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The First Example of Isomerization of a Dimetal Complex Involving the Switch of a Metal−Metal Bond Order from 3 to 0. Synthesis and Characterization of the Paramagnetic Mixed-Valence Complex Cation $[(XylNC)(OC)Re(\mu\text{-}Cl)_2(\mu\text{-dppm})_2ReCl(CNXyl)]^+$ [1]

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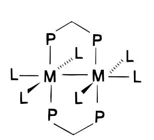
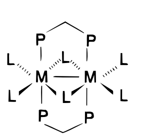
In the course of studying the factors which control the stereochemistry of multiply metal−metal bonded complexes with structures based on open bioctahedral and edge-sharing bioctahedral geometries (**A** and **B**, respectively; P−P represents a bridging bidentate phosphine), we have identified a reaction that is unprecedented in metal−metal multiple bond chemistry,[2] involving a simple isomerization in which a complex of type **A** converts to an isomeric form of type **B** with complete loss of the metal-metal bond.



A

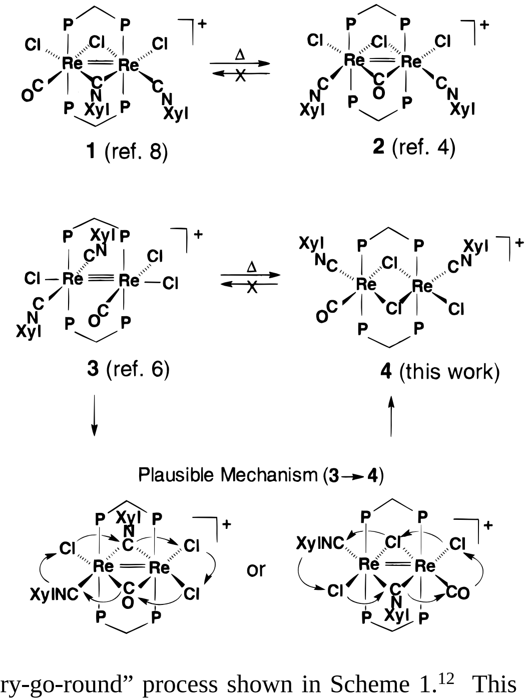


B

The genesis of this work was our discovery that an extensive series of stable geometrical isomers can be isolated and characterized from the reactions of the triply bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with various combinations of CO and RNC ligands.[3−8] An especially noteworthy example is the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ cation (Xyl = 2,6-dimethylphenyl), whose salts have been identified in three distinct isomeric forms **1**−**3** (see Scheme 1).[3,4,6,8] Of the two edge-sharing bioctahedral isomers **1** and **2**, the most thermodynamically stable form is **2**,[3,4,8] but neither converts to or is formed from **3**, which is prepared by a quite different synthetic route.[6] We have now found that the thermolysis of **3** converts it quantitatively to the new isomeric form **4** (see Scheme 1). This isomerization represents the transformation of diamagnetic triply bonded compound to a paramagnetic isomer in which there is no metal−metal bond present.

The transformation of the orange-brown isomer **3** to the blue isomer **4** occurs upon heating solutions of the triflate salt of **3** in 1,2-dichloroethane for 24 h.[9] This thermal isomerization can also be carried out in benzene or acetonitrile but requires longer reaction times. The analogous bromo analogue of **3** can, in a similar fashion, be converted to the di-μ-bromo complex $[(XylNC)(OC)Re(\mu\text{-}Br)_2(\mu\text{-dppm})_2ReBr(CNXyl)]O_3SCF_3$.[10] In contrast to the open bioctahedral structure of **3**,[6] the cation of **4** has a di-μ-halo-bridged edge-sharing bioctahedral geometry. The structure of the dirhenium cation is shown in Figure 1.[11] A plausible mechanism for the conversion of **3** to **4** is the type of “merry-go-round” process shown in Scheme 1.[12] This mechanism has previously[13] been used to explain the fluxionality of the multiply bonded edge-sharing bioctahedral complex $Re_2Cl_4(\mu\text{-dppm})_2(CO)_2$. We have not found any conditions under which **4** converts to **1**, **2**, or **3**.

Scheme 1. Isomers of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ (**1**−**4**)



Complex **4** has IR-active ν(CO) and ν(CN) modes which agree with the presence of terminal CO and XylNC ligands.

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[1] Part 12. *Reactions of the Dirhenium Complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides.* For the previous paper in this series, see: Wu, W.; Subramony, J. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1996**, *35*, 6784.

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[3] Anderson, L. B.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Price, A. C.; Reid, A. H.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 2717.

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[9] A typical procedure is as follows. A sample of **3** as its triflate salt (133 mg, 0.079 mmol) was dissolved in 45 mL of 1,2-$C_2H_4Cl_2$ and the resulting orange-yellow solution heated at reflux for 24 h. The solution changed color to green and, finally, to blue during this period. The reaction mixture was then cooled to room temperature, the solvents removed by rotary evaporator, and the residue dissolved in a minimum volume of dichloromethane (ca. 2 mL). An excess of diethyl ether was added to precipitate the blue isomer $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$, **4**; yield 126 mg (95%). Anal. Calcd for $C_{70}H_{62}Cl_3F_3N_2O_4SP_4Re_2$: C, 49.84; H, 3.70; N, 1.66. Found: C, 48.61; H, 3.61; N, 1.84. IR (Nujol mull, ν(cm^{-1})): 2134 (s, CN), 2066 (s, CN), 2028 (sh, CN), 1862 (vs, CO). ^{1}H NMR (δ in $CDCl_3$): 17.2 (d, 3H), 16.4 (d, 2H), 13.3 (d, 4H), 12.9 (m, br, 4H), 10.9 (m, 6H), 9.8 (m, 9H), 9.4 (t, 1H), 9.0 (t,2H), 8.5 (t, 2H), 5.6 (d, 3H), 5.4 (m, 6H), 4.5 (s, br, 4H), 4.0 (t, 1H), 3.1 (s, 6H), −2.6 (s, 6H), −4.0 (d, 1H), −15.3 (d, 1H). UV-vis (nm in CH_2Cl_2, ϵ values given in parentheses): 302 (24.8×10^3), ∼430 sh ($\sim 2.3 \times 10^3$), 660 (3.2×10^3), ∼1550 (<300). Conductivity (1.0×10^{-3} M solution in acetone, Λ_m): 118 Ω^{-1} cm^2 mol^{-1}.

[10] Full details on the synthesis and characterization of the bromo analogue will be published in due course. Its spectroscopic and electrochemical properties resemble closely those of **4**.

[11] Crystals of composition $[Re_2(\mu\text{-}Cl)_2Cl(\mu\text{-dppm})_2(CO)(CNxyl)_2](O_3SCF_3)_{0.71}Cl_{0.29}{\cdot}2.5C_7H_8$ (**4**) were grown from 1,2-dichloroethane/toluene (1:1) by slow evaporation. Crystal data for **4** (−50 °C): space group $P\bar{1}$ (No. 2); a = 15.751(7) Å, b = 16.645(7) Å, c = 18.886(9) Å, α = 80.27(4)°, β = 65.06(4)°, γ = 83.72(4)°; V = 4420(4) Å^3, Z = 2, d_{calcd} = 1.415 g/cm^3; Enraf−Nonius CAD-4 diffractometer, Mo Kα radiation; 10 996 unique reflections with $6.0° < 2\theta < 45.6°$ collected and used in the refinement; all non-hydrogen atoms of the cation (except CO group atoms) refined anisotropically, hydrogen atoms included but not refined; empirical absorption correction applied (μ = 3.022 mm^{-1}); a cutoff $F_o^2 > 2\sigma(F_o^2)$ used for R-factor calculations, $R(F_o)$ = 0.052, $R_w(F_o^2)$ = 0.158, GOF = 1.085. *Note*: the cation is disordered about a pseudo 2-fold axis through Cl(3) and Cl(4), one toluene molecule is disordered about a crystallographic inversion center, two toluene molecules are located about general positions; fractional triflate and chloride occupancies for the anion with $M(Cl^-) + M(O_3SCF_3^-) = 1$.

[12] As depicted in Scheme 1, this merry-go-round process can proceed in a clockwise or anticlockwise direction to convert **3** to **4** through the agency of either of two possible intermediates. However, when the course of the reaction was monitored by IR spectroscopy, we found no evidence for the presence of any intermediate.

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S0002-7863(96)02910-1 CCC: $12.00

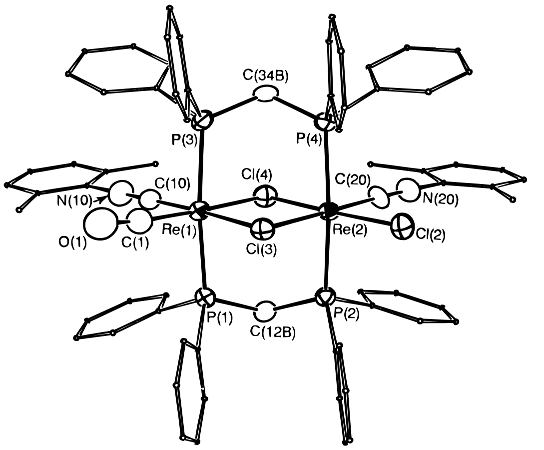

Figure 1. ORTEP representation of the structure of the $[Re_2(\mu\text{-}Cl)_2Cl(\mu\text{-}dppm)_2(CO)(CNXyl)_2]^+$ cation in **4**. This representation shows half of the disorder involving the terminal CO and Cl ligands (about a pseudo 2-fold axis through Cl(3) and Cl(4)). Selected bond distances (Å) and bond angles (deg): Re(1)−Re(2) 3.321(2), Re(1)−C(1) 1.86(4), Re(1)−C(10) 1.981(13), Re(1)−Cl(3) 2.484(3), Re(1)−Cl(4) 2.447(3), Re(2)−Cl(2) 2.309(13), Re(2)−C(20) 1.948(12), Re(2)−Cl(3) 2.488(3), Re(2)−Cl(4) 2.458(3); Re(1)−Cl(3)−Re(2) 83.83(9), Re(1)−Cl(4)−Re(2) 85.22(9), Re(1)−C(10)−N(10) 177.7(11), Re(2)−C(20)−N(20) 178.2(11).

Cyclic voltammetric (CV) measurements on solutions of the blue isomeric form **4** in 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$ exhibit four redox processes (corresponding to two one-electron oxidations and two one-electron reductions of the bulk complex) with $E_{1/2}(ox)(2) = +1.50$ V, $E_{1/2}(ox)(1) = +0.74$ V, $E_{1/2}(red)(1) = -0.03$ V and $E_{1/2}(red)(2) = -0.98$ V vs Ag/AgCl. The reduction at −0.03 V is accessible chemically through the use of 1 equiv of $(\eta^5\text{-}C_5H_5)_2Co$ as the reductant (in dichloromethane at 25 °C) to produce the red, neutral complex $Re_2(\mu\text{-}Cl)_2Cl(\mu\text{-}dppm)_2(CO)(CNXyl)_2$ (**5**) in essentially quantitative yield.[14] The CV of **5** is identical to that of **4** with the exception that the process at $E_{1/2} = -0.03$V corresponds to a one-electron oxidation. Complex **5** is readily reoxidized to the PF_6^- salt of **4** upon its reaction with $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in dichloromethane at 25 °C.

The very long Re−Re distance in the structure of **4** (3.321(1) Å) is in agreement with the absence of a metal−metal bond; this can be contrasted with a Re≡Re bond distance of 2.383(1) Å in the bioctahedral isomer **3**.[6] Accordingly, complex **4** would be expected to be paramagnetic, and this is confirmed both by its magnetic moment ($\mu_{eff} = 1.8(\pm 0.2)\ \mu_B$ as measured by the Evans method in chloroform) and its Knight-shifted ^1H NMR spectrum; the latter shows 17 distinct, sharp resonances between δ +17.2 and −15.3. It seems reasonable to formulate **4** as a charge-separated Re(III)−Re(I) mixed-valence species, since both the magnetic moment and ^1H NMR spectral properties are consistent with the presence of a paramagnetic d^4 "Re(III) center".[15−17] The reduction of **4** to its neutral congener **5** can then be viewed as the reduction of the relatively electron-poor Re(III) center to Re(II). This is accompanied by a shift and pronounced broadening for all the resonances in the ^1H NMR spectrum of **5**. Both **4** and **5** show a single broad resonance in their $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) at δ −121.9 and −14.5, respectively. We attribute this feature to the pair of dppm P atoms that are bound to the diamagnetic Re(I) centers, but which are Knight-shifted through their interaction, via the Re−Cl−Re bridges, with the paramagnetic Re(III) and Re(II) centers within the dirhenium units of **4** and **5**, respectively.

While a few examples of mixed-valence multiply bonded dimetal complexes, which are formally the products of intramolecular disproportionation reactions, are known,[2,18] the conversion of **3** to **4** represents the first documented case of an *isomerization* in which an electron-rich triple bond converts to a formally mixed-valence charge-separated species in which no metal−metal bond is present. This thermal reaction pathway may show some parallels with the excited state photochemistry of dimetal multiply bonded complexes which lead to mixed-valence species.[19] We believe that the scope of this chemistry as it relates to the thermal reactions of other multiply bonded bioctahedral complexes of type **A** is quite extensive. Studies are underway to exploit and develop these findings.

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Supporting Information Available: Tables giving full details for the crystal data and data collection parameters, atomic positional parameters, anisotropic thermal parameters, bond distances, and bond angles for **4** (12 pages). See any current masthead page for ordering and Internet access instructions.

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[14] Anal. Calcd for $C_{69}H_{62}Cl_3N_2OP_4Re_2$: C, 53.89; H, 4.06; N, 1.82. Found: C, 53.86; H, 4.06; N, 1.92. IR (Nujol mull, ν(cm^{-1})): 2050 (sh, CN), 2010 (vs, CN), 1958 (s, vbr, CN), 1830 (vs, CO).

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[19] See, for example, the photochemistry of the Tc≡Tc bond: Cotton, F. A.; Haefner, S. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1996**, *108*, 5486.