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# Mixed carbonyl–nitrile complexes of dirhenium(II). The structural characterization and reactivity of salts of the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)_n]^+$ cations (dppm = $Ph_2PCH_2PPh_2$, $n = 1$ or 2)

James Chantler, Phillip E. Fanwick, Richard A. Walton *

*Department of Chemistry, Purdue University, 1393 Brown Building, West Lafayette, IN 47907-1393, USA*

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## Abstract

The monocarbonyl complexes $Re_2X_4(\mu\text{-dppm})_2(CO)$ (X = Cl or Br) react with stoichiometric quantities of the nitriles RCN (R = Me or Ph) in the presence of TlY (Y = $PF_6$ or $O_3SCF_3$) to afford complexes of the type $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)]Y$ and $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)_2]Y$ in high yield. Crystal structure determinations on the salts $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)]O_3SCF_3$ and $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)_2]ReO_4$ have shown that the former has the unsymmetrical structure $[(MeCN)(CO)ClRe(\mu\text{-dppm})_2ReCl_2]^+$ with a Re≡Re bond (Re–Re distance 2.2881(7) Å), while the bis-nitrile complex is the edge-sharing bioctahedron $[(MeCN)ClRe(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2ReCl(NCMe)]^+$, with an all-*cis* arrangement of the μ-CO and two MeCN ligands and a Re=Re bond (Re–Re distance 2.5669(4) Å). The species $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCMe)]^+$ and $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCMe)_2]^+$ readily interconvert upon the addition or loss of an acetonitrile ligand and, along with their benzonitrile analogues, they react with halide, XylNC and acetylene to afford $Re_2X_4(\mu\text{-dppm})_2(CO)$, $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$ and $[Re_2X_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}C_2H_2)]Y$, respectively.

*Keywords:* Rhenium complexes; Carbonyl complexes; Nitrile complexes; Dirhenium(II) complexes; Crystal structures

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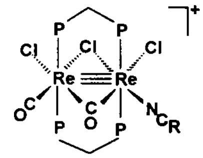
## 1. Introduction

The electron-rich triply bonded $[Re_2(\mu\text{-dppm})_2]^{4+}$ core (dppm = $Ph_2PCH_2PPh_2$) has been found to accommodate two or four organic nitrile ligands in salts of the cationic species $[Re_2Cl_3(\mu\text{-dppm})_2(NCR)_2]^+$ [1–3] and $[Re_2Cl_2(\mu\text{-dppm})_2(NCR)_4]^{2+}$ [3]. Whereas the nitrile ligands in the former monocationic species are not very labile [1], partial or complete displacement of the nitrile ligands has been encountered in the reactions of $[Re_2Cl_2(\mu\text{-dppm})_2(NCR)_4]^{2+}$ [3]. An interesting variant in this chemistry is found in the case of the stable, neutral dirhenium(II) complex $Re_2(\mu\text{-dppm})_2(NCBH_3)_4\text{-}(H_2O)_2\cdot THF$ [4], which contains four N-bound $[NCBH_3]^-$ ligands.

The coordination of organic nitriles to the $[Re_2(\mu\text{-dppm})_2]^{4+}$ core has also been encountered in the case of the mixed carbonyl–nitrile complexes $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCR)_2]PF_6$ (R = Me, Et or Ph) [5] and $[Re_2Cl_3(\mu\text{-dppm})_2(CO)_2(NCR)]PF_6$ (R = Me, Et or Ph) [6]. These complexes are most easily prepared from the monocarbonyl and dicarbonyl precursors $Re_2Cl_4(\mu\text{-dppm})_2(CO)$ [5,7] and $Re_2Cl_4(\mu\text{-dppm})_2(CO)_2$ [6,7], respectively.

While the complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)_2(NCEt)]\text{-}PF_6$ [6] has been structurally characterized (structure **I**), the structure of the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCR)_2]^+$ cations has not been definitively established, although based upon the spectroscopic and electrochemical properties of these complexes, structure **II** was favored [5] .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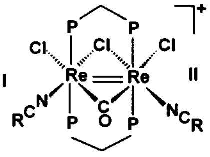
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* Corresponding author. Tel.: + 1-765-4945464; fax: + 1-765-4940239.

*E-mail address:* rawalton@purdue.edu (R.A. Walton).

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The absence of an unambiguous structure determination of a salt of one of the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCR)_2]^+$ cations has hindered the development of the chemistry of this group of complexes.

In the present report we provide details of the structure determination of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)_2]^+$, along with that of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)]^+$, and describe the reactions of salts of these two cations, and other complexes of the same type, with halide ion, xylyl isocyanide and acetylene.

## 2. Experimental

### 2.1. Starting materials and reaction procedures

The compounds $Re_2Cl_4(\mu\text{-dppm})_2(CO)$ (**1a**) [7], $Re_2Br_4(\mu\text{-dppm})_2(CO)$ (**1b**) [5], $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)_2]PF_6$ (**2a**) [5], $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCPh)_2]PF_6$ (**2b**) [5] and thallium(I) triflate [8] were prepared according to the known literature procedures. Xylyl isocyanide (2,6-dimethylphenylisocyanide, abbreviated XylNC) was purchased from Fluka Chemicals, thallium(I) hexafluorophosphate from Strem Chemicals, and acetylene from the Matheson Gas Products. All other reagents were purchased from Aldrich Chemical. Solvents were obtained from commercial sources and thoroughly deoxygenated prior to use. Syntheses were performed using standard Schlenk techniques under an atmosphere of dry nitrogen.

IR spectra (Nujol mulls), $^{31}P\{^1H\}$-NMR spectra and single scan cyclic voltammetric (CV) measurements (recorded in 0.1 M $n\text{-}Bu_4NPF_6\text{–}CH_2Cl_2$ with a scan rate of 200 mV $s^{-1}$ at a Pt-bead electrode) were determined as previously described. [9]

### 2.2. Synthesis of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(NCR)_2]PF_6$

#### 2.2.1. R = Me (3a)

Acetonitrile (5 ml) was added to a mixture of **1b** (0.200 g, 0.134 mmol) and $TlPF_6$ (0.055 g, 0.158 mmol) in acetone (5 ml). The suspension was stirred for 24 h at room temperature (r.t.). The resulting reaction mixture was filtered to remove solid TlBr. This filtrate was evaporated to dryness, extracted into dichloromethane (10 ml) and filtered to remove further quantities of TlBr. An excess of diethyl ether was then added to the extract, resulting in the precipitation of a yellow solid which was washed with an additional quantity of diethyl ether and dried in vacuo. Yield 0.165 g (75%). This product was identified based on a comparison of its electrochemical and spectroscopic properties with the analogous chloro complex [5]; a satisfactory C and H microanalysis was not obtained due to partial loss of acetonitrile ligands (see Section 3).

#### 2.2.2. R = Ph (3b)

A quantity of benzonitrile (1.5 ml) was added to a suspension of **1b** (0.200 g, 0.134 mmol) and $TlPF_6$ (0.055 g, 0.158 mmol) in acetone (5 ml). A yellow–brown solution resulted after this reaction mixture was stirred at r.t. for 24 h. A work-up procedure identical to that described in Section 2.2.1 was utilized to afford a yellow–brown solid. Yield 0.171 g (72%). Anal. Calc. for $C_{65}H_{54}Br_3F_6N_2OP_5Re_2$: C, 44.36; H, 3.09. Found: C, 44.03; H, 3.13%.

### 2.3. Synthesis of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCR)]O_3SCF_3$

#### 2.3.1. R = Me (4a)

A solution of acetonitrile (40 μl) in dichloromethane (100 ml) was prepared and a 10.0 ml aliquot (containing 0.075 mmol of acetonitrile) was added to a mixture of **1a** (0.100 g, 0.076 mmol) and $TlO_3SCF_3$ (0.030 g, 0.085 mmol). The resulting suspension was stirred at r.t. for 24 h. The reaction mixture was filtered to remove insoluble thallium(I) salts and then reduced in volume to ca. 2 ml. Subsequent addition of diethyl ether to the green filtrate caused the precipitation of a green solid which was filtered off, washed with diethyl ether and dried in vacuo. Yield 0.102 g (91%). Anal. Calc. for $C_{54}H_{47}Cl_3F_3NO_4P_4Re_2S$: C, 44.25; H, 3.23. Found: C, 44.34; H, 3.58%.

#### 2.3.2. R = Ph (4b)

A solution of benzonitrile (7.7 μl) in 5 ml of dichloromethane was combined with **1a** (0.100 g, 0.076 mmol) and $TlO_3SCF_3$ (0.030 g, 0.085 mmol), and the mixture was stirred at r.t. for 24 h. A work-up procedure similar to that described in Section 2.3.1 afforded the green title complex. Yield 0.089 g (76%). This compound was identified as $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCPh)]O_3SCF_3$ based on the similarity of its spectroscopic properties to those of **4a**.

### 2.4. Synthesis of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(NCMe)]O_3SCF_3$ (5a)

A procedure similar to that described in Section 2.3.1 was used to convert **1b** to the title complex **5a**. Yield 85%. Anal. Calc. for $C_{54}H_{47}Br_3F_3NO_4P_4Re_2S$: C, 40.56; H, 2.96. Found: C, 40.45; H, 2.84%.

### 2.5. Reactions of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCR)_2]PF_6$ with halide

#### 2.5.1. R = Me (2a) with chloride

A solution of **2a** (0.050 g, 0.033 mmol) in dichloromethane (10 ml) was treated with a stoichiometric quantity of $[Ph_4As]Cl$ (0.014 g, 0.033 mmol). The color of the solution immediately changed from yellow to orange–brown. After 30 min, the mixture was filtered and the filtrate evaporated to leave a brown solid which was identified by IR and NMR spectroscopy to be pure $Re_2Cl_4(\mu\text{-dppm})_2(CO)$ (**1a**) [7]. Yield 0.041 g (94%). The reaction course was the same when an excess of $[Ph_4As]Cl$ was used.

#### 2.5.2. R = Ph (2b) with chloride

Compound **1a** was formed in essentially quantitative yield through the use of this same procedure (see Section 2.5.1). Yield 95%.

#### 2.5.3. R = Me (2a) with iodide

The reaction of **2a** with one equivalent of $[n\text{-}Bu_4N]I$ gave a product which $^{31}P\{^1H\}$-NMR spectroscopy showed was a mixture of species of the type $Re_2Cl_{4-n}I_n(\mu\text{-dppm})_2(CO)$; each component of the mixture displayed a characteristic AA′BB′ pattern [7]. Attempts to separate the individual components were unsuccessful.

### 2.6. Reaction of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(NCMe)_2]PF_6$ (3a) with bromide

Compound **3a** converted to $Re_2Br_4(\mu\text{-dppm})_2(CO)$ (**1b**) upon reaction with one equivalent of $[n\text{-}Bu_4N]Br$. Yield 96%. The identity of the product was based upon its spectroscopic properties [5].

### 2.7. Reactions of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCR)]O_3SCF_3$ with chloride

#### 2.7.1. R = Me (4a)

Compound **1a** was formed upon reacting **4a** and $[Ph_4As]Cl$ with use of the procedure described in Section 2.5.1. Yield 89%.

#### 2.7.2. R = Ph (4b)

A similar reaction afforded **1a** following use of the above procedure. Yield 93%.

### 2.8. Reaction of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(NCMe)]O_3SCF_3$ (5a) with bromide

The product formed from the reaction of **5a** with one equivalent of $[n\text{-}Bu_4N]Br$ in dichloromethane was $Re_2Br_4(\mu\text{-dppm})_2(CO)$ (**1b**). Yield 93%.

### 2.9. Reactions of $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)_2]PF_6$ with XylNC

#### 2.9.1. X = Cl, R = Me (2a)

A solution containing **2a** (0.050 g, 0.033 mmol) and XylNC (0.009 g, 0.069 mmol) in dichloromethane (5 ml) was stirred at r.t. for 6 h. The resulting yellow precipitate was filtered off, washed with diethyl ether to remove any excess XylNC, and dried in vacuo. Yield 0.048 g (86%). This complex was identified as one of the known structural isomers of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]PF_6$, based on its IR spectrum which was identical to that previously reported [10].

A repetition of the above reaction but with the use of refluxing 1,2-dichloroethane as the solvent and a large excess of XylNC yielded the same product. Yield 82%.

#### 2.9.2. X = Cl, R = Ph (2b)

The reaction between **2b** (0.050 g, 0.031 mmol) and XylNC (0.0085 g, 0.065 mmol) in 5 ml of dichloromethane yielded this same XylNC product following the usual work-up. Yield 0.043 g (82%).

#### 2.9.3. X = Br, R = Me (3a)

A quantity of **3a** (0.050 g, 0.031 mmol) was combined with XylNC (0.0085 g, 0.065 mmol) and dichloromethane (5 ml) and the mixture was stirred at r.t. for 2 days. The brown solution was reduced in volume to ca. 2 ml and added to ca. 25 ml of diethyl ether which led to the precipitation of a yellow–brown solid. The solid was filtered off, washed with diethyl ether and dried in vacuo. Yield 0.049 g (88%). IR spectroscopy showed the product to be the same isomeric form of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]PF_6$ [10,11] as that of the analogous chloro complex which was prepared in Section 2.9.1.

### 2.10. Reactions of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)]O_3SCF_3$ (4a) with XylNC

A solution that contained **4a** (0.050 g, 0.034 mmol), XylNC (0.009 g, 0.069 mmol) and dichloromethane (5 ml) was stirred for 1 min at r.t. A large quantity of diethyl ether was then added to the solution, quenching the reaction and precipitating a green solid. This solid was filtered off and washed with diethyl ether and dried in vacuo. Yield 0.048 g (90%). The IR spectrum showed the green product to be a mixture of two compounds; the starting complex **4a** (the minority species), and $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)]O_3SCF_3$ which was identified based on a comparison of its properties with those obtained in a previous study [12].

When this same reaction was carried out for 2 days the yellow product which precipitated was shown to be the same structural isomer of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$ as that formed in the reactions described in Sections 2.9.1 and 2.9.2 which afford the analogous $[PF_6]^-$ salt. Yield 89%. This result is consistent with a previous study [10] which showed that $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)]O_3SCF_3$ is the precursor to this isomeric form of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$.

### 2.11. Reactions of [$Re_2X_3$(μ-dppm)$_2$(CO)(NCR)$_2$]$PF_6$ with $C_2H_2$

#### 2.11.1. X = Cl, R = Me (**2a**)

A sample of **2a** (0.150 g, 0.100 mmol) was dissolved in dichloromethane (15 ml) and the solution was then treated with a stream of $C_2H_2$ gas for 2 h, during which time the volume of the mixture was reduced to ca. 5 ml. The reaction mixture was then stirred at r.t. for 3 days under an atmosphere of acetylene. The resulting tan colored precipitate of [$Re_2Cl_3$(μ-dppm)$_2$(CO)(η$^2$-HCCH)]$PF_6$ was filtered off, washed with diethyl ether and dried in vacuo. Yield 0.110 g (76%). Anal. Calc. for $C_{53}H_{46}Cl_3F_6OP_5Re_2$: C, 44.01; H, 3.21. Found: C, 43.57; H, 3.15%. IR and NMR spectroscopic data showed that both nitrile ligands had been lost and that the product was identical to that of this same stoichiometry which had been prepared previously from the reaction between $Re_2Cl_4$(μ-dppm)$_2$(CO), $TlPF_6$ and acetylene [13].

#### 2.11.2. X = Cl, R = Ph (**2b**)

The same acetylene complex as described in Section 2.11.1 was prepared by the reaction of the benzonitrile complex **2b** with acetylene in dichloromethane. Yield 70%.

#### 2.11.3. X = Br, R = Me (**3a**)

The analogous bromo complex [$Re_2Br_3$(μ-dppm)$_2$(CO)(η$^2$-HCCH)]$PF_6$ was prepared by the use of a procedure similar to that described in Section 2.11.1. Yield 61%. This complex was identified as a close structural analogue of the related chloro complex on the basis of its spectroscopic and electrochemical properties [13].

Table 1
Crystallographic data for the complexes [$Re_2Cl_3$(μ-dppm)$_2$(CO)(NCMe)$_2$]$ReO_4$·MeCN (**2a**′) and [$Re_2Cl_3$(μ-dppm)$_2$(CO)(NCMe)]$O_3SCF_3$ (**4a**)

| | **2a**′ | **4a** |
|---|---|---|
| Chemical formula | $Re_3Cl_3P_4O_5N_3$-$C_{57}H_{53}$ | $Re_2Cl_3SP_4F_3O_4$-$NC_{54}H_{47}$ |
| Formula weight | 1648.93 | 1465.70 |
| Space group | $P\bar{1}$ (no. 2) | $C2/c$ (no. 15) |
| $a$ (A) | 13.0124(5) | 26.6998(15) |
| $b$ (A) | 14.5980(5) | 12.2824(6) |
| $c$ (A) | 17.1187(7) | 16.8438(10) |
| $\alpha$ (°) | 75.573(3) | 90 |
| $\beta$ (°) | 75.7886(18) | 93.457(3) |
| $\gamma$ (°) | 73.467(2) | 90 |
| $V$ (Å$^3$) | 2965.2(3) | 5513.7(9) |
| $Z$ | 2 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.847 | 1.766 |
| $\mu$ (Mo–K$_\alpha$) (mm$^{-1}$) | 6.483 | 4.799 |
| Transmission factors (min./max.) | 0.16/0.38 | 0.37/0.58 |
| $R$ [a]/$R_w$ [b] | 0.062/0.140 | 0.049/0.116 |
| Largest shift/estimated S.D. in final cycle | 0.08 | 0.00 |
| GOF | 1.006 | 0.998 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$.

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

### 2.12. Reactions of [$Re_2X_3$(μ-dppm)$_2$(CO)(NCMe)]$O_3SCF_3$ (X = Cl or Br)

The use of the monoacetonitrile complexes **4a** (X = Cl) and **5a** (X = Br) in place of [$Re_2X_3$(μ-dppm)$_2$(CO)(NCR)$_2$]$PF_6$ (see Section 2.11) afforded the complexes [$Re_2X_3$(μ-dppm)$_2$(CO)(η$^2$-HCCH)]$O_3SCF_3$ in yields of ca. 70%. The identity of these tan colored products was established on the basis of their spectroscopic and electrochemical properties (see Section 3).

### 2.13. X-ray crystallography

Suitable single crystals of **2a** (brown) and **4a** (olive-green) were obtained by the slow evaporation of a solution of **2a** in acetonitrile–toluene and the diffusion of diethyl ether into a dichloromethane solution of **4a**, respectively.

The data collections were performed at 294 ± 1 K with graphite-monochromated Mo–K$_\alpha$ radiation on a Nonius Kappa CCD diffractometer. Lorentz and polarization corrections were applied to the data. The crystallographic data are presented in Table 1.

The structures were solved using the structure solutions program PATTY in DIRDIF [14]. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with C–H = 0.95 Å and $U$(H) = 1.3 $U_{eq}$(C). They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK [15] was applied. The final refinements were performed by the use of the program SHELX-97 [16].

The crystal obtained from the recrystallization of [$Re_2Cl_3$(μ-dppm)$_2$(CO)(NCMe)$_2$]$PF_6$ (**2a**) that was selected for the X-ray structure analysis was found to be that of the [$ReO_4$]$^-$ salt (subsequently designated **2a**′), with disorder of the anion being observed in which there were two positions for the Re atom. The formation of [$ReO_4$]$^-$ is due to the degradation of a small quantity of the dirhenium complex, presumably due to its reaction with $O_2$ which diffuses into the system during the crystal growing process. This type of behavior has been observed previously during such crystal growing procedures [11,17]. The refinement gave occupancies of 0.696 and 0.304 for these two positions. This crystal was also found to contain a molecule of lattice acetonitrile.

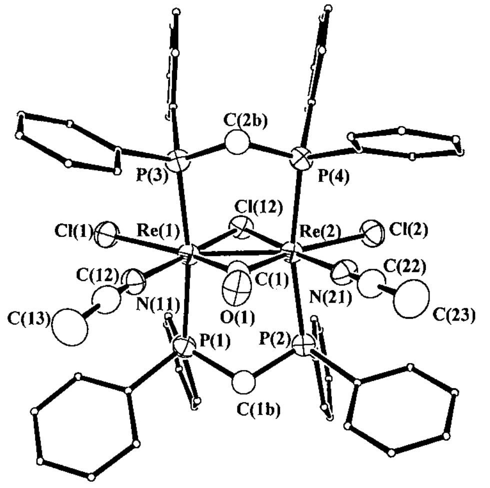


Fig. 1. ORTEP [18] representation of the structure of the dirhenium cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)_2]^+$ as present in **2a**′. The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands which are circles of arbitrary radius.

The structure refinement of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)]O_3SCF_3$ (**4a**) revealed that the molecule exhibited two types of disorder. The triflate anion was found at an inversion center, thereby resulting in disorder between the $F_3C$ and $SO_3$ fragments. In the dirhenium cation, the two rhenium atoms and a chlorine atom were found to lie on a two-fold crystallographic rotation axis. The presence of this axis imposed a chair conformation on the $Re_2(\mu\text{-dppm})_2$ unit and led to a disorder between the CO and acetonitrile ligands.

The structures were refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = 1/[\sigma^2(F_o)^2 + (AP)^2]$ with $A = 0.0877$ for **2a**′ and 0.0760 for **4a** and $P = (F_o^2 + 2F_c^2)/3$ for both structures. The highest peaks observed in the final difference Fouriers had heights of 1.95 and 3.51 e Å$^{-3}$ for **2a**′ and **4a**, respectively.

## 3. Results and discussion

### 3.1. Synthesis and structural characterization of complexes of the type $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)_2]PF_6$

In an earlier report [5] we had established that complexes of the type $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCR)_2]PF_6$ (R = Me, Et or Ph) can be prepared by the procedure shown in Eq. (1).

$$Re_2Cl_4(\mu\text{-dppm})_2(CO) + 2RCN + TlPF_6 \rightarrow [Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCR)_2]PF_6 + TlCl \quad (1)$$

In the present study we have shown that the analogous bromo complexes $[Re_2Br_3(\mu\text{-dppm})_2(CO)(NCR)_2]PF_6$ (R = Me (**3a**) or Ph (**3b**)) are prepared by a very similar procedure through the use of $Re_2Br_4(\mu\text{-dppm})_2(CO)$ and $TlPF_6$. The important spectroscopic and cyclic voltammetric properties of the complexes **3a** and **3b**, which are summarized in Table 2, are very similar to those of their chloro analogues (R = Me (**2a**), Et or Ph (**2b**)) which were previously reported [5]. These complexes show a bridging ν(CO) mode in their IR spectra, a singlet in their $^{31}P\{^1H\}$-NMR spectra, and a one-electron oxidation and two one-electron reductions in their cyclic voltammograms. These properties imply that the $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)_2]^+$ cations possess a symmetric structure. This has been confirmed by an X-ray structure determination of a crystal obtained from a solution of **2a** in acetonitrile–toluene. The crystal proved to be that of the perrhenate salt **2a**′ of composition $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)_2]ReO_4\cdot MeCN$ (see Section 2 for further details). To further confirm the identity of this crystal, a sample of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)_2]ReO_4$ was prepared by the reaction shown in Eq. (1) but with the use of $TlReO_4$ in place of $TlPF_6$. Its properties were the same as those of **2a**′, with ν(CO) and $\nu(ReO_4)$ bands at 1688(s) and 906(vs) cm$^{-1}$, respectively, in the IR spectrum, a singlet at $\delta$ −17.3 in the $^{31}P\{^1H\}$-NMR spectrum (recorded in $CDCl_3$), and a CV essentially identical to that of the analogous $[PF_6]^-$ salt **2a** [5]. An ORTEP [18] representation of the structure of the dirhenium cation present in **2a**′ is given in Fig. 1 and key structural parameters are listed in Table 3. The presence of an edge-sharing bioctahedral geometry, with an all-*cis* arrangement of the μ-CO and two acetonitrile ligands is confirmed. The Re–Re distance of 2.5669(4) Å is typical for a dirhenium complex of this type which possess a Re–Re double bond. For example, the complex cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$, which possesses the same structure as that of the cation in **2a**′, has a Re–Re distance of 2.576(1) Å [19], while in the isostructural tricarbonyl complex cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)_3]^+$ this double bond length is 2.582(1) Å [20]. The eight-membered ring formed by the Re atoms and the two bridging dppm ligands adopts a boat conformation in both the nitrile (**2a**′) and XylNC [19] structures with the $CH_2$ bridges of both dppm ligands directed towards that side of the molecule which contains the nitrile (or isocyanide) ligands. Although the XylNC ligand usually acts as a π-acceptor, while acetonitrile is a σ-donor with no significant π-accepting ability, the structures of the cation of **2a**′ and $[Re_2Cl_3(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_2]^+$ [19] are remarkably similar, and possess essentially identical Re–P, Re–Cl and Re–C bond distances. The bond angles associated with each cation are also closely matched. This same type of structure was also shown to be present in crystals of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(NCPh)_2]PF_6$ (**3b**) that had been grown

Table 2
Spectroscopic and cyclic voltammetric properties of mixed carbonyl–nitrile dirhenium(II) complexes

| Compound | Compound no. | IR spectra (cm$^{-1}$) [a] | | | $^{31}$P{$^1$H}-NMR, $\delta$ [b] | CV half-wave potentials(V) [c] | | |
|---|---|---|---|---|---|---|---|---|
| | | $\nu$(CO) | $\nu$(CN) | $\nu$(P–F) or $\nu$(S–O) | | $E_{1/2}$(ox) | $E_{1/2}$(red)(1) | $E_{1/2}$(red)(2) |
| [$Re_2Br_3$(μ-dppm)$_2$(CO)(NCMe)$_2$]$PF_6$ | **3a** | 1690(s) | 2291(vw) | 841(s) | −23.5(s) [e] | +1.05(60) | −0.43(70) | −1.40(70) |
| [$Re_2Br_3$(μ-dppm)$_2$(CO)(NCPh)$_2$]$PF_6$ | **3b** | 1690(s) | 2253(m) | 840(s) | −24.5(s) [e] | +0.99(70) | −0.36(70) | −1.26(80) |
| [$Re_2Cl_3$(μ-dppm)$_2$(CO)(NCMe)]$O_3SCF_3$ | **4a** | 2003(s) | [d] | 1258(s) | −1.8(m,br),<br>−11.6(m) [f,g] | +0.90(70) | −0.97 [i] | |
| [$Re_2Cl_3$(μ-dppm)$_2$(CO)(NCPh)]$O_3SCF_3$ | **4b** | 2006(s) | 2256(w) | 1260(s) | [h] | | [j] | |
| [$Re_2Br_3$(μ-dppm)$_2$(CO)(NCMe)]$O_3SCF_3$ | **5a** | 2000(s) | [d] | 1263(s) | −6.6(m,br),<br>−11.0(m,br) [g] | | [j] | |

[a] Recorded as Nujol mulls. Abbreviations: s = strong, m = medium, w = weak.

[b] Spectra recorded in $CDCl_3$ unless otherwise stated. Abbreviations: s = singlet, m = multiplet, br = broad.

[c] Measurements carried out on 0.1 M $n$-$Bu_4NPF_6$–$CH_2Cl_2$ solutions and referenced to the Ag/AgCl electrode with a scan rate of 200 mV/s at a Pt-bead electrode. Under these experimental conditions, $E_{1/2} = +0.47$ V vs. Ag/AgCl for the ferrocenium/ferrocene couple. $\Delta E_p(E_{p,a} - E_{p,c})$ values are given in parentheses.

[d] $\nu$(CN) mode too weak to be observed.

[e] Additional septet observed at ca. $\delta$ −144 due to the $[PF_6]^-$ anion.

[f] Spectrum recorded in $CD_2Cl_2$.

[g] AA′BB′ pattern with $\delta$ values quoted for the approximate centers of the multiplets.

[h] Spectrum not recorded.

[i] $E_{p,c}$ value.

[j] CV poorly defined.

from a solution of this complex in di-isopropyl ether–1,2-dichloroethane. However, the quality of the data did not merit full refinement of the structure. The Re–Re bond distance of 2.567 Å was essentially identical to that of **2a′**.

During our attempts to grow single crystals of the bis-acetonitrile complex **2a**, we observed that it decomposed with loss of acetonitrile. Accordingly, crystals were grown in the presence of excess acetonitrile (see Section 2). Decomposition of samples **2a** and its bromo analog **3a** also occurred in the solid state; IR spectral measurements showed that the species $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCMe)]^+$ (see Section 3.2) and $Re_2X_4(\mu\text{-dppm})_2(CO)$ were among the products of these decompositions. In contrast, the benzonitrile analogs **2b** and **3b** are much more stable to loss of the nitrile ligands.

Table 3
Important bond distances (Å) and angles (°) for the complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)_2]ReO_4\cdot MeCN$ (**2a′**) [a]

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Re(1)–Re(2) | 2.5669(4) | Re(2)–Cl(2) | 2.443(2) |
| Re(1)–C(1) | 2.028(8) | Re(2)–Cl(12) | 2.4436(19) |
| Re(1)–N(11) | 2.049(7) | Re(2)–P(2) | 2.466(2) |
| Re(1)–Cl(12) | 2.427(2) | Re(2)–P(4) | 2.470(2) |
| Re(1)–Cl(1) | 2.448(2) | C(1)–O(1) | 1.204(10) |
| Re(1)–P(3) | 2.465(2) | N(11)–C(12) | 1.107(11) |
| Re(1)–P(1) | 2.491(2) | N(21)–C(22) | 1.107(11) |
| Re(2)–C(1) | 2.026(8) | C(12)–C(13) | 1.465(14) |
| Re(2)–N(21) | 2.060(7) | C(22)–C(23) | 1.465(14) |
| *Bond angles* | | | |
| C(1)–Re(1)–N(11) | 76.9(3) | Cl(2)–Re(2)–Cl(12) | 89.19(7) |
| C(1)–Re(1)–Cl(12) | 109.2(2) | C(1)–Re(2)–P(2) | 93.2(2) |
| N(11)–Re(1)–Cl(12) | 173.08(19) | N(21)–Re(2)–P(2) | 85.61(19) |
| C(1)–Re(1)–Cl(1) | 158.8(2) | Cl(2)–Re(2)–P(2) | 85.93(7) |
| N(11)–Re(1)–Cl(1) | 82.7(2) | Cl(12)–Re(2)–P(2) | 94.14(7) |
| Cl(12)–Re(1)–Cl(1) | 91.54(8) | C(1)–Re(2)–P(4) | 91.0(2) |
| C(1)–Re(1)–P(3) | 90.1(2) | N(21)–Re(2)–P(4) | 83.51(19) |
| N(11)–Re(1)–P(3) | 89.32(19) | Cl(2)–Re(2)–P(4) | 86.29(7) |
| Cl(12)–Re(1)–P(3) | 93.87(7) | Cl(12)–Re(2)–P(4) | 96.07(7) |
| Cl(1)–Re(1)–P(3) | 83.83(7) | P(2)–Re(2)–P(4) | 167.07(7) |
| C(1)–Re(1)–P(1) | 95.1(2) | C(1)–Re(2)–Re(1) | 50.7(2) |
| N(11)–Re(1)–P(1) | 85.03(19) | N(21)–Re(2)–Re(1) | 127.3(2) |
| Cl(12)–Re(1)–P(1) | 91.06(7) | Cl(2)–Re(2)–Re(1) | 147.09(6) |
| Cl(1)–Re(1)–P(1) | 88.87(7) | Cl(12)–Re(2)–Re(1) | 57.89(5) |
| P(3)–Re(1)–P(1) | 171.29(7) | P(2)–Re(2)–Re(1) | 95.63(5) |
| C(1)–Re(1)–Re(2) | 50.7(2) | P(4)–Re(2)–Re(1) | 96.52(5) |
| N(11)–Re(1)–Re(2) | 127.44(19) | Re(1)–Cl(12)–Re(2) | 63.60(5) |
| Cl(12)–Re(1)–Re(2) | 58.51(5) | C(12)–N(11)–Re(1) | 173.9(7) |
| Cl(1)–Re(1)–Re(2) | 149.82(6) | C(22)–N(21)–Re(2) | 177.2(7) |
| C(1)–Re(2)–N(21) | 76.6(3) | O(1)–C(1)–Re(2) | 141.3(7) |
| C(1)–Re(2)–Cl(2) | 162.2(2) | O(1)–C(1)–Re(1) | 140.0(6) |
| N(21)–Re(2)–Cl(2) | 85.6(2) | Re(2)–C(1)–Re(1) | 78.6(3) |
| C(1)–Re(2)–Cl(12) | 108.6(2) | N(11)–C(12)–C(13) | 177.7(11) |
| N(21)–Re(2)–Cl(12) | 174.8(2) | N(21)–C(22)–C(23) | 179.0(12) |

[a] Numbers in parentheses are estimated S.D. values to the least significant decimal point.

### *3.2. Synthesis and structural characterization of complexes of the type $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)]O_3SCF_3$*

As mentioned in the preceding section, the bis-acetonitrile complexes **2a** and **3a** lose acetonitrile in the solid state and solution to afford, amongst other products, the mononitrile species $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCMe)]^+$. The triflate salts of these complexes and their benzonitrile analogs were prepared in high yield by use of the procedure shown in Eq. (2).

$$\begin{aligned} &Re_2X_4(\mu\text{-dppm})_2(CO) + RCN + TlO_3SCF_3 \\ &\quad \rightarrow [Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)]O_3SCF_3 + TlX \\ &\qquad (X = Cl \text{ or } Br;\ R = Me \text{ or } Ph) \end{aligned} \tag{2}$$

To maximize the yield of the complexes **4a** (X = Cl, R = Me), **4b** (X = Cl, R = Ph) and **5a** (X = Br, R = Me), it was necessary to ensure that the mole ratio of reagents was close to 1:1:1. These complexes were stable to loss of nitrile, and when the acetonitrile complexes **4a** and **5a** were exposed to an excess of acetonitrile they converted quantitatively to the bis-acetonitrile complexes $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCMe)_2]O_3SCF_3$ (as confirmed by IR spectroscopy).

The important spectroscopic and cyclic voltammetric properties of **4a**, **4b** and **5a** are summarized in Table 2. Each complex shows a strong band at ca. 2000 $cm^{-1}$ in its IR spectrum due to a terminal $\nu(CO)$ mode, and an AA′BB′ pattern in the $^{31}P\{^1H\}$-NMR spectrum, which accords with an unsymmetrical structure for the dirhenium(II) cations. Conductivity measurements on $1.0 \times 10^{-3}$ M solutions of **4a** and **5a** in acetone showed the expected behavior for 1:1 electrolytes, with $\Lambda_m$ values of 92 and 95 $\Omega^{-1}$ $cm^2$ $mol^{-1}$, respectively. These properties are consistent with the results of a single-crystal X-ray structure determination of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)]O_3SCF_3$ (**4a**). The ORTEP [18] representation of the structure of the dirhenium cation present in **4a** is shown in Fig. 2 and the important structural parameters are listed in Table 4.

The structure of **4a** closely resembles those of structurally characterized salts of the cations $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]^+$ [9] and $[Re_2Cl_3(\mu\text{-dppm})_2(NCR)_2]^+$ (R = Et, Ph, 1,2-DCB or 1,4-DCB, where DCB = dicyanobenzene) [1–3,21]. Formally, the dirhenium cation present in the structure of **4a** contains a Re–Re triple bond; this is supported by the observed Re–Re distance of 2.2881(7) Å, which is very similar to the Re–Re distance of 2.289(1) Å present in the analogous XylNC-containing cation $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]^+$ [9], and compares closely with the Re–Re bond distances in the range 2.264–2.270 Å which have been found for the $[Re_2Cl_3(\mu\text{-dppm})_2(NCR)_2]^+$ complexes [1–3,21].

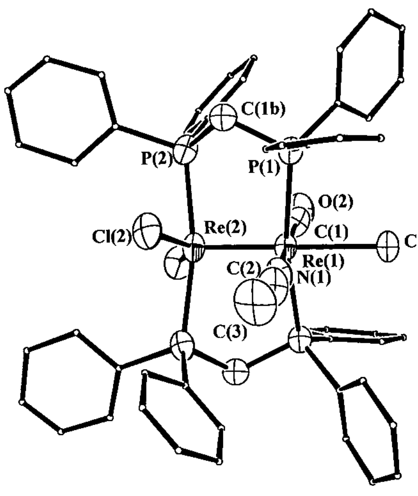


Fig. 2. ORTEP [18] representation of the structure of the dirhenium cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)]^+$ as present in **4a**. This representation is of one half the disorder involving the CO and MeCN ligands which are related by two-fold rotation axis coincident with Re(2)–Re(1)–Cl(1). 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.

Table 4
Important bond distances (Å) and angles (°) for the complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(NCMe)]O_3SCF_3$ (**4a**) [a]

| | | | |
|---|---|---|---|
| *Bond distances* [b] | | | |
| Re(1)–Re(2) | 2.2881(7) | Re(2)–Cl(2) | 2.354(2) |
| Re(1)–N(1)/C(1) | 1.994(10) | Re(2)–P(2) | 2.441(3) |
| Re(1)–P(1) | 2.490(3) | N(1)/C(1)–C(2)/O(2) | 1.146 |
| Re(1)–Cl(1) | 2.508(3) | C(2)–C(3) | 1.53(2) |
| *Bond angles* [b] | | | |
| N(1)–Re(1)–C(1) | 176.3(4) | Re(1)–Re(2)–Cl(2) | 108.72(6) |
| N(1)/C(1)–Re(1)–Re(2) | 91.9(2) | Cl(2)–Re(2)–Cl(2) | 142.56(13) |
| N(1)/C(1)–Re(1)–P(1) | 87.0(3) | Re(1)–Re(2)–P(2) | 95.82(6) |
| Re(2)–Re(1)–P(1) | 95.50(5) | Cl(2)–Re(2)–P(2) | 84.54(9) |
| N(1)/C(1)–Re(1)–P(1) | 92.7(3) | Cl(2)–Re(2)–P(2) | 91.72(9) |
| P(1)–Re(1)–P(1) | 169.01(11) | P(2)–Re(2)–P(2) | 168.36(12) |
| Re(2)–Re(1)–Cl(1) | 180.0(2) | Re(1)–N(1)/C(1)–C(2)/O(2) | 175.21 |
| P(1)–Re(1)–Cl(1) | 84.50(5) | | |
| N(1)/C(1)–Re(1)–Cl(1) | 88.1(2) | N(1)–C(2)–C(3) | 173.20 |

[a] Numbers in parentheses are estimated S.D. values to the least significant decimal point.

[b] As a consequence of the disorder between the terminal CO and MeCN ligands, the atoms labeled N(1) and C(2) occupy equivalent positions to those labeled C(1) and O(2), respectively. Accordingly these atoms are labeled as N(1)/C(1) and C(2)/O(2) in this table.

The Re–Cl bond distance Re(1)–Cl(1) is 2.508(3) Å and ca. 0.15 Å longer than the identical pair of equatorial Re–Cl bonds (Re(2)–Cl(2) = 2.354(2) Å). This difference reflects both the difference in coordination numbers at the two Re centers (Re(2) is the ligand deficient center), and the fact that Re(1)–Cl(1) is colinear with the Re≡Re bond and therefore subject to a *trans* lengthening effect. Similar differences between these two types of Re–Cl bond lengths are found in the structures of $[Re_2Cl_3(\mu\text{-dppm})_2(NCR)_2]^+$ [1–3,21]. The torsional angles P(1)–Re(1)–Re(2)–P(2) and N(1)–Re(1)–Re(2)–Cl(2) have values of 27.7 and 28.6°, respectively, which reflects the presence of a partially staggered rotational geometry. This accords with similar behavior in the case of $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]O_3SCF_3$ [9] and salts of the $[Re_2Cl_3(\mu\text{-dppm})_2(NCR)_2]^+$ cations [1–3,21].

A comparison of the spectroscopic and electrochemical properties of **4a** (Table 2) with those of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)]O_3SCF_3$ [22], which presumably has the same structure as its bromo analog [9], show striking similarities, implying that these chloro complexes are structurally very similar. The difference between the σ-donor/π-acceptor properties of MeCN and XylNC, leads to the $\nu$(CO) mode being shifted by about 30 $cm^{-1}$ to higher frequency in the case of the XylNC complex in which the degree of Re → π*(CO) back-bonding is decreased (relative to that in **4a**). The CV of **4a**, which shows processes at $E_{1/2}(ox) = +0.90$ V and $E_{p,c} = -0.97$ V vs. Ag/AgCl, compares closely with that for $[Re_2Cl_3(\mu\text{-dppm})_2)(CO)(CNXyl)]O_3SCF_3$ [22], which has $E_{1/2}(ox) = +0.96$ V and $E_{p,c} = -0.89$ V vs. Ag/AgCl. For the bis-nitrile complexes $[Re_2Cl_3(\mu\text{-dppm})_2(NCR)_2]^+$, the $E_{1/2}$ values for these two processes are ca. + 0.6 and − 1.3 V, respectively [1–3,21]. This shift of ca. + 0.3 V to more negative potentials reflects the absence of a strongly π-back bonding CO ligand and therefore a decrease in the relative positive charge at the dirhenium core.

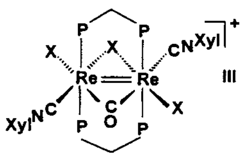
### 3.3. Reactivities of the complexes $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)_2]PF_6$ and $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)]O_3SCF_3$ (X = Cl or Br; R = Me or Ph)

We described in Sections 3.1 and 3.2 that the bis-acetonitrile complexes **2a** and **3a** readily lose an acetonitrile ligand to afford **4a** and **5a**, respectively, and that the latter react with an excess of acetonitrile to regenerate **2a** and **3a** (Eq. (3)).

$$[Re_2X_3(\mu\text{-dppm})_2(CO)(NCMe)]^+ + MeCN \rightleftarrows [Re_2X_3(\mu\text{-dppm})_2(CO)(NCMe)_2]^+ \qquad (3)$$

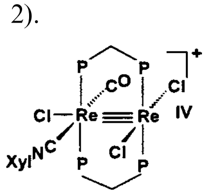
When any of these 1:2 and 1:1 acetonitrile complexes (**2a**–**5a**), or their benzonitrile analogues **2b**, **3b** or **4b**, are treated with one equivalent of $[Ph_4As]Cl$ or $[n\text{-}Bu_4N]Br$, the neutral monocarbonyl starting materials $Re_2X_4(\mu\text{-dppm})_2(CO)$ (X = Cl (**1a**) or Br(**1b**)) are formed in essentially quantitative yield. This clearly demonstrates the lability of the nitrile ligands in these complexes and, therefore, their potential use as precursors to other dirhenium(II) complexes.

In accord with the preceding observations, the reactions of $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)_2]PF_6$, where R = Me when X = Cl or Br and R = Ph when X = Cl, with xylyl isocyanide (XylNC) in dichloromethane were found to afford complexes of the type $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]PF_6$ in which the dirhenium cation was shown to have the edge-sharing bioctahedral structure **III** [10,11].



III

This is one of several isomeric forms known for these cations [23]. A similar reaction course ensued when the monoacetonitrile complex **4a** was reacted with two equivalents of XylNC over a period of two days. However, in this case, the formation of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$, in which the cation also possessed structure **III**, proceeded through the intermediacy of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)]O_3SCF_3$. The dirhenium cation in this complex has the same structure (**IV**), as that of the acetonitrile complex **4a** from which it is derived (Fig. 2).



IV

This XylNC-containing cation, and its bromo analogue, have been isolated and characterized previously [9,22], and are known [10] to be intermediates in the formation of the isomer of $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ which has structure **III**. The high yields (> 80%) achieved in the present reactions from convenient starting materials offer advantages over the previous synthetic procedure [9,22].

Another illustration of the usefulness of these mixed CO–nitrile complexes as synthons are the conversions of **2a**, **2b**, **3a**, **4a** and **5a** to $[Re_2X_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}C_2H_2)]Y$ ($Y = PF_6$ or $O_3SCF_3$) in high yields when these complexes are reacted with acetylene. This procedure provides an alternative route to that in which $Re_2X_4(\mu\text{-dppm})_2(CO)$ (X = Cl or Br) are reacted with $C_2H_2$ in the presence of TlY [13].

## 4. Conclusions

The present study has firmly established the structures of complexes of the types $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)_2]Y$ and $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)]Y$ ($Y = PF_6$ or $O_3SCF_3$) and the ease with which these complexes can be interconverted through the loss or addition of a RCN ligand. In contrast to the lack of ligand lability in the case of complexes of the type $[Re_2X_3(\mu\text{-dppm})_2(NCR)_2]Y$ [1–3], these mixed CO–nitrile complexes show reactivity towards halide ion, XylNC and acetylene to afford the complexes $Re_2X_4(\mu\text{-dppm})_2(CO)$, $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$ and $[Re_2X_3(\mu\text{-dppm})_2(CO)(\eta^2\text{-}C_2H_2)]Y$, respectively, with complete loss of nitrile. Similar instances of nitrile lability have been encountered previously in the case of salts of dirhenium cations of the types $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNR)(NCR)]^+$ [22–24] and $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCMe)]^+$ [25] towards CO and RNC ligands. Further studies of the reactivities of $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)_2]Y$ and $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCR)]Y$ are underway.

## 5. Supplementary material

Full details for the crystal data and data collection parameters, atomic positional parameters, anisotropic thermal parameters, bond distances and bond angles for **2a′** and **4a** have been deposited with the Cambridge Crystallographic Data Center (deposit numbers 145479 and 145480). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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