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Reactions of the dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with isocyanides. Part XVII[1]. Isomerizations of triply bonded dirhenium complexes of the type $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)(CNR)]^+$ (R = Xyl or *t*-Bu) with open bioctahedral structures to di-μ-chloro edge-sharing bioctahedral structures with no Re–Re bond[2]

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Abstract

The diamagnetic dirhenium(II) complexes $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$, where dppm = $Ph_2PCH_2PPh_2$, XylNC = xylyl isocyanide and X = Cl (**3a**) or Br(**3b**), in which the cations possess the Re–Re triply bonded, open bioctahedral structure $[(XylNC)_2XRe(\mu\text{-dppm})_2ReX_2(CO)]O_3SCF_3$, convert to the paramagnetic di-μ-halo bridged complexes $[(XylNC)(CO)Re(\mu\text{-}X)_2(\mu\text{-dppm})_2ReX(CNXyl)]O_3SCF_3$, X = Cl (**4a**) or Br (**4b**), in very high yield when their solutions in 1,2-dichloroethane are heated to reflux for ca. 24 h. This isomerization involves a switch from a Re≡Re bonded structure (Re–Re distance = 2.383(1) Å in **3a**) to one in which no Re–Re bond is present (Re–Re distance = 3.321(1) Å in **4a**). The complex cations in **4a** and **4b** are formulated as mixed-valence Re(I)–Re(III) species, and their formation represents the first example of the isomerization of a multiply bonded dimetal complex to one in which no metal–metal bond is present. The related thermal isomerizations of the Re–Re triply bonded, mixed-isocyanide ligand complexes $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]O_3SCF_3$, X = Cl or Br, have also been examined. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; Dirhenium(II) complexes; Isocyanide complexes; Isomers; Rhenium complexes

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1. Introduction

The seminal discoveries in the field of metal–metal quadruple bond chemistry by F.A. Cotton and co-workers occurred in the early-to-mid 1960's [2] and included important contributions from Brian Johnson [3,4]. While Brian Johnson's interests and contributions have evolved in many different directions since this time, the field of multiple metal–metal bond chemistry has continued to grow and flourish, and now encompasses the chemistry of most of the transition elements and includes compounds which possess metal–metal bond orders of 4, 3.5, 3, 2.5, 2 and 1.5 [2]. Within the myriad of compounds that contain M≡M bonds, there are two important classes, viz., electron-poor and electron-rich triple bonds, which are characterized by $\sigma^2\pi^4$ and $\sigma^2\pi^4\delta^2\delta^{*2}$ ground

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[1] For Part XVI see Ref. [1].

[2] Dedicated to Professor Brian Johnson on the occasion of his 60th Birthday in recognition of his outstanding contributions to inorganic and organometallic chemistry and appreciation (by R.A.W.) for thirty-five years of friendship.

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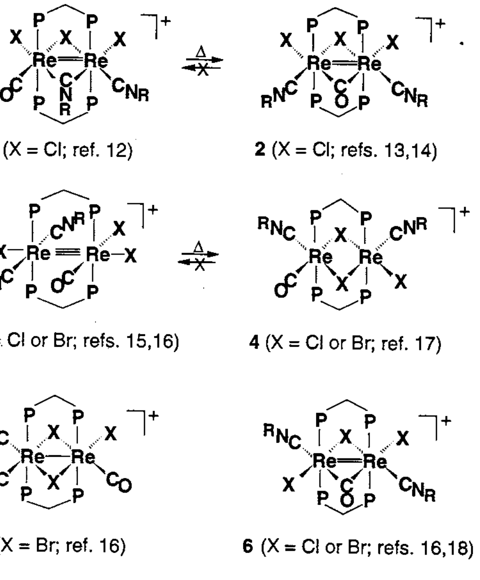
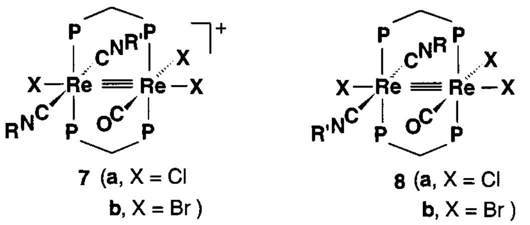
state configurations, respectively [2]. The former configuration is commonly encountered in dimolybdenum(III) and ditungsten(III) compounds, whose chemistry has been extensively investigated by M.H. Chisholm and co-workers [5], while compounds which possess the electron-rich triple bond are found most frequently in dirhenium(II) chemistry [6]. However, the existence of diosmium(III) complexes with the $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration is also well documented [7,8], and the discovery of triply bonded compounds of ditechnetium(II) is an important recent development [9].

We have recently been exploring the isomer chemistry of salts of the monocationic species $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$; Xyl = 2,6-dimethylphenyl) which are derived from the triply bonded dirhenium(II) synthons $Re_2X_4(\mu\text{-dppm})_2$ [2,10,11]. Six isomers of $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$, which have structures based upon open bioctahedral and edge-sharing bioctahedral geometries, have so far been identified (Scheme 1) [12–18]. Of these six isomeric forms, two are formed by the thermal isomerization of other forms, i.e. **1**→**2** and **3**→**4** in Scheme 1. The second of these conversions (**3**→**4**) has been the subject of a preliminary communication [17]. In the present report, we provide full details of the isomerizations of the triply bonded xylyl isocyanide-containing complexes **3a** (X = Cl) and **3b** (X = Br) to the edge-sharing bioctahedral complexes **4a** (X = Cl) and **4b** (X = Br), along with data relating to the analogous isomerization behavior of the triply bonded mixed-isocyanide complexes $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]O_3SCF_3$ (**7** and **8**; R = Xyl and R′ = *t*-Bu), which differ only in the relative dispositions of the XylNC and *t*-BuNC ligands (Fig. 1). The synthesis and spectroscopic characterization of salts of the chloro cations **7a** and **8a** have been reported previously [19,20]; these constitute two of four isomers of the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]^+$ cation that have so far been isolated (the others have edge-sharing bioctahedral structures). The analogous bromo derivatives **7b** and **8b** are reported here for the first time.



1 (X = Cl; ref. 12)
2 (X = Cl; refs. 13,14)
3 (X = Cl or Br; refs. 15,16)
4 (X = Cl or Br; ref. 17)
5 (X = Br; ref. 16)
6 (X = Cl or Br; refs. 16,18)

Scheme 1.



7 (a, X = Cl
b, X = Br)
8 (a, X = Cl
b, X = Br)

Fig. 1.

2. Experimental details

2.1. Starting materials and reaction procedures

The chloro complexes $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$ (isomer **3a**) [15], $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]O_3SCF_3$ (isomers **7a** and **8a**) [19,20] were prepared by established procedures from $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$, $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)$ and $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$, respectively. The bromo complexes $Re_2Br_4(\mu\text{-dppm})_2(CO)$ [21], $Re_2Br_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)$ [22] and $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNXyl)$ [22] were obtained from $Re_2Br_4(\mu\text{-dppm})_2$ according to the literature procedures. The reagents $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ [23] and TlO_3SCF_3 [24] were synthesized by the literature methods, while $(\eta^5\text{-}C_5H_5)_2Co$ and tert-butyl isocyanide (*t*-BuNC) were purchased from Aldrich Chemical and 2,6-dimethylphenyl isocyanide (XylNC) from Fluka Chemical Corp. The commercial reagents were 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. Infrared spectra, ^1H and $^{31}P\{^1H\}$-NMR spectra and cyclic voltammetric measurements were determined as described previously [22]. Elemental microanalyses were carried out by Dr H.D. Lee of the Purdue University Microanalytical Laboratory.

2.2. Synthesis of [Re_2Br_3(μ-dppm)$_2$(CO)(CNXyl)$_2$]O_3SCF_3 (isomer **3b**)

This complex has been synthesized in only low yield previously [16]. The preferred synthetic route involves the use of the acetonitrile complex [Re_2Br_3(μ-dppm)$_2$(CO)(CNXyl)($NCCH_3$)]O_3SCF_3 as an intermediate. A mixture of Re_2Br_4(μ-dppm)$_2$(CO) [21] (0.180 g, 0.121 mmol), TlO_3SCF_3 (0.0450 g, 0.127 mmol) and XylNC (0.0170 g, 0.125 mmol) in acetonitrile (30 ml) was stirred at room temperature for 20 h. The white precipitate (TlBr) was filtered off, and the red–brown filtrate was evaporated to a volume of ca. 5 ml under a stream of N_2 gas. The solution was layered with diethyl ether (ca. 35 ml) to induce precipitation of the brown complex [Re_2Br_3(μ-dppm)$_2$(CO)(CNXyl)($NCCH_3$)]O_3SCF_3 (**9**) which was filtered off, washed with diethyl ether (2 × 10 ml) and dried under vacuum; yield 0.185 g (88%). The identity of this product was based upon the close similarity of its IR spectral properties (Nujol mull, ν (cm^{-1}): 2288 (vw) [ν(CN) of CH_3CN], 2090 (s) [ν(CN) of XylNC], 1954 (vs) [ν(CO)]) to those reported for its chloro analogue [20].

A mixture of **9** (0.150 g, 0.087 mmol) and XylNC (0.011 g, 0.084 mmol) was treated with 30 ml of dichloromethane and stirred at 25°C for 48 h to produce a clear red–brown solution. The solvent was removed with the use of a rotary evaporator and the residue redissolved in 3 ml of dichloromethane and the solution treated with ca. 40 ml of diethyl ether. The title complex **3b** was filtered off and dried; yield 0.125 g (79%). The identity of this product was established by its IR and NMR spectroscopic properties, which were identical with those of a sample of this complex which had been prepared in very low yield by an alternative route and its structure established by X-ray crystallography [16].

2.3. Synthesis of [Re_2Br_3(μ-dppm)$_2$(CO)(CNXyl)(CN-*t*-Bu)]O_3SCF_3

2.3.1. Isomer **7b**

This isomer was obtained via the intermediate [Re_2Br_3(μ-dppm)$_2$(CO)(CN-*t*-Bu)($NCCH_3$)]O_3SCF_3 (**10**) which was itself prepared by a procedure analogous to that described for the mixed XylNC/CH_3CN complex **9** (see Section 2.2); yield 83%. The IR spectral properties of **10** were similar to those of **9** (Nujol mull, ν(cm^{-1}): 2283 (vw)[ν(CN) of CH_3CN], 2151(s) [ν(CN) of *t*-BuNC], 1949(s) [ν(CO)]).

A mixture of **10** (0.0589 g, 0.035 mmol), XylNC (0.0049 g, 0.035 mmol), and dichloromethane (10 ml) was stirred at room temperature overnight. The volume of the reaction mixture was then reduced to ca. 2 ml and diethylether (ca. 20 ml) added to precipitate **7b** as a light red solid, which was filtered off, washed with diethyl ether (2 × 5 ml) and dried under vacuum; yield 0.0524 g (86%). Anal. Calcd. for $C_{66}H_{62}Br_3F_3N_2O_4P_4Re_2S$: C, 44.73; H, 3.53. Found: C, 44.67; H, 3.54%. $^{31}P\{^1H\}$-NMR spectrum (in CD_2Cl_2): AA'BB' pattern with multiplets at δ ca. −14.0 and −15.5.

2.3.2. Isomer **8b**

A solution of the acetonitrile complex **9** (0.120 g, 0.069 mmol) in 30 ml of dichloromethane was treated with a stoichiometric amount of *t*-BuNC (7.5 µl, 0.072 mmol) and the mixture stirred for 48 h. The solvent was then evaporated to a volume of ca. 5 ml by the use of a stream of N_2 gas, and the resulting solution layered with 30 ml of diethyl ether to induce precipitation of **8b**. The product was filtered off, washed with diethyl ether (2 × 10 ml) and dried under vacuum; yield 0.110 g (90%). Anal. Calcd. for $C_{66}H_{62}Br_3F_3N_2O_4Re_2S$: C, 44.73; H, 3.53. Found: C, 44.03; H, 3.37%. $^{31}P\{^1H\}$-NMR spectrum (in $CDCl_3$): AA'BB' pattern with multiplets centered at δ ca. −15.3 and −17.4.

2.4. Thermal isomerization of **3a** to **4a**

A sample of **3a** (0.133 g, 0.079 mmol) was dissolved in 45 ml of 1,2-dichloroethane and the resulting orange–yellow solution heated at reflux for 24 h. The solution changed color to green and, eventually, to blue during this period. The reaction mixture was cooled to room temperature, the solvent removed by use of a 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 **4a**; yield 0.126 g (95%). Anal. Calcd. for $C_{70}H_{62}Cl_3F_3N_2O_4P_4Re_2S$: C, 49.84; H, 3.70; N, 1.66. Found: C, 48.61; H, 3.61; N, 1.84%. The isomerization of **3a** to **4a** also occurs when acetonitrile or benzene is used in place of 1,2-dichloroethane but in these cases requires longer reaction times.

2.5. Thermal isomerization of **3b** to **4b**

A sample of the bromo complex **3b** (0.042 g, 0.023 mmol) was treated with 10 ml of 1,2-dichloroethane and the mixture refluxed for 20 h. The solvent was removed by use of a rotary evaporator and the brown–purple residue recrystallized from 1,2-dichloroethane/toluene (1:1); yield 0.035 g (83%). Anal. Calcd. for $C_{70}H_{62}Br_3F_3N_2O_4P_4Re_2S$: C, 46.19; H, 3.43. Found: C, 46.31; H, 3.53%.

2.6. Thermal isomerizations of **7a** and **8a** to **11**

A quantity of **7a** (0.050 g, 0.031 mmol) was dissolved in 1,2-dichloroethane (10 ml) and the solution refluxed for 2 days. The solvent was removed by the use of a rotary evaporator and the blue solid dried under vacuum; yield 0.050 g (100%). Anal. Calcd. for $C_{66}H_{62}Cl_3F_3N_2O_4P_4Re_2S$: C, 48.37; H, 3.81. Found: C, 48.84; H, 4.13%.

The use of **8a** in place of **7a** led to its quantitative conversion to **11** by the use of this same procedure. Anal. Calcd. for $C_{66}H_{62}Cl_3F_3N_2O_4P_4Re_2S$: C, 48.37; H, 3.81; Cl, 6.49. Found: C, 48.16; H, 4.00; Cl, 6.78%.

2.7. Redox chemistry of ***4a***

2.7.1. Reduction to $Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2Cl(CO)(CNXyl)_2$ (***4a'***)

A mixture of **4a** (0.055 g, 0.033 mmol) and cobaltocene (0.0065, 0.0344 mmol) in 15 ml of dichloromethane was stirred at 25°C for 2 h. The initial blue colored solution changed to red during this period. The reaction mixture was then filtered, the volume of the filtrate reduced to ca. 2 ml, and diethyl ether (10 ml) added. A quantity of yellow–green solid ($[(\eta^5\text{-}C_5H_5)_2Co]O_3SCF_3$) precipitated and was filtered off. The remaining filtrate was evaporated to dryness to afford a red solid (**4a'**); yield 0.048 g (95%). 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%.

2.7.2. Oxidation of ***4a'*** to $[Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2Cl(CO)(CNXyl)_2]PF_6$

A mixture of **4a'** (0.035 g, 0.023 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.0080 g, 0.024 mmol) in 15 ml of dichloromethane was stirred at 25°C for 16 h. Early in the course of the reaction, the color changed from orange to blue. The reaction mixture was filtered, the blue filtrate reduced in volume to ca. 1 ml, and 20 ml of diethyl ether added to induce precipitation of the salt $[Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2(CO)(CNXyl)_2]PF_6$, a complex which contains the same cation as present in the triflate salt **4a**. This product was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.0345 g (90%). The spectroscopic and electrochemical properties of this product were the same as those of **4a** (see Section 3), with the exception of differences in the IR spectra due to the different anions which are present ($[O_3SCF_3]^-$ and $[PF_6]^-$).

2.8. X-ray crystallography

Suitable single crystals of composition $[Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2Cl(CO)(CNXyl)_2](O_3SCF_3)_{0.71}Cl_{0.29}\cdot 2.5C_7H_8$ were obtained by slow evaporation of the solvents from a solution of **4a** in 1,2-dichloroethane/toluene (1/1). A brown plate of **4a** was mounted on a glass fiber in a random orientation. The data collection was performed at 223 K on an Enraf-Nonius CAD4 computer controlled diffractometer with the use of graphite-monochromatized Mo–K_α radiation. The cell constants were based on 25 reflections obtained in the range $11 < \theta < 25°$ 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 [25] was also applied, but no correction for extinction was made. Calculations were performed on an AlphaServer 2100 computer in conjunction with the MolEN structure determination package [26] and the SHELXL-93 refinement program [27].

Compound **4a** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and subsequently confirmed by the successful solution and refinement of the structure. 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. During the course of the structure analysis a disorder within the cation was recognized. This disorder involved the terminal chlorine atom and the CO ligand and is generated by a pseudo two-fold axis through the bridging chlorine atoms Cl(3) and Cl(4). Two different sets of positions for these terminal ligands were produced, one set about each Re center (i.e. C(1), O(1) and Cl(1) about Re(1), and C(2), O(2) and Cl(2) about Re(2)). The atoms of these two sets of ligands were located from the difference Fourier and a 50/50 disorder mode was refined satisfactorily. In addition, a fractional O_3SCF_3 group and a fractional Cl atom were found in the anion site. The positions of these two groups were independent and their occupancies were refined to 0.709(13) for $O_3SCF_3^-$ and 0.291(13) for Cl^-, respectively, with the restriction that $M(Cl^-) = 1 - M(O_3SCF_3^-)$. The asymmetric unit also contained two toluene solvent molecules which were located about general positions and a third toluene molecule which was disordered about an inversion center. All non-hydrogen atoms of the dirhenium cation, except those of the disordered CO groups, were refined anisotropically. All other non-hydrogen atoms in the structure were refined with isotropic thermal parameters. The positions of the hydrogen atoms were calculated according to the idealized geometries with $C–H = 0.95$ Å and $U_{eq}(H) = 1.3\ U_{eq}(C)$. 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 $\Sigma w\ (|F_o^2| - |F_c^2|)^2$, where w is the weighting factor defined as $w = 1/[\sigma^2(F_o^2) + (0.0969P)^2 + 48.8517P]$ where $P = (F_o^2 + 2F_c^2)/3$. Corrections for anomalous scattering were applied to all non-hydrogen atoms [28]. The final residuals for **4a** were $R = 0.052$ and $Rw = 0.158$ with GOF = 1.085. The highest peak in the final difference Fourier was 2.49 e Å^{-3}, and was located in the region of the disordered $O_3SCF_3^-/Cl^-$ anion.

The crystallographic data for **4a** are listed in Table 1. The important intramolecular bond distances and angles are given in Table 2.

3. Results and discussion

This study is focused on the thermal isomerization behavior of the triply-bonded dirhenium(II) complexes $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$ (**3a**, X = Cl; **3b**, X = Br) and the isomeric forms of $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]O_3SCF_3$ (**7a** and **8a**, X = Cl; **7b** and **8b**, X = Br), the structures of which are represented in Scheme 1 and the Fig. 1. The chloro complexes **3a**, **7a** and **8a** have been synthesized and characterized previously [15,19,20], while the analogous bromo complexes **3b**, **7b** and **8b** are reported here for the first time. The synthetic routes to the three bromo complexes are represented in the set of reactions (1)–(3) shown below:

$$Re_2Br_4(\mu\text{-dppm})_2(CO) + XylNC \xrightarrow[CH_3CN]{TlO_3SCF_3} [Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3(\mathbf{9}) \xrightarrow[CH_2Cl_2]{XylNC} [Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SOCF_3\ (\mathbf{3b}) \qquad (1)$$

$$Re_2Br_4(\mu\text{-dppm})_2(CO) + t\text{-}BuNC \xrightarrow[CH_3CN]{TlO_3SCF_3} [Re_2Br_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)(NCCH_3)]O_3SCF_3(\mathbf{10}) \xrightarrow[CH_2Cl_2]{XylNC} [Re_2Br_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)(CNXyl)O_3SCF_3\ (\mathbf{7b}) \qquad (2)$$

$$[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3\ (\mathbf{9}) \xrightarrow[CH_2Cl_2]{t-BuNC} [Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]O_3SCF_3\ (\mathbf{8b}) \qquad (3)$$

A comparison of the IR spectral properties of the bromo complexes **3b**, **7b** and **8b** with those of their chloro analogues is provided in Table 3.

In previous studies [12–14] we established that salts of the chloro complex **1** (Scheme 1) undergo thermal isomerization to **2** when their solutions in 1,2-dichloroethane are heated. In the present study we find that solutions of the isomeric form **3** in 1,2-dichloroethane are converted to a fourth isomer **4** when they are refluxed for periods of up to 24 h. The salts $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$ (**3a**, X = Cl; **3b**, X = Br) convert to the isomeric forms **4a** and **4b** in close to quantitative yield. The structures of the dirhenium cations present in **4a** and **4b** are represented in Scheme 1, and have been established by a single crystal X-ray structure analysis of a crystal of composition $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2](O_3SCF_3)_{0.71}\text{-}Cl_{0.29}\cdot 2.5C_7H_8$, which was obtained by recrystallization of **4a** from a 1,2-dichloroethane/toluene solvent mixture. Spectroscopic characterization of these crystals shows that the nature of the dirhenium cation is identical to that present in the bulk preparative samples. The partial chloride for triflate substitution apparently occurs during the crystal growing process. An ORTEP representation [29] of the structure is given in Fig. 2 and key structural parameters are listed in Table 2. In contrast to the open bioctahedral structure of the precursor complex **3a**, the dirhenium cation present in the isomerized product **4a** possesses a di-μ-chloro bridged edge-sharing bioctahedral structure. The very long Re–Re distance in the structure of **4a** (3.321(2) Å) is in accordance with the absence of a Re–Re bond and can be contrasted with the triple bonded Re≡Re distance of 2.383(1) Å present in the isomer **3a** [15]. With a couple of exceptions, the other structural parameters given in

Table 1
Crystallographic data for the complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2](O_3SCF_3)_{0.71}Cl_{0.29}\cdot 2.5C_7H_8$ (**4a**)

Chem formula	$Re_2Cl_{3.29}S_{0.71}P_4F_{2.13}O_{3.13}N_2C_{87.21}H_{82}$	Z	2
FW	1884.29	ρ_{calcd}, g cm^{-3}	1.415
Space group	$P\bar{1}$ (No. 2)	Crystal dimensions, mm	0.60 × 0.45 × 0.15
a (Å)	15.751(7)	μ, mm^{-1} (Mo–K$_\alpha$)	3.022
b (Å)	16.645(7)	Transmission factors, min/max	0.59/0.90
c (Å)	18.886(9)	$R(F_o)$[a]	0.052
α (°)	80.27(4)	$R_w(F_o^2)$[b]	0.158
β (°)	65.06(4)	Largest shift/error	0.03
γ (°)	83.72(4)	GOF	1.085
V (Å^3)	4420(4)		

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

Table 2
Bond distances (Å) and bond angles (°) for the complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2](O_3SCF_3)_{0.71}Cl_{0.29}\cdot 2.5C_7H_8$ (4a)[a]

Distances			
Re(1)–Re(2)	3.321(2)	Re(2)–P(4)	2.424(3)
Re(1)–C(1)	1.86(4)[b]	Re(2)–P(2)	2.440(3)
Re(1)–C(10)	1.981(13)	Re(2)–Cl(4)	2.458(3)
Re(1)–Cl(1)	2.332(12)[b]	Re(2)–Cl(3)	2.488(3)
Re(1)–P(3)	2.441(3)	N(10)–C(10)	1.16(2)
Re(1)–Cl(4)	2.447(3)	N(10)–C(11)	1.37(2)
Re(1)–P(1)	2.451(3)	N(20)–C(20)	1.161(14)
Re(1)–Cl(3)	2.484(3)	N(20)–C(21)	1.41(2)
Re(2)–C(2)	1.91(4)[b]	O(1)–C(1)	1.16(5)[b]
Re(2)–C(20)	1.948(12)	O(2)–C(2)	1.15(4)[b]
Re(2)–Cl(2)	2.309(13)[b]		
Angles			
C(2)–Re(2)–C(20)	87.4(15)[b]	C(1)–Re(1)–C(10)	84.6(15)[b]
C(20)–Re(2)–Cl(2)	85.8(4)[b]	P(1)–Re(1)–Cl(3)	88.16(9)
C(2)–Re(2)–P(4)	93.3(15)[b]	C(10)–Re(1)–Cl(1)	85.9(4)[b]
C(20)–Re(2)–P(4)	89.2(3)	C(1)–Re(1)–P(3)	93.8(15)[b]
Cl(2)–Re(2)–P(4)	93.6(3)[b]	C(10)–Re(1)–P(3)	89.7(3)
C(2)–Re(2)–P(2)	93.0(15)[b]	Cl(1)–Re(1)–P(3)	92.5(3)[b]
C(20)–Re(2)–P(2)	90.6(3)	C(1)–Re(1)–Cl(4)	171.7(15)[b]
Cl(2)–Re(2)–P(2)	92.7(3)[b]	C(10)–Re(1)–Cl(4)	87.1(3)
P(4)–Re(2)–P(2)	173.69(9)	Cl(1)–Re(1)–Cl(4)	172.9(2)[b]
C(2)–Re(2)–Cl(4)	173.8(15)[b]	P(3)–Re(1)–Cl(4)	86.01(10)
C(20)–Re(2)–Cl(4)	86.5(3)	C(1)–Re(1)–P(1)	93.4(15)[b]
Cl(2)–Re(2)–Cl(4)	172.2(3)[b]	C(10)–Re(1)–P(1)	90.5(3)
P(4)–Re(2)–Cl(4)	87.63(10)	Cl(1)–Re(1)–P(1)	94.7(3)[b]
P(2)–Re(2)–Cl(4)	86.06(10)	P(3)–Re(1)–P(1)	172.84(9)
C(2)–Re(2)–Cl(3)	90.8(15)[b]	Cl(4)–Re(1)–P(1)	86.86(10)
C(20)–Re(2)–Cl(3)	177.8(3)	C(1)–Re(1)–Cl(3)	92.6(15)[b]
Cl(2)–Re(2)–Cl(3)	92.5(3)[b]	C(10)–Re(1)–Cl(3)	176.9(3)
P(4)–Re(2)–Cl(3)	89.68(10)	Cl(1)–Re(1)–Cl(3)	91.3(3)[b]
P(2)–Re(2)–Cl(3)	90.76(9)	P(3)–Re(1)–Cl(3)	91.92(10)
Cl(4)–Re(2)–Cl(3)	95.27(10)	Cl(4)–Re(1)–Cl(3)	95.67(10)
Re(1)–Cl(3)–Re(2)	83.83(9)	O(1)–C(1)–Re(1)	175(5)
Re(1)–Cl(4)–Re(2)	85.22(9)	N(10)–C(10)–Re(1)	177.7(11)
C(10)–N(10)–C(11)	178.8(14)	N(20)–C(20)–Re(2)	178.2(11)
C(20)–N(20)–C(21)	178.2(12)	O(2)–C(2)–Re(2)	171(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.[b] Parameter associated with disordered group.

Table 2 are unexceptional and do not merit further discussion. First, the half atoms Cl(1), Cl(2), C(1), C(2), O(1) and O(2) characterize the disordered terminal Cl and CO ligands and, therefore, have rather large esd's for their associated bond lengths and angles. Second, the eight-membered $Re_2(\mu\text{-dppm})_2$ ring assumes a boat conformation, which is commonly encountered in complexes derived from $Re_2X_4(\mu\text{-dppm})_2$ upon incorporation of CO and RNC ligands [1,30].

Complexes **4a** and **4b** have IR-active ν(CN) and ν(CO) modes which accord with the presence of terminal XylNC and CO ligands (Table 4). The similarity of these IR spectra to one another, along with the striking similarity of the cyclic voltammetric properties of **4a** and **4b** (Table 4), imply that these complexes have essentially the same structure. Both complexes display two one-electron oxidations and two one-electron reductions in their CV's. The process at -0.03 V in the CV of **4a** was shown to be chemically accessible through the use of one equivalent of $(\eta^5\text{-}C_5H_5)_2Co$ as the reductant to produce the red, neutral complex $Re_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2Cl(CO)(CNXyl)_2$, **4a'**, in essentially quantitative yield. The CV properties of **4a'** are the same as those of **4a**, while the IR-active ν(CN) and ν(CO) modes of **4a'** are shifted to lower frequencies relative to those of **4a**. These properties are consistent with **4a** and **4a'** being one-electron congeners. This is confirmed by the reoxidation of **4a'** to the $[PF_6]^-$ salt of **4a** by the use of the one-electron oxidant $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$. The properties of this product are identical with those of **4a** that are presented in Table 4.

The very long Re–Re distance in the structure of **4a** (3.321(1) Å) is consistent with the absence of a metal–metal bond and, therefore, this complex is expected to be paramagnetic. This is confirmed both by its magnetic moment ($\mu_{eff} = 1.8(\pm 0.2)$ BM as measured by the Evans method in chloroform), and its Knight-shifted ^{1}H-NMR spectrum (recorded in $CDCl_3$), which shows seventeen distinct, sharp resonances between $\delta + 18$ and $\delta - 15$ [i.e. 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)]. Based upon these observations, it seems reasonable to formulate **4a** as a charge separated Re(III)–Re(I) mixed-valence species since both the magnetic moment and ^{1}H-NMR spectral properties are consistent with the presence of a paramagnetic d^4 'Re(III) center' [31–33] within this dimetal complex. By implication, a similar conclusion can be drawn in the case of the bromo analogue **4b**, which has an IR spectrum and CV very similar to those of **4a** (see Table 4). However, the ^{1}H-NMR spectrum of a solution of **4b** in $CDCl_3$ shows broad, poorly defined features, unlike the very sharp resonances observed in the ^{1}H-NMR spectrum of **4a**, so that some charge differences may exist between **4a** and **4b**, although the essential structural similarity between these two complexes can reasonably be assumed.

The reduction of **4a** to its neutral congener **4a'** can 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 ^{1}H-NMR spectrum of **4a'**. Both **4a** and **4a'** show a single broad resonance in their $^{31}P\{^1H\}$-NMR spectra (recorded in $CDCl_3$) at $\delta - 121.9$ and $\delta - 14.5$, 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

Table 3
IR spectroscopic data for the dirhenium(II) complexes **3a**, **3b**, **7a**, **7b**, **8a** and **8b**[a]

Complex	ν(CN) cm^{-1}	ν(CO) cm^{-1}	Reference
3a	2144(m), 2116(vs)	1944(s)	[15]
3b	2142(m), 2112(vs)	1948(s)	b
7a[c]	2161(s), 2134(vs)	1927(s)	[19]
7b	2157(m), 2132(vs)	1927(s)	b
8a	2172(m), 2112(vs)	1962(vs)	[20]
8b	2170(m–s), 2118(vs)	1959(vs)	b

[a] All spectra recorded as Nujol mulls of the triflate salts of the dirhenium complexes unless otherwise stated.[b] This work.[c] Data are for the analogous $[PF_6]^-$ salt of **7a**.

within the dirhenium units of **4a** and **4a'**, respectively. No resonance is seen in the $^{31}P\{^1H\}$-NMR spectrum of **4b**, again reflecting some differences in the charge distribution within the paramagnetic complexes **4a** and **4b**.

A plausible mechanism for the isomerization of **3a** to **4a** and **3b** to **4b** is the 'merry-go-round' process shown in Scheme 2, which could proceed in a clockwise or anti-clockwise direction through the agency of two different edge-sharing bioctahedral species. Such a mechanism has been used [34] to explain the fluxionality of the edge-sharing bioctahedral complex $Re_2Cl_4(\mu\text{-dppm})_2(CO)_2$. However, when the isomerization of **3a** to **4a** was monitored by IR spectroscopy, we were unable to detect the presence of any intermediates, including those depicted in Scheme 2.

The non-dissociative mechanism shown in Scheme 2 is further supported by our observation that when 1,2-dichloroethane solutions of **3a** are refluxed in the presence of one equivalent of *t*-BuNC, complex **4a** remains the dominant product and there is little evidence for the incorporation of *t*-BuNC into the final product. However, we cannot rule out the possibility that isomerization reactions which are closely related to the isomerization of **3** to **4** may involve isocyanide ligand dissociation and recoordination. This has been established in the case of the isomerization of **1** to **2** shown in Scheme 1 [12], and isocyanide ligand dissociation must be involved in the thermal isomerization behavior of the mixed-isocyanide complexes **7a** and **8a**, which are isomeric forms of the dirhenium(II) complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]O_3SCF_3$ and possess open bioctahedral structures with a Re≡Re bond. When 1,2-dichloroethane solutions of **7a** and **8a** are refluxed for 2 days they convert to the same blue isomer **11** in essentially quantitative yield. This product is also isolated when a mixture of **7a** and **8a** is heated in 1,2-dichloroethane. The paramagnetic complex **11** shows very broad, poorly defined resonances in its ^1H-NMR spectrum (recorded in $CDCl_3$) and no discernible resonances in its $^{31}P\{^1H\}$-NMR spectrum. The Nujol mull IR spectrum of **11** displays ν(CN) and ν(CO) modes at 2124(vs), 2064(m–s), 2001(sh) and 1861(m–s) cm^{-1}; this is consistent with the presence of terminal isocyanide and CO ligands and resembles closely the spectrum of **4a**. Since **11** is formed from both isomer **7a** and isomer **8a**, the mechanism for its formation must involve dissociation and recoordination of an isocyanide ligand for at least one of these isomerizations, so the non-dissociative mechanism represented in Scheme 2 cannot hold in this case. Preliminary experiments indicate that 1,2-dichloroethane solutions of the bromo complexes **7b** and **8b** likewise convert to a complex, **12**, which is the bromo analogue of **11**. However, we have been unsuccessful in obtaining single crystals of **11** or **12** which are of a quality suitable for a single crystal X-ray structure determination, so the exact structural identity of these isomeric forms remains uncertain although they may have structures similar to those of **4a** and **4b**.

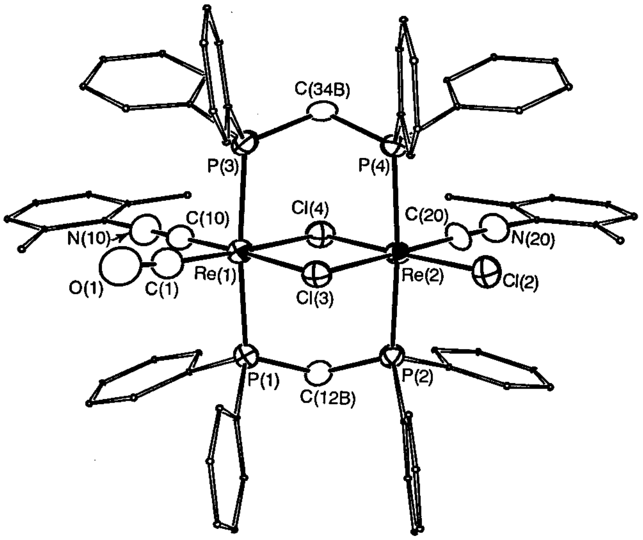


Fig. 2. ORTEP representation of the structure of the $[Re_2(\mu\text{-}Cl)_2(\mu\text{-dppm})_2Cl(CO)(CNXyl)_2]^+$ cation as present in **4a**. This representation shows half of the disorder involving the terminal CO and Cl ligands (about a pseudo two-fold axis through Cl(3) and Cl(4)). Disordered atoms not shown are Cl(1), C(2) and O(2).

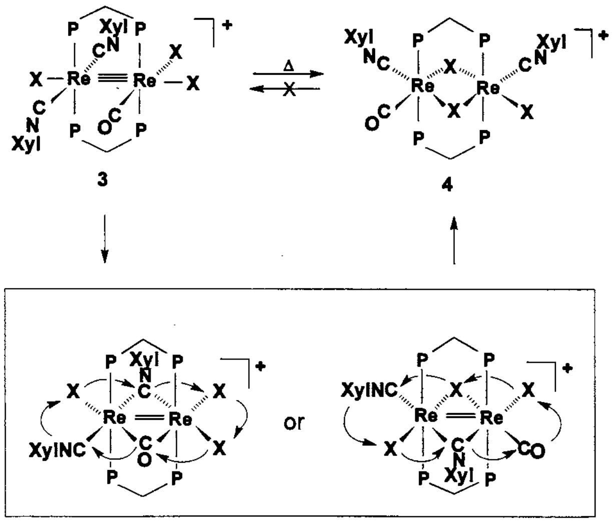
4. Conclusions

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. We believe that the scope of this chemistry as it relates to the thermal reactions of other multiply bonded bioctahedral complexes may be quite extensive and may show some parallels with the

Table 4
IR spectra and cyclic voltammetric data for the dirhenium(II) complexes **4a** and **4b**

	IR spectra, cm^{-1} [a]		CV half-wave potentials, V[b]			
Complex	ν(CN)	ν(CO)	$E_{1/2}$(ox)(2)	$E_{1/2}$(ox)(1)	$E_{1/2}$(red)(1)	$E_{1/2}$(red)(2)
4a	2134(s), 2066(s), 2028(m–s)	1862(vs)	+1.50(~100)	+0.74(75)	−0.03(70)	−0.98(80)
4b	2136(s), 2077(vs), 2017(m–s)	1877(vs)	+1.48(~110)	+0.65(65)	−0.07(80)	−0.96(~100)
4a'	2050(sh), 2010(vs), 1958(s, vbr)	1830(vs)	+1.50(100)	+0.75(75)	−0.03(70)[c]	−1.00(80)

[a] IR spectra recorded as Nujol mulls.[b] Measured on 0.1 M n-Bu_4NPF_6–CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (v) of 200 mV s^{-1} at a Pt-bead electrode. Under our experimental conditions $E_{1/2} = +0.47$ V versus Ag/AgCl for the ferrocenium/ferrocene couple. ΔEp ($E_{p,a} - E_{p,c}$) values are given in parentheses.[c] This process corresponds to a one-electron oxidation of the bulk samples of **4a'**.



Scheme 2. Plausible mechanism for the conversion of **3** to **4**.

excited state photochemistry of dimetal multiply bonded complexes which can lead to mixed-valence species [35].

5. Supplementary material

Tables giving full details for the crystal data and data collection parameters, atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles, and observed and calculated structure factors for **4a** are available on request from author R.A.W.

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