Perfluoroalkyl- and Perfluoroaryl-amidato Derivatives of Ruthenium, Osmium and Iridium *

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Trifluoroacetamide reacted with $[RuCl_2(PPh_3)_3]$–NEt_3 in boiling toluene to afford the binuclear species $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)CF_3\}_2(PPh_3)_4]$ **1a** ('head-to-tail' N,O-amidato bridged isomer). In contrast use of $[RuH(Cl)(PPh_3)_3]$ as the ruthenium precursor led to formation of **1a** as a mixture of 'head-to-tail' and 'head-to-head' isomers plus a small amount of another product **2a** which is tentatively formulated as $[Ru_2(\mu\text{-}H)\{\mu\text{-}NHC(O)CF_3\}_3(PPh_3)_4]$ with one N- and two N,O-bridging amidate ligands. Carbonylation of these products in boiling toluene yielded dicarbonyl species $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)CF_3\}_2(CO)_2(PPh_3)_2]$ **3a** ('head-to-tail' and 'head-to-head' isomers) plus a trace of $[Ru_2(\mu\text{-}H)\{\mu\text{-}NHC(O)CF_3\}_3(CO)_2(PPh_3)_2]$ **4a**. Under similar conditions trifluoroacetamide reacted with $[RuH_2(CO)(PPh_3)_3]$, $[Ru(CO)_3(PPh_3)_2]$, $[OsH_2(CO)(PPh_3)_3]$ and *mer*-$[IrH_3(PPh_3)_3]$ to yield the mononuclear products $[Ru\{NHC(O)CF_3\}_2(CO)(H_2O)(PPh_3)_2]$ **5a**, $[Ru\{NHC(O)CF_3\}_2(CO)_2(PPh_3)_2]$ **6a**, $[OsH\{NHC(O)CF_3\}(CO)(PPh_3)_3]$ **7a** and $[IrH_2\{NHC(O)CF_3\}(PPh_3)_3]$ **8a** respectively, all of which contain monodentate N-bonded trifluoroacetamidate ligands. Pentafluoropropionamide and pentafluorobenzamide yielded analogous products **1b**, **2b**, **3b** and **8b**, and **1c** respectively. The crystal structure of $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_2F_5\}_2(PPh_3)_4]$ **1b** has been determined. All other products were characterised by infrared and NMR spectroscopy.

As part of our ongoing study of heteroallylic ligands we have examined the co-ordination tendencies of trifluoroacetic acid CF_3CO_2H[2] and trifluoroacetamidine $CF_3C(NH)NH_2$[1] towards a variety of platinum-metal hydride complexes and have observed very dissimilar behaviour patterns. The trifluoroacetate anion binds primarily as a monodentate ligand and displays only modest appetite for chelation,[2] whereas the trifluoroacetamidinate anion undergoes condensation with a molecule of free amidine to form the N^1,N^5-chelate anion $NHC(CF_3)NC(CF_3)NH^-$. It therefore seemed appropriate to examine the co-ordination chemistry of the middle member of the series $CF_3C(O)NH_2$ and some related perfluoroamides with similar platinum-metal precursors. The results of this investigation reveal a tendency to monodentate co-ordination similar to that found for $CF_3CO_2^-$ but also a readiness to adopt a bridging bidentate mode not encountered in the corresponding trifluoroacetate reactions. A preliminary account of this work has appeared.[3]

Experimental

Platinum-metal salts were supplied by Johnson Matthey plc. The phosphine-containing ruthenium, osmium and iridium complex precursors were prepared by standard literature procedure.[4,5] The perfluoroalkyl- and perfluoroaryl-amides were obtained from Fluorochem Ltd. and used as purchased. Organic solvents were reagent grade and dried over molecular sieves. Reactions were performed under nitrogen but the products were worked up in open flasks. Elemental analyses were performed in the microanalytical laboratory at University College London. Melting points were taken in sealed tubes under nitrogen. Infrared spectra were recorded on a Perkin-Elmer 983G spectrometer using Nujol mulls, NMR spectra on a Bruker AM 360 (^1H, 360.13; $^{13}C\text{-}\{^1H\}$, 90.56; ^{19}F, 338.87 MHz) or a Bruker WM 250 spectrometer ($^{31}P\text{-}\{^1H\}$, 101.2 MHz).

Complexes **1a**–**1c** and **3a**, **3b** were usually obtained as *ca.* 60 : 40 mixtures of 'head-to-tail' and 'head-to-head' isomers (see Discussion section).

$[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)CF_3\}_2(PPh_3)_4]\cdot 0.5CH_2Cl_2\cdot H_2O$ **1a**.—*Method A*. Dichlorotris(triphenylphosphine)ruthenium (0.8 g, 0.84 mmol), triethylamine (4 cm^3) and trifluoroacetamide (0.5 g, 4.42 mmol) were heated together under reflux in toluene (40 cm^3) for *ca.* 4 h. One further portion (4 cm^3) of triethylamine was added after 2 h. The dark reddish brown solution was cooled to ambient temperature and then concentrated under reduced pressure to leave an oil. Crystallisation from CH_2Cl_2–MeOH gave orange crystals (0.46 g, 71%) m.p. 253–255 °C Found: C, 57.7, H, 3.8; N, 1.7. Calc. for $C_{76}H_{63}ClF_6N_2O_2P_4Ru_2\cdot 0.5CH_2Cl_2\cdot H_2O$: C, 58.3; H, 4.2; N, 1.8%).

Method B. Chlorohydridotris(triphenylphosphine)ruthenium (0.82 g, 0.88 mmol) and trifluoroacetamide (0.4 g, 3.5 mmol) were added to degassed toluene (40 cm^3) and the mixture heated under reflux for *ca.* 1.5 h. The dark red-brown solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation from CH_2Cl_2–MeOH afforded the product as orange microcrystals (0.54 g, 82%). Spectroscopic examination of this product revealed the presence of traces of a further compound **2a** (see Discussion section).

The following were similarly prepared by method A using the appropriate amides: $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_2F_5\}_2(PPh_3)_4]\cdot 0.5CH_2Cl_2$ **1b** as orange crystals (52%), decomp. 190–192 °C (Found: C, 56.3; H, 3.95; N, 1.3. Calc. for $C_{78}H_{63}ClF_{10}N_2O_2P_4Ru_2\cdot 0.5CH_2Cl_2$: C, 56.9; H, 3.85; N, 1.65%); $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_6F_5\}_2(PPh_3)_4]\cdot 0.5CH_2Cl_2$ **1c** as orange crystals (42%). The following were similarly prepared by method B using the appropriate amides: **1b** as orange microcrystals (71%), spectroscopic examination revealed the presence of traces of a further complex **2b** (see

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* Complexes of the Platinum Metals. Part 47.[1]

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Discussion section); **1c** as dark orange plates (60%), decomp. 210–212 °C (Found: C, 59.45; H, 3.75; N, 1.65. Calc. for $C_{86}H_{63}ClF_{10}N_2O_2P_4Ru_2{\cdot}0.5CH_2Cl_2$: C, 59.35; H, 3.7; N, 1.6%).

$[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)CF_3\}_2(CO)_2(PPh_3)_2]$ **3a**.—Complex **1a** (0.14g, 0.09 mmol) was dissolved in toluene (30 cm^3) and the solution heated under reflux in the presence of a slow stream of carbon monoxide for *ca.* 4 h. During this period the solution changed from orange to yellow. Cooling to ambient temperature and concentration under reduced pressure gave a yellow solid which was crystallised from CH_2Cl_2–MeOH to afford the product as yellow microcrystals (0.08 g, 88%) (Found: C, 48.05; H, 2.95; N, 2.5. Calc. for $C_{42}H_{33}ClF_6N_2O_4P_2Ru_2$: C, 48.3; H, 3.2; N, 2.7%). This product contained a small amount of a further complex **4a** thought to arise from carbonylation of traces of **2a** present in the sample of **1a** used.

The complex $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_2F_5\}_2(CO)_2(PPh_3)_2]$ **3b** was similarly obtained as yellow microcrystals (82%) m.p. 235–237 °C (Found: C, 46.45; H, 3.05; N, 2.8. Calc. for $C_{44}H_{33}ClF_{10}N_2O_4P_2Ru_2$: C, 46.2; H, 2.9; N, 2.45%).

$[Ru\{NHC(O)CF_3\}_2(CO)(H_2O)(PPh_3)_2]$ **5a**.—Carbonyldihydridotris(triphenylphosphine)ruthenium (0.8 g, 0.87 mmol) and trifluoroacetamide (0.3 g, 2.65 mmol) were heated together under reflux in toluene (40 cm^3) for *ca.* 6 h. The dark green solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation from CH_2Cl_2–MeOH afforded pale yellow microcrystals (0.48 g, 62%), decomp. 198–200 °C (Found: C, 55.55; H, 3.7; N, 2.95. Calc. for $C_{41}H_{34}F_6N_2O_4P_2Ru$: C, 55.0; H, 3.8; N, 3.1%).

The complex $[Ru\{NHC(O)C_2F_5\}_2(CO)(H_2O)(PPh_3)_2]$ **5b** was similarly obtained using the appropriate amide and isolated as pale yellow microcrystals (59%), m.p. 156–158 °C (Found: C, 51.2; H, 3.95; N, 2.45. Calc. for $C_{43}H_{34}F_{10}N_2O_4P_2Ru$: C, 51.85; H, 3.45; N, 2.8%).

$[Ru\{NHC(O)CF_3\}_2(CO)_2(PPh_3)_2]$ **6a**.—*Method A*. Tricarbonylbis(triphenylphosphine)ruthenium (0.83 g, 1.17 mmol) and trifluoroacetamide (0.4 g, 3.5 mmol) were heated together under reflux in toluene (40 cm^3) for *ca.* 9 h. The yellow-green solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation from CH_2Cl_2–MeOH afforded pale yellow microcrystals (0.53 g, 50%), m.p. 208–210 °C (Found: C, 55.5; H, 3.45; N, 2.75. Calc. for $C_{42}H_{32}F_6N_2O_4P_2Ru$: C, 55.65; H, 3.55; N, 3.1%).

Method B. A solution of complex **5a** (0.28 g, 0.31 mmol) in toluene (30 cm^3) was heated under reflux in a slow stream of carbon monoxide for *ca.* 4 h. The yellow solution was cooled to ambient temperature and then concentrated under reduced pressure to leave an oil. Crystallisation from CH_2Cl_2–MeOH afforded the product as pale yellow microcrystals (0.22 g, 78%).

$[OsH\{NHC(O)CF_3\}(CO)(PPh_3)_3]{\cdot}CH_2Cl_2$ **7a**.—Carbonyldihydridotris(triphenylphosphine)osmium (0.4 g, 0.4 mmol) and trifluoroacetamide (0.16 g, 1.41 mmol) were heated together under reflux in toluene (30 cm^3) for *ca.* 24 h. The yellow solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure. A small amount of unreacted $[OsH_2(CO)(PPh_3)_3]$ deposited as a white solid and was filtered off. The filtrate was then further concentrated under reduced pressure to yield an oil. Crystallisation from CH_2Cl_2–MeOH afforded the product as white microcrystals (0.24 g, 55%), m.p. 220–222 °C (Found: C, 57.15; H, 3.7; N, 1.45. Calc. for $C_{57}H_{47}F_3NO_2OsP_3{\cdot}CH_2Cl_2$: C, 57.9; H, 4.05; N, 1.15%).

$[IrH_2\{NHC(O)CF_3\}(PPh_3)_3]{\cdot}0.5CH_2Cl_2$ **8a**.—*mer*-Trihydridotris(triphenylphosphine)iridium (0.35 g, 0.44 mmol) and trifluoroacetamide (0.15 g, 1.33 mmol) were heated together under reflux in toluene (30 cm^3) for 3 h. The yellow-green solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation from CH_2Cl_2–MeOH afforded white microcrystals (0.24 g, 50%), m.p. 215–217 °C (Found: C, 60.55; H, 4.25; N, 0.95. Calc. for $C_{56}H_{48}F_3IrNOP_3{\cdot}0.5CH_2Cl_2$: C, 59.75; H, 4.35; N, 1.25%).

The complex $[IrH_2\{NHC(O)C_2F_5\}(PPh_3)_3]{\cdot}0.5CH_2Cl_2$ **8b** was similarly prepared using pentafluoropropionamide and isolated as white microcrystals (74%), m.p. 218–220 °C (Found: C, 57.85; H, 4.45; N, 1.0. Calc. for $C_{57}H_{48}F_5IrNOP_3{\cdot}0.5CH_2Cl_2$: C, 58.25; H, 4.15; N, 1.2%).

Crystallography.—Crystal structures have previously been reported[3] for complexes **1a** and **5a**. The crystal structure determination for $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_2F_5\}_2(PPh_3)_4]{\cdot}0.5CH_2Cl_2$ **1b** is described below.

An orange single crystal of approximate size 0.76 × 0.56 × 0.18 mm was mounted on a glass fibre. All geometric and intensity data were taken from this sample at 293 K using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-Kα radiation (λ = 0.710 73 Å).

The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 31 reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure 7154 reflections (6519 unique) in the range $5 \leqslant 2\theta \leqslant 50°$. 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 empirically for absorption. The 4265 unique data with $I \geqslant 3.0\sigma(I)$ were used to solve and refine the structure in the orthorhombic space group *Pbna*.

Crystal data. $C_{78}H_{63}ClF_{10}N_2O_2P_4Ru_2{\cdot}0.5CH_2Cl_2$, M = 1654.31, orthorhombic, space group *Pbna*, a = 16.612(5), b = 19.893(7), c = 22.791(7) Å, U = 7530 Å^3, Z = 4, D_c = 1.46 g cm^{-3}, $F(000)$ 3348, μ(Mo-Kα) 6.17 cm^{-1}.

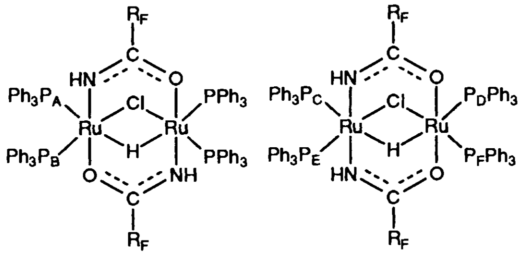
The structure was solved by direct methods and developed by using alternating cycles of least-squares refinement and Fourier-difference synthesis. The asymmetric unit contains one half of the molecule, which resides on a two-fold axis passing through atoms Cl(1) and H(1). The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter (U = 0.08 Å^2). In the latter stages of the refinement the presence of a solvent molecule (dichloromethane) in the lattice was apparent. This resides on a two-fold axis and was refined (C, Cl only) satisfactorily with an occupancy of 25%. The final cycle of least-squares refinement included 461 parameters for 4265 variables and did not shift any parameter by more than 0.001 times its standard deviation. The final R values were 0.0538 and 0.0609 [weighting scheme $w^{-1} = \sigma^2(F) + 0.001\,95F^2$] and the final Fourier-difference map was featureless with no peaks greater than 1.1 e Å^{-3}.

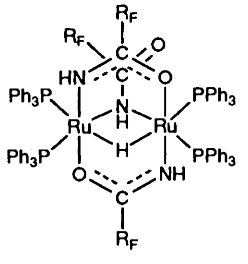
Structure solution used the SHELXTL PLUS program package[6] on a microVax II computer. The molecular structure is shown in Fig. 1, positional parameters for non-hydrogen atoms are given in Table 2, selected bond length and angle data in Table 3.

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

Results and Discussion

Spectroscopic data for the complexes discussed below are presented in Table 1.


Head-to-tail **1** Head-to-head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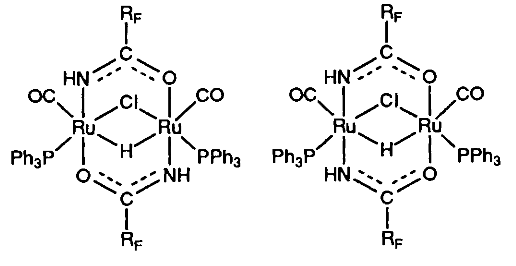
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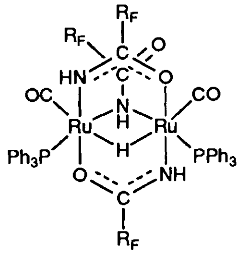
4

[Ru_2(μ-Cl)(μ-H){μ-NHC(O)R_F}$_2$(PPh_3)$_4$](R_F = CF_3,C_2F_5 *or* C_6F_5).—The reaction of [$RuCl_2(PPh_3)_3$] with triethylamine and trifluoroacetamide in refluxing toluene afforded a solution from which an orange crystalline hydrido complex was isolated in good yield. Analytical and spectroscopic data for this product are consistent with the binuclear formulation [Ru_2(μ-Cl)(μ-H){μ-NHC(O)CF_3}$_2$(PPh_3)$_4$] **1a**. The high-field proton NMR spectrum comprises a triplet of triplets at δ −7.52 indicative of a bridging hydride ligand coupled to two pairs of equivalent phosphorus nuclei. The presence of the latter was verified by the ^{31}P-{^{1}H} NMR spectrum which consists of an A′XX′ pattern. The proposed binuclear structure and, in particular, the head-to-tail orientation of the bridging amidate ligands were confirmed by a crystal structure determination, details of which have previously been published.[3] When the same reaction was performed using pentafluoropropionamide an orange crystalline product **1b** similar in appearance to **1a** was obtained. However, the high-field proton NMR spectrum revealed not one but two hydride resonances of very similar intensity, each consisting of a triplet of triplets. The two resonances are close together (δ −7.27, −7.72) and have virtually identical coupling constants. The ^{31}P-{^{1}H} NMR spectrum displays an A′XX′ pattern, similar to that observed for **1a**, plus four separate resonances, two doublets each with a further very small doublet splitting and two triplets. Finally the ^{19}F NMR spectrum shows two sets of resonances attributable to two C_2F_5 fragments in very similar but not identical environments. We conclude on the basis of this evidence that **1b** is a *ca.* 60:40 mixture of 'head-to-tail' and 'head-to-head' isomers. Inspection of the 'head-to-head' isomer reveals that all four ^{31}P nuclei are chemically non-equivalent, hence the four separate ^{31}P-{^{1}H} NMR signals of equal intensity. Since phosphorus–phosphorus coupling through Ru–H–Ru is likely to be stronger than that through Ru–Cl–Ru and since *trans* couplings are generally larger than *cis* it seems that the 'triplet' signals can be attributed to P_C and P_D coupling to P_E and P_F respectively as well as each other, with all the couplings having essentially the same magnitude. The doublet patterns can then be attributed to P_E and P_F coupling to P_C and P_D respectively with an additional, very small coupling ^4J(PP′) between P_E and P_F. Given that the four phosphorus nuclei are all in different chemical environments and resonate at different radiofrequencies it is at first sight surprising that we do not see more evidence of asymmetry in the high-field proton spectrum of the 'head-to-head' isomer which is very sharp with apparently equal couplings to the *cis* pair and to the *trans* pair of phosphorus nuclei. However the magnitudes of ^2J(PH) couplings between phosphine and hydride ligands are not strongly influenced by the nature of other ligands situated *cis* to the coupled nuclei. We therefore conclude that in the present instances the apparent equivalence of coupling constants is purely fortuitous. Crystalline samples of **1b** appear homogeneous with no visible evidence of different crystal forms. In an effort structurally to characterise the proposed 'head-to-head' isomer a crystal suitable for X-ray diffraction study was selected at random from a crystalline sample of **1b** relatively rich in the second isomer. Unfortunately it proved to be of the 'head-to-tail' isomer. The molecular structure is shown in Fig. 1; molecular dimensions are collected in Table 3. The structural characteristics of this isomer of **1b** are very similar to those previously reported[3] for the same isomer of complex **1a**. Once more the hydride ligand was located but not fully refined. Its presence has been amply demonstrated by the high-field proton NMR spectrum and is confirmed by the stereochemical arrangement of the remaining ligands. Unit-cell parameters were determined for two other crystals obtained by the same route. Their dimensions were indistinguishable from those used in the full X-ray analysis.

An orange crystalline product was also obtained from the reaction of pentafluorobenzamide with [$RuCl_2(PPh_3)_3$] in the presence of NEt_3. This was formulated on the basis of spectroscopic data as a mixture of 'head-to-tail' and 'head-to-head' isomers of [Ru_2(μ-Cl)(μ-H){μ-NHC(O)C_6F_5}$_2$(PPh_3)$_4$] **1c**.

When the same reactions were undertaken using preformed [RuH(Cl)(PPh_3)$_3$] in place of [$RuCl_2(PPh_3)_3$]–NEt_3 a significantly different product pattern emerged. With trifluoroacetamide an orange product very similar in appearance to that obtained using [$RuCl_2(PPh_3)_3$]–NEt_3 was formed. However, the high-field proton NMR spectrum of this product showed no fewer than three overlapping hydride resonances each consisting of a triplet of triplets. Two of these can be readily assigned to the 'head-to-tail' and 'head-to-head' isomers of **1a**. These assignments are confirmed by the presence of the corresponding resonance patterns in the ^{31}P-{^{1}H} NMR spectrum. The third triplet of triplets pattern is of relatively low intensity and shows some broadening of individual peaks. The associated ^{31}P-{^{1}H} NMR pattern consists of a single complex resonance at *ca.* δ 30.9 and (probably) a similar one masked by the resonance of **1a** at *ca.* δ 25.2. We tentatively attribute these resonances to a product with 'head-to-tail' orientation as in **1a** but with a bridging μ-N-trifluoroacetamidate ligand in place of

Table 1 Spectroscopic data

			NMR (δ, *J*/Hz)		
Compound	Isomer	IR (cm^{-1})	^{1}H	^{19}F	^{31}P-{^{1}H}
1a	Head-to-tail	ν(RuHRu) masked	−7.52 (t of t, $^2J_{HP}$ 50, 15.5, Ru*H*Ru)	−76.17 (s, C*F*$_3$)	51.16, 31.76 (AA′XX′, *N* = 33)
	Head-to-head	ν(RuHRu) masked	−7.28 (t of t, $^2J_{HP}$ 50, 16, Ru*H*Ru)	−75.2 (s, C*F*$_3$)	52.8 (d, 28), 50.37 (d, 28), 35.05 (t, *ca.* 30), 25.3 (t, *ca.* 30)
1b	Head-to-tail	ν(RuHRu) masked	−7.27 (t of t, $^2J_{HP}$ 49.5, 16, Ru*H*Ru)	−76.34(s, C*F*$_3$), −111.0, −111.2 (s, C*F*$_2$)	51.2, 31.8 (AA′XX′, *N* = 33)
	Head-to-head	ν(RuHRu) masked	−7.72 (t of t, $^2J_{HP}$ 49, 16, Ru*H*Ru)	−76.4 (s, C*F*$_3$), −110.9, −111.1 (s, C*F*$_2$)	52.96 (d, 28), 52.38 (d, 28), 34.51 (t, 28), 24.47 (t, *ca.* 28)
1c	Head-to-tail	ν(RuHRu) masked	−6.70 (t of t, $^2J_{HP}$ 49.5, 16, Ru*H*Ru)		50.8, 32.5 (AA′XX′, *N* = 33)
	Head-to-head	ν(RuHRu) masked	−7.33 (t of t, $^2J_{HP}$ 50, 16, Ru*H*Ru)		54.2 (d, *ca.* 28), 53.2 (d, *ca.* 28), 34.4 (t, *ca.* 28), 29.65 (t, *ca.* 28)
2a		ν(RuHRu) masked	−7.95 (t of t, $^2J_{HP}$ 50, 17, Ru*H*Ru)		
2b		ν(RuHRu) masked	−7.08 (t of t, $^2J_{HP}$ 49, 16, Ru*H*Ru)		54.25 (d, *ca.* 28), 50.52 (d, *ca.* 28), 30.5 (t, *ca.* 28), 24.75 (t, *ca.* 28)
3a	Head-to-tail	ν(CO) 1981, ν(RuHRu) masked	−2.43 (t, $^2J_{HP}$ 11.5, Ru*H*Ru)		55.29 (s)
	Head-to-head		−2.23 (t, $^2J_{HP}$ 12.3, Ru*H*Ru)		58.1 (s), 52.75 (s)
3b	Head-to-tail	ν(CO) 1980 (br), ν(RuHRu) masked	−2.38 (t, $^2J_{HP}$ 11.2, Ru*H*Ru)		55.5 (s)
	Head-to-head	ν(CO) 1980 (br), ν(RuHRu) masked	−2.14 (t, $^2J_{HP}$ 12.2, Ru*H*Ru)		57.6 (s), 53.2 (s)
4a		ν(RuHRu) masked	1.35 (t, $^2J_{HP}$ *ca.* 11, Ru*H*Ru)		53.06 (s)
5a		ν(CO) 1945			31.5 (s)
5b		ν(CO) 1940			32.65 (s)
6a		ν(CO) 1995, 1958			31.90 (s)
7a		ν(OsH) 2130, ν(CO) 1920	6.71 (d of t, $^2J_{HP}$ 86, 25, OsH)		8.31 (d), 1.60 (t, $^2J_{PP'}$ *ca.* 10)
8a		ν(IrH) 2180, 2150	−11.06 (d of t of d, $^2J_{HP}$ 134, 20, $^2J_{HH}$ 5.0, Ir*H*), −18.41 (t of d of d, $^2J_{HP}$ 20, 10, $^2J_{HH'}$ 5.0, Ir*H*)		7.0 (d), 3.6 (t, $^2J_{PP'}$ *ca.* 12)
8b		ν(IrH) 2179, 2139	−10.60 (d of t of d, $^2J_{HP}$ 135, 20, $^2J_{HH'}$ 5, Ir*H*), −18.58 (t of d of d, $^2J_{HP}$ 20, 10, $^2J_{HH'}$ 5, Ir*H*)		7.7 (d), 4.28 (t, $^2J_{PP'}$ *ca.* 13)

References and solvents for NMR spectroscopy: internal $SiMe_4$ (^{1}H and ^{13}C), internal $CFCl_3$ (^{19}F) and external 85% H_3PO_4 (^{31}P); $C_6D_5CD_3$ (binuclear complexes), CD_2Cl_2 (mononuclear complexes).

Table 2 Atomic coordinates (× 10^4) for $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_2F_5\}_2(PPh_3)_4]\cdot 0.5CH_2Cl_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	7 416(1)	2 347(1)	5 607(1)	C(31)	5 357(4)	2 752(4)	5 884(3)
Cl(1)	8 608(1)	2 500	5 000	C(32)	4 626(5)	2 652(6)	6 151(5)
P(1)	6 273(1)	2 332(1)	6 174(1)	C(33)	3 951(6)	2 970(7)	5 961(7)
P(2)	8 346(1)	2 188(1)	6 368(1)	C(34)	3 996(6)	3 416(6)	5 512(5)
N(1)	7 458(3)	3 375(3)	5 708(2)	C(35)	4 685(6)	3 516(5)	5 240(4)
O(1)	7 428(3)	3 672(2)	4 716(2)	C(36)	5 389(5)	3 203(4)	5 433(3)
C(1)	7 483(4)	3 791(3)	5 271(3)	C(41)	9 286(4)	1 723(3)	6 187(3)
C(2)	7 626(7)	4 531(4)	5 424(4)	C(42)	9 986(5)	1 841(4)	6 493(3)
C(3)	7 146(22)	5 018(6)	5 216(11)	C(43)	10 656(5)	1 441(5)	6 409(4)
F(1)	8 414(5)	4 736(3)	5 196(3)	C(44)	10 613(5)	904(5)	6 028(4)
F(2)	7 706(4)	4 636(3)	5 999(2)	C(45)	9 926(6)	807(5)	5 710(4)
F(3)	6 373(5)	4 817(4)	5 286(6)	C(46)	9 252(5)	1 202(4)	5 794(4)
F(4)	7 227(9)	5 094(4)	4 602(5)	C(51)	8 099(4)	1 679(4)	7 014(3)
F(5)	7 238(7)	5 635(3)	5 433(4)	C(52)	8 344(5)	1 792(5)	7 583(3)
C(11)	5 836(4)	1 526(3)	6 412(3)	C(53)	8 128(6)	1 346(6)	8 025(4)
C(12)	5 409(5)	1 421(4)	6 926(3)	C(54)	7 661(6)	796(6)	7 911(5)
C(13)	5 097(5)	790(4)	7 061(4)	C(55)	7 429(6)	655(5)	7 329(5)
C(14)	5 177(5)	265(4)	6 678(4)	C(56)	7 649(5)	1 096(4)	6 886(4)
C(15)	5 584(6)	361(4)	6 166(5)	C(61)	8 739(4)	2 992(3)	6 628(3)
C(16)	5 909(5)	979(4)	6 019(4)	C(62)	9 312(5)	3 326(4)	6 286(3)
C(21)	6 363(4)	2 830(4)	6 863(3)	C(63)	9 564(6)	3 957(4)	6 433(4)
C(22)	6 547(4)	2 546(4)	7 410(3)	C(64)	9 265(7)	4 271(5)	6 931(5)
C(23)	6 617(5)	2 934(5)	7 897(4)	C(65)	8 723(7)	3 965(5)	7 256(5)
C(24)	6 530(6)	3 619(5)	7 865(4)	C(66)	8 453(5)	3 330(4)	7 116(3)
C(25)	6 369(5)	3 922(5)	7 344(5)	Cl(70)	6 442(5)	1 916(5)	402(3)
C(26)	6 261(5)	3 526(4)	6 831(3)	C(70)	5 923(14)	2 500	0

Table 3 Selected bond lengths (Å) and angles (°) for $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_2F_5\}_2(PPh_3)_4]\cdot 0.5CH_2Cl_2$

Ru(1)–Cl(1)	2.434(2)	Ru(1)–P(1)	2.298(2)	P(2)–C(51)	1.834(7)	P(2)–C(61)	1.826(7)
Ru(1)–P(2)	2.344(2)	Ru(1)–N(1)	2.059(5)	N(1)–C(1)	1.295(8)	O(1)–C(1)	1.289(8)
Ru(1)–H(1)	1.664[a]	Ru(1)–Ru(1a)	2.833(1)[b]	O(1)–Ru(1a)	2.158(4)	C(1)–C(2)	1.531(10)
Ru(1)–O(1a)	2.158(4)	Cl(1)–Ru(1a)	2.434(2)	C(2)–C(3)	1.341(27)	C(2)–F(1)	1.467(13)
P(1)–C(11)	1.841(7)	P(1)–C(21)	1.863(7)	C(2)–F(2)	1.334(10)	C(3)–F(3)	1.354(36)
P(1)–C(31)	1.857(7)	P(2)–C(41)	1.860(7)	C(3)–F(4)	1.414(28)	C(3)–F(5)	1.333(16)
Cl(1)–Ru(1)–P(1)	173.5(1)	Cl(1)–Ru(1)–P(2)	84.3(1)	Ru(1)–P(2)–C(51)	121.4(2)	C(41)–P(2)–C(51)	95.2(3)
P(1)–Ru(1)–P(2)	97.3(1)	Cl(1)–Ru(1)–N(1)	84.9(1)	Ru(1)–P(2)–C(61)	110.9(2)	C(41)–P(2)–C(61)	102.0(3)
P(1)–Ru(1)–N(1)	88.7(1)	P(2)–Ru(1)–N(1)	91.7(1)	C(51)–P(2)–C(61)	107.6(3)	Ru(1)–N(1)–C(1)	123.4(4)
Cl(1)–Ru(1)–Ru(1a)	54.4(1)	P(1)–Ru(1)–Ru(1a)	123.5(1)	C(1)–O(1)–Ru(1a)	120.5(4)	N(1)–C(1)–O(1)	129.4(6)
P(2)–Ru(1)–Ru(1a)	138.7(1)	N(1)–Ru(1)–Ru(1a)	84.0(1)	N(1)–C(1)–C(2)	116.4(6)	O(1)–C(1)–C(2)	114.2(6)
Cl(1)–Ru(1)–O(1a)	85.2(1)	P(1)–Ru(1)–O(1a)	100.8(1)	C(1)–C(2)–C(3)	121.5(13)	C(1)–C(2)–F(1)	108.9(7)
P(2)–Ru(1)–O(1a)	96.9(1)	N(1)–Ru(1)–O(1a)	166.2(2)	C(3)–C(2)–F(1)	101.8(14)	C(1)–C(2)–F(2)	113.0(6)
Ru(1a)–Ru(1)–O(1a)	82.5(1)	Ru(1)–Cl(1)–Ru(1a)	71.2(1)	C(3)–C(2)–F(2)	107.1(12)	F(1)–C(2)–F(2)	102.4(8)
Ru(1)–H(1)–Ru(1a)	116.7[a]	Ru(1)–P(1)–C(11)	120.1(2)	C(2)–C(3)–F(3)	108.0(14)	C(2)–C(3)–F(4)	111.8(20)
Ru(1)–P(1)–C(21)	113.6(2)	C(11)–P(1)–C(21)	104.3(3)	F(3)–C(3)–F(4)	103.7(22)	C(2)–C(3)–F(5)	117.8(24)
Ru(1)–P(1)–C(31)	118.1(2)	C(11)–P(1)–C(31)	100.0(3)	F(3)–C(3)–F(5)	109.7(21)	F(4)–C(3)–F(5)	104.9(13)
C(21)–P(1)–C(31)	97.3(3)	Ru(1)–P(2)–C(41)	117.2(2)				

[a] Coordinates of hydride ligand not refined. [b] Non-bonding distance.

chloride. This product, designated **2a**, was present only in very small amounts and has not been isolated or comprehensively characterised.

A similar reaction of $[RuH(Cl)(PPh_3)_3]$ with pentafluoropropionamide gave a good yield of the 'head-to-tail' and 'head-to-head' isomers of $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_2F_5\}_2(PPh_3)_4]$ **1b** plus a trace of the pentafluoropropionamidate analogue of **2a** which we designate **2b**.

Extending the same reaction to pentafluorobenzamide led to isolation of the anticipated product $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_6F_5\}_2(PPh_3)_4]$ **1c** as a mixture of 'head-to-tail' and 'head-to-head' isomers with no evidence for the analogue of **2a**, **2b**. We suggest that the significant broadening observed in the high-field proton resonance of complexes **2a** and **2b** is due to restricted rotation of the N-bridging amidate ligand about the N–C bond in a relatively congested site and that as the size of this ligand increases $NHC(O)CF_3 < NHC(O)C_2F_5 < NHC(O)C_6F_5$ its presence in the bridging location becomes steadily less tenable.

$[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)R_F\}_2(CO)_2(PPh_3)_2]$ ($R_F = CF_3$ *or* C_2F_5).—Carbonylation of the complexes $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)R_F\}_2(PPh_3)_4]$ gave dicarbonyl products $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)R_F\}_2(CO)_2(PPh_3)_2]$. These also exist in 'head-to-tail' and 'head-to-head' configurations. Thus carbonylation of the main ('head-to-tail') isomer of $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)CF_3\}_2(PPh_3)_4]$ **1a** gave a pale yellow crystalline material **3a**, the high-field ^1H NMR spectrum of which displays a single triplet pattern. In contrast, carbonylation of a mixture of 'head-to-tail' and 'head-to-head' isomers of **1b** gave a pale yellow product which displays two triplet hydride signals attributable to 'head-to-tail' and 'head-to-head' isomers of $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_2F_5\}_2(CO)_2(PPh_3)_2]$ **3b**. In order further to confirm our structural assignments, $^{31}P\text{-}\{^1H\}$ NMR spectra of the dicarbonyl products were recorded. Complex **3a** obtained from the isomerically pure precursor **1a** displays a singlet consistent with its formulation as the 'head-to-tail' isomer, whereas the corresponding product **3b** obtained from the mixed-isomer precursor **1b** displays a singlet ('head-to-tail'

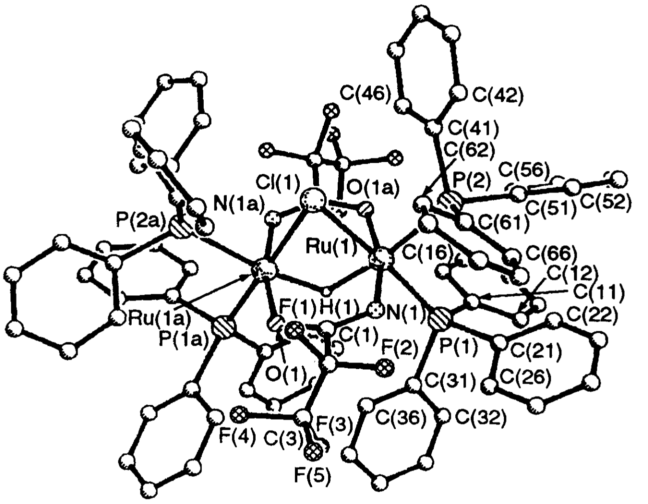

Fig. 1 Molecular structure of $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_2F_5\}_2(PPh_3)_4]$

isomer) plus two singlets ('head-to-head' isomer). Samples of **1a** made by method B gave on carbonylation a mixture of isomers of **3a** plus a trace of **4a** formed by carbonylation of the impurity **2a**.

The formation of the binuclear quadruply bridged complexes **1a**–**1c** and **2a**, **2b**, and their carbonylated derivatives **3a**–**3c** and **4a** is at first sight unexpected since corresponding reactions with closely related species such as amidines and carboxylic acids generated mononuclear complexes under similar circumstances. However, we have previously encountered parallel behaviour with arylamides, $NH_2C(O)R$, and it now appears that amidate anions display a general reluctance to co-ordinate in a chelate manner in these platinum-metal-based systems. This behaviour can be tentatively accounted for in terms of delocalisation energies. It seems feasible that the four-membered metallocycles generated by ligands of the type under discussion rely to a significant extent on delocalisation energy for their stability. If this is the case then asymmetric anions such as the amidates would be expected to possess less delocalisation than their symmetrical counterparts and therefore be less able to chelate.

$[Ru\{NHC(O)R_F\}_2(CO)(H_2O)(PPh_3)_2]$ ($R_F = CF_3$ **5a** *or* C_2F_5 **5b**).—The treatment of $[RuH_2(CO)(PPh_3)_3]$ with trifluoroacetamide (*ca.* 1:3 molar ratio) in boiling toluene affords a solution from which the product **5a** can be isolated as air-stable pale yellow microcrystals. The corresponding reaction with pentafluoropropionamide gave **5b** as air-stable white microcrystals. Spectroscopic data (Table 1) did not permit an unambiguous assignment of stereochemistry. Therefore, in order to resolve this problem and also compare the structure with that previously reported for the closely related complex $[Ru\{OC(O)CF_3\}_2(CO)(MeOH)(PPh_3)_2]$[7] a crystal structure determination was undertaken on **5a**. Details of this structure have previously been reported,[3] so only salient features are noted below. The essentially octahedral ruthenium(II) centre is co-ordinated to a *trans* pair of triphenylphosphines, a *trans* pair of N-bound trifluoroacetamidate anions, a carbonyl and a molecule of water. Angles subtended at ruthenium by *cis* pairs of donor atoms range from 84.6(2)° for O(4)–Ru–P(2) to 98.0(3)° for C(1)–Ru–N(1). With the possible exception of one rather long Ru–P bond [2.445(3) Å] the ruthenium–ligand distances are entirely consistent with bonding to an octahedral ruthenium(II) centre. The presence of a molecule of water within the co-ordination sphere adjacent to a monodentate trifluoroacetamidate ligand attests to the poor chelating capacity of the latter. However, intramolecular hydrogen bonding between the co-ordinated water molecule and the oxygen atom of an amidate ligand (O–H $\cdots$ O 2.600 Å) no doubt plays a significant role in stabilising this particular arrangement. The *trans*-phosphines *trans*-amidates stereochemistry found for **5a** was unexpected since two closely related structures $[Ru\{OC(O)CF_3\}_2(CO)(MeOH)(PPh_3)_2]$[7] and $[Ru\{OS(O)_2CF_3\}_2(CO)(H_2O)(PPh_3)_2]$[8] have both been shown to possess *cis cis* configurations. Given that $CF_3CO_2^-$, $CF_3SO_3^-$ and $CF_3C(O)NH^-$ ligands have very similar steric characteristics it seems probable that the different geometry adopted by complex **5a** reflects electronic effects arising from the change from O- to N-donor ligands.

$[Ru\{NHC(O)CF_3\}_2(CO)_2(PPh_3)_2]$ **6a**.—This complex was obtained in good yield from the reaction of $[Ru(CO)_3(PPh_3)_2]$ with trifluoroacetamide in boiling toluene. It was also produced by treatment of **5a** with a steady stream of carbon monoxide. The spectroscopic data (Table 1) clearly establish the presence of equivalent PPh_3 ligands and a *cis* pair of carbonyl ligands. The ν(CO) frequencies for the latter favour CO *trans* to $NHC(O)CF_3$ rather than PPh_3 and thus support a *trans*-phosphines, *cis*-carbonyls stereochemistry for **6a**.

$[OsH\{NHC(O)CF_3\}(CO)(PPh_3)_3]$ **7a**.—In marked contrast to its more substitution-labile ruthenium analogue, the osmium complex $[OsH_2(CO)(PPh_3)_3]$ reacts only slowly with trifluoroacetamide to yield the hydride **7a** in which only one amidate ligand has been introduced and all three phosphine ligands have been retained. The spectroscopic data (Table 1) are indicative of a *mer*-phosphines stereochemistry with hydride *trans* to phosphine.

$[Ir(H)_2\{NHC(O)R_F\}(PPh_3)_3]$ ($R = CF_3$ **8a** *or* C_2F_5 **8b**).—Reactions of *mer*-$[IrH_3(PPh_3)_3]$ with the appropriate amides in boiling toluene afford the products **8a** and **8b** as air-stable white crystals. Spectroscopic data clearly establish a *mer*-phosphines, *cis*-hydrides stereochemistry for these products. The high-field chemical shifts recorded for hydride *trans* to amidate in these complexes are *ca.* 5 ppm to low field of those reported[2] for hydride *trans* to perfluorocarboxylate in the related complexes $[IrH_2(O_2CR_F)(PPh_3)_3]$ and thus clearly indicate that the amidate ligands are N- rather than O-bonded.

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