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Syntheses, characterization and redox properties of homoleptic ruthenium(II)–diphosphine and diarsine complexes: deviations from ligand additivity

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Homoleptic Ru(II)–diphosphine and Ru(II)–diarsine complexes, $[Ru(L–L)_3]^{2+}$, have been synthesized by two routes. Treatment of $[RuCl_2(PPh_3)_3]$ with excess ligand in EtOH gave $[Ru(L–L)_3]Cl_2$ only for L–L = 1,2-$(Me_2As)_2C_6H_4$ (diars) **1a** and $Me_2PCH_2PMe_2$ (dmpm) **2a**. In the latter reaction, neutral *trans*-$[RuCl_2$(dmpm–*P,P′*)(dmpm–*P*)$_2]$ **3** was also a product (detected by $^{31}P\{^1H\}$ NMR spectroscopy). A more widely-applicable synthesis was treatment of the halide-free starting material $[Ru(dmf)_6](OTf)_3$ (dmf = Me_2NCHO; OTf = $CF_3SO_3^-$) with excess ligand in EtOH. This gave the triflate salts $[Ru(L–L)_3](OTf)_2$ (L–L = diars **1b**, dmpm **2b**, $Me_2PCH_2CH_2PMe_2$ (dmpe) **4** and $Et_2PCH_2CH_2PEt_2$ (depe) **5**. The complexes were characterized by microanalysis, infrared and electronic spectroscopies, multinuclear NMR spectroscopy, and FAB mass spectrometry. The crystal structure of $[Ru(diars)_3]Cl_2·0.5dmf·H_2O$ has been determined. The mean Ru–As bond length, 2.4468(15) Å, is significantly longer than for typical *trans*-$[Ru^{II}(diars)_2]$ moieties (2.425 Å; mean of 14 structures), suggesting steric crowding. X-Ray quality crystals of the diphosphine complexes were not obtained. However, Ru K-edge EXAFS measurements on $[Ru(dmpe)_3](OTf)_2$ were fitted well by a shell of six phosphorus atoms at Ru–P = 2.38(1) Å, compared with 2.31 Å for published structures containing *trans*-$[Ru^{II}(dmpe)_2]$, again indicative of steric crowding. Electrochemical studies, in extremely anhydrous media, revealed an irreversible oxidation for $[Ru(L–L)_3](OTf)_2$ assigned as Ru(II)/Ru(III), at E_P^A *ca.* +2.3 V *vs.* ferrocene/ferrocinium. Digital simulation showed that the oxidations are kinetically slow, and the formal Ru(II)/Ru(III) potentials are around +1.8 V. This is more positive than the value predicted using published electrochemical ligand parameters (E_L). The latter were checked, for diars and dmpe, by synthesizing and measuring the Ru(II)/Ru(III) redox potentials of [Ru(2,2′-bipyridine)$_2$(L–L)](OTf)$_2$ (L–L = dmpe **6** and diars **7**). The crystal structure of **7** was determined. The mean Ru–As bond length, 2.4066(3) Å, lends further support to the contention that the homoleptic cation **1** is sterically crowded. Attempts to synthesise pure samples of related complexes with monodentate phosphines (PR_3) or aryldiphosphines were unsuccessful.

Introduction

The development of thioether macrocycles well-suited to octahedral coordination (in particular, 1,4,7-trithiacyclononane, [9]aneS_3, and 1,4,7,10,13,16-hexathiacyclooctadecane, [18]aneS_6) has led to the development of unusual homoleptic thioether complexes of both 3d and platinum group metals, and the elucidation of some unusual redox properties for the complexes, most notably the generation of d^7 mononuclear Pd(III), Pt(III) and Rh(II) species.[1] With ruthenium(II), homoleptic thioether coordination resulted in the low spin d^6 state being greatly stabilised towards redox processes.[2] For example, the Ru(II)/Ru(III) couple for $[Ru([9]aneS_3)_2]^{2+}$ is at +1.41 V (*vs.* ferrocene/ferrocinium),[2] compared with, for instance, $[Ru(bipy)_3]^{2+}$ (+0.85 V)[3] or $[Ru(amine)_6]^{2+}$ (*ca.* −0.4 V).[4] Interestingly, macrocyclic ligands are not a prerequisite for achieving homoleptic thioether coordination; treatment of halide-free Ru(II) starting materials (*e.g.* $[Ru(dmso)_6](BF_4)_2$) with 2,5,8-trithianonane (ttn) afforded $[Ru(ttn)_2](BF_4)_2$, with similar redox and spectroscopic properties to $[Ru([9]aneS_3)_2]^{2+}$ and $[Ru([12]aneS_3)_2]^{2+}$.[2] Recently, complexes $[Ru\{MeC(CH_2EMe)_3\}_2](OTf)_2$ (E = Se, Te), the first examples of homoleptic hexaselenoand hexatelluroether transition metal complexes, have been described.[5] These were made by reaction of the appropriate ligand with $[Ru(dmf)_6](OTf)_3$. Again, the soft donor set stabilises Ru(II) with respect to oxidation.

Recently, there has been much interest in the establishment of a ligand electrochemical series, based on the premise that the effects exerted by a set of ligands on the electronic properties of the complex are essentially additive.[6] In particular, Lever used the extensive data set available for Ru(III)/Ru(II) redox processes, mostly for species $[Ru^{II}(bipy)_2L_2]^{n+}$ in CH_3CN, to derive E_L for a ligand L, defined as one-sixth of the value of the Ru(III)/Ru(II) potential (*vs.* NHE) for the corresponding $[Ru^{II}L_6]^{n+}$. As might be expected for 'soft' Lewis bases, E_L for thioethers R_2S and related ligands are quite positive (*e.g.* +0.35 V for Et_2S). Thus, a value of +1.44 V (*vs.* ferrocene/ferrocinium) would be predicted for the Ru(II)/Ru(III) redox potential of a homoleptic complex of type $[Ru(R_2S)_6]^{2+}$, in good agreement with the measured value for $[Ru([9]aneS_3)_2]^{2+}$.[2]

The [9]aneS_3 chemistry prompted us to investigate the synthesis and redox properties of homoleptic Ru(II)–phosphine and arsine complexes. There is great current interest in Ru(II)–phosphine coordination chemistry[7] (prompted partly by developments in homogeneous catalysis[8]) and a very large number of Ru(II)–phosphine complexes has been prepared. However, there are few claims for homoleptic Ru(II)–phosphorus coordination, and none at all for homoleptic Ru(II)–

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arsine coordination. Moreover, until this study, no structural data had been obtained.

Complexes $[Ru(P\{OR\}_3)_6]^{2+}$ (R = Me, Et), made by reaction of $[RuCl_2(PPh_3)_3]$ or $[\{RuCl_2(bicyclo[2,2,1]hepta\text{-}2,5\text{-}diene)\}_n]$ with excess $P(OR)_3$ in ROH, have been characterised spectroscopically.[9] The complex $[Ru(dmpm)_3]Cl_2$ (dmpm = $Me_2PCH_2PMe_2$), made from $[RuCl_2(PPh_3)_3]$ and excess dmpm in refluxing EtOH, has been briefly described.[10] The related Fe(II) complexes $[Fe(L–L)_3]^{2+}$ (L–L = diars, *cis*-$Me_2AsCH{=}CHAsMe_2$)[11] have been known for some time, although analogous diphosphine complexes do not appear to have been made. Interestingly, the Fe(II)–diars complex could be oxidized to Fe(III) under forcing conditions (hot nitric acid). Isoelectronic Co(III) complexes $[Co(L–L)_3]^{3+}$ (L–L = 1,2-$C_6H_4(EMe_2)_2$, E = P [diphos], E = As [diars], 1,2-$C_6H_4(PPh_2)_2$, $Me_2PCH_2CH_2PMe_2$ [dmpe]) are well-characterized, and the crystal structure of $[Co(diars)_3](BF_4)_3$ has been determined.[12] Low-valent d^6 homoleptic phosphine complexes, for instance $[M(dmpe)_3]$[13] and $[Mo(PMe_3)_6]$[14] (M = Cr, Mo, W), are also known.

We have investigated the reaction of the convenient halide-free starting material $[Ru(dmf)_6](OTf)_3$ ($^-OTf = CF_3SO_3^-$)[15] with $Me_2PCH_2PMe_2$ (dmpm), dmpe, $Et_2PCH_2CH_2PEt_2$ (depe) and diars, and found that all these ligands give the desired $[RuE_6]^{2+}$. Additionally, we have investigated the reaction of $[RuCl_2(PPh_3)_3]$ with excess dmpm, dmpe and diars in EtOH. We have also examined the redox properties of the complexes, and found an anomaly between their behavior, and predictions made using Lever's well-known electrochemical ligand parameter approach,[6] which was originally developed using Ru(II)/Ru(III) couples. In an effort to explore the reasons for this, we widened our investigation to encompass some examples of $[Ru(bipy)_2(L–L)]^{2+}$ (L–L = diars, dmpe). We report details of these studies here, together with the crystal structures of $[Ru(diars)_3]Cl_2{\cdot}2H_2O$ and $[Ru(bipy)_2(diars)](OTf)_2$, and attempts to prepare homoleptic complexes with PMe_3 and $Ph_2P(CH_2)_nPPh_2$ (*n* = 1, dppm; *n* = 2, dppe). A preliminary communication describing some aspects of this work has appeared.[16]

Experimental

General considerations

Reactions were carried out under nitrogen using standard Schlenk line techniques. Dmf was anhydrous grade (≤0.005% water). Perdeuterated solvents for NMR studies were used as received. The ligands dmpe and dmpm (Strem Chemicals) and PMe_3 (1.0 M solution in thf; Aldrich) were used as received, and diars was prepared by a literature method.[17] The complexes $[RuCl_2(PPh_3)_3]$[18] and $[Ru(dmf)_6](OTf)_3$[15] were prepared by literature routes. The hexafluoroantimonate $[Ru(dmf)_6](SbF_6)_3$ was prepared as for $[Ru(dmf)_6](OTf)_3$[15] but using $AgSbF_6$ in place of AgOTf. It was characterised by IR and electronic spectroscopy. General experimental and characterisation methods were as recently described;[19] ^1H NMR spectra were recorded at 400 MHz (Bruker Avance) and $^{31}P\{^1H\}$ NMR spectra at 101 MHz (Bruker AC 250 spectrometer) unless otherwise noted.

Electrochemical measurements

Tetraethylammonium tetrafluoroborate (TEAT) and tetrabutylammonium hexafluorophosphate (TBAH) were used as supporting electrolyte. TEAT was recrystallised from ethanol and dried at 60 °C *in vacuo*; TBAH (puriss. from Fluka) was used as received. Acetonitrile (spectroscopy grade from Merck), after being refluxed over CaH_2, was distilled under vacuum at room temperature with a high refluxing ratio, utilizing 1 m length distillation column filled with glass rings. Dichloromethane (from Fluka) was successively refluxed over, and distilled from, P_4O_{10}, CaH_2 and activated molecular sieves. The solvents were stored in Schlenk flasks over 3 Å activated molecular sieves, protected from light.

Electrochemical experiments from −2.4 to +1.6 V (*vs.* ferrocene/ferrocinium) were conducted using an EcoChemie PGSTAT 20 system, using Au disc working electrodes; 0.2 M TEAT in CH_3CN was employed. The reference electrode was an aqueous SCE, but potentials are quoted with respect to the ferrocene/ferrocinium couple, which was routinely monitored after each set of voltammetric measurements to reduce errors due to junction potentials. Positive feedback compensation was employed to reduce errors due to cell resistance.

Later measurements, under careful exclusion of water and any other proton-donors, were conducted over a wider potential window (*i.e.*, in the range ≈ −3.4 and +3.5 V *vs.* ferrocinium/ferrocene couple) in acetonitrile or in dichloromethane. The solvent, purified as described above, was distilled *via* a closed system into an electrochemical cell containing the supporting electrolyte and the species under examination, soon before performing the experiment. Experiments were carried out in an airtight single-compartment cell described elsewhere,[20] by using platinum as working and counter electrodes and a silver spiral as a quasi-reference electrode. The drift of the quasi-reference electrode was negligible for the time required for an experiment. The potential values have been determined by adding, at the end of each experiment, ferrocene as an internal standard (its $E_{1/2}$ in acetonitrile was 0.39 V at 25 °C and 0.37 V at −45 °C *vs.* SCE). The working electrode consisted either of a 0.5 mm-diameter platinum wire (area *ca.* 0.09 cm^2) sealed in glass, or a Pt disc ultramicroelectrode (UME; diameter either 125 or 25 μm) also sealed in glass.

The cell containing the supporting electrolyte and the electroactive compound was dried under vacuum at 100–120 °C for at least 60 h before each experiment. The pressure measured in the electrochemical cell prior to performing the trap-to-trap distillation of the solvent was typically $1–2 \times 10^{-5}$ mbar.

Voltammograms were recorded with an AMEL Model 552 potentiostat or a custom made fast potentiostat controlled by either an AMEL Model 568 function generator or an ELCHEMA Model FG-206F. Data acquisition was performed by a Nicolet Model 3091 digital oscilloscope interfaced to a PC.

Digital simulations of cyclic voltammetric experiments were performed using either the DigiSim 3.0 software by Bioanalytical Systems Inc., or the Antigona software developed by Dr. Loic Mottier. The parameters were chosen so as to obtain a visual best fit over a 10^2-fold range of scan rates.

Syntheses

$[Ru(diars)_3]Cl_2$ 1a. To $[RuCl_2(PPh_3)_3]$ (0.2034 g, 0.21 mmol) in EtOH (35 cm^3) was added the ligand (0.16 g, 0.57 mmol). The solution was refluxed for 4 h, then cooled to room temperature. A small amount of insoluble material was filtered off, the pale yellow solution was evaporated to small volume and the product was precipitated with diethyl ether. The white solid was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 0.149 g, 75%. Found: C, 32.98; H, 4.78%. $C_{30}H_{48}As_6Cl_2Ru{\cdot}2H_2O$ requires C, 33.23; H, 5.02%. Mass spectrum (FAB, Xe^+): *m*/*z* 994 (21) $[M–Cl]^+$, 959 (31) $[M–Cl–HCl]^+$ and 945 (100) $[M–2Cl–Me]^+$. IR data (Nujol mull, cm^{-1}) 3400 (br); $\nu_{O–H}$. Electronic spectral data: $E_{max}/10^{-3}$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 27.03 sh (85), 33.55 (1300), 37.04 (2360). ^1H NMR (CD_3OD) δ 8.07, 7.80 [12H, AA′BB′, C_6H_4], 2.05 [18H, $AsCH_3$], 1.56 (18H, $AsCH_3$).

$[Ru(dmpm)_3]Cl_2$ 2a. This was prepared using an adaptation of the literature method.[10] Workup consisted of evaporating the reaction mixture to dryness, and extracting with the minimum volume of ethanol. Addition of diethyl ether gave a white precipitate of **2a** (50% on Ru; identified by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy by comparison with literature data[10] and with **2b**, below), and a yellow mother liquor. This was evaporated to dryness and examined using $^{31}P\{^1H\}$ NMR spectroscopy, which showed it to consist of *trans*-$[RuCl_2(\eta^2\text{-dmpm})(\eta^1\text{-dmpm})_2]$ (**3**), free PPh_3 and traces of $Me_2P(O)CH_2PMe_2$ (see Results).

$[Ru(diars)_3](OTf)_2$ 1b. *From $[Ru(dmf)_6](OTf)_3$ and the ligand.* Diars (0.16 g, 0.57 mmol) and $[Ru(dmf)_6](OTf)_3$ (0.184 g, 0.19 mmol) were combined in EtOH (35 cm^3) and the mixture was refluxed for 3.5 h, giving a pale pink solution. This was rotary evaporated to dryness, the residue was taken up in the minimum volume of EtOH and the product was precipitated by addition of diethyl ether. It was filtered off, washed with ether and dried *in vacuo*. Yield 0.12 g, 48%. Found: C, 30.06; H, 3.71%. $C_{32}H_{48}As_6F_6S_2O_6Ru$ requires C, 30.57; H, 3.85%. Mass spectrum (FAB, Xe^+): *m*/*z* 1109 (100) $[M–OTf]^+$, 945 (62) $[M–2OTf–Me]^+$ and 823 (84) $[M–diars–OTf]^+$. IR (Nujol mull, cm^{-1}): 1269 (s), 1155 (m), 1029 (s) (uncoordinated OTf^-). Electronic spectral data: $E_{max}/10^{-3}$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 33.56 sh (1090), 37.31 sh (1860). ^1H NMR (CD_3OD) δ 8.05, 7.78 [12H, AA′BB′, C_6H_4], 1.99 [18H, AsCH_3], 1.55 [18H, AsCH_3].

*By metathesis of **1a**.* Silver trifluoromethanesufonate (0.25 g, 0.097 mmol) was added to a solution of $[Ru(diars)_3]Cl_2$ (0.23 g 0.022 mmol) in ethanol (20 cm^3) and the mixture was stirred for 1 h at room temperature. The AgCl which precipitated was removed by filtration under gravity and the product was precipitated by the addition of excess diethyl ether to the filtrate. Yield 0.16 g, 57%. Found: C, 29.85; H, 3.64%. $C_{32}H_{48}As_6F_6S_2O_6Ru$ requires C: 30.57 H: 3.85%. Spectroscopic data were as above.

$[Ru(diars)_3](SbF_6)_2$ 1c. This was prepared as for **1b**, from diars and $[Ru(dmf)_6](SbF_6)_3$, except that 18 h reflux was necessary. Yield 51%. Found: C, 24.92; H, 3.38%. $C_{30}H_{48}As_6F_{12}Sb_2Ru$ requires C, 25.18; H, 3.38%. Mass spectrum (FAB, Xe^+): *m*/*z* 1194 (100) $[M–SbF_6]^+$ and 479 (90) $[(M–2\ SbF_6)]^{2+}$. ^1H NMR (CD_3OD) δ 8.08, 7.83 [12H, AA′BB′, C_6H_4], 2.01 [18H, AsCH_3], 1.57 [18H, AsCH_3].

$[Ru(dmpm)_3](OTf)_2$ 2b. This was prepared from $[Ru(dmf)_6](OTf)_3$ as for **1b**, but using 6 mol. equiv. of dmpm. On reflux, the solution went from orange, through deep red, then purple, to colorless. Yield 61% (on Ru). Found: C, 24.88; H, 5.03; P, 22.93; Ru, 12.58; S, 7.48%. $C_{17}H_{42}F_6P_6S_2O_6Ru$ requires C, 25.29; H, 5.24; P, 23.01; Ru, 12.51; S, 7.94%. Mass spectrum (FAB, Xe^+): *m*/*z* 658 (63) $[M–OTf]^+$, 522 (94) $[M–OTf–dmpm]^+$ and 508 (100). IR data (Nujol mull, cm^{-1}): 1265 (s), 1154 (m), 1033 (s) (uncoordinated OTf^-). Electronic spectral data: $E_{max}/10^{-3}$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 36.23 sh (3600), 38.91 (4800). ^1H NMR(CD_3OD): δ 3.79 [6H, br m, PCH_2P], 1.92 [12H, m, PCH_3], 1.85 [12H, m, PCH_3]. $^{31}P\{^1H\}$ NMR (CH_3OH, CD_2Cl_2 lock): δ −33.82 (s).

$[Ru(dmpe)_3](OTf)_2$ 4. The ligand (1.00 g, 6.70 mmol) and $[Ru(dmf)_6](OTf)_3$ (1.053 g, 1.00 mmol) were combined in EtOH (35 cm^3) and the mixture was refluxed until no further color change occurred (1.5 h). The color changed from yellow, through burgundy and purple, to colorless. Workup was as for **1b**. Yield 0.866 g, 96% (on Ru). Found: C, 27.92; H, 5.50; P, 21.67; Ru 11.28; S, 7.36%. $C_{20}H_{48}F_6P_6S_2O_6Ru$ requires C, 28.27; H, 5.69; P, 21.87; Ru, 11.89; S, 7.55%. Mass spectrum (FAB, Xe^+): *m*/*z* 700 (13) $[M–OTf]^+$; 550 (100) $[M–OTf–dmpe]^+$, 400 (32) $[M–OTf–2\ dmpe]^+$. IR (Nujol mull, cm^{-1}): 1262 (s), 1158 (m), 1028 (s) (uncoordinated OTf^-). Electronic spectrum: $E_{max}/10^{-3}$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 37.04 sh (1430), 39.06 (1650). ^1H NMR (CD_3OD): δ 2.08, 1.90 [12H, br ms, PCH_2CH_2P], 1.68 [36H, s, PCH_3]. $^{13}C\{^1H\}$ NMR (CD_3OD) δ 30.0 (s, PCH_2CH_2P), 19.6, 18.36 (br ms, PCH_3). $^{31}P\{^1H\}$ NMR (CH_3OH, CD_2Cl_2 lock): δ + 27.8 (s).

$[Ru(depe)_3](OTf)_2$ 5. This complex was prepared as for **4**, using depe (0.18 g, 0.87 mmol), and $[Ru(dmf)_6](CF_3SO_3)_3$ (0.03 g, 0.032 mmol). The crude product was recrystallized from EtOH/Et_2O at 0 °C. Yield: 0.015 g, 45% (on Ru). Found: C, 36.51; H, 7.02%. $C_{32}H_{72}P_6O_6F_6S_2Ru$ requires C, 37.76; H, 7.13%. Mass spectrum (FAB, Xe^+): *m*/*z* 869 (29) $[M–OTf]^+$ and 663 (100) $[M–OTf–depe]^+$. IR (KBr disc, cm^{-1}): 1275 (s), 1145 (s), 1032 (s) (uncoordinated OTf^-). Electronic spectrum: $E_{max}/10^{-3}$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 34.48 (sh) (1680), 37.04 (1840). ^1H NMR (CD_3OD): δ 1.85 and 1.52 [each 6H, br ms, PCH_2CH_2P], 0.82 [60H, br ms, Et_2P]. $^{31}P\{^1H\}$ NMR (CH_3OH, CD_2Cl_2 lock): δ + 42.0 (s).

$[Ru(bipy)_2(dmpe)](CF_3SO_3)_2$ 6. $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (0.17 g, 0.29 mmol) and AgOTf (0.15 g, 0.6 mmol) were stirred in acetone (50 cm^3) under argon for 14 h. The AgCl precipitate was removed by filtration under gravity. The resulting red solution was degassed, then syringed into a solution of dmpe (0.27 g, 1.8 mmol) in acetone (50 cm^3). The mixture was refluxed for 24 h and, after cooling to room temperature, the solvent was removed *in vacuo*. The black/brown residue was taken up in the minimum volume of acetone. Addition of excess diethyl ether afforded a brown/yellow solid which was filtered off and dried *in vacuo*. Yield: 0.1 g, 41%. Microanalyses were not performed owing to high fluorine content. Mass spectrum (FAB, Xe^+): *m*/*z* 712 (7) $[M–OTf]^+$, 556 (7) $[M–2\ OTf–H]^+$. Accurate mass determination: found 712.645, calculated for $[M–OTf]^+$ 712.662. IR (KBr disc, cm^{-1}): 1265 (s), 1143 (s), 1032 (non-coordinated triflate). Selected ^1H NMR (CD_3OD) δ 8.71 [d, J_{HH} 5.8], 8.44 [d, J_{HH} 8.2], 8.35 [d, J_{HH} 8.2], 8.09 [t, J_{HH} 8.3], 7.88 [t, J_{HH} 7.8], 7.59 [t, J_{HH} 6.6], 7.30 [d, J_{HH} 8.3], 7.25 [t, J_{HH} 5.8]. $^{31}P\{^1H\}$ NMR (d^6 acetone): δ +47.0 (s).

$[Ru(bipy)_2(diars)](CF_3SO_3)_2$ 7. $AgCF_3SO_3$ (0.109 g, 0.42 mmol) was added to $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (0.11 g, 0.21 mmol) in acetone (10 cm^3) and the mixture was stirred under argon for 21 h. The AgCl, which precipitated, was removed by filtration, and the red solution was treated with diars (0.06 g, 0.21 mmol). The reaction was then refluxed for 21 h. The solvent was removed *in vacuo* and the red/brown residue was triturated repeatedly with EtOH/Et_2O (1 : 30), until a fine brown powder was obtained, which was filtered off. Recrystallisation from ethanol/diethyl ether gave the pure product, which required prolonged drying under vacuum at 50 °C to remove all residual diethyl ether. Crystals suitable for X-ray diffraction were grown from MeOH/Et_2O. Yield 0.1636 g, 78%. Found: C, 38.13; H, 3.16; N, 5.76%. $C_{32}H_{32}N_4As_2F_6O_6S_2Ru$ requires C, 38.52; H, 3.23; N, 5.61%. Mass spectrum (FAB, Xe^+): *m*/*z* 849 (100) $[M–OTf]^+$, 693 ((55) $[M–OTf–bipy]^+$. ^1H NMR (CD_3OD): δ 8.70 [d, 2H, J_{HH} 8.2], 8.63 [d, 2H, J_{HH} 8.2], 8.53 [d, 2H, J_{HH} 5.8], 8.24 [dt, 2H, J_{HH} 7.9, 1.7], 8.12 [dt, 2H, J_{HH} 7.9, 1.7], 8.02, 7.73 [AA′XX′, 4H, *o*-C_6H_4], 7.73 [d, 2H, J_{HH} 5.8], 7.61 [m, 2H], 7.49 [m, 2H], 1.83 [s, 6H, AsCH_3], 0.73 [s, 6H, AsCH_3]. Selected $^{13}C\{^1H\}$ NMR (CD_3OD): δ 159.4, 157.5, 151.6, 141.5, 140.5, 133.4, 132.3, 129.9, 129.4, 126.6, 126.0. ^{19}F (CD_3OD): δ −80.0 [s, non-coordinated triflate].

EXAFS studies

The sample for EXAFS spectroscopy was lightly ground with BN in a pestle and mortar, and packed in an aluminum sample holder between Sellotape windows. Data were collected at the Ru K-edge using a liquid nitrogen-cooled cryostat, in transmission mode on Station 9.2 of the Daresbury Synchrotron Radiation Source. A Si(220) double crystal monochromator, detuned to reject 50% of the incident signal to minimise harmonic contamination, was employed. Data were processed using the Daresbury program EXCALIB, the background was subtracted using EXBACK and the isolated EXAFS data were

Table 1 Crystallographic data for **1a**·0.5dmf·H_2O and **7**

	1a·0.5dmf·H_2O	**7**
Formula	$C_{31.5}H_{54}As_6Cl_2N_{0.5}O_{1.5}Ru$	$C_{32}H_{32}As_2F_6N_4O_6RuS_2$
M_r	1085.35	997.65
Space group (no.)	$P\bar{1}$ (2)	*Pbca* (61)
a/Å	11.6861(16)	19.4220(14)
b/Å	16.900(2)	13.4406(10)
c/Å	20.774(3)	28.171(2)
α/°	94.833(17)	90
β/°	102.402(16)	90
γ/°	92.756(17)	90
V/Å^3	3983.5(10)	7353.9(9)
Z	4	8
T/K	213(2)	150(2)
ρ_{calcd}/g cm^{-3}	1.810	1.802
μ/mm^{-1}	5.320	2.406
R_1,^{a} wR_2^{b}	0.0481, 0.1016	0.0240, 0.0598

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$ for $I > 2\sigma(I)$.

analysed by fitting a theoretical curve to the experimental k^3-weighted EXAFS spectra using EXCURV98. The phase shifts had previously been validated by the excellent agreement between EXAFS and single crystal X-ray determination of Ru–P (and Ru–Cl) distances in *cis*-[RuCl$_2$(dppm)$_2$], as part of an earlier study.[19] The theoretical fit was obtained by adding shells of backscattering atoms around the central absorber atom, and refining the Fermi energy E_f, the absorber–scatterer distances r, and the Debye–Waller factors to minimise the R-factor. The number of scatterers, N, were taken as integer values giving the best fit. Only shells giving a significant improvement in the R-factor were included in the final fit.

X-Ray crystallography

Crystal data and refinement parameters for complexes **1a**·0.5dmf·H_2O and **7** are given in Table 1.

CCDC reference numbers 138795 and 188771.

See http://www.rsc.org/suppdata/dt/b2/b206234h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Syntheses and spectroscopic properties of diphosphine and diarsine complexes

We were intrigued by the report that treatment of [RuCl$_2$(PPh$_3$)$_3$] with excess dmpm gave [Ru(dmpm)$_3$]Cl$_2$,[10] and we therefore investigated the reaction of [RuCl$_2$(PPh$_3$)$_3$] in a polar solvent (EtOH) with excess of the related ligands diars, dmpm and dmpe. With diars, we obtained the white, ethanol-soluble [Ru(diars)$_3$]Cl$_2$·2H_2O (**1a**) in good yield. Microanalytical data were consistent with this formulation, and the FAB mass spectrum showed a cluster of peaks at *m*/*z* 994 consistent with [M–Cl]$^+$. The ^{1}H NMR spectrum showed one AA′BB′ system in the aromatic region, and two equally intense As methyl resonances. As confirmed by the crystal structure determination (below), each As is equivalent, and has one methyl substituent oriented towards a neighbouring diars aromatic ring, and the other oriented towards one of the two opposite triangular faces of the octahedron which include an As from each of three different diars ligands. The presence of water was confirmed by ^{1}H NMR and infrared spectroscopy.

In our hands, treatment of [RuCl$_2$(PPh$_3$)$_3$] in EtOH with 3 mol. of dmpm[10] gave a moderate yield of [Ru(dmpm)$_3$]Cl$_2$ (**2a**) with the published spectroscopic characteristics, but it also invariably gave a light yellow by-product. The ^{31}P{^{1}H} NMR spectrum of this consisted of three equally intense resonances. Two were complex multiplets, at δ 4.9 and −30.7 ppm, with one large coupling (peak separation 297 Hz), consistent with mutually *trans* phosphines. The third was an apparent doublet (*J ca.* 3 Hz) at δ −59.0 ppm. The latter chemical shift is near that of the free ligand (−54.5 ppm). This, and its small couplings to the other phosphorus nuclei, suggests one monodentate dmpm, and hence the formulation *trans*-[RuCl$_2$(η^2-dmpm)(η^1-dmpm)$_2$] (**3**). It is possible that **3** is an intermediate in the reaction to form **2a**. We were unable to separate **3** from free PPh$_3$ (singlet at −5.5 ppm) and traces of Me$_2$P(O)CH$_2$-PMe$_2$ (doublets at 49.8 and −54.9 ppm; J_{PP} 39 Hz). Interestingly, treatment of [OsCl$_2$(PPh$_3$)$_3$] in petroleum ether with excess dmpm gave *trans*-[OsCl$_2$(η^2-dmpm)(η^1-dmpm)$_2$], and this also proved impossible to free from PPh$_3$.[21]

Less satisfactory was the result of prolonged reflux of EtOH solutions of [RuCl$_2$(PPh$_3$)$_3$] with 3.5 mol or 6 mol of dmpe, which gave only *trans*-[RuCl$_2$(dmpe)$_2$], identified by microanalyses and by the similarity of its NMR spectra to those published.[22]

We therefore decided to employ a halide-free ruthenium starting material. The complex [Ru(dmf)$_6$](OTf)$_3$[15] is proving to be a useful synthon, particularly for homoleptic complexes with neutral ligands.[5,23] Treatment of [Ru(dmf)$_6$](OTf)$_3$ with excess diars, dmpm, dmpe or depe in refluxing EtOH gave reasonable yields of [Ru(diars)$_3$](OTf)$_2$ (**1b**), [Ru(dmpm)$_3$]-(OTf)$_2$ (**2b**), [Ru(dmpe)$_3$](OTf)$_2$ (**4**) and [Ru(depe)$_3$](OTf)$_2$ (**5**) respectively. Optimum results were obtained when a significant excess (>4.5 mol. equiv.) of ligand was employed. A remarkable series of colour changes was seen during the reactions with the diphosphine ligands. Initially, the solutions were pale yellow (the colour of the Ru(III) starting material), but the colour deepened to burgundy, then deep blue–purple, before clearing to colourless. These colours may be due to intermediate, mixed-valence [Ru(II)Ru(III)] binuclear complexes. As expected for low spin Ru(II) with strong field ligands, the isolated complexes were white.

Throughout this study, we had considerable trouble obtaining satisfactory microanalyses (C and H) by combustion for these triflate salts, although the spectroscopic data (*q.v.*) adequately established the composition and purity of the complexes. The high fluorine content may have caused difficulties with complete combustion.†

The FAB mass spectra of the complexes showed significant peak clusters at *m*/*z* corresponding to [M–OTf]$^+$, and to fragmentation products involving loss of one and, in some cases, two ligands. The infrared spectra showed bands consistent with exclusively uncoordinated OTf$^-$ ions, in addition to bands similar to those seen for the chloride salts in the case of **1b** and

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† After the conclusion of this study, an ICP-OES facility was commissioned at Liverpool, and samples remaining from this study were analysed for other elements using this technique; results are included in the Experimental section, and they support the contention that the complexes are pure, but do not burn well.

Table 2 $10D_q$ and B values for $[Ru(diphosphine)_3]^{2+}$ complexes[a]

Complex	$10D_q$/cm^{-1}	B/cm^{-1}
$[Ru(dmpm)_3](OTf)_2$	37900	130
$[Ru(dmpe)_3](OTf)_2$	38300	170
$[Ru(depe)_3](OTf)_2$	36500	120

[a] Spectra all recorded in CH_3CN. $10D_q$ and B values calculated on the basis that the energy of the $^1T_{1g}$ state is $10D_q - C$,[25] and that $C = 10B$, as for $[Fe(diars)_3]^{2+}$.[11]

2b. The NMR (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) spectra were also diagnostic; the spectra of **1b** and **2b** were very similar to those of the corresponding chloride salts **1a** and **2a**. The $^{31}P\{^1H\}$ NMR spectrum of **4** showed a singlet at 27.8 ppm, a value significantly shifted compared with *trans*-$[RuX_2(dmpe)_2]$ (X = halide) which have resonances around 40–43 ppm[22] The $^{31}P\{^1H\}$ NMR spectrum of **5** showed a singlet, at 42 ppm, also shifted upfield compared with *trans*-$[RuCl_2(depe)_2]$ (48 ppm).[24] The ^1H NMR spectrum of **4** showed a very complex pair of broad multiplets due to the PCH_2CH_2P moiety, and an apparent singlet, albeit also broad, for the PMe groups. This is surprising since there should be two different environments for the methyl groups, as for **1b**. However, the isoelectronic $[Co(dmpe)_3]^{3+}$ also has closely-spaced PMe resonances, at 1.90 and 1.95 ppm.[12] Moreover, the $^{13}C\{^1H\}$ NMR spectrum of **4** showed one broad multiplet for the PCH_2CH_2P moiety at 30.0 ppm and two distinct broad multiplets at 19.6 and 18.4 ppm due to the two different PMe groups, confirming that the proton resonances for the latter are simply coincident.

The electronic spectra of the alkyldiphosphine complexes showed a shoulder at between 35000–37000 cm^{-1}, and a peak at between 37000 and 39000 cm^{-1}. Although these bands are at very high energy for d–d transitions, and although they have quite high molar extinction coefficients, we assign them to the $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$ transitions, respectively, expected for a pseudooctahedral low spin d^6 complex.[25] Table 2 shows the values of $10D_q$ and B calculated from the data. In the case of the diars complexes, the band at 33600 cm^{-1} is assigned to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition, but the energy of the $^1T_{2g} \leftarrow {}^1A_{1g}$ transition cannot be determined. The shoulder at *ca.* 37000 cm^{-1} in the spectra of **1a** and **1b** has vibrational structure, and is assigned to the diars-localised $\pi^* \leftarrow \pi$ transition, which occurs at this energy in the free ligand.[26] The $^1T_{2g} \leftarrow {}^1A_{1g}$ transition evidently overlaps this band. Nevertheless, it is clear that $10D_q$ for the diarsine is significantly less than for the diphosphine ligands, as expected. The bulkier depe ligand has a marginally lower $10D_q$ value than the methyl-substituted diphosphines, perhaps owing to even greater steric crowding in **5** than in **2** or **4**.

The very low values of B for these complexes follows from the small energy separation between the d–d bands, since this is approximately $16B$.[25] Interestingly, homoleptic thioether complexes, such as $[Ru(1,4,7\text{-trithiacyclononane})_2]^{2+}$ [1] and $[Ru(MeC\{CH_2SMe\}_3)_2]^{2+}$ [5,27] show similar spectra, except that the d–d transitions are at somewhat lower energy. Although the thioether B values, 250–290 cm^{-1}, are larger than for the diphosphines, these too are considerably smaller than for 'classical' ligands such as ammonia or 1,2-diaminoethane.[2]

Attempts to synthesise $[Ru(PR_3)_6]^{2+}$

Some time ago, it was reported that complexes $[RuCl(P\{OR\}_3)_5]^+$ and $[Ru(P\{OR\}_3)_6]^{2+}$ could be isolated after prolonged reaction of $[RuCl_2(PPh_3)_3]$ with a very large excess of the ligand in MeOH.[9] Treatment of $[Ru(dmf)_6](OTf)_3$ with a large excess of PMe_3 in EtOH/thf at reflux gave a colorless solution, from which an impure, white solid product was obtained on workup. The $^{31}P\{^1H\}$ NMR spectrum of this showed the presence of some Me_3PO (singlet at δ 45.3 ppm), and another singlet, at δ 31.7 ppm. The FAB mass spectrum (Xe^+) showed the presence of a molecular ion at 706 u, correct for $[M–OTf]^+$, and a succession of peak clusters due to progressive loss of the phosphines, and we therefore tentatively assign the peak at 31.7 ppm to $[Ru(PMe_3)_6](OTf)_2$ (**8**). However, we have been unable to obtain **8** free from Me_3PO. Unlike complexes **1**, **2**, **4** and **5**, (impure) **8** is air-sensitive in solution. On leaving a solution in EtOH to stand in air, a very intense blue–purple colour developed over a period of about 1 week at room temperature. Further details of this chemistry will be reported elsewhere.

Attempts to use aryldialkylphosphines in similar reactions (to promote crystallization of the $[RuP_6]^{2+}$ species) failed, and no evidence could be obtained for the formation of $[Ru(PhPMe_2)_6]^{2+}$ from $[Ru(dmf)_6](OTf)_3$ and $PhPMe_2$.

Attempts to synthesize $[Ru(aryldiphosphine)_3]^{2+}$

Reactions between $[Ru(dmf)_6](OTf)_3$ and dppe (up to 6 equivalents) did not give $[Ru(dppe)_3](OTf)_2$, but produced an intractable yellow gum, after separation from excess ligand by trituration with diethyl ether, the analytical and spectroscopic properties of which suggested the formulation *trans*-$[Ru(OTf)_2(dppe)_2]$, but we have not isolated this pure. Since we have devised better routes to complexes $[Ru(OTf)_2(diphosphine)_2]$, (albeit *cis*, in this case)[28] we have not pursued this further.

Prolonged reflux of $[Ru(dmf)_6](OTf)_3$ with 6.8 mol. equivalents of dppm in MeOH failed to give an analytically satisfactory sample of $[Ru(dppm)_3](OTf)_2$, although mass spectral (FAB, Xe^+) and NMR data supported this formulation. We have previously reported the synthesis and crystal structure of *cis*-$[Ru(dppm)_2(P\{OEt\}_3)_2](OTf)_2$, and this was considerably distorted from octahedral geometry owing to steric crowding.[28] It is perhaps not surprising, therefore, that $[Ru(dppm)_3](OTf)_2$ could not be isolated pure.

Structural studies on $[Ru(L–L)_3]^{2+}$ (L–L = diars, dmpe)

We were keen to obtain structural data on these novel homoleptic complexes. In attempts to obtain crystals of the cation $[Ru(diars)_3]^{2+}$, we tried a range of anions and were successful in obtaining crystals of $[Ru(diars)_3](SbF_6)_2$ (**1c**), but these invariably crystallized with non-stoichiometric, disordered solvent molecules, which prevented satisfactory refinement. Eventually, crystals of **1a** were grown, as $[Ru(diars)_3]Cl_2\cdot 0.5dmf\cdot H_2O$, from dmf and diethyl ether by solvent diffusion; details of the structure determination were reported in the preliminary communication.[16] The complex crystallized with two crystallographically distinct, but very similar, cations per asymmetric unit. The structure (Table 1; Fig. 1) is similar to that of the isoelectronic $[Co(diars)_3](BF_4)_3$.[12] Selected bond lengths and angles are shown in Table 3. Recently, a considerable number of structures of derivatives of *trans*-$[RuCl(4,4'\text{-bipyridine})(diars)_2]^+$ has been published,[29] and the mean Ru–As distance in complexes containing the *trans*-$[Ru^{II}(diars)_2]$ moiety (14 structures) is 2.425 Å. The mean Ru–As bond length in **1a** (over both independent molecules) is 2.4468(15) Å, suggesting some steric crowding compared with *trans*-$[Ru^{II}(diars)_2]$ complexes. Two further characteristics quoted to show the existence of steric crowding in $[Co(diars)_3](BF_4)_3$[12] were: unusually small Me–As–Me angles, and large Co–As–Me angles. Complex **1a** has a mean Me–As–Me angle of 98.8(5)° and a mean Ru–As–Me angle of 122.0(4)°, compared with means of 100.1 and 120.5°, respectively, for complexes containing the *trans*-$[Ru^{II}(diars)_2]$ moiety.[29]

In spite of considerable efforts, including anion metatheses, we have been unable to obtain X-ray diffraction-quality single crystals of any of the diphosphine complexes **2**, **4** or **5**. We therefore used Ru K-edge EXAFS spectroscopy to obtain structural information on **4**. Fig. 2 shows the EXAFS spectrum and Fourier transform. An excellent fit to the spectrum was obtained with a shell of six P atoms at a distance of 2.38(1) Å

Table 3 Selected bond lengths (Å) and angles (°) for **1a**[a]

Ru(1)–As(11)	2.4706(15)	Ru(1)–As(21)	2.4532(16)
Ru(1)–As(31)	2.4566(14)	Ru(1)–As(12)	2.4446(13)
Ru(1)–As(22)	2.4462(14)	Ru(1)–As(32)	2.4399(13)
As–C(Me) (mean)	1.935(12)	As–C(aryl) (mean)	1.927(10)
As(12)–Ru(1)–As(11)	83.19(5)	As(22)–Ru(1)–As(21)	84.13(5)
As(32)–Ru(1)–As(31)	84.00(4)	As(11)–Ru(1)–As(21)	170.94(6)
As(12)–Ru(1)–As(32)	176.64(6)	As(22)–Ru(1)–As(31)	170.98(5)
As(12)–Ru(1)–As(22)	92.52(5)	As(21)–Ru(1)–As(32)	90.67(5)
As(11)–Ru(1)–As(31)	98.64(5)	As(22)–Ru(1)–As(32)	90.19(4)
As(12)–Ru(1)–As(21)	91.59(5)	As(12)–Ru(1)–As(31)	93.55(5)
As(21)–Ru(1)–As(31)	89.04(5)	As(11)–Ru(1)–As(31)	94.89(5)
As(11)–Ru(1)–As(22)	88.70(5)	Me–As–Me (mean)	98.8(5)
Me–As–Ru(1) (mean)	122.0(4)		

[a] Two slightly different cations in asymmetric unit; data for one cation shown.

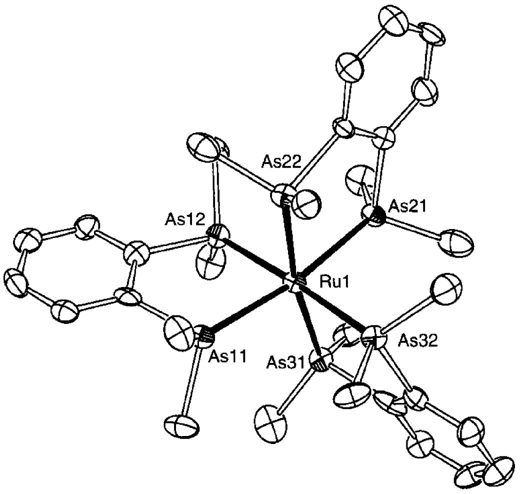

Fig. 1 ORTEP plot of one of the two slightly different cations, $[Ru(diars)_3]^{2+}$, from the crystal structure of **1a**·0.5dmf·H_2O.

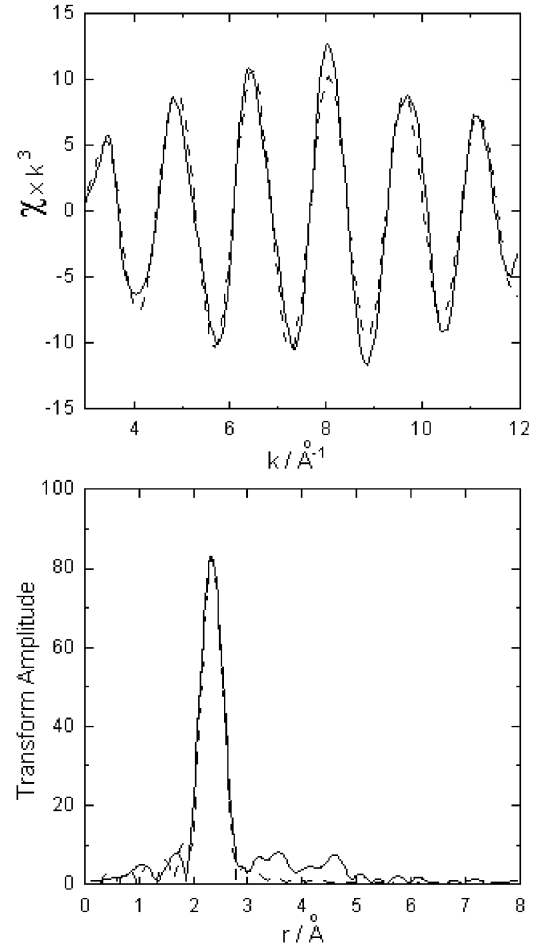

Fig. 2 Ruthenium K-edge EXAFS data (top) and Fourier transform (bottom) for complex **4**. The solid lines are experimental data, and the dotted lines are for the best fit; see Results and discussion.

(Debye–Waller factor 0.005 Å^2, residual 24.1). Although the Fourier transform indicates the presence of some minor shells between 3 and 5 Å, presumably ligand C atoms, the addition of additional backscatterers to the model did not significantly improve the fit.

The mean Ru–P distance in the 14 complexes containing *trans*-$[Ru^{II}(dmpe)_2]$ moieties in the Cambridge Crystallographic Database[30] is 2.31 Å, so clearly, the Ru–P distance in **4** is considerably lengthened by steric hindrance, to a degree significantly greater than for **1**.

Electrochemical and theoretical studies

None of the homoleptic complexes $[M(L–L)_3]^{2+}$ showed any evidence of a Ru(II)/Ru(III) redox process within the normal electrochemical 'window' of CH_3CN/0.2 M TEAT (*i.e.* up to + 1.6 V *vs.* ferrocene/ferrocinium).

In order to extend the useful potential window to $+ 3.5 \geq E \geq -3.4$ V, thereby excluding any non-intrinsic follow up reactions of electrogenerated species, the voltammetry of **1b**, **2b** and **4** was examined under strictly dry conditions, using a microelectrode (Experimental).[20,31] Cyclic voltammograms for the complexes are shown in Fig. 3. The dmpm complex, **2b**, shows two closely-spaced one-electron, chemically and electrochemically irreversible processes, at E_p^A *ca.* + 2.4 V. When the positive limit is extended to ≥ +2.9 V, there is a further irreversible, multi-electron process, which is strongly affected by adsorption phenomena, as evidenced by the linear dependence of its peak current with scan rate. Moreover, severe passivation effects are seen when these peaks are included in the potential sweep. The dmpe and diars complexes, **4b** and **1b**, show a one-electron, electrochemically and chemically irreversible process, at E_p^A + 2.29 and +2.1 V respectively. Digital simulation of these curves was used to provide parameters for the heterogeneous electron transfer processes, and the kinetic constants for the chemical steps associated with the redox processes; the simulation used an EC mechanism for **4b** and an ECEC mechanism for **2b**. The simulated curves are also shown in Fig. 3 and the data are tabulated in Table 4. Agreement with the experimental curves is good; the apparently less satisfactory agreement for complex **2b** arises because the second oxidation process is just at the foot of the multi-electron wave (occurring at potential > +2.9 V), which increases the experimental current compared with the simulated curve. It is noteworthy that the oxidations show rather sluggish kinetics (rate constants *ca.* 10^{-4} cm s^{-1} and transfer coefficients 0.70–0.75).

Table 4 Electrochemical data (potential/V; first order rate constants/s^{-1})

Ligand	E(Ru$^{III/II}$)^a	E_L^{b}	E(Ru$^{III/II}$)^c	E_L^{d}	E(Ru$^{III/II}$)^e	E_{formal}^{f}	$k_{decomp.}$^{g}
diars	+0.62	+0.28	+1.72	+0.34	+1.05, +1.41	+1.75	1×10^5
dmpe	+0.55	+0.26	+1.68	+0.32	+0.93, +1.29	+1.80	1×10^5
dmpm	–	–	–	–	unknown	+1.76, +2.10	1×10^5, 1×10^6

[a] For the appropriate *trans*-[RuCl$_2$(L–L)$_2$]$^+$, in CH$_3$CN, *vs.* NHE assuming that the ferrocene/ferrocenium couple is at +0.630 V *vs.* NHE.[33,42] [b] Electrochemical ligand parameter,[6] calculated from *a*, using E_L for chloride of −0.24 V.[6] [c] For the appropriate [Ru(bipy)$_2$(L–L)]$^{2+}$ in CH$_3$CN, *vs.* NHE, this work (dmpe and diars). [d] Electrochemical ligand parameter E_L, calculated from *c*, using E_L for bipy of +0.259 V.[6] [e] Potential *vs.* ferrocene/ferrocinium[42] calculated for [Ru(L–L)$_3$]$^{2+}$, using the appropriate E_L value. The left-hand value is calculated using E_L derived from *trans*-[RuCl$_2$-(L–L)$_2$]$^+$, and the right-hand value is calculated using E_L derived from [Ru(bipy)$_2$(L–L)]$^{2+}$. [f] Totally irreversible at all scan rates; formal potential derived by curve fitting; see Experimental section. [g] From curve fitting, assuming EC mechanism, except for dmpm complex, for which an ECEC mechanism was assumed, hence two rate constants. The values of the rate constants are the lower limit.

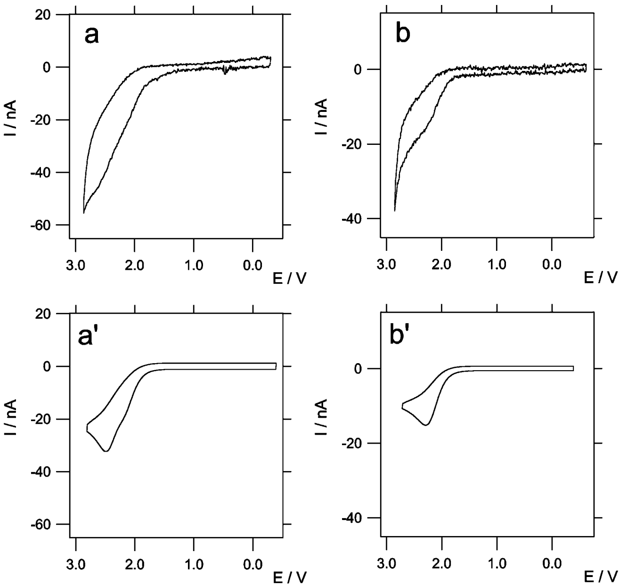

Fig. 3 (a) Cyclic voltammetric curve for a 1 mM [Ru(dmpm)$_3$]$^{2+}$, 0.08 M TBAH/CH$_3$CN solution. Working electrode: Pt disc microelectrode, radius 125 μm; T = 25 °C; scan rate 1 V s^{-1}. (a′) Simulated cyclic voltammetric curve for the species [Ru(dmpm)$_3$]$^{2+}$ under the conditions of (a) calculated for an ECEC mechanism (see text). (b) Cyclic voltammetric curve for a 1 mM [Ru(dmpe)$_3$]$^{2+}$, 0.08 M TBAH/CH$_3$CN solution. Working electrode: Pt disc microelectrode, radius 125 μm; T = 25 °C; scan rate 1 V s^{-1}. (b′) Simulated cyclic voltammetric curve for the species [Ru(dmpe)$_3$]$^{2+}$ under the conditions of (b) calculated for a EC mechanism (see text).

Table 5 Significant bond lengths (Å) and angles (°) for **7**

Ru(1)–As(1)	2.4113(3)	Ru(1)–As(2)	2.4019(3)
Ru(1)–N(1)	2.1045(15)	Ru(1)–N(2)	2.0841(15)
Ru(1)–N(3)	2.0713(15)	Ru(1)–N(4)	2.0855(15)
As–C(Me) (mean)	1.943(2)	As–C(aryl) (mean)	1.9457(19)
As(1)–Ru(1)–As(2)	84.042(8)	N(1)–Ru(1)–N(2)	77.82(6)
N(3)–Ru(1)–N(4)	78.20(6)	N(1)–Ru(1)–As(1)	97.68(4)
N(1)–Ru(1)–As(2)	178.09(4)	N(2)–Ru(1)–As(1)	89.79(4)
N(2)–Ru(1)–As(2)	103.05(4)	N(3)–Ru(1)–As(1)	97.64(5)
N(3)–Ru(1)–As(2)	86.18(4)	N(4)–Ru(1)–As(1)	173.44(4)
N(4)–Ru(1)–As(2)	90.58(4)	N(1)–Ru(1)–N(3)	92.77(6)
N(1)–Ru(1)–N(4)	87.65(6)	N(2)–Ru(1)–N(3)	168.75(6)
N(2)–Ru(1)–N(4)	95.09(6)	C(21)–As(1)–C(22)	100.21(10)
C(29)–As(2)–C(30)	100.80(9)	C(21)–As(1)–Ru(1)	121.80(7)
C(22)–As(1)–Ru(1)	119.62(7)	C(29)–As(2)–Ru(1)	124.99(6)
C(30)–As(2)–Ru(1)	113.56(6)		

Consistent with these results, when complex **1b** was dissolved in conc. HNO$_3$, a reagent which is capable of oxidizing [Fe(diars)$_3$]$^{2+}$ to [Fe(diars)$_3$]$^{3+}$,[32] there was no obvious colour change, and the addition of 60% HClO$_4$ simply precipitated [Ru(diars)$_3$](ClO$_4$)$_2$ (**1d**), the cation of which was spectroscopically identical to that of **1a**–**c**.

The electrochemical ligand parameter (E_L) for chloride is particularly well-established (−0.24 V, over 45 complexes[6]). The Ru(III)/Ru(II) potentials have been measured in CH$_3$CN for a range of complexes *trans*-[RuCl$_2$(L–L)$_2$]$^+$ (L–L = diphosphine, diarsine *etc.*).[33] Table 4 compares values of E_L for representative diphosphine and diarsine ligands, calculated using these potentials. Clearly, these values predict that one should observe a Ru(II)/Ru(III) process at between +0.9 and +1.1 V, about 0.7 V negative of the formal potentials for **1**–**4**.

We wished to check whether this discrepancy was due to a breakdown in ligand additivity caused by unusually strong ligand–ligand cooperativity; halide ions are π-donors, and these neutral ligands have significant π-acceptor ability. Some quite extreme examples of cases where this clearly causes ligand additivity to break down have been published.[34]

Bipy has the advantages that it is not a π-donor, its E_L value is particularly well-determined (+0.259 V, 94 examples),[6] and the half-wave potential for the Ru(II)–Ru(III) process for a complex [Ru(bipy)$_2$(L–L)]$^{2+}$ should lie within the normal potential window of CH$_3$CN electrolytes, obviating the need for the very time-consuming and painstaking precautions necessary to determine the redox properties of **1**, **2** and **4**. Electrochemical and photophysical measurements on both [Ru(bipy)$_2$(dmpe)]$^{2+}$ and [Ru(bipy)$_2$(diars)]$^{2+}$ have been reported,[35] but spectroscopic and structural data were not given. Moreover, the ligand written as 'dmpe' in the text of ref. 35 was illustrated as Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe). We have therefore prepared and characterized [Ru(bipy)$_2$(dmpe)](OTf)$_2$ (**6**) and [Ru(bipy)$_2$-(diars)](OTf)$_2$ (**7**), and have re-examined their electrochemistry (Table 4).

Crystals of **7** suitable for X-ray diffraction were grown from MeOH/Et$_2$O by diffusion. A summary of the crystal data and refinement results is given in Table 2. Significant bond lengths and angles are in Table 5, and Fig. 4 shows the cation. The structure makes an interesting comparison with that of **1a**. The mean Ru–As distance in **7** is 2.4066(3) Å, shorter than in **1a**, and also shorter than the mean of 2.425 Å for complexes containing the *trans*-[Ru^{II}(diars)$_2$] moiety.[30] The mean Me–As–Me angle is 100.5°, and the mean Ru–As–Me angle is 120°, similar to the means of 100.1 and 120.5°, respectively, for *trans*-[Ru^{II}(diars)$_2$] moieties.[30] The structure confirms that there is no significant steric strain in complex **7**.

In CH$_3$CN, **6** and **7** show a Ru(II)/Ru(III) redox process, and two bipy-based one-electron reductions. The half-wave potentials of these agree with the published values, within experimental error.[35] The E_L values we calculate for dmpe and diars using **6** and **7** are somewhat larger than those determined using [RuCl$_2$(L–L)$_2$] (Table 4). Because E_L must be multiplied by 6 to estimate the Ru(II)/Ru(III) potentials of our [Ru(L–L)$_3$]$^{2+}$, these differences become significant. However, the oxidations we observe for [Ru(L–L)$_3$]$^{2+}$ have formal potentials at least 0.4 V positive of the Ru(II)/Ru(III) potential calculated using even these E_L values, and, moreover, they are irreversible.

It is interesting to compare these observations with the situation for related donor atoms. The complex [Ru(1,5,9-

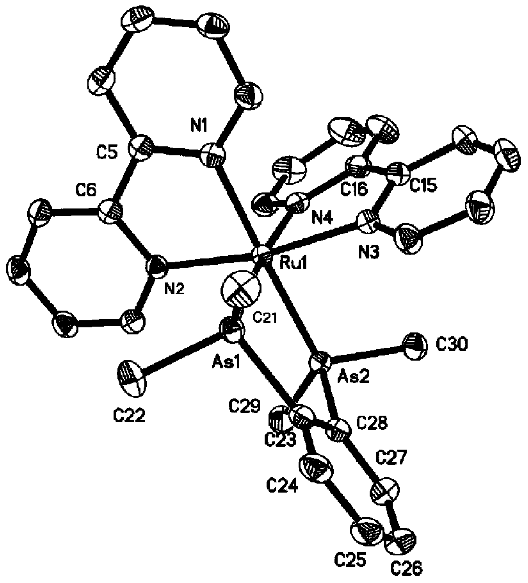

Fig. 4 ORTEP plot of the cation of complex **7**.

trithiacyclododecane$)_2]^{2+}$ has a Ru(II)/Ru(III) redox process at +1.03 V, and [Ru(1,4,7-trithiacyclononane$)_2]^{2+}$ at +1.36 V. Similarly, the recently-described homoleptic selenoether complex $[\mathrm{Ru(MeC\{CH_2SeMe\}_3)_2}]^{2+}$ has a quasi-reversible Ru(II)/Ru(III) process at +1.18 V.[5] The published E_L values for alkylthioethers[6] range from +0.31 to +0.35 V, giving a predicted Ru(II)/Ru(III) potential for a complex $[\mathrm{Ru(R_2S)_6}]^{2+}$ in the range +1.2 to +1.5 V; to a first approximation, $[\mathrm{Ru(R_2Se)_6}]^{2+}$ should be similar. Thus the Ru(II) homoleptic complexes of thio- and selenoethers show redox behaviour which agrees well with Lever's predictions, while the homoleptic phosphine and arsine complexes do not.

It is clear from the structural data that the Ru(II) centre is sterically crowded in our complexes. Oxidation to the smaller Ru(III) will thus be unusually unfavourable. The diphosphine complexes are more strongly affected by this; the bond length difference observed between **4b** and *trans*-$[\mathrm{Ru^{II}(dmpe)_2}]$ moieties is somewhat larger than that between **1a** and *trans*-$[\mathrm{Ru^{II}(diars)_2}]$ moieties. It is significant that the crystal structures of the various thioether complexes show that there is little or no steric strain in the homoleptic complexes, compared with non-homoleptic complexes with the same ligands.[5,27]

Quantum chemical calculations

We hoped to shed more light on the unusual Ru(II)/Ru(III) redox potentials of **1**, **2** and **4** using theoretical methods. Calculations at different levels of theory have been used, applying density functional theory (DFT) and *ab initio* methods (gas phase only). The geometry optimization of the complexes, investigated by HF/3-21G*[36] and DFT[37] (using B3LYP[38] and BP86[39] functionals with 3-21G* and effective core potential (i) split valence CEP-31G and (ii) double zeta LanL2DZ[40] basis set), has shown that better results are obtained with DFT/3-21G.

Calculations were performed on complexes **1**, **2**, **4** and (as a model complex where steric effects are minimal) **6**. For the last three, geometry optimization was done both at molecular mechanics and DFT/3-21G* level, while for the first one the geometry from the crystal structure was used. Since no X-ray data are available for the homoleptic phosphine complexes, the EXAFS results reported above for complex **4**, and the crystal structure of heteroleptic Ru(II) complexes, are the only reference data available. The geometry obtained for complex **4** by DFT calculations is in a fairly good agreement with the data, showing the overestimation of bond lengths with an average deviation of 0.03 Å, whereas that from molecular mechanics show an average Ru–P bond length of 2.31 Å, a typical bond length shown by heteroleptic species. The σ-donor and π-acceptor properties of the two ligands dmpm and dmpe should be very similar, and both the molecular orbital (MO) and electrochemical results confirm this. The following discussion therefore focuses on one of the two diphosphine complexes studied.

The single point MO calculations for the two geometries of **2b** (Fig. 5a and 5b) show that the lengthening of Ru–P bonds from 2.31 to 2.41 Å stabilizes the LUMO by 1.02 eV. Rather surprisingly, it also stabilizes the HOMO by 0.66 eV. Moreover, as determined by the Mulliken population analyses,[41] the contribution of ruthenium to the HOMO increases dramatically with the lengthening of the Ru–P bonds, passing from 41 to 72%, whereas the LUMO remains nearly unaffected (from 41 to 45%). This indicates that the steric hindrance at the metal centre influences the electronic properties of the complex, making it both more difficult to oxidize, and easier to reduce.

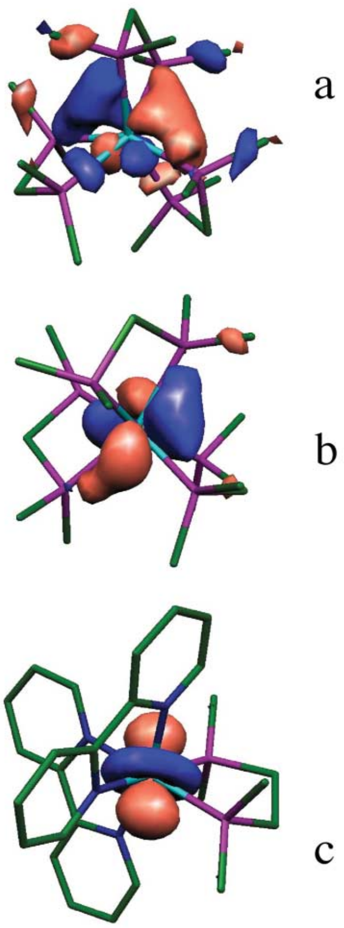

Fig. 5 Calculated HOMO surfaces at B3LYP/3-21G* level of (a) $[\mathrm{Ru(dmpm)_3}]^{2+}$ with geometry optimized by molecular mechanics (mean Ru–P bond length 2.31 Å); (b) $[\mathrm{Ru(dmpm)_3}]^{2+}$ with geometry optimized at DFT level (mean Ru–P bond length 2.41 Å); (c) $[\mathrm{Ru(bpy)_2(dmpe)}]^{2+}$ with DFT optimized geometry.

The calculations on species $[\mathrm{Ru(bpy)_2(dmpe)}]^{2+}$, performed for comparison purposes, show, for the optimized geometry at B3LYP/3-21G*, that not only is the HOMO completely ruthenium-centered (Fig. 5c), but its energy is about 1 eV higher than the HOMO of the homoleptic complex $[\mathrm{Ru(dmpe)_3}]^{2+}$ (**4**). This is in line with the electrochemical results indicating that the complex $[\mathrm{Ru(bpy)_2(dmpe)}]^{2+}$ is significantly easier to oxidize than species **4**.

As for the slow kinetics observed for the oxidation processes, two possible explanations are, firstly, a high electron transfer reorganization energy, and secondly, the fact that the HOMO, having almost completely d-metal character, is buried inside a phosphorus shell and a less polarizable carbon shell. Since the electron transfer reorganization energy for a low spin d^6/low spin d^5 process should not be large, the latter explanation appears more likely.

Conclusions

We have shown that it is possible to prepare octahedral homoleptic Ru(II)–phosphine and Ru(II)–arsine complexes. Steric factors alone seem to control which complexes can be made. Thus, P-donors with small substituents can give $[Ru(P)_6]^{2+}$, whether they are electron-rich (*e.g.* dmpe) or electron-poor (*e.g.* $P\{OEt\}_3$),[9] while larger ligands (*e.g.* dppe) cannot. We have found evidence, from metal–ligand bond lengths, of steric crowding, in $[Ru(diars)_3]^{2+}$ by X-ray crystallography, and $[Ru(dmpe)_3]^{2+}$ by EXAFS. In spite of this, the electronic spectra indicate that these ligands exert an extremely large ligand field at Ru(II). The complexes are remarkably resistant to oxidation to Ru(III), apparently more so than Lever's electrochemical ligand parameters would suggest, and our theoretical calculations strongly suggest that steric crowding is responsible for this.

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References

1 (*a*) D. G. De Wit, *Coord. Chem. Rev.*, 1996, **147**, 209; (*b*) A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1; (*c*) S. R. Cooper, *Acc. Chem. Res.*, 1988, **21**, 141.

2 (*a*) M. N. Bell, A. J. Blake, A. J. Holder, T. I. Hyde and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1990, 3841; (*b*) S. C. Rawle, T. J. Sewell and S. R. Cooper, *Inorg. Chem.*, 1987, **26**, 3769.

3 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belper and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.

4 E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984.

5 W. Levason, S. D. Orchard and G. Reid, *Chem. Commun.*, 1999, 1071.

6 (*a*) A. B. P. Lever, *Inorg. Chem.*, 1990, **29**, 1271; (*b*) S. S. Fielder, M. C. Osborne, A. B. P. Lever and W. J. Pietro, *J. Am. Chem. Soc.*, 1995, **117**, 6990.

7 (*a*) K. M. Sung, S. Huh and M. J. Jun, *Polyhedron*, 1998, **18**, 469; (*b*) S. P. Nolan, T. R. Belderrain and R. H. Grubbs, *Organometallics*, 1997, **16**, 5569.

8 (*a*) E. P. Kundig, C. M. Saudan and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 1220; (*b*) M. E. Cucullu, S. P. Nolan, T. R. Belderrain and R. H. Grubbs, *Organometallics*, 1999, **18**, 1299; (*c*) Y. Nishibayashi, I. Takei, S. Uemura and M. Hidai, *Organometallics*, 1998, **17**, 3420; (*d*) H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. England, T. Ikariya and R. Noyori, *Angew. Chem., Int. Ed.*, 1998, **37**, 1703.

9 D. A. Couch and S. D. Robinson, *Inorg. Chim. Acta*, 1974, **9**, 39.

10 W. K. Wong, K. W. Chiu, G. Wilkinson, A. J. Howes, M. Motevalli and M. B. Hursthouse, *Polyhedron*, 1985, **4**, 603.

11 R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, 1968, **7**, 1154.

12 (*a*) H. C. Jewiss, W. Levason and M. Webster, *Inorg. Chem.*, 1986, **25**, 1997; (*b*) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570; (*c*) T. Ohishi, K. Kashiwabara and J. Fujita, *Chem. Lett.*, 1981, 1371.

13 (*a*) F. G. N. Cloke, P. J. Fyne, V. C. Gibson, M. L. H. Green, M. J. Ledoux, R. N. Perutz, A. Dix, A. Gourdon and K. Prout, *J. Organomet. Chem.*, 1984, **277**, 61; (*b*) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 1962, 2545.

14 M. Brookhart, K. Cox, F. G. N. Cloke, J. C. Green, M. L. H. Green, J. Bashkin, A. E. Derome and P. D. Grebenik, *J. Chem. Soc., Dalton Trans.*, 1985, 423.

15 R. J. Judd, R. Cao, M. Biner, T. Armbruster, H. B. Bürgi, A. E. Merbach and A. Ludi, *Inorg. Chem.*, 1995, **34**, 5080.

16 A. A. La Pensée, S. J. Higgins, C. A. Stuart and J. F. Bickley, *Inorg. Chem. Commun.*, 1999, **2**, 524.

17 R. D. Feltham, A. Kasenally and R. S. Nyholm, *J. Organomet. Chem.*, 1967, **7**, 285.

18 P. S. Hallman, T. A. Stevenson and G. Wilkinson, *Inorg. Synth.*, 1970, **12**, 237.

19 (*a*) J. V. Barkley, S. J. Higgins, M. K. McCart and T. J. Pounds, *Inorg. Chem.*, 1997, **36**, 6188; (*b*) S.J. Higgins, A. L. La Pensée, C.A. Stuart and J.M. Charnock, *J. Chem. Soc., Dalton Trans.*, 2001, 902.

20 (*a*) F. Paolucci, M. Marcaccio, C. Paradisi, S. Roffia, C. A. Bignozzi and A. Amatore, *J. Phys. Chem. B*, 1998, **102**, 4759; (*b*) M. Marcaccio, F. Paolucci, C. Paradisi, S. Roffia, C. Fontanasi, L. J. Yellowlees, S. Serroni, S. Campagna, G. Denti and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 10081.

21 P. Palma-Ramirez, D. J. Cole-Hamilton, P. Pogorzelec and J. Campora, *Polyhedron*, 1990, **9**, 1107.

22 C. A. Tolman, S. D. Ittel, A. D. English and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 4080.

23 (*a*) I. R. Baird, S. J. Rettig, B. R. James and K. A. Skov, *Can. J. Chem.*, 1998, **76**, 1379; (*b*) N. J. Holmes, W. Levason and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1998, 3457.

24 L. D. Field, A. V. George, D. C. R. Hockless, G. R. Purches and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1996, 2011.

25 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1984.

26 J. R. Preer, F. D. Tsay and H. B. Gray, *J. Am. Chem. Soc.*, 1972, **94**, 1875.

27 W. Levason, S. D. Orchard and G. Reid, *Inorg. Chem.*, 2000, **39**, 3853.

28 J. F. Bickley, S. J. Higgins, C. A. Stuart and A. Steiner, *Inorg. Chem. Commun.*, 2000, **3**, 211.

29 (*a*) B. J. Coe, M. Chery, R. L. Beddoes, H. Hope and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1996, 3917; (*b*) B. J. Coe, S. Hayat, R. L. Beddoes, M. Helliwell, J. C. Jeffrey, S. R. Batten and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1997, 591; (*c*) B. J. Coe, T. Beyer, J. C. Jeffrey, S. J. Coles, T. Gelbrich, M. B. Hursthouse and M. E. Light, *J. Chem. Soc., Dalton Trans.*, 2000, 797; (*d*) B. J. Coe, C. I. McDonald, S. J. Coles and M. B. Hursthouse, *Acta Crystallogr., Sect. C*, 2000, **56**, 963.

30 D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746.

31 (*a*) F. Paolucci, M. Marcaccio, S. Roffia, G. Orlandi, F. Zerbetto, M. Prato, M. Maggini and M. Scorrano, *J. Am. Chem. Soc.*, 1995, **117**, 6572; (*b*) M. Carano, M. Careri, F. Cicogna, I. D'Ambra, J. L. Houben, G. Ingrosso, M. Marcaccio, F. Paolucci, C. Pinzino and S. Roffia, *Organometallics*, 2001, **20**, 3478.

32 R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, 1970, **9**, 1207.

33 N. R. Champness, W. Levason, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1992, 3243.

34 (*a*) G. A. Heath and D. G. Humphrey, *J. Chem. Soc., Chem. Commun.*, 1991, 1668; (*b*) C. M. Duff and R. A. Schmid, *Inorg. Chem.*, 1991, **30**, 2938.

35 J. V. Caspar and T. J. Meyer, *Inorg. Chem.*, 1983, **22**, 2444.

36 (*a*) A. A. Granovsky, *Gamess*, http://classic.chem.msu.su/gran/gamess/index.html; M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347; (*b*) J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939; (*c*) M. S. Gordon, J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.*, 1982, **104**, 2797; (*d*) K. D. Dobbs and W. J. Hehre, *J. Comput. Chem.*, 1987, **8**, 880.

37 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98*, Gaussian, Inc., Pittsburgh, PA, 1998.

38 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Wang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

39 (*a*) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (*b*) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.

40 (*a*) T. H. Dunning, Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, ed. H. F. Schaefer III, Plenum, New York, 1976; (*b*) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; (*c*) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 284; (*d*) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

41 (*a*) R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1841; (*b*) R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 2338; (*c*) R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 2343; (*d*) S. I. Gorelsky and A. B. P. Lever, *MOMIX*, York University, Ontario, 2000.

42 V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, **298**, 97.