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Reactions of the Dirhenium(II) Complexes $Re_2X_4(dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides. 10.[1] Synthesis and Characterization of the Complex $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]O_3SCF_3$ and Several Isomeric Forms of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$ (Y = PF_6, O_3SCF_3)[†]

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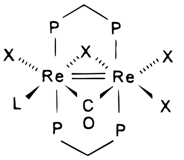
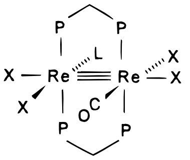
The reactions of the unsymmetrical, coordinatively unsaturated dirhenium(II) complexes $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]Y$ (XylNC = 2,6-dimethylphenyl isocyanide; Y = O_3SCF_3 (**3a**), PF_6 (**3b**)) with XylNC afford at least three isomeric forms of the complex cation $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$. Two forms have very similar bis(μ-halo)-bridged edge-sharing bioctahedral structures of the type $[(CO)BrRe(\mu\text{-}Br)_2(\mu\text{-dppm})_2Re(CNXyl)_2]Y$ (Y = O_3SCF_3 (**4a/4a′**), PF_6 (**4b/4b′**)), while the third is an open bioctahedron $[(XylNC)_2BrRe(\mu\text{-dppm})_2ReBr_2(CO)]Y$ (Y = O_3SCF_3 (**5a**), PF_6 (**5b**)). While the analogous chloro complex cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ was previously shown to exist in three isomeric forms, only one of these has been found to be structurally similar to the bromo complexes (i.e. the isomer analogous to **5a** and **5b**). The reaction of **3a** with CO gives the salt $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]O_3SCF_3$ (**7**), in which the edge-sharing bioctahedral cation $[(XylNC)BrRe(\mu\text{-}Br)(\mu\text{-}CO)(\mu\text{-dppm})_2ReBr(CO)]^+$ has an all-cis arrangement of π-acceptor ligands. The Re−Re distances in the structures of **4b′**, **5a**, and **7** are 3.0456(8), 2.3792(7), and 2.5853(13) Å, respectively, and accord with formal Re−Re bond orders of 1, 3, and 2, respectively. Crystal data for $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2](PF_6)_{0.78}(ReO_4)_{0.22}\cdot CH_2Cl_2$ (**4b′**) at 295 K: monoclinic space group $P2_1/n$ (No. 14) with $a = 19.845(4)$ Å, $b = 16.945(5)$ Å, $c = 21.759(3)$ Å, $\beta = 105.856(13)°$, $V = 7038(5)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.060$ ($R_w = 0.145$) for 14 245 data ($F_o^2 > 2\sigma(F_o^2)$). Crystal data for $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3\cdot C_6H_6$ (**5a**) at 173 K: monoclinic space group $P2_1/n$ (No. 14) with $a = 14.785(3)$ Å, $b = 15.289(4)$ Å, $c = 32.067(5)$ Å, $\beta = 100.87(2)°$, $V = 7118(5)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.046$ ($R_w = 0.055$) for 6962 data ($I > 3.0\sigma(I)$). Crystal data for $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]O_3SCF_3\cdot Me_2CHC(O)Me$ (**7**) at 295 K: monoclinic space group $P2_1/n$ (No. 14) with $a = 14.951(2)$ Å, $b = 12.4180(19)$ Å, $c = 40.600(5)$ Å, $\beta = 89.993(11)°$, $V = 7537(3)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.074$ ($R_w = 0.088$) for 6595 data ($I > 3.0\sigma(I)$).

Introduction

The triply-bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (dppm = $Ph_2PCH_2PPh_2$) react in a stepwise fashion with carbon monoxide to afford the mono- and dicarbonyl complexes $Re_2X_4(\mu\text{-dppm})_2(CO)$ (**1a**, X = Cl; **1b**, X = Br) and $Re_2X_4(\mu\text{-dppm})_2(CO)_2$ (**2a**, X = Cl; **2b**, X = Br).[2,3] While the monocarbonyls exist in two isomeric forms,[2−4] the dicarbonyl complexes have been found to possess only the edge-sharing bioctahedral structure depicted in **I** (L = CO). In contrast, mixed carbonyl−isocyanide complexes of composition $Re_2X_4(\mu\text{-dppm})_2(CO)(CNR)$ (i.e. L = RNC), which are formed by the reactions of isocyanide ligands with **1a** and **1b**, exist in two quite distinct structural forms; when X = Cl and R = xylyl or mesityl,[3] the edge-sharing bioctahedral structure **I** is adopted, while the open bioctahedral structure **II** is found in the cases where X = Cl or Br when R = *t*-Bu or xylyl.[1,4] To date, only in the case of $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$ have any of these compounds been isolated in both of the isomeric forms **I** and **II**.[1,3] The particular isomer which is obtained when the monocarbonyl **1a** is reacted with 1 equiv of XylNC depends entirely upon the choice of reaction solvent; isomer **I** is formed when dichloromethane or acetone is the solvent, while isomer **II** is formed in acetonitrile.



I



II

In the presence of Tl^+ and additional equivalents of a ligand L′, one of the Re−X bonds of the complexes of structure types **I** and **II** is labilized and salts of the $[Re_2X_3(\mu\text{-dppm})_2(CO)(L)(L′)]^+$ cations can be isolated (L = CO, RNC; L′ = CO, RNC, RCN, PR_3), in which the same basic edge-sharing or open bioctahedral geometries of the parent species are retained.[1,4−10] However, when the reactions between Tl^+ and $Re_2X_4(\mu\text{-dppm})_2(CO)(CNR)$ are carried out *in the absence of L′*, then quite

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[†] This article is dedicated to Lord Lewis on the occasion of his retirement as Professor of Inorganic Chemistry from the University of Cambridge, U.K. Various aspects of this work were presented at a Symposium, Metal−Metal Bonds in Chemistry, which was held in honor of Professor Lewis and sponsored by the Dalton Division of the Royal Society of Chemistry, Sept 14−15, 1995, Cambridge, U.K.

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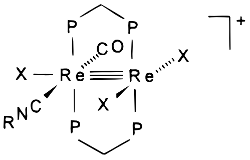
different behavior is observed from that cited above. The isomers with the open bioctahedral structure **II** (X = Br) react to afford the unsymmetrical, coordinatively unsaturated complexes of type **III**;[4] these result from the labilization of the Re−X bond that is trans to the RNC ligand, followed by transfer of CO from the adjacent Re center to give a trans disposition of CO and RNC ligands in the final product.[11]



III

In the present report we describe the reactions of salts of a representative complex cation of type **III**, *viz.* $[Re_2Br_3(\mu\text{-}dppm)_2(CO)(CNXyl)]Y$ (Y = PF_6, O_3SCF_3), with carbon monoxide and xylyl isocyanide. This work has led to the formation of a variety of isomeric forms of the complex cation $[Re_2Br_3(\mu\text{-}dppm)_2(CO)(CNXyl)_2]^+$, which differ in the nature of the Re−Re bonds that are present.

Experimental Section

Starting Materials and General Procedures. The compounds $[Re_2Br_3(dppm)_2(CO)(CNXyl)]O_3SCF_3$, **3a**,[4] $Re_2Br_4(dppm)_2(CO)(CNXyl)$,[4] $Re_2Br_4(dppm)_2(CO)$,[3] and TlO_3SCF_3[12] were prepared according to the literature procedures. 2,6-Dimethylphenyl isocyanide, XylNC, was purchased from Fluka Chemical Corp., CO gas from Matheson Gas Products Co., and $TlPF_6$ from Strem Chemicals. These reagents were used as received. Solvents were obtained from commercial sources and were deoxygenated by purging with nitrogen gas prior to use. All reactions were performed under an atmosphere of dry nitrogen. Infrared spectra, ^1H and $^{31}P\{^1H\}$ NMR spectra, and cyclic voltammetric measurements were determined as described previously.[4] Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

A. Synthesis of $[Re_2Br_3(dppm)_2(CO)(CNXyl)]PF_6$, 3b. (i) From $Re_2Br_4(dppm)_2(CO)(CNXyl)$. A mixture of $Re_2Br_4(dppm)_2(CO)(CNXyl)$ (200 mg, 0.123 mmol) and $TlPF_6$ (45.0 mg, 0.129 mmol) in 20 mL of CH_2Cl_2 was stirred at 25 °C for 4 h. The white precipitate (TlBr) was filtered off, and the green filtrate was reduced in volume to ca. 3 mL. An equal volume of isopropyl ether (3 mL) was then added to the solution, and the mixture was allowed to evaporate slowly at 25 °C to afford a crop of green crystals; yield 202 mg (96%). IR spectrum (ν, cm^{-1}): 2160 (m, CN), 2028 (s, CO). ^1H NMR spectrum (δ in $CDCl_3$): 7.80−6.90 (m, 43H, Ph), 6.17 (m, 2H, CH_2 of dppm), 5.87 (m, 2H, CH_2 of dppm), 2.03 and 1.98 (s, 6H, CH_3 of xylyl). $^{31}P\{^1H\}$ NMR spectrum (δ in $CDCl_3$): −9.0 (m), −14.5 (m).

(ii) From $Re_2Br_4(dppm)_2(CO)$. A mixture of $Re_2Br_4(dppm)_2(CO)$ (250 mg, 0.168 mmol), XylNC (23.0 mg, 0.175 mmol), and $TlPF_6$ (65.0 mg, 0.186 mmol) was stirred in 30 mL of CH_2Cl_2 for 6 h to give a pale green suspension. The workup was similar to that described in part A(i); yield 241 mg (84%).

B. Reactions of $[Re_2Br_3(dppm)_2(CO)(CNXyl)]Y$ (Y = O_3SCF_3, 3a; PF_6, 3b) with XylNC. (i) Y = O_3SCF_3 in CH_2Cl_2. A mixture of **3a** (56 mg, 0.033 mmol) and XylNC (5.0 mg, 0.038 mmol) was treated with CH_2Cl_2 (20 mL) at 25 °C. A color change from green to red-brown was observed immediately. The resulting solution was stirred at 25 °C for 3 h and then filtered. The volume of the filtrate was reduced to 2 mL, and ca. 20 mL of diethyl ether was then added to induce precipitation. A brown solid was collected by filtration, washed with diethyl ether (2 mL × 3), and dried under vacuum. Since an IR spectrum of this crude product showed it to be a mixture, attempts were made to separate the possible components. The recrystallization of the solid from a CH_2Cl_2/C_6H_6 solvent mixture (2/1) was partially successful; this gave a crop of yellow-brown platelike crystals, which was a mixture of structurally similar isomers (**4a**/**4a′**) of composition $[Re_2Br_3(\mu\text{-}dppm)_2(CO)(CNXyl)_2]O_3SCF_3$, along with a small quantity of red diamond-shaped crystals (**5a**), which was a third isomeric form of this complex. We were unable to cleanly separate the **4a**/**4a′** mixture, the components of which were reproducibly obtained in a 95/5 ratio (as judged by ^1H NMR spectroscopy) by the use of this procedure. Yields: **4a**/**4a′**, 25.1 mg (42%); **5a**, 1.2 mg (2%). Additional runs gave yields for **4a**/**4a′** in the range 40−65%, while for **5a** the yields ranged from 0 to 10%. Anal. Calcd for $C_{70}H_{62}Br_3F_3N_2O_4P_4Re_2S$: C, 46.19; H, 3.43; N, 1.54. Found for **4a**/**4a′**: C, 46.31; H, 3.35; N, 1.63. Found for **5a**: C, 46.56; H, 3.55; N, 1.40.

Our attempts to determine the single-crystal X-ray structures of **4a** and **4a′** have to date been unsuccessful; a disorder problem thwarted our attempts to solve the structure of **4a**, while good-quality crystals of **4a′** were not obtained from the **4a**/**4a′** mixtures. The structure of **5a** was solved successfully.

(ii) Y = O_3SCF_3 in $(CH_3)_2CO$. A sample of **3a** (140 mg, 0.083 mmol) was combined with a stoichiometric amount of XylNC (11.0 mg, 0.084 mmol) and the mixture stirred in 25 mL of $(CH_3)_2CO$ at 25 °C for 1.5 h. A brown solution formed, and 133 mg of a brown solid was collected following the addition of an excess of diethyl ether. As described above, the IR spectrum of this brown solid showed it to be a mixture. Recrystallization from a CH_2Cl_2/C_6H_6 solvent mixture afforded **4a**/**4a′** (ca. 95/5) and **5a**: yields, **4a**/**4a′**, 100 mg (66%); **5a**, 9.5 mg (6%).

(iii) Y = PF_6 in CH_2Cl_2. A mixture comprising equimolar amounts of **3b** (70.0 mg, 0.042 mmol) and XylNC (5.5 mg, 0.042 mmol) in 15 mL of CH_2Cl_2 was stirred for 24 h. The reaction solution was then reduced in volume to ca. 3 mL, and a very small quantity of yellow-brown solid was filtered off. This product is believed to be an isomeric form of $[Re_2Br_3(\mu\text{-}dppm)_2(CO)(CNXyl)_2]PF_6$, **6**, that had not been obtained as its analogous triflate salt (see sections B(i) and B(ii)). Because of the poor solubility properties of **6** and the very small amounts obtained, this product was not fully characterized. The identity of **6** is based upon its IR spectral properties (see Results and Discussion). Following the removal of the small amount of **6**, the red reaction filtrate was treated with ca. 3 mL of *i*-Pr_2O and the solvent mixture allowed to evaporate slowly at 25 °C. This afforded a crop of yellow crystals, which was a mixture of isomers of $[Re_2Br_3(\mu\text{-}dppm)_2(CO)(CNXyl)_2]PF_6$, **4b**/**4b′** (ca. 95/5), admixed with a very small quantity of red crystals of another isomeric form, **5b**. The yellow and red crystals could be separated by hand. Yields: **4b**/**4b′**, 48.2 mg (64%); **5b**, (<2%). Anal. Calcd for $C_{69}H_{62}Br_3F_6N_2OP_5Re_2$: C, 45.63; H, 3.44; N, 1.54. Found for **5b**: C, 45.70; H, 3.47; N, 1.39.

(iv) Y = PF_6 in $(CH_3)_2CO$. A procedure similar to that described in section B(iii), involving the reaction of **3b** (65.0 mg, 0.039 mmol) with XylNC (5.0 mg, 0.038 mmol) in 10 mL of acetone and a reaction time of 17 h, afforded an isomeric mixture **4b**/**4b′** (ca. 95/5), along with trace amounts of **5b** and **6** (which were identified spectroscopically); yield of **4b**/**4b′** 46.3 mg (66%).

C. Reactions of $Re_2Br_4(dppm)_2(CO)(CNXyl)$ with XylNC in the Presence of TlY (Y = PF_6, O_3SCF_3). (i) Y = O_3SCF_3. A suspension of $Re_2Br_4(dppm)_2(CO)(CNXyl)$ (75.0 mg, 0.046 mmol), TlO_3SCF_3 (17.0 mg, 0.048 mmol), and XylNC (6.0 mg, 0.046 mmol) in 20 mL of CH_2Cl_2 was stirred at 25 °C for 20 h. The white precipitate (TlBr) was filtered off, the volume of the red-brown filtrate was reduced to ca. 2 mL, and 20 mL of diethyl ether was then added to induce precipitation of a brown solid. This product was found to be the isomeric mixture **4a**/**4a′** (ca. 50/50); yield 72.5 mg (86%). A trace of the isomer **5a** was also present in the crude products (as detected by ^1H NMR spectroscopy). Attempts to separate **4a** and **4a′** were unsuccessful.

(ii) Y = PF_6. A procedure very similar to that in section C(i), but with $TlPF_6$ in place of TlO_3SCF_3, afforded a mixture of **4b**/**4b′** (ca. 50/50); yield 73%. Recrystallization of this mixture using a CH_2Cl_2/

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C_6H_6 solvent mixture allowed for the separation of **4b** and **4b′**; the yellow crystals of **4b** were very unstable, while the red-brown crystals of **4b′** were quite stable.

D. Reaction of [Re_2Br_3(dppm)$_2$(CO)(CNXyl)]O_3SCF_3 with CO. A solution of **3a** (60 mg, 0.036 mmol) in CH_2Cl_2 (15 mL) was treated with CO (slow purge through the solution) for ca. 30 s. The resulting mixture was then stirred at 25 °C for 24 h. The volume of the solution was reduced to 2 mL, ca. 2 mL of C_6H_6 was added, and the crystalline product was obtained by the slow evaporation of the solvent mixture at 25 °C. The complex [Re_2Br_3(dppm)$_2$(CO)$_2$(CNXyl)]O_3SCF_3, **7**, was collected as brown crystals; yield 49.2 mg (81%). Anal. Calcd for $C_{62}H_{53}Br_3F_3NO_5P_4Re_2S$: C, 43.37; H, 3.11; N, 0.82. Found: C, 43.24; H, 3.08; N, 0.82.

E. Attempts To Interconvert Isomers. Various attempts to convert one isomeric form of [Re_2Br_3(μ-dppm)$_2$(CO)(CNXyl)$_2$]Y to another were carried out. When the isomeric mixtures **4a/4a′** (ca. 95/5) and **4b/4b′** (ca. 50/50) and pure **5a** were stirred at room temperature in CH_2Cl_2, or refluxed in CH_2Cl_2 for several hours, the original materials were recovered unchanged.

F. X-ray Crystallography. Suitable single crystals of compounds **4b′**, **5a**, and **7** were obtained by slow evaporation of solvents at 25 °C from solutions of **4b′** in CH_2Cl_2/*i*-Pr_2O (2/1), **5a** in CH_2Cl_2/C_6H_6 (1/1), and **7** in CH_2Cl_2/$(CH_3)_2CHC(O)CH_3$ (1/1).

The data collections were performed on an Enraf-Nonius CAD4 computer controlled diffractometer; graphite-monochromatized Mo Kα radiation was used in all cases. Data collections on the crystals were carried out at 295 ± 1 K for **4b′** and **7** and at 173 ± 1 K for **5a**. The cell constants were based on 25 reflections obtained in the ranges $18 < \theta < 25°$ for **4b′**, $17 < \theta < 20°$ for **5a**, and $16 < \theta < 20°$ for **7**, as measured by the computer-controlled diagonal-slit method of centering. Three standard reflections were measured after every 5000 s of beam time during data collection to monitor the crystal stability. Lorentz and polarization corrections were applied to the data sets. An empirical absorption correction[13] was also applied, but no correction for extinction was made. Calculations for structure solving were performed on VAX computers using the program MolEN. For **5a** and **7**, structure refinements were also done using MolEN, while for **4b′**, the structure refinement was finished by use of the SHELXL-93 program[14] on a PC with a Pentium processor.

All three compounds crystallized in the monoclinic crystal system, with the space group $P2_1/n$. The structures were solved by use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. For **4b′** and **5a** all non-hydrogen atoms were refined anisotropically.[15] Only atoms heavier than oxygen were anisotropically refined for **7**;[15] all other non-hydrogen atoms were refined with isotropic thermal parameters. For all three structures, the positions of the hydrogen atoms were calculated by the use of idealized geometries with C−H = 0.95 Å and B(H) = 1.3B_{iso}(C). Their contributions were added to the structure factor calculations, but their positions were not refined.

During the course of the structure refinement of **4b′**, it became apparent that the anion could not be refined as $[PF_6]^-$ with full occupancy. This was reflected by unusually small thermal parameters for the P atom and very large parameters for the F atoms and by the presence of several very large peaks in the remaining difference Fourier map. Since the IR spectrum of the crystals showed a band of moderate intensity at 904 cm^{-1}, which is characteristic of the ν(Re−O) mode of the $[ReO_4]^-$ anion, in addition to the expected ν(P−F) mode of $[PF_6]^-$ at 846 (s) cm^{-1}, the formation of $[ReO_4]^-$ is presumably due to the degradation of a very small quantity of the dirhenium cation through its reaction with O_2 which diffuses into the system during the slow crystal-growing process. We modeled the anion site as containing disordered $[PF_6]^-$ and $[ReO_4]^-$. With this model, the R factors of the refinement parameters improved from $R = 0.077$ and $R_w = 0.194$ to $R = 0.060$ and $R_w = 0.145$ and the remaining highest peak in the difference Fourier map decreased from 7.00 to 1.73 e/Å^3. The atoms of these two groups were located and refined satisfactorily to the occupancies of 0.777(4) for $[PF_6]^-$ and 0.223(4) for $[ReO_4]^-$, respectively. The octahedral $[PF_6]^-$ group and the tetrahedral $[ReO_4]^-$ group were found to be partially overlapped, so that two sets of the fluorine and oxygen atoms, F(1)/O(1) and F(2)/O(2), occupy the same positions. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$, where w is the weighing factor defined as $w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 129.4751P]$ and $P = (F_o^2 + 2F_c^2)/3$. The final residuals for **4b′** were $R = 0.060$ and $R_w = 0.145$ with GOF = 1.05. The highest peak in the final difference Fourier was 1.73 e/Å^3.

For compound **5a**, a molecule of C_6H_6 from the crystallization solvent was found to be present in the asymmetric unit. This solvent molecule was included in the analysis and was satisfactorily refined. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighing factor defined as $w = 1/\sigma^2(|F_o|)$. The final residuals for **5a** were $R = 0.046$ and $R_w = 0.055$ with GOF = 1.299. The highest peak in the final difference Fourier was 2.66 e/Å^3.

In the case of compound **7**, a molecule of the crystallization solvent $(CH_3)_2CHC(O)CH_3$ was found in the asymmetric unit during the latter stages of the refinement. However, only four of the non-hydrogen atoms of this solvent molecule were located and refined satisfactorily. Due to a disorder problem, the carbon atoms of the two methyl groups of the isopropyl group as well as the hydrogen atoms of this solvent molecule were not included in this analysis. As a result, the final residuals for **7**, $R = 0.074$ and $R_w = 0.088$, were fairly high and GOF = 1.791. The highest peak in the final difference Fourier was 2.63 e/Å^3. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighing factor defined as $w = 1/\sigma^2(|F_o|)$.

The crystallographic data for compounds **4b′**, **5a**, and **7** are listed in Table 1. The intramolecular bond distances and angles for these structures are given in Tables 2−4.

Results and Discussion

We have established previously that the reactions of the mixed carbonyl−isocyanide complexes Re_2X_4(μ-dppm)$_2$(CO)(CNR), where X = Cl or Br and R = *t*-Bu or xylyl, which possess the open bioctahedral structure **II**, react with Tl$^+$ salts in the *absence* of additional equivalents of CO or RNC to afford the unsymmetrical halide-deficient species of structure type **III**.[4,11] This is represented as step A in Scheme 1. When these reactions are carried out in the presence of an additional 1 equiv of RNC, they proceed according to step B (Scheme 1) in the case of X = Cl.[1,7] In the present report we have established the following: (1) step B in Scheme 1 is not followed when Re_2Br_4(μ-dppm)$_2$(CO)(CNXyl) (i.e. X = Br) is reacted with TlY (Y = O_3SCF_3 or PF_6); (2) the reactions of [Re_2Br_3(μ-dppm)$_2$(CO)(CNXyl)]Y (Y = O_3SCF_3 (**3a**); PF_6 (**3b**)) with XylNC afford at least three isomeric forms of the complex cation [Re_2Br_3(μ-dppm)$_2$(CO)(CNXyl)$_2$]$^+$; (3) [Re_2Br_3(μ-dppm)$_2$(CO)(CNXyl)]O_3SCF_3 (**3a**) reacts with CO to give the all-cis isomer of [Re_2Br_3(μ-dppm)$_2$(CO)$_2$(CNXyl)]O_3SCF_3. This chemistry is summarized in Scheme 2.

Synthesis, Spectroscopic Characterizations, and Structural Studies. The primary focus of our work has been the reactions of the salts [Re_2Br_3(μ-dppm)$_2$(CO)(CNXyl)]Y (Y = O_3SCF_3 (**3a**), PF_6 (**3b**)) with XylNC. Reactions in dichloromethane and acetone gave similar results; the major product (40−70% yield) is a mixture of isomers **4a/4a′** (Y = O_3SCF_3) or **4b/4b′** (Y = PF_6) along with a small quantity of **5a** (Y = O_3SCF_3) or **5b** (Y = PF_6). The structures of these isomeric forms of [Re_2Br_3(μ-dppm)$_2$(CO)(CNXyl)$_2$]Y are represented in Scheme 2. The ratio of isomers in the mixtures **4a/4a′** and **4b/4b′** was reproducibly close to 95/5; while we were unable to effect a clean separation

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(15) (a) Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. C, Table 4.2.6.8. (b) Maslen, E. N.; Fox, A. G.; O'Keefe, M. A. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. C, Table 6.1.1.4.

Table 1. Crystallographic Data for $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2](PF_6)_{0.78}(ReO_4)_{0.22}\cdot CH_2Cl_2$ (**4b′**), $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3\cdot C_6H_6$ (**5a**), and $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]O_3SCF_3\cdot Me_2CHC(O)Me$ (**7**)

	4b′	**5a**	**7**
empirical formula	$Re_{2.22}Br_3Cl_2P_{4.78}F_{4.66}O_{1.88}N_2C_{70}H_{64}$	$Re_2Br_3SP_4F_3O_4N_2C_{61}H_{53}$	$Re_2Br_3SP_4F_3O_6NC_{67}H_{63}$
fw	1924.67	1898.48	1803.33
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	19.845(4)	14.785(3)	14.951(2)
b, Å	16.945(5)	15.289(4)	12.4180(19)
c, Å	21.759(3)	32.067(5)	40.600(5)
β, deg	105.856(13)	100.87(2)	89.993(11)
V, Å^3	7038(5)	7118(5)	7537(3)
Z	4	4	4
ρ_{calcd}, g/cm^3	1.816	1.771	1.589
μ, cm^{-1} (Mo, Kα)	54.85	52.87	49.90
transm factors, min/max	0.11/0.25	0.59/1.00	0.04/0.37
R^a/R_w^b	0.060/0.145	0.046/0.055	0.074/0.088
largest shift/error	0.06	0.02	0.02
GOF	1.046	1.299	1.791

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$ for **4b′**; $R = \sum|F_o| - |F_c|/\sum|F_o|$ with $F_o > 3\sigma(F_o)$ for **5a** and **7**. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 129.4751P]$ where $P = (F_o^2 + 2F_c^2)/3$, for **4b′**; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o^2|)]^{1/2}$, $w = 1/\sigma^2(F_o)$, for **5a** and **7**.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for the Dirhenium Cation of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2](PF_6)_{0.78}(ReO_4)_{0.22}\cdot CH_2Cl_2$ (**4b′**)[a]

Distances

Re(1)−Re(2)	3.0456(8)	Re(2)−P(2)	2.423(3)
Re(1)−C(10)	2.01(2)	Re(2)−P(4)	2.423(3)
Re(1)−P(1)	2.426(3)	Re(2)−Br(2)	2.5905(15)
Re(1)−P(3)	2.442(3)	Re(2)−Br(3)	2.533(2)
Re(1)−Br(1)	2.556(2)	O(10)−C(10)	1.02(2)
Re(1)−Br(2)	2.5038(14)	N(20)−C(20)	1.15(2)
Re(1)−Br(3)	2.498(2)	N(20)−C(21)	1.38(2)
Re(2)−C(20)	1.991(12)	N(30)−C(30)	1.133(15)
Re(2)−C(30)	2.018(12)	N(30)−C(31)	1.39(2)

Angles

C(10)−Re(1)−P(1)	88.3(4)	Br(3)−Re(1)−Re(2)	53.28(5)
C(10)−Re(1)−P(3)	89.9(4)	Br(2)−Re(1)−Re(2)	54.60(3)
P(1)−Re(1)−P(3)	176.51(11)	Br(1)−Re(1)−Re(2)	144.46(5)
C(10)−Re(1)−Br(3)	167.9(4)	C(20)−Re(2)−C(30)	89.8(5)
P(1)−Re(1)−Br(3)	88.20(10)	C(20)−Re(2)−P(4)	89.5(4)
P(3)−Re(1)−Br(3)	94.15(10)	C(30)−Re(2)−P(4)	90.2(3)
C(10)−Re(1)−Br(2)	83.7(4)	C(20)−Re(2)−P(2)	90.5(4)
P(1)−Re(1)−Br(2)	90.65(9)	C(30)−Re(2)−P(2)	89.2(3)
P(3)−Re(1)−Br(2)	86.17(9)	P(4)−Re(2)−P(2)	179.46(11)
Br(3)−Re(1)−Br(2)	107.88(6)	C(20)−Re(2)−Br(3)	86.4(4)
C(10)−Re(1)−Br(1)	77.3(4)	C(30)−Re(2)−Br(3)	176.1(3)
P(1)−Re(1)−Br(1)	94.07(9)	P(4)−Re(2)−Br(3)	88.77(10)
P(3)−Re(1)−Br(1)	88.46(9)	P(2)−Re(2)−Br(3)	91.76(10)
Br(3)−Re(1)−Br(1)	91.42(7)	C(20)−Re(2)−Br(2)	169.4(4)
Br(2)−Re(1)−Br(1)	160.27(6)	C(30)−Re(2)−Br(2)	79.5(3)
C(10)−Re(1)−Re(2)	138.2(4)	P(4)−Re(2)−Br(2)	91.05(8)
P(1)−Re(1)−Re(2)	89.23(9)	P(2)−Re(2)−Br(2)	88.92(9)
P(3)−Re(1)−Re(2)	90.11(8)	Br(3)−Re(2)−Br(2)	104.22(6)
C(20)−Re(2)−Re(1)	138.6(4)	Re(1)−Br(3)−Re(2)	74.49(7)
C(30)−Re(2)−Re(1)	131.5(3)	C(20)−N(20)−C(21)	171.1(15)
P(4)−Re(2)−Re(1)	89.65(8)	C(30)−N(30)−C(31)	173.1(13)
P(2)−Re(2)−Re(1)	90.76(8)	O(10)−C(10)−Re(1)	176.5(14)
Br(3)−Re(2)−Re(1)	52.23(6)	N(20)−C(20)−Re(2)	178.5(12)
Br(2)−Re(2)−Re(1)	51.99(3)	N(30)−C(30)−Re(2)	173.0(11)
Re(1)−Br(2)−Re(2)	73.41(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for the Dirhenium Cation of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3\cdot C_6H_6$ (**5a**)[a]

Distances

Re(1)−Re(2)	2.3792(7)	Re(2)−P(4)	2.480(3)
Re(1)−Br(11)	2.699(1)	Re(2)−C(20)	2.05(1)
Re(1)−Br(12)	2.547(1)	Re(2)−C(30)	2.06(1)
Re(1)−P(1)	2.493(3)	O(1)−C(1)	1.15(1)
Re(1)−P(3)	2.490(3)	N(20)−C(20)	1.18(2)
Re(1)−C(1)	1.91(1)	N(20)−C(21)	1.42(2)
Re(2)−Br(21)	2.629(2)	N(30)−C(30)	1.16(2)
Re(2)−P(2)	2.494(3)	N(30)−C(31)	1.38(2)

Angles

Re(2)−Re(1)−Br(11)	161.71(4)	Re(1)−Re(2)−C(20)	92.5(3)
Re(2)−Re(1)−Br(12)	106.51(4)	Re(1)−Re(2)−C(30)	106.2(3)
Re(2)−Re(1)−P(1)	96.53(8)	Br(21)−Re(2)−P(2)	77.80(8)
Re(2)−Re(1)−P(3)	97.90(8)	Br(21)−Re(2)−P(4)	88.32(8)
Re(2)−Re(1)−C(1)	84.2(4)	Br(21)−Re(2)−C(20)	82.7(3)
Br(11)−Re(1)−Br(12)	91.67(5)	Br(21)−Re(2)−C(30)	79.3(3)
Br(11)−Re(1)−P(1)	82.02(8)	P(2)−Re(2)−P(4)	162.4(1)
Br(11)−Re(1)−P(3)	84.66(8)	P(2)−Re(2)−C(20)	87.5(3)
Br(11)−Re(1)−C(1)	77.6(4)	P(2)−Re(2)−C(30)	96.1(3)
Br(12)−Re(1)−P(1)	87.45(9)	P(4)−Re(2)−C(20)	80.0(3)
Br(12)−Re(1)−P(3)	87.28(9)	P(4)−Re(2)−C(30)	91.8(3)
Br(12)−Re(1)−C(1)	169.3(4)	C(20)−Re(2)−C(30)	160.4(5)
P(1)−Re(1)−P(3)	165.5(1)	C(20)−N(20)−C(21)	172(1)
P(1)−Re(1)−C(1)	91.0(4)	C(30)−N(30)−C(31)	175(1)
P(3)−Re(1)−C(1)	91.7(4)	Re(1)−C(1)−O(1)	176(1)
Re(1)−Re(2)−Br(21)	172.39(4)	Re(2)−C(20)−N(20)	172(1)
Re(1)−Re(2)−P(2)	96.14(8)	Re(2)−C(30)−N(30)	174(1)
Re(1)−Re(2)−P(4)	96.70(8)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

of the components of the bulk material, individual crystals of the isomeric forms could be separated by hand. In the case of the reaction between $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]PF_6$ (**3b**) and XylNC in dichloromethane, a small quantity of a yellow-brown product was obtained, which we believe may be a fourth isomeric form of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]PF_6$ (**6**). Unfortunately, **6** has very poor solubility in solvents such as CH_2Cl_2 and $CHCl_3$, so its characterization is based on its Nujol mull IR spectrum, which shows two terminal ν(CN) modes at 2162 (vs) and 2104 (vs) cm^{-1} and a bridging ν(CO) mode at 1736 (m) cm^{-1}. These spectral properties closely resemble those of the chloro analogue of **6**, i.e. $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$, which we recently isolated as a major product in the reaction between $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)]O_3SCF_3$ and XylNC[11] and whose dirhenium cation is believed to have an unsymmetrical structure $[(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-dppm})_2ReCl(CNXyl)]^+$. This chloro complex has terminal ν(CN) modes at 2170 (s) and 2114 (vs) cm^{-1} and a bridging ν(CO) mode at 1722 (s) cm^{-1}.

In contrast to the relative complexity of the reactions of XylNC with **3a** and **3b**, the analogous reaction involving CO is quite straightforward. A single isomer of $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]O_3SCF_3$ (**7**) is formed upon reacting **3a** with CO (Scheme 2).

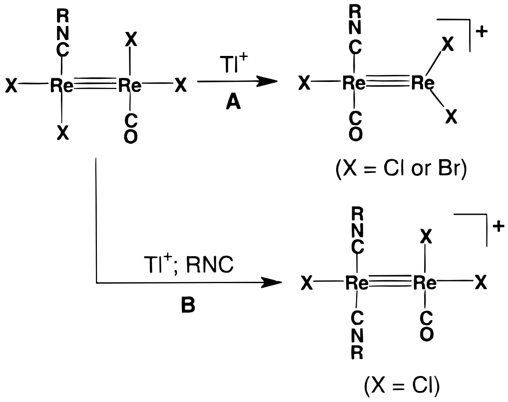
An alternative procedure for the preparation of **4a**/**4a′** and **4b**/**4b′** is to react the neutral complex $Re_2Br_4(\mu\text{-dppm})_2$-

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for the Dirhenium Cation of $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]SO_3CF_3{\cdot}Me_2CHC(O)Me$ (**7**)[a]

	Distances		
Re(1)−Re(2)	2.5853(13)	Re(2)−P(2)	2.477(10)
Re(1)−Br(1)	2.554(3)	Re(2)−P(4)	2.468(9)
Re(1)−Br(12)	2.579(2)	Re(2)−C(12)	2.111(18)
Re(1)−P(1)	2.457(9)	Re(2)−C(21)	1.85(3)
Re(1)−P(3)	2.478(10)	O(12)−C(12)	1.11(2)
Re(1)−C(1)	2.012(18)	O(21)−C(21)	1.17(3)
Re(1)−C(12)	2.11(2)	N(1)−C(1)	1.11(2)
Re(2)−Br(2)	2.536(3)	N(1)−C(2)	1.47(3)
Re(2)−Br(12)	2.569(3)		
	Angles		
Re(2)−Re(1)−Br(1)	148.86(6)	P(3)−Re(1)−C(1)	85.4(10)
Re(2)−Re(1)−Br(12)	59.67(7)	P(3)−Re(1)−C(12)	94.5(9)
Re(2)−Re(1)−P(1)	96.54(18)	C(1)−Re(1)−C(12)	74.1(9)
Re(2)−Re(1)−P(3)	95.63(17)	Re(1)−Re(2)−Br(2)	152.66(9)
Re(2)−Re(1)−C(1)	126.3(7)	Re(1)−Re(2)−Br(12)	60.05(6)
Re(2)−Re(1)−C(12)	52.2(5)	Re(1)−Re(2)−P(2)	95.10(17)
Br(1)−Re(1)−Br(12)	89.25(9)	Re(1)−Re(2)−P(4)	94.80(18)
Br(1)−Re(1)−P(1)	86.1(2)	Re(1)−Re(2)−C(12)	52.3(7)
Br(1)−Re(1)−P(3)	84.0(2)	Re(1)−Re(2)−C(21)	121.4(7)
Br(1)−Re(1)−C(1)	84.8(7)	Br(2)−Re(2)−Br(12)	92.61(10)
Br(1)−Re(1)−C(12)	158.9(5)	Br(2)−Re(2)−P(2)	84.74(18)
Br(12)−Re(1)−P(1)	92.79(16)	Br(2)−Re(2)−P(4)	85.51(18)
Br(12)−Re(1)−P(3)	94.19(16)	Br(2)−Re(2)−C(12)	155.0(7)
Br(12)−Re(1)−C(1)	174.0(7)	Br(2)−Re(2)−C(21)	86.0(7)
Br(12)−Re(1)−C(12)	111.9(5)	Br(12)−Re(2)−P(2)	90.9(2)
P(1)−Re(1)−P(3)	167.8(2)	Br(12)−Re(2)−P(4)	92.28(19)
P(1)−Re(1)−C(1)	86.7(9)	Br(12)−Re(2)−C(12)	112.3(6)
P(1)−Re(1)−C(12)	92.1(9)	Br(12)−Re(2)−C(21)	176.6(11)
P(2)−Re(2)−P(4)	169.9(2)	C(1)−N(1)−C(2)	169(3)
P(2)−Re(2)−C(12)	92.3(9)	Re(1)−C(1)−N(1)	177.0(18)
P(2)−Re(2)−C(21)	85.9(11)	Re(1)−C(12)−Re(2)	75.5(7)
P(4)−Re(2)−C(12)	95.4(9)	Re(1)−C(12)−O(12)	140.4(17)
P(4)−Re(2)−C(21)	90.7(11)	Re(2)−C(12)−O(12)	143(2)
C(12)−Re(2)−C(21)	69.1(9)	Re(2)−C(21)−O(21)	167(3)
Re(1)−Br(12)−Re(2)	60.29(6)		

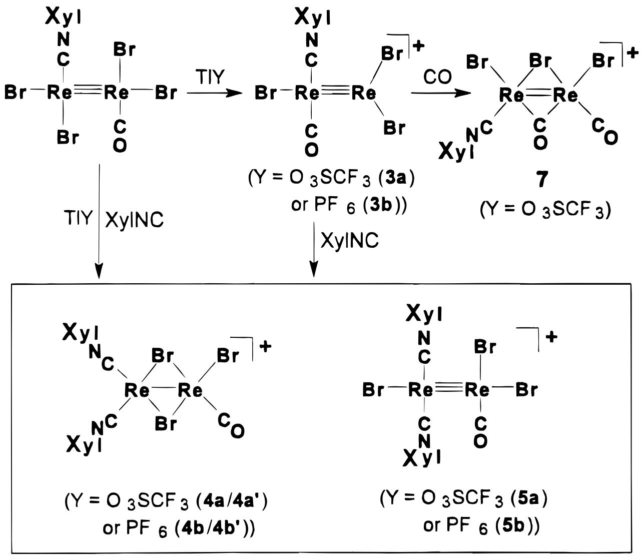
[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Scheme 1. Reactions between the $Re_2X_4(\mu\text{-dppm})_2(CO)(CNR)$ Complexes of Structure Type **II** and Thallium(I) Salts



(CO)(CNXyl) with 1 equiv of XylNC in the presence of TlO_3SCF_3 (for **4a/4a′**) or $TlPF_6$ (for **4b/4b′**) (see Scheme 2). There are two consequences of using the $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNXyl)/TlY$ mixtures as starting materials in place of **3a** and **3b**. First, the ratio of isomers in the isomeric mixtures **4a/4a′** and **4b/4b′** is ca. 50/50, compared to ca. 95/5 when **3a** and **3b** are used. Second, **5a** (and **5b**) are obtained at best in trace amounts (<1%) as detected by IR and ^1H NMR spectroscopy. In the case of **4b/4b′**, we were able to effect a clean separation of the 50/50 mixture of isomers by recrystallization from CH_2Cl_2/C_6H_6. This enabled us to confirm the spectroscopic and electrochemical properties of the different isomeric forms **4a**, **4a′**, **4b**, and **4b′**. These properties, along with those for the other isomeric forms of these complexes, **5a** and **5b**, as well as those for $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]O_3SCF_3$ (**7**), are summarized in Table 5.

Scheme 2. Reactions of $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNXyl)$ and the Halide-Deficient Complexes $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]Y$ (Y = O_3SCF_3 (**3a**), PF_6 (**3b**)) with Xylyl Isocyanide and Carbon Monoxide



The electrochemical and spectroscopic properties of analogous $[O_3SCF_3]^-$ and $[PF_6]^-$ salts are essentially identical to one another. The principal spectroscopic differences are the presence of characteristic bands at ca. 1265 (vs) cm^{-1} (for $[O_3SCF_3]^-$ salts) and ca. 840 (vs) cm^{-1} (for $[PF_6]^-$ salts) in the Nujol mull IR spectra and a binomial heptet centered at δ ca. −143.5 in the ^{31}P NMR spectra of the $[PF_6]^-$ salts. The other important spectroscopic characteristics are given in Table 5.

The mixtures of isomers **4a/4a′** and **4b/4b′** differ only in the identity of the anions. The similarity in their electrochemical and spectroscopic properties is clear from the data in Table 5. The electrochemical properties, as measured by the CV technique, reveal two accessible one-electron oxidations and two one-electron reductions in the potential range +1.50 to −0.90 V vs Ag/AgCl. These characteristics differ from the analogous electrochemical data reported for chloro complexes which have the same stoichiometry as **4a**, **4a′**, **4b**, and **4b′**, *viz.*, $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNR)_2]Y$ (Y = Cl, ReO_4, O_3SCF_3, or PF_6; R = *t*-Bu, Xyl)[6,7,10,11] but which possess edge-sharing bioctahedral structures with one bridging Cl and a bridging CO or RNC ligand. These chloro compounds possess one oxidation and two reductions within the larger potential range of +1.50 to −1.30 V.[6,10] Support for the conclusion that **4a**, **4a′**, **4b**, and **4b′** differ structurally from the chloro complexes $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$ is apparent from an examination of their IR spectra (Table 5), which show the presence of terminally bound XylNC and CO ligands only. This conclusion has been confirmed by a single-crystal X-ray structure determination on a crystal of **4b′**, which we obtained from a solution of this complex in $CH_2Cl_2/i\text{-}Pr_2O$. Although the slow crystal-growing process led to the decomposition of a small quantity of the dirhenium complex and the incorporation of some $[ReO_4]^-$ anion into the complex, thereby complicating the structure refinement (see Experimental Section), the identity of the cation as $[Re_2(\mu\text{-Br})_2(\mu\text{-dppm})_2Br(CO)(CNXyl)_2]^+$ was firmly established.

Table 5. Electrochemical and Spectroscopic Data for Isomers of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$ (Y = O_3SCF_3, PF_6; **4a, 4a′**, **4b, 4b′**, **5a**, **5b**) and for the Complex $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]O_3SCF_3$ (**7**)

	CV half-wave potentials, V[a]				IR, cm^{-1} [c]			
compd	$E_{1/2}$(ox)(2)[b]	$E_{1/2}$(ox)(1)[b]	$E_{1/2}$(red)(1)[b]	$E_{1/2}$(red)(2)[b]	ν(CN)	ν(CO)	^{1}H NMR, δ[d,e]	^{31}P{^{1}H} NMR, δ[d,f]
4a	+1.45 (130)	+0.65 (120)	+0.11 (125)	−0.84 (120)	2102 (vs)	1964 (s, br)	+2.30 (s), +1.76 (s) [CH_3 of xylyl]	−28.8 (m, br), −134.1 (m, br)
					2078 (sh)		+3.64 (m), +2.93 (m) [CH_2 of dppm]	
4a′	+1.43 (120)	+0.64 (120)	+0.13 (120)	−0.81 (120)	2108 (s)	1998 (vs)	+2.40 (s), +1.65 (s) [CH_3 of xylyl]	−30.1 (m, br), −163.7 (m, br)
					2056 (s)		+3.64 (m), +2.57 (m) [CH_2 of dppm]	
4b	+1.45 (120)	+0.64 (110)	+0.12 (120)	−0.81 (120)	2102 (vs)	∼1965 (s, br)[i]	+2.30 (s), +1.77 (s) [CH_3 of xylyl]	−29.3 (m, br), −134.7 (m, br)
					2082 (vs)		+3.64 (m), +2.91 (m) [CH_2 of dppm]	
4b′	+1.44 (130)	+0.64 (120)	+0.13 (120)	−0.84 (130)	2102 (s)	1996 (vs)	+2.40 (s), +1.67 (s) [CH_3 of xylyl]	−29.7 (m, br), −160.2 (m, br)
					2060 (s)		+3.66 (m), +2.58 (m) [CH_2 of dppm]	
5a			−0.53[g, h]	−1.00 (120)[h]	2144 (m)	1956 (s, br)	+1.80 (m) [CH_3 of xylyl][j]	−15.2 (m), −16.5 (m)[j]
					2110 (vs)		∼+6.25 (m) [CH_2 of dppm][j, k]	
5b			−0.56[g]	−0.98 (110)	2146 (m)	1954 (s)	+1.83 (m) [CH_3 of xylyl]	−15.2 (m), −16.8 (m)
					2106 (vs)		∼+6.25 [CH_2 of dppm][k]	
7		+0.11 (130)	−0.90 (130)		2164 (s)	2014 (vs)	+3.00 (s, br), +1.15 (s, br)	−19.2 (m), −24.2 (m)
						1734 (m)	+4.90 (m), +4.45 (m)	

[a] Measured in 0.1 M TBAH−CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (*v*) of 200 mV/s at a Pt-bead electrode. Under our experimental conditions $E_{1/2}$ = +0.47 V vs Ag/AgCl for the ferrocenium/ferrocene couple. [b] ΔE_p ($E_{p,a} - E_{p,c}$) values are given in parentheses at a scan rate of 200 mV/s. [c] IR spectra recorded as Nujol mulls. [d] Spectra recorded in $CDCl_3$ unless otherwise stated. [e] Phenyl group resonances occur within the range δ +8.1 to δ +6.6. [f] Chemical shifts are those of the centers of complex multiplets. [g] $E_{p,c}$ value. [h] These electrochemical properties resemble those for the chloro analogue of **5a** (see ref 1), which has this same structure, the principal difference being the appearance of a second irreversible process in the CV of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$, data for which have not been reported previously ($E_{p,c}$ = −0.56, $E_{p,c}$ = −0.79, and $E_{1/2}$(red) = −1.10 V vs Ag/AgCl with *v* = 200 mV/s). [i] Some samples of this complex showed a splitting of this peak (1974 (s) and 1952 (s) cm^{-1}). [j] Spectrum recorded in CD_2Cl_2. [k] Two overlapping multiplets.

An ORTEP[16] representation of the structure of the dirhenium cation of **4b′**, as present in a crystal of composition $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2](PF_6)_{0.78}(ReO_4)_{0.22}\cdot CH_2Cl_2$, is shown in Figure 1. The key crystallographic data and important structural parameters are given in Tables 1 and 2. The structure is that of unsymmetrical edge-sharing bioctahedra, with two μ-Br ligands and the two XylNC ligands bound to one of the Re centers. This same structure is also believed to be present in the triflate salt **4a′**. This is demonstrated by the similarity between the spectroscopic and electrochemical properties of **4a′** and **4b′** (Table 5). The compounds **4a′** and **4b′** are the first examples of mixed halide/isocyanide and/or carbonyl complexes which are derived from the triply bonded synthons $Re_2X_4(\mu\text{-dppm})_2$ and have bis(μ-halo) edge-sharing bioctahedral structures.

The bis(μ-bromo) bridge is unsymmetrical, with the distances to the formally higher oxidation state rhenium center (Re(1)) being significantly shorter (2.504(1) and 2.498(2) Å) than those to Re(2) (2.591(2) and 2.533(2) Å). The distances Re(1)−Br(2) and Re(1)−Br(3) are also shorter (by ca. 0.05 Å) than that of the terminal Re−Br bond (Re(1)−Br(1) = 2.556(2) Å). The two xylyl isocyanide ligands are bound in a linear fashion, as signified by values of 173.0(1) and 178.5(12)° for N(30)−C(30)−Re(2) and N(20)−C(20)−Re(2), respectively. The Re−Re distance of 3.0456(8) Å is consistent with the presence of a metal−metal single bond. This distance is much longer than Re−Re distances in other dirhenium cations of composition $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNR)_2]^+$ (X = Cl, Br), which contain either edge-sharing bioctahedral structures of the type $[Re_2(\mu\text{-}X)(\mu\text{-}CO)(\mu\text{-dppm})_2X_2(CNR)_2]^{+}$ [10] or open bioctahedral structures such as that found in complexes **5a** and **5b** (vide infra). In the two latter structure types, the formal Re−Re bond orders are 2 and 3, respectively. In the structure of **4a′** and **4b′**,

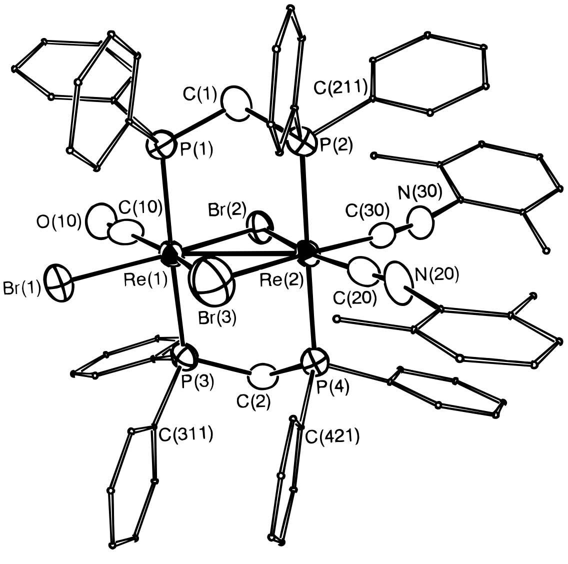


Figure 1. ORTEP[16] representation of the structure of the dirhenium cation $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ as present in **4b′**. The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligands, which are circles of arbitrary radius.

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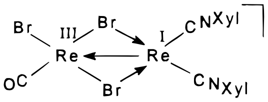
(16) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

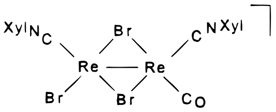
electron-counting procedures would lead to the prediction of a Re−Re single bond if we invoke the EAN rule and assume that each bridging bromide contributes three electrons. However, with such an unsymmetrical molecular structure for **4a′** and **4b′**, we are loath to speculate further as to the details of the electronic structure of the dirhenium cation.

The close similarities between the electrochemical and spectroscopic properties of the pairs **4a**/**4a′** and **4b**/**4b′** (Table 5) imply that **4a** and **4b** must have very structures similar to those of **4a′** and **4b′**. The electrochemical properties of all four complexes are essentially identical, and their ^{31}P{^{1}H} NMR spectra not only show similar patterns but have one of the two multiplets of an AA′BB′ type pattern at an unusually high field: δ ca. −135 for **4a** and **4b**; δ ca. −160 for **4a′** and **4b′**. We had previously reported a similar high-field resonance in the ^{31}P{^{1}H} NMR spectrum of the symmetical dirhenium(III) complex $Re_2(\mu\text{-}Cl)_2Cl_4(\mu\text{-dppm})_2$ (δ = −140.6).[17] Although the explanation for this phenomenon is uncertain, it may be characteristic of a "Re(III)-like" center in bis(μ-halo)-bridged dirhenium complexes. In the case of **4a**/**4a′** and **4b**/**4b′**, a bonding description in terms of Re(III)−Re(I) centers is not implausible, with the upfield resonance then being assigned to the pair of phosphines which are bound to the Re(III) center. A formal description in these terms for the structurally characterized cation of **4a′** and **4b′**, with a dative metal−metal bond ($Re^{III}\leftarrow Re^{I}$), is represented in **IV** (dppm ligands omitted).

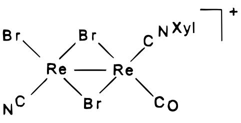


IV

Two structures are plausible for the cation of **4a** and **4b** (see **V** and **VI**), both of which maintain a formal Re(III)−Re(I) description and accord with their possessing a very close electronic and molecular structural similarity to **4a′** and **4b′** (as implied by their electrochemical and spectroscopic properties). However, an alternative, and rather intriguing, possibility is that the pairs **4a**/**4a′** and **4b**/**4b′** differ structurally only in the conformation of the two fused five-membered rings which comprise the bridging unit P−CH$_2$−P−Re−Re−P−CH$_2$−P. The structure determination of **4b′** has established that this unit possesses a "boat (tub)" conformation (Figure 1). If a "chair" conformation is present in **4a** and **4b**, this could well explain the very minor differences in the properties of **4a**/**4b** and **4a′**/**4b′** (Table 5). While we were able to grow single crystals of **4a** (from a toluene/1,2-dichloroethane solution at 25 °C) the complete structure solution and refinement were hindered by a disorder problem. It was found that a crystallographic 2-fold axis, which is coincident with the Re−Re bond, existed in the cation of **4a**, the consequence of which would be a disorder between the CO and the terminal bromide ligand if **4a** is structurally very similar to **4a′**. Such a 2-fold disorder would also require that the P−CH$_2$−P−Re−Re−P−CH$_2$−P fused-ring system possesses a chair conformation. Further work is underway to try to definitively establish the structures of **4a** and **4b**.



V



VI

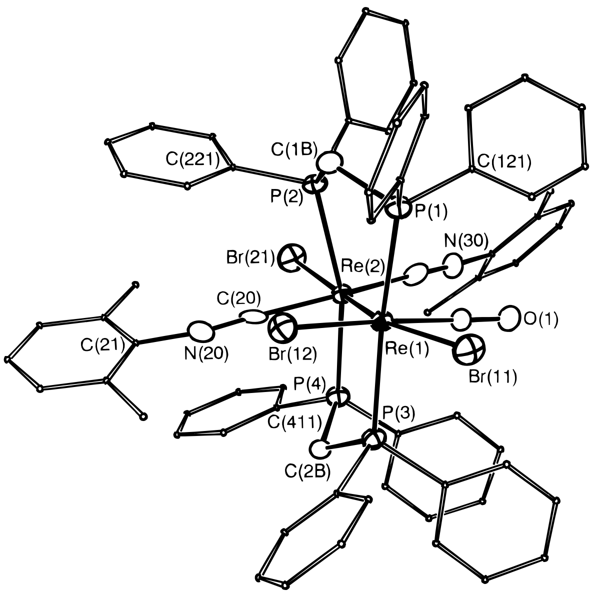


Figure 2. ORTEP[16] representation of the structure of the dirhenium cation $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ as present in **5a**. The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligands, which are circles of arbitrary radius.

The other isomers of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$, **5a** and **5b** (see Scheme 2), while possessing terminal CO and XylNC ligands just like **4a**/**4b** and **4a′**/**4b′**, have very different electrochemical properties (Table 5) and, therefore, possess different molecular structures. This has been confirmed by an X-ray crystal structure determination of **5a**. An ORTEP[16] representation of the dirhenium cation of **5a** is shown in Figure 2, while important crystallographic data and structural parameters are given in Tables 1 and 3. This structure, which is an open bioctahedron, is the same as that of the chloro complex $[(XylNC)_2ClRe(\mu\text{-dppm})_2ReCl_2(CO)]O_3SCF_3$ (**8**).[1] Complex **8** is one of at least four different structural isomers of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$ (Y = Cl, ReO_4, O_3SCF_3);[1,6,10,11] the others which have been structurally characterized possess edge-sharing bioctahedral geometries with (μ-Cl)(μ-CO) or (μ-Cl)(μ-CNXyl) bridging ligands, and they are therefore quite different structurally from the bromo complexes **4a**/**4b** and **4a′**/**4b′**. The Re−Re distance for **5a** (2.3792(7) Å) is essentially identical to that in **8** (2.3833(8) Å)[1] and the *t*-BuNC analogue of **8**, *viz.* $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)_2]PF_6$ (2.3787(5) Å).[7] Complex **5a**, like **8**, has a partially staggered rotational geometry, which is not unexpected since there is no electronic barrier to rotation about the Re≡Re bond.[18] However, the values for the torsional angles P(1)−Re(1)−Re(2)−P(2), P(3)−Re(1)−Re(2)−P(4), C(1)−Re(1)−Re(2)−C(30), and Br(12)−Re(1)−Re(2)−C(20), which are 17.9(1), 7.1(1), 10.0(5), and 16.4(3)°, respectively, are on average less than are those for **8** (20.2(1), 10.6(1), 17.8(6), and 24.3(4)°) although the trend is the same.

In contrast to the products that are formed upon reacting $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]Y$ (Y = O_3SCF_3 (**3a**), PF_6 (**3b**)) with XylNC (Scheme 2), the product of the reaction of **3a** with CO is an edge-sharing bioctahedral complex $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]O_3SCF_3$ (**7**), in which one of the bridging groups is a μ-CO ligand. This is clearly implied by the IR spectrum of this complex, which shows a bridging ν(CO) mode (1734 cm^{-1}) as well as terminal ν(CO) and ν(CN) modes (Table 5),

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(17) Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.

(18) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, U.K., 1993.

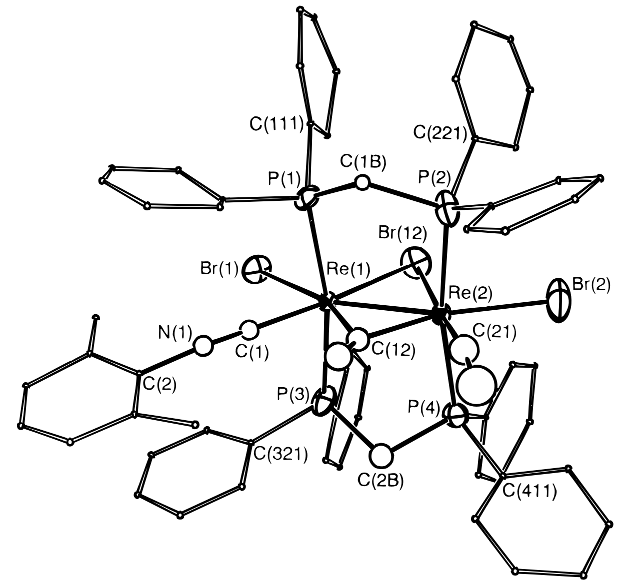
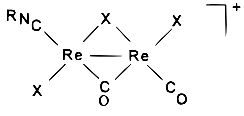


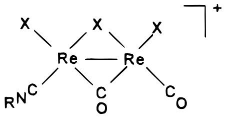
Figure 3. ORTEP[16] representation of the dirhenium cation $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]^+$ as present in **7**. The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligand, which are circles of arbitrary radius.

and has been confirmed by an X-ray crystal structure determination. An ORTEP[16] representation of the dirhenium cation of **7** is shown in Figure 3, and important crystallographic data and structural parameters are given in Tables 1 and 4. The edge-sharing bioctahedron, in which all three π-acceptor ligands are located on the same side of the Re_2P_4 skeleton in an all-cis arrangement, is a common geometry for dirhenium complexes of this general type.[10] The Re−Re distance in **7** of 2.5853(13) Å is in the range observed for other complexes that contain Re═Re bonds, such as $[Re_2Cl_3(\mu\text{-dppm})_2(CO)_2(NCEt)]PF_6$ (2.586(1) Å)[5] and $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]ReO_4$ (2.576(1) Å),[10] in which there is also an all-cis arrangement of π-acceptor ligands.

Previous work has shown[5,6] that the chloro complexes $[Re_2Cl_3(\mu\text{-dppm})_2(CO)_2(CNR)]^+$ (R = *t*-Bu, Xyl) exist in two isomeric edge-sharing bioctahedral structural forms (see **VII** and **VIII**) and that **VIII** is the most thermodynamically stable



VII



VIII

form of the two. In the case of the bromo complex **7**, only the isomer with structure **VIII** was isolated, in spite of the mild reaction conditions used; the other isomeric form **VII** may be very unstable when X = Br. In view of the known structure of the precursor complex **3a** (see structure **III**), attack by CO at either Re center on the same side of the molecule as the terminally bound CO would be expected to give the edge-sharing bioctahedral complex $[Re_2Br_3(\mu\text{-dppm})_2(CO)_2(CNXyl)]O_3SCF_3$ with structure **VII**. This isomer must undergo a facile isomerization to the thermodynamically stable isomeric form **VIII**. Such a process is well established in the case of the analogous chloro complexes.[5,6]

Concluding Remarks

In contrast to the reaction between **3a** and CO in which a single isomer is formed, the reactions of XylNC with **3a** and **3b** are decidedly more complicated (Scheme 2). While three isomeric forms of the complex cation $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ are produced, we do not yet know the mechanism of these reactions. Nonetheless, some general conclusions are possible.

Complexes **5a** and **5b**, which contain an open bioctahedral structure, are very minor products of these reactions. It is clear that these complexes are *not* formed by the same high-yield route which is used to obtain the analogous chloro complex **8** (i.e. $[(XylNC)_2ClRe(\mu\text{-dppm})_2ReCl_2(CO)]O_3SCF_3$),[1] namely, the reaction of $Re_2X_4(\mu\text{-dppm})_2(CO)(CNXyl)$ (X = Cl) with XylNC in the presence of TlY (Y = PF_6, O_3SCF_3). The difference between the chloro and bromo systems can be explained by the supposition that, following labilization of the Re−X bond that is trans to the XylNC ligand of $Re_2X_4(\mu\text{-dppm})_2(CO)(CNXyl)$, CO migration to form **3a** and **3b** is much more rapid than coordination of the second XylNC ligand when X = Br. The reverse situation holds when X = Cl.[1] It is also apparent that **5a** and **5b** are not formed by isomerization of **4a**/**4a′** and **4b**/**4b′**; in fact, we find no evidence for interconversions between any of the three isomeric forms of $[Re_2Br_3(\mu\text{-dppm})_2(CNXyl)_2(CO)]Y$.

In the case of the reactions of $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNXyl)$/TlY mixtures with XylNC and $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]Y$ with XylNC (see Scheme 2), the structural isomers **4a**/**4a′** and **4b**/**4b′** predominate. However, the product ratios **4a**/**4a′** (and **4b**/**4b′**) change from ca. 50/50 to ca. 95/5 depending upon which dirhenium starting material is used. One explanation for this difference may lie in the presence of a much more heterogeneous reaction system in the case of the $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNXyl)$/TlY mixtures; the use of the preformed complexes **3a** and **3b** (i.e. $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]Y$) gives a more soluble and homogeneous starting material. This difference may influence the relative rates of formation of **4a** and **4a′** (and **4b** and **4b′**).

A further point to be emphasized is the large range of metal−metal bond orders that can be accommodated within the various isomeric forms of the complex cations of the type $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$. For those chloro species which have already been reported, we have seen both the retention of the Re−Re triple bond in salts of the open bioctahedral cation $[(XylNC)_2ClRe(\mu\text{-dppm})_2ReCl_2(CO)]^+$ [1] and the presence of a formal double bond in an edge-sharing bioctahedral isomer of the type $[(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2ReCl(CNXyl)]^+$.[10] In the case of the bromo species $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$, we find that a Re−Re triple bond is present in **5a** and **5b** but that the edge-sharing bioctahedral isomers **4a**/**4b** and **4a′**/**4b′** possess the unexpected bis(μ-bromo)-bridged structures in which a Re−Re single bond is present. The search for bis(μ-chloro) complexes of the latter type is underway.

Acknowledgment. We thank the National Science Foundation, through Grant No. CHE94-09932 to R.A.W., for support of this work.

Supporting Information Available: Tables giving full details for the crystal data and data collection parameters (Tables S1, S7, and S13), atomic positional parameters (Tables S2, S3, S8, S9, S14, and S15), anisotropic thermal parameters (Tables S4, S10, and S16), bond distances (Tables S5, S11, and S17), and bond angles (Tables S6, S12, and S18) for **4b′**, **5a**, and **7** (33 pages). Ordering information is given on any current masthead page.

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