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Synthesis, Characterization and Photochemistry of $[Rh_2(diisocyanide)_4Re_2(CO)_{10}](PF_6)_2$ Complexes (diisocyanide = 1,3-diisocyanopropane; 2,5-diisocyano-2,5-dimethylhexane; 1,8-diisocyano-*p*-menthane)

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Abstract

The syntheses, characterization and photochemistry of a series of tetranuclear complexes of the form $[Rh_2(diisocyanide)_4Re_2(CO)_{10}]^{2+}$ (diisocyanide = 1,3-diisocyanopropane (bridge), 2,5-diisocyano-2,5-dimethylhexane (TM4), or 1,8-diisocyano-*p*-menthane (dimen)) are reported. The syntheses of $Rh_2(dimen)_4Mn_2(CO)_{10}(PF_6)_2$ and $Rh_2(bridge)_4Mn_2(CO)_{10}(BF_4)_2$ were successful, but the complexes could not be purified. The syntheses of similar tetranuclear complexes with $[MoCp(CO)_3]_2$ (Cp = cyclopentadienyl) and $[FeCp(CO)_2]_2$ as the terminal metal groups were not successful. All of the complexes exhibit an intense allowed ($\epsilon > 50000$ M^{-1} cm^{-1}) electronic transition in the visible spectral region attributable to a metal localized transition in the linear tetranuclear core. Shifts in the energy of this transition with changes in the tetranuclear species accord with the predictions of simple Hückel MO theory for a highly delocalized, four orbital, four metal atom system. Photochemical studies of $[Rh_2(TM4)_4Re_2(CO)_{10}](PF_6)_2$ that address three types of potential photochemical reactivity are reported: stability in the absence of substrates, terminal metal group radical exchange and ligand substitution. The complex is inert upon $\sigma \rightarrow \sigma^*$ excitation in the absence of substrates and does not exhibit radical exchange of the terminal metal groups. Photochemical ligand substitution occurs in the presence of phosphine ligands, but the complex undergoes primary diisocyanide substitution at Rh rather than CO substitution at Re. These results contrast the photochemical behavior of binuclear species ($M_2(CO)_{10}$) that contain a single metal–metal bond.

Introduction

In a previous paper [1] we investigated the mechanism of formation, X-ray structure and the photochemical stability of a tetranuclear mixed metal complex, $[Rh_2(TM4)_4Mn_2(CO)_{10}](PF_6)_2$ (TM4 = 2,5-diisocyano-2,5-dimethylhexane). This complex exhibits a structure that contains two $Mn(CO)_5$ groups bound through Rh–Mn bonds to both ends of the parent $Rh_2(TM4)_4{}^{2+}$ complex (see Fig. 1 for a schematic representation). The complex exhibits an intense, low energy electronic transition attributable to an allowed transition of the d^7–d^8–d^8–d^7 chromophore. The considerable thermal and photochemical stability of this system has prompted us to investigate the effects of varying the bridging diisocyanide ligand and the terminal metal units on the stability and reactivity of the resulting tetranuclear species. In this regard, we have synthesized a new series of stable $[Rh_2(diisocyanide)_4Re_2(CO)_{10}]^{2+}$ complexes (where diisocyanide = 1,3-diisocyanopropane (bridge), 2,5-diisocyano-2,5-dimethylhexane (TM4) and 1,8-diisocyano-*p*-menthane (dimen); structures of the three ligands are shown in Fig. 2. Preliminary photochemical investigations of the $[Rh_2(TM4)_4Re_2(CO)_{10}]^{2+}$ complex are also reported.

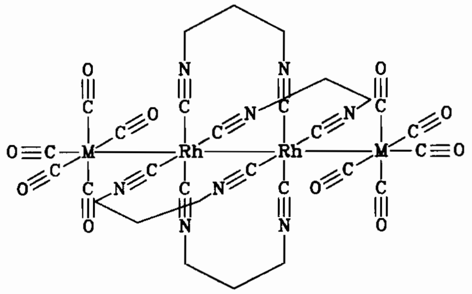

Fig. 1. Schematic drawing of $Rh_2(bridge)_4M_2(CO)_{10}{}^{2+}$.

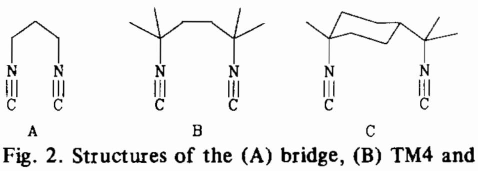

Fig. 2. Structures of the (A) bridge, (B) TM4 and (C) dimen ligands.

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Experimental

General

The solvents used were of spectroscopic quality. In addition, solvents for photochemical syntheses (acetone and acetonitrile) were purified further by drying over B_2O_3 or P_2O_5 respectively for 24 h followed by distillation immediately before use [2]. The following reagents were used as received: $RhCl_3 \cdot 3H_2O$ (Johnson-Matthey, Inc.); COD (COD = 1,5-cyclooctadiene), diamines and benzyltriethylammonium chloride (Aldrich Chemical Company); 50% $NaOH/H_2O$, KH_2PO_4 (Mallinckrodt, Inc.); carbon monoxide (C.P. grade 99.5%) K_2HPO_4 (Matheson, Coleman, & Bell); B_2O_3, $AgBF_4$, $[CpFe(CO)_2]_2$ (Alfa Products); NH_4PF_6 (Ozark-Mahoning Pennwalt); and $Re_2(CO)_{10}$ and bis(diphenyl phosphino (Strem Chemicals). Triphenylphosphine (Aldrich Chemical Company) was recrystallized from hot ethanol before use. $[CpMo(CO)_3]_2$ was a gift of Professor John Ellis.

The new complexes were characterized by IR and UV–Vis spectroscopy, ^{31}P NMR and elemental analyses. Previously characterized intermediate materials ($Rh_2(diisocyanide)_4^{2+}$ complexes) were checked for purity before use through comparison of physical properties and/or spectra to literature data. IR spectra were obtained on a Beckman 4250 IR spectrophotometer; UV–Vis spectra with a Cary 17D spectrophotometer; and NMR spectra with either a Varian Associates CFT-20 NMR spectrometer equipped with a 79.5 MHz proton accessory or a Nicollet NT-300W-B instrument. Chemical shifts for ^{31}P NMR are reported in units of δ, referenced to 85% phosphoric acid as an external standard. Elemental analyses were performed by Galbraith Laboratories of Knoxville, TN, or Schwarzkopf Microanalytical Laboratory of Woodside, NY.

Photochemical Reactions

Reactant solutions were purged with dry, oxygen free* nitrogen or in some cases degassed by 3 to 5 freeze–pump–thaw cycles. Photochemical reactions were carried out with a medium pressure mercury vapor lamp or, when possible, sunlight. In general, wherever sunlight was used as the photon source, the Hg lamp could be substituted; the reverse was not necessarily true. In some cases where the product was found to be photosensitive, a Dow Corning Filter #7-51 (strong absorption below 295 nm and from 425 to 675 nm), protected the tetranuclear products while it allowed photolysis into the $\sigma \rightarrow \sigma^*$ band of $Re_2(CO)_{10}$ [3] at 308 nm. Dark control reactions indicate that exposure of the solutions to light is necessary for the syntheses of the tetranuclear complexes as well as all reported photochemical reactions.

Syntheses of Starting Materials

$[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) [4] and the diisocyanide ligands were prepared by the published procedures. Other starting materials were prepared with some variations.

$[Rh(COD)(CH_3CN)_2]BF_4$ [5]. A sample of 1.57 g $AgBF_4$ (8.00 mmol) was added to a solution of 1.955 g $[Rh(COD)Cl]_2$ (3.97 mmol) in 75 ml of acetonitrile. AgCl precipitated immediately from the orange solution. The mixture was then stirred an additional 15 min to insure complete reaction. After the silver chloride was filtered off, the product was isolated from the filtrate by rotary evaporation of the solvent. Yield: 96% (2.913 g, 7.66 mmol).

$[Rh_2(bridge)_4](BF_4)_2$. Prepared in 81% yield via the method outlined in ref. 6.

$[Rh_2(TM4)_4](PF_6)_2$. Prepared in 82% yield via the method outlined in ref. 7.

$[Rh_2(dimen)_4](PF_6)_2$. Prepared in 84% yield via the method outlined in ref. 8.

$Re_2(CO)_8(PPh_3)_2$. Prepared in 33% yield via the thermal reaction method in refs. 9 and 10.

$[Rh_2(TM4)_4Mn_2(CO)_{10}]PF_6$. Prepared by the method of Bohling *et al.* [1].

Syntheses of the Compounds

$[Rh_2(bridge)_4Re_2(CO)_{10}](BF_4)_2$

$Re_2(CO)_{10}$ (0.195 g, 0.299 mmol) and 0.073 g $[Rh_2(bridge)_4](BF_4)_2$ (0.0966 mmol) (3:1 Re:Rh) were placed in a 250 ml round bottom flask. After pumping on the flask for 20 min, 50 ml of dry degassed acetonitrile were distilled into the reaction flask. The solution was photolyzed for 2 h, with a medium pressure Hg vapor lamp fitted with a 7-51 Corning filter. During the photolysis the solution color changed from purple to bright burgundy. After the solvent was removed under vacuum the resulting solid was recrystallized from acetone/hexane under vacuum. During the crystallization, the flask was covered with foil to protect the product from light. After three days of slow recrystallization, the solids were removed by filtration. The desired product was extracted from this powder into acetone and reprecipitated from acetone/hexane. Yield: 13% (0.018 g, 0.013 mmol) IR(acetone): $\tilde{\nu}$(CN), 2193 cm^{-1}; $\tilde{\nu}$(CO), 2058, 1995, 1956 (shoulder) cm^{-1}. *Anal.* Calc. for $Rh_2Re_2C_{30}H_{24}N_8O_{10}B_2F_8$: C, 25.58; H, 1.72; N, 7.96. Found: C, 25.51; H, 1.91; N, 8.22%.

$[Rh_2(TM4)_4Re_2(CO)_{10}](PF_6)_2 \cdot acetone$

A 0.101 g sample of $[Rh_2(TM4)_4](PF_6)_2$ (0.0874 mmol) was placed in a test tube with 0.1204 g

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*Oxyclear rechargeable gas purifier, #RGP-250.

$Re_2(CO)_{10}$ (0.185 mmol) and 20 ml of acetone. The solution was purged with nitrogen for 20 min and then photolyzed in sunlight for $2\frac{1}{2}$ h. Upon exposure to sunlight the reaction solution turned from red to royal blue. After photolysis, the solvent was removed via rotary evaporation, and the crude product was washed several times with hexane. Slow recrystallization from acetone/hexane gave the compound in 91% yield (0.1519 g, 0.0815 mmol). IR(acetone): $\bar{\nu}$(CN), 2168 cm^{-1}; ν(CO), 2065, 1990 cm^{-1}. *Anal.* Calc. for $Rh_2Re_2C_{53}H_{70}N_8O_{11}P_2F_{12}$: C, 34.16; H, 3.79; N, 6.01. Found: C, 34.28; H, 4.06; N, 5.87%.

$[Rh_2(dimen)_4Re_2(CO)_{10}](PF_6)_2$

A 25 ml acetone solution of 0.137 g $[Rh_2(dimen)_4](PF_6)_2$ (0.109 mmol) and 0.198 g $Re_2(CO)_{10}$ (0.303 mmol) was purged with nitrogen for 25 min. The solution color changed from orange to green upon exposure to sunlight (3 h and 10 min). The green solid was isolated by rotary evaporation of the solvent, washed with hexane, and reprecipitated from acetone/hexane. Yield: 99% (0.205 g, 0.107 mmol). IR(acetone): $\bar{\nu}$(CN), 2150 cm^{-1}; $\bar{\nu}$(CO), 2063, 1989 cm^{-1}. *Anal.* Calc. for $Rh_2Re_2C_{58}H_{72}N_8O_{10}P_2F_{12}$: C, 36.48; H, 3.80; N, 5.87. Found: C, 36.15; H, 3.90; N, 5.30%.

$[Rh_2(TM4)_4Re_2(CO)_8(PPh_3)_2](PF_6)_2$

A sample of 0.0521 g $[Rh_2(TM4)_4](PF_6)_2$ (0.0452 mmol) was placed in a pyrex test tube with 0.110 g $Re_2(CO)_8(PPh_3)_2$ (0.0981 mmol). Twenty-five ml of dried acetone were distilled into the vacuum-line degassed reaction vessel after the solvent was also degassed via four freeze–pump–thaw cycles. The solution was then photolyzed for 2.5 h, with a medium pressure Hg vapor lamp equipped with a 7-51 filter. During this time the solution color changed from red to deep blue. After photolysis the solvent was removed by rotary evaporation, and the blue solid was washed with cyclohexane and ether. A slow recrystallization from acetone/hexane followed by reprecipitation from acetone/ether afforded the desired compound as a blue powder. IR(acetone): $\bar{\nu}$(CN), 2163 cm^{-1}; $\bar{\nu}$(CO), 2012, 1932 cm^{-1}. ^{31}P NMR (acetone): 19.5 ppm (singlet). *Anal.* Calc. for $Rh_2Re_2C_{84}H_{94}N_8O_8P_4F_{12}$: C, 44.40; H, 4.17; N, 4.93. Found: C, 44.29; H, 4.26; N, 4.78%.

Reaction of $Mn_2(CO)_{10}$ with $Rh_2(bridge)_4(BF_4)_2$

A solution of 0.1523 g of $Rh_2(bridge)_4(BF_4)_2$ (0.0215 mmol) and 0.900 g of $Mn_2(CO)_{10}$ (0.2308 mmol) in 190 ml of CH_3CN was bubble degassed for 1.5 h with N_2. The solution was photolyzed for 2 h with the unfiltered output of a medium pressure Hg lamp. After the solvent was removed by rotary evaporation, the infrared spectrum of an acetone solution of the blue–green solid revealed product peaks at 2195, 1969 and 2030 cm^{-1} and impurities at 2240 and 1910 cm^{-1}. Recrystallization from acetone/hexane did not affect further purification.

Reaction of $Mn_2(CO)_{10}$ with $Rh_2(dimen)_4(PF_6)_2$

A solution of 0.0789 g of $Rh_2(dimen)_4(PF_6)_2$ (0.0628 mmol) and 0.5047 g of $Mn_2(CO)_{10}$ (1.294 mmol) (Mn:Rh = 20:1) in 20 ml of acetone was bubble degassed with N_2 for 20 min. The solution was photolyzed for 2.25 h with a medium pressure Hg lamp equipped with a 7-51 filter. Removal of the solvent yielded a dark green solid. Twenty-five, 2 to 4 ml washings with hexane removed yellow $Mn_2(CO)_{10}$ and yielded 0.1002 g of $Rh_2(dimen)_4Mn_2(CO)_{10}(PF_6)_2$ (0.0608 mmol) in 97% yield. The infrared spectrum of an acetone solution of the green solid revealed product peaks at 2165, 1979, 2035 cm^{-1} and an impurity peak, at 1920 cm^{-1}. Attempts to purify the green solid by recrystallization or chromatography led to the regeneration of $Rh_2(dimen)_4(PF_6)_2$ and $Mn_2(CO)_{10}$.

Reaction of $[CpMo(CO)_3]_2$ with $Rh_2(dimen)_4(PF_6)_2$

A solution of 0.0803 g of $Rh_2(dimen)_4(PF_6)$ (0.0639 mmol) and 0.0957 g of $[CpMo(CO)_3]_2$ (0.195 mmol) in 20 ml of acetone was degassed with N_2 for 20 min. The red solution was photolyzed with the unfiltered output of a medium pressure Hg lamp for 3.5 h. A UV–Vis spectrum of the solution after photolysis revealed only the presence of starting materials. Two days of additional photolysis gave no conversion to products.

Reaction of $[CpFe(CO)_2]_2$ with $Rh_2(TM4)_4(PF_6)_2$

A solution of 0.1027 g of $Rh_2(TM4)_4(PF_6)_2$ (0.0891 mmol) and 0.0914 g of $[CpFe(CO)_2]_2$ (0.258 mmol) in 30 ml of acetone was degassed with N_2 for 20 min. Sunlight photolysis for 4 h gave no color change. Infrared analysis of the solution revealed only peaks due to the starting materials.

Photochemical Reactions of $Rh_2(TM4)_4Re_2(CO)_{10}(PF_6)_2$

Photochemical stability of $Rh_2(TM4)_4Re_2(CO)_{10}(PF_6)_2$ in degassed acetone

A stir bar and 0.0325 g of $Rh_2(TM4)_4Re_2(CO)_{10}(PF_6)_2$ acetone (0.0174 mmol) were placed in a quartz cell equipped with a vacuum stopcock. After evacuation of the cell on a vacuum line, 5 ml of dry acetone was distilled into the cell. After four freeze–pump–thaw cycles, the cell was sealed and photolyzed for 12 days with a medium pressure Hg lamp equipped with a 578 nm interference filter. IR analysis of the photolyte indicated only the presence of starting material within experimental error (±5%).

Radical scrambling experiments

Several experiments were performed with the same general method. Mixtures of (~0.01 mmol each) $Rh_2(TM4)_4Re_2(CO)_{10}(PF_6)_2$ and $Mn_2(CO)_{10}$, $Rh_2(TM4)_4Re_2(CO)_{10}(PF_6)_2$ and $Rh_2(TM4)_4Mn_2(CO)_{10}(PF_6)_2$, and $Rh_2(TM4)_4Mn_2(CO)_{10}(PF_6)_2$ and $Re_2(CO)_{10}$ were placed in quartz test tubes with ~6 ml of dry acetone and degassed with N_2. After photolysis with the unfiltered output of a medium pressure Hg lamp for 5 h the IR spectra of the solutions revealed only peaks due to the starting materials.

Reaction of $Rh_2(TM4)_4(PF_6)_2$ with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$

A solution of 0.0988 g of $Rh_2(TM4)_4(PF_6)_2$ (0.0857 mmol), 0.0338 g $Mn_2(CO)_8$ (0.0867 mmol) and 0.0593 g $Re_2(CO)_8$ (0.0909 mmol) in 20 ml of acetone was bubble degassed with N_2 for 20 min. The solution was photolyzed for 2.5 h with a medium pressure Hg vapor lamp equipped with a 7-51 corning filter. Within 5 min the red solution had turned purple. After rotary evaporation of the solution, the blue–green solid was washed with 6 × 15 ml portions of hexane. IR analysis of an acetone solution of the solid revealed it to be mostly $[Rh_2(TM4)_4Mn_2(CO)_{10}](PF_6)_2$ and a small amount of $Re_2(CO)_{10}$.

Photochemical reaction of $[Rh_2(TM4)_4Re_2(CO)_{10}](PF_6)_2$ with PPh_3

A degassed solution of 0.021 g of $[Rh_2(TM4)_4Re_2(CO)_{10}](PF_6)_2\cdot$acetone (0.011 mmol) and a large excess of PPh_3 (0.26a g, 1.13 mmol) in 5 ml of acetone was degassed with N_2 for 10 min and photolyzed with a medium pressure Hg lamp equipped with a 313 nm interference filter for 23.5 h. The IR spectrum of the solution exhibited large peaks due to unreacted $Rh_2(TM4)_4Re_2(CO)_{10}{}^{2+}$ at 2168, 1989 and 2063 cm^{-1}. Major product peaks are at 2130, 2030 and 1959 cm^{-1}. The peak at 2130 cm^{-1} is tentatively assigned to $\tilde{\nu}$(CN) of $Rh_2(TM4)_2(PPh_3)_4(PF_6)_2$ (identified by comparison with the thermal reaction product of $Rh_2(TM4)_4(PF_6)_2$ and PPh_3). The peak at 1959 cm^{-1} is assigned to $\tilde{\nu}$(CO) of $Re_2(CO)_8(PPh_3)_2$ by comparison to an authentic sample. No peaks attributable to $Rh_2(TM4)_4Re_2(CO)_8(PPh_3)_2(PF_6)_2$ were present in the IR spectrum.

Results and Discussion

Photochemical Syntheses of the $[Rh_2(diisocyanide)_4Re_2(CO)_{10}](PF_6)_2$ Complexes

The general synthetic route to the compounds follows the method developed for $[Rh_2(TM4)_4Mn_2(CO)_{10}](PF_6)_2$ (eqn. (1)). As in this previous case, the synthetic reactions only proceed on exposure to light. Three tetranuclear complexes of the form $[Rh_2(L)_4Re_2(CO)_{10}]^{2+}$ (L = dimen, TM4), and $[Rh_2(TM4)_4Re_2(CO)_4(PPh_3)_2]^{2+}$ were synthesized in greater than 85% yield and fully characterized. The complex with L = bridge was formed in high yield but was difficult to purify because of the relative insolubility of $Rh_2(bridge)_4(BF_4)_2$ and the presence of an unidentified Re-carbonyl containing side product.

$$[Rh_2L_4]^{2+} + M_2(CO)_{10} \xrightarrow{h\nu} Rh_2L_4M_2(CO)_{10}{}^{2+} \qquad (1)$$

Attempts to isolate the previously uncharacterized Mn compounds $[Rh_2(dimen)_4Mn_2(CO)_{10}](PF_6)_2$ and $[Rh_2(bridge)_4Mn_2(CO)_{10}](BF_4)_2$ in analytically pure form were unsuccessful. As in the case of $Rh_2(bridge)_4Re_2(CO)_{10}(BF_4)_2$, the Mn complexes were formed in high yield but the removal of unidentified CO containing contaminants was not successful. However, adequate spectroscopic data for these compounds to allow comparisons with the Re analogs were obtained and are included in Tables 1 and 2.

TABLE 1. Infrared stretching frequencies[a]

Compound	$\tilde{\nu}$(CN)	$\tilde{\nu}$(CO)
Bridge[b]	2149	
TM4[c]	2131	
Dimen[c]	2132	
$Rh_2(bridge)_4{}^{2+}$	2172	
$Rh_2(TM4)_4{}^{2+}$	2160	
$Rh_2(dimen)_4{}^{2+}$	2162	
$Rh_2(bridge)_4Mn_2(CO)_{10}{}^{2+}$	2195	1969, 2030
$Rh_2(TM4)_4Mn_2(CO)_{10}{}^{2+}$	2178	1978, 2038[d]
$Rh_2(dimen)_4Mn_2(CO)_{10}{}^{2+}$	2165	1979, 2035
$Rh_2(bridge)_4Re_2(CO)_{10}{}^{2+}$	2193	1995, 2069
$Rh_2(TM4)_4Re_2(CO)_{10}{}^{2+}$	2168	1989, 2063
$Rh_2(dimen)_4Re_2(CO)_{10}{}^{2+}$	2150	1989, 2063
$Rh_2(TM4)_4Re_2(CO)_8(PPh_3)_2{}^{2+}$	2163	1932, 2012

[a]All spectra obtained for acetone solutions except where noted; all data in cm^{-1}. [b]Neat oil. [c]Nujol mull. [d]Data from ref. 1.

TABLE 2. Lowest energy electronic absorption for $Rh_2(diisocyanide)_4M_2(CO)_8(L)_2{}^{2+}$ complexes[a]

Compound	λ_{max} [b](ϵ_{max} [c])
$Rh_2(bridge)_4Re_2(CO)_{10}(BF_4)_2$	566(55800)
$Rh_2(TM4)_4Mn_2(CO)_{10}(PF_6)_2$ [d]	600(106000)
$Rh_2(TM4)_4Re_2(CO)_{10}(PF_6)_2$	585(59800)
$Rh_2(dimen)_4Mn_2(CO)_{10}(PF_6)_2$	635[e]
$Rh_2(dimen)_4Re_2(CO)_{10}(PF_6)_2$	618(71000)
$Rh_2(TM4)_4Re_2(CO)_8(PPh_3)_2(PF_6)_2$	592 (106000)

[a]Determined in acetone solution. [b]In nm. [c]In M^{-1} cm^{-1}. [d]Data from ref. 1. [e]Extinction coefficient was not determined.

The behavior of $[Rh_2(dimen)_4Mn_2(CO)_{10}](PF_6)_2$ deserves additional comment. This species forms in the photochemical synthetic reaction in appreciable amounts only if a large (20:1) Mn to Rh ratio is used. After the excess $Mn_2(CO)_{10}$ was removed from the sample by hexane washings, some decomposition of the complex was observed. When the isolated, $Mn_2(CO)_{10}$ free complex was redissolved in acetone, the adduct rapidly regenerated the starting binuclear materials. This behavior suggests that the rigid dimen ligand maintains a longer Rh–Rh distance in $[Rh_2(dimen)_4Mn_2(CO)_{10}]^{2+}$ than one required to maintain stable rhodium–manganese bonds in the absence of substantial amounts of free $Mn_2(CO)_{10}$. The successful synthesis of the corresponding Re complex suggests that the rhodium–rhenium bonds of the tetranuclear complex formed in this case have higher thermodynamic stability.

Extension of the synthetic reaction was also attempted with two other binuclear complexes with single metal–metal bonds ($[CpFe(CO)_2]_2$ and $[CpMo(CO)_3]_2$, Cp = η^5-$C_5H_5^-$). The photochemical reactions of $[CpMo(CO)_3]_2$ with $[Rh_2(dimen)_4](PF_6)_2$ with $[CpFe(CO)_2]_2$ and $[Rh_2(TM4)_4](PF_6)_2$ gave no evidence for net conversion to tetranuclear complexes. These results are consistent with either or both low reactivity of $CpFe(CO)_2$ and $CpMo(CO)_3$ radicals and low thermodynamic stability of the tetranuclear products due to unfavorable steric interactions between the $CpM(CO)_3$ and $Rh_2(L)_4^{2+}$ units.

Characterization of the Tetranuclear Complexes

The tetranuclear complexes were characterized by IR, UV–Vis spectroscopies, elemental analyses and in one case, ^{31}P NMR.

The $Re_2(CO)_{10}$ and the $Mn_2(CO)_{10}$ derivatives of the dirhodium complexes, exhibit IR spectra with one $\bar{\nu}$(CN) and two $\bar{\nu}$(CO) stretching frequencies. The values for the CN and CO vibrational stretching frequencies of the free ligands, the parent Rh complexes and the new compounds are presented in Table 1. The $\bar{\nu}$(CO) stretching frequencies are nearly independent of the bridging isocyanide, but are ~3 cm^{-1} higher for the Re complexes. On average, the $\bar{\nu}$(CN) vibrational stretching frequency increases very slightly in the tetranuclear species as compared with the parent binuclear species. These observed increases for $\bar{\nu}$(CN) result from electron density decreases at rhodium via an electron withdrawing effect through the Rh–M bonds into the $M(CO)_5$ unit as electron density is removed from the dσ^* level of the $Rh_2(L)_4^{2+}$ unit and the Rh–Rh distance decreases. The increases in the $\bar{\nu}$(CN) stretching frequencies in these compounds are much smaller than the increases observed for the corresponding $Rh_2L_4Cl_2^{2+}$ complexes that result from transanular oxidative addition of Cl_2 across the Rh Rh interaction [12]. This observation is consistent with a smaller degree of electron density removal in both $M(CO)_5$ cases as compared with the Cl case. Data for the bridge and TM4 complexes are consistent with relatively small decreases in the Rh–Rh distance on adding the $M(CO)_5$ units, but in the case of $Rh_2(dimen)_4Re_2(CO)_{10}^{2+}$, the decrease of $\bar{\nu}$(CN) relative to $Rh_2(dimen)_4^{2+}$ indicates that a larger shortening of the Rh–Rh distance occurs. The larger decrease of the Rh–Rh distance upon formation of the Re containing tetranuclear species in the dimen case is further supported by analysis of the energetics of the $\sigma \rightarrow \sigma^*$ electronic transitions exhibited by these complexes (*vide infra*). The small magnitude of the inductive effect that the terminal metal atom exerts on Rh is also apparent in the IR and ^{31}P NMR spectra of $[Rh_2(TM4)_4Re_2(CO)_4(PPh_3)_2](PF_6)_2$, for which we assign the *trans* geometry. Although the $\bar{\nu}$(CO) bands in this PPh_3 complex are shifted to lower energy relative to $[Rh_2(TM4)_4Re_2(CO)_{10}](PF_6)_2$ by approximately 55 cm^{-1} in agreement with an increase in the electron density at rhenium, the $\bar{\nu}$(CN) stretching frequency at 2163 cm^{-1} is nearly identical with the 2168 cm^{-1} value observed for $Rh_2(dimen)_4Re_2(CO)_{10}^{2+}$. The ^{31}P NMR spectrum of this compound exhibits a singlet, with no indication of coupling to rhodium through the Rh–Re bonds.

All of the tetranuclear species reported here exhibit an intense ($\epsilon > 50000$ M^{-1} cm^{-1}) electronic transition in the visible region of the spectrum. We attribute this transition in each case to an allowed transition characteristic of complexes containing single metal–metal bonds. (Data are tabulated in Table 2.) As in the previous paper [1] we adopt the $\sigma \rightarrow \sigma^*$ label for this transition; however, the transition is fully delocalized [1, 13] over all four metal atoms rather than only the two central metal atoms as is the case for the binuclear complexes $Mn_2(CO)_{10}$ (M = Mn, Re) and $[Rh_2L_4Cl_2]^{2+}$ (L = bridge, TM4) [14]. As previously discussed, delocalization over all four metals implies that a significant Rh → M or M → Rh charge transfer component is also important in this transition.

The dominance of the electronic spectra of these complexes by transitions localized within the metal–metal bonding network suggested that simple MO theory might be applicable. Hückel theory was used to ascertain how changes in metal–metal distances, orbital energies and orbital interaction energies effect the electronic structure and electronic transitions in these tetranuclear complexes. For these calculations, a four orbital basis set consisting of a d_{z^2} orbital on each metal atom was used. Non-zero interactions were allowed only between adjacent metals. Different interaction energies were used between the inner metals ($\beta_{2,3}$) and the inner and outer metals ($\beta_{1,2}$ and $\beta_{3,4}$). Overlap integrals (S_{ij}) were assumed to be 1 for $i = j$ and 0 for $i \neq j$. $\alpha_1 = \alpha_4$ and $\alpha_2 = \alpha_3$ values were estimated from spectroscopic and crystallographic data for the appropriate $Rh_2(diisocyanide)_4^{2+}$ or $M_2(CO)_{10}$ complex. For example, evidence for the increase in the strength of the rhodium–rhodium interaction on binding of the two terminal metal units was obtained through comparison of the rhodium–rhodium distances in $Rh_2(TM4)_4^{2+}$ with those of $[Rh_2(TM4)_4Mn_2(CO)_{10}]^{2+}$. For this representative case, there is a significant shortening of the Rh–Rh distance, from 3.25 Å [7] in the binuclear to 2.92 Å [1] in the tetranuclear species. This increase in the Rh–Rh interaction upon binding of the two terminal metal units was taken into account in the calculations.

Variation of the four available parameters (α_1, α_2, $\beta_{1,2}$, $\beta_{2,3}$) over a range to produce spectroscopically reasonable values for the lowest $\sigma \rightarrow \sigma^*$ transition indicates that in all cases, four nondegenerate energy levels result with 0, 1, 2 and 3 nodes, respectively, in the direction of increased energy. The lower three levels are filled with a total of six electrons so that the lowest allowed electronic transition results from excitation of one electron from level 3 (g symmetry) to level 4 (u symmetry). The calculations predict that the energy of the $3 \rightarrow 4$ transition increases for the following situations: (i) the energies (α_1, α_4) of the terminal metal d_{z^2} orbitals are made more negative (a shift from Mn to Re); (ii) the interaction energies ($\beta_{1,2}$ and $\beta_{3,4}$) between the terminal and inner metal atoms are increased (shorten Rh–M distance or increase bonding); (iii) the interaction energy ($\beta_{2,3}$) between the two Rh atoms is increased (i.e. a decrease in the Rh–Rh distance).

The experimental data available in Table 2 are consistent with the calculations in each case. The strongest Rh–Rh interactions occur in the bridge complexes with the shortest carbon chain length (the shortest Rh–Rh distances and the smallest decrease in Rh–Rh distance), while the weakest Rh–Rh interactions are present in the dimen complexes with the longest carbon chain lengths (the longest Rh–Rh distance and the largest decrease in Rh–Rh distance). In complexes of the same bridging ligand, the $3 \rightarrow 4$ transition occurs at higher energy in the Re as opposed to the Mn complex. This result is consistent with stronger rhodium–rhenium bonds as compared with rhodium–manganese bonds.

Photochemical Reactivity Studies of $Rh_2(TM4)_4Re_2(CO)_{10}(PF_6)_2$

In the previous study, preliminary photochemical measurements determined the mechanism of complex formation and some of the possible photochemical reaction pathways of $[Rh_2(TM4)_4Mn_2(CO)_{10}](PF_6)_2$ [1]. We believe the proposed mechanism for the formation of $[Rh_2(TM4)_4Mn_2(CO)_{10}(PF_6)_2$ is also consistent with the formation of the new complexes synthesized here. The proposed mechanism of formation involves photolytic cleavage of $Mn_2(CO)_{10}$ to form 17 electron manganese pentacarbonyl fragments which add to the ends of the binuclear rhodium complexes. Previously, the excited state reactivity pattern of $[Rh_2(TM4)_4Mn_2(CO)_{10}]^{2+}$ was studied. The complex was photolyzed in the presence and absence of O_2 with a HeNe laser ($\lambda = 632.8$ nm). In the absence of O_2, the complex was stable upon excitation of the $\sigma \rightarrow \sigma^*$ transition. With O_2 present, the complex decomposed to give $[Rh_2(TM4)_4](PF_6)_2$ and manganese products that were not characterized. In the degassed experiment, no $Mn_2(CO)_{10}$ was observed, ruling out the production of $Mn(CO)_5$ upon photolysis of the complex. Apparently, elimination of metal–metal bond cleavage as a primary photochemical pathway upon $\sigma \rightarrow \sigma^*$ excitation has been achieved by extending the metal–metal chain. The photochemical reaction in the presence of oxygen may be the result of excited state electron transfer behavior.

The previous photochemical reactivity studies of $Rh_2(TM4)_4Mn_2(CO)_{10}^{2+}$, and the isoelectronic $[Rh_2(bridge)_4]_2^{6+}$ complex [15] utilized excitation of the low lying $\sigma \rightarrow \sigma^*$ transition. We assume that the photochemically active state is the $\sigma \rightarrow \sigma^*$ triplet excited state populated via intersystem crossing from the $^1(\sigma \rightarrow \sigma^*)$ state reached on excitation. The Hückel calculations indicate that the $^3(\sigma \rightarrow \sigma^*)$ state features a decrease in bonding with respect to the two inner metal atoms while the outer metal–metal interactions are not significantly affected. In $[Rh_2(bridge)_4]_2^{6+}$ with no ligands bridging the central metals, rapid homolytic cleavage to $[Rh_2(bridge)_4]^{3+}$ radical fragments occurs [15]. In $[Rh_2(TM4)_4Mn_2(CO)_{10}]^{2+}$, the bridging ligands restrain the tetranuclear species from splitting at the Rh–Rh bond. In essence, this Rh–Rh bond cleavage becomes another non-radiative excited state decay path. At an early stage in the development of the present study, we speculated that if Rh–Re bonding differs significantly from Rh–Mn bonding, accompanying changes in the strengths of the Rh–Rh interaction might modify the photochemical reactivity pattern. For this reason, three types of photochemical reactions were examined for $[Rh_2(TM4)_4Re_2(CO)_{10}](PF_6)_2$: photostability and decomposition reactions, terminal metal radical exchange and ligand substitution.

Upon excitation of the $\sigma \rightarrow \sigma^*$ transition at 578 nm, $[Rh_2(TM4)_4Re_2(CO)_{10}](PF_6)_2$ was found to be very stable in degassed acetone solutions. After 12 days of photolysis, less than 5% decomposition of the tetranuclear species was observed. However, higher energy photolysis led to slow decomposition to $[Rh_2(TM4)_4](PF_6)_2$ and $[Re(CO)_3OH]_4$ [16, 17]. Although the solvents were thoroughly dried, we believe trace amounts of water are required for this reaction to occur. The identification of the rhenium product is based on the agreement of the observed IR spectrum (peaks at 2030 and 1925 cm^{-1}) with those previously reported for $[Re(CO)_3OH]_4$ [17].

The mechanism that leads to the formation of $[Re(CO)_3OH]_4$ in this system is unclear at this time. The loss of CO from $[Rh_2(TM4)_4Re_2(CO)_{10}]^{2+}$ as a primary step that eventually leads to $[Re(CO)_3OH]_4$ is not likely because photolysis of $[Rh_2(TM4)_4Re_2(CO)_{10}]^{2+}$ in the presence of CO did not affect the decomposition of $[Rh_2(TM4)_4Re_2(CO)_{10}]^{2+}$. The intermediacy of $Re(CO)_5$ in this reaction is also unlikely in view of the failure to observe terminal metal group exchange (*vide infra*). Further mechanistic studies will be necessary to resolve this question.

The second type of potential photochemical reaction investigated was radical exchange of the terminal metal groups. This type of reaction is commonly observed in binuclear species that contain a single metal–metal bond and has been interpreted as the result of M–M bond and M′–M′ cleavage followed by M and M′ recombination. For example, excitation of the $\sigma \rightarrow \sigma^*$ transitions of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ gives $ReMn(CO)_{10}$ [18–20]. Mixtures of $[Rh_2(TM4)_4Re_2(CO)_{10}]^{2+}$ and $[Rh_2(TM4)_4Mn_2(CO)_{10}]^{2+}$, $[Rh_2(TM4)_4Re_2(CO)_{10}]^{2+}$ and $Mn_2(CO)_{10}$, and $[Rh_2(TM4)_4Mn_2(CO)_{10}]^{2+}$ and $Re_2(CO)_{10}$ were photolyzed, but no evidence of radical scrambling was observed. A solution of $[Rh_2(TM4)_4](PF_6)_2$ was also photolyzed with broad band radiation in the presence of equimolar amounts of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$. Curiously, $[Rh_2(TM4)_4Mn_2(CO)_{10}]^{2+}$ was the exclusive product. At least three competitive processes control this result: The relative rates of $Mn(CO)_5$ radical formation, relative reactivity of the $M(CO)_5$ radicals, and the relative absorption of light by the $M_2(CO)_{10}$ complexes. The combination of these three processes that causes the result is not known, but the result is consistent with the photochemical stability of the Rh–Mn bonds once formed in view of the apparent greater thermodynamic stability of Rh–Re bonds. The tetranuclear species do not appear to undergo facile photochemical bond cleavage reactions similar to those of the binuclear species $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.

Finally, as a potential photochemical reaction, ligand substitution was investigated. In view of the facile substitution reactions observed for many M–CO complexes, an expected product from the photochemical reaction of $[Rh_2(TM4)_4Re_2(CO)_{10}]^{2+}$ and PPh_3 was $[Rh_2(TM4)_4Re_2(CO)_8(PPh_3)_2](PF_6)_2$. Photolysis of $Rh_2(TM4)_4Re_2(CO)_{10}{}^{2+}$ in the presence of PPh_3 gave no evidence for the formation of a CO substitution product*. To insure that kinetic constraints rather than unfavorable thermodynamic parameters controlled this result, the photochemical reaction of $[Rh_2(TM4)_4Re_2(CO)_8(PPh_3)_2](PF_6)_2$ with CO was also studied, but again substitution (CO for PPh_3 on the terminal metal) was not observed. The lack of CO substitution in the tetranuclear species is consistent with our observation that no radical scrambling occurs, if substitution at Re must occur via the release of $Re(CO)_5$ radicals produced by the cleavage of a Rh–Re bond.

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*Although CO substitution at Re does not occur when $Rh_2(TM4)_4Re_2(CO)_{10}(PF_6)_2$ is photolyzed in the presence of PPh_3, a slow reaction that proceeds over the course of 3 days occurs with disruption of the tetranuclear complex (see 'Experimental' for details).