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Syntheses, characterisation and some ligand substitution chemistry of Ru(II)–diphosphine triflate complexes †

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The complexes *cis*-[Ru(OTf)$_2$(L–L)$_2$] {L–L = $Ph_2PCH_2PPh_2$, dppm (**1a**); $(Ph_2P)_2C{=}CH_2$, dppen (**1b**)} react with halide ions, with retention of stereochemistry, to give *cis*-[RuX_2(L–L)$_2$] {L–L = dppm, dppen; X = Br (**2**), I (**3**)}. With MeCN, **1a**, **b** yield *cis*-[Ru(L–L)$_2$(MeCN)$_2$](OTf)$_2$ (**4a**, **b**), but *cis*-[Ru(OTf)$_2$(dppe)$_2$] (**1c**; dppe = $Ph_2PCH_2CH_2PPh_2$) reacts to give *trans*-[Ru(dppe)$_2$(MeCN)$_2$](OTf)$_2$ (**4c**). Whereas **1a** reacts readily with 1,2-diaminoethane (en) to give [Ru(dppm)$_2$(en)](OTf)$_2$ (**5a**) cleanly, **1a**, **b** only react under forcing conditions with 2,2′-bipyridine (bipy) to provide [Ru(L–L)$_2$(bipy)](OTf)$_2$ (**6a**, **b**); in addition to **6a** (L–L = dppm), some [Ru(dppm)(bipy)$_2$](OTf)$_2$ is also formed *via* diphosphine displacement. Attempts to obtain [Ru(dppe)$_2$(bipy)](OTf)$_2$ (**6c**) by this route were unsuccessful. The outcome of reactions of **1a**, **b** with phosphorus donors is governed by steric considerations. For example, while reaction of **1a**, **b** with PMe_3 failed to provide [Ru(L–L)$_2$(PMe_3)$_2$](OTf)$_2$ complexes, $P(OMe)_3$ reacted readily to yield [Ru(L–L)$_2${$P(OMe)_3$}$_2$](OTf)$_2$ (**7a**, **b**). The reaction of **1a** with one equivalent of $Me_2PCH_2CH_2PMe_2$ (dmpe) gave [Ru(dppm)$_2$(dmpe)](OTf)$_2$ (**8a**) and [Ru(dppm)(dmpe)$_2$](OTf)$_2$ (**9a**) in a 5 : 1 ratio, although [Ru(dppen)$_2$(dmpe)](OTf)$_2$ (**8b**) was the only product from an analogous reaction with **1b**. However, with one equivalent of $Me_2PCH_2PMe_2$ (dmpm), **1a** reacted to form exclusively [Ru(dppm)(dmpm)$_2$](OTf)$_2$ (**10a**). The complexes have been characterised by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, FAB mass spectrometry, and X-ray crystallography in the case of **4a** and **7b**.

We recently showed that homoleptic Ru(II)–phosphine complexes of the form [Ru(L–L)$_3$]$^{2+}$ can be prepared from [Ru(dmf)$_6$](OTf)$_3$ and excess L–L in EtOH when L–L is small {*e.g.* $Me_2P(CH_2)_nPMe_2$, n = 1, 2; $Et_2PCH_2CH_2PEt_2$; 1,2-$(AsMe_2)_2C_6H_4$}, but not for bulkier aryldiphosphines.[1,2] Motivated by the desire to probe further the steric control over the outcome of these reactions, as well as by an interest in the origin of the unusual redox properties of the homoleptic complexes,[1,2] we wished to study the mixed-ligand complexes [Ru(L–L)$_2$(L′)$_2$]$^{2+}$, [Ru(L–L)$_2$(L′–L′)]$^{2+}$ (L–L = aryldiphosphine; L′ = trialkylphosphine or phosphite; L′–L′ = alkyldiphosphine), and [Ru(L–L)$_2$(diamine)]$^{2+}$.

An obvious possible route to such complexes is silver-mediated halide abstraction from the appropriate *trans*-[$RuCl_2$(L–L)$_2$] complex, followed by addition of the requisite neutral or anionic ligand. Whereas treatment of Ru(II)–phosphine complexes with Ag(I) or Tl(I) salts often results in the coordination of solvent to Ru(II)[3] or the formation of Ru–Cl–M adducts,[4–6] we found that prolonged treatment of *trans*-[$RuCl_2$(L–L)$_2$] {L–L = $Ph_2PCH_2PPh_2$ (dppm), $(Ph_2P)_2C{=}CH_2$ (dppen), $Ph_2PCH_2CH_2PPh_2$ (dppe)} with 2 equiv. of AgOTf (OTf = $CF_3SO_3^-$) in 1,2-dichloroethane (DCE) under anhydrous conditions gave *cis*-[Ru(OTf)$_2$(L–L)$_2$] (**1a**–**c**, respectively).[7]

In this paper, we report the outcome of the reactions of these triflate complexes with a range of neutral and anionic mono- and bidentate ligands, and we show that whereas some of the reactions cleanly give triflate ligand substitution, in other cases, unexpected products resulting from both triflate and aryldiphosphine ligand substitution are formed.

† Electronic supplementary information (ESI) available: synthesis and characterisation of **1a**–**c**, and X-ray crystallographic data and crystal structures of the adventitious aquo complexes *cis*-[Ru(OTf)(H_2O)(dppm)$_2$]OTf **S2a** and *cis*-[Ru(H_2O)$_2$(dppm)$_2$](OTf)$_2$ **S2b**. See http://www.rsc.org/suppdata/dt/b3/b306552a/

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Results and discussion

Metathesis of triflate complexes with other anionic ligands

Prior to investigating the reactions of **1a**–**c** with neutral ligands, we investigated the metatheses of triflate with halide ions. It was anticipated this would afford a mild route to heavier halide complexes of Ru(II) with these diphosphine ligands, which avoids the possibility of incomplete reaction arising in attempts at metathesis from [$RuCl_2$(L–L)$_2$][8] and also avoids the rather tedious preparation of halide-free starting materials, such as [Ru(H_2O)$_6$]$^{2+}$ [9] or [Ru(dmf)$_6$]$^{3+}$.[8] We were also interested in examining the stereochemical outcome of these ligand substitutions.

Treatment of solutions of **1a** or **1b** (prepared *in situ* from *trans*-[$RuCl_2$(dppm)$_2$] or *trans*-[$RuCl_2$(dppen)$_2$] and AgOTf) in DCE with Et_4NBr gave *cis*-[$RuBr_2$(dppm)$_2$] (**2a**) and *cis*-[$RuBr_2$(dppen)$_2$] (**2b**). Reaction with Et_4NI required more forcing conditions; treatment of **1a**, **b** with Et_4NI at room temperature gave olive green solutions, which only became orange on reflux. The complexes *cis*-[RuI_2(dppm)$_2$] (**3a**) and *cis*-[RuI_2(dppen)$_2$] (**3b**) were isolated on workup. It is possible that the green colour is due to a five-coordinate intermediate, [RuI(L–L)$_2$]$^+$.[10]

Sullivan and Meyer reported that solutions of *cis*-[$RuCl_2$(dppm)$_2$] were photochemically converted to *trans*-[$RuCl_2$(dppm)$_2$] over several days.[11] When $CDCl_3$ solutions of **2a**, **b** and **3a**, **b** were left in ambient light for up to one week, partial conversion to the *trans* isomer was observed ($^{31}P\{^1H\}$ NMR monitoring), but these reactions did not go to completion.

Reactions of 1 with acetonitrile

Nitriles represent a class of sterically undemanding, neutral monodentate ligands, and again, we wished to examine the stereochemical outcome of triflate metathesis with such ligands.

Table 1 Crystallographic data and details of data collection and structure refinement for complexes **4a** and **7b**

	4a	**7b**
Formula	$C_{54}H_{50}B_2F_8N_2P_4Ru$	$C_{61}H_{64}Cl_2F_6O_{12}P_6RuS_2$
M/g mol^{-1}	1125.63	1525.16
T/K	293(2)	213(2)
Crystal system; space group	Monoclinic; C_c	Monoclinic; $P2_1/n$
a/Å; α/°	13.7375(17); 90.00	19.540(2); 90.00
b/Å; β/°	19.564(2); 95.270(14)	13.8934(14); 106.126(13)
c/Å; γ/°	20.201(2); 90.00	25.426(3); 90.00
V/Å^3; Z	5406.5(11)	6630.8(13); 4
D_c/g mol^{-1}	1.383	1.519
F(000); μ(Mo-Kα)/mm^{-1}	2296; 0.409	3120; 0.528
θ Range/°	2.08–22.48	1.82–22.49
hkl Range	−14/14, −21/21, −21/21	−20/21, −14/14, −27/27
Unique diffractions[a]	6982	8644
Observed reflections	14445	31220
Parameters	644	828
R; wR (observed diffractions)[b]	0.0341; 0.0523	0.0658; 0.1004
R; wR (all data)[b]	0.0700; 0.0604	0.1167; 0.1311
GOF (all data)	0.628	0.869
Residual electron density/e Å^{-3}	0.36, −0.34	0.7, −0.5

[a] Diffractions with $F^2 > 2\sigma(F^2)$. [b] Weighting scheme for **4a**: $w = 1/[\sigma^2(F_o^2)]$; for **7b**: $w = 1/[\sigma^2(F_o^2) + (0.0373P)^2]$, $P = (F_o^2 + 2F_c^2)/3$. $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}]^{1/2}$. [c] GOF $= [\Sigma\{w(F_o^2 - F_c^2)^2\}/(N_{diffrs} - N_{params})]^{1/2}$.

Treatment of **1a**, **b** {prepared *in situ* from *trans*-$[RuCl_2(L–L)_2]$ and AgOTf} with excess acetonitrile in hot DCE rapidly gave *cis*-$[Ru(L–L)_2(MeCN)_2](OTf)_2$ {L–L = dppm (**4a**),[12] dppen (**4b**)}, isolated as colourless crystalline solids after recrystallisation from CH_2Cl_2–hexanes. Interestingly, the same reaction conditions for **1c** gave exclusively *trans*-$[Ru(dppe)_2(MeCN)_2](OTf)_2$ (**4c**), revealed by the singlet at +45 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Presumably, the slightly greater steric demands of the five-membered chelate rings favour attainment of the *trans* geometry with this ligand, as was found for $[Ru(dmpe)_2(MeCN)_2](BPh_4)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$), prepared by refluxing *trans*-$[RuCl_2(dmpe)_2]$ with $NaBPh_4$ in MeCN.[13] Complexes **4a**–**c** were also readily formed (as tetrafluoroborate salts) on treatment of the appropriate *trans*-$[RuCl_2(L–L)_2]$ complex with two equivalents of $AgBF_4$ in MeCN–DCE.

The crystal structure of **4a** (BF_4 salt) was determined. This is evidently the first crystal structure of a $[Ru(diphosphine)_2(RCN)_2]^{2+}$ salt. Details of the structure determination and refinement are summarised in Table 1, and significant bond lengths and angles are listed in Table 2. The molecular structure is illustrated in Fig. 1. Bond lengths and angles within the Ru(II)$(dppm)_2$ unit are similar to those in other complexes containing this moiety, and they have already been extensively discussed.[14,15] The Ru–$NCCH_3$ bond lengths (Table 2) are longer than those found in *trans*, *mer*-$[RuCl(PPh_3)_2(CH_3CN)_3]^+$ (2.004, 1.997, 1.969 Å), as might be expected, since a phosphine is a better π-acceptor than a nitrile. However, they are slightly shorter than in some other complexes in which MeCN is also *trans* to an arylphosphine, *e.g.* in *fac*-$[Ru\{Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}(MeCN)_3]^{2+}$ {2.13(1) Å}[16] or $[Ru(Ph_2P\{CH_2\}_4PPh_2)(MeCN)_4]^{2+}$ {2.108(2), 2.120(2) Å}.[17] When MeCN is *trans* to a better π-acceptor than an arylphosphine, the Ru–N bond is longer, such as in *cis*, *fac*-$[\{Ru(P[OMe]_3)_2(MeCN)_3\}_2(\mu\text{-}cyclo\text{-}(S_2CH_2CMe{=}CMeCH_2)]$, for example, in which the Ru–N–*trans*–P bond lengths are 2.138 and 2.114 Å.[18]

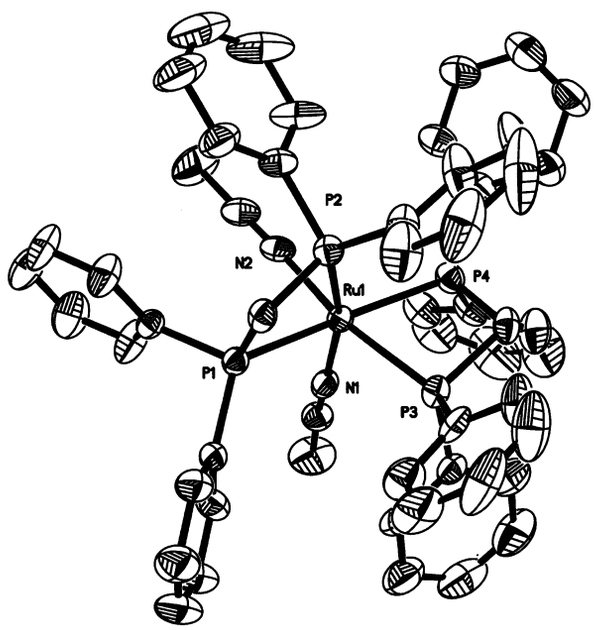

Fig. 1 Molecular structure of the cation of *cis*-$[Ru(dppm)_2(MeCN)_2](BF_4)_2$ (**4a**). Ellipsoids drawn at the 50% probability level.

Reactions of 1 with diamine and diimine ligands

Treatment of **1a**, generated *in situ* from $[RuCl_2(dppm)_2]$ and AgOTf, with a small excess of 1,2-diaminoethane (en) at room temperature yielded white $[Ru(dppm)_2(en)](OTf)_2$ (**5**) after recrystallisation from CH_2Cl_2–hexanes. This was characterised from its $^{31}P\{^1H\}$ NMR spectrum (AA′XX′) and FAB^+ mass spectrum (highest mass peak 1079 a.m.u., due to $[M - OTf]^+$). Reaction of **1b** with en gave a mixture of products, evidently due to some reaction of the diamine with the coordinated $(Ph_2P)_2C{=}CH_2$ ligand,[15] so this was not pursued further.

The photophysical and redox properties of mixed-ligand complexes of Ru(II) with 2,2′-bipyridine (bipy) and related ligands continue to be a topic of great interest.[19–22] Although several $[Ru(diphosphine)(bipy)_2]^{2+}$ complexes have been reported,[19,23,24] the sole $[Ru(diphosphine)_2(bipy)]^{2+}$ complex which is claimed to have been prepared is $[Ru(dppe)_2(bipy)](PF_6)_2$,[25] reportedly the product of refluxing $[RuCl_3(bipy)]$ with excess dppe in water for two weeks, followed by anion metathesis and chromatography. The product was characterised only from microanalytical data.

Earlier, we reported that treatment of **1a** or **1b** in DCE with bipy at room temperature yielded red solutions, but pure $[Ru(L–L)_2(bipy)]^{2+}$ complexes could not be isolated.[7] We have since found that substitution does take place, but only under more forcing conditions. Reaction of **1a** with a small excess of bipy in DCE under reflux for 24 h gave a yellow solid after recrystallisation (MeOH–Et_2O). The FAB^+ mass spectrum of

Table 2 Significant bond lengths (Å) and angles (°) for complex **4a** (BF_4 salt)

Ru(1)–P(1)	2.3661(18)	Ru(1)–P(2)	2.3230(19)
Ru(1)–P(3)	2.3372(18)	Ru(1)–P(4)	2.371(2)
Ru(1)–N(1)	2.058(6)	Ru(1)–N(2)	2.053(7)
N(1)–C(1)	1.152(8)	N(2)–C(3)	1.164(9)
C(1)–C(2)	1.466(10)	C(3)–C(4)	1.437(11)
P(1)–Ru(1)–P(2)	70.65(6)	P(3)–Ru(1)–P(4)	70.49(7)
P(1)–C(5)–P(2)	96.2(3)	P(3)–C(30)–P(4)	95.1(3)
N(1)–Ru(1)–N(2)	86.5(2)	P(3)–Ru(1)–N(2)	166.55(16)
P(2)–Ru(1)–N(1)	164.84(16)	Ru(1)–N(1)–C(1)	177.7(6)
Ru(1)–N(2)–C(3)	176.7(6)	N(1)–C(1)–C(2)	176.9(9)
N(2)–C(3)–C(4)	175.7(9)	P(1)–Ru(1)–P(4)	170.57(7)

this shows a cluster of peaks centred at 1175 a.m.u., correct for the $[M - OTf]^+$ ion from $[Ru(dppm)_2(bipy)](OTf)_2$ (**6a**), but also a weaker cluster of peaks centred at 947 a.m.u., correct for $\{[Ru(dppm)(bipy)_2](OTf)\}^+$. The $^{31}P\{^1H\}$ NMR spectrum shows two triplets, assigned to the AA′XX′ spin system of **6a**, and a weaker singlet at +0.5 ppm, assigned to $[Ru(dppm)(bipy)_2](OTf)_2$ on the basis of the FAB^+ results. By integration, 14% of the product is $[Ru(dppm)(bipy)_2](OTf)_2$. The microanalytical data further support this conclusion, being deficient in C, but high in N, for pure **6a**. The calculated figures in the Experimental section take this composition, and the fact that the ^1H NMR spectrum shows the presence of CH_2Cl_2 of solvation, into account. Apart from this, the ^1H NMR spectrum was of little use in structure assignment, since the product was only soluble to a significant degree in CD_3OD, and even in this solvent, the peaks were broad and the signal/noise ratio was not high.

Similar treatment of **1b** with bipy did give $[Ru(dppen)_2(bipy)](OTf)_2$ (**6b**) as a pure yellow solid after recrystallisation. The FAB^+ mass spectrum of **6b** shows a cluster of peaks at 1199, with the correct isotope pattern, due to $[M - OTf]^+$, and the absence of any peaks attributable to $[Ru(dppen)(bipy)_2](OTf)_2$. The $^{31}P\{^1H\}$ spectrum shows only two equally intense, broad resonances at 9.2 and 0.6 ppm, as expected for a *cis*-$[Ru(dppen)_2]$ moiety,[15] and no peak at 18.2 ppm, the literature value for $[Ru(dppen)(bipy)_2]^{2+}$.[19] Interestingly, in spite of the previous report of the preparation of $[Ru(bipy)(dppe)_2](PF_6)_2$,[25] our attempts to make $[Ru(dppe)_2(bipy)](OTf)_2$ (**6c**) from **1c** under the same conditions as **6a**, **b** failed.

Reaction of 1 with phosphorus ligands

In order to confirm that steric effects were responsible for our earlier failure to prepare homoleptic Ru(II)–diphosphine complexes with aryldiphosphines,[24] we have explored the reaction of **1a**–**c** with other phosphine and phosphite ligands. Treatment of **1a** or **1b** with $P(OMe)_3$ readily gave colourless $[Ru(L–L)_2(P\{OMe\}_3)_2](OTf)_2$ (**7a** and **7b**). The $^{31}P\{^1H\}$ NMR spectra of **7a**, **b** show three, equally intense, complex multiplets, with one of these in the chemical shift range expected for coordinated phosphites. The latter resonance, and one of the two phosphine resonances, share large $^2J_{PP}$ (**7a**, 297;**7b**, 320 Hz) values, typical for P–*trans*–P at Ru(II), consistent with retention of *cis* stereochemistry. This was confirmed for **7b** by an X-ray crystal structure determination.

Crystallographic data and refinement details for **7b** are summarised in Table 1, and significant bond lengths and angles are listed in Table 3. The structure is illustrated in Fig. 2. This is the first X-ray crystal structure of a Ru(II) complex with six P donor ligands. The geometry is clearly much distorted from octahedral by the steric requirements of the ligands, and this lends support to our conclusion, based on EXAFS evidence, that $[Ru(dmpe)_3]^{2+}$ is sterically crowded.[24] It appears that the phosphite ligands are quite strongly bound to Ru(II) since, although the Ru(II)–$P(OMe)_3$ distances {2.303(2), 2.325(2) Å} are quite long, they are within the range previously found

Table 3 Significant bond lengths (Å) and angles (°) for complex **7b**

Ru(1)–P(1)	2.409(2)	Ru(1)–P(2)	2.4782(19)
Ru(1)–P(3)	2.4764(19)	Ru(1)–P(4)	2.396(2)
Ru(1)–P(5)	2.303(2)	Ru(1)–P(6)	2.325(2)
P(1)–C(13)	1.809(7)	P(2)–C(13)	1.826(8)
P(3)–C(39)	1.832(8)	P(4)–C(39)	1.820(7)
C(13)–C(14)	1.329(10)	C(39)–C(40)	1.316(11)
P(1)–Ru(1)–P(2)	70.55(7)	P(3)–Ru(1)–P(4)	70.57(7)
P(5)–Ru(1)–P(6)	84.96(7)	P(1)–Ru(1)–P(6)	103.36(8)
P(2)–Ru(1)–P(3)	101.57(6)	P(4)–Ru(1)–P(5)	101.73(7)
P(1)–Ru(1)–P(4)	166.05(7)	P(2)–Ru(1)–P(5)	156.85(7)
P(3)–Ru(1)–P(6)	156.19(7)	Ru(1)–P(1)–C(13)	93.5(3)
P(1)–C(13)–P(2)	101.9(4)	Ru(1)–P(2)–C(13)	90.8(2)
Ru(1)–P(3)–C(39)	94.0(3)	Ru(1)–P(4)–C(39)	94.0(3)

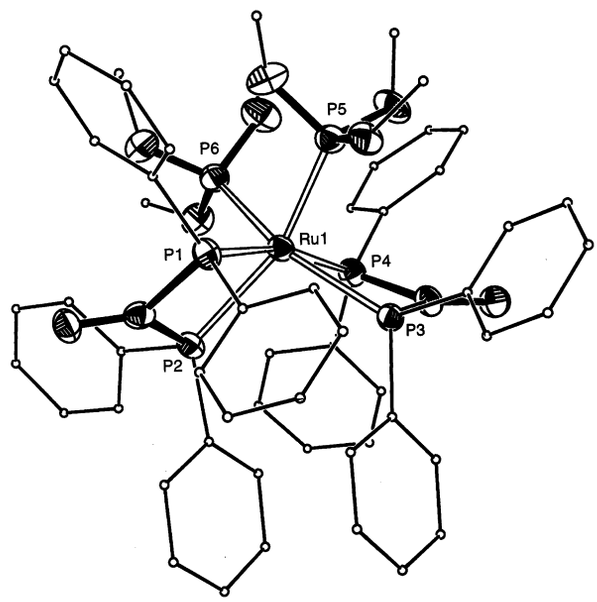

Fig. 2 Molecular structure of the cation of *cis*-$[Ru(dppen)_2(P\{OMe\}_3)_2](OTf)_2$ (**7b**). Ellipsoids drawn at the 50% probability level.

for Ru(II)–$P(OMe)_3$ distances. For example, in *cis*, *cis*-[{Ru$(P[OMe]_3)_4\}_2WS_4$], the Ru–P bonds range from 2.271(5) to 2.368(7) Å {mean: 2.316(7) Å}.[26] Other examples include *trans*, *mer*-$[RuCl_2\{Me_2P(CH_2)_3P(Me)(CH_2)_3PMe_2\}\{P(OMe)_3\}]$ {2.280(5) Å},[27] *fac*-$[Ru(\eta^3\text{-}S_5)\{P(OMe)_3\}_3]$ {2.248(5), 2.236(6), 2.233(6) Å}[28] and *trans*-$[Ru(Me_2C{=}NNH_2)_2\{P(OMe)_3\}_4](BPh_4)_2$ {2.35(1) Å}.[29] In contrast, the two PPh_2 ligands *trans* to the strong π-acceptor phosphite ligands in **7b** have by far the longest Ru(II)–P bonds {2.4782(19) and 2.4764(19) Å} yet found for four-membered chelate diphosphines of this type (there are 40 examples in the Cambridge Crystallographic Database). For comparison, the Ru(II)–(η^2-Ph_2P–C–PPh_2) distances of *trans*-$[RuCl_2(dppen)_2]$ {2.344(1), 2.331(1) Å}[30] and *trans*-$[RuCl_2(dppm)_2]$ {2.340(1), 2.367(1) Å} are typical;[14] the longest bonds observed previously have been found in cases where there are bulky and/or strongly bonded co-ligands {*e.g.* *trans*-$[RuCl(dppm)_2(CN^tBu)]PF_6$; 2.360(2), 2.373(2), 2.394(2) Å,[12] *trans*-[RuCl{=C=C=C(*o*-C_6H_4)CPh=CH}$(dppm)_2$]PF_6; mean 2.375(8) Å[31]}. Moreover, it is clear that the two dppen ligands in **7b** are distorted away from ideal octahedral coordination by the binding of the two $P(OMe)_3$ ligands. The mutually *trans* PPh_2 donors have a P–Ru–P angle of 166.05(7)°, bent away from the phosphites. A combination of steric effects and the strained four-membered chelate rings of the dppen ligands causes the plane containing the Ru(II) and the phosphite donors to be twisted considerably with respect to the plane containing the Ru(II) and the PPh_2 donors *trans* to the phosphites {inter-planar angle 30.45(8)°}.

In contrast to the reactions with $P(OMe)_3$, treatment of **1a**, **b** with PMe_3 gave dark red solutions with extremely complex

$^{31}P\{^1H\}$ NMR spectra, and no $[Ru(L–L)_2(PMe_3)_2]^{2+}$ species could be isolated. The dark red colour is characteristic of five-coordinate Ru(II)–phosphine coordination, and it is likely that, although PMe_3 is a better σ-donor than $P(OMe)_3$, its somewhat larger cone angle {PMe_3, 118°; $P(OMe)_3$, 107°} precludes six-coordination. This nicely illustrates the steric limits of $Ru(II)P_6$ coordination with these ligands.

We therefore attempted to use the small, chelating diphosphines dmpm (dmpm = $Me_2PCH_2PMe_2$) and dmpe to prepare mixed complexes $[Ru(L–L)_2(L'–L')]^{2+}$. Treatment of **1a** with one equivalent of dmpe gave a white product (expected for a $Ru(II)P_6$ complex) after workup. The FAB^+ mass spectrum of this shows highest mass peaks clustered around 1169 a.m.u., with the isotope pattern expected for the $[M - OTf]^+$ peak of $[Ru(dppm)_2(dmpe)](OTf)_2$ (**8a**). However, it also showed a weaker cluster of peaks at 935 a.m.u. While this is not attributable to any likely fragmentation of **8a**, it is consistent with the $[M - OTf]^+$ peak of $[Ru(dppm)(dmpe)_2](OTf)_2$ (**9a**). The microanalyses are consistent with a mixture of **8a** and **9a**, as are both the $^{31}P\{^1H\}$ and ^1H NMR spectra. The $^{31}P\{^1H\}$ spectrum, although rendered complicated by second-order coupling, clearly shows one major and one minor product, in approximately a 5 : 1 ratio. The major product, **8a**, gives rise to three resonances of equal intensity: a complex multiplet at +28.7 ppm with one large J_{PP} (190 Hz), assigned to the dmpe, and two overlapping resonances, one at −26.2 ppm with one large J_{PP} (190 Hz), assigned to the two dppm Ps that are *trans* to the dmpe ligand, and the other at −25.5 ppm, assigned to the two dppm Ps *cis* to dmpe. The minor product, **9a**, also produces three resonances of equal intensity, one at +33.5 ppm with one large J_{PP} (200 Hz), due to the dmpe Ps that are *trans* to dppm, another at +27.2 ppm, due to the dmpe Ps *cis* to dppm, and a third at −23.9 ppm with one large J_{PP} (200 Hz), which is assigned to the single dppm ligand.

This conclusion is supported by the ^1H NMR spectrum, recorded in CD_3OD. In particular, the ratio of aromatic protons to dmpe protons is correct for the 5 : 1 **8a** : **9a** formulation. The dppm methylene resonance appears to be under the –OH peak and is unresolved. The dmpe methyl resonances are helpful, however. One would expect a complex with the symmetry of **8a** to have two dmpe methyl environments, and there are two, equally intense, apparent doublets at 1.84 and 0.22 ppm. Clearly, the environments are very different, unlike the two environments in the homoleptic complex $[Ru(dmpe)_3](OTf)_2$.[24] This is probably a consequence of the steric crowding in **8a**, and the likely proximity of aromatic rings to the dmpe methyl groups. Similarly, complex **9a** should have four different methyl environments, and four equally intense resonances are found at 1.99, 1.56, 1.20 and 0.62 ppm, the first of these overlapping the multiplets due to the dmpe backbone protons.

Attempts to obtain pure **8a** by separating it from **9a** were unsuccessful. We therefore tried to prepare a pure sample of **9a** by reacting **1a** with two equivalents of dmpe, but this also gave an inseparable mixture.

Interestingly, however, reaction of **1a** with *one equivalent* of dmpm in DCE resulted in the precipitation of a *pure* sample of $[Ru(dppm)(dmpm)_2](OTf)_2$ (**10a**) in moderate yield (based on dmpm). The FAB^+ mass spectrum is consistent with this formulation and, in particular, shows no peak clusters attributable to $[Ru(dppm)_2(dmpm)](OTf)_2$. The $^{31}P\{^1H\}$ NMR spectrum of **10a** is shown in Fig. 3. The complex multiplet at −11.2 ppm is due to the single dppm ligand and, as expected, shows one large J_{PP} (177 Hz) owing to coupling to the *trans* dmpm Ps, which, in turn, resonate at −31.4 ppm. The *cis* dmpm Ps are responsible for the apparent septet resonance at −34.8 ppm

Conclusion

In summary, we have studied the ligand substitution chemistry of the novel complexes *cis*-$[Ru(OTf)_2(diphosphine)_2]$ (diphosphine = dppm, dppen, dppe) with a range of anionic and neutral ligands. We have found that the triflates are readily displaced by halide anions or acetonitrile, with retention of *cis* stereochemistry in the case of four-membered ring diphosphines, or by en. The displacement of triflate by bipy is less straightforward, and although $[Ru(dppen)_2(bipy)](OTf)_2$ could be isolated pure, the reaction of **1a** with bipy resulted in some diphosphine displacement by bipy under the conditions required to give triflate substitution, and $[Ru(dppe)_2(bipy)](OTf)_2$ could not be prepared. This is most likely due to steric limitations. Similarly, although $P(OMe)_3$ reacted with **1a**, **b** to give RuP_6 dications [and we were thus able to obtain the first X-ray crystal structure of a Ru(II) complex with hexa(phosphorus) coordination], this did not work for the larger PMe_3, and even the reactions of **1a**, **b** with chelating methyldiphosphines sometimes resulted in partial displacement of the aryldiphosphine as well as triflate ligand substitution.

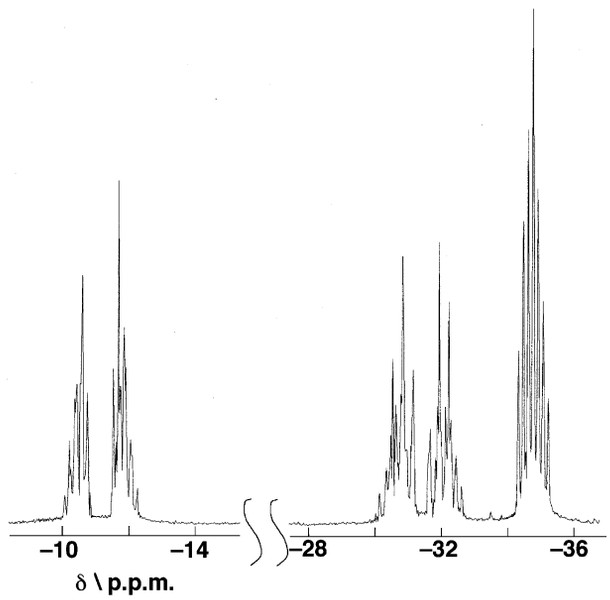

Fig. 3 $^{31}P\{^1H\}$ NMR spectrum (161 MHz) of $[Ru(dppm)(dmpm)_2](OTf)_2$ (**10a**) in $CD_3CN–CH_3CN$.

Experimental

Reactions were carried out under nitrogen using standard Schlenk line techniques. Perdeuterated solvents for NMR studies were used as received. The ligands dppen,[32] dppm[33] and dppe[33] were prepared using literature methods. *trans*-$[RuCl_2(L–L)_2]$ complexes were prepared as described previously for the dppen complex,[15] and the triflates were prepared from these as described previously;[7] full details of the syntheses and characterisation of the triflate complexes **1a**–**c**, and of attempts to obtain crystal structures (which led to partial or complete triflate substitution by trace water), are included in the ESI.† General experimental and characterisation methods were as previously described.[15] Infrared spectra of all bis(triflate) salts showed the characteristic ν_{SO} of non-coordinated triflate at 1270 ± 8 cm^{-1}.[34]

Syntheses

***cis*-[RuBr$_2$(dppm)$_2$] (2a).** A solution of **1a** was prepared *in situ* in DCE (50 cm^3) from $[RuCl_2(dppm)_2]$ (0.200 g, 0.213 mmol) and AgOTf (0.115 g, 0.447 mmol).[7] After filtering out the AgCl, the yellow solution was treated with Et_4NBr (0.1 g, 0.48 mmol) and the mixture was stirred at room temperature for 1 h. The solvent was removed *in vacuo* and the residue was recrystallised from acetone–hexane to provide a bright yellow solid, which was filtered off and dried *in vacuo*. Yield 0.134 g, 61%. Anal. calcd. for $C_{50}H_{44}Br_2P_4Ru$: C, 58.32; H, 4.31; found:

C, 58.22; H, 4.15%. FAB MS: *m/z* 949 (100) $[M - Br]^+$, 869 (62) $[M - 2Br - H]^+$. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ −1.7 (t, $J_{|AX + AX'|}$ 71 Hz), −30.8 (t).

***cis*-[RuBr$_2$(dppen)$_2$] (2b).** This was prepared as for **2a** from **1b**. Yield 69%. Anal. calcd. for $C_{52}H_{44}Br_2P_4Ru$: C, 59.27; H, 4.21; found: C, 59.50; H, 4.26%. FAB MS: *m/z* 1053 (31) $[M]^+$, 973 (97) $[M - Br]^+$, 893 (100) $[M - 2Br - H]^+$. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 15.1, −9.3 (2br s).

***cis*-[RuI$_2$(dppm)$_2$] (3a).** To a solution of **1a** (0.0432 g, 0.037 mmol) in DCE (10 cm^3) was added Et_4NI (0.031 g, 0.12 mmol). The reaction mixture turned green. It was then refluxed for 1.5 h, becoming orange during this time. The volume was reduced to *ca*. 1 cm^3 under reduced pressure and the product was precipitated by the addition of MeOH, filtered off and dried *in vacuo*. Yield 0.036 g, 87%. Anal. calcd. for $C_{50}H_{44}I_2P_4Ru$: C, 53.45; H, 3.95; found: C, 53.10; H, 3.85%. FAB MS: *m/z* 997 (92) $[M - I]^+$, 869 (56) $[M - 2I - H]^+$. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ −8.0 (t, $J_{|AX + AX'|}$ 73 Hz), −12.9 (s; *trans* isomer), −37.0 (t). Selected ^1H NMR data ($CDCl_3$): δ 5.30 (br m, CH_AH_B), 4.90 (br m, CH_AH_B).

***cis*-[RuI$_2$(dppen)$_2$] (3b).** This was prepared as for **3a** from **1b**. Yield 60%. Anal. calcd. for $C_{52}H_{44}I_2P_4Ru$: C, 54.42; H, 3.86; found: C, 54.08; H, 3.77%. FAB MS: *m/z* 1021 (21) $[M - I]^+$, 893 (72) $[M - 2I - H]^+$. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 15.1 (br s), 12.9 (s; *trans* isomer), −3.4 (br s). Selected ^1H NMR data ($CDCl_3$) δ: 6.20 (m, 2H, C=CH_AH_B), 6.00 (m, 2H, C=CH_AH_B).

***cis*-[Ru(dppm)$_2$(MeCN)$_2$](OTf)$_2$ (4a).** To a solution of **1a**, prepared from $[RuCl_2(dppm)_2]$ (0.216 g, 0.23 mmol) and AgOTf (0.125 g, 0.486 mmol) in DCE (50 cm^3) as described above, and with the AgCl filtered out, was added MeCN (10 cm^3). The mixture was refluxed for 10 min, and then evaporated to dryness. The off-white residue was recrystallised from CH_2Cl_2–hexane, filtered off and dried in *vacuo*. Yield 0.172 g, 73%. Anal. calcd. for $C_{56}H_{50}F_6N_2O_6P_4RuS_2$: C, 53.80; H, 4.03; N, 2.24; found: C, 53.61; H, 3.95; N, 2.10%. FAB MS: *m/z* 1100 (12) $[M - OTf]^+$, 1019 (100) $[M - 2MeCN - OTf]^+$, 910 (10) $[M - MeCN - 2OTf - H]^+$. $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ: −3.2 (t, $J_{|AX + AX'|}$ 71 Hz), −18.1 (t).

***cis*-[Ru(dppen)$_2$(MeCN)$_2$](OTf)$_2$ (4b).** This was prepared as for **4a** from **1b**. Yield 73%. Anal. calcd. for $C_{58}H_{50}F_6N_2O_6P_4RuS_2$: C, 54.68; H, 3.96; N, 2.20; found: C, 54.41; H, 3.99; N, 2.05%. FAB MS: *m/z* 1125 (8) $[M - OTf]^+$, 1042 (100) $[M - 2MeCN - OTf]^+$, 934 (7) $[M - MeCN - 2OTf - H]^+$. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 16.8 (br s), 2.8 (br s).

***cis*-[Ru(dppm)$_2$(MeCN)$_2$](BF$_4$)$_2$ (4a; tetrafluoroborate).** To a solution of *trans*-$[RuCl_2(dppm)_2]$ (0.22 g, 0.23 mmol) in DCE (50 cm^3) and MeCN (10 cm^3) at reflux was added $AgBF_4$ (0.094 g, 0.48 mmol). The solution was refluxed for 1 h and allowed to cool to room temperature. It was then filtered, the solution evaporated to dryness, and the residue taken up in CH_2Cl_2 and filtered through diatomaceous earth. The product was precipitated by the addition of hexane, filtered off and dried *in vacuo*. Yield 0.16 g, 68%. FAB MS: *m/z* 1038 (10) $[M - BF_4]^+$, 910 (11) $[M - MeCN - 2BF_4 - H]^+$, 889 (100) $[M - 2MeCN - BF_4 - BF_3]^+$. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ −3.8 (t, $J_{|AX + AX'|}$ 71 Hz), −18.3 (t).

[Ru(dppm)$_2$(en)](OTf)$_2$ (5a). A solution of **1a** in DCE (50 cm^3) was prepared from $[RuCl_2(dppm)_2]$ (0.30 g, 0.32 mmol) and AgOTf (0.18 g, 0.70 mmol) as described above, and the filtrate was treated with 1,2-diaminoethane (0.03 cm^3, 0.34 mmol). Immediately, the yellow solution became almost colourless. It was refluxed for 20 min, then cooled and evaporated to dryness. The residue was recrystallised from CH_2Cl_2–hexane. Yield 0.20 g, 52%. Anal. calcd. for $C_{54}H_{52}F_6N_2O_6P_4RuS_2$: C, 52.81; H, 4.27; N, 2.28; found: C, 52.58; H, 3.98; N, 2.20%. FAB MS: *m/z* 1079 (19) $[M - OTf]^+$, 1019 (100) $[M - en - OTf]^+$. $^{31}P\{^1H\}$ NMR (DMSO): δ 0.1 (t, $J_{|AX + AX'|}$ 61 Hz), −14.6 (t).

[Ru(dppm)$_2$(bipy)](OTf)$_2$ (6a). To $[RuCl_2(dppm)_2]$ (0.0715 g, 0.076 mmol) in DCE (10 cm^3) was added AgOTf (0.0386 g, 0.15 mmol) and the mixture was refluxed for 40 min. It was then cooled to room temperature and filtered, and the filtrate was treated with bipy (0.0125 g, 0.08 mmol). The mixture was refluxed for 24 h, then cooled and evaporated to dryness. The pale yellow residue was recrystallised from MeOH–CH_2Cl_2–Et_2O. Yield 0.055 g, 55%. Anal. calcd. for $C_{59.6}H_{50}F_6N_{2.28}O_6P_{3.72}RuS_2 \cdot CH_2Cl_2$: C, 52.99; H, 3.78; N, 2.32; found: C, 52.80; H, 3.72; N, 2.87%. FAB MS: *m/z* 1175 (87) $[M - OTf]^+$, 947 (100) $[M - OTf]^+$ of $[Ru(dppm)(bipy)_2](OTf)_2$. $^{31}P\{^1H\}$ NMR (EtOH): δ 0.5 {s, $[Ru(dppm)(bipy)_2](OTf)_2$}; −12.0, −19.9 (triplets, $J_{|AX + AX'|}$ 61 Hz). ^1H NMR (CD_3OD): δ 8.6–6.4 (multiplets, aromatic H), 5.4 (br m, PCH_2P).

[Ru(dppen)$_2$(bipy)](OTf)$_2$ (6b). This was prepared on the same scale and in the same way as **6a**, using $[RuCl_2(dppen)_2]$. Yield 0.056 g, 43%. Anal. calcd. for $C_{64}H_{52}F_6N_2O_6P_4RuS_2 \cdot CH_2Cl_2$: C, 54.48; H, 3.80; N, 1.95; found: C, 54.90; H, 3.97; N, 2.57%. FAB MS: *m/z* 1199 (26) $[M - OTf]^+$, 803 (100) $[M - dppen - OTf]^+$. $^{31}P\{^1H\}$ NMR (EtOH): δ 0.5, −9.2 (2br s).

[Ru(dppm)$_2${P(OMe)$_3$}$_2$](OTf)$_2$ (7a). A solution of **1a** in DCE (50 cm^3) was prepared from $[RuCl_2(dppm)_2]$ (0.30 g, 0.32 mmol) and AgOTf (0.087 g, 0.34 mmol) as described above. To the filtrate from this reaction was added $P(OMe)_3$ (0.078 cm^3, 0.66 mmol). Immediately, the yellow solution became almost colourless. It was refluxed for 20 min, then cooled and evaporated to dryness. The residue was recrystallised from CH_2Cl_2–hexane. Yield 0.349 g, 77%. Anal. calcd. for $C_{58}H_{62}F_6O_{12}P_6RuS_2$: C, 49.19; H, 4.41; found: C, 49.45; H, 4.20%. FAB MS: *m/z* 1267 (38) $[M - OTf]^+$, 1143 (13) $[M - P(OMe)_3 - OTf]^+$, 1117 (41) $[M - 2OTf - H]^+$. $^{31}P\{^1H\}$ NMR (DMSO): δ 123.3 [2P, complex m, $P(OMe)_3$, $J_{PP\,trans}$ 297 Hz], −14.2 (2P, complex m, mutually *trans* dppm Ps), −31.2 (2P, complex m, mutually *cis* dppm Ps, $J_{PP\,trans}$ 297 Hz).

[Ru(dppen)$_2${P(OMe)$_3$}$_2$](OTf)$_2$ (7b). A solution of **1b** in DCE (50 cm^3) was prepared from $[RuCl_2(dppen)_2]$ (0.52 g, 0.54 mmol) and AgOTf (0.087 g, 0.34 mmol) as described above for **1a**. To the filtrate from this reaction was added $P(OMe)_3$ (0.10 cm^3, 1.13 mmol). Immediately, the yellow solution became almost colourless. It was refluxed for 20 min, then cooled and evaporated to dryness. The residue was triturated with Et_2O and dried *in vacuo*. Yield 0.68 g, 88%. Anal. calcd. for $C_{60}H_{62}F_6O_{12}P_6RuS_2$: C, 50.04; H, 4.34; found: C, 50.17; H, 4.44%. FAB MS: *m/z* 1291 $[M - OTf]^+$, 1167 $[M - P(OMe)_3 - OTf]^+$, 1141 $[M - 2OTf - H]^+$. $^{31}P\{^1H\}$ NMR (DMSO): δ 124.5 [2P, complex m, $P(OMe)_3$, $J_{PP\,trans}$ 320 Hz], 1.3 (2P, complex m, mutually *trans* dppen Ps), −8.6 (2P, complex m, mutually *cis* dppm Ps, $J_{PP\,trans}$ 320 Hz).

Attempted synthesis of [Ru(dppm)$_2$(dmpe)](OTf)$_2$ (8a). A solution of **1a** (0.26 mmol) was prepared in DCE (12 cm^3) as described above. The AgCl was removed by filtering the solution through a cannula into a fresh solution of dmpe (0.04 g, 0.25 mmol) in DCE (4 cm^3). The reaction mixture was refluxed for 16 h, then the solvent was evaporated to a low volume. Diethyl ether (5 cm^3) was slowly added to precipitate the product, which was filtered off and dried *in vacuo*. Yield 0.26 g. Spectroscopic data indicates a 5 : 1 mixture of **8a** and $[Ru(dppm)(dmpe)_2](OTf)_2$ (**9a**). Anal. calcd. (for a 5 : 1 ratio of **8a** : **9a**) for $C_{54.8}H_{59}F_6O_6P_6RuS_2 \cdot$DCE: C, 49.38; H, 4.62; found: C, 49.19; H, 4.48%. FAB MS: *m/z* 1169 [M(**8a**) − OTf]$^+$, 1019

[M(**8a**) − 2OTf − H]$^+$, 935 [M(**9a**) − OTf]$^+$. $^{31}P\{^1H\}$ NMR (DMSO) 5 : 1 ratio of **8a** : **9a**: (**8a**) δ 28.7 (2P, complex m, dmpe, $J_{PP_{trans}}$ 190), −25.5 (2P, complex m, mutually *trans* dppm Ps), −26.2 (2P, complex m, mutually *cis* dppm Ps, $J_{PP_{trans}}$ 190); (**9a**) δ 33.5 (2P, complex m, mutually *cis* dmpe Ps, $J_{PP_{trans}}$ 200), 27.2 (2P, complex m, mutually *trans* dmpe Ps), −23.9 (complex m, dppm Ps, $J_{PP_{trans}}$ 200 Hz). ^1H NMR (CD_3OD): δ 6.69–7.79 (multiplets, C_6H_5 of dppm), 2.20–1.85 (multiplets, PCH_2CH_2P), 1.84, 0.22 (2d, PCH_3 of **8a**), 1.99, 1.56, 1.20, 0.62 (4m, PCH_3 of **9a**).

[Ru(dppm)(dmpm)$_2$](OTf)$_2$ (10a). A solution of **1a** (0.18 mmol) was prepared in DCE (10 cm^3) as described above. To the filtered solution was added dmpm (0.025 g, 0.18 mmol). The reaction mixture was refluxed for 24 h, then allowed to cool to room temperature. The white product which precipitated was filtered off and dried *in vacuo*. Yield 0.037 g, 40% (w.r.t. dmpm). Anal. calcd. for $C_{37}H_{48}F_6O_6P_6RuS_2$: C, 42.17; H, 4.59; found: C, 42.08; H, 4.38%. FAB MS: *m*/*z* 907 [M − OTf]$^+$, 757 [M − 2OTf − H]$^+$. $^{31}P\{^1H\}$ NMR (MeOH): δ −11.2 (2P, complex m, dppm, $J_{PP_{trans}}$ 177), −31.4 (2P, complex m, mutually *cis* dmpm Ps), −34.8 (2P, complex m, mutually *trans* dmpm Ps, $J_{PP_{trans}}$ 177 Hz). ^1H NMR (CD_3OD): δ 7.73, 7.53 (2m, C_6H_5 of dppm), 5.00 (m, PCH_2P of dppm), 2.85 (br m, PCH_2P of dmpm), 2.03, 0.65 (2m, PCH_3).

Crystal structures

Single crystals of **4a** and **7b** suitable for X-ray diffraction were grown from CH_2Cl_2–hexane by slow solvent diffusion. Intensity data (Table 1) were collected using a STOE-IPDS image plate diffractometer (Mo-Kα, graphite monochromator, λ = 0.71073 Å) at 293 (**4a**) or 213 (**7b**) ± 2 K, in the φ rotation scan mode. A total of 6982 (**4a**) and 8644 (**7b**) unique reflections were measured, and these were used in the refinements. The structures were solved by direct methods using the SHELXS97 package and refined using full-matrix least squares on F^2 (SHELXL97).[35,36] For **4a**, refinement converged to R = 0.0341 for the reflections with $F^2 > 2\sigma(F^2)$. For **7b**, refinement converged to R = 0.0658 for the reflections with $F^2 > 2\sigma(F^2)$.

CCDC reference numbers 144522 and 212388.

See http://www.rsc.org/suppdata/dt/b3/b306552a/ for crystallographic data in CIF or other electronic format.

Comparison of bond length and angle data with other structures was achieved by using the Chemical Database Service at the CCLRC Daresbury Laboratory, Warrington, UK.[37]

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