Synthesis, Characterisation and Crystal Structure of a Dirhodium(II) Compound with Two Bridging Trifluoroacetamidate Ligands†

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The compound [$Rh_2(HNCOCF_3)_4$] reacts with 1,10-phenanthroline (phen) in the presence of HCl to give two isomers of [$Rh_2(HNCOCF_3)_2$(phen)$_2Cl_2$], **1a** and **1b**, which are readily distinguished by ^1H NMR spectroscopy. In contrast if the reaction is carried out in the presence of a non-acidic chloride source, tetrabutylammonium chloride, only a single isomer, **1a**, is formed in appreciable amounts. Complex **1a** reacts with pyridine in the presence of K[PF_6] to give [$Rh_2(HNCOCF_3)_2$(phen)$_2$($C_5H_5N)_2$][PF_6]$_2$, **2**, which has been characterised by X-ray crystallography. For comparative purposes [$Rh_2(O_2CCH_3)_2$(phen)$_2$($C_5H_5N)_2$][PF_6]$_2$, **3**, has been prepared and crystallographically characterised.

While the chemistry of dirhodium(II) compounds containing four bridging carboxylato ligands has been extensively studied [1–3] the chemistry, as opposed to the electrochemical and structural properties, of many other dirhodium(II) compounds has been sadly neglected. For example the first amidato bridged compound, [$Rh_2(HNCOCF_3)_4$] was reported[4] in 1982 and many other [$Rh_2(RNCOR')_4$] compounds are now known.[5–12] However despite the enormous potential interest in these compounds the studies which have been reported in the literature, with few exceptions,[13] largely concentrated only on X-ray crystallographic characterisation and electrochemical/spectroelectrochemical investigations. Similar comments might be made about many other classes of dirhodium(II) compounds. One of the few groups of compound whose *chemistry* has received close attention is, for obvious reasons, that in which there are orthometallated tertiary phosphine bridging ligands.[14–17]

As the first step towards redressing this situation we now report the results obtained during our investigation of the reaction of [$Rh_2(HNCOCF_3)_4$] with 1,10-phenanthroline (phen).

Experimental

Proton NMR spectra were recorded on a Varian XL400 spectrometer. Cyclic voltammetric measurements were performed using a Metrohm E506 potentiostat interfaced with a Metrohm E612 VA Scanner and Hewlett Packard 7035B XY recorder. Electrolyte solutions were 0.2 mol dm^{-3} in tetrabutylammonium tetrafluoroborate. Deaeration of the solution was performed before commencing the experiment and a stream of nitrogen was passed throughout. The working electrode was a platinum wire (Metrohm EA285). A non-aqueous Ag–AgCl–Cl$^-$, CH_2Cl_2 electrode was used as a reference electrode (Metrohm EA441/5) and a platinum wire as the auxiliary electrode. All potentials are reported with respect to the Ag–AgCl electrode, against which ferrocene is oxidised at a potential of +0.60 V.

The complexes [$Rh_2(O_2CCH_3)_4$], [$Rh_2(HNCOCF_3)_4$] and [$Rh_2(O_2CCH_3)_2$(phen)$_2Cl_2$] were prepared by literature methods.[5,18,19] All other reagents were supplied by commercial suppliers. Solvents were of analytical grade and were distilled under nitrogen prior to use.

Preparations.—[$Rh_2(HNCOCF_3)_2$(phen)$_2Cl_2$]**1a**.1,10-Phenanthroline (0.10 g, 0.55 mmol) was added to a solution of [$Rh_2(HNCOCF_3)_4$] (0.11 g, 0.16 mmol) in methanol (5 cm^3). Tetrabutylammonium chloride (0.12 g, 0.45 mmol) was then added and the solution stirred at 25 °C for 60 h. The red-brown solid which formed was filtered off, washed with methanol and dried *in vacuo*. Yield 0.05 g, 24% (Found: C, 38.7; H, 2.4; Cl, 8.0; N, 9.2. Calc. for $C_{28}H_{18}Cl_2F_6N_6O_2Rh_2$: C, 39.0; H, 2.1; Cl, 8.2; N, 9.7%). ^1H NMR (CD_3NO_2): 1,10-phenanthroline, δ 8.74 (d, 2 H), 8.36 (d, 2 H), 8.25 (d, 2 H), 7.96 (d, 2 H), 7.76 (dd, 2 H), 7.65 (AB, 4 H) and 7.27 (dd, 2 H); CF_3CONH^-, δ 9.20 (br s, 2 H).

[$Rh_2(HNCOCF_3)_2$(phen)$_2$($C_5H_5N)_2$][PF_6]$_2$ **2**. Pyridine (0.05 cm^3) was added to a suspension of [$Rh_2(HNCOCF_3)_2$(phen)$_2Cl_2$] (0.10 g, 0.11 mmol) in methanol (5 cm^3). The mixture was stirred at 25 °C for 2 h, in which time a yellow solution was formed. Solid K[PF_6] (0.05 g, 0.27 mmol) was added and the volume reduced to 2 cm^3. A yellow solid precipitated and was collected by filtration and dried *in vacuo*. Yield 0.08 g, 58% (Found: C, 36.1; H, 2.2; N, 9.4. Calc. for $C_{38}H_{28}F_{18}N_8O_2P_2Rh_2$: C, 36.8; H, 2.3; N, 9.0%). ^1H NMR [$(CD_3)_2CO$]: 1,10-phenanthroline, δ 8.91 (d, 2 H), 8.87 (d, 2 H), 8.48 (d, 2 H), 8.40 (d, 2 H), 7.86 (m, 6 H) and 7.72 (m, 2 H); pyridine, δ 8.03 (d, 4 H), 7.78 (t, 2 H) and 7.26 (dd, 4 H); CF_3CONH^-, δ 9.05 (br s, 2 H).

[$Rh_2(O_2CCH_3)_2$(phen)$_2$($C_5H_5N)_2$][PF_6]$_2$ **3**. Pyridine (0.05 cm^3) was added to a suspension of [$Rh_2(O_2CCH_3)_2$(phen)$_2Cl_2$] (0.10 g, 0.13 mmol) in methanol (5 cm^3). The mixture was stirred at 25 °C for 2 h, in which time a yellow solution was formed. Solid K[PF_6] (0.05 g, 0.27 mmol) was added and the volume reduced to 2 cm^3. A yellow solid precipitated and was collected by filtration and dried *in vacuo*. Yield 0.09 g, 70% (Found: C, 39.7; H, 2.6; N, 7.2. Calc. for $C_{38}H_{32}F_{12}N_6O_4P_2Rh_2$: C, 40.3; H, 2.8; N, 7.4%). ^1H NMR (CD_3NO_2): 1,10-phenanthroline, δ 8.69 (d, 4 H), 8.25 (d, 4 H), 7.70 (s, 4 H) and 7.66 (dd, 4 H); pyridine, δ 8.19 (d, 4 H), 7.78 (t, 2 H) and 7.27 (dd, 4 H); $O_2CCH_3^-$, δ 2.62 (s, 6 H).

Crystal Structure Determinations.—Single crystals of [$Rh_2(HNCOCF_3)_2$(phen)$_2$($C_5H_5N)_2$][PF_6]$_2$·($C_2H_5)_2O$ **2** were prepared by vapour diffusion of diethyl ether into a dichloromethane solution of the compound while those of

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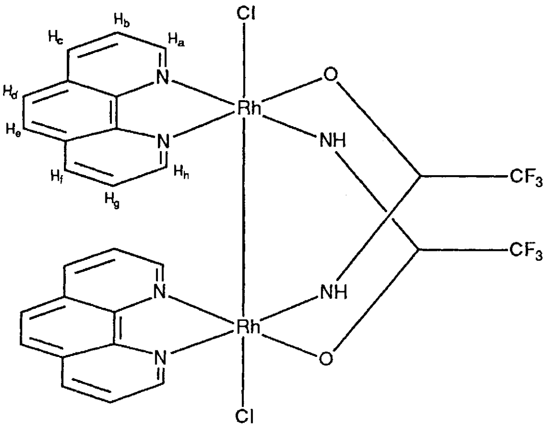
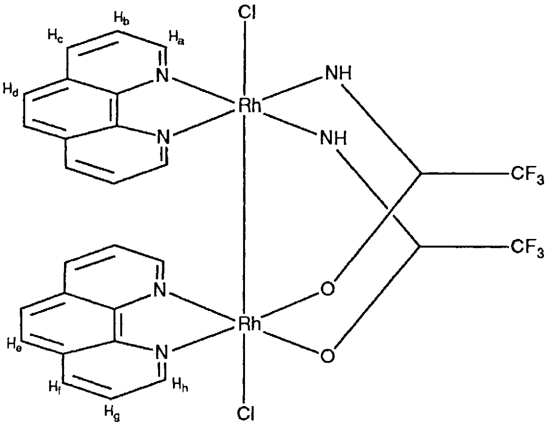
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



1a



1b

$[Rh_2(O_2CCH_3)_2(phen)_2(C_5H_5N)_2][PF_6]_2 \cdot (CH_3)_2CO$ **3** were obtained by slow evaporation of an acetone solution.

Crystal data for complex **2**. $C_{42}H_{38}F_{18}N_8O_3P_2Rh_2$, M = 1312.6, triclinic, space group $P\bar{1}$, a = 13.669(2), b = 14.179(2), c = 14.879(3) Å, α = 84.61(1), β = 72.07(1), γ = 64.92(1)°, U = 2483(1) Å^3 (by least-squares refinement of diffractometer angles for 30 automatically centred reflections in the range $16 \leqslant 2\theta \leqslant 27°$, λ = 0.710 73 Å), Z = 2, D_c = 1.76 g cm^{-3}, $F(000)$ = 1304, μ(Mo-Kα) = 8.3 cm^{-1}. Orange block, 0.40 × 0.30 × 0.50 mm.

Data collection and processing. Nicolet R3mV diffractometer equipped with graphite-monochromated Mo-Kα radiation. Intensities of $5 \leqslant 2\theta \leqslant 50°$ were collected by θ–2θ scans at variable speeds from 4 to 29° min^{-1} depending on the intensity of a 2 s prescan; the range was 0.6° below Kα1 to 0.6° above Kα2 and backgrounds were measured at each side for a quarter of the scan time. Three standard reflections remeasured every 97 scans showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction applied. Of the 8732 unique data measured ($+h$, $\pm k$, $\pm l$) some 7244 were judged to be observed [$I \geqslant 3\sigma(I)$] and were employed in structure analysis.

Structure analysis and refinement. Direct methods (Rh atoms) followed by alternating cycles of full-matrix least-squares refinement and Fourier-difference synthesis. Non-hydrogen atoms of cation and anions refined anisotropically. Each of the CF_3 groups on the bridging trifluoroacetamidate ligands are disordered over two positions. Occupancies were refined in the initial stages but fixed for the final least-squares cycles. Atoms of a poorly defined lattice diethyl ether were modelled isotropically. The final least-squares refinement including 707 parameters for 7244 variables gave R = 0.0549, R' = 0.0631 [weighting scheme $w^{-1} = \sigma^2(F) + 0.0033F^2$], and did not shift any parameter by more than 0.2 times its standard deviation. The final Fourier difference map was featureless with the largest peak 0.8 e Å^{-3}.

Crystal data for complex **3**. $C_{41}H_{38}F_{12}N_6O_5P_2Rh_2$, M = 1190.6, triclinic, space group $P\bar{1}$, a = 12.583(2), b = 13.390(2), c = 15.366(3), Å, α = 67.37(1), β = 83.74(1), γ = 80.26°, U = 2353(1) Å^3 (by least-squares refinement of diffractometer angles for 30 reflections in the range $14 \leqslant 2\theta \leqslant 29°$, λ = 0.710 73 Å), Z = 2, D_c = 1.68 g cm^{-3}, $F(000)$ = 1188, μ(Mo-Kα) = 8.5 cm^{-1}. Orange block, 0.40 × 0.40 × 0.35 mm.

Data collection and processing. As described above. Of the 8684 unique data measured some 6692 were judged to be observed [$I \geqslant 3\sigma(I)$] and were employed in structure analysis.

Structure analysis and refinement. Direct methods (Rh atoms) followed by alternating cycles of least-squares refinement and Fourier-difference synthesis. The asymmetric unit contains one badly disordered molecule of acetone. Equivocal identification of the oxygen atom and the methyl groups proved impossible and these have been assigned arbitrarily. This resulted in a few unsatisfactory thermal and structural parameters. However as the lattice solvent molecule makes no short contacts with the chemically important parts of the structure this imperfect solution has been accepted. Non-hydrogen atoms were refined anisotropically and hydrogens were placed in calculated positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter (U = 0.08 Å^2). The final least-squares refinement including 613 parameters for 6692 variables gave R = 0.0474, R' = 0.0574 [weighting scheme $w^{-1} = \sigma^2(F) + 0.0054F^2$], and did not shift any parameter by more than 0.3 times its standard deviations. The final Fourier-difference map was featureless with the largest peak 1.1 e Å^{-3}, close to one of the rhodium atoms.

The structure was solved, refined, and is displayed using the SHELXTL PLUS program package[20] on a Microvax II computer.

Additional material for both structures available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Although the vast majority of dirhodium(II) carboxylates contain four bridging ligands there are several well documented compounds known with fewer carboxylato bridging ligands. These include the compound $[Rh_2(O_2CCH_3)_4(bipy)]$ (bipy = 2,2′-bipyridine), in which only three of the carboxylato ligands bridge the rhodium–rhodium bond,[21] a series of compounds $[Rh_2(O_2CR)_2(R'COCHCOR'')_2(C_5H_5N)_n]$ (n = 1 or 2; R, R′, R″ = CH_3 or CF_3),[22–24] a series of complexes $[Rh_2(O_2CCH_3)_2(chel)_2(mim)_2][ClO_4]_2$ (chel = phen, 4,7-dimethyl- or 3,4,7,8-tetramethyl-1,10-phenanthroline; mim = N-methylimidazole),[19] and the compound $[Rh_2(O_2CCH_3)_2(dmg)_2(PPh_3)_2]$ (dmg = the monoanion of dimethylglyoxime).[25] Analogous compounds with alternative three-atom monoanionic bridging ligands such as monothiocarboxylates, $[SCOR]^-$, or amidates, $[RNCOR']^-$, are unknown. As the first step toward remedying this situation we have investigated the reaction of $[Rh_2(HNCOCF_3)_4]$ with 1,10-phenanthroline.

The reaction of the dinuclear rhodium(II) compound $[Rh_2(HNCOCF_3)_4]$ with 1,10-phenanthroline and HCl in methanol proceeds smoothly at room temperature to give a red-brown powder. Microanalytical data are consistent with the empirical formula $[Rh(HNCOCF_3)(C_{12}H_8N_2)Cl]$ and given the known chemistry of rhodium(II) it seems likely that the structure consists of two such units linked *via* a rhodium–rhodium single bond which is also bridged by two trifluoroacetamidato ligands. Close examination of the ^{1}H NMR spectrum of the compound reveals no less than sixteen signals

Table 1 Fractional atomic coordinates (× 10^4) for $[Rh_2(HNCOCF_3)_2(phen)_2(C_5H_5N)_2][PF_6]_2{\cdot}(C_2H_5)_2O$ **2**

Atom	*x*	*y*	*z*
Rh(1)	8 808(1)	8 434(1)	−2 837(1)
Rh(2)	10 623(1)	7 128(1)	−2 415(1)
O(1)	9 491(3)	9 491(3)	−2 936(3)
O(2)	11 184(4)	6 529(3)	−3 783(3)
N(1)	8 051(4)	7 451(3)	−2 683(3)
N(2)	7 782(4)	8 865(3)	−1 484(3)
N(3)	9 937(4)	6 106(3)	−1 820(3)
N(4)	10 057(4)	7 646(3)	−1 053(3)
N(5)	7 417(4)	9 689(4)	−3 314(3)
N(6)	12 313(4)	6 011(3)	−2 276(3)
N(7)	11 227(4)	8 231(3)	−2 923(3)
N(8)	9 784(4)	7 914(4)	−4 195(3)
F(1)	10 855(23)	6 864(47)	−5 975(20)
F(2)	12 137(37)	5 840(23)	−5 529(22)
F(3)	12 022(43)	7 312(35)	−5 775(18)
F(4)	10 681(19)	10 705(15)	−2 817(14)
F(5)	10 654(18)	10 416(16)	−4 210(15)
F(6)	12 091(12)	9 607(12)	−3 782(19)
F(1A)	11 052(25)	7 379(22)	−6 000(11)
F(2A)	12 412(18)	6 284(36)	−5 598(18)
F(3A)	11 036(33)	5 932(19)	−5 560(14)
F(4A)	10 299(19)	10 831(14)	−3 530(28)
F(5A)	11 834(35)	9 622(29)	−4 124(29)
F(6A)	11 422(36)	10 093(21)	−2 701(24)
C(1)	8 165(6)	6 783(5)	−3 337(5)
C(2)	7 523(8)	6 179(6)	−3 105(7)
C(3)	6 791(7)	6 237(6)	−2 219(7)
C(4)	6 653(6)	6 945(6)	−1 518(6)
C(5)	5 885(6)	7 104(7)	−572(6)
C(6)	5 746(6)	7 843(6)	44(6)
C(7)	6 368(6)	8 492(5)	−241(5)
C(8)	6 258(6)	9 282(6)	342(5)
C(9)	6 852(6)	9 855(5)	−14(5)
C(10)	7 645(5)	9 649(5)	−925(4)
C(11)	7 151(5)	8 310(4)	−1 154(4)
C(12)	7 296(5)	7 546(4)	−1 799(4)
C(13)	9 926(6)	5 307(4)	−2 249(5)
C(14)	9 347(6)	4 710(5)	−1 731(5)
C(15)	8 758(6)	4 943(5)	−778(5)
C(16)	8 790(5)	5 771(5)	−318(4)
C(17)	8 240(6)	6 049(5)	671(5)
C(18)	8 330(6)	6 836(6)	1 073(4)
C(19)	8 963(5)	7 378(5)	527(4)
C(20)	9 134(6)	8 156(5)	912(5)
C(21)	9 748(6)	8 648(5)	305(5)
C(22)	10 192(6)	8 388(4)	−672(4)
C(23)	9 472(5)	7 144(4)	−451(4)
C(24)	9 385(5)	6 318(4)	−877(4)
C(25)	6 791(7)	9 491(6)	−3 709(6)
C(26)	5 799(9)	10 253(7)	−3 864(8)
C(27)	5 513(9)	11 284(7)	−3 637(8)
C(28)	6 214(9)	11 477(6)	−3 243(8)
C(29)	7 159(7)	10 662(5)	−3 090(6)
C(30)	12 873(5)	5 113(5)	−2 821(4)
C(31)	13 906(6)	4 366(5)	−2 757(5)
C(32)	14 390(6)	4 515(6)	−2 119(6)
C(33)	13 808(7)	5 424(6)	−1 549(5)
C(34)	12 769(5)	6 155(5)	−1 655(5)
C(35)	10 736(6)	7 088(5)	−4 383(4)
C(36)	11 404(9)	6 718(8)	−5 413(5)
C(37)	10 565(5)	9 154(4)	−3 077(4)
C(38)	11 019(8)	9 975(6)	−3 432(7)
P(1)	2 707(2)	7 228(2)	1 055(1)
P(2)	7 742(2)	7 417(2)	4 028(1)
F(7)	2 006(6)	6 840(5)	643(6)
F(8)	2 960(9)	7 754(7)	80(5)
F(9)	1 660(5)	8 268(5)	1 462(7)
F(10)	3 793(6)	6 225(5)	612(6)
F(11)	2 497(10)	6 656(7)	1 970(5)
F(12)	3 464(5)	7 639(6)	1 375(6)
F(13)	6 701(7)	7 715(8)	4 935(5)
F(14)	7 159(5)	6 922(5)	3 548(4)
F(15)	8 786(6)	7 109(6)	3 115(4)
F(16)	7 164(7)	8 468(5)	3 609(7)
F(17)	8 322(5)	7 904(5)	4 519(4)
F(18)	8 323(9)	6 353(6)	4 431(7)
O(3)	6 269(6)	2 432(5)	3 284(5)
C(39)	5 627(17)	1 919(15)	3 208(14)
C(40)	6 156(14)	1 391(12)	2 313(11)
C(41)	5 024(27)	3 706(23)	4 194(21)
C(42)	5 816(16)	3 115(14)	4 333(13)

arising from the phenanthroline ligands suggesting that two isomers, **1a** and **1b**, are present. The two isomers are not present in equal amounts but in approximate ratio of 60:40. This ratio is reproducible from one batch of the compound to another. A series of homonuclear decoupling experiments allowed the assignment of two unique sets of eight phenanthroline signals. The occurrence of similar amounts of the two isomers was a little surprising in that although any compound of the type $[Rh_2(RNCOR')_4]$, containing four unsymmetrical bridging ligands, can potentially exist as any one of four geometric isomers it is almost without exception the centrosymmetric *cis* isomer which predominates.[8–10] Attempts to separate **1a** from **1b** by column or thin-layer chromatography proved unsuccessful. Since the acidic media in which the compound was prepared might act to labilise the bridging ligands and therefore cause rearrangement reactions, and hence the observed isomeric mixture of products, we decided to repeat the reaction using a non-protic source of chloride ions. When a synthetic procedure is followed in which the HCl is replaced by tetrabutylammonium chloride a red-brown solid is again obtained. The ^1H NMR spectrum of this compound contains only eight resonances for the phenanthroline ligands and the structure is believed to be **1a**. This assignment is principally based upon the appearance of the signals for protons H_d and H_e. In **1a** these protons give rise to an AB quartet, while in isomer **1b** two singlet resonances should be observed.

The axial halide ligands are readily replaced by a variety of Lewis bases. For example adding a drop of pyridine to a methanolic solution of complex **1a** rapidly gives a yellow solution which upon addition of $K[PF_6]$ yields $[Rh_2(HNCOCF_3)_2(phen)_2(C_5H_5N)_2][PF_6]_2$ **2**. Importantly during this reaction there is no (^1H NMR) evidence of any isomerisation taking place. Recrystallisation of this compound from diethyl ether–dichloromethane gave the ether solvate which has been characterised by X-ray crystallography, see below. Although several related compounds containing carboxylato ligands have been characterised none of these[19,26] has axial pyridine ligands or hexafluorophosphate anions and therefore for the purposes of making relevant comparisons we have synthesised (see Experimental section) and crystallographically characterised the analogous carboxylato compound $[Rh_2(O_2CCH_3)_2(phen)_2(C_5H_5N)_2][PF_6]_2$ **3**.

The basic geometries of complexes **2** and **3** are similar to those already described in the literature[19] for the series of dications $[Rh_2(O_2CCH_3)_2(chel)_2(mim)_2]^{2+}$. The atomic coordinates are listed in Tables 1 and 2 respectively, while important molecular dimensions are presented in Tables 3 and 4. The structure of the cations are shown in Figs. 1 and 2.

X-Ray crystallographic analysis of complex **2** confirms the *cis* head-to-tail arrangement of the bridging trifluoroacetamidate ligands such that the co-ordination sphere of each rhodium ion consists of two phenanthroline nitrogens, a pyridine nitrogen atom, an oxygen and nitrogen atom from two different amidate ligands, and the second metal ion. The geometry about each of the metal centres is that of a distorted octahedron with the angles between adjacent atoms in the metal co-ordination

Table 2 Fractional atomic coordinates (× 10^4) for $[Rh_2(O_2CCH_3)_2(phen)_2(C_5H_5N)_2][PF_6]_2{\cdot}(CH_3)_2CO$ **3**

Atom	*x*	*y*	*z*
Rh(1)	953(1)	9 248(1)	8 011(1)
Rh(2)	1 921(1)	7 332(1)	8 905(1)
O(1)	−167(3)	8 842(3)	9 112(3)
O(2)	873(3)	7 375(3)	10 012(2)
O(3)	1 823(3)	9 726(3)	8 795(3)
O(4)	2 884(3)	8 128(3)	9 312(3)
N(1)	1 992(3)	9 638(3)	6 880(3)
N(2)	191(3)	8 803(3)	7 168(3)
N(3)	2 868(3)	7 203(3)	7 807(3)
N(4)	1 030(3)	6 492(3)	8 509(3)
N(5)	15(4)	10 931(4)	7 513(3)
N(6)	2 760(4)	5 816(4)	9 908(3)
C(1)	2 862(4)	10 129(4)	6 730(4)
C(2)	3 490(5)	10 357(5)	5 900(5)
C(3)	3 232(5)	10 072(5)	5 191(4)
C(4)	2 323(5)	9 548(4)	5 327(3)
C(5)	1 980(5)	9 194(5)	4 651(4)
C(6)	1 058(6)	8 737(5)	4 816(4)
C(7)	397(5)	8 588(5)	5 663(4)
C(8)	−572(5)	8 151(5)	5 869(4)
C(9)	−1 157(5)	8 091(5)	6 679(5)
C(10)	−754(4)	8 416(4)	7 331(4)
C(11)	750(4)	8 902(4)	6 337(3)
C(12)	1 709(4)	9 360(4)	6 178(3)
C(13)	3 829(4)	7 537(5)	7 502(4)
C(14)	4 383(5)	7 393(6)	6 735(5)
C(15)	3 979(5)	6 890(6)	6 243(5)
C(16)	2 956(5)	6 531(5)	6 549(4)
C(17)	2 421(7)	5 982(6)	6 109(5)
C(18)	1 495(6)	5 602(6)	6 478(5)
C(19)	971(5)	5 730(5)	7 308(4)
C(20)	17(5)	5 323(5)	7 746(5)
C(21)	−377(5)	5 492(5)	8 547(5)
C(22)	123(5)	6 091(4)	8 907(4)
C(23)	1 448(4)	6 294(4)	7 717(3)
C(24)	2 451(4)	6 697(4)	7 337(3)
C(25)	−1 035(5)	11 060(5)	7 733(5)
C(26)	−1 659(6)	12 062(6)	7 439(6)
C(27)	−1 199(7)	12 974(6)	6 872(7)
C(28)	−143(6)	12 841(5)	6 669(5)
C(29)	454(5)	11 823(5)	6 970(4)
C(30)	2 964(6)	5 758(6)	10 761(5)
C(31)	3 380(7)	4 832(8)	11 454(6)
C(32)	3 603(10)	3 891(8)	11 301(8)
C(33)	3 496(12)	3 933(8)	10 427(8)
C(34)	3 020(7)	4 890(6)	9 742(6)
C(35)	48(4)	8 075(5)	9 882(4)
C(36)	−757(6)	7 960(6)	10 696(5)
C(37)	2 591(4)	9 093(5)	9 265(3)
C(38)	3 194(5)	9 507(6)	9 804(5)
P(1)	7 346(1)	6 259(1)	5 493(1)
P(2)	4 039(1)	10 358(2)	2 106(1)
F(1)	6 762(6)	5 332(6)	6 241(5)
F(2)	8 369(5)	5 826(6)	6 083(6)
F(3)	7 710(7)	5 540(8)	4 946(7)
F(4)	6 974(5)	7 029(6)	6 079(5)
F(5)	6 273(5)	6 753(6)	4 985(5)
F(6)	7 919(5)	7 228(5)	4 761(4)
F(7)	3 614(16)	11 210(9)	1 293(8)
F(8)	3 873(9)	11 037(7)	2 744(6)
F(9)	4 566(14)	9 465(10)	2 897(13)
F(10)	4 225(7)	9 661(8)	1 506(6)
F(11)	2 979(7)	9 972(11)	2 419(7)
F(12)	5 060(9)	10 808(18)	1 817(11)
O(5)	6 827(13)	6 220(10)	1 730(9)
C(39)	6 115(22)	6 652(15)	2 207(18)
C(40)	6 625(13)	7 400(12)	2 410(11)
C(41)	5 125(15)	6 694(19)	2 528(21)

Table 3 Selected bond distances (Å) and angles (°) for $[Rh_2(HNCOCF_3)_2(phen)_2(C_5H_5N)_2][PF_6]_2{\cdot}(C_2H_5)_2O$ **2**

Rh(1)–Rh(2)	2.612(1)	Rh(2)–N(3)	2.040(5)
Rh(1)–N(1)	2.020(6)	Rh(2)–N(4)	2.019(5)
Rh(1)–N(2)	2.040(4)	Rh(2)–N(6)	2.241(5)
Rh(1)–N(5)	2.238(5)	Rh(2)–N(7)	2.046(6)
Rh(1)–N(8)	2.048(4)	Rh(2)–O(2)	2.065(4)
Rh(1)–O(1)	2.049(5)	O(2)–C(35)	1.262(8)
O(1)–C(37)	1.289(8)	N(8)–C(35)	1.299(7)
N(7)–C(37)	1.285(7)		
N(1)–Rh(1)–N(2)	81.2(2)	N(3)–Rh(2)–N(4)	81.2(2)
N(1)–Rh(1)–N(8)	94.1(2)	N(3)–Rh(2)–O(2)	95.8(2)
N(2)–Rh(1)–O(1)	95.8(2)	N(4)–Rh(2)–N(7)	94.6(2)
N(8)–Rh(1)–O(1)	89.0(2)	N(7)–Rh(2)–O(2)	88.4(2)
Rh(2)–Rh(1)–N(1)	97.0(1)	Rh(1)–Rh(2)–N(3)	94.1(1)
Rh(2)–Rh(1)–N(2)	97.0(1)	Rh(1)–Rh(2)–N(4)	95.0(1)
Rh(2)–Rh(1)–N(5)	171.0(2)	Rh(1)–Rh(2)–N(6)	171.6(1)
Rh(2)–Rh(1)–N(8)	83.5(1)	Rh(1)–Rh(2)–N(7)	84.4(1)
Rh(2)–Rh(1)–O(1)	84.9(1)	Rh(1)–Rh(2)–O(2)	85.8(1)
N(5)–Rh(1)–N(1)	91.4(2)	N(6)–Rh(2)–N(3)	90.8(2)
N(5)–Rh(1)–N(2)	87.5(2)	N(6)–Rh(2)–N(4)	92.4(2)
N(5)–Rh(1)–N(8)	92.6(2)	N(6)–Rh(2)–N(7)	91.1(2)
N(5)–Rh(1)–O(1)	86.9(2)	N(6)–Rh(2)–O(2)	87.1(2)

sphere falling in the range 81.2(1)–97.0(1)°. The smallest of these angles is that formed by the 'bite' of the phenanthroline ligands, while the largest occur between Rh–Rh and Rh–N(phen) vectors. The rhodium–pyridine bonds are not collinear with the rhodium–rhodium bond but form an average angle of 171.3(2)° with it. This deviation from linearity is not uncommon but is usually ascribed[23,27] to steric interactions between axial and bridging ligands, which are unlikely to be present in this instance. The geometries about the metal centres in **3** are very similar (Table 4).

Table 4 Selected bond distances (Å) and angles (°) for $[Rh_2(O_2CCH_3)_2(phen)_2(C_5H_5N)_2][PF_6]_2{\cdot}(CH_3)_2CO$ **3**

Rh(1)–Rh(2)	2.559(1)	Rh(2)–N(3)	2.003(4)
Rh(1)–N(1)	2.010(4)	Rh(2)–N(4)	1.999(5)
Rh(1)–N(2)	2.001(5)	Rh(2)–N(6)	2.199(4)
Rh(1)–N(5)	2.242(4)	Rh(2)–O(2)	2.048(4)
Rh(1)–O(1)	2.044(3)	Rh(2)–O(4)	2.028(5)
Rh(1)–O(3)	2.045(5)	O(3)–C(37)	1.256(6)
O(1)–C(35)	1.252(5)	O(4)–C(37)	1.258(7)
O(2)–C(35)	1.252(6)		
N(1)–Rh(1)–N(2)	81.4(2)	N(3)–Rh(2)–N(4)	81.5(2)
N(1)–Rh(1)–O(3)	94.3(2)	N(3)–Rh(2)–O(4)	97.0(2)
N(2)–Rh(1)–O(1)	95.4(2)	N(4)–Rh(2)–O(2)	93.5(2)
O(1)–Rh(1)–O(3)	88.9(2)	O(2)–Rh(2)–O(4)	87.9(2)
Rh(2)–Rh(1)–N(1)	97.1(1)	Rh(1)–Rh(2)–N(3)	96.2(1)
Rh(2)–Rh(1)–N(2)	95.4(1)	Rh(1)–Rh(2)–N(4)	97.8(1)
Rh(2)–Rh(1)–N(5)	168.6(1)	Rh(1)–Rh(2)–N(6)	168.0(2)
Rh(2)–Rh(1)–O(1)	83.9(1)	Rh(1)–Rh(2)–O(2)	85.0(1)
Rh(2)–Rh(1)–O(3)	84.7(1)	Rh(1)–Rh(2)–O(4)	84.5(1)
N(5)–Rh(1)–N(1)	92.4(2)	N(6)–Rh(2)–N(3)	92.7(2)
N(5)–Rh(1)–N(2)	92.2(2)	N(6)–Rh(2)–N(4)	91.4(2)
N(5)–Rh(1)–O(1)	87.0(1)	N(6)–Rh(2)–O(2)	86.8(2)
N(5)–Rh(1)–O(3)	88.4(2)	N(6)–Rh(2)–O(4)	86.5(2)

The rhodium–rhodium bond length in complex **2** is 2.612(1) Å, which is significantly greater than that in **3**, 2.559(1) Å. It can usefully be compared with that observed in $[Rh_2(HNCOCF_3)_4(C_5H_5N)_2]$, 2.472(3) Å.[8] Other tetraamidato bridged species $[Rh_2(HNCOR)_4L_2]$ have exhibited similar metal–metal bond lengths [*e.g.* R = Ph, L = C_5H_5N, 2.437(1) Å;[10] R = Ph, L = $SbPh_3$, 2.463(1) Å;[10] R = CH_3, L = H_2O, 2.415(1) Å[9]]. The difference in Rh–Rh bond length on comparing similar doubly and quadruply bridged trifluoroacetamidato compounds, 0.14 Å, is similar to that observed on making the

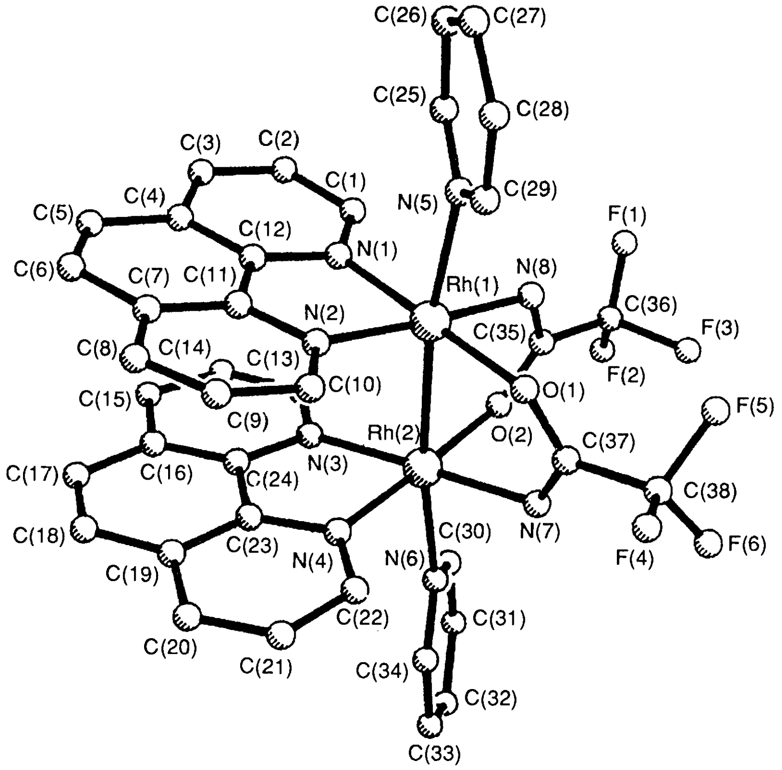


Fig. 1 The structure of the cation $[Rh_2(HNCOCF_3)_2(phen)_2(C_5H_5N)_2]^{2+}$ showing the atom labelling scheme

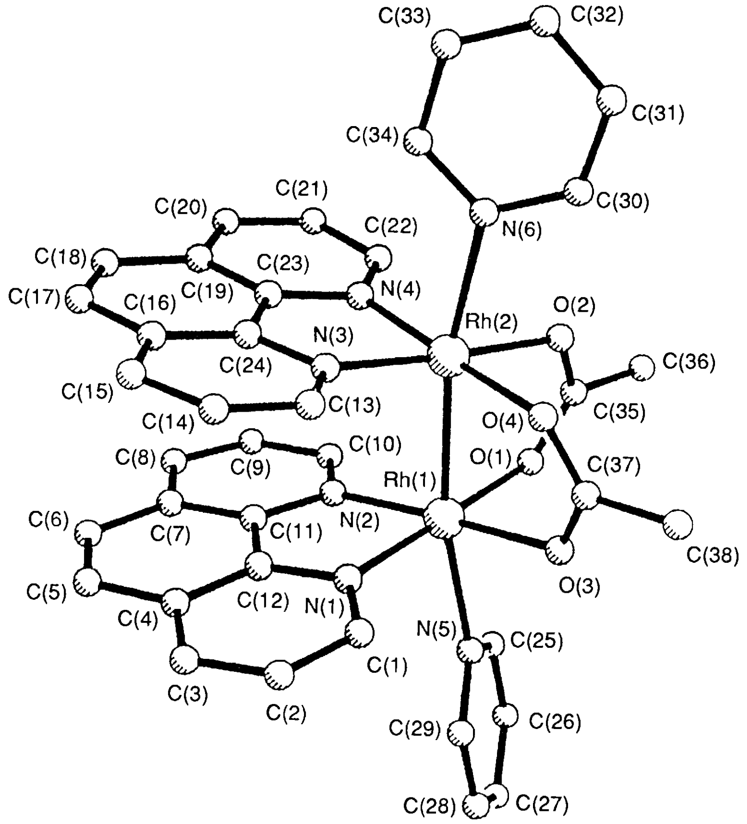


Fig. 2 The structure of the cation $[Rh_2(O_2CCH_3)_2(phen)_2(C_5H_5N)_2]^{2+}$ showing the atom labelling scheme

analogous comparison for acetato bridged species {*i.e.* comparison of that found in **3** with that for $[Rh_2(O_2CCH_3)_4(C_5H_5N)_2]$, 2.396(1) Å[28]}. The increase in metal–metal bond lengths on reducing the number of bridging ligands is hardly surprising, however it is interesting that the Rh–Rh distance in **2** closely approximates that observed in the cation $[Rh_2(CH_3CN)_{10}]^{4+}$, 2.624(1) Å,[29] in which there are no bridging ligands. The rhodium–pyridine bond lengths in **2** and **3** are closely similar and unremarkable. As has been found previously[8,9] the bonds to the oxygen atoms of the bridging amidate ligands are longer than those to the nitrogen atoms of these ligands [Rh–N$_{av}$ 2.047(5) Å, Rh–O$_{av}$ 2.057(5) Å] although in this instance the difference is not statistically significant. Nevertheless if the *trans* Rh–N(phen) bond lengths are examined the different *trans* influences of the two types of donor atom can clearly be distinguished [Rh–N(phen) *trans* to O, 2.020(6); Rh–N(phen) *trans* to NH, 2.040(5) Å]. In contrast the four Rh–N(phen) bonds in **3** are indistinguishable [1.999(5)–2.010(4) Å].

In each of the compounds **2** and **3** there are substantial torsion angles about the rhodium–rhodium bond. The phenanthroline ligands are rotated from a totally eclipsed conformation by 15.8° in **2** and 15.4° in **3**. The torsion angles in the bridging ligands are somewhat less [**2**, O(1)–Rh(1)–Rh(2)–N(7) −14.6(2), O(2)–Rh(2)–Rh(1)–N(8) −13.8(2); **3**, O(1)–Rh(1)–Rh(2)–O(2) −13.7(2), O(3)–Rh(1)–Rh(2)–O(4) −12.6(2)°]. The mean planes of the phenanthroline ligands are not parallel in either structure. In **2** the angle between the two ligand planes is 9.5(1)°, while in **3** it is 10.6(1)°. These deviations from coplanarity are substantially less than those observed in the closely related compounds $[Rh_2(O_2CR)_2(R'COCHCOR'')_2(C_5H_5N)_2]$[23,30] where there are substantial steric interactions between the pairs of chelating equatorially co-ordinated ligands. The closest approach (ring centroid to ring centroid) of phenanthroline ligands is 3.46(1) Å. The most obvious difference between the two structures is the relative angles of inclination of the two axially co-ordinated pyridine ligands. In **2** the ligands are almost coplanar [24.8(2)°] and lie in the region between the bridging and chelating ligands while in **3** the two planes are almost orthogonal [84.9(2)°] and the mean plane of one ligand [N(6)C(30)C(31)C(32)C(33)C(34)] almost bisects the N(3)–Rh(2)–N(4) angle.

In view of the rich redox chemistry of dirhodium(II) compounds we have undertaken a brief survey of the electrochemical properties of the compounds described in this paper using cyclic voltammetry. In dichloromethane solution complex **2** undergoes a quasi-reversible oxidation at a potential of +1.30 V (*vs.* Ag–AgCl; ferrocene–ferrocenium +0.60 V) while complex **3** is oxidised at +1.75 V. The observations of a potential difference of 0.45 V is interesting in that in a series of studies carried out by Bear, Kadish and co-workers[7,31,32] on the compounds $[Rh_2(O_2CCH_3)_4(HNCOCH_3)_{4-n}]$ ($n = 0$–4) it was observed that the complete replacement of four bridging acetate ligands by the corresponding acetamidate resulted in the shifting of the potential for the $[Rh_2]^{4+}$–$[Rh_2]^{5+}$ couple to a value *ca.* 1.0 V more cathodic and, within experimental error, the shifting of the potential occurred in four equal steps. Hence the observed difference in potential observed in this study can be readily understood within the framework already described in the earlier reports. Owing to the low solubility of the neutral chloro adducts it has not been possible to carry out a parallel pair of experiments on $[Rh_2(O_2CCH_3)_2(phen)_2Cl_2]$ and **1**.

Acknowledgements

We would like to thank Johnson Matthey plc for generous loans of rhodium trichloride and the SERC for provision of the X-ray diffractometer.

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Received 30*th April* 1991; *Paper* 1/02008K