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# Monocarbonyl Complexes of the Type Re$_2$X$_4$($\mu$-dppm)$_2$(CO) (X = Cl, Br; dppm = Ph$_2$PCH$_2$PPh$_2$) Revisited. Reactions of the Bromo Complex Re$_2$Br$_4$($\mu$-dppm)$_2$(CO) with *tert*-Butyl and Xylyl Isocyanides[†]

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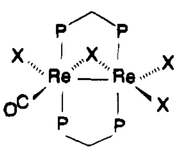
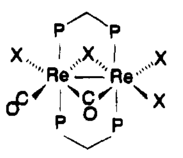
One of the two isomeric forms of the complex Re$_2$Br$_4$($\mu$-dppm)$_2$(CO) (**1b**), both of which are formed by the reaction of the triply bonded complex Re$_2$Br$_4$($\mu$-dppm)$_2$ with CO, is shown to have the same A-frame-like structure as that characterized previously for Re$_2$Cl$_4$($\mu$-dppm)$_2$(CO) (**1a**) by X-ray crystallography. Crystal data for Re$_2$Br$_4$($\mu$-dppm)$_2$(CO)·CH$_2$Cl$_2$ (**1b**) at 293 K: monoclinic space group *Cc* (No. 9) with $a$ = 19.584(5) Å, $b$ = 17.109(2) Å, $c$ = 17.649(6) Å, $\beta$ = 105.92(2)°, $V$ = 5686(5) Å$^3$, $Z$ = 4. The structure was refined to $R$ = 0.055 ($R_w$ = 0.073) for 4891 data with $I > 3.0\sigma(I)$. The CO ligand is terminally bound, and the Re−Re distance of 2.336(1) Å accords with the retention of a Re≡Re bond. The second isomeric form of Re$_2$X$_4$($\mu$-dppm)$_2$(CO) has been identified as having an open unsymmetrical structure X$_3$Re($\mu$-dppm)$_2$ReX(CO). The reaction of **1b** with xylyl and *tert*-butyl isocyanides produces bioctahedral complexes of the type (RNC)Br$_2$Re($\mu$-dppm)$_2$ReBr$_2$(CO) (R = xylyl (**3a**), *t*-Bu (**3b**)), in which two Re−Br bonds are collinear with the Re≡Re bond, and the terminally bound RNC and CO ligands are anti to one another on separate Re centers. This structure has been established by a single-crystal X-ray structure determination of **3b**. Crystal data for Re$_2$Br$_4$($\mu$-dppm)$_2$(CO)(CN-*t*-Bu)·CH$_2$Cl$_2$·2.5C$_6$H$_6$ (**3b**) at 203 K: monoclinic space group $P2_1/n$ (No. 14) with $a$ = 12.892(2) Å, $b$ = 19.478(4) Å, $c$ = 27.231(4) Å, $\beta$ = 93.623(13)°, $V$ = 6824(4) Å$^3$, $Z$ = 4. The structure was refined to $R$ = 0.066 ($R_w$ = 0.084) for 5166 data with $I > 3.0\sigma(I)$. The Re−Re distance is 2.381(1) Å. The mixed carbonyl−isocyanide complexes **3a** and **3b** react with TlO$_3$SCF$_3$ in dichloromethane to give the triply-bonded compounds [Re$_2$Br$_3$($\mu$-dppm)$_2$(CO)(CNR)]O$_3$SCF$_3$ (R = xylyl (**4a**), *t*-Bu (**4b**)), which have an unsymmetrical structure with the two metal centers possessing different coordination numbers and the CO and RNC ligands trans to one another. This conclusion is based upon a single-crystal X-ray structure determination of **4a**. Crystal data for [Re$_2$Br$_3$($\mu$-dppm)$_2$(CO)(CNxyl)]O$_3$SCF$_3$ (**4a**) at 293 K: monoclinic space group P2$_1$/c (No. 14) with $a$ = 14.182(3) Å, $b$ = 15.749(4) Å, $c$ = 31.580(5) Å, $\beta$ = 98.58(2)°, $V$ = 6974(5) Å$^3$, $Z$ = 4. The structure was refined to $R$ = 0.066 ($R_w$ = 0.088) for 5333 data with $I > 3.0\sigma(I)$. A comparison is made between these results and those obtained previously for the related dirhenium chloro complexes which contain CO and RNC ligands.

## Introduction

The triply-bonded dirhenium(II) chloro complex Re$_2$Cl$_4$($\mu$-dppm)$_2$ (dppm = Ph$_2$PCH$_2$PPh$_2$) displays an extensive reaction chemistry toward carbon monoxide, organic isocyanides, and nitriles.[1] Included among the many dirhenium derivatives that have been isolated and characterized are the mono- and dicarbonyl complexes **1a** and **2a**.[2,3] The structures of these



1a X = Cl
1b X = Br



2a X = Cl
2b X = Br

complexes have been established on the basis of single-crystal X-ray structure determinations and the spectroscopic properties of **1a** and **2a**. While the reactions of **1a** and **2a** with organic isocyanides and nitriles,[3−6] tertiary phosphine and phosphite ligands,[7,8] and alkynes[9,10] have been examined in considerable detail, little chemistry has been developed using the analogous bromo−carbonyl species **1b** and **2b**, although both these complexes have been prepared and characterized spectroscopically and cyclic voltammetrically.[3,11]

In order to establish the influence, if any, of the nature of the halide ligand on the reactions of complexes of types **1** and **2**, we are currently examining the reactions of **1b** and **2b** with various $\sigma$-donor and $\pi$-acceptor ligands. In the present report, we describe the reactions of the monocarbonyl Re$_2$Br$_4$($\mu$-dppm)$_2$(CO), **1b**, with the isocyanide ligands *t*-BuNC and xylNC (xyl = xylyl). In some instances, the resulting complexes show

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[†] Reactions of the Dirhenium(II) Complexes Re$_2$X$_4$(dppm)$_2$ (X = Cl, Br; dppm = Ph$_2$PCH$_2$PPh$_2$) with Isocyanides. 7. For part 6, see ref 24.

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significant structural differences from the products that are formed from the reactions of the analogous chloro complex **1a**.

## Experimental Section

**Starting Materials and Reaction Procedures.** The compounds Re$_2$Br$_4$($\mu$-dppm)$_2$(CO) (**1b**) and TlO$_3$SCF$_3$ were prepared according to the literature procedures.[3,12] The isocyanide ligands RNC (R = xyl, *t*-Bu) were purchased from Fluka Chemicals and used as received. Solvents were obtained from commercial sources and were deoxygenated by purging with dinitrogen prior to use. All reactions were performed under an atmosphere of dry dinitrogen.

**A. Synthesis of Re$_2$Br$_4$($\mu$-dppm)$_2$(CO)(CNR) (i) R = xyl (3a).** A mixture of Re$_2$Br$_4$(dppm)$_2$(CO) (**1b**) (300 mg, 0.201 mmol) and xylNC (30.0 mg, 0.229 mmol) was treated with 20 mL of acetone and the resulting suspension stirred at 25 °C for 10 h. A green solid precipitate formed during this period. This was filtered off, washed with diethyl ether, and dried under vacuum, affording the complex Re$_2$Br$_4$(dppm)$_2$(CO)(CNxyl); yield 229 mg (70%). When CH$_2$Cl$_2$ was used as the reaction solvent in place of acetone, **3a** was obtained in similar yield upon the addition of a large excess of diethyl ether to precipitate the complex. Anal. Calcd for C$_{60}$H$_{53}$Br$_4$NOP$_4$Re$_2$: C, 44.48; H, 3.30; N, 0.86. Found: C, 44.83; H, 3.45; N, 0.91.

**(ii) R = *t*-Bu (3b).** A solution of **1b** (100 mg, 0.067 mmol) in 8 mL of acetone was treated with 8 $\mu$L of *t*-BuNC (0.07 mmol). The resulting mixture was kept stirring at 25 °C for 16 h. Compound **3b** precipitated as a pink solid and was collected by filtration of the reaction mixture. This product was found to contain one molecule of acetone on the basis of spectroscopic characterizations (both IR and $^1$H NMR); yield 74.3 mg (70%). It was found that the quantities of both solvent and isocyanide used in this reaction are critical. The pink precipitate would not form with the use of either a large volume of acetone solvent or an excess of isocyanide. Anal. Calcd for C$_{59}$H$_{59}$Br$_4$NOP$_4$Re$_2$ (i.e. Re$_2$Br$_4$(dppm)$_2$(CO)(CN-*t*-Bu)·(CH$_3$)$_2$CO): C, 43.47; H, 3.64; N, 0.86. Found: C, 43.76; H, 3.58; N, 0.86. Conductivity: $\Lambda_m = 56\ \Omega^{-1}$ cm$^2$ mol$^{-1}$ in acetone solution, and $\Lambda_m = 134\ \Omega^{-1}$ cm$^2$ mol$^{-1}$ in acetonitrile.

**B. Synthesis of [Re$_2$Br$_3$($\mu$-dppm)$_2$(CO)(CNR)]O$_3$SCF$_3$. (i) R = xyl (4a).** A mixture of **3a** (123 mg, 0.076 mmol) and 27 mg of TlO$_3$SCF$_3$ (0.076 mmol) was treated with 25 mL of CH$_2$Cl$_2$, and the resulting mixture was stirred at 25 °C for 6 h. A color change from brown to pale green was observed during this period. The white precipitate was filtered off, and the volume of the green filtrate was reduced to ~3 mL. An equal volume of isopropyl ether was added to the solution and crystals were produced upon slow evaporation of the solvents at 25 °C. Green diamond shaped crystals of [Re$_2$Br$_3$(dppm)$_2$(CO)(CNxyl)]O$_3$SCF$_3$, **4a**, were harvested after 6 h; yield 137 mg (98%). Anal. Calcd for C$_{61}$H$_{53}$Br$_3$F$_3$NO$_4$P$_4$Re$_2$S: C, 43.37; H, 3.16; N, 0.83. Found: C, 43.52; H, 3.14; N, 0.74.

An alternative procedure for obtaining **4a** involved the reaction of 100 mg of **1b** (0.067 mmol), 9.0 mg of xylNC (0.069 mmol), and 24.0 mg of TlO$_3$SCF$_3$ (0.068 mmol) in 15 mL of CH$_2$Cl$_2$; yield 88 mg (78%).

**(ii) R = *t*-Bu (4b).** A procedure similar to that described in paragraph B(i) was used to prepare the compound [Re$_2$Br$_3$($\mu$-dppm)$_2$(CO)(CN-*t*-Bu)]O$_3$SCF$_3$, **4b**, except that **3b** was used as the precursor complex. The reaction of 133 mg of **3b** (0.085 mmol) and 32 mg of TlO$_3$SCF$_3$ (0.091 mmol) in 25 mL of CH$_2$Cl$_2$ yielded green crystals of **4b**; yield 101 mg (73%). Anal. Calcd for C$_{57}$H$_{53}$Br$_3$F$_3$NO$_4$P$_4$Re$_2$S: C, 41.72; H, 3.26; N, 0.85. Found: C, 42.17; H, 3.32; N, 0.92. Conductivity: $\Lambda_m = 124\ \Omega^{-1}$ cm$^2$ mol$^{-1}$ in acetone solution, and $\Lambda_m = 119\ \Omega^{-1}$ cm$^2$ mol$^{-1}$ in acetonitrile.

The alternative preparation of **4b** by the direct reaction of **1b** with *t*-BuNC in the presence of TlO$_3$SCF$_3$ proved to be difficult. The formation of **4b** by this procedure was identified by IR spectroscopy, but attempts to isolate **4b** in pure form from the reaction mixture were not successful.

**X-ray Crystallography.** Suitable single crystals of the complexes Re$_2$Br$_4$($\mu$-dppm)$_2$(CO) (**1b**), Re$_2$Br$_4$($\mu$-dppm)$_2$(CO)(CN-*t*-Bu) (**3b**), and [Re$_2$Br$_3$($\mu$-dppm)$_2$(CO)(CNxyl)]O$_3$SCF$_3$ (**4a**) were obtained by the slow evaporation at 25 °C of the solvents from various mixed-solvent systems. Thus, for **1b** a mixed CH$_2$Cl$_2$/ethanol (2/1) solvent system was used and for **3b** CH$_2$Cl$_2$/CHCl$_3$/C$_6$H$_6$ (1/1/2) was used, while in the case of **4a** X-ray-quality crystals were obtained from CH$_2$Cl$_2$/C$_6$H$_6$ (1/1).

In all cases, the data collection was performed on an Enraf-Nonius CAD4 computer-controlled diffractometer; graphite-monochromatized Cu K$\alpha$ radiation was used in the case of **1b**, and Mo K$\alpha$ radiation for **3b** and **4a**. Data collection on the crystal of **3b** was carried out at 203 ± 1 K because of the instability of the crystals at room temperature. The cell constants were based on 25 reflections obtained in the ranges $20 < \theta < 25°$ for **1b**, $16 < \theta < 19°$ for **3b**, and $17 < \theta < 21°$ for **4a**, 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. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. Lorentz and polarization corrections were applied to the data set. An empirical absorption correction[13] was also applied, but no correction for extinction was made.

Compound **1b** crystallized in the monoclinic crystal system. The systematic absences observed in the data set were consistent with either space group *Cc* or *C2/c*. As $Z = 4$, the acentric space group *Cc* was assumed and subsequently confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (SHELXS-86) and difference Fourier syntheses. Due to a total loss of 18.9% in the intensity of three standard reflections, a linear decay correction was applied to the data set. The structure was found to have a disorder between the CO group and a terminal Br atom. This generated two different positions for the CO group (C(1), O(1) and C(2), O(2)) and the Br atom (Br(1) and Br(2)); a 50/50 percent disorder model was satisfactorily refined. The nature of this disorder is shown in Figure S1 (Supporting Information) and is typical of the type of positional disorder found in dirhenium complexes which contain a trans Re$_2$($\mu$-dppm)$_2$ unit.[3,10,14] All non-hydrogen atoms, except the carbon and oxygen atoms of the disordered CO group but including the C and Cl atoms of the CH$_2$Cl$_2$ solvent molecule, were anisotropically refined. The atoms belonging to the disordered CO group, C(1), C(2), O(1), and O(2), were refined with isotropic thermal parameters. Hydrogen atoms on the phenyl rings and solvent CH$_2$Cl$_2$ molecules were located and added to the structure factor calculations, but their positions were not 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 weighting factor defined as $w = 1/\sigma^2(|F_o|)$. Corrections for anomalous scattering were applied to the anisotropically refined atoms.[15] The final residuals for **1b** were $R = 0.055$ ($R_w = 0.073$) and GOF = 1.795. The highest peak in the final difference Fourier map was 2.07 e/Å$^3$. In the final stage of the structure analysis, the refined values for the other absolute structure were calculated as $R = 0.059$ ($R_w = 0.077$) and GOF = 1.905. These values were slightly higher than those for the first enantiomorph and thus were discarded.

Compound **3b** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was determined from the systematic absences observed in the data set. The structure was solved by the 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. All atoms heavier than carbon in this structure were refined with anisotropic thermal parameters; the carbon atoms were refined either anisotropically or isotropically. It was found that one CH$_2$Cl$_2$ and two and one-half benzene molecules from the crystallization solvents were present in the asymmetric unit. All non-hydrogen atoms of these solvent molecules were located and refined satisfactorily. The one-half benzene molecule was located on a crystallographic inversion center. All hydrogen atoms were calculated by using idealized geometries with C−H = 0.95 Å and $B_{iso}$(H) = 1.3$B_{iso}$(C). Their contributions were added to the structure factor calculations, but their positions were not 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 weighting factor defined as $w = 1/\sigma^2(|F_o|)$. Corrections for anomalous scattering were applied to the anisotropically refined

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[15] Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) Table 2.3.1; (b) Table 2.2B.

**Table 1.** Crystallographic Data for $Re_2Br_4(\mu\text{-dppm})_2(CO)\cdot CH_2Cl_2$ (**1b**), $Re_2Br_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-Bu})\cdot CH_2Cl_2\cdot 2.5C_6H_6$ (**3b**), and $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNxyl)]O_3SCF_3$ (**4a**)

| | 1b | 3b | 4a |
|---|---|---|---|
| chem formula | $Re_2Br_4Cl_2P_4OC_{52}H_{46}$ | $Re_2Br_4Cl_2P_4ONC_{72}H_{70}$ | $Re_2Br_3SP_4F_3O_4NC_{61}H_{53}$ |
| fw | 1573.78 | 1852.20 | 1689.19 |
| space group | *Cc* (No. 9) | *P*2₁/*n* (No. 14) | *P*2₁/*c* (No. 14) |
| *a*, Å | 19.584(5) | 12.892(2) | 14.182(3) |
| *b*, Å | 17.109(2) | 19.478(4) | 15.749(4) |
| *c*, Å | 17.649(6) | 27.231(4) | 31.580(5) |
| β, deg | 105.92(2) | 93.623(13) | 98.58(2) |
| *V*, Å$^3$ | 5686(5) | 6824(4) | 6974(5) |
| *Z* | 4 | 4 | 4 |
| *T*, K | 293 | 203 | 293 |
| λ, Å | 1.541 84 (Cu Kα) | 0.710 73 (Mo Kα) | 0.710 73 (Mo Kα) |
| $\rho_{calc}$, g/cm$^3$ | 1.838 | 1.803 | 1.609 |
| μ, cm$^{-1}$ | 134.78 | 61.28 | 53.85 |
| transmissn coeff | 1.00−0.28 | 0.27−0.17 | 1.00−0.12 |
| *R*[a] | 0.055 | 0.066 | 0.066 |
| $R_w$[b] | 0.073 | 0.084 | 0.088 |
| GOF | 1.795 | 1.896 | 2.100 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

**Table 2.** Positional Parameters and Equivalent Isotropic Displacement Parameters (Å$^2$) for the Important Atoms of $Re_2Br_4(\mu\text{-dppm})_2(CO)\cdot CH_2Cl_2$ (**1b**) and Their Estimated Standard Deviations[a]

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Re(1) | 0 | 0.79182(5) | 0 | 1.91(1) |
| Re(2) | −0.00587(5) | 0.69338(5) | 0.08974(6) | 2.14(1) |
| Br(1) | −0.1284(3) | 0.8254(3) | −0.0607(3) | 3.8(1) |
| Br(2) | −0.1365(2) | 0.6683(3) | 0.0767(3) | 3.47(9) |
| Br(3) | 0.0585(2) | 0.8908(2) | −0.0777(2) | 5.25(6) |
| Br(4) | 0.0372(2) | 0.5900(2) | 0.2020(2) | 4.28(6) |
| Br(12) | 0.1222(1) | 0.7314(2) | 0.0835(2) | 4.10(6) |
| P(1) | 0.0027(2) | 0.9050(3) | 0.0860(3) | 2.44(9) |
| P(2) | −0.0067(2) | 0.7792(3) | 0.2000(3) | 2.21(9) |
| P(3) | −0.0117(2) | 0.7074(3) | −0.1151(3) | 2.15(9) |
| P(4) | −0.0158(2) | 0.5812(3) | 0.0005(3) | 2.3(1) |
| O(1) | −0.163(2) | 0.818(3) | −0.048(3) | 5.7(9)* |
| O(2) | −0.162(2) | 0.692(2) | 0.047(2) | 4.2(7)* |
| C(1) | −0.093(2) | 0.805(2) | −0.032(2) | 1.7(5)* |
| C(2) | −0.102(2) | 0.692(2) | 0.057(2) | 2.3(6)* |
| C(1B) | −0.0441(9) | 0.873(1) | 0.157(1) | 2.7(4) |
| C(2B) | −0.0579(9) | 0.619(1) | −0.0962(9) | 1.9(3) |
| Cl(901) | 0.7387(5) | 0.0729(5) | 0.2736(7) | 8.3(2) |
| Cl(902) | 0.8469(5) | −0.0274(7) | 0.2489(6) | 9.3(3) |
| C(900) | 0.829(2) | 0.052(2) | 0.301(2) | 6.5(9) |

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the phenyl group atoms of the dppm ligands are available as Supporting Information.

**Table 3.** Positional Parameters and Equivalent Isotropic Displacement Parameters (Å$^2$) for the Important Atoms of $Re_2Br_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-Bu})\cdot CH_2Cl_2\cdot 2.5C_6H_6$ (**3b**) and Their Estimated Standard Deviations[a]

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Re(1) | 0.33364(7) | 0.22398(5) | 0.12640(4) | 1.375(18) |
| Re(2) | 0.16435(7) | 0.17468(5) | 0.12098(3) | 1.411(18) |
| Br(11) | 0.50107(19) | 0.29510(13) | 0.16166(10) | 2.26(6) |
| Br(12) | 0.4314(3) | 0.1904(2) | 0.05207(13) | 5.33(9) |
| Br(21) | −0.0058(2) | 0.11305(15) | 0.08416(10) | 2.64(6) |
| Br(22) | 0.0979(2) | 0.15910(16) | 0.20740(11) | 3.63(7) |
| Cl(1) | 0.8136(9) | 0.2391(6) | 0.2209(4) | 8.3(3) |
| Cl(2) | 0.7597(12) | 0.3302(6) | 0.2962(5) | 10.9(4) |
| P(1) | 0.4221(5) | 0.1308(3) | 0.1736(2) | 1.62(13) |
| P(2) | 0.2243(5) | 0.0560(3) | 0.1327(2) | 1.94(14) |
| P(3) | 0.2923(5) | 0.3337(3) | 0.0831(2) | 1.91(14) |
| P(4) | 0.0765(5) | 0.2851(3) | 0.1022(2) | 1.74(13) |
| O(10) | 0.2684(13) | 0.2773(9) | 0.2251(6) | 2.9(4) |
| N(10) | 0.1861(15) | 0.1602(10) | 0.0076(7) | 2.2(5) |
| C(1) | 0.3369(17) | 0.0544(12) | 0.1777(8) | 1.5(4)* |
| C(2) | 0.1529(17) | 0.3287(12) | 0.0572(8) | 1.4(4)* |
| C(10) | 0.2881(18) | 0.2548(14) | 0.1849(8) | 2.3(6) |
| C(20) | 0.1878(16) | 0.1683(13) | 0.0505(9) | 2.2(5)* |
| C(21) | 0.1869(19) | 0.1458(13) | −0.0451(9) | 2.2(5)* |
| C(22) | 0.182(3) | 0.2141(19) | −0.0725(12) | 7.4(11) |
| C(23) | 0.085(2) | 0.1038(16) | −0.0563(11) | 3.9(7)* |
| C(24) | 0.286(2) | 0.1056(16) | −0.0558(10) | 3.5(7) |
| C(901) | 0.748(3) | 0.315(2) | 0.2316(19) | 9.4(14) |
| C(911) | 0.084(2) | 0.0119(17) | 0.6618(12) | 4.6(8) |
| C(912) | 0.164(2) | 0.0466(16) | 0.6398(15) | 5.9(9) |
| C(913) | 0.261(3) | 0.0289(18) | 0.6550(14) | 6.6(11) |
| C(914) | 0.274(3) | −0.0250(17) | 0.6872(15) | 6.7(10) |
| C(915) | 0.190(3) | −0.057(2) | 0.7077(16) | 8.0(12) |
| C(916) | 0.097(2) | −0.0359(17) | 0.6931(11) | 4.5(8) |
| C(921) | 0.619(3) | 0.249(2) | 0.8357(11) | 7.5(12) |
| C(922) | 0.653(3) | 0.225(3) | 0.8796(14) | 12.2(17) |
| C(923) | 0.555(6) | 0.197(3) | 0.907(3) | 22(3) |
| C(924) | 0.513(5) | 0.241(2) | 0.9130(14) | 27.6(16) |
| C(925) | 0.469(5) | 0.280(3) | 0.868(2) | 26.4(19) |
| C(926) | 0.522(3) | 0.278(3) | 0.8319(15) | 9.0(13) |
| C(931) | 0.429(3) | −0.016(2) | 0.5329(15) | 6.8(10)* |
| C(932) | 0.419(3) | 0.042(2) | 0.5049(15) | 6.8(10)* |
| C(933) | 0.520(3) | −0.059(2) | 0.5280(17) | 8.2(12)* |

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the phenyl group atoms of the dppm ligands are available as Supporting Information.

atoms.[15] The final residuals for **3b** were $R = 0.066$ ($R_w = 0.084$) and GOF = 1.90. The highest peak in the final difference Fourier map was 1.43 e/Å$^3$.

Compound **4a** crystallized in the monoclinic crystal system. On the basis of systematic absences in the data set, the space group P2₁/c was uniquely identified. The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Most non-hydrogen atoms in this structure were refined with anisotropic thermal parameters. The hydrogen atoms were located from difference Fourier maps and added to the structure factor calculations, but their positions were not refined. The structure was refined in full-matrix least squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where *w* is the weighting factor defined as $w = 1/\sigma^2(|F_o|)$. Corrections for anomalous scattering were applied to the anisotropically refined atoms.[15] The final residuals for **4a** were $R = 0.066$ ($R_w = 0.088$) and GOF = 2.100. The highest peak in the final difference Fourier map was 1.70 e/Å$^3$.

The basic crystallographic parameters for **1b**, **3b**, and **4a** are listed in Table 1. Positional parameters and their errors are listed in Tables 2−4, and important intramolecular bond distances and angles of **1b**, **3b**, and **4a** are listed in Tables 5−7.

**Physical Measurements.** Infrared spectra were recorded as Nujol mulls between NaCl or KBr plates on a Perkin-Elmer 1800 FT-IR

**Table 4.** Positional Parameters and Equivalent Isotropic Displacement Parameters (Å$^2$) for the Important Atoms of [$Re_2Br_3$(μ-dppm)$_2$(CO)(CNxyl)]$O_3SCF_3$ (**4a**) and Their Estimated Standard Deviations[a]

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Re(1) | 0.27910(6) | 0.14345(7) | 0.10500(3) | 3.34(2) |
| Re(2) | 0.22577(6) | 0.14017(7) | 0.16993(3) | 3.22(2) |
| Br(11) | 0.3257(2) | 0.1419(2) | 0.02633(8) | 5.91(7) |
| Br(21) | 0.3443(2) | 0.0799(2) | 0.2262(1) | 5.62(7) |
| Br(22) | 0.0655(2) | 0.2059(2) | 0.1632(1) | 6.29(8) |
| P(1) | 0.3087(4) | −0.0136(4) | 0.1047(2) | 3.5(1) |
| P(2) | 0.1625(4) | −0.0046(4) | 0.1633(2) | 3.5(1) |
| P(3) | 0.2580(5) | 0.3006(4) | 0.0967(2) | 4.0(2) |
| P(4) | 0.2817(5) | 0.2813(4) | 0.1930(2) | 3.7(1) |
| O(1) | 0.069(1) | 0.135(1) | 0.0585(6) | 6.9(5) |
| N(10) | 0.507(1) | 0.146(2) | 0.1339(7) | 5.9(6) |
| C(1) | 0.143(2) | 0.135(2) | 0.0738(8) | 4.8(6) |
| C(10) | 0.426(2) | 0.150(2) | 0.1263(7) | 5.0(6) |
| C(11) | 0.608(2) | 0.150(2) | 0.140(1) | 7.3(8) |
| C(12) | 0.648(2) | 0.134(2) | 0.184(1) | 8.8(9) |
| C(13) | 0.753(2) | 0.139(3) | 0.200(2) | 14(2) |
| C(14) | 0.797(4) | 0.154(3) | 0.168(2) | 14(2)* |
| C(15) | 0.763(2) | 0.172(2) | 0.124(1) | 11(1) |
| C(16) | 0.655(2) | 0.166(2) | 0.103(1) | 9.6(9) |
| C(17) | 0.594(2) | 0.115(2) | 0.218(1) | 9(1) |
| C(18) | 0.606(3) | 0.169(3) | 0.061(1) | 12(1) |
| C(1B) | 0.264(2) | −0.064(2) | 0.1519(8) | 4.8(6) |
| C(2B) | 0.244(2) | 0.349(2) | 0.1485(7) | 4.8(6) |
| S(100) | 0.7852(9) | 0.1345(6) | 0.3466(5) | 13.0(5) |
| F(101) | 0.936(2) | 0.046(2) | 0.3608(9) | 16(1) |
| F(102) | 0.960(2) | 0.170(2) | 0.365(1) | 19(1) |
| F(103) | 0.881(4) | 0.140(3) | 0.298(1) | 30(2) |
| O(100) | 0.763(2) | 0.215(2) | 0.3403(8) | 9.6(7)* |
| O(102) | 0.730(2) | 0.067(2) | 0.3308(9) | 11.0(8)* |
| O(103) | 0.808(3) | 0.111(3) | 0.402(1) | 19(1)* |
| C(101) | 0.902(4) | 0.119(4) | 0.342(2) | 15(2)* |

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent temperature factor defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$. Data for the phenyl group atoms of the dppm ligands are available as Supporting Information.

**Table 5.** Selected Bond Distances (Å) and Bond Angles (deg) for $Re_2Br_4$(μ-dppm)$_2$(CO)·$CH_2Cl_2$ (**1b**)[a]

| Distances | | | |
|---|---|---|---|
| Re(1)−Re(2) | 2.336(1) | Re(2)−Br(4) | 2.617(3) |
| Re(1)−Br(1) | 2.514(6) | Re(2)−Br(12) | 2.623(3) |
| Re(1)−Br(3) | 2.632(3) | Re(2)−P(2) | 2.442(6) |
| Re(1)−Br(12) | 2.653(3) | Re(2)−P(4) | 2.457(6) |
| Re(1)−P(1) | 2.452(6) | Re(2)−C(2) | 1.82(4) |
| Re(1)−P(3) | 2.452(6) | O(1)−C(1) | 1.34(6) |
| Re(1)−C(1) | 1.77(4) | O(2)−C(2) | 1.13(6) |
| Re(2)−Br(2) | 2.541(6) | | |

| Angles[b] | | | |
|---|---|---|---|
| Re(2)−Re(1)−Br(3) | 157.9(1) | Re(1)−Re(2)−Br(4) | 159.22(9) |
| Re(2)−Re(1)−Br(12) | 63.07(8) | Re(1)−Re(2)−Br(12) | 64.37(7) |
| Re(2)−Re(1)−P(1) | 98.4(2) | Re(1)−Re(2)−P(2) | 96.8(1) |
| Re(2)−Re(1)−P(3) | 97.3(1) | Re(1)−Re(2)−P(4) | 97.9(1) |
| Re(2)−Re(1)−C(1) | 94(1) | Br(2)−Re(2)−Br(4) | 93.5(2) |
| Br(3)−Re(1)−Br(12) | 94.9(1) | Br(2)−Re(2)−Br(12) | 171.4(2) |
| Br(3)−Re(1)−P(1) | 82.9(2) | Br(2)−Re(2)−P(2) | 87.0(2) |
| Br(3)−Re(1)−P(3) | 84.4(2) | Br(2)−Re(2)−P(4) | 84.8(2) |
| Br(3)−Re(1)−C(1) | 108(1) | Br(4)−Re(2)−Br(12) | 94.9(1) |
| Br(12)−Re(1)−P(1) | 95.8(2) | Br(4)−Re(2)−P(2) | 82.8(2) |
| Br(12)−Re(1)−P(3) | 95.5(2) | Br(4)−Re(2)−P(4) | 84.8(2) |
| Br(12)−Re(1)−C(1) | 157(1) | Br(12)−Re(2)−P(2) | 95.7(2) |
| P(1)−Re(1)−P(3) | 163.6(2) | Br(12)−Re(2)−P(4) | 94.3(1) |
| P(1)−Re(1)−C(1) | 87(1) | P(2)−Re(2)−P(4) | 164.7(2) |
| P(3)−Re(1)−C(1) | 87(1) | Re(1)−C(1)−O(1) | 173(4) |
| Re(1)−Re(2)−Br(2) | 107.2(1) | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Angles for one-half of the disorder only are given; atoms not included are C(2), O(2), and Br(2). Full data are available as Supporting Information.

**Table 6.** Selected Bond Distances (Å) and Bond Angles (deg) for $Re_2Br_4$(μ-dppm)$_2$(CO)(CN-*t*-Bu)·$CH_2Cl_2$·2.5$C_6H_6$ (**3b**)[a]

| Distances | | | |
|---|---|---|---|
| Re(1)−Re(2) | 2.3805(14) | Re(2)−Br(22) | 2.572(3) |
| Re(1)−Br(11) | 2.690(3) | Re(2)−P(2) | 2.452(7) |
| Re(1)−Br(12) | 2.537(4) | Re(2)−P(4) | 2.469(7) |
| Re(1)−P(1) | 2.463(7) | Re(2)−C(20) | 1.96(3) |
| Re(1)−P(3) | 2.483(7) | O(10)−C(10) | 1.22(3) |
| Re(1)−C(10) | 1.83(3) | N(10)−C(20) | 1.18(3) |
| Re(2)−Br(21) | 2.642(3) | N(10)−C(21) | 1.46(3) |

| Angles | | | |
|---|---|---|---|
| Re(2)−Re(1)−Br(11) | 160.32(8) | Re(1)−Re(2)−Br(22) | 110.35(8) |
| Re(2)−Re(1)−Br(12) | 110.28(10) | Re(1)−Re(2)−P(2) | 95.27(17) |
| Re(2)−Re(1)−P(1) | 97.31(16) | Re(1)−Re(2)−P(4) | 93.90(16) |
| Re(2)−Re(1)−P(3) | 98.60(16) | Re(1)−Re(2)−C(20) | 83.6(7) |
| Re(2)−Re(1)−C(10) | 81.0(7) | Br(21)−Re(2)−Br(22) | 88.70(10) |
| Br(11)−Re(1)−Br(12) | 89.39(11) | Br(21)−Re(2)−P(2) | 82.45(18) |
| Br(11)−Re(1)−P(1) | 81.88(16) | Br(21)−Re(2)−P(4) | 87.62(17) |
| Br(11)−Re(1)−P(3) | 82.50(17) | Br(21)−Re(2)−C(20) | 77.1(7) |
| Br(11)−Re(1)−C(10) | 79.3(7) | Br(22)−Re(2)−P(2) | 83.67(18) |
| Br(12)−Re(1)−P(1) | 89.42(18) | Br(22)−Re(2)−P(4) | 96.75(17) |
| Br(12)−Re(1)−P(3) | 86.87(19) | Br(22)−Re(2)−C(20) | 165.1(7) |
| Br(12)−Re(1)−C(10) | 168.6(7) | P(2)−Re(2)−P(4) | 170.1(2) |
| P(1)−Re(1)−P(3) | 164.0(2) | P(2)−Re(2)−C(20) | 90.1(8) |
| P(1)−Re(1)−C(10) | 87.2(8) | P(4)−Re(2)−C(20) | 87.1(8) |
| P(3)−Re(1)−C(10) | 93.4(9) | Re(1)−C(10)−O(10) | 173(2) |
| Re(1)−Re(2)−Br(21) | 160.53(8) | Re(2)−C(20)−N(10) | 169(2) |

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

spectrometer. $^1$H NMR spectra were obtained with the use of either a Varian Gemini-200 or a GE QE-300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. A GE QE-300 spectrometer equipped with a multinuclear Quad probe operated at 121.5 MHz, with 85% $H_3PO_4$ as an external standard, was used to obtain the $^{31}P\{^1H\}$ NMR spectra. Electrochemical measurements were carried out with use of a BAS Inc. Model CV-27 instrument in conjunction with a BAS Model RXY recorder and were recorded on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at 25 °C and were uncorrected for junction potentials. Under our experimental conditions, $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Conductivity measurements were obtained by the use of a YSI Model 35 conductance meter. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

## Results and Discussion

The coordinatively unsaturated monocarbonyl dirhenium complex $Re_2Br_4$(μ-dppm)$_2$(CO) (**1b**) was used as the starting material in the present study. Its synthesis and physicochemical properties, which have been described in a previous report,[3] resemble closely those of its chloro analogue $Re_2Cl_4$(μ-dppm)$_2$(CO) (**1a**).[2,3] Both **1a** and **1b** react with an excess of CO to afford the edge-sharing bioctahedral species $Re_2X_4$(μ-dppm)$_2$(CO)$_2$ (**2a** and **2b**), possessing the structure (CO)XRe(μ-X)(μ-CO)(μ-dppm)$_2$ReX$_2$, wherein which there is a cis arrangement of CO ligands. In the present study, we find that the bromo complex **1b** reacts with *tert*-butyl isocyanide and xylyl isocyanide to give the bioctahedral complexes $Re_2Br_4$(μ-dppm)$_2$(CO)(CNR) (eq 1).

$$Re_2Br_4(\mu\text{-dppm})_2(CO) + RNC \xrightarrow{\text{acetone}} Re_2Br_4(\mu\text{-dppm})_2(CO)(CNR) \quad (1)$$

**3a** (R = xyl)
**3b** (R = *t*-Bu)

One of the bromide ligands of **3a** and **3b** is labilized in the presence of thallium(I) triflate to produce the salts [$Re_2Br_3$(μ-

**Table 7.** Selected Bond Distances (Å) and Bond Angles (deg) for $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNxyl)]SO_3CF_3$ (**4a**)

| | | | |
|---|---|---|---|
| | Distances | | |
| Re(1)−Re(2) | 2.289(1) | Re(2)−Br(22) | 2.478(3) |
| Re(1)−Br(11) | 2.665(3) | Re(2)−P(2) | 2.448(7) |
| Re(1)−P(1) | 2.510(7) | Re(2)−P(4) | 2.435(7) |
| Re(1)−P(3) | 2.502(7) | O(1)−C(1) | 1.09(3) |
| Re(1)−C(1) | 2.03(3) | N(10)−C(10) | 1.14(3) |
| Re(1)−C(10) | 2.09(3) | N(10)−C(11) | 1.42(3) |
| Re(2)−Br(21) | 2.448(3) | | |
| | Angles | | |
| Re(2)−Re(1)−Br(11) | 174.81(9) | C(1)−Re(1)−C(10) | 170(1) |
| Re(2)−Re(1)−P(1) | 93.4(2) | Re(1)−Re(2)−Br(21) | 112.06(9) |
| Re(2)−Re(1)−P(3) | 93.8(2) | Re(1)−Re(2)−Br(22) | 109.6(1) |
| Re(2)−Re(1)−C(1) | 91.0(8) | Re(1)−Re(2)−P(2) | 96.3(2) |
| Re(2)−Re(1)−C(10) | 99.1(7) | Re(1)−Re(2)−P(4) | 96.4(2) |
| Br(11)−Re(1)−P(1) | 85.6(2) | Br(21)−Re(2)−Br(22) | 138.2(1) |
| Br(11)−Re(1)−P(3) | 87.4(2) | Br(21)−Re(2)−P(2) | 84.5(2) |
| Br(11)−Re(1)−C(1) | 84.0(8) | Br(21)−Re(2)−P(4) | 88.8(2) |
| Br(11)−Re(1)−C(10) | 85.8(7) | Br(22)−Re(2)−P(2) | 93.6(2) |
| P(1)−Re(1)−P(3) | 172.8(2) | Br(22)−Re(2)−P(4) | 84.2(2) |
| P(1)−Re(1)−C(1) | 94.5(8) | P(2)−Re(2)−P(4) | 167.1(2) |
| P(1)−Re(1)−C(10) | 83.7(9) | Re(1)−C(1)−O(1) | 175(3) |
| P(3)−Re(1)−C(1) | 85.7(8) | Re(1)−C(10)−N(10) | 171(2) |
| P(3)−Re(1)−C(10) | 94.8(9) | | |

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

$dppm)_2(CO)(CNR)]SO_3CF_3$ (eq 2).

$$\mathrm{Re_2Br_4(\mu\text{-}dppm)_2(CO)(CNR) + TlO_3SCF_3 \xrightarrow{CH_2Cl_2} [Re_2Br_3(\mu\text{-}dppm)_2(CO)(CNR)]O_3SCF_3 + TlBr} \quad (2)$$

**4a** (R = xyl)
**4b** (R = *t*-Bu)

**(a) Structures of the Monocarbonyl Starting Materials.** During the course of the present study, we revisited the structural chemistry of the monocarbonyls **1a** and **1b**. We had previously observed[2,3] that these complexes crystallize in the solid state as a mixture of two isomers, which possess $\nu$(CO) bands at ca. 1970 and 1900 cm$^{-1}$. We will refer to these as the "1970 cm$^{-1}$" and "1900 cm$^{-1}$" isomers. This isomeric mixture persists in solution when the crystalline products are dissolved in a wide range of solvents. IR spectroscopy shows that the 1970 cm$^{-1}$ isomer is the dominant form in $CH_2Cl_2$ solutions of **1a**, while the reverse situation holds in the case of $CH_2Cl_2$ solutions of **1b**.[2,3] The addition of a second solvent to $CH_2Cl_2$ solutions of **1a** leads to crystallization of either the 1970 cm$^{-1}$ or the 1900 cm$^{-1}$ isomer, depending upon which solvent is added; $(i\text{-Pr})_2O$, $Et_2O$, acetone, and MeEtCO give the former, while the addition of MeOH, EtOH, benzene, and toluene produces the latter isomer. In the case of the bromo complex **1b**, the addition of any common solvent to a $CH_2Cl_2$ solution of this complex (e.g. MeOH, EtOH, $Et_2O$, benzene, etc.) affords almost exclusively crystals of the 1900 cm$^{-1}$ isomer.[16] However, we find no solvent mixture which favors the crystallization of the 1970 cm$^{-1}$ isomer of **1b**. In all cases, irrespective of the isomeric makeup of the crystalline materials **1a** and **1b**, the same IR spectral patterns are reproducibly obtained for $CH_2Cl_2$ solutions of **1a** and **1b**; this implies that there is a solvent-dependent equilibrium of isomers.

In the case of **1a**, the 1900 cm$^{-1}$ isomer was obtained in a pure state (crystals grown from $CH_2Cl_2$/benzene) and was shown[3] by X-ray crystallography to have the A-frame-like structure **I** (the trans pair of dppm ligands is omitted for clarity).

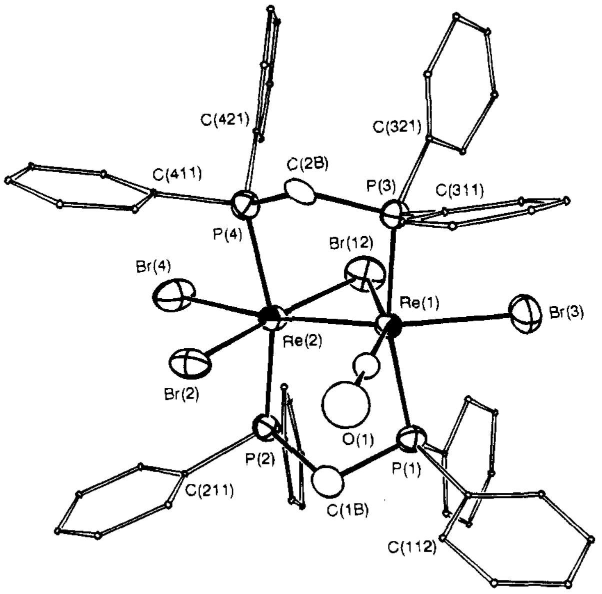
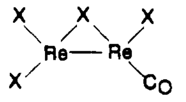
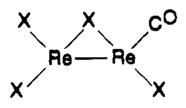


**Figure 1.** ORTEP[17] representation of the structure of the A-frame-like isomeric form of the $Re_2Br_4(\mu\text{-dppm})_2(CO)$ molecule (**1b**). The thermal ellipsoids are drawn at the 50% probability level, except for the phenyl group atoms of the dppm ligands, which are circles of arbitrary radius.

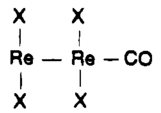
It was proposed,[3] but not proven, that the other isomer (1970 cm$^{-1}$) most likely has the structure **II** or **III**. This tentative



I



II



III

conclusion was based upon the IR (terminal $\nu$(CO) mode only) and NMR spectral properties of **1a** and **1b**. We are now able to clarify this structural picture.

We have established in the present study that the 1900 cm$^{-1}$ isomer of the bromo complex **1b** has the same structure as its chloro analogue. An X-ray structure determination was carried out on a single crystal obtained from a $CH_2Cl_2$/ethanol mixture. An ORTEP[17] representation of the structure is shown in Figure 1, and key crystallographic data and important structural parameters are given in Tables 1, 2, and 5. While the molecule has no crystallographically imposed symmetry, it has the same type of terminal halide/CO disorder as found in the structure of **1a**.[3] The full-disorder model is available in the Supporting Information (Figure S1); one-half of the disorder is shown in Figure 1. The Re−Re distance of 2.336(1) Å in the structure of **1b** accords with the preservation of a Re≡Re bond[18] and is essentially identical to the analogous distance for **1a** (2.338(1) Å).[3]

While we have not been able to isolate the 1970 cm$^{-1}$ isomer of **1b** free of the structurally characterized A-frame-like form (1900 cm$^{-1}$ isomer), in the case of its chloro analogue **1a**, the 1970 cm$^{-1}$ isomer predominates when the complex is crystallized from $CH_2Cl_2/(i\text{-Pr})_2O$, $CH_2Cl_2$/MeEtCO, or $CH_2Cl_2$/acetone solvent mixtures (*vida supra*). A single-crystal X-ray structure determination was attempted on a crystal of this isomer

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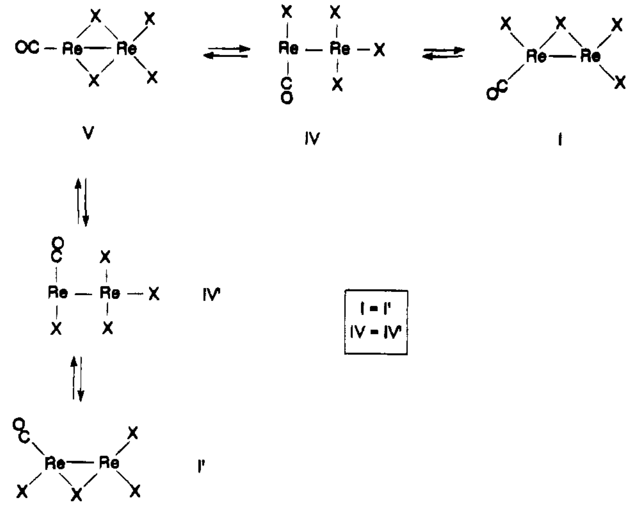
[16] The solution IR spectra of **1a** and **1b** in benzene and toluene show that the 1900 cm$^{-1}$ isomer is also the majority species in these two solvents.[2,3]

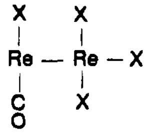
[17] Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

[18] Anderson, L. B.; Barder, T. J.; Esjornson, D.; Walton, R. A.; Bursten, B. E. *J. Chem. Soc., Dalton Trans.* **1986**, 2607.

**Scheme 1.** Proposed Mechanism for the Interconversion of the Isomers of $Re_2X_4(\mu$-dppm$)_2$CO (X = Cl, Br)



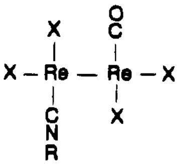
of **1a** as grown from the $CH_2Cl_2/(i$-Pr$)_2O$ (9/1) solvent mixture. While we were unable to complete the refinement of the structure due to a disorder involving the CO group and one of the Cl ligands,[19] the structure was clearly that of an isomeric form different from either **II** or **III**, namely, structure **IV**, in which all CO and Cl ligands are terminal. The Re−Re distance is ca. 2.27 Å.

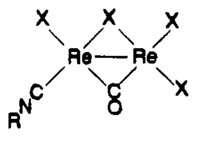

IV

The conclusion that the 1900 cm$^{-1}$ isomer has structure **I** and the 1970 cm$^{-1}$ isomer has structure **IV** also accords with the previously reported $^1$H, $^{13}$C, and $^{31}$P NMR spectral data for **1a** and **1b**.[2,3] The fluxionality of these compounds[2,3] can be explained by the rapid interconversion of **I** and **IV** along with the presumed, but undetected, symmetric form **V** (Scheme 1). This would explain why the bridgehead $-CH_2-$ protons of the dppm ligands appear as a binomial pentet (i.e. the two sides of the molecule appear equivalent), the $^{13}C\{^1H\}$ NMR spectrum reveals that the CO ligand remains attached to only one Re center and is coupled to only one pair of trans P atoms during the fluxional process, and the $^{31}P\{^1H\}$ NMR spectrum remains an AA'BB' pattern throughout, thereby signifying that the two ends of the molecule are always inequivalent.

**(b) Properties of $Re_2Br_4(\mu$-dppm$)_2$(CO)(CNR) (R = xyl (3a), *t*-Bu (3b)) and a Comparison with the Analogous Chloro Complexes.** The mixed carbonyl−isocyanide complexes $Re_2Br_4(\mu$-dppm$)_2$(CO)(CNR) (R = xyl (**3a**), *t*-Bu (**3b**)) have IR Nujol mull spectra and $^{31}P\{^1H\}$ NMR spectra (see Table 8) which signify the presence of terminal CO and RNC ligands and imply the structural similarity of these two complexes. The structure of the *t*-BuNC-containing species **3b** was confirmed by X-ray crystallography; an ORTEP[17] representation of the structure is shown in Figure 2. The key crystallographic data and important structural parameters for **3b** are provided in Tables 1, 3, and 6. In this open bioctahedral structure, the CO and *t*-BuNC ligands are anti to one another. The Re−Re distance of 2.381(1) Å is consistent with the presence of a $Re\equiv Re$ bond. It is similar to the Re−Re distances for the monocarbonyl complexes $Re_2X_4(\mu$-dppm$)_2$(CO) (2.338(1) Å for X = Cl[3] and 2.336(1) Å for X = Br (Table 5)) but considerably shorter than those observed for edge-shared bioctahedral species such as $Re_2(\mu$-Cl$)(\mu$-CO$)(\mu$-dppm$)_2Cl_3$(L) which are 2.584(1) Å for L = CO[2] and 2.581(2) Å for L = xylNC.[3] The structure most closely resembles that found[6] for the bioctahedral dirhenium(II) cation $[Re_2Cl_3(\mu$-dppm$)_2$(CO)(CN-*t*-Bu$)_2]^+$ (i.e. $[Cl_2$(CO)Re$(\mu$-dppm$)_2$Re(CN-*t*-Bu$)_2Cl]^+$) which contains one additional $\pi$-acceptor ligand compared to the case of **3b**. The Re−Re distance of 2.379(1) Å for this bis(isocyanide) species is essentially identical to that for **3b** and shows the minor effect that an isocyanide for halide ligand substitution has upon the Re−Re distance. The axial Re−Br bonds are, as expected, significantly longer than the corresponding equatorial Re−Br bonds, although this difference is very dependent upon which $\pi$-acceptor ligand is bound to which Re atom; the difference is ca. 0.15 Å for Re(1) and ca. 0.07 Å for Re(2). In accord with the presence of a $Re\equiv Re$ bond and the absence of an electronic barrier to rotation, we note that the molecule shows a significant deviation from an eclipsed rotational geometry. This is reflected in the values for the torsional angles P(1)−Re(1)−Re(2)−P(2), P(3)−Re(1)−Re(2)−P(4), C(10)−Re(1)−Re(2)−Br(22), and Br(12)−Re(1)−Re(2)−C(20) of 23.4(2), 17.6(2), 24.1(8), and 20.8(8)°, respectively.

The structure found for **3b**, and the spectroscopic evidence that the xylNC-containing derivative **3a** has exactly this same structure (**VI**), can be contrasted with the structures found for


VI


VII

the analogous chloro complexes $Re_2Cl_4(\mu$-dppm$)_2$(CO)(CNR) (R = xyl, *t*-Bu).[3] When R = xyl, the structure of the chloro complex is that of an edge-shared bioctahedron (**VII**), as determined by X-ray crystallography,[3] whereas in the case of R = *t*-Bu, the open bioctahedral structure **VI** can be confidently inferred from the results of IR spectral measurements[3] and, indirectly, by a single-crystal X-ray structure determination on the derivative $[Re_2Cl_3(\mu$-dppm$)_2$(CO)(CN-*t*-Bu$)_2]^+$, which can be prepared directly from $Re_2Cl_4(\mu$-dppm$)_2$(CO)(CN-*t*-Bu).[6] Accordingly, these results imply that subtle electronic factors dictate whether structure **VI** or **VII** will be favored and that the switch in structure type can be triggered by a change in the halide and/or isocyanide ligand.

The structural integrity of **3a** and **3b** in chlorocarbon solvents is reflected by the NMR spectral properties of $CDCl_3$ solutions of these complexes (Table 8). This was also demonstrated by IR spectral measurements on $CH_2Cl_2$ solutions of **3a** and **3b**, which showed $\nu$(CN) and $\nu$(CO) peaks at 2069 (s) and 1963 (s) cm$^{-1}$ for **3a** and 2120 (s) and 1944 (s, br) cm$^{-1}$ for **3b**, very similar to the values for Nujol mulls. The electrochemical behavior of **3a** and **3b** was examined for 0.1 M TBAH−$CH_2Cl_2$ solutions by use of the cyclic voltammetric technique. Neither complex showed reversible electrochemical behavior, although both cyclic voltammograms were very similar (scan rate 200 mV s$^{-1}$, potentials vs Ag/AgCl): **3a**, $E_{p,a}$ = +1.04 V (coupled wave at $E_{p,c} \approx$ +0.73V), $E_{p,c}$ = −1.07 V (product wave at $E_{p,a} \approx$ −0.29 V); **3b**, $E_{p,a}$ = +1.15 V (coupled wave

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(19) The complete structure solution and refinement were also hindered by a relatively poor data set because of the small crystal size. Preliminary crystal data at 293 K: monoclinic space group *Cc* (No. 9) or *C*2/*c* (No. 15), *a* = 12.132(4) Å, *b* = 22.43(1) Å, *c* = 42.24(2) Å, $\beta$ = 91.13(3)°, *V* = 11494(8) Å$^3$, *Z* = 8.

**Table 8.** Spectroscopic Data for $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNR)$ (R = xyl (**3a**), *t*-Bu (**3b**)) and $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNR)]O_3SCF_3$ (R = xyl (**4a**), *t*-Bu (**4b**))

| | IR, $cm^{-1}$ [a] | | | |
|---|---|---|---|---|
| | $\nu$(CN) | $\nu$(CO) | $^1H$ NMR, $\delta$[b] | $^{31}P\{^1H\}$ NMR, $\delta$[c] |
| **3a** | 2066 (s) | 1968 (vs) | 8.20−6.90 (m, 43H, Ph and xyl), 6.00−5.60 (m, vbr, 4H, $CH_2$ of dppm), 2.05 (s, 3H, $CH_3$ of xyl), 1.90 (s, 3H, $CH_3$ of xyl) | −9.8, −14.5, −21.5, −25.5[e] |
| **3b** | 2128 (s) | 1962 (vs) | 8.08−7.08 (m, 40H, Ph), 5.82 (m, 2H, $CH_2$ of dppm), 5.67 (m, 2H, $CH_2$ of dppm), 1.40 (s, 9H, $CH_3$ of *t*-Bu) | −10.7, −14.2, −21.4, −23.3 |
| **4a** | 2164 (m) | 2024 (vs) | 7.80−6.90 (m, 43H, Ph and xyl), 6.22 (m, br, 2H, $CH_2$ of dppm), 5.90 (m, br, 2H, $CH_2$ of dppm), 1.98 (s, br, 6H, $CH_3$ of xyl)[d] | −9.0, −14.5 |
| **4b** | 2198 (m) | 2026 (vs) | 8.05−7.02 (m, 40H, Ph), 6.20 (m, br, 4H, $CH_2$ of dppm), 0.65 (s, br, 9H, $CH_3$ of *t*-Bu)[d] | −11.5, −15.2 |

[a] IR spectra recorded as Nujol mulls. The spectra of **4a** and **4b** also show an intense, fairly broad band at 1260−1264 $cm^{-1}$ which is characteristic of the $[O_3SCF_3]^-$ anion. [b] Spectra recorded in $CDCl_3$. Abbreviations: m = multiplet, br = broad, s = singlet. [c] Spectra recorded in $CDCl_3$. Resonances quoted are those of multiplets which are characteristic of ABCD or AA'BB' type patterns. [d] These resonances are split due to slight inequivalences between the $CH_3$ groups of the RNC ligands. [e] The $^{31}P\{^1H\}$ NMR spectrum of **3a** gives only broad, poorly resolved multiplets as a consequence of the poor solubility properties of this complex.

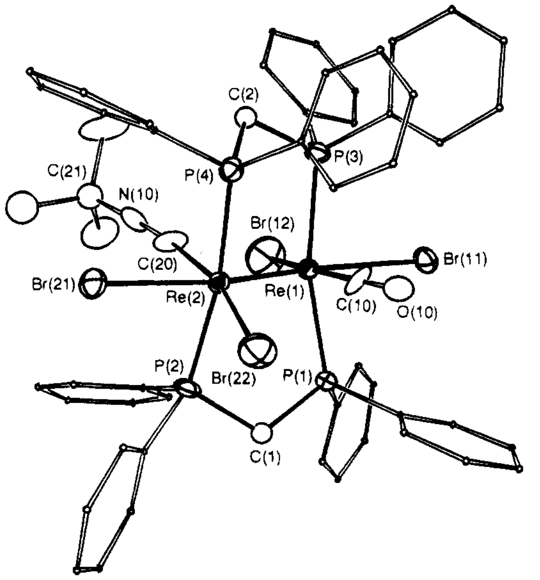
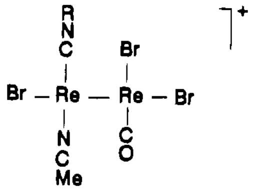


**Figure 2.** ORTEP[17] representation of the structure of the $Re_2Br_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-Bu})$ molecule (**3b**). The thermal ellipsoids are drawn at the 50% probability level, except for the phenyl group atoms of the dppm ligands, which are circles of arbitrary radius.

at $E_{p,c} \approx +0.83$ V), $E_{p,c} = -1.10$ V (product wave at $E_{p,a} \approx -0.20$ V).

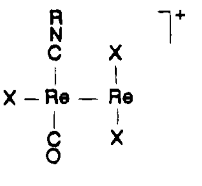
In contrast to the behavior of **3a** and **3b** in $CDCl_3$ and $CH_2Cl_2$, their properties in more polar solvents such as acetone and acetonitrile are consistent with ionic behavior. Thus, conductivity measurements on acetone solutions of **3a** and **3b** ($\Lambda_m$ = 34 and 56 $\Omega^{-1}$ $cm^2$ $mol^{-1}$, respectively, for $c_m = 1.0 \times 10^{-3}$ M) indicate partial dissociation of $Br^-$, whereas in acetonitrile the conductance values are consistent with complete 1:1 electrolyte behavior ($\Lambda_m$ = 122 and 123 $\Omega^{-1}$ $cm^2$ $mol^{-1}$ for $c_m = 1.0 \times 10^{-3}$ M). The species formed in the latter solution are most likely the mono(acetonitrile) complexes $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNR)(NCMe)]Br$. The solution IR spectra of **3a** and **3b** in acetonitrile show that these new species are characterized by strong bands for the $\nu$(CN) mode of the RNC ligand and $\nu$(CO) mode of the carbonyl group at 2097 and 1962 $cm^{-1}$, respectively, for the species derived from **3a** and at 2152 and 1951 $cm^{-1}$ for that which is formed from **3b**. Note that the $\nu$(CO) band of these acetonitrile complexes occurs at a frequency very similar to $\nu$(CO) of the parent complexes **3a** and **3b**. When these acetonitrile solutions are taken to dryness and then pumped under a vacuum, the weakly bound acetonitrile ligand is lost and **3a** and **3b** are reconstituted. Since it is the $\nu$(CN) mode which is shifted the most upon the dissolution of **3a** and **3b** in acetonitrile, we assume that it is the Re−Br bond trans to the Re−CNR unit which is labilized; i.e., the species which is formed has the structure **VIII**. Also, the Re−Br bond



VIII

which is trans to the isocyanide ligand is the longest of the two Re−Br bonds which are trans to the $\pi$-acceptor CO and RNC ligands (Table 6). This postulate is supported further by the structure of the complex cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-Bu})_2]^+$, which has a structure like that of **VIII** with the *t*-BuNC ligands trans to one another,[6] and by the $^{31}P\{^1H\}$ NMR spectrum of a $CD_3CN$ solution of **3b**, which shows an AA'BB' pattern with multiplets at $\delta$ −13.8 and −15.3. This pattern resembles that displayed by $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-Bu})_2]^+$ [5] but is quite different from the spectrum of a solution of **3b** in $CDCl_3$ (Table 8). The consequences of labilizing this particular Re−Br bond *in the absence of a coordinating solvent* are discussed in the following section.

**(c) Reactions of $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNR)$ (R = xyl (3a), *t*-Bu (3b)) with Thallium(I) Triflate.** When edge-shared bioctahedral species with structure **VII** are treated with $Tl^+$ reagents, the Re−X bond cis to the bridging carbonyl ligand is labilized, and in the presence of ligands (L) dirhenium complexes of the type $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNR)(L)]^+$ are usually formed with preservation of the edge-shared bioctahedral geometry.[4,5,11] As mentioned in the previous section, when the bioctahedral complexes **3a** and **3b** (structure **VI**) are treated with the coordinating solvent acetonitrile, the Re−Br bond trans to the RNC ligand is labilized. However, when **3a** and **3b** are treated with $TlO_3SCF_3$ in the absence of a coordinating solvent, the salts $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNR)]O_3SCF_3$ are formed (R = xyl (**4a**), *t*-Bu (**4b**)) via a major structural rearrangement. Loss of the bromide ligand which is trans to the isocyanide is accompanied by migration of the CO ligand from the adjacent Re atom to occupy the vacated ligand site. This leads to structure **IX**, in which the RNC and CO ligands are trans to



IX

one another and the two Re centers possess different coordina-

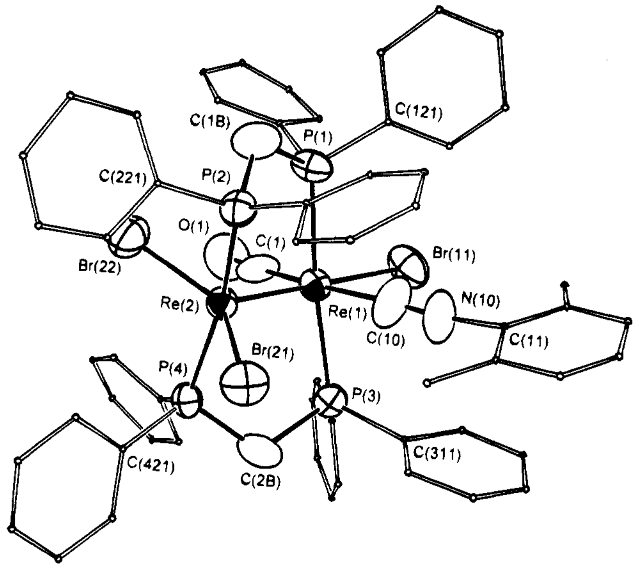


**Figure 3.** ORTEP[17] representation of the structure of the dirhenium cation $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNxyl)]^+$ present in complex **4a**. The thermal ellipsoids are drawn at the 50% probability level, except for the phenyl group atoms of the dppm ligands, which are circles of arbitrary radius.

tion numbers. A single-crystal X-ray structure determination on the xylNC derivative **4a** has confirmed this result. An ORTEP[17] representation of the structure of the dirhenium cation of **4a** is shown in Figure 3. The key crystallographic data and important structural parameters are provided in Tables 1, 4, and 7.

The structure of **4a** resembles closely that determined by X-ray crystallography for the bis(nitrile) chloro complex cations of the type $[Re_2Cl_3(\mu\text{-dppm})_2(L)(L')]^+$ (L and L′ = EtCN, PhCN, or 1,2-$NCC_6H_4CN$)[20-22] and inferred by spectroscopic and electrochemical measurements in those cases where L and L′ = CO[11] or *t*-BuNC[23] and L = *t*-BuNC or xylNC when L′ = MeCN, EtCN, or PhCN.[23] The Re−Re distance of 2.289(1) Å is similar to those determined for the bis(nitrile) complexes (in the range 2.265(1)−2.270(1) Å).[20-22] The Re−Br distances involving the two metal centers are appreciably different (Table 7). The distances Re(2)−Br(21) and Re(2)−Br(22), which average to 2.463 Å, are ca. 0.2 Å shorter than the axial Re(1)−Br(11) distance of 2.665(3) Å. This reflects both the difference in coordination numbrs at the metal centers (Re(2) has the lower coordination number) and the structural trans effect of the Re≡Re bond on the distance Re(1)−Br(11). The "ligand-deficient" Re atom has a Br−Re−Br angle of 138.2(1)°, which compares with Cl−Re−Cl angles that range from 140.5 to 146.5° in the structures of the bis(nitrile) chloro dirhenium(II) complexes mentioned previously. Compared to the structure of **3b**, that of **4a** shows an even closer approach to a fully staggered rotational geometry. 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)−Br(22), and C(10)−Re(1)−Re(2)−Br(21) are 29.3(2), 31.0(2), 30.7(7), and 26.8(8)°, respectively.

The IR spectra of **4a** and **4b** (Table 8), in which the CO and RNC ligands are trans to one another, show that the ν(CO) and ν(CN) modes are at appreciably higher frequencies (signifying less net Re → π* back-bonding to each ligand) compared to the analogous spectra of **3a** and **3b**, where these two π-acceptor ligands are trans to Re−Br bonds.

The cyclic voltammetric properties of **4a** and **4b** in 0.1 M TBAH−$CH_2Cl_2$ (scan rate 200 mV $s^{-1}$, potentials vs Ag/AgCl) are very similar to one another and show a reversible couple, corresponding to a one-electron oxidation of the bulk complexes; the $E_{1/2}$ values for this couple are +0.99 V and +0.93 V for **4a** and **4b**, respectively. Each CV also shows an irreversible reduction, with $E_{p,c} = -0.77$ V for **4a** and two closely-spaced reduction processes at $E_{p,c} = -0.93$ and $-1.05$ V for **4b**. This electrochemical behavior resembles that reported previously for other dirhenium complex cations of the type $[Re_2X_3(\mu\text{-dppm})_2(L)(L')]^+$ which have this same structure (**IX**).[11,20,23]

(**d**) **Concluding Remarks.** The present study has clarified the structural nature of the two isomeric forms (**I** and **IV**) of the monocarbonyl complexes $Re_2X_4(\mu\text{-dppm})_2(CO)$ (X = Cl, Br) which are formed upon reacting $Re_2X_4(\mu\text{-dppm})_2$ with CO.[2,3] The reactions of the bromo complex $Re_2Br_4(\mu\text{-dppm})_2(CO)$ with xylyl and *tert*-butyl isocyanides afford the complexes $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNR)$, whose structures are that of a bioctahedron **VI**, in which the CO and RNC ligands are on different Re atoms and are anti to one another. While this structure is the same as that possessed by the analogous chloro complex $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)$,[6] it differs from the structure of $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNxyl)$, which is that of an edge-shared bioctahedron.[3] This implies that the stereochemistry of complexes of the type $Re_2X_4(\mu\text{-dppm})_2(L)(L')$ is determined by electronic rather than steric factors. An intriguing possibility is that, for any particular choice of X and R groups, both structure types **VI** and **VII** might be isolable for $Re_2X_4(\mu\text{-dppm})_2(CO)(CNR)$. This possibility is being explored.

The reactions of $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNR)$ with $Tl^+$ salts proceed with the loss of the bromide ligand that is trans to the isocyanide and the transfer of the CO from the adjacent Re atom to give complex cations in which the two metal centers have different coordination numbers and the RNC and CO ligands are trans to one another. These experiments contribute to our understanding of the factors which determine the nature of the different stereoisomers that can be obtained[24] when the triply-bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ are reacted with CO, RNC, RCN, and related ligands, either alone or in combination with one another.

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**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 **1b**, **3b**, and **4a** and a figure (Figure S1) showing the disorder model for **1a** (60 pages). Ordering information is given on any current masthead page.

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