}$, $\text{diene}=\text{nbid}$; $\text{HL}=\text{2-pyridinethiol}$, $\text{diene}=\text{1,5-cyclo-octadiene}$ or nbid) have been prepared by treatment of the corresponding $[\text{Ru}(\text{diene})\text{L}_2]$ with methyl iodide (114).

Long range $^{31}\text{P}\text{-}^1\text{H}$ coupling in $[\text{Ru}(\eta^4\text{-C}_5\text{H}_6)(\text{CO})(\text{PPh}_3)_2]$, $[\text{Ru}(\eta^4\text{-C}_5\text{H}_6)\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}]$, and $[\text{Ru}(\eta^4\text{-C}_5\text{H}_6)\{\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}]$ was examined. The coupling constants were used to assign the stereochemistry of 5-substituted $\eta^4\text{-cyclopentadiene}$ compounds. No $^1\text{H}_{\text{endo}}\text{-}^{31}\text{P}$ coupling was seen but H_{exo} was coupled with $J_{\text{PH}} \sim 8\text{-}20$ Hz (115).

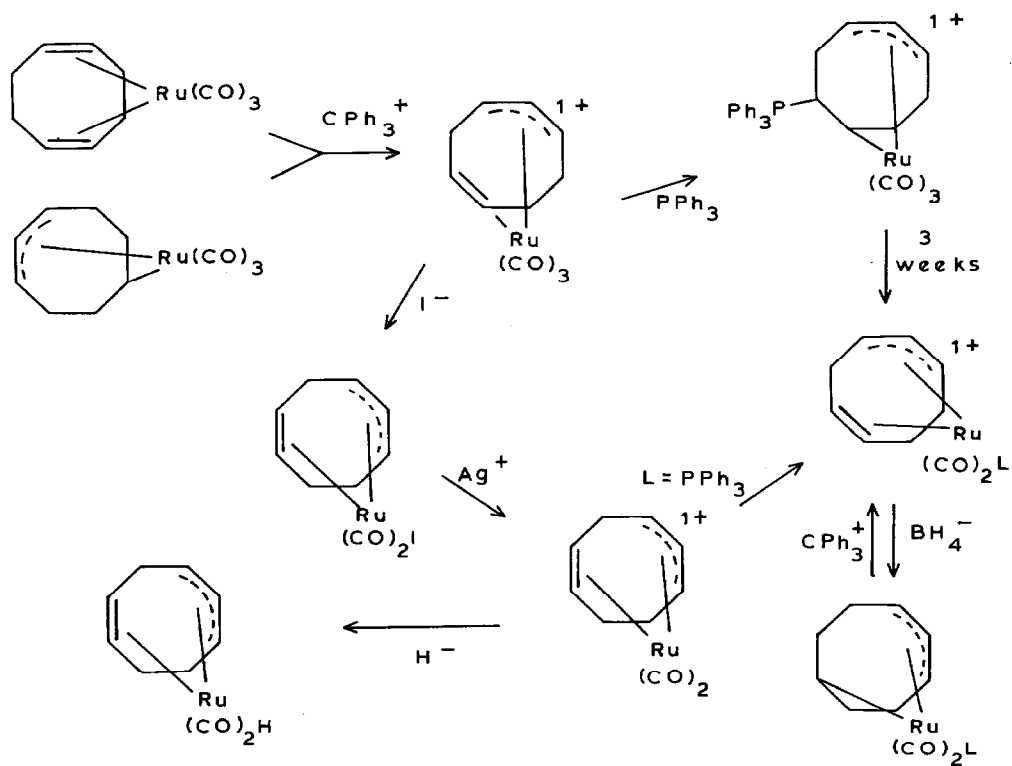
Trimethylphosphite reacts with $[\text{Ru}(1-2:5-6-\eta\text{-cyclo-octa-1,5-diene})(1-6-\eta\text{-cyclo-octa-1,3,5-triene})]$, forming $[\text{Ru}(1-2:5-6-\eta\text{-cyclo-octa-1,5-diene})(1-4-\eta\text{-cyclo-octa-1,3,5-triene})\{\text{P}(\text{OMe})_3\}]$ [60] (90%). The product was characterized by X-ray crystallography (116).

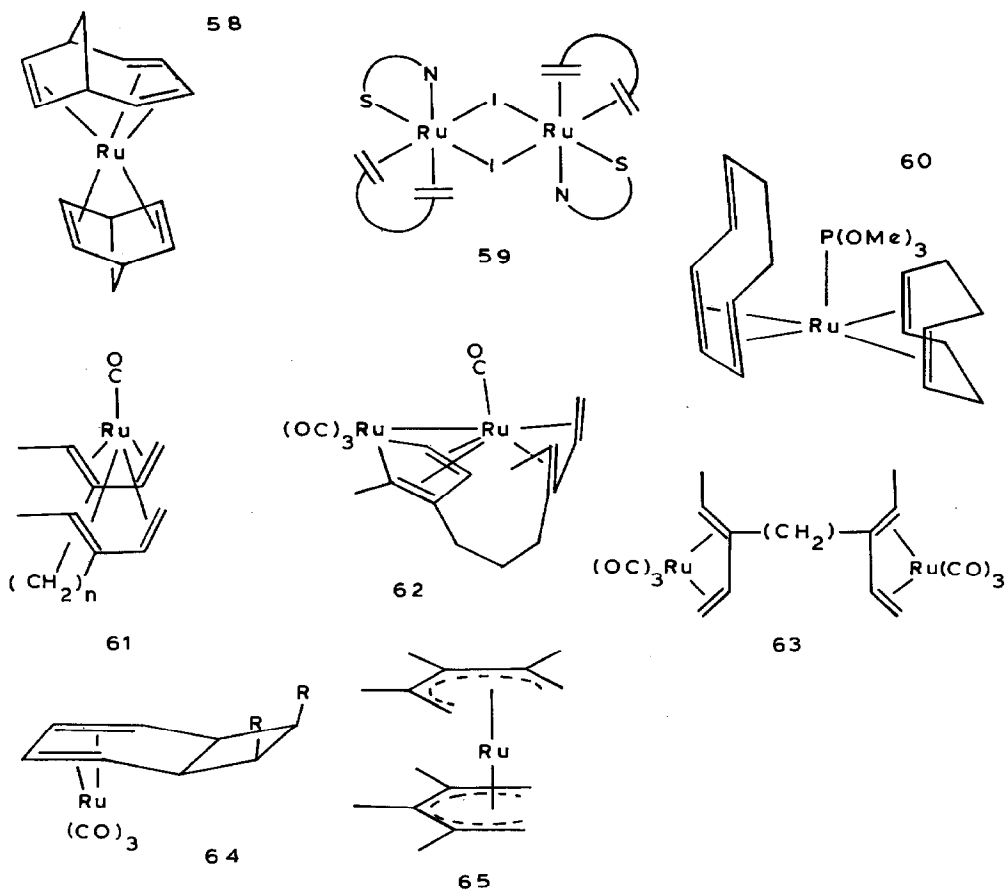
At 140° $[\text{Ru}_3(\text{CO})_{12}]$ and 3,7-divinyl-1,8-nonadiene form $[\text{Ru}(\text{CO})(\text{C}_{13}\text{H}_{20})]$ [61] ($n=3$) (49%) and $[\text{Ru}_2(\text{CO})_4(\text{C}_{13}\text{H}_{18})]$ [62] ($n=3$) (12%); both products were crystallographically characterized. Similar reactions of 3,8-vinyl-1,9-decadiene and 3,9-divinyl-1,10-undecadiene form $[(\mu\text{-polymethylene})\{\text{Ru}(\text{CO})_3(\eta^4\text{-C}_5\text{H}_7)\}_2]$ [63], while 1,3,7,9-decatetraene yields $[\text{Ru}(\text{CO})_3(\text{bicyclo[4.2.0]2,4-}$

Scheme 14

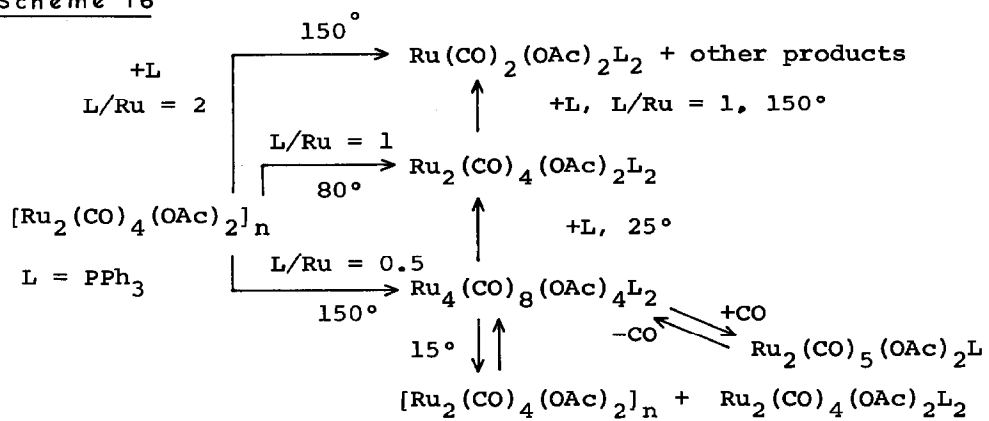


Scheme 15





Scheme 16



octadiene] [64] (117).

In the presence of 2,3,4-trimethyl-1,3-pentadiene, reduction of ethanolic $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with zinc yields $[\text{Ru}(2,3,4\text{-C}_8\text{H}_{13})_2]$ [65], characterized by spectroscopic methods and by crystallography. Bis(2,4-dimethylpentadienyl)-ruthenium was prepared in the same manner. Yields of ca. 30% were achieved (118).

CLUSTER COMPOUNDS

Dinuclear Clusters

The relationships between various ruthenium complexes derived from $[\text{Ru}_2(\text{CO})_4(\text{O}_2\text{CR})_2]$ and PR_3 ligands during the homogeneous hydrogenation of carboxylic acids were investigated. Species identified include $[\text{Ru}(\text{CO})_2(\text{OAc})_2(\text{PR}_3)_2]$, $[\text{Ru}_2(\text{CO})_4(\text{OAc})_2(\text{PR}_3)_2]$, $[\text{Ru}_4(\text{CO})_8(\text{OAc})_4(\text{PR}_3)_2]$, and $[\text{Ru}_2(\text{CO})_5(\text{OAc})_2(\text{PR}_3)]$, the species observed depending upon the identity of the phosphine ($\text{R}=\text{Bu}, \text{Cyc}, \text{Ph}, \text{OEt}$), the PR_3/Ru ratio, and the temperature (Scheme 16) (119).

Hydride-bridged dimers have been synthesized by hydrogenation of $[\text{Ru}(\text{styrene})_2(\text{PPh}_3)_2]$. The initial product, formulated as $[\text{RuH}_n(\text{PPh}_3)_2]$, is proposed to be a mixture of $[\text{RuH}_6(\text{PPh}_3)_2]$ and [66]. Under nitrogen $[\text{RuH}_6(\text{PPh}_3)_2]$ dimerizes to $[\text{Ru}_2\text{H}_6(\text{N}_2)(\text{PPh}_3)_4]$ [67], characterized by X-ray crystallography (120).

Photolysis of $[\text{OsH}_4\text{L}_3]$ ($\text{L}=\text{PMe}_2\text{Ph}$) in benzene or THF forms $[\text{Os}_2\text{H}_4\text{L}_6]$ [68] (50% yield), characterized by X-ray crystallography. Also formed in this process is *cis*- $[\text{OsH}_2\text{L}_4]$. In solution phosphine dissociation from [68] was indicated by the ^{31}P NMR spectrum. Protonation of [68] gives $[\text{Os}_2\text{H}_3\text{L}_6][\text{PF}_4]$ [69], which was structurally characterized (121).

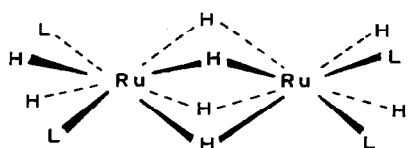
The reaction between $[\text{Os}(\text{CO})_5]$ and GeCl_4 at 60° forms $[\text{Os}_2(\text{CO})_8(\text{GeCl}_3)_2\text{Cl}]$ [70] in 60% yield. The product was structurally characterized. The proposed mechanism of formation involves initial oxidative addition, forming $[\text{Os}(\text{CO})_4(\text{GeCl}_3)\text{Cl}]$, followed by CO loss and condensation with $[\text{Os}(\text{CO})_5]$ (122).

Mononuclear and binuclear alkene complexes $[\text{Os}(\text{CO})_4(\text{CH}_2=\text{CHCO}_2\text{Me})]$ and $[\text{Os}_2(\text{CO})_8(\text{CH}_2=\text{CHCO}_2\text{Me})]$ [71] (30%) are prepared by photolysis of $[\text{Os}_3(\text{CO})_{12}]$ in the presence of methyl acrylate. The X-ray structural determination of [71] was reported; the Os_2C_2 ring is puckered (123).

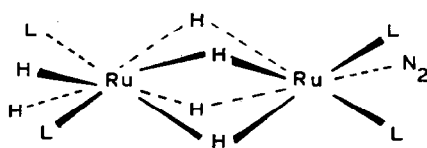
Pyrolysis of $[\text{Os}_2(\text{CO})_8\text{I}_2]$ yields $[\text{Os}_2(\text{CO})_6\text{I}_2]$ [72] (8%), characterized crystallographically (124).

$[\text{Ru}_2(\text{CO})_6(\text{R-dab})]$ ($\text{R-dab}=\text{RN}=\text{CHCH}=\text{NR}$; $\text{R}=\underline{i}\text{-Pr}, \text{Cyc}$) reacts quantitatively with ketene, forming [73]; the complex where $\text{R}=\underline{i}\text{-Pr}$ was crystallographically analyzed (125).

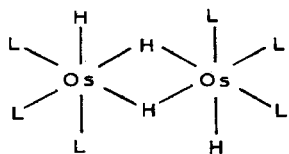
Thermolysis of $[\text{Ru}_3(\text{CO})_{10}(2\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2)]$ at 80° produces $[\text{Ru}_2(\text{MeCC}_6\text{H}_4\text{PPh}_2)(\text{CO})_6]$ [74] (8%) and $[\text{Ru}_3\text{H}_2(\mu\text{-}\eta^2\text{-P-HC}_2\text{C}_6\text{H}_4\text{PPh}_2)(\text{CO})_8]$ (65%). The



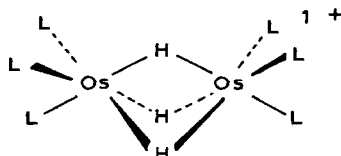
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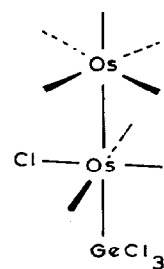
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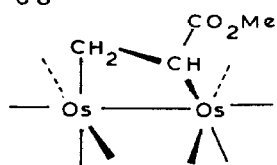
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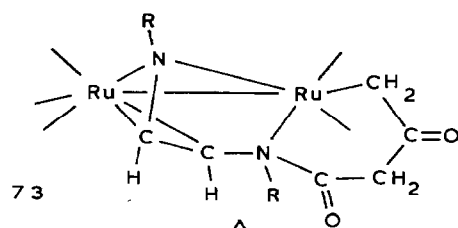
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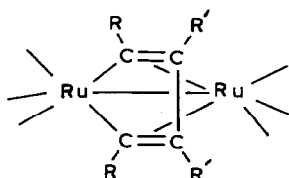
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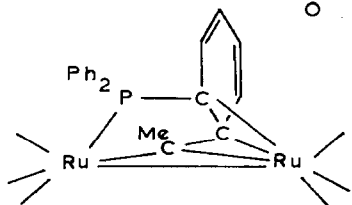
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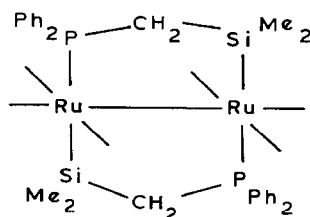
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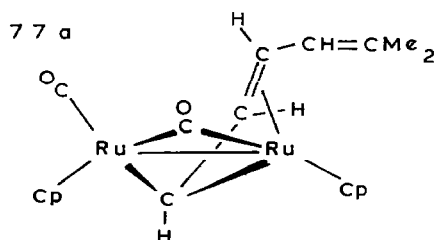
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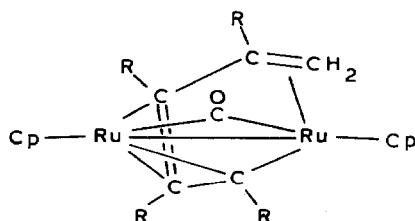
74



76



77 a



77 b

latter reacts with CO at 80° to form [74] and $[\text{Ru}_3(\text{CO})_{12}]$. The X-ray crystal structure of [74] was reported (126).

Metallocyclopentadienyl-containing dimers have been prepared through alkyne coupling reactions with $[\text{Ru}_3(\text{CO})_{12}]$. The X-ray crystal structures of $[\text{Ru}_2(\text{CO})_6(\text{C}_4\text{R}_2\text{R}'_2)]$ [75] ($\text{R}=\text{R}'=\text{CH}_2\text{OH}$ (127), $\text{R}=\text{R}'=\text{CO}_2\text{Me}$ (128), $\text{R}=\text{CH}_2\text{OH}$, $\text{R}'=\text{Et}$ (127)) were reported. Also formed in the reaction with $\text{C}_2(\text{CO}_2\text{Me})_2$ was $[\text{Ru}_3(\text{CO})_7(\text{C}_4(\text{CO}_2\text{Me})_4)]$ (128).

The syntheses of $[\text{M}_2(\text{CO})_6(\text{Ph}_2\text{PCH}_2\text{SiMe}_2)]$ [76] ($\text{M}=\text{Ru}, \text{Os}$) were accomplished by reactions of the corresponding $[\text{M}_3(\text{CO})_{12}]$ with $\text{Ph}_2\text{PCH}_2\text{SiMe}_2\text{H}$. The crystal structure of the Ru compound was reported (8).

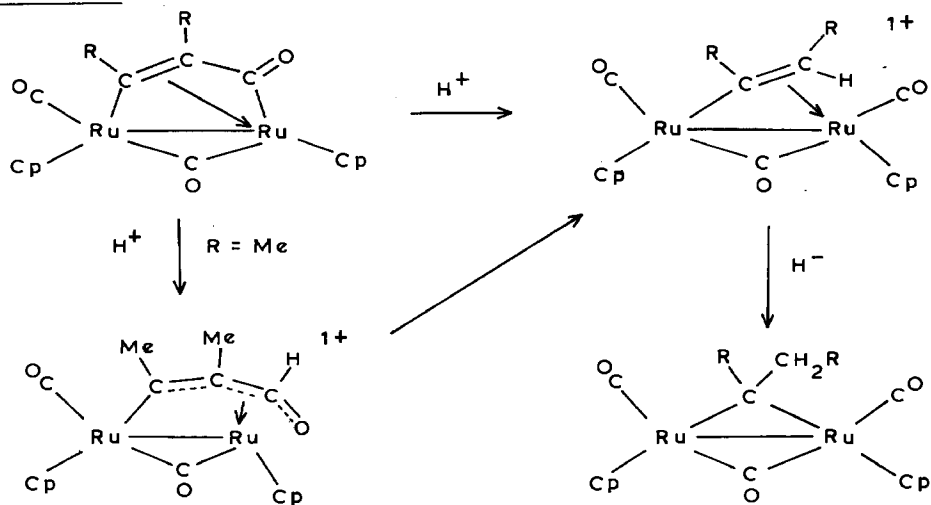
Photolysis of $[\text{Ru}_2(\text{CO})_3(\mu\text{-CMe}_2)\text{Cp}_2]$ in the presence of acetylene forms $[\text{Ru}_2(\mu\text{-CO})(\mu\text{-CHCH}=\text{CHCH}=\text{CMe}_2)(\text{CO})\text{Cp}_2]$ [77a] ($\text{R}=\text{Me}$) by alkyne insertion stereospecifically trans; the product was characterized by X-ray crystallography. Photolysis of $[\text{Ru}_2(\text{CO})_3(\mu\text{-CH}_2)\text{Cp}_2]$ in the presence of $\text{C}_2(\text{CO}_2\text{Me})_2$ yields $[\text{Ru}_2(\mu\text{-CO})(\mu\text{-CR}=\text{CR}=\text{CH}_2)\text{Cp}_2]$ [77b] ($\text{R}=\text{CO}_2\text{Me}$) with cis stereochemistry; this product was also crystallographically characterized. Steric crowding was proposed to account for the difference in the stereochemistry (129).

Protonation of $[\text{Ru}_2(\text{CO})_2\{\text{C}(\text{O})\text{C}_2\text{R}_2\}\text{Cp}_2]$ ($\text{R}_2=\text{H}_2, \text{Ph}_2, \text{H}(\text{Me}), \text{H}(\text{Ph})$) with HBF_4 forms $[\text{Ru}_2(\text{CO})_3(\text{CR}=\text{CHR})\text{Cp}_2]^+$. When $\text{R}_2=\text{Me}_2$, the initial product is $[\text{Ru}_2(\text{CO})_2\{\text{CH}(\text{O})\text{C}_2\text{Me}_2\}\text{Cp}_2]^+$, which then rearranges to the vinyl complex $[\text{Ru}_2(\text{CO})_3(\text{CRCH}_2\text{R})\text{Cp}_2]$. Hydride addition to the α -carbon when $\text{R}_2=\text{H}_2$ also forms $[\text{Ru}_2(\text{CO})_3(\text{C}_2\text{H}_4)\text{Cp}_2]$ in low yield. Reduction of $[\text{Ru}_2(\text{CO})_2(\text{CH}(\text{O})\text{C}_2\text{Me}_2)\text{Cp}_2]^+$ with sodium borohydride forms $[\text{Ru}_2(\text{CO})_2(\text{CH}_2\text{CMeCMe})\text{Cp}_2]$. Hydride abstraction from $[\text{Ru}_2(\text{CO})_3(\text{CHMe})\text{Cp}_2]$ by trityl cation yields $[\text{Ru}_2(\text{CO})_3(\text{CH}=\text{CH}_2)\text{Cp}_2]^+$. These reactions are summarized in Scheme 17 (130).

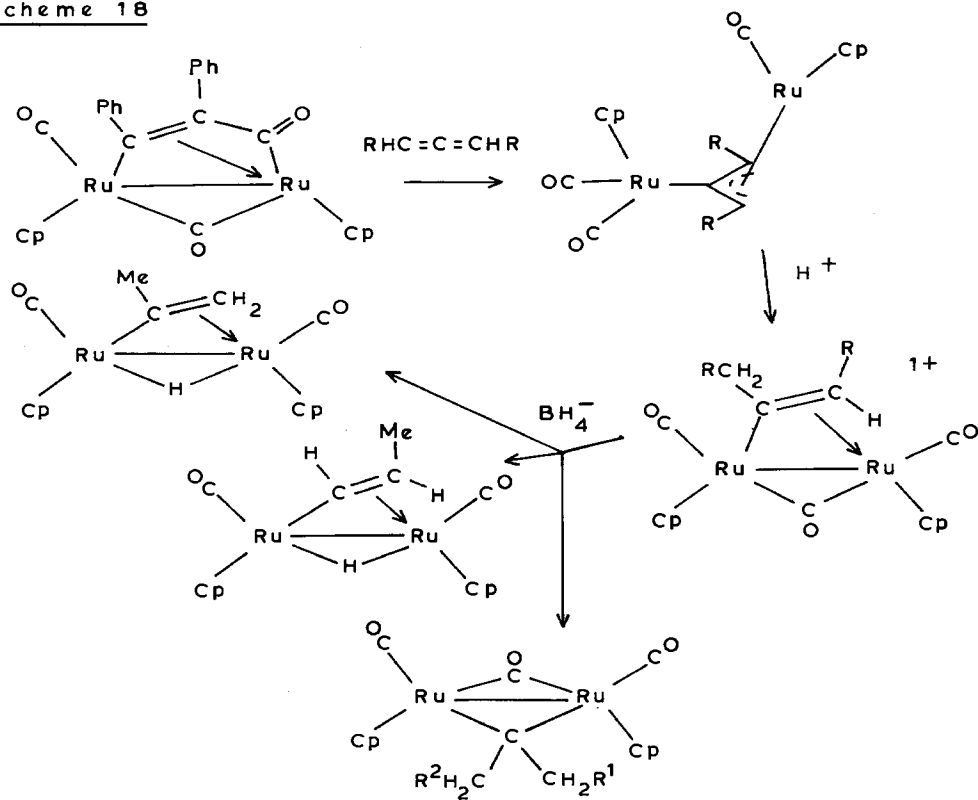
Allenes $\text{RCH}=\text{C}=\text{CHR}'$ ($\text{R}=\text{R}'=\text{H}$ or Me ; $\text{R}=\text{H}, \text{R}'=\text{Me}$) and $[\text{Ru}_2(\text{CO})_2\{\mu\text{-C}(\text{O})\text{C}_2\text{Ph}_2\}\text{Cp}_2]$ at 100° give $[\text{Ru}(\text{CO})(\eta^3\text{-C}_3\text{H}_4\text{-n}\text{Me}_n\{2\text{-Ru}(\text{CO})_2\text{Cp}\}\text{Cp})]$ ($n=0$, 90%; $n=1$, 70%; $n=2$, 10%). Protonation of the product where $n=0$ forms $[\text{Ru}_2(\text{CO})_3(\mu\text{-CMe}=\text{CH}_2)\text{Cp}_2][\text{BF}_4]$, which can be reduced with sodium borohydride to $[\text{Ru}_2(\text{CO})_3(\mu\text{-CMe}_2)\text{Cp}_2]$ (77%), characterized by X-ray crystallography. This sequence was used to prepare $[\text{Ru}_2(\text{CO})_3(\mu\text{-CMeEt})\text{Cp}_2]$ (60%). Cis-trans isomerization occurs via bridge-terminal carbene migration. Other products found during the synthesis of the CMe_2 complex are isomers $[\text{Ru}_2(\text{CO})_2(\mu\text{-H})(\mu\text{-CMe}=\text{CH}_2)\text{Cp}_2]$ and $[\text{Ru}_2(\text{CO})_2(\mu\text{-H})(\mu\text{-CH}=\text{CHMe})\text{Cp}_2]$; the former is dominant in solution, but the latter was found in the crystal structure. These reactions are shown in Scheme 18 (131).

Pyrolysis of $[\text{Ru}_2(\text{CO})_2\{\text{C}(\text{O})\text{C}_2\text{HR}\}\text{Cp}_2]$ in refluxing toluene gives $[\text{Ru}_2(\text{CO})_3(\mu\text{-CCHR})\text{Cp}_2]$ by an intramolecular hydrogen shift. Protonation of the product with HBF_4 yields $[\text{Ru}_2(\text{CO})_3(\mu\text{-CMe})\text{Cp}_2][\text{BF}_4]$, which can be deprotonated

Scheme 17



Scheme 18



with bases such as water, triethylamine or methyllithium. However, $[\text{Ru}_2(\text{CO})_3(\mu\text{-CHMe})\text{Cp}_2]$ is obtained by treatment of the carbyne complex with sodium borohydride. Successive addition of methyllithium and HBF_4 to $[\text{Ru}_2(\text{CO})_4\text{Cp}_2]$ also gives $[\text{Ru}_2(\text{CO})_3(\mu\text{-CMe})\text{Cp}_2][\text{BF}_4]$ and the analogous process with phenyllithium/ HBF_4 and sodium borohydride was used to prepare $[\text{Ru}_2(\text{CO})_3(\mu\text{-CHPh})\text{Cp}_2]$ in high yield. The crystal structures of *cis*- $[\text{Ru}_2(\text{CO})_3(\mu\text{-CCH}_2)\text{Cp}_2]$ [78] and *cis*- $[\text{Ru}_2(\text{CO})_3(\mu\text{-CMe})\text{Cp}_2][\text{BF}_4]$ [79] were determined (132).

The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with dihydrofulvalene in refluxing glyme yields [80] (78%), characterized by X-ray crystallography. Oxidation of [80] with iodine gives $[\text{I}(\text{CO})_2\text{Ru}(\text{C}_5\text{H}_4\text{C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{I}]$; the reaction is reversed upon treatment with LiBHET_3 . Photolysis of [80] in the presence of alkynes generates [81]. Photolysis of [80] alone forms [82] by an intramolecular process; the reaction can be reversed thermally. The crystal structure of [81] was reported (133).

Dimers $[\text{Ru}_2(\text{CO})_6(\text{C}_{16}\text{H}_{22})]$ [83], $[\text{RuFe}(\text{CO})_6(\text{C}_{16}\text{H}_{22})]$ [84], and $[\text{Ru}_2(\text{CO})_6(\text{C}_{16}\text{H}_{20})]$ [85] were prepared. The first two were prepared from $[\text{Ru}(\text{CO})_3(1,2,1',2'\text{-}\eta^4\text{-C}_{16}\text{H}_{22})]$ [86] and the appropriate $[\text{M}_3(\text{CO})_{12}]$. The preparation of [86] (80% yield) involves the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with bi-2,7-cyclo-octadienyl at 140° . The reaction also produces [85]. Crystal structures of [84] and [85] were reported (134).

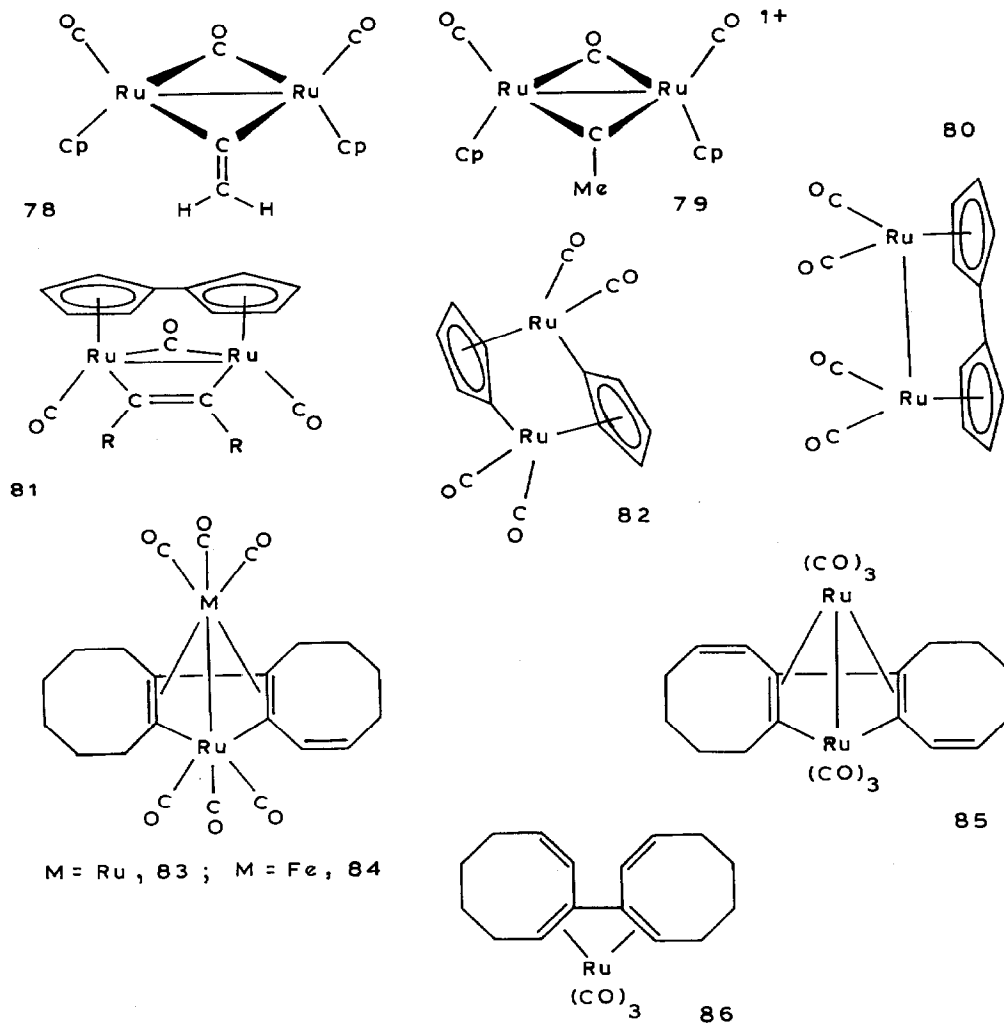
Trinuclear Clusters

Ultraviolet photoelectron spectra and Fenske-Hall molecular orbital calculations for $[\text{Os}_3\text{HX}(\text{CO})_{10}]$ and $[\text{Os}_3\text{X}_2(\text{CO})_{10}]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) were reported. These results suggest that the only direct Os-Os bonds in these molecules are the two $(\text{OC})_4\text{Os-Os}(\text{CO})_3$ bonds. The $(\text{OC})_3\text{Os-Os}(\text{CO})_3$ interaction in the $(\mu\text{-H})(\mu\text{-X})$ series is weakly bonding, but in the $(\mu\text{-X})_2$ series is weakly antibonding (135).

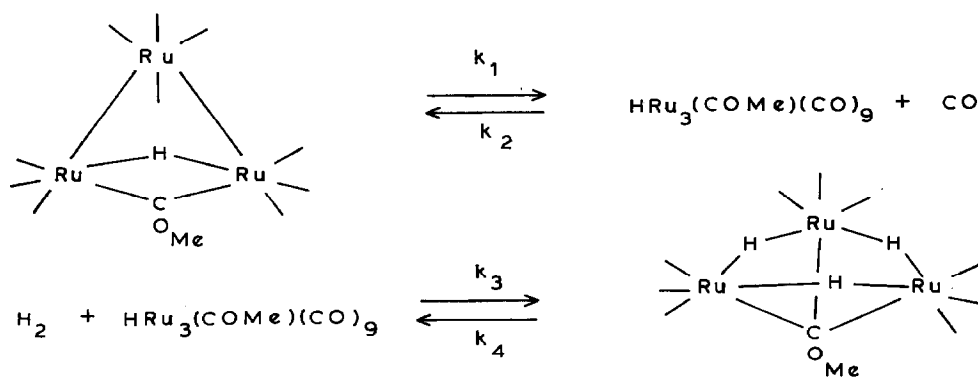
The ^{17}O spin-lattice relaxation times at 54.25 MHz and 298 K were measured for a series of metal carbonyls, including $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ and $[\text{Os}_3\text{Br}_2(\text{CO})_{12}]$ (136).

Protonation of $[\text{Os}_3\text{HX}(\text{CO})_{10}]$ ($\text{X}=\text{H}, \text{NHPH}, \text{OPh}$) with trifluoroacetic acid gives $[\text{Os}_3\text{H}_2\text{X}(\text{CO})_{10}]^+$, but reactions of $[\text{Os}_3\text{H}(\text{OH})(\text{CO})_{10}]$ with RCO_2H ($\text{R}=\text{CF}_3, \text{CH}_3, \text{CD}_3, \text{H}$) produce $[\text{Os}_3\text{H}(\text{O}_2\text{CR})(\text{CO})_{10}]$. The compounds were spectroscopically characterized (137).

Hydrogenation of $[\text{M}_3\text{H}(\mu\text{-COMe})(\text{CO})_{10}]$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$) at 1 atm and $60\text{-}120^\circ$ forms $[\text{M}_3\text{H}_3(\mu_3\text{-COMe})(\text{CO})_9]$. For Fe the product is unstable and reverts to the starting material in the absence of hydrogen, but in the presence of SbPh_3 the stable product $[\text{Fe}_3\text{H}_3(\mu_3\text{-COMe})(\text{CO})_7(\text{SbPh}_3)_2]$ can be isolated. Similarly, although $[\text{Ru}_3\text{H}(\mu\text{-CNMeBz})(\text{CO})_{10}]$ cannot be hydrogenated to a stable product, in the presence of SbPh_3 $[\text{Ru}_3\text{H}_3(\mu\text{-CNMeBz})(\text{CO})_6(\text{SbPh}_3)_3]$ can be



Scheme 19



isolated in good yield (138). The kinetics and mechanism of hydrogenation of $[\text{Ru}_3\text{H}(\mu\text{-COMe})(\text{CO})_{10}]$ to $[\text{Ru}_3\text{H}_3(\mu_3\text{-COMe})(\text{CO})_9]$ have been investigated. The reaction is quantitatively reversible; for the carbonylation of the trihydride activation parameters are $\Delta H_4^\ddagger = 31.0$ kcal and $\Delta S_4^\ddagger = +8$ eu and $k_4^{\text{H}}/k_4^{\text{D}} = 1.4$. The proposed mechanism is given in Scheme 19. An unusually small competition ratio for hydrogen to CO (k_3/k_2) was noted. It was suggested that this might be due to hydrogen addition and CO addition at different metal sites (139).

Substitution by CNR on $[\text{Ru}_3(\text{CO})_{12}]$ produces $[\text{Ru}_3(\text{CO})_{12-n}(\text{CNR})_n]$ ($\text{R}=\text{CMe}_3$, $n=1,2,3$; $\text{R}=\text{Cyc}$, $n=1$; $\text{R}=\text{C}_6\text{H}_4\text{OMe-4}$, $n=1,2$; $\text{R}=\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{Me-4}$, $n=3$). The crystal structures of $[\text{Ru}_3(\text{CO})_{12-n}(\text{CNCMe}_3)_n]$, $n=1$ [87] and 2 [88] were reported (140).

Thermally induced substitution on $[\text{Ru}_3(\text{CO})_{12}]$ by $\text{MeSi}(\text{PEt}_2)_3$ forms $[\text{Ru}_3(\text{CO})_9(\text{MeSi}(\text{PEt}_2)_3)_3]$ [89] (14% yield). The $\text{MeSi}(\text{PPr}_2)_3$ derivative was also prepared (141).

The crystal structures of $[\text{Ru}_3(\text{CO})_{11}(\text{PCyc}_3)]$, $[\text{Ru}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$, and $[\text{Ru}_3(\text{CO})_9(\text{PMe}_3)_3]$ [90] were reported (142).

Ligand substitution reactions of $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ are initiated by sodium diphenylketyl. Ligands used include isocyanides, phosphines, phosphites, arsines, and SbPh_3 . High specificity and high conversion are obtained and mixed ligand substituted products easily obtained (143).

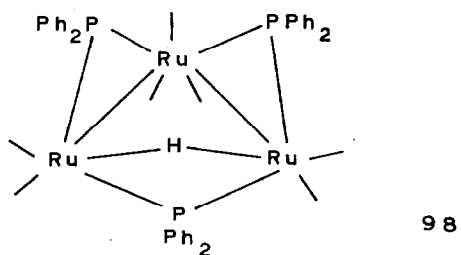
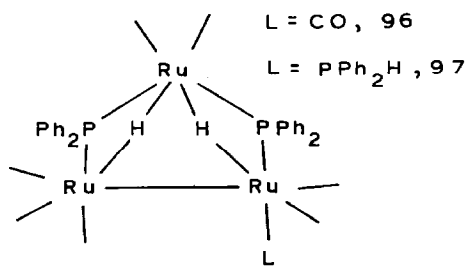
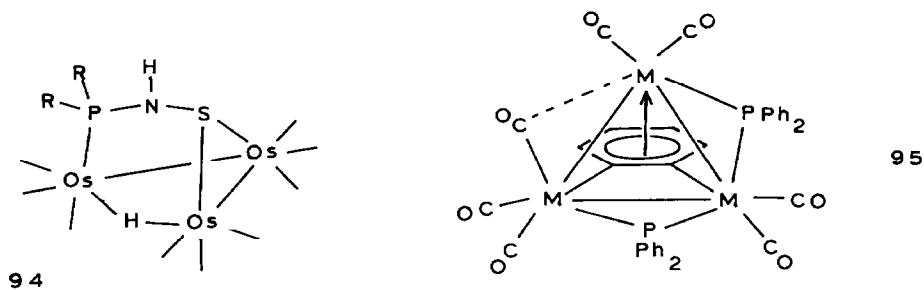
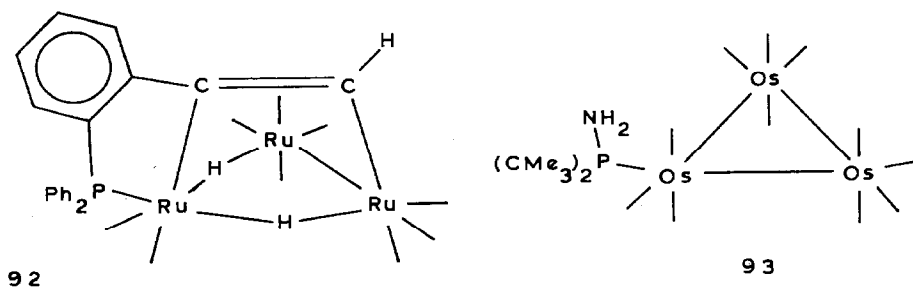
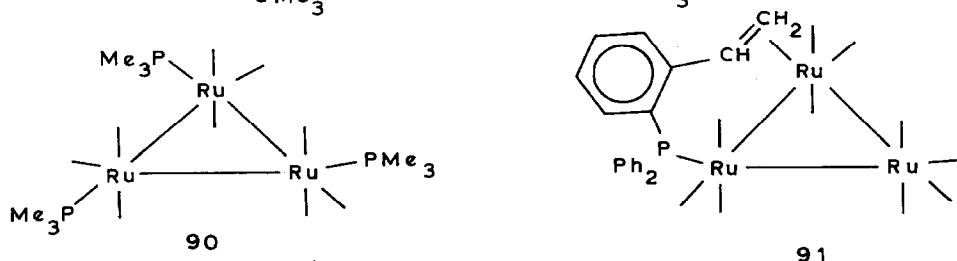
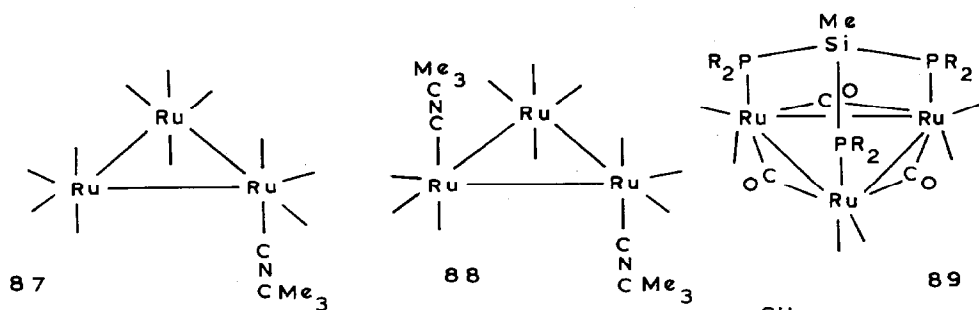
Sodium diphenylketyl was also used to initiate the reaction between $[\text{Ru}_3(\text{CO})_{12}]$ and $2\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{CH}_2$ to $[\text{Ru}_3(\text{CO})_{10}(2\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{CH}_2)]$ [91] in 74% yield. The product was characterized by X-ray crystallography. Pyrolysis of [91] in refluxing cyclohexane forms $[\text{Ru}_3\text{H}_2(\mu_3\text{-HCCC}_6\text{H}_4\text{PPh}_2)(\text{CO})_8]$ [92], the structure of which was determined by X-ray methods (144).

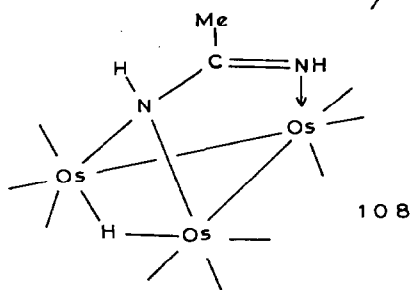
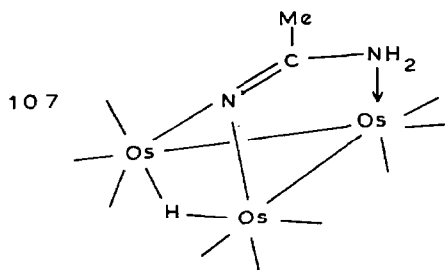
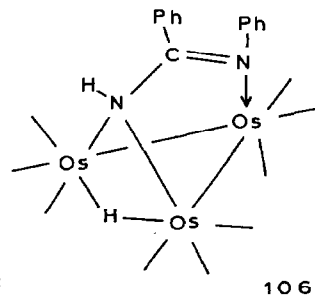
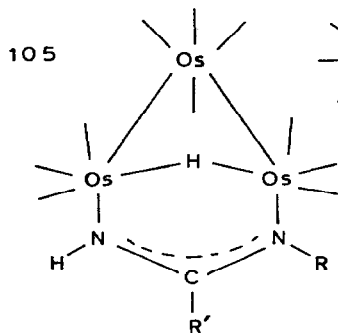
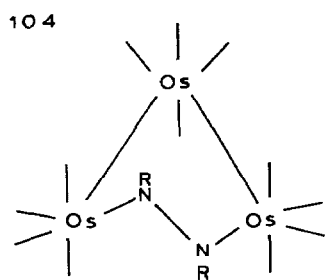
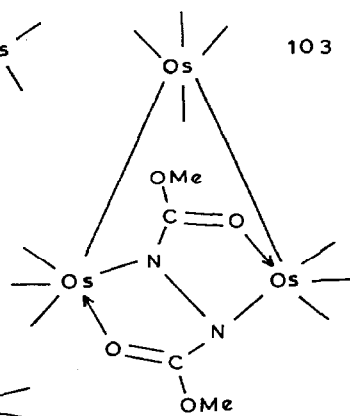
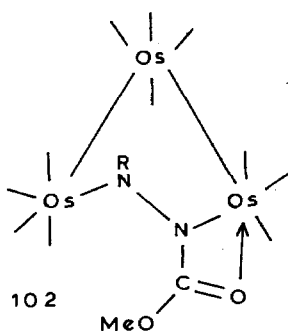
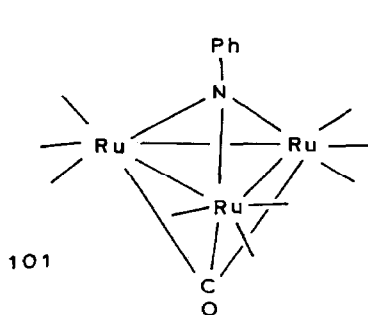
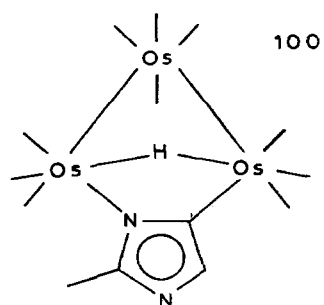
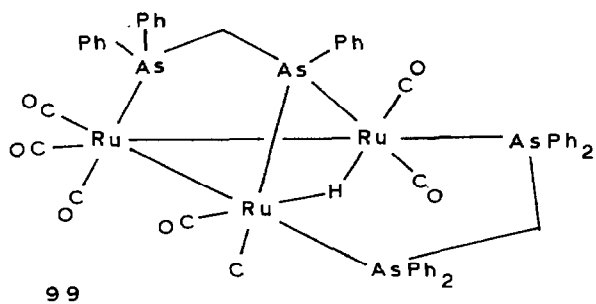
The reaction between "lightly stabilized" $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ and $\text{S}(\text{NP}(\text{CMe}_3)_2)_2$ yields $[\text{Os}_3(\text{CO})_{11}\{\text{P}(\text{CMe}_3)_2(\text{NH}_2)\}]$ [93] while the product from $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ is $[\text{Os}_3\text{H}(\text{CO})_9\text{P}(\text{CMe}_3)_2(\text{NHS})]$ [94]. The products were characterized by ^{13}C NMR spectroscopy and X-ray crystallography (145).

The crystal structures of $[\text{M}_3(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-PPh}_2)_2(\text{CO})_7]$ ($\text{M}=\text{Ru}, \text{Os}$) [95] were reported (146).

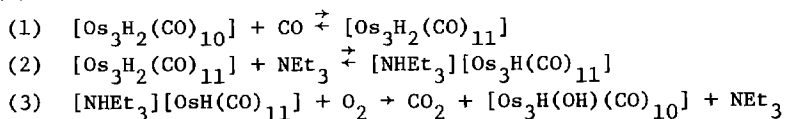
Ligand substitution on $[\text{Ru}_3(\text{CO})_{12}]$ by PPh_2H forms $[\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{H})_3]$, which on photolysis yields $[\text{Ru}_2(\mu\text{-PPh}_2)_2(\text{CO})_6]$, $[\text{Ru}_3\text{H}_2(\mu\text{-PPh}_2)_2(\text{CO})_8]$ [96], $[\text{Ru}_3\text{H}_2(\mu\text{-PPh}_2)_2(\text{CO})_7(\text{PPh}_2\text{H})]$ [97] and $[\text{Ru}_3\text{H}(\mu\text{-PPh}_2)_3(\text{CO})_7]$ [98]. All complexes were characterized spectroscopically; the crystal structure of [98] was determined (147).

Both X-ray and neutron diffraction studies of the structure of $[\text{Ru}_3\text{H}(\text{CO})_7(\text{AsPhCH}_2\text{AsPh}_2)(\text{Ph}_2\text{AsCH}_2\text{AsPh}_2)]$ [99] were described. The Ru-H bond distances are 1.791 and 1.818 Å and the Ru-H-Ru angle is 107.5° (148).





In the presence of bases such as py or DMF $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ is oxidized under CO/O_2 to $[\text{OsH}(\text{OH})(\text{CO})_{10}]$ and CO_2 in almost quantitative yield (149). The hydroxide-containing product reacts with $d_5\text{-py}$ at 20° to displace water, generating $[\text{Os}_3\text{D}(\mu\text{-NC}_5\text{D}_4)(\text{CO})_{10}]$. The oxidation reaction was shown to proceed through $[\text{Os}_3\text{H}(\text{CO})_{11}]^-$. The reaction sequence is shown in Equations (1)-(3).



The crystal structure of $[\text{Os}_3\text{H}\{\mu\text{-}3,4\text{-}\eta^2\text{-C}_3\text{N}_2\text{H}_2(2\text{-Me})\}(\text{CO})_{10}]$ [100] was determined. The angle between the Os_3 plane and the plane at the C_3N_2 ring is 100° . The $\text{Os}-\text{C}$ bond distance (2.089 Å) is slightly shorter than the $\text{Os}-\text{N}$ distance (2.153 Å) (150).

Reduction of nitrobenzene by $[\text{Ru}_3(\text{CO})_{12}]$ at 100° produces $[\text{Ru}_3(\text{CO})_{10}^-(\text{NPh})]$ [101], $[\text{Ru}_3(\text{CO})_9(\text{NPh})_2]$, and carbon dioxide in yields of 5-15%. The crystal structure of [101] was reported (151).

Dimethyl azodicarboxylate and $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ at room temperature form $[\text{Os}_3(\text{CO})_{11}(\text{MeOC}(\text{O})\text{N}_2\text{CO}_2\text{Me})]$ [102]. At 70° for 10 min. [102] is converted into $[\text{Os}_3(\text{CO})_{10}(\text{MeOC}(\text{O})\text{N}_2\text{CO}_2\text{Me})]$ [103] in 50% yield; the same product may be obtained quantitatively from $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ and dimethyl azodicarboxylate. Carbonylation of either [102] (0°) or [103] (25°) gives $[\text{Os}_3(\text{CO})_{12}(\text{MeOC}(\text{O})\text{N}_2\text{CO}_2\text{Me})]$ [104], which was characterized by X-ray crystallography (152).

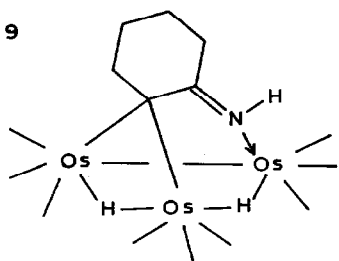
Reactions of amidines $\text{NH}=\text{CR}'\text{NHR}$ with $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ were used to prepare $[\text{Os}_3\text{H}\{\text{NRC}(\text{R}')\text{NH}\}(\text{CO})_{10}]$ [105] ($\text{R}=\text{H}$, $\text{R}'=\text{Me}$; $\text{R}=\text{R}'=\text{Ph}$). Pyrolysis of these products yields the corresponding $[\text{OsH}\{\text{NRC}(\text{R}')\text{NH}\}(\text{CO})_9]$ [106]; the crystal structure of the product with $\text{R}=\text{R}'=\text{Ph}$ was determined. In solution two tautomeric forms can be observed when $\text{R}'=\text{Me}$ and $\text{R}=\text{H}$, corresponding to [107] and [108] (153).

Both NH and CH bond activation occur as competing processes upon thermolysis of $[\text{Os}_3(\text{CO})_{11}\{\text{NHC}(\text{CH}_2)_5\}]$, forming $[\text{Os}_3\text{H}_2(\text{CO})_9\{\text{NHC}(\text{CH}_2)_4\text{C}\}]$ [109] (11%) and $[\text{Os}_3\text{H}(\text{CO})_{10}\{\text{NC}(\text{CH}_2)_5\}]$ [110] (34%); the crystal structure of [109] was reported (154).

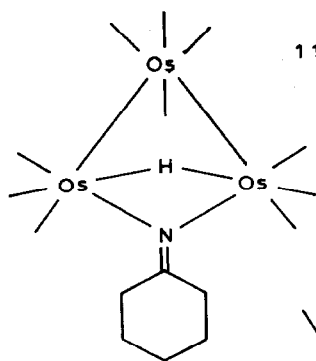
In refluxing benzene $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ and $\text{PhCH}_2\text{N}=\text{CHC}_6\text{H}_4\text{OH}-2$ produce $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{OC}_6\text{H}_3\text{CH}=\text{NHCH}_2\text{Ph})]$ [111]. In refluxing heptane this product is converted into three isomers $[\text{Os}_3\text{H}(\text{CO})_9(\text{OC}_6\text{H}_3\text{CHNHCH}_2\text{Ph})]$ [112] (6%), $[\text{Os}_3\text{H}(\text{CO})_9(\text{OC}_6\text{H}_4\text{CHNCH}_2\text{Ph})]$ [113] (8%), and $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{OC}_6\text{H}_2\text{CHNHCH}_2\text{Ph})]$ [114] (30%). The products were characterized by spectroscopic methods (155).

In refluxing acetic acid $[\text{Ru}_3\text{H}(\text{CO})_{10}(\text{NHBz})]$ [115] (8-10%) is synthesized from $[\text{Ru}_3(\text{CO})_{12}]$ and benzonitrile; $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ is also a product. The

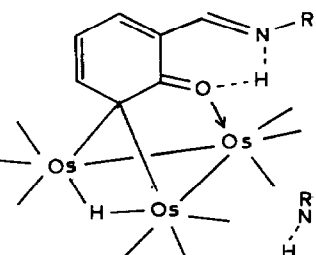
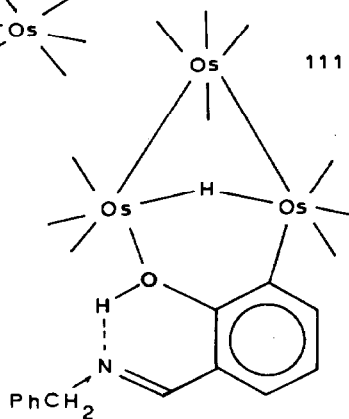
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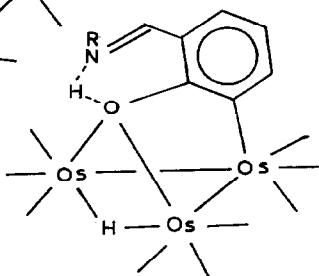


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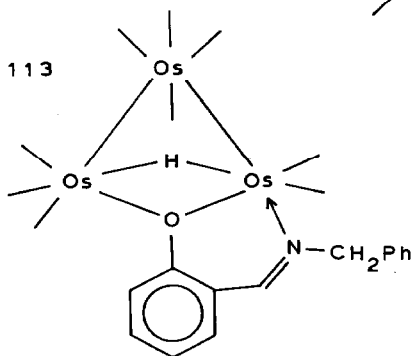


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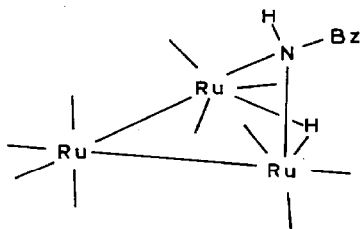
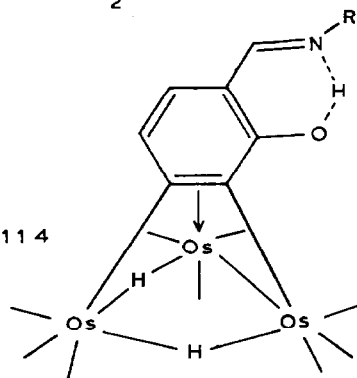
or



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115

structure of [115] was established by X-ray methods (156).

The new nitrosyl-containing clusters $[M_3(CO)_{10}(NO)]^-$ ($M=Ru, Os$) have been prepared by treatment of the appropriate $[M_3(CO)_{12}]$ with $[PPN][NO_2]$. Protonations of the anions produce the previously reported nitrosyls $[M_3H(CO)_{10}(NO)]$. In a similar fashion, $[PPN][Ru_6C(CO)_{15}(NO)]$ was prepared from $[Ru_6C(CO)_{17}]$ (157).

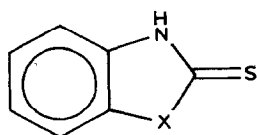
Reactions of heterocycles HL^{1-6} [116]-[121] with $[Os_3(CO)_{10}(NCMe)_2]$ generate oxidative addition products $[Os_3H(CO)_{10}L]$. The crystal structure of $[Os_3H(CO)_{10}L^5]$ [122] was reported. Decarbonylation of $[Os_3H(CO)_{10}L]$ ($L=L^1, L^2, L^6$) with trimethylamine-N-oxide or by heating ($L=L^5$) produces the corresponding $[Os_3H(CO)_9L]$ [123]. In refluxing octane $[Os_3H(CO)_9L^5]$ is converted to [124]. Both [123] and [124] exist as mixtures of two isomers differing in the position of the bridging hydride (158).

A number of products result from the reaction of $[Os_3H_2(CO)_{10}]$ with RNCS (Scheme 20). The crystal structures of $[Os_3H(SCH=NC_6H_4F-4)(CO)_{10}]$ [125], $[Os_3H(SCH=NC_6H_4F-4)(CO)_9]$ [126], and $[Os_3H(SCHNC_6H_5)(CO)_9(PMe_2Ph)]$ [127] were reported (159).

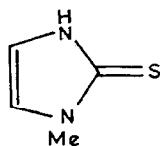
Carboxylate ligands were attached to the Ru_3 unit through reactions of $[PPN][O_2CR]$ ($R=H, Me$) with $[Ru_3(CO)_{12}]$ in THF. The crystal structure of $[PPN][Ru_3(O_2CH)(CO)_{10}]$ [128] was determined. Qualitatively, the rate of ^{13}CO exchange was found to decrease in the order: $[Ru_3(O_2CMe)(CO)_{10}]^- > [Ru_3(O_2CH)(CO)_{10}]^- > [Ru_3(N_2C_4H_4)(CO)_{10}]$. The carbonyls of [128] are fluxional, with the process with the lowest activation energy involving exchange of six CO's in the Ru_3 plane. The formate complex reacts reversibly with CO at elevated temperatures, giving $[Ru_3H(CO)_{11}]^-$ and carbon dioxide (160).

Insertion of ethylene into a Ru-H bond and then CO insertion generates $[Ru_3(X)(O=CET)(CO)_{10}]$ [129] ($X=Cl, Br$; 60-80%) from $[Ru_3HX(CO)_{10}]$ under a C_2H_4/CO atmosphere. Propene reacts in a similar fashion, forming $[Ru_3Br(O=CPr)(CO)_{10}]$ with the $n\text{-Pr}/i\text{-Pr}$ ratio of 10. Ethylene and $Na[M_3H(CO)_{11}]$ form a product which can be protonated to $[M_3H(O=CET)(CO)_{10}]$ [130]. When $M=Ru$, [130] reacts further with ethylene, yielding $[Ru_3(CO)_{12}]$ and $[Ru_2(O=CET)_2(CO)_6]$ [131] (91%), characterized by X-ray crystallography. Similarly, $[Ru_3H(O=CR)(CO)_{10}]$ ($R=Me, Ph, NMe_2$) and ethylene yield $[Ru_2(O=CET)(O=CR)(CO)_6]$ [132] (90-100%) (161).

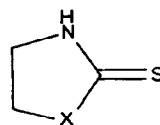
Treatment of $[Ru_3H(O=CMe)(CO)_{10}]$ with methyllithium at -30° yields $[Ru_3(\eta^1\text{-C(O)Me})(\mu\text{-H})(\mu\text{-O=CMe})(CO)_9]^-$ [133], which, when treated with ethyl trifluoromethanesulfonate, forms $[Ru_3H_2(\mu_3\text{-}\eta^2\text{-EtOC=CH})(CO)_9]$ [134] (80%) and acetaldehyde. Labeling studies prove that the starting acetyl is lost as acetaldehyde. Analogous reactions with other nucleophiles were investigated (Scheme 21) (162).



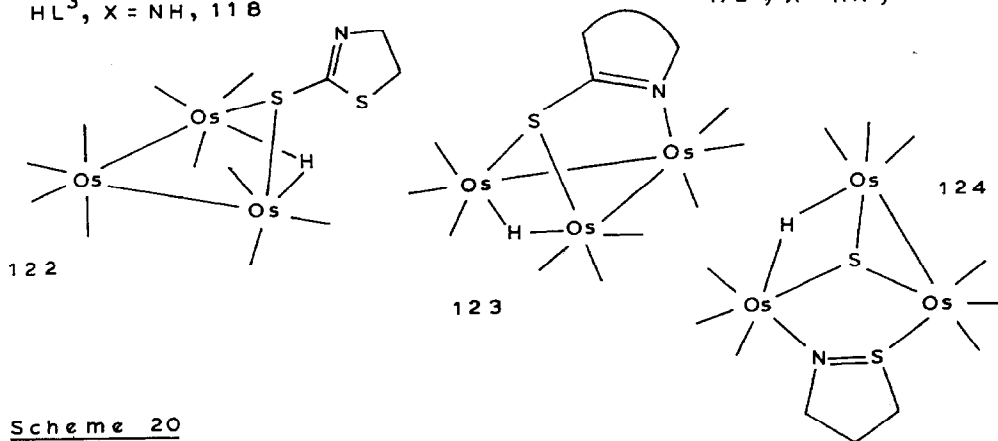
HL¹, X = O, 116
 HL², X = S, 117
 HL³, X = NH, 118



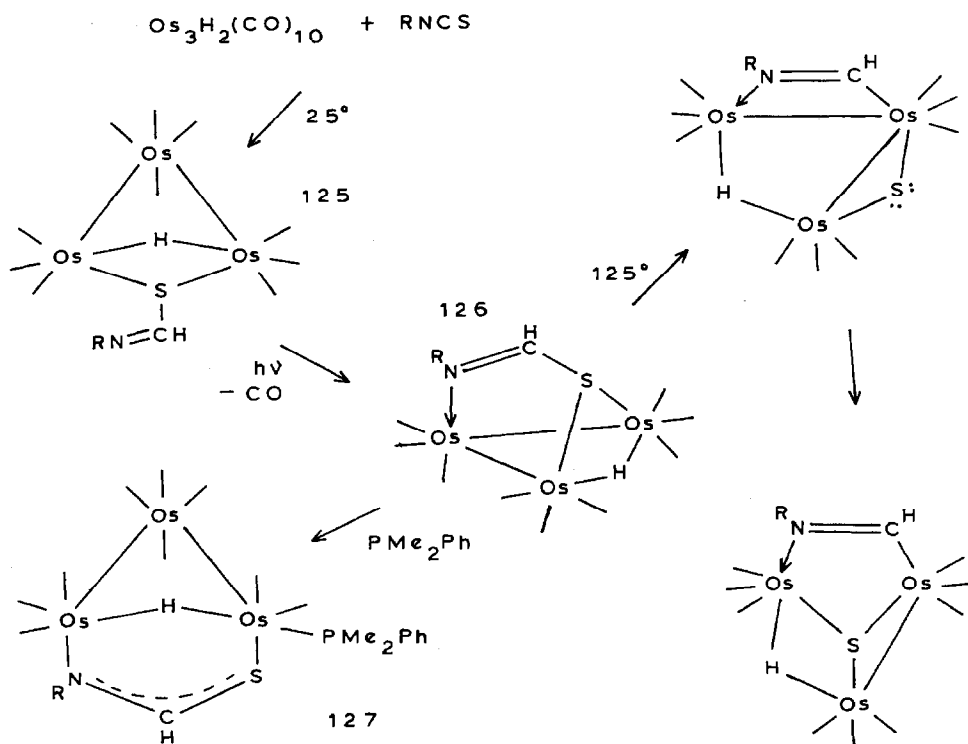
HL⁴, 119

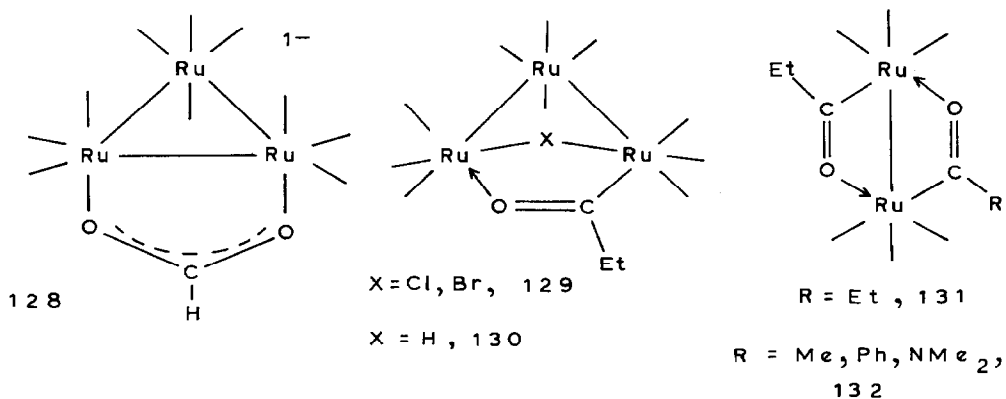


HL⁵, X = S, 120
 HL⁶, X = NH, 121

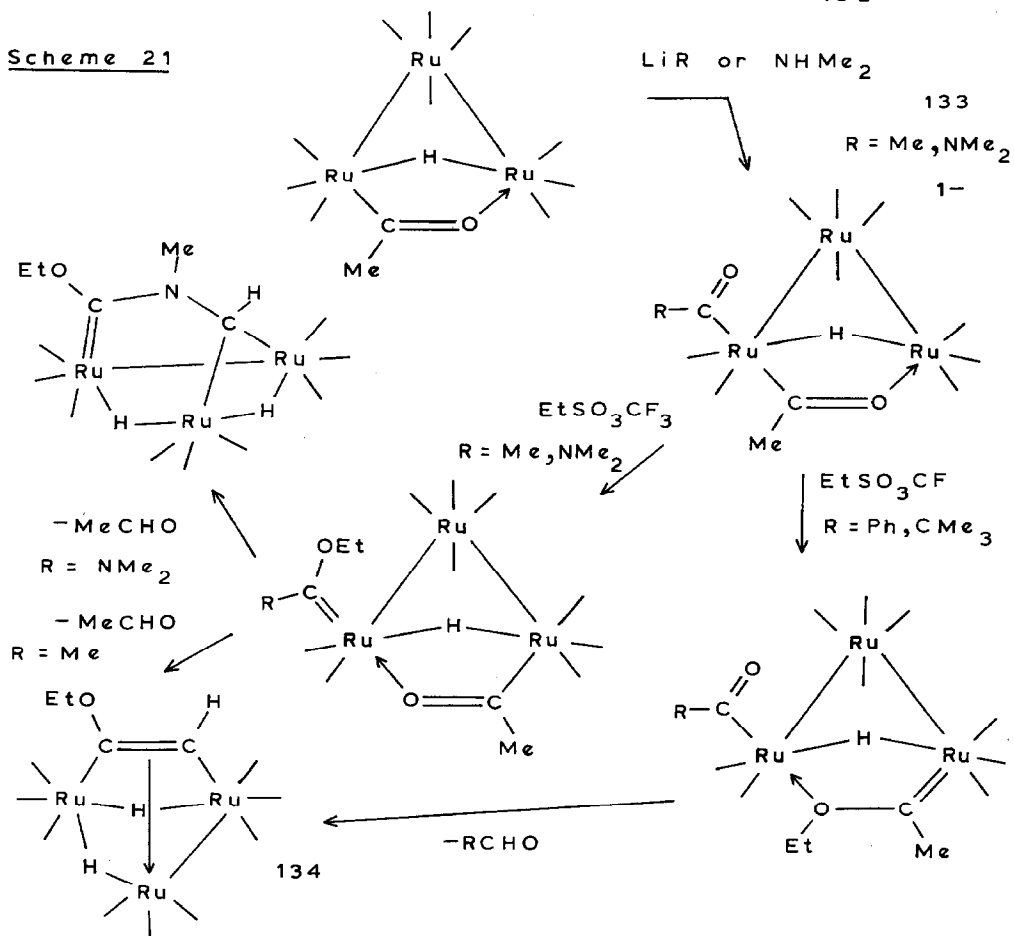


Scheme 20





Scheme 21



A polarographic study was made of the reduction of $[\text{Os}_3(\mu\text{-X})_2(\text{CO})_8\text{L}_2]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$; $\text{L}=\text{CO}, \text{PPh}_3, \text{P}(\text{OPh})_3$). The reduction potential depends little upon the halogen (376).

The photoelectron spectrum of $[\text{Ru}_3\text{H}_2(\text{CO})_9(\mu_3\text{-S})]$ was recorded and Fenske-Hall calculations were used to assign the bands. Results were compared with those from studies of the Fe and Fe-Co analogs (163). Photoelectron spectra of $[\text{M}_3\text{H}_2(\text{CO})_9(\mu_3\text{-S})]$ (M=Ru,Os), when compared with the corresponding $[\text{M}_3(\text{CO})_{12}]$, indicate a loss of direct M-M interactions and the appearance of bands due to a mixture of energy-equivalent M-H-M and M-S interactions (164).

Reactions of thiobenzophenone with Os_3 clusters have been investigated. The product from $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ is $[\text{Os}_3\text{H}(\text{SCHPh}_2)(\text{CO})_{10}]$ [135] (165). With $[\text{OsH}_2(\text{CO})_9(\text{NMe}_3)]$, fast addition yields $[\text{Os}_3\text{H}_2(\text{CO})_8(\text{C}(\text{O})\text{CPh}_2\text{S})(\text{SCHPh}_2)]$ [136], while slow addition yields $[\text{Os}_3\text{H}(\text{SCHPh}_2)(\text{CO})_9(\text{SCHPh}_2)]$ [137] (166). All products were characterized by X-ray crystallography.

Coupling of two Os_3 units was achieved through the reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with $\text{HS}(\text{CH}_2)_3\text{SH}$. The product, $[\{\text{Os}_3\text{H}(\text{CO})_{10}(\text{SCH}_2)_2\text{CH}_2\}]$, was formed in 20% yield and its crystal structure was determined (167).

Oxidative addition of HSiPh_3 to $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ at 70° produces $[\text{Os}_3\text{H}_3(\text{CO})_9(\text{SiPh}_3)]$ [138] in 58% yield. The product was characterized by ^{13}C and ^1H NMR spectroscopy and by X-ray crystallography. Exchange of the hydride ligands on the doubly bridged edge was established by spin saturation transfer experiments at 25° . At 75° the third hydride begins to exchange (168).

Oxidative addition of HSiCl_2X to $[\text{Os}_3(\text{CO})_{12}]$ at 140° yields trans- $[\text{Os}(\text{CO})_4(\text{SiCl}_2\text{X})_2]$ (25%) and $[\text{Os}_3(\text{CO})_{12}(\text{SiXCl}_2)_2]$ [139] (X=Cl (46%), Me (61%)). The crystal structure of the chloride derivative was determined. The same reaction involving $[\text{Ru}_3(\text{CO})_{12}]$ produces only $[\text{Ru}(\text{CO})_4(\text{SiCl}_3)_2]$ and $[\{\text{Ru}(\text{CO})_4(\text{SiCl}_3)\}_2]$. The crystal structure of $[\text{Os}_3\text{H}_3(\text{CO})_9(\text{SiCl}_3)_3]$ [140] was also reported (169).

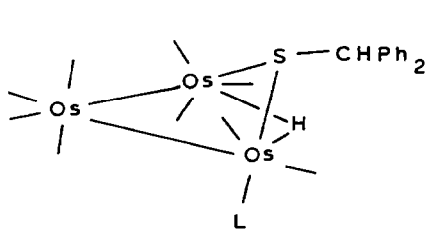
The reaction of PR_3 with $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{10}(\text{SiR}'_2\text{R}'')_2]$ forms $[\text{Ru}_3(\text{CO})_9(\text{SiR}'_2\text{-R}'')(\text{PR}_3)_2]^-$, isolated as the PPN salts. The proposed structure of the products is [141] (170).

The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with PhC_2X (X=Cl,Br) yields $[\text{Ru}_3(\text{CO})_9\text{X}(\mu_3\text{-}\eta^2\text{-C}_2\text{Ph})]$ [142]. The crystal structure of the chloride derivative was determined (171).

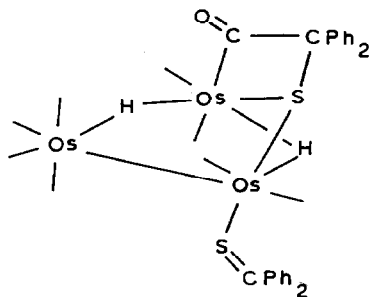
The crystal structure of $[\text{Os}_3(\text{CHSiMe}_3)(\text{CO})_{11}]$ [143] was reported (172).

Insertion of CO into the Os- CH_2 bond of $[\text{Os}_3(\text{CO})_{11}(\text{CH}_2)]$ generates $[\text{Os}_3(\text{CO})_{12}(\eta^2(\text{C,C}), \mu\text{-CH}_2\text{CO})]$ [144], characterized by X-ray crystallography and spectroscopic methods. Labeling studies showed that an equilibrium between $[\text{Os}_3(\text{CO})_{11}(\text{CH}_2)]$ and $[\text{Os}_3(\text{CO})_{10}(\text{CH}_2\text{CO})]$ precedes CO addition. $[\text{Os}_3(\text{CO})_{12}(\text{CH}_2\text{CO})]$ reacts further with CO, producing $[\text{Os}_3(\text{CO})_{12}]$, and with ROH to give $\text{CH}_3\text{CO}_2\text{R}$ (R=H,Me) and $[\text{Os}_3(\text{CO})_{12}]$ (173).

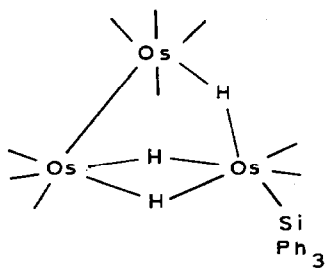
Attack by LiBHET_3 on the carbyne ligand of $[\text{Os}_3\text{H}(\text{COMe})(\text{CO})_{10}]$ gives initially $[\text{Os}_3\text{H}(\text{CHOMe})(\text{CO})_{10}]^-$ (70%); protonation of the product with



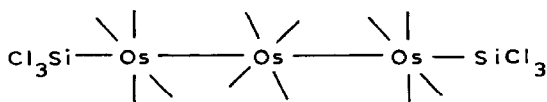
135, L = CO



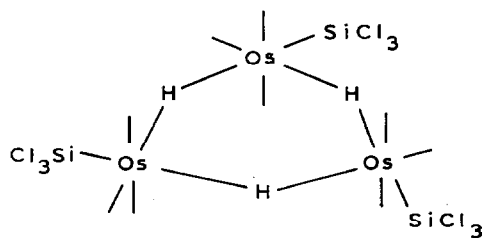
136

137, L = S C Ph₂

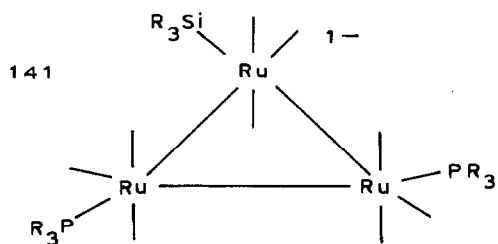
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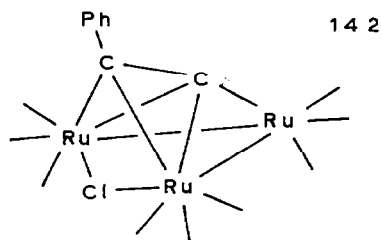
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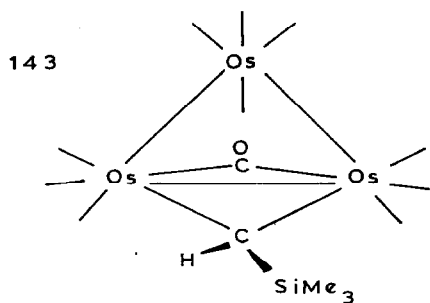
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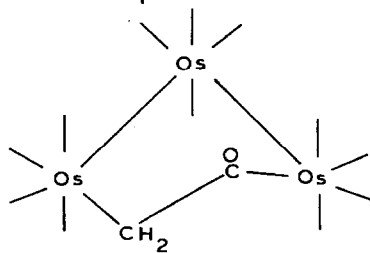
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142



143



144

trifluoroacetic acid at -60° forms $[\text{Os}_3\text{H}(\text{CH})(\text{CO})_{10}]$ [145] (70%). The crystal structure of [145] reveals an asymmetrical μ_3 -CH ligand with the C-H vector bent toward the unique Os atom; this is attributed to the donor-acceptor nature of the $\text{Os}\rightarrow\text{CH}$ bond. Displacement of this interaction by py generates an adduct between the py and methylidyne. The methylidyne complex was also reacted with LiBHET_3 and N_2CHR , forming $[\text{Os}_3\text{H}(\text{CH}_2)(\text{CO})_{10}]^-$ and $[\text{OsH}(\text{CH}=\text{CHR})(\text{CO})_{10}]$, respectively. These reactions are summarized in Scheme 22 (174).

Hydride migration to the coordinated vinyl group of $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{CF}_3\text{C}=\text{CHCF}_3)]$ [146] is induced by bromide ion, yielding $[\text{Os}_3(\text{CO})_{10}(\text{trans-CF}_3\text{CH}=\text{CHCF}_3)\text{Br}]^-$ [147] (75%), characterized by X-ray crystallography. At 40° in dichloromethane [147] is converted into $[\text{Os}_3(\text{CO})_9(\text{trans-CF}_3\text{CH}=\text{CHCF}_3)\text{Br}]^-$ [148] (40%), also characterized by X-ray crystallography. Treatment with Me_3O^+ converts [147] into approximately equal amounts of $[\text{Os}_3\text{HBr}(\text{CO})_{10}]$ and $[\text{Os}_3(\text{CO})_{11}(\text{trans-CF}_3\text{CH}=\text{CHCF}_3)]$ [149]. On the other hand, treatment of [147] with methyl fluorosulfonate produces [149] and $[\text{Os}_3\text{H}(\text{CO})_9(\text{trans-CF}_3\text{CH}=\text{CHCF}_3)\text{Br}]$ [150], characterized by X-ray crystallography (175).

The alkyne complex $[\text{Os}_3(\text{CO})_{10}(\text{HC}_2\text{CH}_2\text{CH}_2\text{OH})]$, formed from $\text{HC}_2\text{CH}_2\text{CH}_2\text{OH}$ and $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$, is converted in refluxing heptane to $[\text{Os}_3\text{H}(\text{C}_2\text{CH}_2\text{CH}_2\text{OH})(\text{CO})_9]$ (90%); upon treatment with silica, the acetylide product cyclizes to $[\text{Os}_3\text{H}_2(\text{CO})_9(\mu_3\text{-C}=\text{CCH}_2\text{CH}_2\text{O})]$. The cyclized product is also formed in 48% yield through the direct reaction of $[\text{Os}_3(\text{CO})_{12}]$ and $\text{HC}_2\text{CH}_2\text{CH}_2\text{OH}$. These transformations are shown in Scheme 23 (176).

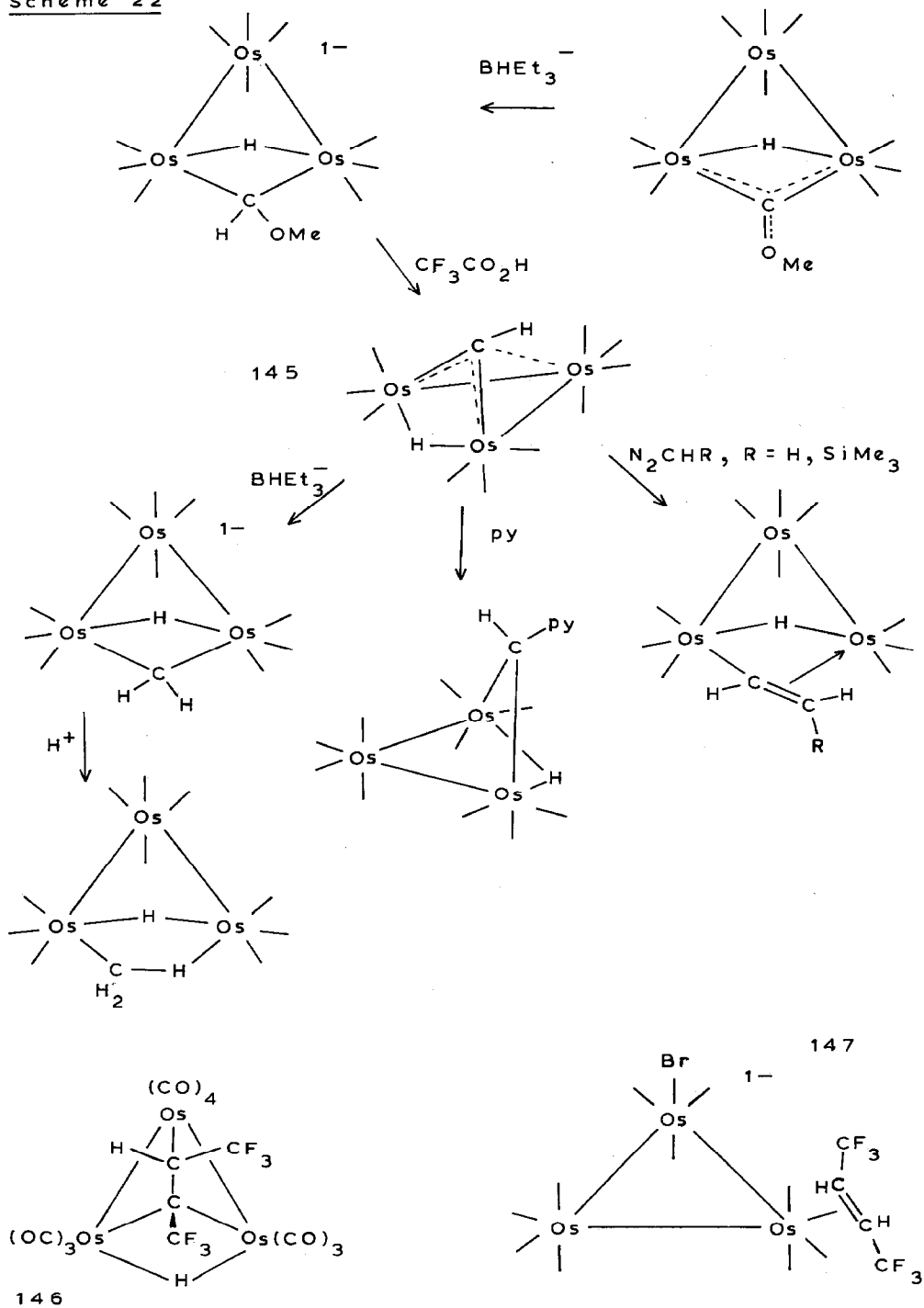
The crystal structure of $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{CH}=\text{CHCMe}_3)]$ [151], formed from $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ and HC_2CMe_3 , was reported. Side products from the synthesis in the presence of excess alkyne include $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{C}=\text{CHCMe}_3)]$ and $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{HC}=\text{CCMe}_3)]$ (177).

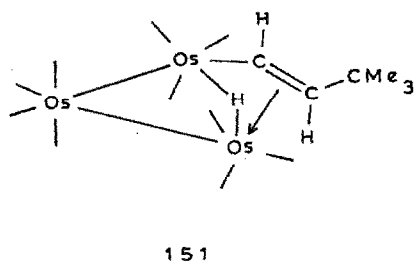
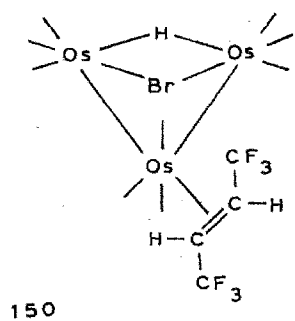
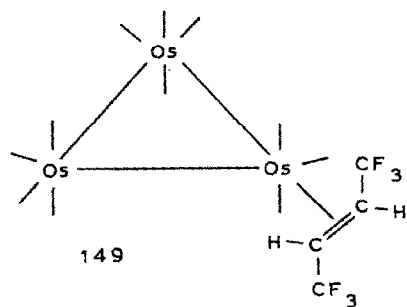
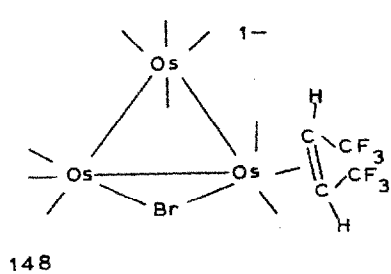
Vibrational modes for C_2H_n units attached to trinuclear clusters have been assigned. The IR and Raman spectra of the C_2H_2 ligand of $[\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-C}_2\text{H}_2)]$ were analyzed and compared with EEL spectra for C_2H_2 on Pt(111) and Pd(111) surfaces (178). Vibrational assignments for the vinyl group of $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{CH}=\text{CH}_2)]$ and the vinylidene of $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{C}=\text{CH}_2)]$ were made from a normal coordinate analysis of $\text{Os}_3(\text{C}_2\text{H}_n)$ ($n=3,2$) fragments and from spectra of deuterated clusters. The principal C=C stretching frequencies were assigned at 1311 and 1331 cm^{-1} , respectively (179).

Photoelectron spectra and CNDO calculations for $[\text{M}_3\text{H}(\text{CO})_9(\text{C}_2\text{R})]$ ($\text{M}=\text{Ru}$, $\text{R}=\text{CMe}_3$; $\text{M}=\text{Os}$, $\text{R}=\text{Me}$; $\text{M}=\text{Os}$, $\text{R}=\text{CMe}_3$) were reported. Bonding of the acetylide to the cluster is described in terms of one sigma and two weaker pi interactions, but the bridging hydride has a low bond overlap population (180).

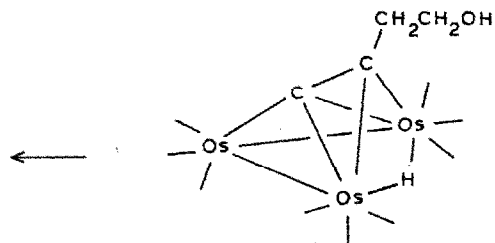
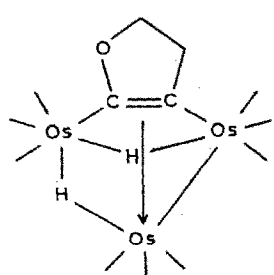
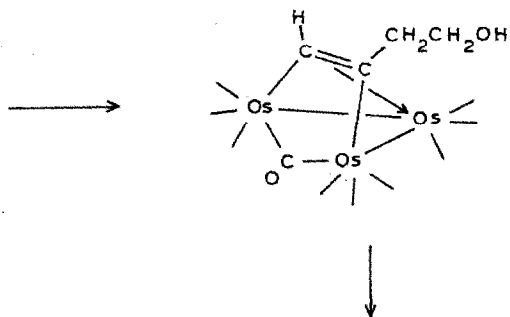
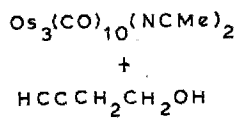
Nucleophilic attack by isocyanides upon coordinated acetylides has

Scheme 22





Scheme 23



been observed. The reaction between $[\text{Ru}_3\text{H}(\text{CO})_9(\text{C}_2\text{Ph})]$ and CNCMe_3 forms $[\text{Ru}_3\text{H}(\text{CO})_9\{\text{C}(\text{CNCMe}_3)\text{CPh}\}]$ [152] in 20% yield and the analogous reaction with $[\text{Os}_3(\text{CO})_9(\text{PPh}_2)(\text{C}_2\text{Ph})]$ gives $[\text{Os}_3(\text{CO})_9(\text{PPh}_2)\{\text{C}(\text{CNCMe}_3)\text{CPh}\}]$ [153] in 94% yield. Nucleophilic addition of butylamine to [153] forms $[\text{Os}_3(\text{CO})_9(\text{PPh}_2)\{\text{C}(\text{C}(\text{NHCMe}_3)\text{NHBu})\text{CPh}\}]$ [154] (98%). Products [152] and [154] were structurally characterized (181).

Oxidative addition of aryl C-H bonds occurs upon reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with $\text{C}_6\text{H}_4\text{RR}'$ to form $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{C}_6\text{H}_4\text{RR}')] (R=\text{H}, R'=\text{H}, \text{Me}, \text{Pr}, \text{CH}=\text{CHPh}, \text{Cl}; R=R'=\text{Me})$ in 20-37% yield. The crystal structure of the C_6H_4 adduct [155] was reported. Two isomers were observed for the products from toluene and from chlorobenzene (182).

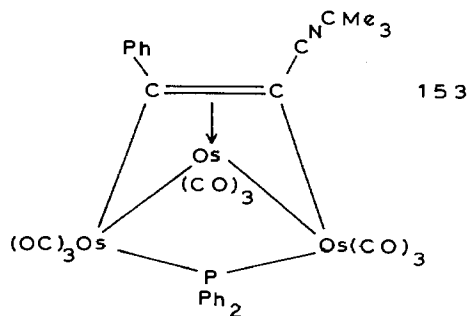
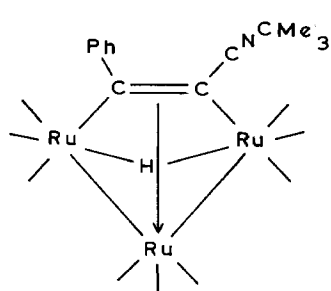
Treatment of $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ with both B_2H_6 and $\text{BH}_3 \cdot \text{NET}_3$ generates $[\text{Os}_3\text{H}_3(\text{CO})_9(\text{BCO})]$ [156] (85%) and hydrogen (91%); the cluster product was characterized by X-ray crystallography. In the presence of excess THF, $[\{\text{Os}_3\text{H}_3(\text{CO})_9\}_3(\text{B}_3\text{O}_3)]$ is formed. Although the CO attached to the B atom of [156] does not exchange with ^{13}CO at 25° , PMe_3 displacement of CO forms $[\text{Os}_3\text{H}_3(\text{CO})_9(\text{BPMe}_3)]$ (183).

The closely related ketylidene cluster $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{CCO})]$ [157] is formed in up to 75% yield by heating $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{CH})]$ [145] (refluxing hexane or sublimation at 85°). The product was structurally characterized; the C-C-O angle is 178.6° and the C-C and C-O bond distances are 1.264 and 1.154 Å, respectively. The mechanism for formation of [145] is proposed to involve thermal rearrangement to $[\text{Os}_3\text{H}(\text{CO})_9(\text{HC}=\text{C}=\text{O})]$. Protonation of [145] gives $[\text{Os}_3\text{H}_3(\text{CO})_9(\text{CCO})]^+$, while hydrogenation in refluxing heptane produces $[\text{Os}_3\text{H}_3(\text{CO})_9(\text{CH})]$ (54%), implying that HC-CO coupling is reversible (184).

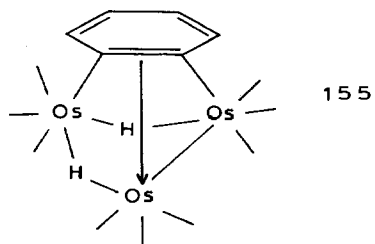
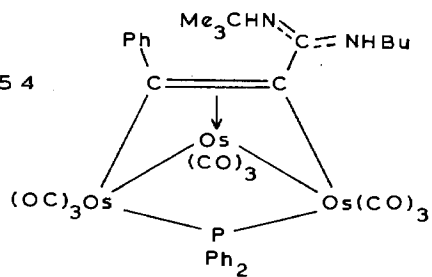
Methylidyne-alkyne coupling occurs upon reaction of either $[\text{Ru}_3\text{H}_3(\text{CO})_9(\mu_3\text{-CX})]$ ($X=\text{OMe}, \text{Me}, \text{Ph}$) or $[\text{Ru}_3\text{H}(\text{CO})_{10}(\mu\text{-CX})]$ ($X=\text{OMe}$) with C_2R_2 , forming $[\text{Ru}_3\text{H}(\text{CO})_9(\mu_3\text{-}\eta^3\text{-XCRCR})]$ [158]. Terminal alkynes give two possible coupled products, the more abundant being $[\text{Ru}_3\text{H}(\text{CO})_9(\mu_3\text{-}\eta^3\text{-XCCHCR})]$. When $X=\text{OMe}$, hydrogenation (1 atm, 90°) generates new alkylidyne clusters $[\text{Ru}_3\text{H}_3(\text{CO})_9(\mu_3\text{-CCHRCH}_2\text{R})(\text{CO})_9]$ (185).

The new cluster $[\text{Ru}_3\text{H}_3(\text{CO})_3\text{Cp}_3]$ [159] was prepared in 40-60% yield by photolysis of $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CHR})\text{Cp}_2]$ ($R=\text{H}, \text{Me}, \text{CO}_2\text{H}$) under hydrogen; the product was characterized by X-ray crystallography. Also formed in the reaction were $[\text{Ru}_3(\mu\text{-CO})_3(\mu_3\text{-CR})\text{Cp}_3]$ (10-20%) and $[\text{Ru}_4(\mu_3\text{-CO})_4\text{Cp}_4]$ (30%). Protonation of [159] with HBF_4 yields $[\text{Ru}_3(\mu\text{-H})_3(\mu_3\text{-H})(\text{CO})_3\text{Cp}_3][\text{BF}_4]$. Pyrolysis of [159] in refluxing toluene and in the presence of ethylene yields $[\text{Ru}_3(\mu\text{-CO})_3(\mu_3\text{-CMe})\text{Cp}_3]$ (56%) and $[\text{Ru}_2(\text{CO})(\text{C}_2\text{H}_4)(\mu\text{-CO})_2\text{Cp}_2]$ (9%). The reaction of [159] with acetylene gives $[\text{Ru}_3(\text{CO})_3(\mu\text{-CH}=\text{CH}_2)\text{Cp}_3]$ (45%) and $[\text{Ru}_3(\mu\text{-CO})_3(\mu_3\text{-CMe})\text{Cp}_3]$ (16%) (186).

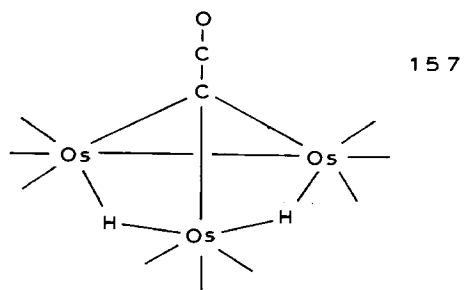
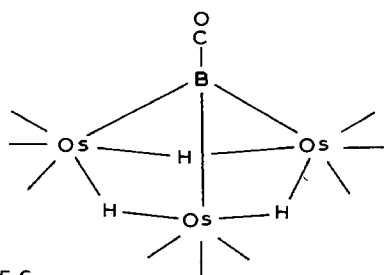
152



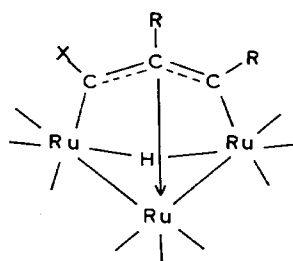
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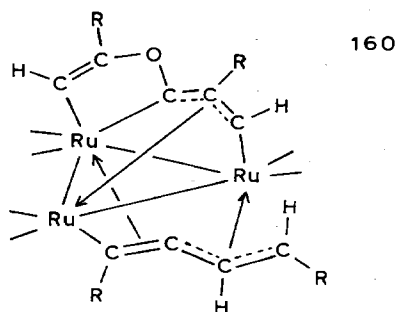
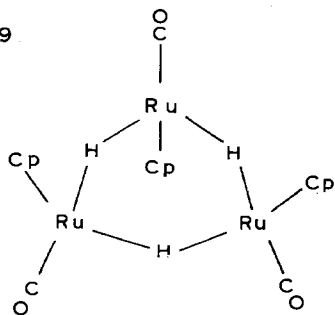
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158



159



The ^1H NMR spectra of the ortho-metallated cluster $[\text{Os}_3\text{H}(\text{CO})_8(\text{C}_4\text{Ph}_4-\text{C}_6\text{H}_4)]$ and the p-chlorinated analog were assigned. The proton ortho to the Os-C bond is strongly deshielded (187).

Excess HC_2CMe_3 reacts with $[\text{Ru}_3(\text{CO})_6(\text{C}_{12}\text{H}_{20})(\text{C}_{13}\text{H}_{20}\text{O})]$ (isomers [160] and [161], $\text{R}=\text{CMe}_3$), forming two isomers $[\text{Ru}_3(\text{CO})_5(\text{C}_{12}\text{H}_{20})(\text{C}_{19}\text{H}_{30}\text{O})]$ ([162] and [163], $\text{R}=\text{CMe}_3$). The crystal structure of [163] was reported. The isomers [160] and [161] arise from coupling of HC_2CMe_3 to $[\text{Ru}_3\text{H}(\text{CO})_9(\text{C}_2\text{CMe}_3)]$ (188).

Hydrogenation of cyclohexadiene by $[\text{Ru}_3\text{H}_3(\mu\text{-CX})(\text{CO})_9]$ ($\text{X}=\text{OMe}, \text{Ph}$) produces one equivalent of cyclohexene and the cyclohexadiene complex $[\text{Ru}_3\text{H}(\mu_3\text{-CX})(\text{CO})_8(\text{C}_6\text{H}_8)]$ [164], characterized by X-ray crystallography for the OMe derivative. The structure of [164] was compared with that of $[\text{Ru}_3\text{H}(\mu\text{-COMe})(\text{CO})_{10}]$, which was re-determined (189).

Tetranuclear and Larger Clusters

The vibrational spectra of $[\text{M}_4\text{H}_4(\text{CO})_{12}]$ ($\text{M}=\text{Ru}, \text{Os}$) were assigned (190).

An X-ray crystallographic study of the chiral cluster $[\text{Ru}_4\text{H}_4(\text{CO})_9(\text{PMe}_2\text{-Ph})\{\text{P}(\text{OC}_6\text{H}_4\text{Me-4})_3\}\{\text{P}(\text{OCH}_2)_3\text{CET}\}]$ was reported (191).

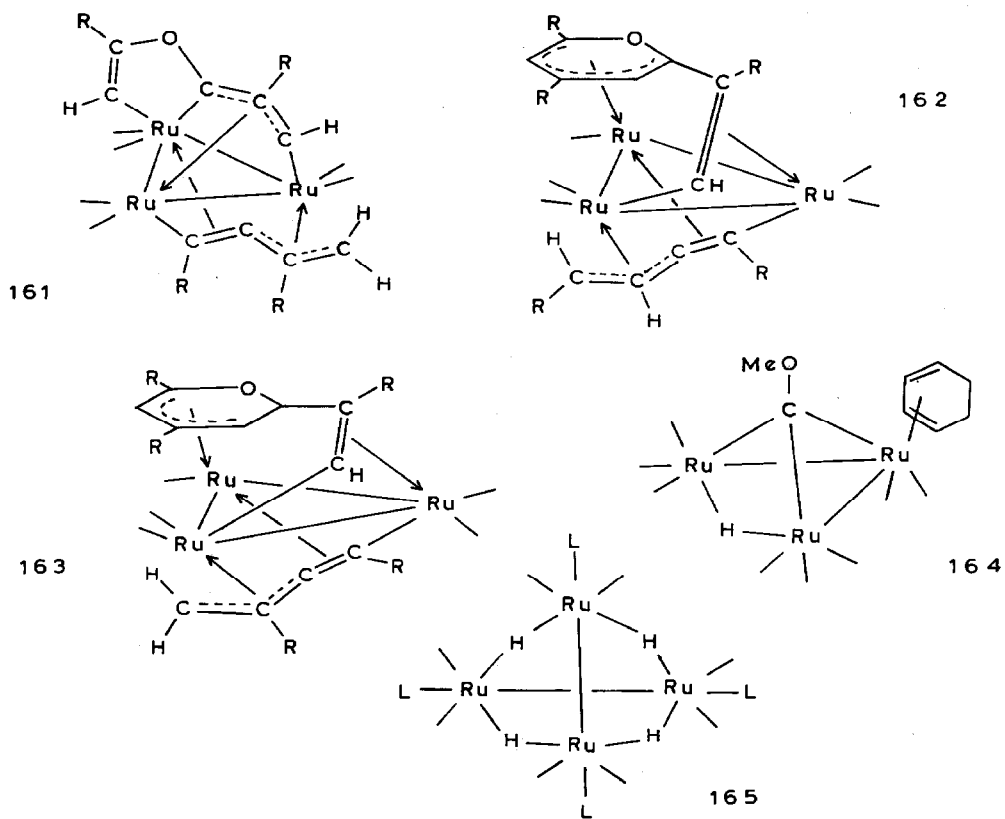
Both X-ray and neutron diffraction at 293 and 20 K, respectively, were used to determine the structure of $[\text{Ru}_4\text{H}_4(\text{CO})_8\{\text{P}(\text{OMe})_3\}_4]$ [165], including location of the hydrides. All Ru-H-Ru bridges are symmetrical (192).

The kinetics and mechanism of fragmentation of $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$ under CO to form $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{Ru}(\text{CO})_5]$ and hydrogen were investigated. The rate law is of the form $k[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$, where $k = a[\text{CO}]/(1+b[\text{CO}])$. A small and normal deuterium isotope effect was found and the reaction is retarded by hydrogen. The proposed mechanism is shown in Scheme 24 (193).

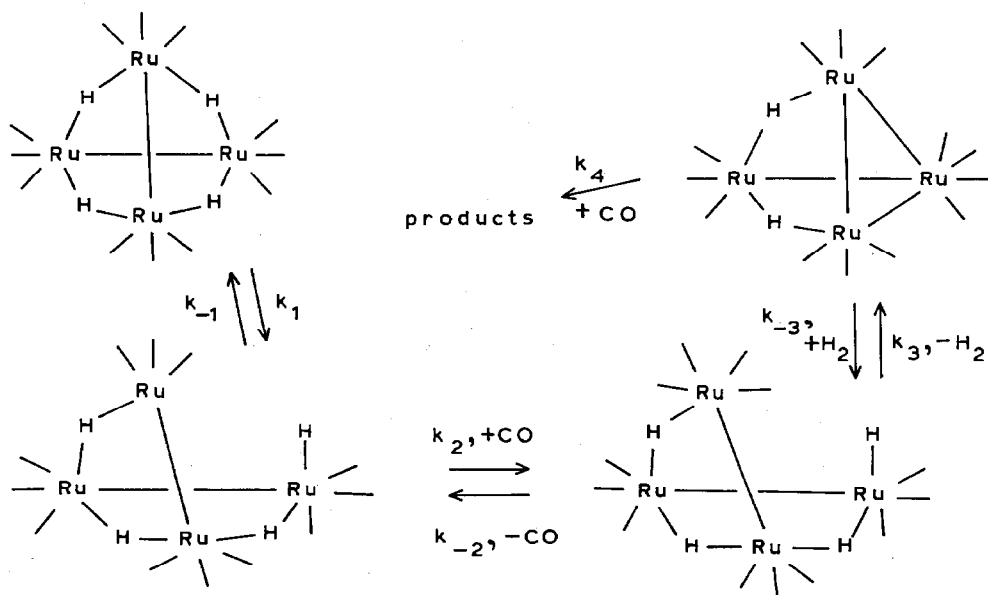
The butterfly cluster $[\text{Ru}_4(\mu_4\text{-}\eta^2\text{-p-HC}_2\text{C}_6\text{H}_4\text{PPh}_2)(\text{CO})_{11}]$ [166] can be prepared in 17% yield by pyrolysis of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta\text{-p-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2)]$ [91] at 135° . The product, which was characterized by X-ray crystallography, can also be obtained from $[\text{Ru}_3\text{H}_2(\mu_3\text{-}\eta^2\text{-p-HC}_2\text{C}_6\text{H}_4\text{PPh}_2)(\text{CO})_8]$ [92] and $[\text{Ru}_3(\text{CO})_{12}]$ (194).

Sodium diphenylketyl reduction of $[\text{Ru}_3(\text{CO})_{12}]$ under carefully controlled conditions can be used to prepare the new cluster anions $[\text{Ru}_4(\text{CO})_{11}]^{6-}$ and $[\text{Ru}_4(\text{CO})_{12}]^{4-}$, in addition to $[\text{Ru}_3(\text{CO})_{11}]^{2-}$, $[\text{Ru}_4(\text{CO})_{13}]^{2-}$, or $[\text{Ru}_6(\text{CO})_{18}]^{2-}$. Reduction of $[\text{Ru}_6(\text{CO})_{18}]^{2-}$ gives either $[\text{Ru}_6(\text{CO})_{17}]^{4-}$ or $[\text{Ru}_6(\text{CO})_{16}]^{6-}$. The stoichiometry determines the cluster anions obtained (195,196).

Photoelectron spectra and CNDO calculations were used to investigate the electronic structure of $[\text{Ru}_4(\text{CO})_{12}(\text{C}_2\text{R}_2)]$. The "hinge" Ru atoms seem to be involved in both donation and back-donation with the alkyne while the wing-tip Ru atoms are involved in donation only (197).



Scheme 24



Oxidation of $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$ with $[\text{NO}][\text{PF}_6]$, obtained from commercial sources, in acetonitrile gave $[\text{Os}_4\text{H}_4(\text{CO})_{12}]$, $[\text{Os}_4\text{H}_3(\text{OH})(\text{CO})_{12}]$ [167], and $[\text{Os}_4\text{H}_3(\mu\text{-OPO}_3\text{H})(\text{CO})_{12}]$ [168]. The crystal structure of a co-crystallized mixture of the last two (1:2 ratio) was determined. The orthophosphate product was believed to be formed from orthophosphoric acid contamination. Under dry conditions the product of the reaction is $[\text{Os}_4\text{H}_4(\mu\text{-NO})(\text{CO})_{12}]$ (198).

Oxidation of $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$ with NOX ($\text{X}=\text{BF}_4$ or PF_6) in acetonitrile produces initially $[\text{Os}_4\text{H}_3(\text{CO})_{12}(\text{NCMe})_2]\text{X}$ [169], characterized by X-ray crystallography. Reactions of [169] with halide ions $\text{Y}^-=\text{Cl}^-$ or Br^- yield $[\text{Os}_4\text{H}_3(\text{CO})_{12}\text{Y}]$; these products can be reversibly deprotonated, forming $[\text{Os}_4\text{H}_2(\text{CO})_{12}\text{Y}]^-$. In the presence of $\text{Z}=\text{NO}_2^-$ or OH^- , [169] can be deprotonated to $[\text{Os}_3\text{H}_2(\text{CO})_{12}(\text{NCMe})_2]$, which rapidly disproportionates into [169] and $[\text{Os}_4\text{H}(\text{CO})_{12}(\text{NCMe})_2]^-$. Treatment of $[\text{Os}_4\text{H}(\text{CO})_{12}(\text{NCMe})_2]^-$ with ClAuPPh_3 generates $[\text{Os}_4\text{H}(\text{CO})_{12}(\text{NCMe})_2(\text{AuPPh}_3)]$ (199).

Oxidation of $[\text{PPN}][\text{Ru}_4\text{H}_3(\text{CO})_{12}]$ with $[\text{NO}][\text{BF}_4]$ yields $[\text{Ru}_4\text{H}(\text{CO})_{12}\text{N}]$, and $[\text{H}_3\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-N})]$ [170], characterized by X-ray crystallography. The former product is converted to $[\text{Ru}_4(\text{CO})_{12}(\mu_4\text{-N})]^-$ by treatment with $[\text{PPN}][\text{NO}_2]$. Oxidation of the Os analog yields $[\text{Os}_4\text{H}_3(\text{CO})_{12}(\text{NO})]$ and $[\text{Os}_4\text{H}(\text{CO})_{12}(\mu_4\text{-N})]$; treatment of the latter with $[\text{PPN}][\text{NO}_2]$ forms $[\text{PPN}][\text{Os}_4(\text{CO})_{12}(\mu_4\text{-N})]$ [171], characterized by X-ray crystallography (200).

The trinuclear isocyanate-containing clusters $[\text{Ru}_3(\text{NCO})(\text{CO})_{11}]^-$ and $[\text{Ru}_3(\mu\text{-NCO})(\text{CO})_{10}]^-$, prepared from $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{PPN}][\text{N}_3]$, agglomerate to $[\text{Ru}_4(\text{NCO})(\text{CO})_{13}]^-$ [172] (up to 70%) at 25°. In refluxing THF, the Ru_3 clusters are converted to both [172] and $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ [173] in up to 92% yield. Characterization of [173] was achieved by IR and ^{13}C and ^{15}N NMR spectroscopy. Under CO, [173] fragments to $[\text{Ru}_5\text{N}(\text{CO})_{14}]^-$ [174], characterized by X-ray crystallography, and $[\text{Ru}_3(\text{CO})_{12}]$. Under 3000 psi of CO and at 70° [173] forms both [174] and [172] (201). Hydrogenation of [172] at 25° yields $[\text{Ru}_4\text{H}_2(\text{NCO})(\text{CO})_{12}]^-$, which is protonated to $[\text{Ru}_4\text{H}_3(\text{NCO})(\text{CO})_{12}]$ (20%) with trifluoromethane sulfonic acid. The latter product was characterized by X-ray crystallography (202). Treatment of [172] with hydroxide yields $[\text{Ru}_4\text{H}(\text{CO})_{13}]^-$ (12%), structurally characterized, and $[\text{Ru}_4(\text{CO})_{13}]^{2-}$ (35%) (203). These reactions are summarized in Scheme 25.

The chloride-bridged cluster $[\text{PPN}]_2[\text{Ru}_4\text{Cl}_4(\text{CO})_{10}]$ [175] was prepared in 5-10% yield by reduction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with $[\text{PPN}][\text{Co}(\text{CO})_4]$ in THF; the crystal structure of the product was reported. Other products were $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{PPN}][\text{RuCo}_3(\text{CO})_{12}]$ and $[\text{PPN}][\text{Ru}_3\text{Co}(\text{CO})_{13}]$. Complex [175] is formally a mixed-valence complex, having two Ru(I) and two Ru(II) centers (204).

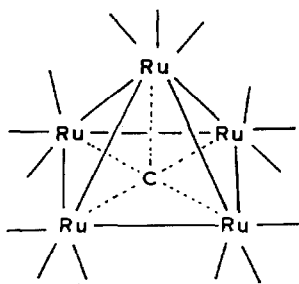
Pyrolysis of $[\text{Ru}_3\text{H}(\mu\text{-PPh}_2)(\text{CO})_9]$ in heptane forms larger clusters $[\text{Ru}_4(\text{CO})_{12}]^-$

$(\mu_3\text{-PPh})$] (40%) and $[\text{Ru}_5(\text{CO})_{16}(\mu\text{-PPh}_2)(\mu_5\text{-P})]$ [176] (15-20%), characterized by X-ray crystallography. The P atom of [176] is partially encapsulated and the cluster has a closed-shell, 80-electron count (205).

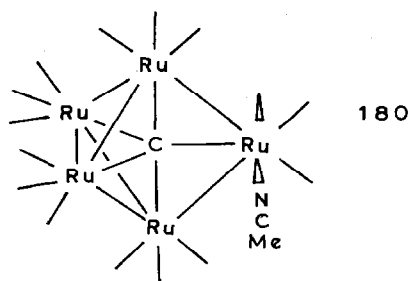
Pyrolysis of $[\text{Ru}_3(\text{CO})_{11}(\text{Ph}_2\text{PC}_2\text{Ph})]$ produces $[\text{Ru}_5(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-C}_2\text{Ph})(\mu\text{-PPh}_2)]$ [177] (30%), structurally characterized. Reversible carbonylation of [177] gives $[\text{Ru}_5(\text{CO})_{14}(\mu_5\text{-}\eta^2\text{-C}_2\text{Ph})(\mu\text{-PPh}_2)]$ [178], also characterized by X-ray crystallography. Other Lewis bases such as NCR (R=Me,Ph), NH_2R (R=i-Pr, s-Bu) and py also add reversibly concomitant with Ru-Ru bond cleavage (206).

Carbonylation (80 atm) of $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ produces $[\text{Ru}_5\text{C}(\text{CO})_{15}]$ [179], characterized by X-ray methods, and $[\text{Ru}(\text{CO})_5]$. Reactions of [179] with a variety of substrates were investigated. $[\text{Ru}_5\text{C}(\text{CO})_{15}(\text{NCMe})]$ [180] is formed from the acetonitrile reaction. Phosphines add to [179], giving $[\text{Ru}_5\text{C}(\text{CO})_{15\text{-}m}(\text{PR}_3)_m]$, ($m=1,2,3$; $\text{PR}_3=\text{PPh}_3, \text{PMePh}_2$) or $[\text{Ru}_5\text{C}(\text{CO})_{13}\{\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2\}]$ ($n=1,2$). The crystal structures of [180], $[\text{Ru}_5\text{C}(\text{CO})_{14}(\text{PPh}_3)]$, and $[\text{Ru}_5\text{C}(\text{CO})_{13}(\text{PPh}_3)_2]$ [181] were described. Hydrogenation of $[\text{Ru}_5\text{C}(\text{CO})_{13}(\text{dppe})]$ forms $[\text{Ru}_5\text{H}_2\text{C}(\text{CO})_{12}(\text{dppe})]$ [182], which was structurally characterized. Halide ions add to [179], forming $[\text{Ru}_5\text{C}(\text{CO})_{15}\text{X}]^-$ (X=F,Cl,Br,I), which can be protonated to $[\text{Ru}_5\text{HC}(\text{CO})_{15}\text{X}]$. With halogens, [179] fragments to $[\text{Ru}_2(\text{CO})_6\text{X}_4]$ (X=Cl,Br) or oxidative cleavage of a Ru-Ru bond produces $[\text{Ru}_5\text{C}(\text{CO})_{15}\text{I}_2]$ (207). Oxidative addition of HX (X=SH,SeH,SEt,SMe) to [179] produces $[\text{Ru}_5\text{C}(\text{CO})_{14}\text{HX}]$ in yields of up to 90%; the crystal structure of the SEt derivative [183] was determined. Pyrolysis of [183] at 80° forms $[\text{Ru}_5\text{C}(\text{CO})_{13}\text{H}(\text{SEt})]$ (82%), and addition of PPh_3 to this product generates $[\text{Ru}_5\text{C}(\text{CO})_{13}(\text{PPh}_3)\text{H}(\text{SEt})]$ [184] (66%), which was structurally characterized. Pyrolysis of [184] generates $[\text{Ru}_5\text{C}(\text{CO})_{12}(\text{PPh}_3)\text{H}(\text{SEt})]$ [185] (71%). Treatment of [183] with MeAuPPh_3 produces $[\text{Ru}_5\text{C}(\text{CO})_{13}(\text{AuPPh}_3)(\text{SEt})]$ (47%). Treatment of [179] with IAuPPh_3 gives $[\text{Ru}_5\text{C}(\text{CO})_{14}(\text{AuPPh}_3)(\mu\text{-I})]$. Pyrolysis of the latter generates $[\text{Ru}_5\text{C}(\text{CO})_{13}(\text{AuPPh}_3)\text{I}]$, which adds PPh_3 , generating $[\text{Ru}_5\text{C}(\text{CO})_{13}(\text{PPh}_3)(\text{AuPPh}_3)\text{I}]$ [184a], which was characterized by X-ray diffraction (208). In a similar fashion, [179] and X AuPPh_3 (X=Cl,Br) form $[\text{Ru}_5\text{C}(\text{CO})_{15}(\text{AuPPh}_3)\text{X}]$ (structurally characterized for X=Cl [186]) which lose CO, forming $[\text{Ru}_5\text{C}(\text{CO})_{14}(\text{AuPPh}_3)\text{X}]$ (structurally characterized for X=Br) (209).

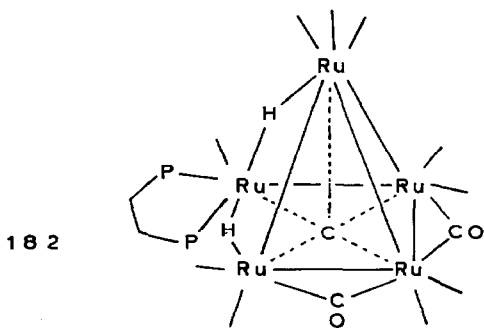
High pressure infrared spectroscopic studies of pentanuclear Ru and Os clusters were conducted. At 20° and under 80 atm of CO, $[\text{Ru}_5\text{C}(\text{CO})_{15}]$ is converted to $[\text{Ru}_5\text{C}(\text{CO})_{16}]$; at 90° the product reverts to the starting material. Similarly, $[\text{Os}_5\text{C}(\text{CO})_{15}]$ can be carbonylated (50 atm) at 70° to $[\text{Os}_5\text{C}(\text{CO})_{16}]$ [187], characterized by X-ray crystallography. Hydrogenation of [187] (75 atm, 90°) produces $[\text{Os}_5\text{C}(\text{CO})_{15}\text{H}_2]$. Reduction of $[\text{M}_5\text{C}(\text{CO})_{15}]$ gives the corresponding $[\text{M}_5\text{C}(\text{CO})_{14}]^{2-}$ [188]; the crystal structure of the [PPN] salt of the Os cluster anion was reported. Treatment of $[\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}$



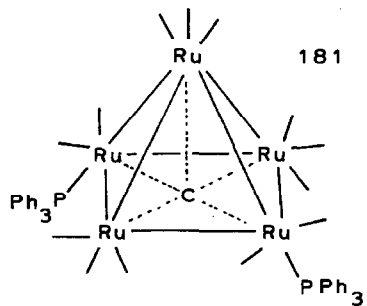
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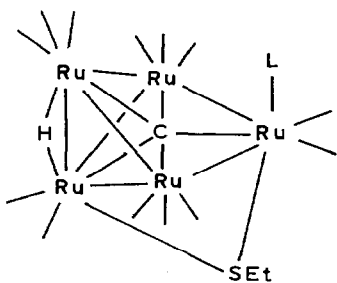
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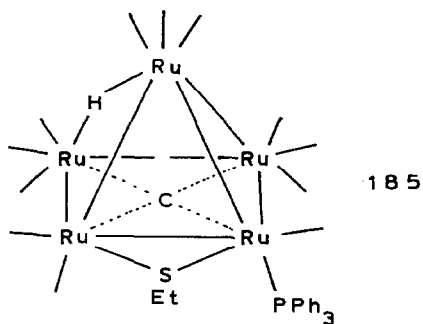
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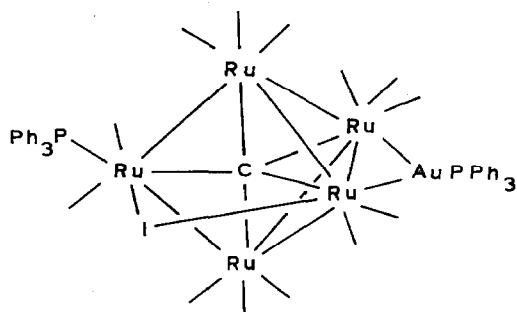
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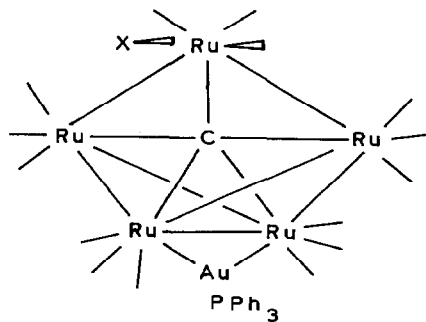
183, L = CO

184, L = PPh₃

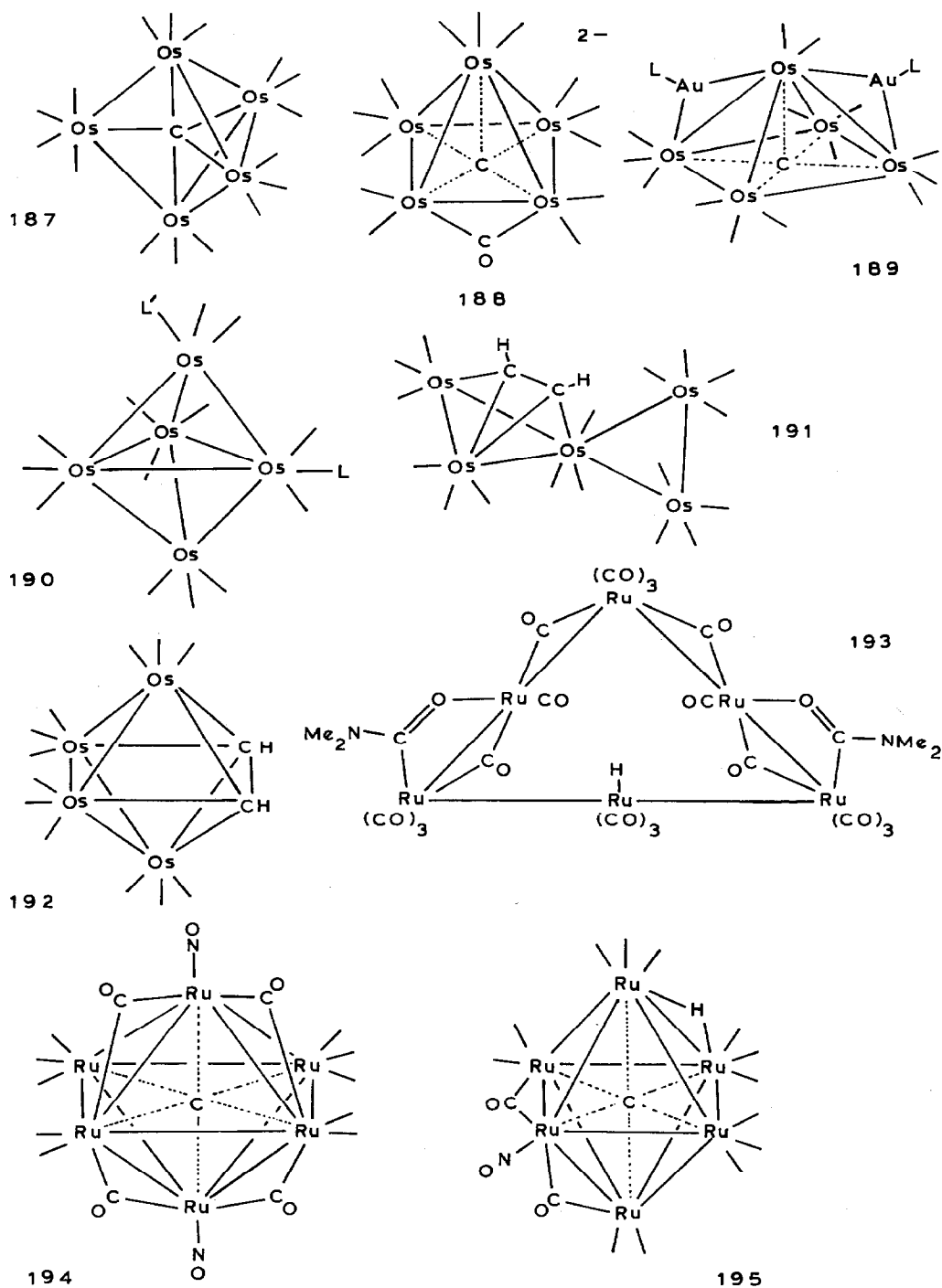
185



184a



186



with 2 equivalents of ClAuPPh₃ produces [Os₅C(CO)₁₄(AuPPh₃)₂] [189], characterized by X-ray methods (210).

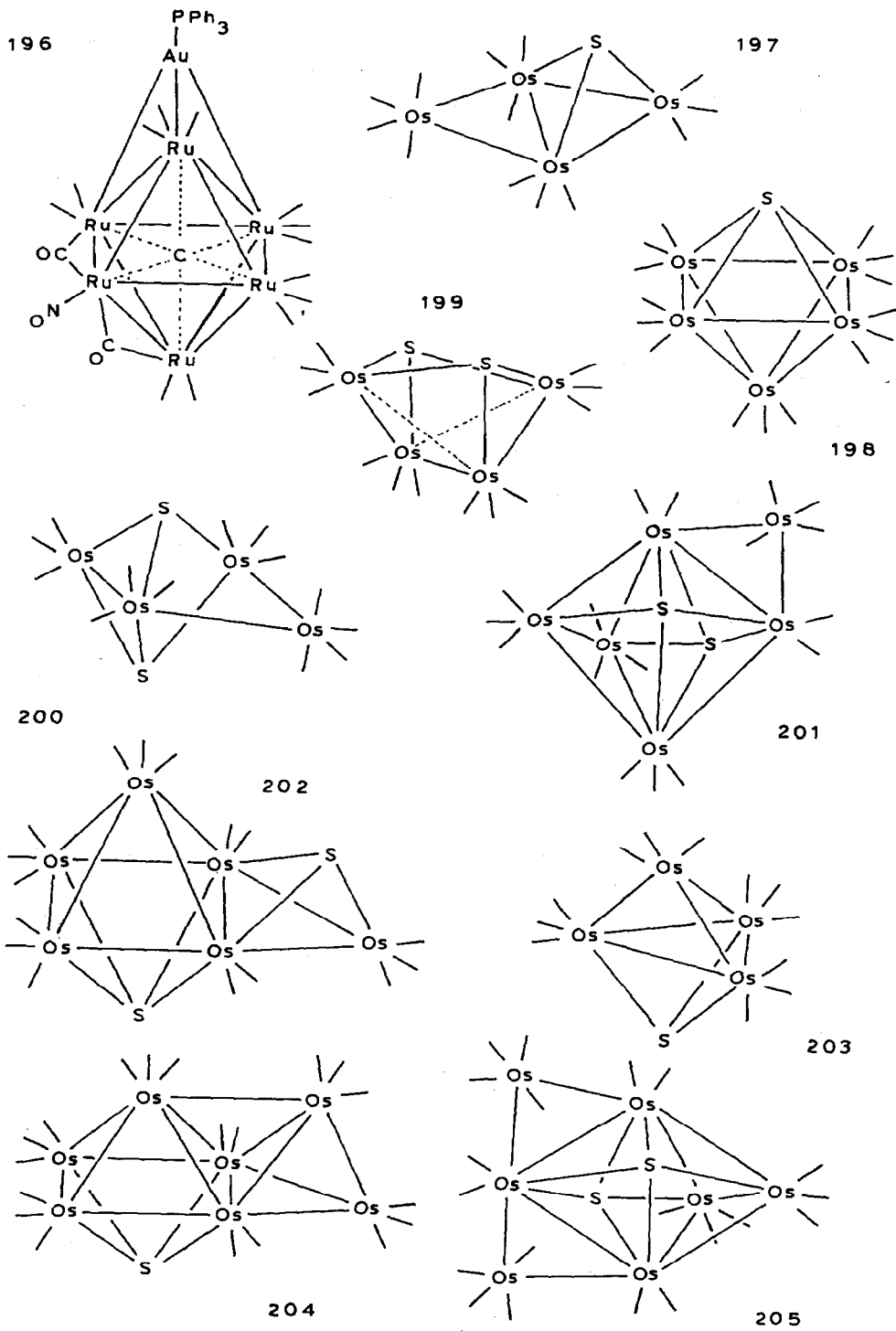
At 120° [Os₅H₂(CO)₁₅L] (L=PPh₃,PEt₃,P(OMe)₃) loses CO to form the corresponding [Os₅H₂(CO)₁₄L] ([190],L'=CO); the PEt₃ derivative being characterized by X-ray diffraction. Substitution of L' on [Os₅H₂(CO)₁₄L] yields [Os₅H₂(CO)₁₃LL'], structurally characterized for L=PEt₃ and L'=P(OMe)₃ [190] (211).

Products from the reaction of acetylene with [Os₅(CO)₁₉] in refluxing heptane are [Os₅(CO)₁₇(C₂H₂)] [191] (15%) and [Os₄(CO)₁₂(C₂H₂)] [192] (55%). With other alkynes HC₂R (R=Me,Ph), the products are [Os₅(CO)₁₇(HC₂R)] and [Os₄(CO)₁₂(HC₂R)], but from RC₂R (R=Ph,CO₂Me) only decarbonylation to [Os₅(CO)₁₆] is observed (212).

In refluxing THF and in the absence of CO, K[Ru₃(O=CNMe₂)(CO)₁₀], formed by deprotonation of [Ru₃H(O=CNMe₂)(CO)₁₀] with KOH/MeOH, dimerizes to [Ru₆H(O=CNMe₂)₂(μ-CO)₄(CO)₁₄]⁻ [193] (45%); the crystal structure of the [AsPh₄] salt was determined (213).

Treatment of [Ru₆C(CO)₁₇] with [PPN][NO₂] in THF produces [Ru₆C(CO)₁₅(NO)]⁻ in 85% yield. Nitrosonium adds to the product to form [Ru₆C(CO)₁₄(NO)₂] [194], characterized by X-ray crystallography. Additions of electrophiles E=H⁺ (H₂SO₄) or AuPPh₃⁺ (ClAuPPh₃) to [Ru₆C(CO)₁₅(NO)]⁻ generate [Ru₆C(CO)₁₅(NO)E]; crystal structures were determined for both adducts [195] and [196] (214,215).

A wide variety of clusters of from 3 to 7 Os atoms have been prepared with sulfur-containing ligands. Under CO (200 psi), pyrolysis of [Os₃H(SPh)-(CO)₁₀] at 150° forms benzene, [Os₄(CO)₁₃(μ₃-S)] [197] (27%), [Os₅(CO)₁₅(μ₄-S)] [198] (7%), [Os₃(CO)₁₂] (17%), and [Os₃(CO)₉(μ₃-S)₂] (38%); the structures of [197] and [198] were determined by X-ray crystallography. Pyrolysis of [197] at 125° yields [Os₄(CO)₁₂(μ₃-S)] (97%). Pyrolysis of [Os₃H(SPh)(CO)₁₀] at 150° and under 1800 psi of CO produces benzene, [Os₃(CO)₉(μ₃-S)₂] and [Os(CO)₅]. Mechanisms for these transformations were proposed (216). Pyrolysis of [Os₃H(SC₆F₅)(CO)₁₀] in refluxing nonane for 1.5 h gives [Os₄(CO)₁₂(μ₃-S)₂] [199] (2-3%), which adds CO at 25°, forming [Os₄(CO)₁₃(μ₃-S)₂] [200] (100%); [200] is converted back to [199] in refluxing hexane. Both [199] and [200] were characterized by X-ray methods. The high reactivity of [199] toward CO is attributed to the presence of two long Os-Os bonds (3.091 and 3.002 Å) (217). Condensation of [Os₃(CO)₉(μ₃-S)₂] with [Os₃(CO)₁₀(NCMe)₂] forms [Os₆(CO)₁₇(μ₄-S)₂] [201] in 29% after 3 h in refluxing hexane. Pyrolysis of [201] in refluxing octane yields [Os₆(CO)₁₆(μ₄-S)(μ₃-S)] [202] quantitatively. Both [201] and [202] were characterized by X-ray crystallography (218). Condensation of [Os₄(CO)₁₂(μ₃-S)] [203] with [Os₃(CO)₁₀(NCMe)₂]

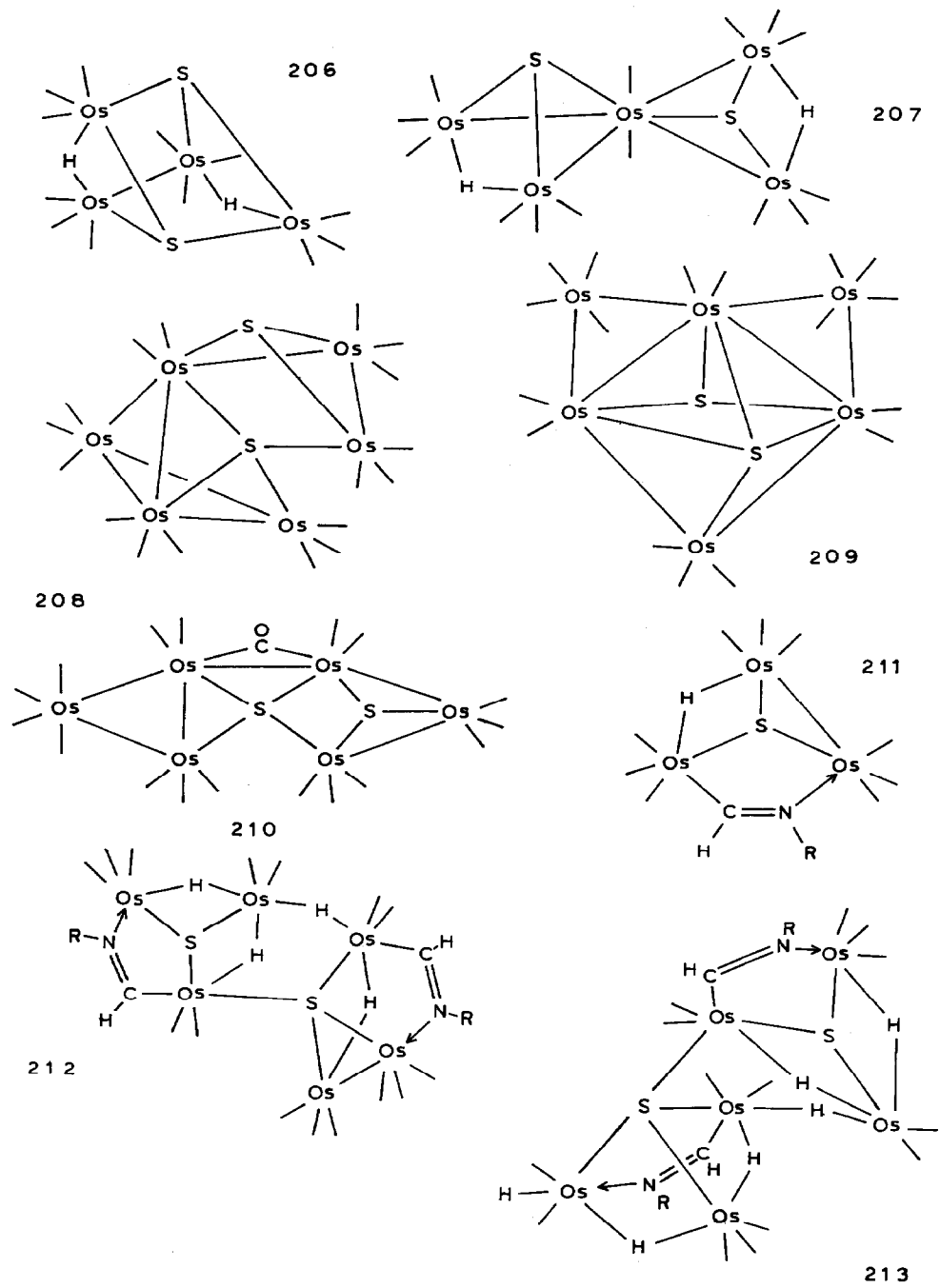


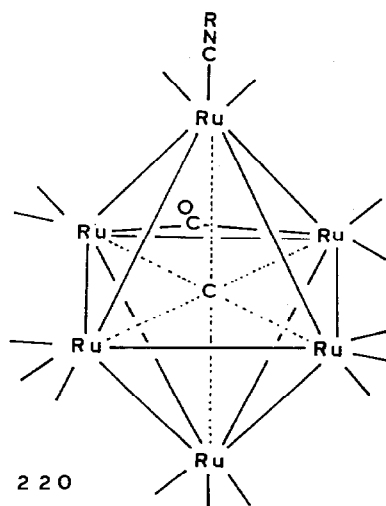
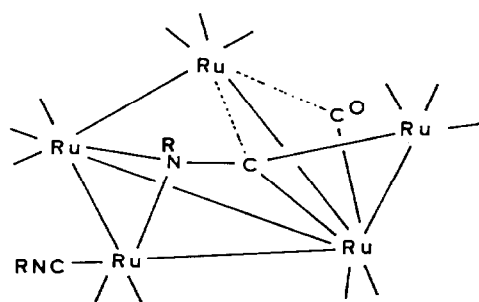
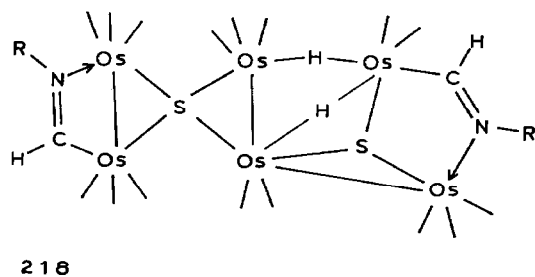
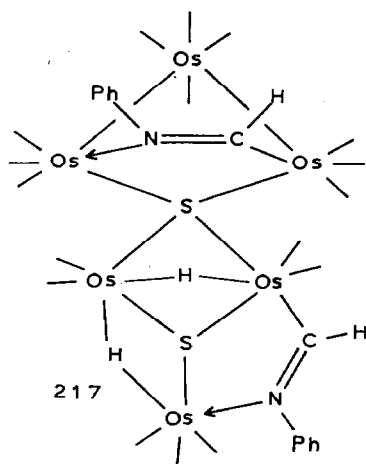
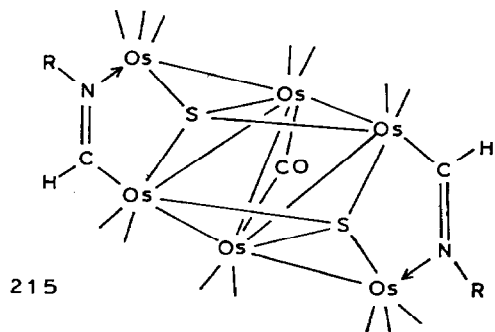
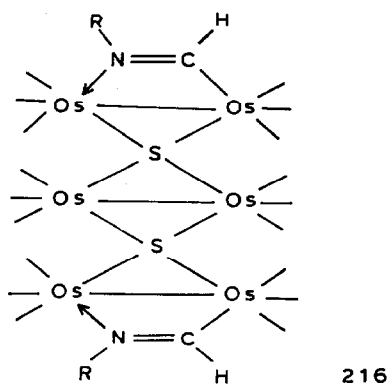
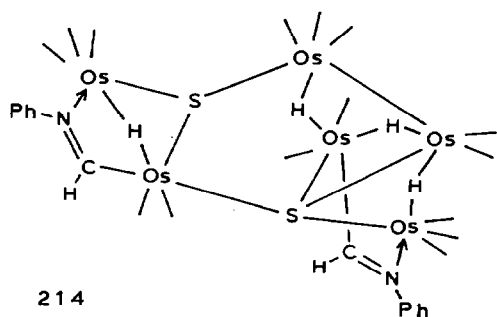
forms $[\text{Os}_7(\text{CO})_{19}(\mu_4\text{-S})]$ [204] in 23% yield after 3 h in refluxing octane. The same product in 4% yield is obtained from $[\text{Os}_3\text{H}_2(\text{CO})_9(\mu_3\text{-S})]$ and $[\text{Os}_3\text{H}(\text{CO})_{10}(\mu\text{-OMe})]$ (nonane reflux, 22 h). The structures of [203] and [204] were determined (219). Condensation of $[\text{Os}_3(\text{CO})_9(\mu_3\text{-S})_2]$ and $[\text{Os}(\text{CO})_5]$, induced by photolysis, produces $[\text{Os}_4(\text{CO})_{13}(\mu_3\text{-S})_2]$ [200] (40%), and condensation of $[\text{Os}_4(\text{CO})_{12}(\mu_3\text{-S})_2]$ [199] with $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ gives $[\text{Os}_7(\text{CO})_{20}(\mu_4\text{-S})_2]$ [205]. Both [200] and [205] were characterized crystallographically (220). Addition of H_2S to $[\text{Os}_4(\text{CO})_{12}(\mu_3\text{-S})]$ [203] in refluxing heptane forms $[\text{Os}_4\text{H}_2(\text{CO})_{12}(\mu_3\text{-S})_2]$ [206] (55%) and $[\text{Os}_3\text{H}_2(\text{CO})_9(\mu_3\text{-S})]$ (35). In refluxing nonane H_2S adds to $[\text{Os}_5(\text{CO})_{15}(\mu_4\text{-S})]$ [198] to produce $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\mu_3\text{-S})_2]$ [207] (94%); the crystal structure of [207] was determined (221). Pyrolysis of $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{SBz})]$ at 150° proceeds by two mechanisms, one to form $[\text{Os}_3(\text{CO})_9(\mu_3\text{-S})_2]$, $[\text{Os}_6(\text{CO})_{16}(\mu_4\text{-S})(\mu_3\text{-S})]$, toluene, and $[\text{Os}_7(\text{CO})_{20}(\mu_4\text{-S})_2]$ [205], and the other mechanism to dibenzyl and red and green isomers of the formula $[\text{Os}_6\text{H}_2(\text{CO})_{17}(\mu_4\text{-S})(\mu_3\text{-S})]$. The red isomer was shown to have structure [208], while the green isomer has structure [209]. Photolysis of $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{SBz})]$ produces dibenzyl and $[\text{Os}_6\text{H}_2(\text{CO})_{18}(\mu_4\text{-S})(\mu_3\text{-S})]$ [210], structurally characterized (222).

A number of Os_6 clusters have been prepared by pyrolysis of $[\text{Os}_3\text{H}(\text{CO})_9(\mu_3\text{-S})(\mu\text{-CH=NR})]$ [211]. Hydrogenation of [211] ($\text{R}=\text{Ph}$) in refluxing octane forms $[\text{Os}_6\text{H}_4(\text{CO})_{15}(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-CH=NPh})_2]$ [212] (47%), $[\text{Os}_6\text{H}_6(\text{CO})_{14}(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-CH=NPh})_2]$ [213] (12%), and $[\text{Os}_6\text{H}_4(\text{CO})_{15}(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-CH=NPh})_2]$ [214] (21%). Under CO and in refluxing octane [212] reverts to [211] in 28% yield, and hydrogenation of [212] gives [213] (17%) and [214] (13%). Under an inert atmosphere [212] is converted to [214]. Pyrolysis of [214] in refluxing nonane gives $[\text{Os}_6(\text{CO})_{15}(\mu_4\text{-S})_2(\mu\text{-CH=NPh})_2]$ [215]. The crystal structures of [212], [213] and [214] were described (223). Pyrolysis of [211] ($\text{R}=\text{Ph}$ or $\text{C}_6\text{H}_4\text{F-4}$) yields $[\text{Os}_6(\text{CO})_{18}(\mu_4\text{-S})_2(\mu\text{-CH=NR})_2]$ [216] ($\text{R}=\text{Ph}$ or $\text{C}_6\text{H}_4\text{F-4}$), $[\text{Os}_6\text{H}_2(\text{CO})_{17}(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-CH=NR})_2]$ [217], which exists as two isomers, $[\text{Os}_6\text{H}_2(\text{CO})_{16}(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-CH=NR})_2]$ [218], which exists as three isomers, and $[\text{Os}_6(\text{CO})_{15}(\mu_4\text{-S})_2(\mu\text{-CH=NR})_2]$ [215]. Crystal structures of one isomer of [217] ($\text{R}=\text{C}_6\text{H}_4\text{F}$), one isomer of [218] ($\text{R}=\text{Ph}$), and [215] ($\text{R}=\text{Ph}$) were reported (224). In another paper the crystal structure of [216] was described (225).

Pyrolysis of $[\text{Ru}_5(\text{CO})_{14}(\text{CNCMe}_3)(\mu_5\text{-CNCMe}_3)]$ [219] in refluxing nonane yields $[\text{Ru}_6\text{C}(\text{CO})_{15}(\text{CNCMe}_3)(\mu\text{-CO})]$ [220] (13%), characterized by X-ray crystallography. ^{13}C labeling was used to determine that the CNCMe_3 ligand is the source of the carbide. Tert-butyl isocyanate is a by-product (226).

The IR spectra for $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ and $[\text{NMe}_4]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$ in the 900-600 cm^{-1} region were assigned. The assignment was aided by shifts for the ^{13}C





enriched clusters. The band patterns are a function of the symmetry of the Ru_6C core, but the frequencies depend upon other features. The $\nu(\text{M-C})$ absorptions for these species are at 838 and 709 cm^{-1} , respectively (227).

EXAFS of $[\text{Os}_3(\text{CO})_{12}]$, $[\text{PPN}][\text{Os}_6(\text{CO})_{18}]$, $[\text{Os}_6(\text{CO})_{18}]$, and $[\text{PPN}]_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$ were used to characterize the Os skeletons and determine the non-bonded Os-Os distances (228).

Treatment of $[\text{Os}_8\text{H}(\text{CO})_{22}]^-$ [221] with iodine yields $[\text{Os}_8\text{H}(\text{CO})_{22}\text{I}]$ [222], characterized by X-ray crystallography (229).

Pyrolysis of $[\text{Os}_3(\text{CO})_{12}]$ forms $[\text{Os}_9(\text{CO})_{21}(\text{HCCMeCH})]^-$ [223] in low yield from refluxing isobutanol and $[\text{Os}_9(\text{CO})_{21}(\text{HCCEtCH})]^-$ from refluxing 2-methylbutanol. The crystal structure of the former anion as the PPN salt was determined (230).

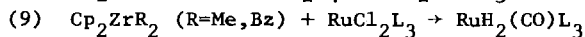
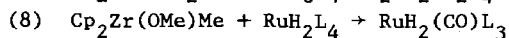
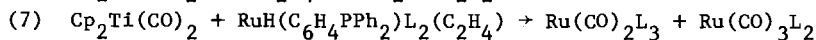
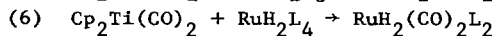
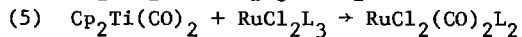
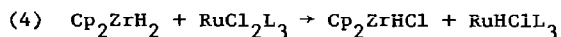
Mixed Metal Clusters

Mixed metal dimers $[\text{RuMn}(\mu\text{-CO})(\text{CO})_3(\mu\text{-dppm})_2\text{Cl}]$ and $[\text{RuMn}(\mu\text{-PPh}_2)(\text{CO})_6(\text{PPh}_3)_2]$ were prepared from reactions of $\text{Na}[\text{Mn}(\text{CO})_5]$ with cis- $[\text{RuCl}_2(\text{dppm})_2]$ and with $[\text{RuCl}_3(\text{PPh}_3)_3]$, respectively (231).

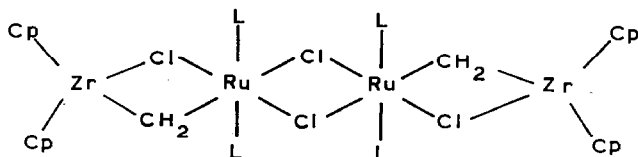
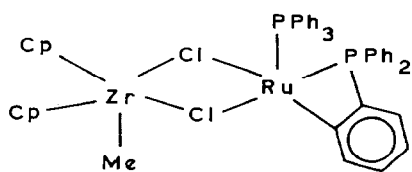
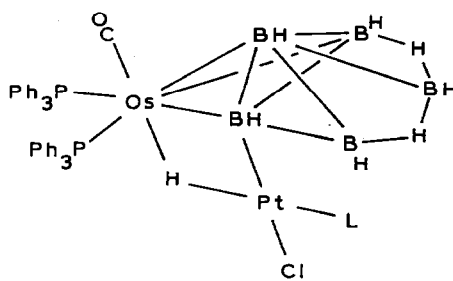
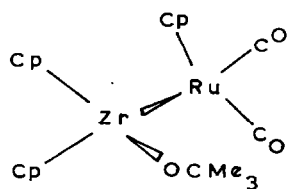
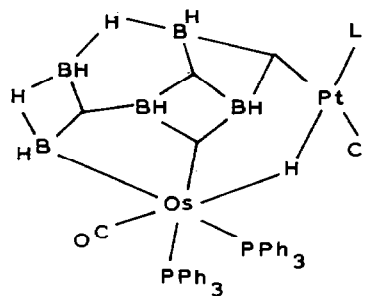
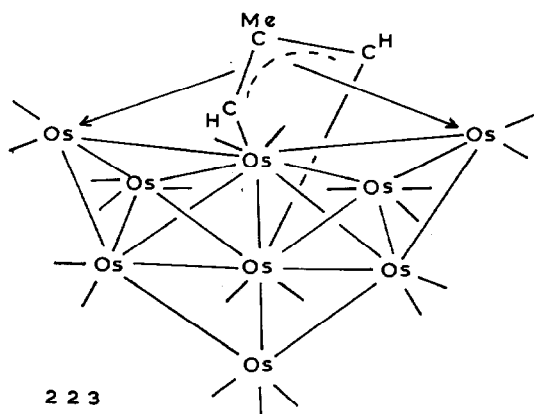
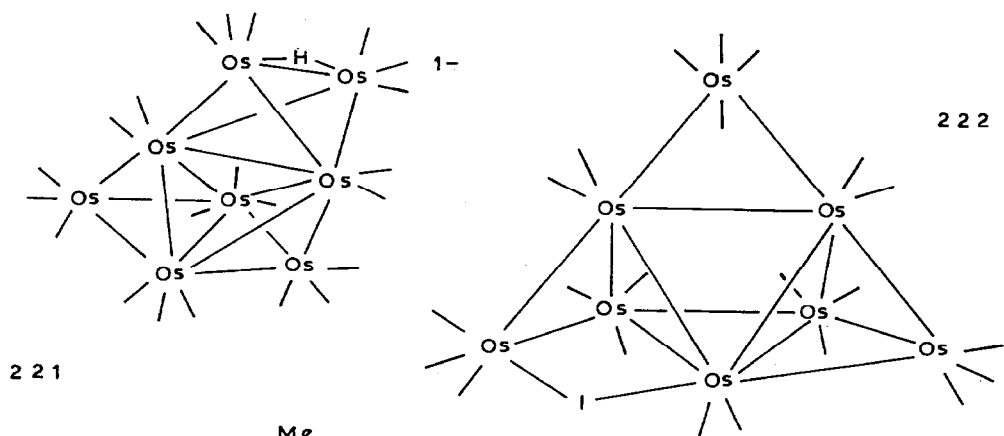
Sequential treatment of nido- $[4,4,4\text{-}(\text{PPh}_3)_2(\text{CO})\text{-}4\text{-OsB}_5\text{H}_9]$ with first sodium hydride and then cis- $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$ produces $[(\text{PPh}_3)_2(\text{CO})\text{Os}(\text{PPhMe}_2)\text{-ClHPtB}_5\text{H}_7]$ [224], characterized by X-ray crystallography (232).

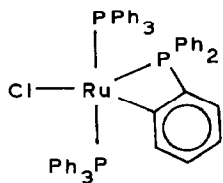
The synthesis of $[\text{Cp}_2\text{ZrMeRu}(\text{CO})_2\text{Cp}]$ in 83% yield was accomplished by the reaction of $[\text{Cp}_2\text{ZrMeCl}]$ with $\text{K}[\text{CpRu}(\text{CO})_2]$. The product reacts with water in air, forming $[(\text{Cp}_2\text{ZrMe})_2\text{O}]$ and $[\text{CpRu}(\text{CO})_2\text{H}]$. In a similar fashion $[\text{Cp}_2\text{Zr}(\text{OCMe}_3)\text{Ru}(\text{CO})_2\text{Cp}]$ [225] was prepared in 75% yield from $[\text{Cp}_2\text{Zr}(\text{OCMe}_3)\text{Cl}]$ and $\text{K}[\text{CpRu}(\text{CO})_2]$ and its crystal structure was determined (233).

The photolytic reaction between $[\text{Cp}_2\text{ZrMeCl}]$ and $[\text{RuCl}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]$ yields $[\text{Cp}_2\text{ZrMeCl}_2\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)]$ (proposed structure [226]), which slowly rearranges to $[(\text{Cp}_2\text{ZrCl}(\text{CH}_2)\text{Ru}(\text{PPh}_3)_2\text{Cl})_2]$ (proposed structure [227]) in ca. 10% yield. Products were characterized by spectroscopic methods. Reactions between Ru phosphine complexes and other Zr or Ti complexes resulted in ligand exchange. Reactions (4)-(9) were reported ($\text{L}=\text{PPh}_3$). The new complex $[\text{RuCl}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]$ [228] was spectroscopically characterized (234).

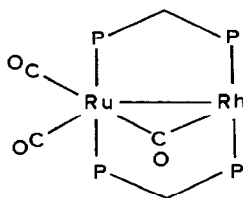


At 80° in toluene $[\text{RuRhCl}(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2]$ [229] is produced from $[\text{Ru}(\text{COD})(\text{dppm})_2]$ and $[\text{Ru}_2\text{Cl}_2(\text{CO})_4]$; other products are $[\text{Ru}(\text{CO})(\text{COD})(\text{dppm})]$

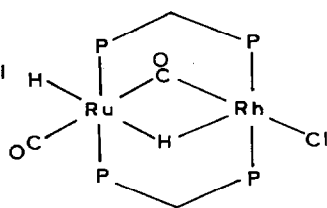




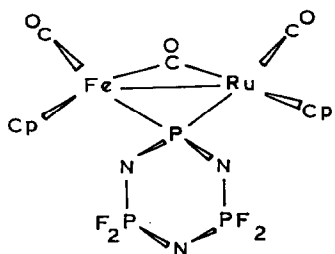
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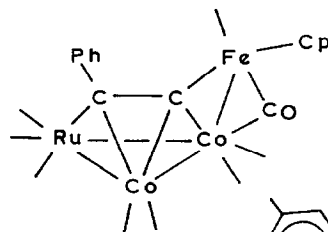
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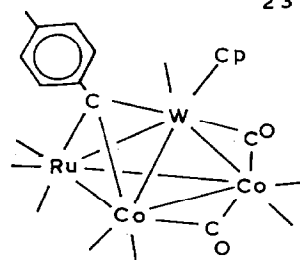
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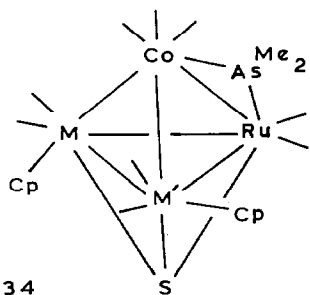
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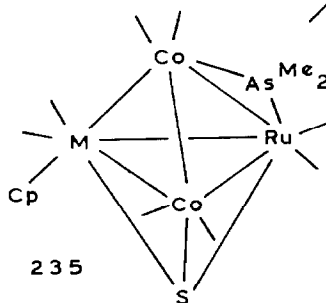
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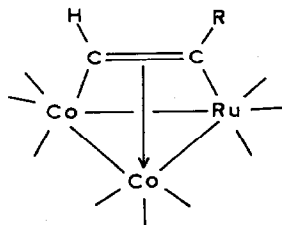
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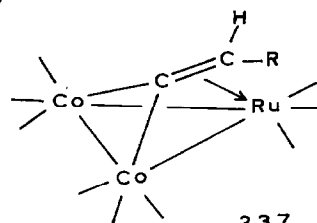
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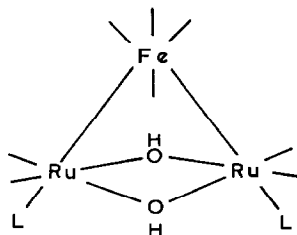
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and $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{dppm})_2]$. The yield of the mixed metal product is improved by conducting the reaction under a CO atmosphere. The complex, characterized spectroscopically, is a hydroformylation catalyst and reacts with sodium borohydride, giving $[\text{RuRhH}_2\text{Cl}(\text{CO})_2(\text{dppm})_2]$ [230] (30%) (235).

The reaction of $[\text{CpRu}(\text{CO})_2]^-$ with $[(\text{NPF}_2)_2(\text{NPFFe}(\text{CO})_2\text{Cp})]$ or with $[\text{CpFe}(\text{CO})_2\text{I}]$ yields $[\text{FeRu}(\text{CO})_4\text{Cp}_2]$. The crystal structure of $[(\text{NPF}_2)_2(\text{NPFFeRu}(\text{CO})_3\text{Cp}_2)]$ [231] was reported (236).

$[\text{RuCo}_2(\text{CO})_{11}]$ reacts with reagents capable of supplying 4-electron donor fragments E to yield $[\text{RuCo}_2(\text{CO})_9(\mu_3\text{-E})]$. Complexes prepared in this manner were E=PMe (37%) from PH_2Me , AsMe (38%) from AsH_2Me , SET (31%) from HSEt, SePh (22%) from Se_2Ph_2 , C_2Ph_2 (73%), $\text{Cp}(\text{CO})_2\text{FeC}_2\text{Ph}$ (69%) [232], and $\text{CpW}(\text{CO})_2^-(\text{CC}_6\text{H}_4\text{Me-4})$ (12%) [233] (237).

Capped trinuclear clusters were also obtained from $[(\mu\text{-PHR})\text{FeCo}(\text{CO})_7]$ and $[\text{Ru}_3(\text{CO})_{12}]$. The products were $[\text{FeRuCoH}(\text{CO})_9(\mu_3\text{-PMe})]$ (31%) and $[\text{Ru}_2\text{CoH}(\text{CO})_9^-(\mu_3\text{-PMe})]$ (29%) (238).

Metal atom substitution on $[\text{RuCo}_2(\text{CO})_9(\mu_3\text{-S})]$ has been used to produce a number of mixed metal clusters. The method involves, first, CO substitution by $[\text{AsMe}_2\text{M}(\text{CO})_3\text{Cp}]$ (M=Me,W) to give $[\text{RuCo}_2(\text{CO})_8(\text{AsMe}_2\text{M}(\text{CO})_3\text{Cp})(\mu_3\text{-S})]$ and then elimination of a Co fragment. Complexes prepared include $[\{\text{Ru}(\text{CO})_3\}\{\text{Co}(\text{CO})_3\}\{\text{M}(\text{CO})_2\text{Cp}\}(\mu_3\text{-S})]$ (M=Mo,W), $[\{\text{Ru}(\text{CO})_3\}\{\text{M}(\text{CO})_2\text{Cp}\}\{\text{Co}(\text{CO})_2^-(\text{AsMe}_2\text{M}'(\text{CO})_2\text{Cp})\}(\mu_3\text{-S})]$ (M=M'=Mo; M=M'=W, M=Mo, M'=W; M=W, M'=Mo), $[\{\text{Ru}(\text{CO})_3\}\{\text{Co}(\text{CO})_3\}\{\text{Co}(\text{CO})_2(\text{AsMe}_2\text{M}(\text{CO})_2\text{Cp})\}(\mu_3\text{-S})]$ (M=Mo,W), $[(\mu_3\text{-S})\{\text{M}(\text{CO})_2\text{Cp}\}\{\text{M}'(\text{CO})_2\text{Cp}\}-\{\text{Ru}(\text{CO})_2\}(\mu\text{-AsMe}_2)\{\text{Co}(\text{CO})_3\}]$ [234] (M=M'=Mo; M=M'=W; M=Mo, M'=W; M=W, M'=Mo), and $[(\mu_3\text{-S})\{\text{Co}(\text{CO})_2\}\{\text{M}(\text{CO})_2\text{Cp}\}\{\text{Ru}(\text{CO})_2\}(\mu\text{-AsMe}_2)\{\text{Co}(\text{CO})_2\}]$ [235] (M=Mo,W). The crystal structure of [235] was reported (239).

Substitution of HC_2R (R=H,Ph) for CO on $[\text{RuCo}_2(\text{CO})_{11}]$ at 25° yields $[\text{RuCo}_2(\text{CO})_9(\text{HC}_2\text{R})]$ [236] in quantitative yield. These products rearrange in refluxing hexane to vinylidene clusters $[\text{RuCo}_2(\text{CO})_9(\text{CCHR})]$ [237] (R=H (25%), Ph (60%)) (240).

In refluxing acetone and in the presence of sodium carbonate, $[\text{FeRu}_2(\mu\text{-Cl})_2(\text{CO})_8\text{L}_2]$ is converted to $[\text{FeRu}_2(\mu\text{-OH})_2(\text{CO})_8\text{L}_2]$ [238] (L=PPh₃,PMe₃,AsPh₃) in yields of 55-95%. The crystal structure of the PPh₃ derivative was reported. Cleavage to $[\text{Ru}_2(\text{CO})_4(\mu\text{-I})_2\text{L}_2]$ occurs upon treatment of the chloride-bridged clusters with potassium iodide. In 2-propanol $[\text{FeRu}_2(\mu\text{-Cl})_2(\text{CO})_8(\text{PPh}_3)_2]$, sodium carbonate, and water react to form [238] (L=PPh₃) (15%) and $[\text{FeRu}_2(\mu\text{-H})(\mu\text{-OH})(\text{CO})_8(\text{PPh}_3)_2]$ (20%) (241).

Treatment of $[\text{CoRu}_3(\text{CO})_{13}]^-$ with NO^+ generates $[\text{CoRu}_3\text{N}(\text{CO})_{12}]$ (8%) and $[\text{Ru}_3(\text{CO})_{12}]$. Hydrogenation of $[\text{CoRu}_3(\text{CO})_{13}]^-$ forms $[\text{CoRu}_3\text{H}_2(\text{CO})_{12}]^-$, isolated in 95% yield as the PPN salt; protonation of the product yields $[\text{CoRu}_3\text{H}_3(\text{CO})_{12}]$. The reaction of $[\text{CoRu}_3(\text{CO})_{13}]^-$ with NO^+ produces a mixture of $[\text{Co}(\text{CO})_3(\text{NO})]$,

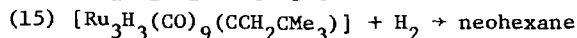
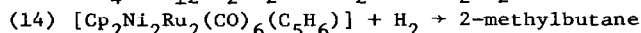
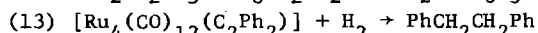
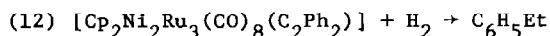
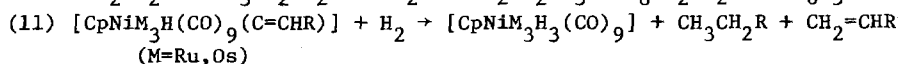
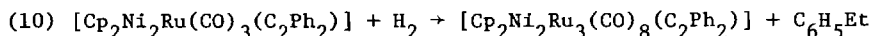
$[\text{CoRu}_3\text{H}_3(\text{CO})_{12}]$, $[\text{Ru}_3(\text{CO})_{12}]$, and small amounts of Ru clusters, including $[\text{Ru}_3\text{H}(\text{CO})_{10}(\text{NO})]$ and $[\text{Ru}_3\text{H}_2(\text{CO})_9(\text{NH})]$ (242).

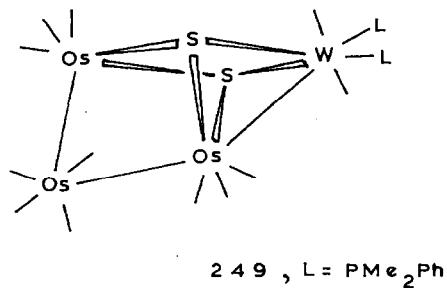
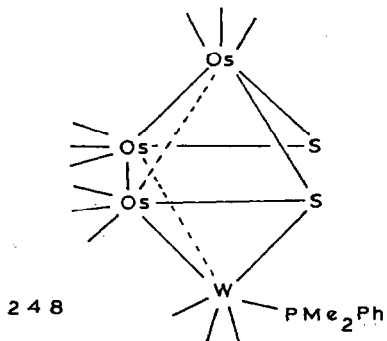
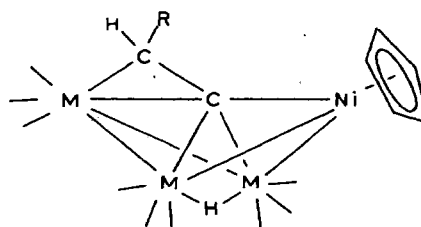
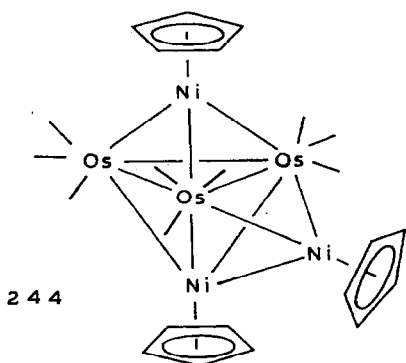
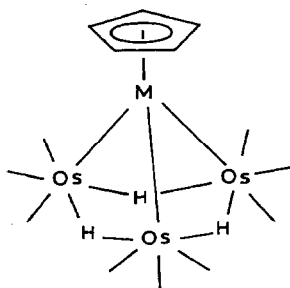
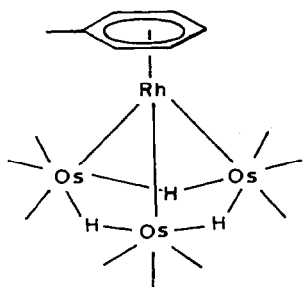
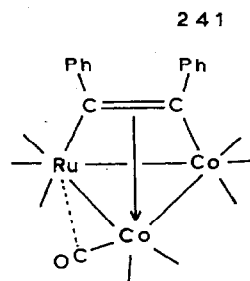
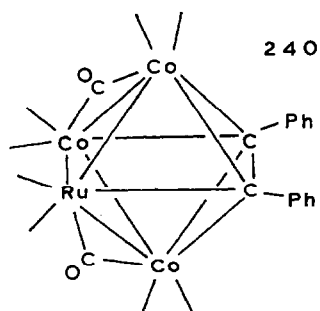
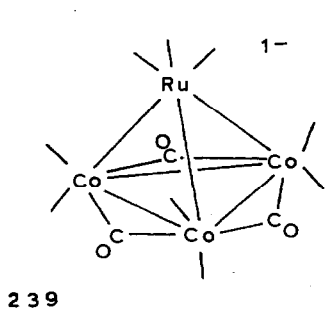
Syntheses and reactions of $[\text{RuCo}_3(\text{CO})_{12}]^-$ have been reported. The sodium salt was prepared in 54% yield from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Na}[\text{Co}(\text{CO})_4]$. Also prepared were the NEt_4 , PPh_4 , and PPN salts, the last of which, [239], was structurally characterized (243). The NEt_4 salt was also prepared in 90% yield from the reaction between $[\text{NEt}_4][\text{RuCl}_4(\text{NCMe})_2]$ and $[\text{Co}_2(\text{CO})_8]$ in THF at 50° for 5 h (244). Protonation of $[\text{RuCo}_3(\text{CO})_{12}]^-$ produces $[\text{RuCo}_3\text{H}(\text{CO})_{12}]$; both of these are catalyst precursors for methanol homologation to ethanol (200° , CO/H_2 1:2, 64% selectivity at 25% conversion) using methyl iodide as a promoter (243). Diphenylacetylene and $[\text{NEt}_4][\text{RuCo}_3(\text{CO})_{12}]$ form $[\text{NEt}_4][\text{RuCo}_3(\text{CO})_{10}(\text{C}_2\text{Ph}_2)]$ [240] in 75% yield from refluxing acetone; the product was characterized by X-ray crystallography. Protonation of [240] with $\text{HCl}/\text{H}_2\text{O}/\text{acetone}$ gave a 20% yield of $[\text{RuCo}_2(\text{CO})_9(\text{C}_2\text{Ph}_2)]$ [241], also characterized structurally (244).

Combination of $[\text{CpRh}(\text{CO})_2]$ and $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ under hydrogen and in an arene solvent produces $[\text{RhOs}_3\text{H}_2(\text{CO})_{10}\text{Cp}]$ and $[\text{RhOs}_3\text{H}_3(\text{CO})_9(\text{arene})]$. In toluene at 90° and 1 atm hydrogen the products are $[\text{RhOs}_3\text{H}_3(\text{CO})_9(\text{C}_6\text{H}_5\text{Me})]$ [242] (25%) and $[\text{RhOs}_3\text{H}_2(\text{CO})_{10}\text{Cp}]$ (8%) (246). X-ray crystallography was used to characterize [242] (247).

In a similar fashion, $[\text{CpNiOs}_3\text{H}_3(\text{CO})_9]$ [243] and $[(\text{CpNi})_3\text{Os}_3(\text{CO})_9]$ [244] were prepared from $[\{\text{CpNi}(\text{CO})\}_2]$ and either $[\text{Os}_3(\text{CO})_{12}]$ or $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$. The product distribution was influenced by the atmosphere under which the reaction was conducted (hydrogen, CO, or nitrogen). The structure of [243] was established by X-ray crystallography (248). In octane reflux under hydrogen, $[\text{Os}_3(\text{CO})_{12}]$ and $[\{\text{CpNi}(\text{CO})\}_2]$ form $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ and $[\text{CpNiOs}_3\text{H}_3(\text{CO})_9]$ [243] which co-crystallize as a 1:2 mixture, characterized by X-ray crystallography. The Ru analog, $[\text{CpNiRu}_3\text{H}_3(\text{CO})_9]$, was prepared in 74% yield from $[\text{Ru}_3(\text{CO})_{12}]$ and $[\{\text{CpNi}(\text{CO})\}_2]$ at 80° in ethoxyethanol and under hydrogen (249). Another group reported the crystal structure of [243] and its isomorphous and paramagnetic analog $[\text{CpCoOs}_3\text{H}_3(\text{CO})_9]$ [245] (250).

The reactivity of alkyne- and vinylidene-containing clusters toward hydrogen was probed. The reactions include those in equations (10)-(15) (251).





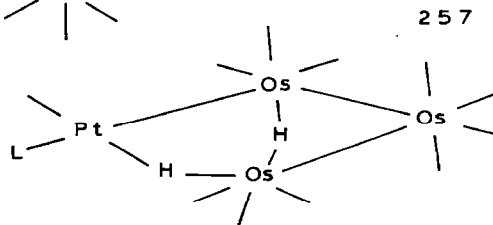
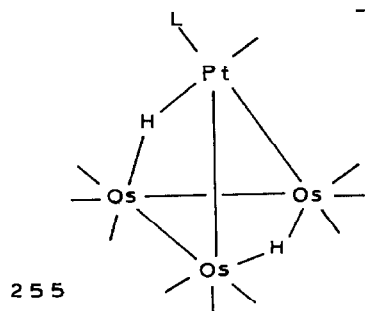
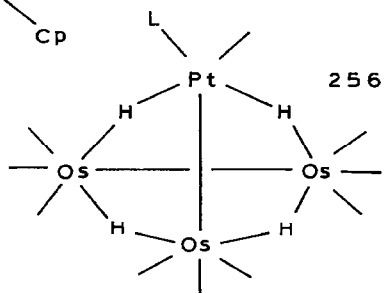
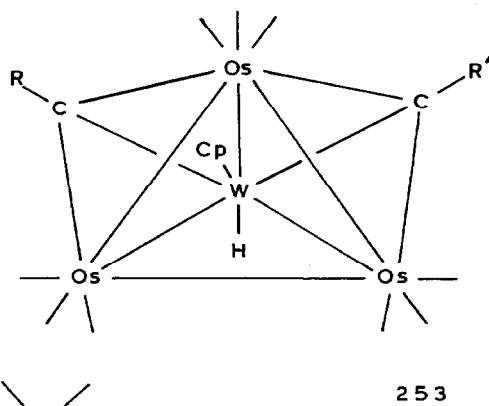
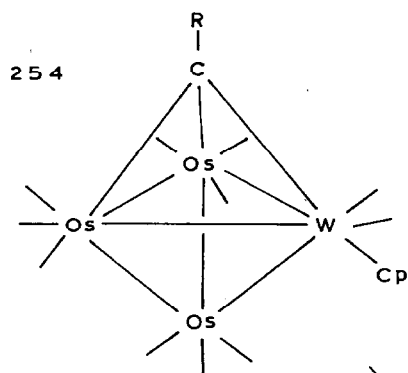
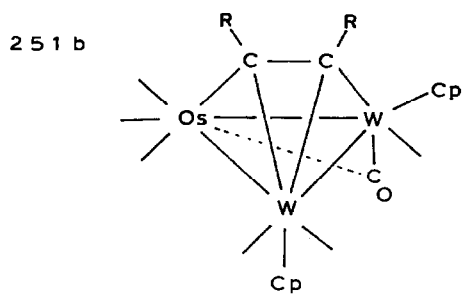
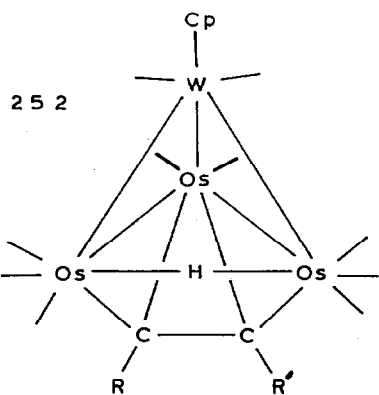
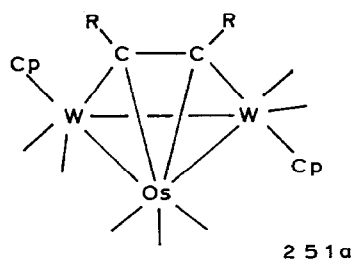
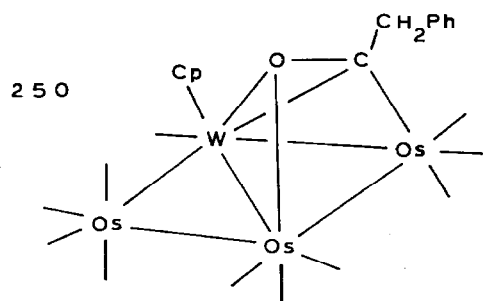
The mixed metal vinylidene $[\text{CpNiRu}_3\text{H}(\text{CO})_9(\text{C}=\text{CH}-i\text{-Pr})]$ [246] was prepared in 40-50% yield from $[\{\text{CpNi}(\text{CO})\}_2]$, $[\text{Ru}_3\text{H}(\text{CO})_9(\text{C}_2-i\text{-Pr})]$, and hydrogen in refluxing octane. The product was characterized by X-ray crystallography and by spectroscopic methods (252).

In a similar manner, reactions of $[\{\text{CpNi}(\text{CO})\}_2]$ with either $[\text{Os}_3\text{H}(\text{CO})_9(\text{C}_2\text{CMe}_3)]$ or $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{HC}=\text{CHCMe}_3)]$ under hydrogen produce $[\text{CpNiOs}_3\text{H}(\text{CO})_9(\text{C}=\text{CHCMe}_3)]$ [247] in low yield; the product was crystallographically characterized (253).

The sulfide-bridged cluster $[\text{Os}_3\text{W}(\text{CO})_{12}(\text{PMe}_2\text{Ph})(\mu_3\text{-S})_2]$ [248] was prepared in 28% yield by pyrolysis of a mixture of $[\text{W}(\text{CO})_5(\text{PMe}_2\text{Ph})]$ and $[\text{Os}_3(\text{CO})_9(\mu_3\text{-S})_2]$ in hexane. The structure of the product, established by X-ray crystallography, was found to contain two long metal-metal bonds. At 25° the compound adds PMe_2Ph , forming the planar cluster $[\text{Os}_3\text{W}(\text{CO})_{12}(\text{PMe}_2\text{Ph})_2(\mu_3\text{-S})_2]$ [249], also crystallographically characterized (254).

A number of Os-W clusters have been prepared from carbyne complexes of W. The reaction between $[\text{CpW}(\text{CO})_2(\text{CC}_6\text{H}_4\text{Me-4})]$ and $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ produces $[\text{CpWOs}_3(\text{CO})_{11}[\text{C}(\text{O})\text{CH}_2\text{C}_6\text{H}_4\text{Me-4}]]$ [250] (21%), $[(\text{CpW})_2\text{Os}(\text{CO})_7[\text{C}_2(\text{C}_6\text{H}_4\text{Me-4})_2]]$ [251] ($\text{R}=\text{C}_6\text{H}_4\text{Me-4}$, 33%), and $[\text{CpWOs}_3\text{H}(\text{CO})_{10}(\text{CC}_6\text{H}_4\text{Me-4})_2]$ [252] ($\text{R}=\text{R}'=\text{C}_6\text{H}_4\text{Me-4}$, 22%). The products are formed by parallel paths. Also produced are $[\text{CpW}(\text{CO})_3\text{H}]$ and $[\text{Os}_2\text{H}_2(\text{CO})_8]$, which are by-products of the paths leading to [252] and [251], respectively. Isotope labeling showed that the source of the benzylic protons of [250] and the hydride of [252] is $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$. The crystal structure of [250] was reported (255). A later paper by these workers described the syntheses of $[\text{CpWOs}_3\text{H}(\text{CO})_{10}(\text{RC}_2\text{R}')] [252]$ by reaction of $[\text{CpWOs}_3\text{H}(\text{CO})_{12}]$ with trimethylamine-N-oxide and alkynes $\text{RC}_2\text{R}'$ ($\text{R}=\text{R}'=\text{C}_6\text{H}_4\text{Me-4}$, $\text{R}=\text{R}'=\text{Ph}$, and $\text{R}=\text{Ph}$, $\text{R}'=\text{C}_6\text{H}_4\text{Me-4}$); the crystal structure of the bis(4-tolyl)acetylene derivative was determined. These products rearrange to the bis(carbyne) clusters $[\text{CpWOs}_3\text{H}(\text{CO})_9(\mu_3\text{-CR})(\mu_3\text{-CR}')] [253]$ in ca. 60% yields after treatment with trimethylamine-N-oxide in acetonitrile, followed by pyrolysis in refluxing toluene. The crystal structure of the bis(4-tolylcarbyne) derivative was reported (256). Mixed W-Os or W-Ru clusters containing alkynes or carbynes have been prepared by others from reactions of $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ or $[\text{Ru}_3(\text{CO})_{12}]$ with $[\text{CpW}(\text{CO})_2(\text{CC}_6\text{H}_4\text{Me-4})]$. In these cases the products are $[(\text{CpW})_2^{\text{M}}(\text{CO})_7(\text{RC}_2\text{R})]$ ($\text{M}=\text{Ru}$ or Os , $\text{R}=\text{C}_6\text{H}_4\text{Me-4}$). The crystal structure of the Os compound contains two isomeric molecules [251a] and [251b]. The carbyne cluster $[\text{CpWOs}_3(\text{CO})_{11}(\text{CR})]$ [254] was prepared from $[\text{CpW}(\text{CO})_2(\text{CR})]$ ($\text{R}=\text{C}_6\text{H}_4\text{Me-4}$) and $[\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2]$ and was characterized by X-ray crystallography (257).

Hydrogenation of the unsaturated cluster $[\text{Os}_3\text{PtH}_2(\text{CO})_{10}(\text{PCyc}_3)] [255]$ yields $[\text{Os}_3\text{PtH}_4(\text{CO})_{10}(\text{PCyc}_3)] [256]$; the reaction may be reversed by purging with nitrogen. Under a CO atmosphere, [255] forms $[\text{Os}_3\text{PtH}_2(\text{CO})_{11}(\text{PCyc}_3)]$



[257]. Both [256] and [257] were characterized by X-ray crystallography (258).

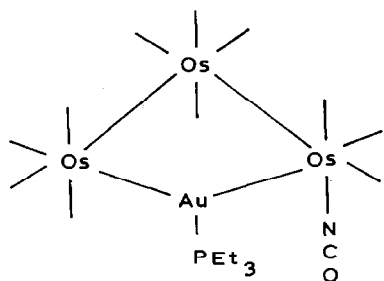
A large number of mixed metal clusters containing Group 11 or 12 metals have been prepared by reactions of cluster anions with sources of ML_n^+ or ML_n^{2+} . These complexes are classified as mixed metal clusters, rather than as salts of homonuclear cluster anions, because of the strong and well-defined heterometallic bonds. A wide variety of methods have been used to prepare these complexes.

Treatment of $[Os_3(CO)_{12}]$ with $[ClAuPEt_3]$, sodium azide and 18-crown-6 formed $[Os_3(AuPEt_3)(CO)_{11}(NCO)]$ [258] (20%) and $[Os_3(AuPEt_3)(CO)_{10}(NCO)]$ [259] (62%). Also prepared were the $AuPPh_3$ analogs. In a related reaction $[Os_3(AuPEt_3)(CO)_{10}(NO)]$ [260] was prepared in 7% yield from $[Os_3(CO)_{12}]$, $[ClAuPEt_3]$, and sodium nitrite. Reactions of [259] with water, methanol, benzylamine, $BH_3 \cdot THF$, PEt_3 , PPh_3 , and $PhNPPH_3$ gave $[Os_3(AuPEt_3)(CO)_{10}(NHC(O)X)]$ [261] ($X=OH, OMe, NHBz$, and H), $[Os_3(CO)_9(PEt_3)_3]$, $[Os_3(AuPEt_3)(CO)_9(PPh_3)(NCO)]$, and $[Os_3(AuPEt_3)(CO)_{10}(NCNPh)]$ [262], respectively. $BH_3 \cdot THF$ and benzylamine react with [262], forming $[Os_3(AuPEt_3)(CO)_{10}(NHC(NPh)X)]$ [263] ($X=H$ or $NHBz$, respectively). The products [259] and [258] are also formed from $[Os_3(CO)_{11}^-(NCMe)]$ and $[OCNAuPEt_3]$, but only [259] from $[Os_3(CO)_{10}(NCMe)_2]$ (259).

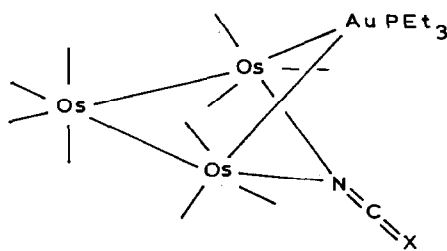
A quantitative yield of $[Os_3(AuPR_3)H(CO)_{11}]$ [264] is obtained by treatment of $[PPN][Os_3H(CO)_{11}]$ with $[ClAuPR_3]$ ($R=Ph, Et$) and $TlPF_6$. Pyrolysis of [264] produces $[Os_3(AuPR_3)H(CO)_{10}]$ [265]. Deprotonation of [264] to $[Os_3^-(AuPR_3)(CO)_{11}]^-$, followed by reaction with $[ClAuPR_3]/TlPF_6$, produces $[Os_3^-(AuPR_3)_2(CO)_{11}]^{2-}$ [266]; this product may also be obtained from $[Os_3(CO)_{11}]^{2-}$ and two equivalents of $[ClAuPR_3]$. Pyrolysis of [266] yields $[Os_3(AuPR_3)_2(CO)_{10}]$ [267], also obtained from $[Os_3H(CO)_{10}(COBz)]$, $[ClAuPEt_3]$, and $TlPF_6$, and characterized by X-ray crystallography. This procedure was used to prepare $[Os_3(AuPEt_3)(CO)_{10}(\mu-OEt)]$. Nucleophiles such as $L=NEt_3$ and PPh_3 add to [266], forming $[Os_3(AuPEt_3)_2(CO)_{11}L]$ (260).

Treatment of hydride-containing Os clusters with, first, lithium diisopropylamide and then $[ClAuPPh_3]/TlPF_6$ was used to prepare $[Os_3(AuPPh_3)(CO)_{10}X]$ [268] ($X=OH, NHO_2C_6H_4Me-4$) and $[Os(AuPPh_3)(CO)_8L(2-NHC_5H_4N)]$ [269] ($L=CO, PPh_3$). The crystal structure of [269] ($L=PPh_3$) was reported. Also prepared was $[Os_3(AuPPh_3)(CO)_9(C_2Ph)]$ by treatment of $[Os_3(CO)_{10}(NCMe)_2]$ with $[PhC_2AuPPh_3]$ (261).

The Ru-Hg clusters $[Ru_3(HgX)(CO)_9(C_2CMe_3)]$ [270] ($X=I$ (80%), Br (45%)) were prepared by reaction of $[Ru_3H(CO)_9(C_2CMe_3)]$ with first KOH and then HgX_2 in THF . These products were reacted further with $[AsPh_4][Ru_3(CO)_9(C_2CMe_3)]$ or with $Na[Mo(CO)_3Cp]$ to produce $[Hg\{Ru_3(CO)_9(C_2CMe_3)\}_2]$ [271] (100%) or $[Hg\{Ru_3(CO)_9(C_2CMe_3)\}\{Mo(CO)_2Cp\}]$ [272] ($X=Mo(CO)_2Cp$), respectively. The crystal structures of [271] and [272] were determined (262).

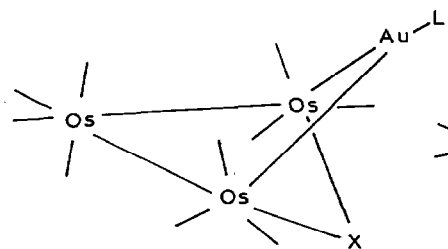


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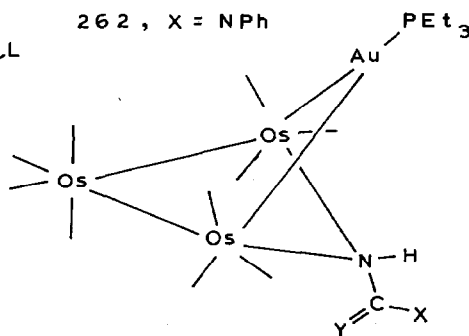
259, X = O

262, X = NPh



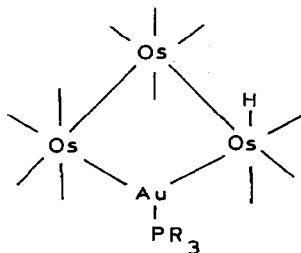
260, X = NO

268, X = OH, NHR

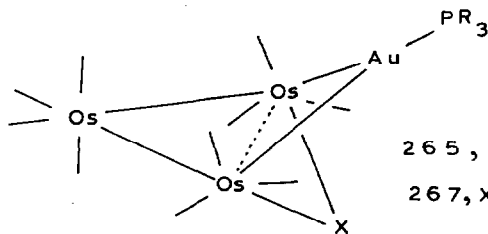


261, Y = O, X = OH, OMe, NHBz, H

263, Y = NPh, X = H, NHBz

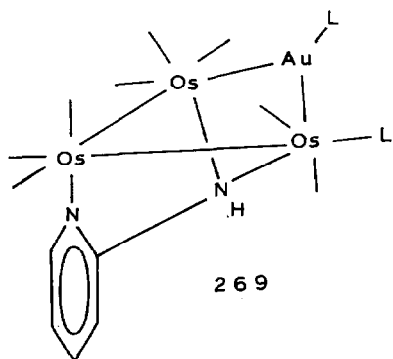


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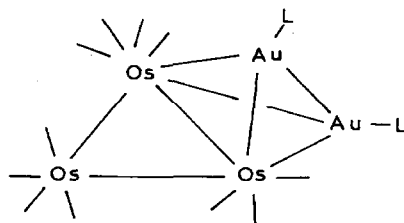


265, X = H

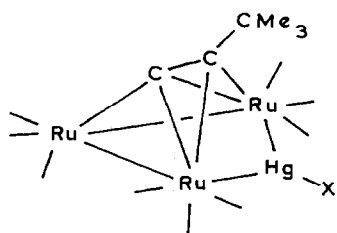
267, X = AuR3



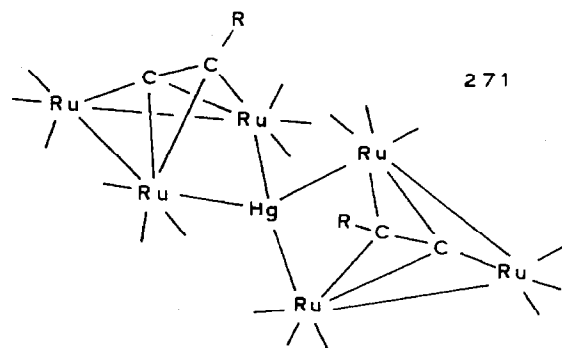
269



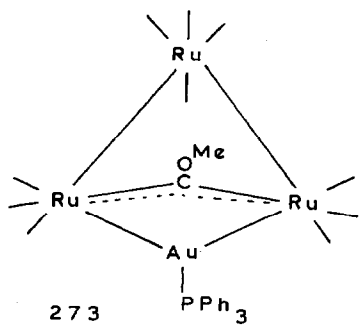
266



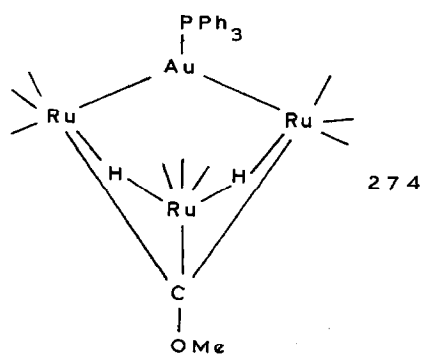
270, X = I, Br

272, X = Mo(CO)₂Cp

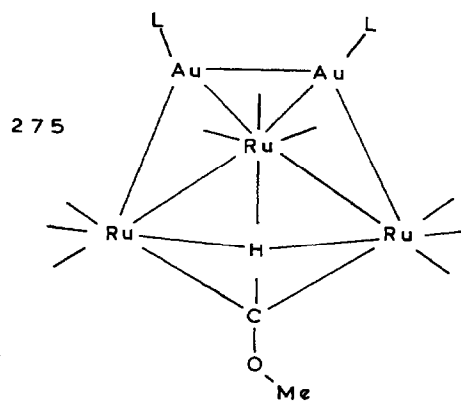
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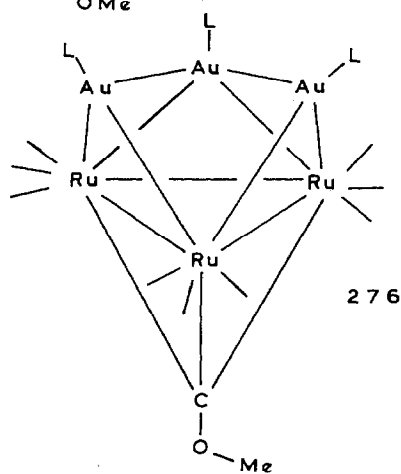
273



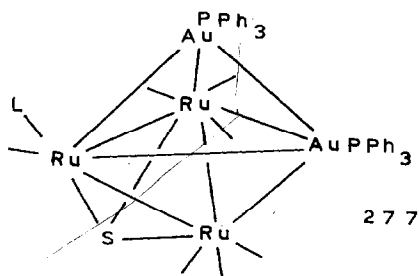
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276



277

Reactions between methyl gold complexes and metal hydrides are also useful for the formation of mixed metal clusters. Combination of $[\text{MeAuPPh}_3]$ and $[\text{Ru}_3\text{H}(\text{CO})_{10}(\mu\text{-COMe})]$ yields $[\text{Ru}(\text{AuPPh}_3)(\text{CO})_{10}(\mu\text{-COMe})]$ [273], characterized by X-ray crystallography. Similarly, $[\text{MeAuPPh}_3]$ and $[\text{Ru}_3\text{H}_3(\text{CO})_9(\mu_3\text{-COMe})]$ form three products: $[\text{Ru}_3(\text{AuPPh}_3)\text{H}_2(\text{CO})_9(\mu_3\text{-COMe})]$ [274], $[\text{Ru}_3(\text{AuPPh}_3)_2\text{H}(\text{CO})_9(\mu_3\text{-COMe})]$ [275], and $[\text{Ru}_3(\text{AuPPh}_3)_3(\text{CO})_9(\mu_3\text{-COMe})]$ [276]; these products were characterized by spectroscopic methods and [274] and [276] by X-ray crystallography (263). The same synthetic method was used to prepare $[\text{Ru}_3(\text{AuPPh}_3)\text{H}(\text{CO})_8\text{L}(\mu_3\text{-S})]$ and $[\text{Ru}_3(\text{AuPPh}_3)_2(\text{CO})_8\text{L}(\mu_3\text{-S})]$ [277] from $[\text{Ru}_3\text{H}_2(\text{CO})_9(\mu_3\text{-S})]$; other products were $[\text{Ru}_3\text{H}_2(\text{CO})_7(\text{PPh}_3)\text{L}(\mu_3\text{-S})]$ (L=CO or PPh_3). The crystal structures of [277] (L= PPh_3) and [275] were reported. Facile Au-Ru bond cleavage was proposed to explain the fluxional behavior of the Au_2Ru_3 complexes (264).

Mixing $[\text{Ru}_4\text{H}_3(\text{CO})_{12}]^-$ and $[(\text{AuPPh}_3)_3\text{O}]^+$ produces $[\text{Ru}_4(\text{AuPPh}_3)\text{H}_3(\text{CO})_{12}]$ (10%), $[\text{Ru}_4(\text{AuPPh}_3)_2\text{H}_2(\text{CO})_{12}]$ (3%), and $[\text{Ru}_4(\text{AuPPh}_3)_3\text{H}(\text{CO})_{12}]$ [278] (15%); the crystal structure of the last of these was reported (265).

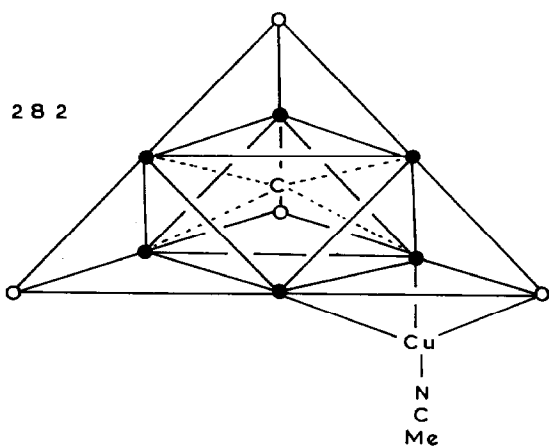
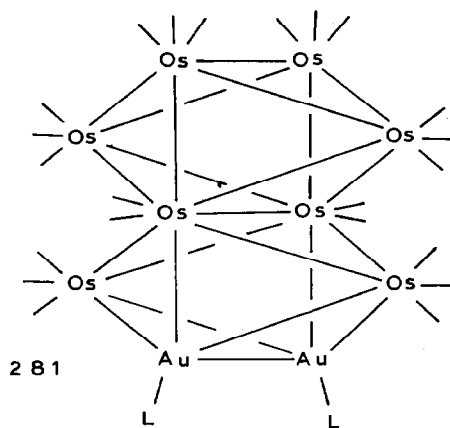
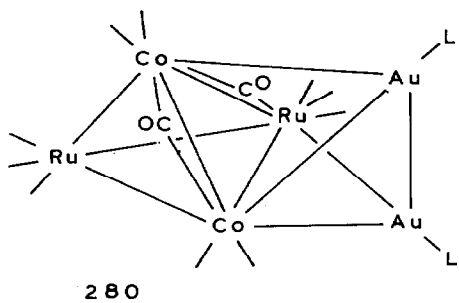
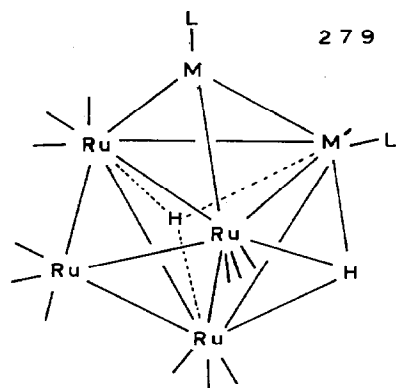
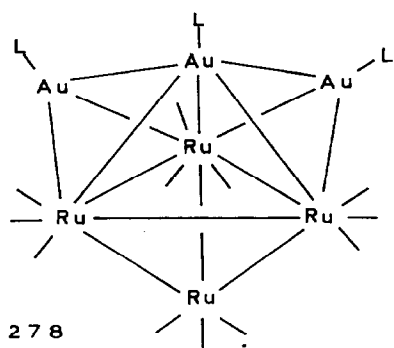
Cu-, Ag-, and Au-Ru clusters $[\text{Ru}_4(\text{MPPh}_3)_2\text{H}_2(\text{CO})_{12}]$ [279] (M=Cu, Ag, or Au) were prepared in ca. 50% yield by treatment of $[\text{PPN}]_2[\text{Ru}_4\text{H}_2(\text{CO})_{12}]$ with TiPF_6 and the appropriate $[\text{XMPPh}_3]$. Also prepared by this method were $[\text{Ru}_4(\text{MPPh}_3)(\text{M}'\text{PPh}_3)\text{H}_2(\text{CO})_{12}]$ (M=Ag, M'=Cu; M=Au; M'=Cu or Ag). The crystal structures of the dicopper-, disilver-, and copper silver tetraruthenium clusters were reported. Two types of Group 11 metal exchange were established: intramolecular exchange on the NMR timescale and intermolecular exchange (266).

The reaction between $[\text{ClAuPPh}_3]$ and $[\text{Ru}_2\text{Co}_2(\text{CO})_{12}]^{2-}$, prepared by deprotonation of $[\text{Ru}_2\text{Co}_2\text{H}_2(\text{CO})_{12}]$ with potassium hydride in THF, was used to prepare $[\text{Ru}_2\text{Co}_2(\text{AuPPh}_3)_2(\text{CO})_{12}]$ [280] in 38% yield. The product was characterized by X-ray crystallography (267).

The synthesis of $[\text{Os}_8(\text{AuPPh}_3)_2(\text{CO})_{22}]$ [281] (65%) was accomplished from $[\text{Os}_8(\text{CO})_{22}]^{2-}$, $[\text{ClAuPPh}_3]$, and TiPF_6 and the crystal structure of the product was determined (268).

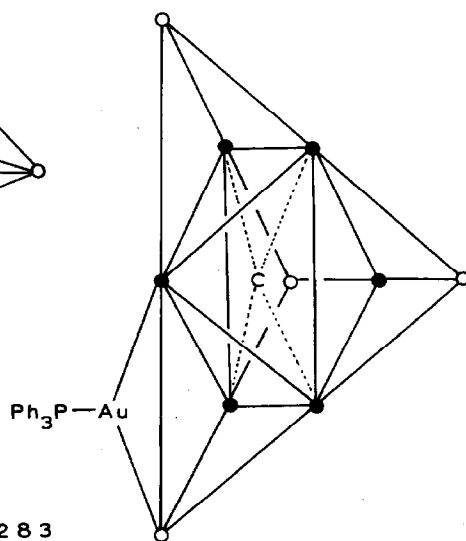
Reactions of $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ with $[\text{Cu}(\text{NCMe})_4][\text{BF}_4]$ or $[\text{ClAuPPh}_3]$ yield $[\text{Os}_{10}(\text{CuNCMe})\text{C}(\text{CO})_{24}]^-$ [282] or $[\text{Os}_{10}(\text{AuPPh}_3)\text{C}(\text{CO})_{24}]^-$ [283], respectively, isolated as the PPh_3Me salts. The products were characterized by X-ray crystallography (269).

Derivatives of $[\text{Os}_{11}\text{C}(\text{CO})_{27}]^{2-}$ [284] were prepared. The large cluster anion was obtained as a minor product from the pyrolysis of $[\text{Os}_3(\text{CO})_{12}]$. The core geometry was established by X-ray crystallography, although disorder prevented refinement. Treatment of the cluster anion with $[\text{Cu}(\text{NCMe})_4][\text{BF}_4]$ gave $[\text{Os}_{11}(\text{CuNCMe})\text{C}(\text{CO})_{27}]^-$ [285], isolated as the PPh_3Me salt and characterized by X-ray methods. The reaction of [284] with $[\text{ClAuPR}_3]$ forms $[\text{Os}_{11}(\text{AuPR}_3)\text{C}(\text{CO})_{27}]^-$ and with iodine gives $[\text{Os}_{11}\text{C}(\text{CO})_{27}\text{I}]^-$; both of these

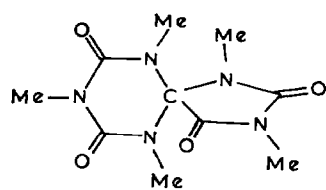
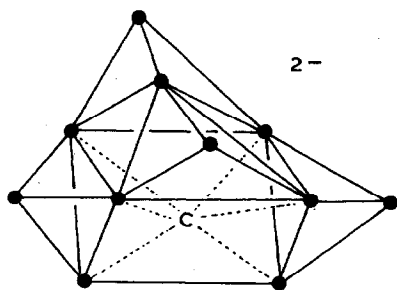


○ = Os(CO)₃

● = Os(CO)₂

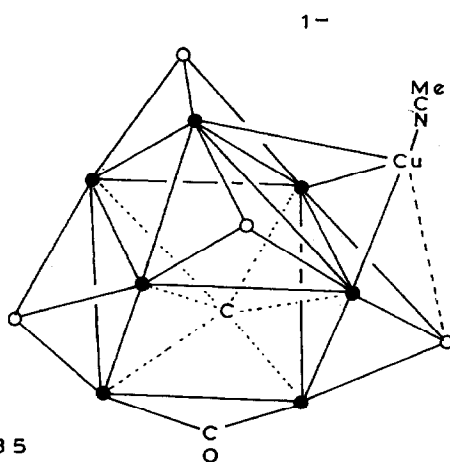


284



286

285

○ = Os(CO)₃● = Os(CO)₂

products decompose to $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ in solution (270).

Catalysis by Clusters and Supported Clusters

Catalysis of spirocyclization of alkyl isocyanates to [4.5]-spiroheterocycles was achieved by $[\text{Ru}_3\text{H}(\text{CO})_{10}(\text{SiEt}_3)_2]^-$ in the presence of triethylsilane. In a typical example, methyl isocyanate, triethylsilane, and $[\text{PPN}][\text{Ru}_3\text{H}(\text{CO})_{10}(\text{SiEt}_3)_2]^-$ (5000:1000:1) in THF at 150° yielded Et_3SiOH and [286]. The cluster does not survive intact, but the residue is an active catalyst, as well (271).

Either $[\text{Ru}_3(\text{CO})_{12}]$ or $[\text{Ru}_4\text{H}_4(\text{CO})_8\{(-)\text{-D1OP}\}_2]$ are catalysts for hydroformylation of pent-1-ene-5- d_3 at 7 to 50 atm of CO and hydrogen, forming primarily linear products. Deuterium retention is high only at high CO pressures. With $[\text{Ru}_3(\text{CO})_{12}]$ deuterium scrambling occurs under all conditions but with $[\text{Ru}_4\text{H}_4(\text{CO})_8\{(-)\text{-D1OP}\}_2]$ deuterium is completely retained and found only in the α , β , and ω positions of the methyl hexanoate after oxidation of the hexanal. Using $[\text{Ru}_3(\text{CO})_{12}]$ as the catalyst (25 mmol alkene, 25 mL benzene, 50 atm CO, 45 atm hydrogen, 0.3 g catalyst, 150°) at 95% conversion the product distribution included alcohol (4.2%), parafin (12.8%), and aldehyde (83%), the last of which was comprised of hexanal (81%), 2-methylpentanal (17%) and 2-ethylbutanal (2.0%). Using $[\text{Ru}_4\text{H}_4(\text{CO})_8\{(-)\text{-D1OP}\}_2]$ under the same conditions gives only a 23% conversion of alcohol (10.5%), parafin (25.5%), and aldehyde (64.0%) as hexanal (85.3%), 2-methylpentanal (14.2%), and 2-ethylbutanal (0.5%) (272).

$[\text{Ru}_4\text{H}_4(\text{CO})_8\{(-)\text{-D1OP}\}_2]$ has also been used as a catalyst for hydrogenation of 2-phenylbutenes to 2-phenylbutane with 8.5% optical purity. Alkene isomerization is responsible for lowering the optical purity (273).

Near UV irradiation of $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$ in heptane induces catalytic hydrogenation of ethylene. For irradiation of 366 n, the quantum yield for ethane is 1.8. CO inhibits the reaction. Photoinduced CO dissociation is proposed as the first step (274).

DBU (1,8-diazabicyclo[5.4.0]decene-7) is an effective co-catalyst with $[\text{M}_3(\text{CO})_{12}]$ (M=Ru,Os) for the water gas shift reaction. In a typical experiment, water (1.0 g), methanol (6 mL), $[\text{Os}_3(\text{CO})_{12}]$ (0.03 mmol), DBU (17 mmol), and CO (10 kg/cm²) were reacted at 150° for 24 h to produce about 175 moles of hydrogen per mole of $[\text{Os}_3(\text{CO})_{12}]$ per day. This compares with 21 moles of hydrogen using triethylamine as the base and 34 moles using potassium hydroxide. Tetranuclear clusters $[\text{M}_4\text{H}_2(\text{CO})_{12}]^{2-}$ and $[\text{M}_4\text{H}_3(\text{CO})_{12}]^-$ could be isolated as the PPN salts from the reaction mixtures (275).

The formation of methyl formate and water from methanol, hydrogen (250 psi) and carbon dioxide (250 psi) is catalyzed by $[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$ or a successor at 125°. A turnover number of 4 per day was found. The formate complex $[\text{Ru}_3(\text{O}_2\text{CH})(\text{CO})_{10}]^-$, formed from either $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{PPN}][\text{O}_2\text{CH}]$ or $[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$ and carbon dioxide, is also a catalyst precursor. After 24 h the

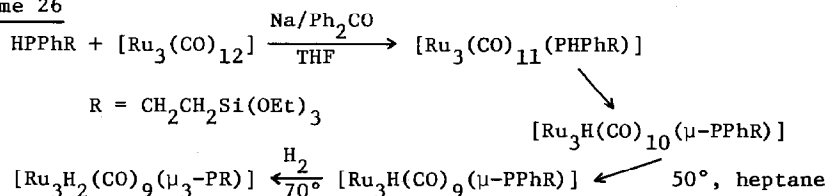
Ru product, recovered nearly quantitatively, is $[\text{Ru}_4\text{H}_3(\text{CO})_{12}]^-$, which is also a catalyst precursor. Under CO the metal product is $[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$, and a higher turnover rate for methyl formate (106 vs. 7) is observed. However, carbon dioxide conversion to methyl formate is not thought to involve CO (276).

$[\text{Ru}_3(\text{CO})_9(\text{dppm})(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)]$ and analogs supported on phosphinated styrene-divinylbenzene copolymer ($[\text{Ru}_3(\text{CO})_9(\text{dppm})(\text{PPh}_2\text{CH}_2\text{-polymer})]$) and on phosphinated silica ($[\text{Ru}_3(\text{CO})_9(\text{dppm})(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}\equiv)]$) were prepared and characterized (277).

Silica supported $[\text{Ru}_4\text{H}_4(\text{CO})_8(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}\equiv)_4]$ was prepared from $[\text{Ru}_4\text{H}_4(\text{CO})_8\text{-PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4]$ and was characterized by IR and UV/visible spectroscopy. This material was tested as a catalyst for ethylene hydrogenation. Activity was higher than for $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ deposited on silica (278).

$[\text{Ru}_3\text{H}_2(\text{CO})_9(\mu_3\text{-PCH}_2\text{CH}_2\text{Si}(\text{OEt})_3)]$ was prepared in overall 67% yield according to Scheme 26. This product was then attached to SiO_2 , Al_2O_3 , TiO_2 , MgO , and ZnO . The supported clusters were characterized by IR spectroscopy and were used for catalysis of alkene isomerization. Cluster breakdown was observed (279).

Scheme 26



Physisorption of $[\text{Ru}_3(\text{CO})_{12}]$ on partially dehydrated silica (500°, 20 h), forms $[\text{Ru}_3\text{H}(\text{CO})_{10}(\text{OSi}\equiv)]$, which decomposes only above ca. 100°C to Ru metal particles and an Ru(II) carbonyl surface species. Characterization was by IR and Raman spectroscopy and by quantitative CO determination (280).

A variety of Ru-containing clusters - $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{Ru}_4\text{H}_2(\text{CO})_{13}]$, $[\text{FeRu}_3\text{H}_2(\text{CO})_{13}]$, and $[\text{PPN}][\text{CoRu}_3(\text{CO})_{13}]$ - adsorbed on Al_2O_3 , SiO_2 , or Na-Y zeolite were found to catalyze CO reduction to methane. Carbon dioxide reduction to methane was also achieved using $[\text{Ru}_3(\text{CO})_{12}]$ on Al_2O_3 (281).

Heterogeneous catalysts prepared from (a) $[\text{Fe}_3(\text{CO})_{12}]$ and $[\text{Ru}_3(\text{CO})_{12}]$, (b) $[\text{FeRu}_3\text{H}_2(\text{CO})_{13}]$, or (c) $[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$ deposited on Cab-O-Sil from hexane solution were examined for the conversion of CO and hydrogen to hydrocarbons. Catalysts (a) and (c) had the same activity; (b) was the least active. Catalysts formed by decomposition under helium were more active than those formed by decomposition under hydrogen. The kinetics for CO reduction were examined and a mechanism proposed (282).

Differences in catalytic behavior are exhibited by $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$ supported on Al_2O_3 and MgO . On Al_2O_3 treatment of $[\text{Ru}_3(\text{CO})_{12}]$

with CO/hydrogen produces Ru metal, identical to supported Ru metal catalysts prepared by classical methods. On MgO $[\text{Ru}_3(\text{CO})_{12}]$ acts as a catalyst precursor for methanol production from CO/hydrogen and after the catalytic experiment $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ was identified on the surface. The hexanuclear cluster was proposed to be formed from $[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$ and $[\text{Ru}_6(\text{CO})_{18}]^{2-}$. On either support $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$ is a catalyst for the production of oxygenates from CO/hydrogen. On the surface $[\text{Ru}_4\text{H}_3(\text{CO})_{12}]^-$ reacts further, forming $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$. Oxygenate selectivity was attributed to the presence of intact clusters. Cluster species were identified by IR spectroscopy and by isolation after extraction from the surface (283).

Photolysis of $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ supported on partially dehydroxylated silica under hydrogen or nitrogen formed the same surface species, proposed to be $\text{Ru}(\text{CO})_4$. Irradiation of $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ also produced what was suggested to be $[\text{Ru}_4\text{H}_4]\text{SiO}_2$; this material can be carbonylated to some extent back to $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ (284).

Photodecomposition of water was achieved using $[\text{Ru}_3(\text{CO})_{12}]$ deposited on TiO_2 as a catalyst precursor (285).

EXAFS characterizations of $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{O-surface})]$, $[\text{Os}_3(\text{CO})_{12}]$, $[\text{Os}_3\text{H}_2^-(\text{CO})_{10}]$, $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{OMe})]$, $[\text{Os}_3(\text{CO})_{10}(\text{OEt})_2]$, $[\text{Os}_3\text{H}(\text{CO})_9(\text{Spr})]$, and $[\text{Os}_3\text{H}(\text{CO})_{10}\{\text{SCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_{3-n}(\text{O-silica})_n\}]$ using the Os L (111) edge spectra were reported (286).

Adsorption of $[\text{Os}_3(\text{CO})_{12}]$ on MgO was examined. When a high content of surface carbonate is present, oxidative addition of hydroxyl to an Os-Os bond forms $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{OMg})]$ or $[\text{Os}_3(\text{CO})_{10}(\text{OMg})_2]$ on the surface. With highly decarbonated MgO, $[\text{Os}_3(\text{CO})_{11}]^{2-}$ is quickly formed. Thermal treatment in all cases gives a mixture of what are probably mononuclear, di- and tricarbonyl Os(II) surface complexes. Treatment with oxygen yields $[\text{Os}(\text{CO})_2(\text{OMg})_4]^{2-}$, which is very stable with respect to further reactions (287).

Surface adsorbed $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{OAl=})]$ was prepared by reaction of $[\text{Os}_3(\text{CO})_{12}]$ with surface hydroxyls on Al_2O_3 . This material was initially catalytically active for 1-hexene isomerization at 120° , but activity decreased to a constant value after 2 h and the IR spectrum indicated break-up of the cluster to mononuclear Os(II) carbonyl. Isomerization was inhibited by CO and promoted by hydrogen (288).

An extraction technique was used to prepare highly dispersed $[\text{Os}_3(\text{CO})_{12}]$ on Al_2O_3 . Partial decarbonylation could be achieved during the extraction or by heating in air, producing $[\text{Os}(\text{CO})_n]^{2+}$, $n=2$ or 3 (289).

$[\text{Os}_3(\text{CO})_{12}]$ and $[\text{Os}_6(\text{CO})_{18}]$ were impregnated on SiO_2 , Al_2O_3 , and TiO_2 . These materials were characterized as initially deposited and again after heating to 523 K. Heating converts these to a family of species (a) of empirical formula $\text{Os}_n(\text{CO})_{xn} \text{C}_{yn}$, where the most likely values are $n=12$,

$2.0 < X < 3.0$, and $0.0 < y < 0.4$. UV/visible reflectance spectroscopy and electron microscopy suggest that Os-Os bonding is retained. Species (a) chemisorbs CO and oxygen at 293 K. Labeled CO, when adsorbed, does not equilibrate with the CO ligands of (a), confirming that these are different states (290,291).

Decomposition of $[\text{RuOs}_3\text{H}_2(\text{CO})_{13}]$ upon Degussa γ -alumina-C produced alumina-supported $\text{Al}^+[\text{RuOs}_3\text{H}(\text{CO})_{13}]^-$ by reaction of Al-OH with the cluster. Treatment at 373-443 K under 1:1 CO/hydrogen resulted in spectral changes attributed to formation of $[\text{RuOs}_3\text{H}_3(\text{CO})_{12}]^-$. Above 373 K and under vacuum, the cluster decomposed. This material was catalytically active for ethylene hydrogenation and butene isomerization (292).

Decomposition of $[\text{CpNiOs}_3\text{H}_3(\text{CO})_9]$ on Al_2O_3 and thermal treatment of 200° for 4 h under hydrogen produced a catalyst for hydrogenation of alkenes, alkynes, and benzene. The catalyst was also active for methanation of carbon monoxide or dioxide (293).

Miscellaneous Studies of Clusters

The ground-state electronic structures and spectra of $[\text{Ru}_2\text{Cl}_9]^{3-}$ and $[\text{Ru}_3\text{Cl}_{12}]^{4-}$ were calculated by the SCF-X α -SW method and the Fenske-Hall method. For $[\text{Ru}_2\text{Cl}_9]^{3-}$ there is a single sigma bond between the metal atoms and for $[\text{Ru}_3\text{Cl}_{12}]^{4-}$ a bond order of 0.5 is assigned (294).

Self-consistent charge extended Huckel calculations for systems consisting of 1-3 CO molecules chemisorbed on 8-10 atom Ru clusters were performed and the results compared to Pd (295).

MO calculations supplemented by symmetry and perturbation theory arguments were used to evaluate the effect of introducing C_{2v} $\text{M}(\text{CO})_4$ fragments into metal clusters derived from $\text{M}(\text{CO})_3$ fragments. Electron-counting rules for predicting geometries were provided and site preferences and conformational consequences were developed (296).

Highly unsaturated metal-containing molecular ions and atomic metal ions were produced by UV/visible multiphoton dissociation/ionization of metal complexes. Ions and precursors were: Ru_2^+ ($[\text{FeRu}_2(\text{CO})_{12}]$, $[\text{Ru}_3(\text{CO})_{12}]$), Ru_3^+ ($[\text{Ru}_3(\text{CO})_{12}]$), Os_2^+ ($[\text{Os}_3(\text{CO})_{12}]$), Os_3^+ ($[\text{Os}_3(\text{CO})_{12}]$), FeRu^+ ($[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$, $[\text{FeRu}_2(\text{CO})_{12}]$), and Fe_2Ru^+ ($[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$). The technique is useful for the production of gas-phase samples of bare homo- and heteronuclear metal dimers and trimers, metal sulfides, and monoligated metal atoms (297). In another paper the technique was used to compare $[\text{Fe}_{3-n}\text{Ru}_n(\text{CO})_{12}]$, $n=0,1,2$, and 3. The extent of fragmentation is correlated with the M-M bond strength. The role of the initial excitation energy is illustrated by the mixed metal clusters, which reflect the influence of the parent electronic structure in the photo-product yields (298).

Kinetic studies of reactions of metal hydrides of the iron triad with methoxide were reported. Deprotonation was considerably slower than for

oxygen or nitrogen acids of comparable strength; this was interpreted in terms of the degree of structural and electronic rearrangements of substrate and solvent. Protonations of the conjugate bases were also relatively slow. The pK_a 's were calculated from rate constants and using indicator/buffers. Bridging hydrides seem more acidic than terminal ones and acidity decreases down the column. Complexes studied and their pK_a 's are $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$ (11.7), $[\text{Ru}_4\text{H}_4(\text{CO})_{11}\{\text{P}(\text{OMe})_3\}]$ (14.7), $[\text{Ru}_4\text{H}_4(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$ (>15), $[\text{Os}_4\text{H}_4(\text{CO})_{12}]$ (12.0), $[\text{FeRu}_3\text{H}_4(\text{CO})_{12}]$ (11.8), $[\text{Ru}_4\text{H}_2(\text{CO})_{13}]$ (11.1), $[\text{FeRu}_3\text{H}_2(\text{CO})_{13}]$ (11.2), $[\text{Os}_3\text{H}_2(\text{CO})_{12}]$ (14.7), and $[\text{OsH}_2(\text{CO})_4]$ (15.2) (299).

The principal components of the ^{13}C NMR chemical shift tensors of metal carbonyls including $[\text{M}_3(\text{CO})_{12}]$ (M=Ru,Os) were determined. The tensors of terminal CO ligands are highly anisotropic (380±60 ppm) and nearly axially symmetric. Those of bridging CO ligands are much less anisotropic (300).

CATALYSIS

Reduction

Hydrogenation catalyzed by $[\text{OsHBr}(\text{CO})(\text{PPh}_3)_3]$ has been investigated (301). In the absence of hydrogen 1-hexene is isomerized to 2-hexenes at 150°, and in the presence of hydrogen (1 atm), 95% conversion to hexane is achieved after 30 min. The complex also catalyzes hydrogenations of propionaldehyde and acetone (30 and 70 atm, 100 and 180 min., 100 and 15% conversion, respectively). Using this catalyst 1-hexene was hydroformylated (150°, 100 atm CO/hydrogen, 1440 min., 30% conversion) to C_7 aldehydes (57%, 70% linear), other products were C_7 alcohols (7%), hexane (5%), and 2-hexene (23%).

Hydrogenation of alkenes is catalyzed by $[\text{RuCl}_2(\text{PPh}_3)\text{L}]$, where L=1-[N,N- α -dimethylaminoethyl]-2-diphenylphosphinoferrocene. The rate of 1-hexene reduction in butanol at 40° is first order in alkene and in hydrogen and inverse order in PPh_3 . The dependence upon catalyst concentration changes from first order to half order with increasing concentration. The catalyst is proposed to be a Ru(I) complex (302).

The kinetics of hydrogenation of allyl alcohol and of allyl bromide using $[\text{RuCl}_2(\text{PPh}_3)_3]$ was investigated. During hydrogenation of allyl alcohol, rapid catalyst deactivation was noted due to formation of $[\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]$ by CO abstraction. For allyl bromide the hydrogenation rate is zero order in both alkene and hydrogen and 0.85 order in catalyst. Phosphine dissociation from $[\text{RuHCl}(\text{PPh}_3)_3]$ is proposed to be rate-determining (373).

Selective hydrogenation of 1,3- and 1,5-cyclooctadiene to cyclooctene is achieved using $[\text{Ru}(1,5\text{-cyclooctadiene})(1,3,5\text{-cyclooctatriene})]$ as the catalyst in THF at 20° and 1 atm. Isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene occurs during the process. Norbornadiene is not hydrogenated

under the same conditions and the solvent influences the selectivity. A mechanism was proposed (303).

Anthracene is hydrogenated to 1,2,3,4-tetrahydroanthracene using $[\text{RuH}_2(\text{PPh}_3)_2(\text{PPh}_2\text{C}_6\text{H}_4)]^-$ as the catalyst. The mechanism was investigated. Under hydrogen, $\text{K}[\text{RuH}_2(\text{PPh}_3)_2(\text{PPh}_2\text{C}_6\text{H}_4)]^-$ forms *fac*- $[\text{RuH}_3(\text{PPh}_3)_3]^-$ in 85% yield over a 24 h period. The trihydride reacts quantitatively with anthracene, forming $[\text{RuH}(\text{PPh}_3)_2(\text{anthracene})]^-$ and 1,2,3,4-tetrahydroanthracene. Under hydrogen $[\text{RuH}(\text{PPh}_3)_2(\text{anthracene})]^-$ yields $[\text{RuH}_5(\text{PPh}_3)_2]^-$ and 1,2,3,4-tetrahydroanthracene. The pentahydride complex reacts in turn with anthracene to give $[\text{RuH}(\text{PPh}_3)_2(\text{anthracene})]^-$ and 1,2,3,4-tetrahydroanthracene, with 1-hexene to give $[\text{RuH}_3(\text{PPh}_3)_2]^-$ and hexane, and with ethylene to form ethane and $[\text{Ru}(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)(\text{C}_2\text{H}_4)_2]^-$. The mechanisms of these hydrogenations were discussed (304).

Catalysis of the hydrogenation of 1,3-pentadiene by RuCl_3 in the presence of polyethylenimine was reported. The Ru(III) precursor was reduced with hydrogen or with sodium borohydride (305).

Poisoning of catalytic hydrogenation of 1-hexene by dibenzo[a,c]cyclooctatetraene was used as evidence for the homogeneity of a number of catalyst systems, including $[\text{RuCl}_2(\text{PPh}_3)_3]$. Catalysis by metal surfaces appears not to be affected (306).

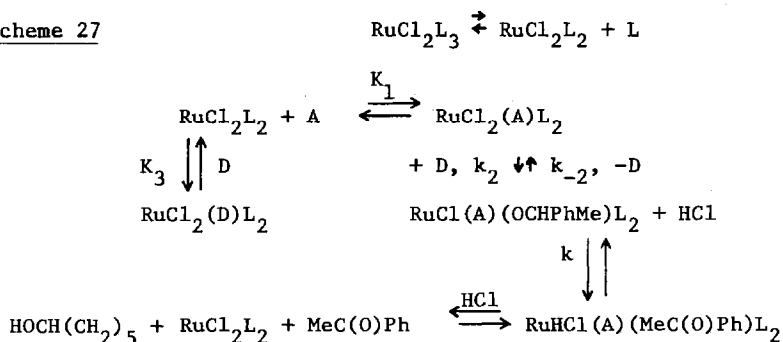
Reduction of nitrobenzene to aniline was achieved using CO and water with $[\text{Ru}_3(\text{CO})_{12}]$ as the catalyst precursor and in the presence of 3,4,7,8-tetramethylphenanthroline, phen, bipy or py. Best results were obtained with the chelating bases, and only 1-2 equivalent of base was required. After 2 h, 97% conversion to aniline was achieved using a 1:1 ratio of 3,4,7,8-tetramethylphenanthroline/Ru ($[\text{Ru}_3(\text{CO})_{12}]$, 8×10^{-7} mol, and aniline/ $[\text{Ru}_3(\text{CO})_{12}]$, 6000, in ethanol at 165° and 30 atm) (307).

Phase-transfer reduction of nitro compounds by CO/hydrogen is catalyzed by $[\text{RuCl}_2(\text{PPh}_3)_3]$ at 25° and 1 atm. Typical reaction conditions used toluene (10 mL), sodium hydroxide solution (5 N, 8 mL), benzyltriethylammonium chloride (0.5 mmol), nitroarene (2.5 mmol), and catalyst (0.25 mmol) for 24 h. The proposed mechanism involves attack of RNO_2 on RuCO to form a cyclic RNORuC(O)O intermediate and then attack of the partially reduced RNO on RuCO to form RNRuC(O)CO (308).

Hydrogen transfer from 1-phenylethanol (D) to cyclohexanone (A) is catalyzed by $[\text{RuCl}_2(\text{PPh}_3)_3]$ (C) in diphenyl ether at 140°. An induction period is found unless $[\text{RuHCl}(\text{PPh}_3)_3]$ is used as the catalyst. The initial rate law is given by equation (16). Based upon this, the mechanism shown in Scheme 27 is proposed (374).

$$(16) \text{ rate} = K_1 k_2 [\text{D}][\text{A}][\text{C}]_t / \{1 + K_3 [\text{D}] + K_1 [\text{A}] + k^{-1} K_1 k_2 [\text{D}][\text{A}]\}$$

Scheme 27



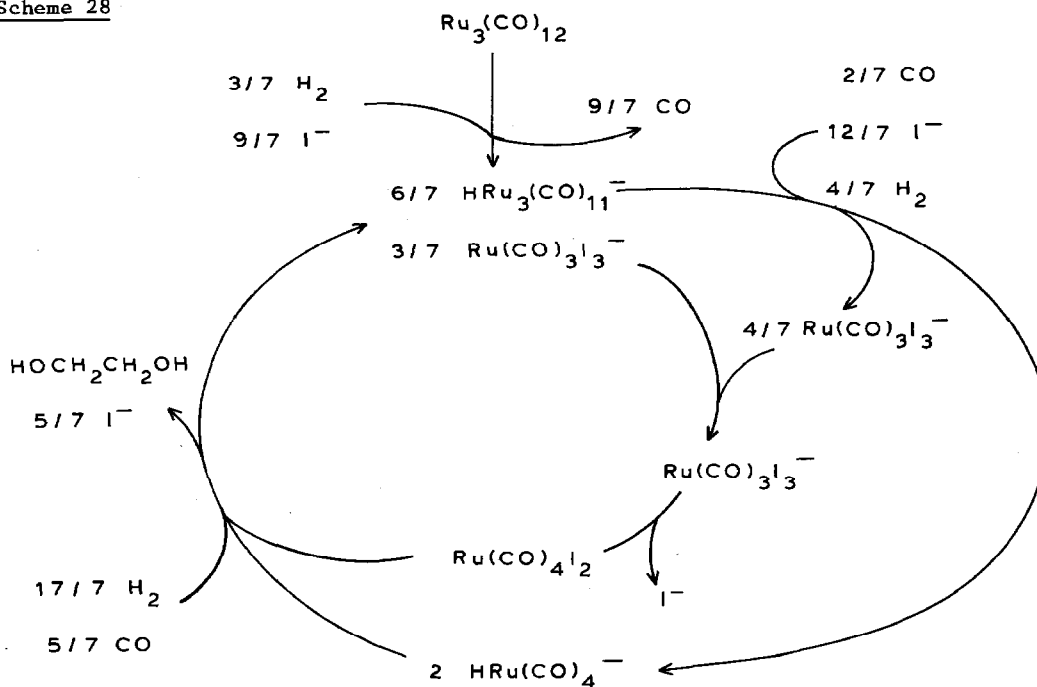
Some Ru complexes catalyze regioselective dehydrogenation of unsymmetrically substituted 1,4- and 1,5-diols, forming β -substituted γ -lactones and γ -substituted δ -lactones, respectively, in the presence of α,β -unsaturated ketones as hydrogen acceptors and triethylamine. Regioselectivity is governed by steric repulsion between the diol substituents and the other ligands in the coordination sphere. Catalysts which are effective are $[\text{RuCl}_2(\text{PPh}_3)_3]$, $[\text{Ru}_2\text{Cl}_4\{(-)\text{-DlOP}\}_3]$, and $[\text{Ru}_2\text{Cl}_4\{1,4\text{-bis}(\text{diphenylphosphine})\text{butane}\}_3]$. Typical reaction conditions: diol (5 mmol), 4-phenyl-3-buten-2-one (10 mmol), catalyst (0.2 mmol), triethylamine (0.12 mL), and toluene (25 mL) at 110° for 10-20 h (309).

Reactions Involving Synthesis Gas

Ru carbonyls in the presence of an iodide source, an acid, and a phosphine oxide are catalysts for the conversion of CO and hydrogen to ethanol at 30-87 MPa and 180-250°. Other products are methanol, methane, acetaldehyde, ethylene glycol, and propanol. Much of the ethanol product is formed by homologation of methanol. The function of the phosphine oxide appears to be to moderate the acidity of the solution (310).

A study of the mechanism of the Ru/I catalyst system for conversion of CO and hydrogen to methanol, ethanol, and ethylene glycol was reported. Variations in activity with the solvent, cation, promoters, catalyst concentration, temperature, and pressure were examined. The major metal species present in the system under operating conditions are $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ and $[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$. Model studies were conducted on reactions of $[\text{RuH}(\text{CO})_4]^-$ with $[\text{Ru}(\text{CO})_4\text{I}_2]$ and of $[\text{RuH}(\text{CO})_4]^-$ with $[\text{CpRe}(\text{CO})_2(\text{NO})]^+$. These studies led to the suggestion that $[\text{RuH}(\text{CO})_4]^-$ attacks $[\text{Ru}(\text{CO})_4\text{I}_2]$ to form the formyl complex $[\text{Ru}(\text{CO})_3\text{I}_2^-(\text{CHO})]^-$, which is the precursor to ethylene glycol and some methanol. The proposed mechanism is shown in Scheme 28 (311).

Scheme 28



Mixed Ru-Rh catalysts have been reported to be effective catalysts for ethylene glycol production from CO and hydrogen. One study examined $[\text{Ru}(\text{acac})_3]$ and $[\text{Rh}(\text{acac})_3]$ as catalyst precursors in $[\text{PBU}_4]\text{Br}$ melts. Products were ethylene glycol, ethylene glycol monoalkyl ether, methanol and ethanol. Maximum activity for ethylene glycol was found at a Ru/Rh ratio of 1. The IR spectrum of the product solution indicated the presence of $[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$ and $[\text{Ru}(\text{CO})_2\text{Br}_4]^{2-}$, while chromatography was used to isolate $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{RhRu}_2(\text{CO})_{12}]^-$ from this mix. At pressures of 300 atm, glycol/alkanol weight ratios of 1:1.37 were achieved with glycol derivatives accounting for greater than 30 wt. % of the liquid products (312). In another study, the catalyst was derived from $[\text{Ru}(\text{acac})_3]$ and $[\text{Rh}(\text{CO})_2(\text{acac})]$ in the presence of acetic acid and triethylamine. This system produced methyl acetate, ethyl acetate and the diacetate of ethylene glycol from CO and hydrogen. Both CO conversion and selectivity to C_2 products were enhanced by the use of both metals. Metal species observed in the product mixture include $[\{\text{Ru}(\text{CO})_3(\text{OAc})\}_2]$, $[\text{Ru}(\text{CO})_5]$, $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{Rh}_6(\text{CO})_{16}]$, and $[\text{Rh}_6(\text{CO})_{15}\text{X}]^-$ ($\text{X}=\text{H}$ or OAc). In a typical example, Ru (2 mmol), Rh (0.2 mmol), triethylamine (4 mmol), acetic acid (50 mL) and CO/hydrogen (1000 atm, 1:1 ratio) were kept at 230° for 2-4 hr, producing 0.182 M/h of methyl acetate, 0.098 M/h of ethyl acetate, and

0.262 M/h of ethylene glycol diacetate (313).

Mixed Co-Ru catalysts were tested for methanol homologation to ethanol. $[\text{CpRu}(\text{PPh}_3)_2\text{Co}(\text{CO})_4]$, prepared in 28% yield by the reaction of $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ with $\text{Tl}[\text{Co}(\text{CO})_4]$, was compared with $[\text{Co}_2(\text{CO})_8]$ alone, with $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ alone, and with mixtures of $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]/[\text{Co}_2(\text{CO})_8]$ and of $[\text{Ru}(\text{acac})_3]/-[\text{Co}_2(\text{CO})_8]$. The bimetallic catalysts containing Co, Ru, and PPh_3 were all superior to $[\text{Co}_2(\text{CO})_8]$ or to $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ alone. The metals are proposed to act independently, Co for homologation of methanol to acetaldehyde, Ru for reduction of acetaldehyde to ethanol. In a typical example, $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ and $[\text{Co}_2(\text{CO})_8]$ were used as catalysts under 27 MPa of 40:60 CO/hydrogen and at 220° in the presence of methyl iodide and methanol (methanol/methyl iodide/metal = 4400/2/1) to produce a 58% conversion of methanol to ethanol (86% selectivity) after 6 h (314).

Promotion of Co-catalyzed carbonylation of methanol to acetaldehyde is achieved by transition metal halides, including $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, in the presence of lithium iodide. The role of the metal halide is apparently to generate HI; $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ is formed under the reaction conditions. Other organic products are methyl acetate, ethanol, acetic acid, and ethyl acetate (315).

Homologation of methyl esters to ethyl esters under CO and hydrogen is catalyzed by $[\text{Co}(\text{OAc})_2]/[\text{Ru}(\text{acac})_3]$ mixtures in the presence of iodide. The optimum Co/Ru ratio is 0.4. Lithium iodide is a better promoter than either methyl iodide or iodine (316).

Homologation of dimethyl ether with CO and hydrogen to methanol and ethanol is achieved using $[\text{Ru}(\text{acac})_3]$ as the catalyst precursor. In acetic acid the corresponding esters are produced. The same catalyst system homologates methyl acetate to ethyl acetate. Improved yields of ethyl acetate are obtained with Ru/Co mixtures. Iodide and a proton source are essential as promoters (317).

The water-soluble porphyrin complex $[\text{Ru}(\text{TPPS})(\text{CO})]^{4-}$ (TPPS=meso-tetra-(4-sulfonatophenyl)porphyrinato) is a catalyst for the water gas shift reaction at 1 atm and 100°. The complex, six times more active than $[\text{Ru}_3(\text{CO})_{12}]$, is prepared by refluxing $\text{Na}_4[\text{TPPS}] \cdot 12 \text{H}_2\text{O}$ and $[\text{Ru}_3(\text{CO})_{12}]$ in DMF for 1-3 weeks (318).

Irradiation with visible light of a solution of triethanolamine and DMF containing $[\text{Ru}(\text{bipy})_3]^{2+}$ and Co^{2+} under a carbon dioxide atmosphere results in catalytic production of either CO and hydrogen or CO alone (319).

Oxidation

The kinetics of ruthenate catalyzed oxidation of allyl, crotyl, cinnamyl, and propargyl alcohols by $[\text{Fe}(\text{CN})_6]^{3-}$ in aqueous alkaline media were determined. The proposed mechanism involves complex formation between the alcohol and

ruthenate; the complex disproportionates to Ru(IV) and aldehyde (320).

A study of the kinetics of oxidation of isopropanol by periodate in the presence of Os(VIII), Ru(III), and mixtures of the two found the order of activity: Os(VIII) < Ru(III) < Os-Ru mixtures. The mechanism was proposed to involve a Os(VIII)-isopropanol complex which reacts with Ru(III) to give the products (321). Also examined was Ru(III) catalyzed oxidation of alkyl acetates (377).

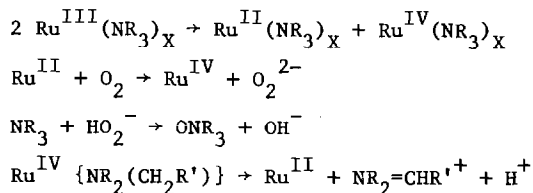
Oxidation of chalcones by Ce(IV) in sulfuric acid/acetic acid is catalyzed by RuCl₃. The initial step is formation and oxidation of a Ru(III)-chalcone complex, which then decomposes to the PhCH=CH·radical (322).

Oxidation of trimethylphenol by 30% hydrogen peroxide in acidic media to the corresponding *p*-benzoquinone is catalyzed by RuCl₃. After 5 h at 25°, 90% conversion of 2,3,6-trimethylphenol to the *p*-benzoquinone is achieved using 1 mol % of the catalyst (323).

Oxidation of sulfides by iodosylbenzene to sulfones is catalyzed by [RuCl₂(PPh₃)₃]. Electron-withdrawing substituents on the arene ring of the oxidant reduce reactivity and improve selectivity. Using *m*-iodosylbenzoic acid, sulfoxides are formed. Aliphatic primary alcohols are converted to aldehydes using *m*-iodosylbenzoic acid but to carboxylic acids using iodosylbenzene. Selenides are also oxidized. The general procedure involves 96 mg of [RuCl₂(PPh₃)₃], 25 mmol of iodosylbenzene, and 10 mmol of the sulfide in dichloromethane for 15 min. (324).

Oxidation of trialkylamines by oxygen, giving trialkylamine-N-oxides and other products, is catalyzed by RuCl₃·3H₂O. In aqueous solution, trimethylamine (10 mmol) reacts at 100° with oxygen (50 lb/m²) over a 16 h period to produce an 80% conversion to trimethylamine-N-oxide (3.4 mmol), formic acid (4.0 mmol as [NMe₃H][O₂CH]), N,N-dimethyl formamide (0.5 mmol), dimethylhydroxylamine (trace) and dimethylamine. The proposed mechanism is shown in Scheme 29 (325).

Scheme 29



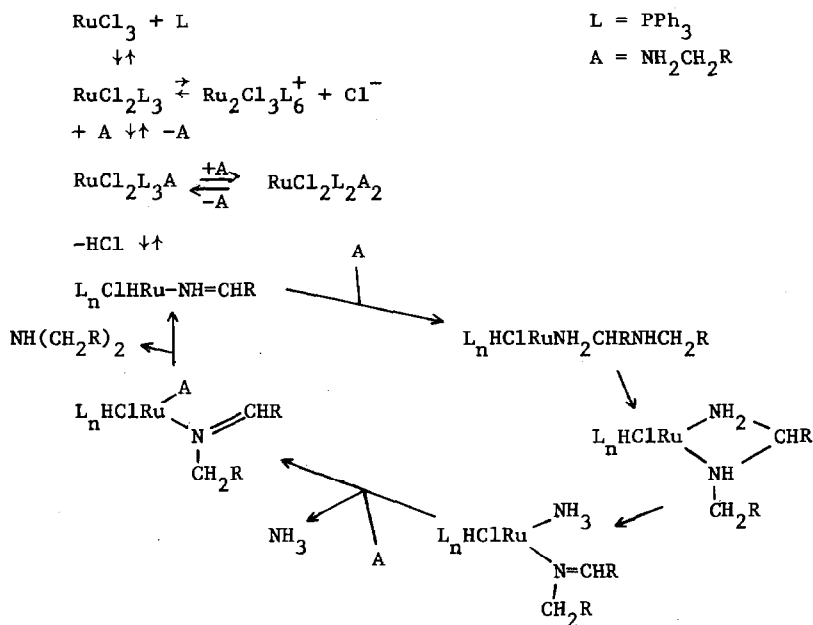
Other Reactions

The reaction between acetic anhydride and amines PhCH₂N(CH₂R)₂ to give PhCH₂N(CH₂R)(C(O)Me) and other products is catalyzed by RuCl₃. A PPh₃-modified catalyst has also been used. Oxidation of the amine by the catalyst is believed to be involved. In one example, benzyldibutylamine and acetic

anhydride were converted in the presence of 6% RuCl_3 to benzylbutylacetylamine (98%) after 7 h at 160° (326).

The effect of phosphines upon the $[\text{RuCl}_2(\text{PPh}_3)_3]$ catalyzed conversion of primary to secondary amines were investigated. Rates and selectivity for conversion of decylamine to didecylamine were determined. The rate was first order in catalyst and in amine initially but in the presence of PPh_3 catalyst decomposition led to a decreasing rate. The major species in equilibrium in solution were shown by ^{31}P NMR spectroscopy to be $[\text{RuCl}_2(\text{PPh}_3)_3]$, $[\text{RuCl}_2(\text{PPh}_3)_2\text{A}_2]$, $[\text{RuHCl}(\text{PPh}_3)_3]$, $[\text{RuHCl}(\text{PPh}_3)_2\text{A}_2]$, and PPh_3 (A=amine). Under deuterium gas, monodeuteration of the α -carbon of the decyl substituent was observed. The mode of catalyst decomposition was P-aryl ortho-metallation and then benzene elimination. The $\text{RuCl}_3/\text{PBu}_3$ system was stable, showing after 5 h, the presence of $[\text{Ru}_2\text{Cl}_3(\text{PBu}_3)_6]\text{Cl}$, $[\text{RuH}_2(\text{PBu}_3)_4]$, and $[\text{RuHCl}(\text{PBu}_3)_3\text{A}]$. About 5% decyl $\text{N}=\text{CH}(\text{CH}_2)_8\text{CH}_3$ was present under steady state conditions. The proposed mechanism is shown in Scheme 30 (327).

Scheme 30



$[\text{RuCl}_2(\text{PPh}_3)_3]$ is a catalyst for the reaction of arenesulfonyl chlorides with vinylarenes in the presence of tertiary amines to form α,β -unsaturated sulfones. Only E isomers are formed. If the arenesulfonyl chloride contains chloride or nitro substituents on the ring, then reactions with 2-methylstyrenes yield 2-aryl-3-(arylsulfonyl)propenes, as well. In one example, benzenesulfonyl chloride (2 mmol), styrene (2 mmol), tributylamine (2 mmol)

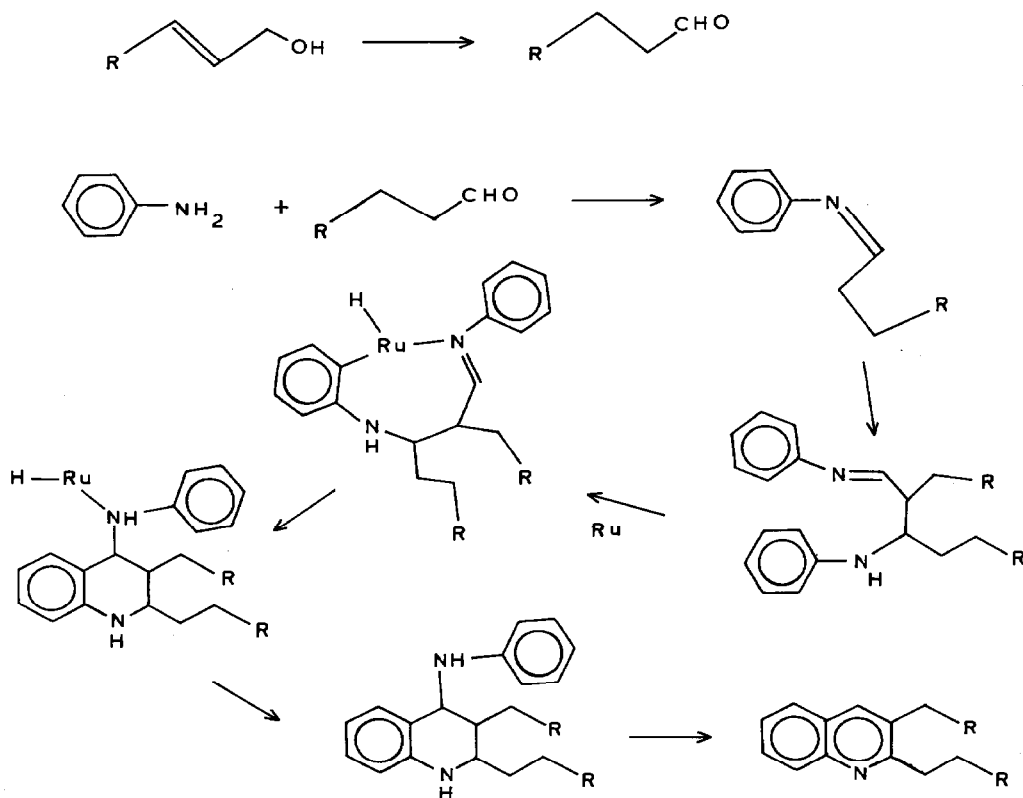
and catalyst (0.02 mmol) is heated at 60° for 72 h in benzene, producing a 71% yield of tributylammonium chloride and E-PhCH=CHSO₂Ph at 75% conversion. A radical mechanism in which Ru(II) reversibly abstracts chloride is proposed (328).

N-monoalkyl amides are formed from amides and primary alcohols using [RuCl₂(PPh₃)₃] as the catalyst. For example, at 180° for 4 h benzamide (10 mmol), ethanol (5 mL), and [RuCl₂(PPh₃)₃] (0.1 mmol) produce N-ethyl benzamide with 85% selectivity at 53% conversion (370).

Quinoline derivatives are formed from aminoarenes and 2-propen-1-ol or 2-buten-1-ol using [RuCl₂(PPh₃)₃] as a catalyst. Standard reaction conditions are, for example, aniline (20 mmol), alcohol (10 mL), [RuCl₂(PPh₃)₃] (0.2 mmol), and nitrobenzene (22 mmol) at 180° for 5 h. The proposed mechanism is shown in Scheme 31 (371).

γ-Butyrolactones were prepared by cyclocondensation of R¹R²C=CHR³ with Cl₂CRCO₂R' (R=H,Cl,Me; R'=H,SiMe₃) in the presence of [RuCl₂(PPh₃)₃] (378,379).

Scheme 31



The addition of aliphatic and aromatic carboxylic acids to alkynes, forming vinyl esters, is catalyzed by $[\text{Ru}_3(\text{CO})_{12}]$ or $[\text{Ru}(\text{CO})_2(\text{OAc})]_n$. Products from diphenylacetylene and acetic acid (1:1, 0.2 M) at 145° for 22 h (55% conversion) are $\text{PhCH}=\text{C}(\text{OAc})\text{Ph}$ (E isomer (82%), Z isomer (9%)) and $\text{Ph}_2\text{C}=\text{CHOAc}$ (9%). The kinetic product is the E isomer, which slowly rearranges. Other alkynes which were examined were phenylacetylene, 4-octyne, and dimethyl acetylenedicarboxylate, and other acids were benzoic acid, 4-fluorobenzoic acid, 4-methylbenzoic acid, and 2,2-dimethylpropionic acid (329).

The addition of methyl formate to ethylene, forming methyl propionate, is catalyzed by $[\text{RuCl}_2(\text{PPh}_3)_3]$. Ethyl formate does not react in this fashion. From 80 mL of methyl formate and ethylene (10 bar) at $190\text{--}200^\circ$ for 18 h and in the presence of 0.14 mmol of catalyst are formed methyl propionate (40 mmol) and CO (55 mmol) (330).

Hydrosilylation of alkenes is catalyzed by Ru(II) and Ru(III) phosphine complexes. Vinylsilanes and 1-alkenes are more reactive than more substituted alkenes. The reaction is enhanced by oxygen and the phosphine ligands are not required for activity. Two general mechanisms were proposed (331).

Hydrosilylation of vinyltrialkoxysilanes by trialkoxysilanes is catalyzed by $[\text{RuCl}_2(\text{PPh}_3)_3]$ and by $[\text{Ru}(\text{acac})_3]$. The major product is 1,2-bis(trialkoxysilyl)ethane. A by-product is 1,2-bis(trialkoxysilyl)ethene when the ethoxy or isopropoxy substituents are present, but the α -substituted addition product for the methoxy-substituted silanes (332).

$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PMe}_3)_2]$ is a catalyst for the reaction of alcohols with triethylsilane. The kinetics for the reaction with $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{Et}$ were examined (333).

REVIEWS AND OTHER WORKS

The following reviews pertinent to the organometallic chemistry of Ru and Os have appeared.

"Chemistry of triosmium carbonyl cluster compounds and its implications for catalysis", by R. D. Adams (334).

"Surface organometallic chemistry: a new approach to heterogeneous catalysis?", by J. M. Basset and A. Choplin (335).

"The chemistry of carbido carbonyl clusters", by J. S. Bradley (336).

"Complexes containing heteronuclear metal-metal bonds. Some recent advances 1980-81. Compounds containing two different transition metals (including mixed metal clusters)", by M. I. Bruce (337).

"Complexes containing heteronuclear metal-metal bonds. Some recent advances 1980-81. B. Heterometallic cluster compounds", by M. I. Bruce (338).

"Vinylidene and propadienyliene (allenylidene) metal complexes", by M. I. Bruce and A. G. Swincer (339).

- "Reduction of trichloromethyl compounds by hydrogen donors induced by transition metal carbonyls, their complexes, or their salts", by E. C. Chukovskaya, R. Kh. Freidlina, and N. A. Kuzmina (340).
- "Factors which determine product selectivity in the homogeneous hydrogenation of carbon monoxide to oxygenates", by L. C. Costa (341).
- "The activation of carbon dioxide by metal complexes", by D. J. Darensbourg and R. A. Kudarowski (342).
- "Binding and rearrangements of small oxy-ligands at metal clusters", by A. J. Deeming (343).
- "Mechanistic aspects of the photosubstitution and photoisomerization reactions of d^6 metal complexes", by P. C. Ford, D. Wink, and J. Dibenedetto (344).
- "Organometallic compounds of ferrocene-based transition metals", by P. N. Goponik, A. I. Lesikovich, and Yu. G. Orlik (345).
- "Bridged hydrocarbyl or hydrocarbon binuclear transition-metal complexes: classification, structures, and chemistry", by J. Holton, M. F. Lappert, R. Pearce, and P. I. W. Yarrow (346).
- "The chemistry of nitrogen fixation and models for reactions of nitrogenase", by R. H. Henderson, G. J. Leigh, and C. J. Pickett (347).
- "Ligand substitution reactions at low-valent, four-, five-, and six-coordinate transition-metal centers", by J. A. S. Howell and P. M. Burkinshaw (348).
- "Metal-carbido complexes of ruthenium and osmium", by B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. N. Nicholls, and M. D. Vargas (349).
- "Comments on the mechanisms of heterogeneous catalysis of the hydrodenitrogenation reaction", by R. M. Laine (350).
- "Modeling heterogeneous catalysts with homogeneous catalysts: modeling the hydrodenitrogenation reaction", by R. M. Laine (351).
- "A possible mechanism for the reactions of electrophiles with polynuclear transition metal carbonyl and related complexes", by A. R. Manning (352).
- "Transition metals in organic synthesis: hydroformylation, reduction, and oxidation. Annual survey covering the year 1981", by L. Markó (353).
- "Organic reactions of selected π -complexes; annual survey covering the year 1981", by G. Marr and B. W. Rockett (354).
- "Organo-transition metal clusters: rational approaches to synthesis, structure, fluxionality and reactivity", by M. J. McGlinchey, M. Mlekuz, P. Bougeard, B. G. Sayer, A. Marinetti, J.-Y. Saillard, and G. Jaouen (355).
- "Homogeneous oxidations catalyzed by transition metals: current evolutions", by B. Meunier (356).
- "Catalysis by molecular metal clusters", by E. L. Muetterties and M. J. Krause (357).

- "Organometallic intramolecular coordination compounds containing diolefin donor ligands", by I. Omae (358).
- "The chemistry of metal carbonato and carbon dioxide complexes", by D. A. Palmer and R. van Eldik (359).
- "Transition metal nitrosyls in organic synthesis and in pollution control", by K. K. Pandey (360).
- "Organometallic catalysis in asymmetric synthesis", by P. Pino and G. Consiglio (361).
- "Kinetic behavior of metal-metal bonded carbonyls", by A. Poe (362).
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- "Homogeneous metal-catalysis in organic photochemistry", by R. G. Salomon (364).
- "Alkyne-substituted homo- and heterometallic carbonyl clusters of the iron, cobalt, and nickel triads", by E. Sappa, A. Tiripicchio, and P. Braunstein (365).
- "Phosphorus ylides in the coordination sphere of transition metals: an inventory", by H. Schmidbauer (366).
- "Metal isocyanide complexes", by E. Singleton and H. E. Oosthuizen (367).
- "Basic metal cluster reactions", by H. Vahrenkamp (368).
- "Electron-rich half-sandwich complexes-metal bases per excellence", by H. Werner (369).

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