Stable boat and chair isomers of dimetal complexes containing the [Re$_2$(μ-dppm)$_2$] unit (M = Re; dppm = Ph$_2$PCH$_2$PPh$_2$)

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Reactions of the triply bonded complexes [Re$_2$Br$_3$(μ-dppm)$_2$(CO)(CNR)]Y (dppm = Ph$_2$PCH$_2$PPh$_2$; R = 2,6-dimethylphenyl; Y = O$_3$SCF$_3$, PF$_6$) with RNC afford edge-sharing bioctahedral complexes of the type [Re$_2$(μ-Br)$_2$(μ-dppm)$_2$Br(CO)(CNR)$_2$]Y, which are shown to contain Re–Re single bonds and exist in novel isomeric forms with boat and chair conformations for the Re$_2$(μ-dppm)$_2$ unit.

In the course of studies aimed at delineating the factors which determine the stabilities of various structural isomers of dimetal complexes of types **A** and **B** (P–P represents a bridging bidentate phosphine), and the mechanisms of the isomer conversions, we have encountered a new class of isomers which have relevance to the structural chemistry of open bioctahedra (**A**) and edge-sharing bioctahedra (**B**), as well as other classes of complexes which contain a M$_2$(μ-dppm)$_2$ unit (dppm = Ph$_2$PCH$_2$PPh$_2$).[1–3]

The mixed carbonyl–isocyanide complexes of the type [Re$_2$X$_3$(μ-dppm)$_2$(CO)(CNR)$_2$]Y (X = Cl, Br; R = 2,6-dimethylphenyl; Y = O$_3$SCF$_3$, PF$_6$) have been identified in at least five different structural forms, with metal–metal bond orders ranging from 3 to 0 (Scheme 1).[4–10] In some instances, isomerizations have been observed to occur at elevated temperatures (*i.e.* **1** → **2** and **3** → **4**).[4–6,9] Previously, the X-ray structural characterizations of salts of **1**–**5** have shown that the Re$_2$(μ-dppm)$_2$ unit (two fused five-membered rings in the cases of **1**, **2**, **3** and **5** and an eight-membered ring for **4**) exists in a stable boat conformation. Further characterizations of the bromo complex **5** have now established that preparative samples of the O$_3$SCF$_3$ and PF$_6$ salts consist of a mixture of two isomers with the same basic structure as that depicted in Scheme 1, but which differ in possessing either a boat (**5a**) or chair (**5b**) conformation for the Re$_2$(μ-dppm)$_2$ unit.

The reactions of the unsymmetrical, coordinatively unsaturated dirhenium(ii) complexes [Re$_2$Br$_3$(μ-dppm)$_2$(CO)-(CNR)]Y (Y = O$_3$SCF$_3$, PF$_6$)[8,10] with 1 equiv. of RNC in CH$_2$Cl$_2$ or acetone afford mixtures which contain the salts of the isomeric pair (**5a**)Y and (**5b**)Y as the major product [yield 40–70%, product ratio (**5a**)Y : (**5b**)Y *ca.* 5 : 95].† The spectroscopic and electrochemical properties of diamagnetic (**5a**)Y and (**5b**)Y are very similar,[8] and do not readily permit a distinction to be made between the structures of the components of the mixture. However, an X-ray structure determination on a crystal of (**5a**)PF$_6$ has shown[8] the structure to be that of the isomer with the boat conformation [the Re–Re distance is 3.0456(8) Å]. Although we have been unable to obtain single crystals of the major isomers (**5b**)O$_3$SCF$_3$ and (**5b**)PF$_6$ directly from the

preparative reaction mixtures which are of a quality suitable for an X-ray structure determination, we have done so by an alternative procedure.

Treatment of (**5b**)O$_3$SCF$_3$ with [Co(η^5-C$_5$H$_5$)$_2$] in CH$_2$Cl$_2$ affords the paramagnetic, one-electron reduced product [Re$_2$Br$_3$(μ-dppm)$_2$(CO)(CNR)$_2$] **6** in high yield. The addition of [Fe(η^5-C$_5$H$_5$)$_2$]PF$_6$ to a CH$_2$Cl$_2$ solution of **6** re-oxidizes it quantitatively to (**5b**)PF$_6$.‡ The structural identities of **6** and (**5b**)PF$_6$ have been established by X-ray crystallography which shows that both possess a chair conformation for the Re$_2$(μ-dppm)$_2$ unit.§ An ORTEP representation of the structure of **6** is shown in Fig. 1; the structure of the dirhenium cation present in (**5b**)PF$_6$ is essentially the same, with the exception of the parameters associated with the Re$_2$(μ-Br)$_2$ unit (see caption for Fig. 1). The Re–Re bond distances in the structures of (**5b**)PF$_6$ and **6** are 3.028(2) and 3.8023(10) Å, respectively; the former is essentially identical to the Re–Re distance in (**5a**)PF$_6$.[8] These distances, along with the magnetic properties of (**5b**)PF$_6$ and **6**, are consistent with the presence of Re–Re bonds of order one and zero, respectively. Accordingly, the one-electron reduction of (**5b**)O$_3$SCF$_3$ leads to a species [(RNC)$_2$Re(μ-Br)$_2$(μ-dppm)$_2$ReBr(CO)] **6** which can best be considered formally as a charge separated Re^I–Re^{II} species (18e–17e) rather than one containing a Re–Re bond of order 0.5.

The properties of (**5b**)PF$_6$ as prepared by the ferrocenium oxidation of **6** are identical to samples which are present in previously reported[8] mixtures of (**5a**)PF$_6$ and (**5b**)PF$_6$. Accordingly, the reduction of (**5b**)O$_3$SCF$_3$ to **6**, and the oxidation of **6** to (**5b**)PF$_6$ occur with preservation of a chair conformation. The

1 (X = Cl, ref. 4)

2 (X = Cl, refs. 5,6)

3 (X = Cl or Br, refs. 7,8)

4 (X = Cl or Br, ref. 9)

5 (X = Br, ref. 8)

A

B
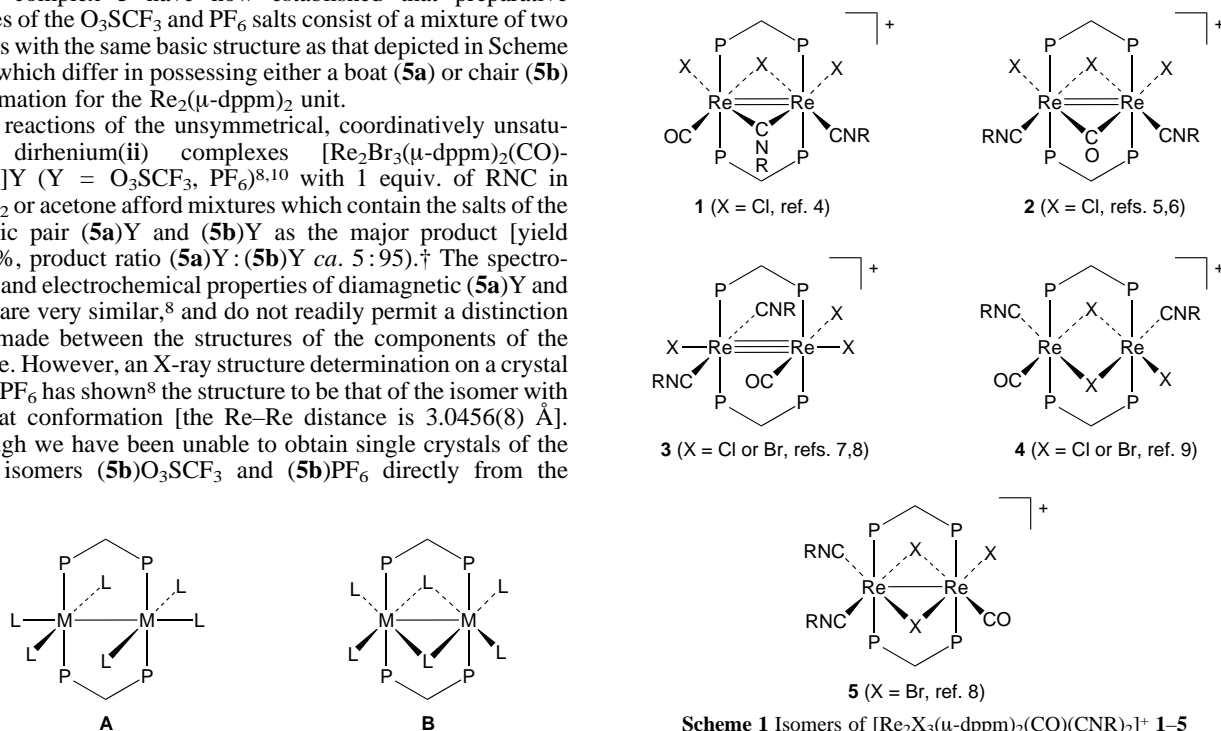
Scheme 1 Isomers of [Re$_2$X$_3$(μ-dppm)$_2$(CO)(CNR)$_2$]$^+$ **1**–**5**
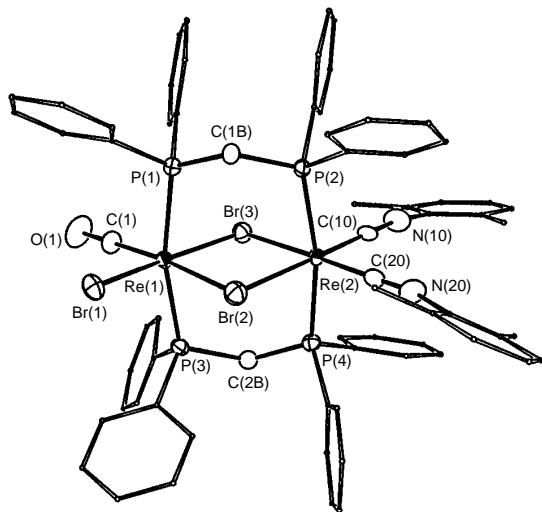
Fig. 1 ORTEP representation of the structure of the dirhenium complex [Re₂Br₃(μ-dppm)₂(CO)(CNR)₂] in crystals of **6**·CH₂Cl₂, showing the chair conformation for the Re₂(μ-dppm)₂ unit. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and the xylyl groups of the RNC ligands which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (°): Re(1)···Re(2) 3.8023(10), Re(1)–C(1) 1.838(14), Re(1)–Br(1) 2.509(2), Re(1)–Br(2) 2.6184(11), Re(1)–Br(3) 2.5813(9), Re(1)–P(1) 2.444(2), Re(1)–P(3) 2.451(2), Re(2)–C(10) 1.929(7), Re(2)–C(20) 1.931(7), Re(2)–Br(2) 2.6289(9), Re(2)–Br(3) 2.6560(11), Re(2)–P(2) 2.407(2), Re(2)–P(4) 2.387(2); P(1)–Re(1)–P(3) 166.02(5), C(1)–Re(1)–Br(1) 91.9(4), C(1)–Re(1)–Br(3) 97.7(4), Br(1)–Re(1)–Br(2) 82.81(4), Br(3)–Re(1)–Br(2) 87.75(3), P(4)–Re(2)–P(2) 168.58(5), C(10)–Re(2)–C(20) 90.1(3), C(20)–Re(2)–Br(2) 94.7(2), C(10)–Re(2)–Br(3) 89.1(2), Br(2)–Re(2)–Br(3) 85.99(3), Re(1)–Br(2)–Re(2) 92.87(3), Re(1)–Br(3)–Re(2) 93.09(3). Note: the structure of the dirhenium cation present in the structure of (**5b**)PF₆·2CH₂Cl₂ is very similar to that of **6**, with the exception of the presence of a Re–Re single bond [3.028(2) Å]. This leads primarily to differences in the parameters for the Re₂(μ-Br)₂ unit between these two structures. The bond distances in the structure of the cation **5b** which correspond to Re(1)–Br(2), Re(1)–Br(3), Re(2)–Br(2), Re(2)–Br(3) in the structure of **6** are 2.556(2), 2.553(2), 2.599(3), and 2.604(3) Å, respectively, while the angles (°) which correspond to Re(1)–Br(2)–Re(2) and Br(2)–Re(1)–Br(3) are 71.95(9) and 109.50(9)°, respectively.

large increase in Re–Re distance which accompanies the reduction of the salts (**5b**)Y to **6** (*ca.* 0.78 Å), would be expected to reduce the ring strain in the Re₂(μ-dppm)₂ unit and allow conversion to the most stable ring conformation. Since no conformation change occurs, we can conclude that the chair conformation, as is already present in (**5b**)Y, is more stable than the boat conformation in (**5a**)Y. This is supported by the observation that solutions of (**5a**)PF₆ in dichloromethane convert slowly to the more thermodynamically stable isomer (**5b**)PF₆ (96 h at 25 °C, 24 h at reflux) in essentially quantitative yield.

Further studies are underway to examine the scope of this chemistry as it relates to other M₂(μ-dppm)₂ complexes, and the redox behaviour of the less stable boat conformer **5a**, which is typically obtained in much lower yield than **5b**.

Footnotes

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† An alternative method for the synthesis of mixtures of (**5a**)Y and (**5b**)Y is the reaction of the triply bonded, neutral complex [Re₂Br₄(μ-dppm)₂(CO)(CNR)] with a mixture of TlY (1 equiv.) and RNC (2 equiv.).

‡ *Synthesis*: **6**: a sample of (**5b**)O₃SCF₃ (120 mg, 0.0659 mmol) was mixed with [Co(η⁵-C₅H₅)₂] (12.5 mg, 0.0661 mmol) in CH₂Cl₂ (15 ml) at 25 °C. The reaction mixture, which changed from red–brown to green within 5 min, was stirred for 30 min, filtered, and the volume of the filtrate reduced to 2 ml. An equal volume of Et₂O was added to induce precipitation of yellow [Co(η⁵-C₅H₅)₂]O₃SCF₃, which was filtered off and the filtrate stripped to dryness. The green residue (**6**) was washed with Et₂O (3×5 ml) and dried; yield 94 mg (85%). Anal. Calc. for C₆₉H₆₂Br₃N₂OP₄Re₂: C, 49.59; H, 3.73; N, 1.68. Found: C, 49.21; H, 3.65; N, 1.48%. Recrystallization from CH₂Cl₂–C₂H₅CO₂Me afforded X-ray quality crystals. IR spectrum (Nujol mull): ν(CN) 2050(sh), 2012s and 1919s, (br) cm⁻¹; ν(CO) 1858vs cm⁻¹. Cyclic voltammogram (0.1 m Buⁿ₄NPF₆–CH₂Cl₂, Pt-bead electrode, ν = 200 mV s⁻¹, potentials *vs.* Ag/AgCl): $E_{\frac{1}{2}}^{\text{ox3}}$ = +1.43 V, $E_{\frac{1}{2}}^{\text{ox2}}$ = +0.65 V, $E_{\frac{1}{2}}^{\text{ox1}}$ = +0.10 V, $E_{\frac{1}{2}}^{\text{red}}$ = −0.83 V. Magnetic moment: μ_eff ≈ 1.4 μ_B (Evans method, CDCl₃).

(**5b**)PF₆: a mixture of **6** (42.0 mg, 0.0251 mmol) and [Fe(η⁵-C₅H₅)₂]PF₆ (9.0 mg, 0.027 mmol) in 10 ml of CH₂Cl₂ was stirred at 25 °C. A change from green to red–brown occurred within a few min. After a period of 1 h the reaction solution was reduced in volume to *ca.* 1 ml, and 15 ml of Et₂O added to induce precipitation of (**5b**)PF₆, which was filtered off and washed with Et₂O (3 × 5 ml); yield 41.5 mg (91%). Recrystallization from CH₂Cl₂–Prⁱ₂O afforded X-ray quality crystals. The properties of (**5b**)PF₆ were identical to those of samples obtained previously[8] as mixtures with (**5a**)PF₆.

§ *Crystal data*: **6**·CH₂Cl₂ at 203 K: space group P1̄ with *a* = 13.330(4), *b* = 16.226(3), *c* = 16.327(6) Å, α = 99.29(2), β = 90.66(3), γ = 91.59(2)°, *Z* = 2, *D*_c = 1.674 g cm⁻³. An empirical absorption correction was applied (μ = 5.434 mm⁻¹). Structure solved using the Enraf-Nonius structure determination package (MolEN) and refined through the use of SHELXL-93. Hydrogen atoms included but not refined. A cut-off *F*_o² > 2σ(*F*_o)² used for *R*-factor calculations to give *R*(*F*_o) = 0.040, *R*_w(*F*_o²) = 0.112, and GOF = 1.099. Disorder between the terminal CO and Br ligands associated with Re(1); a disorder model involving fractional CO and Br occupancies for each site was refined satisfactorily to 0.707(6) CO/0.293(6) Br for one site and 0.293(6)CO/0.707(6)Br for the other.

(**5b**)PF₆·2CH₂Cl₂ at 203 K: space group P1̄ with *a* = 13.800(5), *b* = 16.927(8), *c* = 17.556(5) Å, α = 87.05(7), β = 77.56(6), γ = 69.67(7)°, *Z* = 2, *D*_c = 1.757 g cm⁻³. An empirical absorption correction was applied (μ = 5.153 mm⁻¹). All other procedures as for the structure of **6**·CH₂Cl₂; the final residuals were *R*(*F*_o) = 0.065, *R*_w(*F*_o²) = 0.185, and GOF = 1.021. Disorder between the terminal CO and Br ligands modeled satisfactorily as 0.50/0.50 for both sites. Full structural details for **6**·CH₂Cl₂ and (**5b**)PF₆·2CH₂Cl₂ will be published later.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/393.

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