

**Amide Metallation Reactions: Synthesis and X-Ray Crystal Structures of  
 $[\text{Ru}(\text{NHCOCF}_3)_2(\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_2]$ ,  
 $[\text{Ph}_3\text{P}(\text{OC})\text{Ru}(\mu\text{-NHCOC}_6\text{H}_4\text{-o})(\mu\text{-NHCOPh})(\mu\text{-H})\text{Ru}(\text{CO})(\text{PPh}_3)_2]$  and  
 $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-H})(\mu\text{-NHCOCF}_3)_2(\text{PPh}_3)_4]$**

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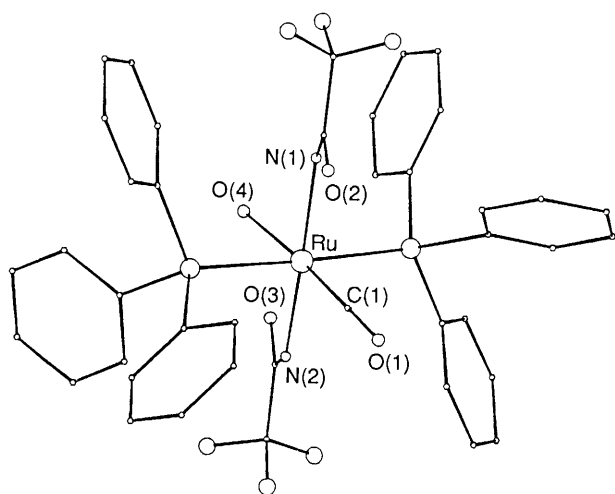
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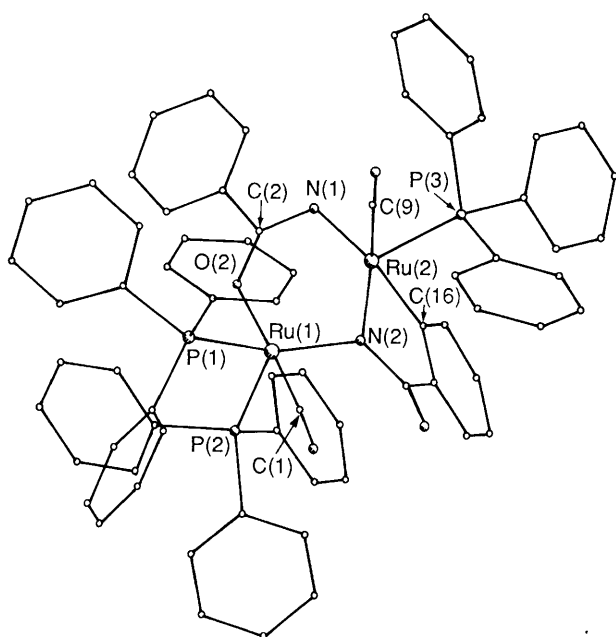
Amides,  $\text{NH}_2\text{COR}$  ( $\text{R} = \text{CF}_3, \text{Ph}$ ), undergo metallation reactions to form mono- and bi-nuclear ruthenium(II) amido complexes, notably  $[\text{Ru}(\text{NHCOCF}_3)_2(\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_2]$ , the cyclometallated (N,C) benzamido derivative  $[\text{Ph}_3\text{P}(\text{OC})\text{Ru}(\mu\text{-NHCOC}_6\text{H}_4\text{-o})(\mu\text{-NHCOPh})(\mu\text{-H})\text{Ru}(\text{CO})(\text{PPh}_3)_2]$  and the quadruply bridged species  $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-H})(\mu\text{-NHCOCF}_3)_2(\text{PPh}_3)_4]$  all of which have been characterised by X-ray diffraction methods.

Whereas the activation and cleavage of C–H bonds by transition metal complexes is now commonplace, and is known to play a key role in many important catalytic processes,<sup>1</sup> the corresponding reactions of N–H bonds are much less familiar.<sup>2,3</sup> However, as others have noted,<sup>3</sup> N–H

bond activation by transition metal complexes in homogeneous solution is of considerable relevance to the important problem of catalytic alkene hydro-amination. Indeed a recently reported catalyst system capable of adding aniline across the double bond of norbornene has been shown



**Fig. 1** Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): P(1)–Ru(1) 2.379(3), P(2)–Ru(1) 2.445(3), O(4)–Ru(1) 2.160(5), N(1)–Ru(1) 2.069(5), N(2)–Ru(1) 2.101(5), C(1)–Ru(1) 1.813(6).



**Fig. 2** Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ru(2)–Ru(1) 2.842(4), P(1)–Ru(1) 2.329(5), P(2)–Ru(1) 2.395(5), C(1)–Ru(1) 1.825(13), O(2)–Ru(1) 2.128(10), N(2)–Ru(1) 2.178(11), P(3)–Ru(2) 2.293(5), N(1)–Ru(2) 2.142(12), C(9)–Ru(2) 1.815(12), N(2)–Ru(2) 2.127(9), C(16)–Ru(2) 2.056(15), P(1)–Ru(1)–Ru(2) 115.1(2), P(2)–Ru(1)–Ru(2) 139.3(1), C(1)–Ru(1)–Ru(2) 99.8(4), O(2)–Ru(1)–Ru(2) 82.2(3), N(2)–Ru(1)–Ru(2) 47.9(2), P(3)–Ru(2)–Ru(1) 150.1(1), N(1)–Ru(2)–Ru(1) 82.9(3), C(9)–Ru(2)–Ru(1) 120.1(5), N(2)–Ru(2)–Ru(1) 49.5(2), C(16)–Ru(2)–Ru(1) 88.4(4).

to involve oxidative addition of the amine across an iridium(I) centre.<sup>4</sup>

We now report reactions between amides  $\text{NH}_2\text{COR}$  ( $\text{R} = \text{CF}_3, \text{Ph}$ ) and various ruthenium(II) triphenylphosphine complexes leading to the formation of ruthenium(II) amido products.

Trifluoroacetamide reacts with  $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$  in boiling toluene to form the amido product  $[\text{Ru}(\text{NHCOCF}_3)_2-$

$(\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_2]$  **1**† as air-stable pale yellow crystals. The X-ray crystal structure of **1**‡ is shown in Fig. 1 together with selected bond lengths and bond angles. The presence of the aquo ligand within the coordination sphere of **1** attests to the relatively poor chelating capacity of the  $\text{CF}_3\text{CONH}^-$  anion. Carbonylation of **1** in boiling toluene affords the dicarbonyl  $[\text{Ru}(\text{NHCOCF}_3)_2(\text{CO})_2(\text{PPh}_3)_2]$ .

In marked contrast benzamide reacts with  $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$  under similar conditions to yield the novel binuclear cyclometallated product  $[(\text{Ph}_3\text{P})(\text{OC})\text{Ru}(\mu\text{-NHCO}\text{C}_6\text{H}_4\text{-o})-(\mu\text{-NHCOPh})(\mu\text{-H})\text{Ru}(\text{CO})(\text{PPh}_3)_2]$  **2**† as air-stable orange needles. The X-ray crystal structure of **2**‡ is shown in Fig. 2 together with bond length and bond angle data.

The formation of products **1** and **2** can be rationalised in terms of a reaction scheme involving a common initial step (1) followed, in the case of the more acidic  $\text{NH}_2\text{COCF}_3$ , by attack on the second hydride ligand (2), and in the case of the less acidic  $\text{NH}_2\text{COPh}$ , by cyclometallation (3), condensation with a second molecule of the intermediate  $\text{RuH}(\text{NHCOPh})(\text{CO})-$

† Selected spectroscopic data for **1**: IR (Nujol mull)  $\nu(\text{CO})$  1945  $\text{cm}^{-1}$ ; NMR ( $\text{CD}_2\text{Cl}_2$ )  $^1\text{H}$   $\delta$  4.4 (s), NH;  $^{31}\text{P}$   $\{^1\text{H}\}$   $\delta$  31.5(s).

For **2**: IR (Nujol mull)  $\nu(\text{CO})$  1912, 1953  $\text{cm}^{-1}$ ;  $\nu(\text{RuHRu})$  masked; NMR ( $\text{CD}_2\text{Cl}_2$ )  $^1\text{H}$   $\delta$  – 11.43 (d of d of d,  $^2J_{\text{HP}}$  63.5, 27.5 and 22.7 Hz), RuHRu;  $^{31}\text{P}$   $\{^1\text{H}\}$   $\delta$  52.55 (d of d,  $J_{\text{PP}}$  17 and 4 Hz), 50.08 (d or d,  $J_{\text{PP}}$  40 and 4 Hz), 22.70 (d or d,  $J_{\text{PP}}$  40 and 17 Hz).

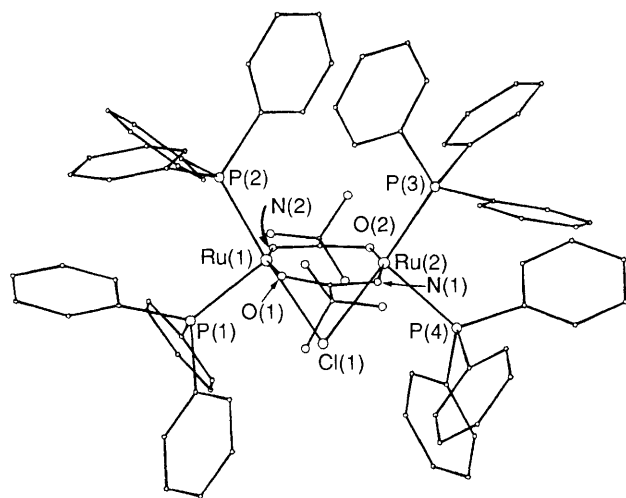
For **3**: IR (Nujol mull)  $\nu(\text{RuHRu})$  masked; NMR ( $\text{CD}_2\text{Cl}_2$ )  $^1\text{H}$   $\delta$  – 7.52 (t of t,  $^2J_{\text{HP}}$  49.8 and 15.5 Hz), RuHRu;  $^{31}\text{P}$   $\{^1\text{H}\}$   $\delta$  51.17 (d of d,  $^2J_{\text{PP}}$  20 Hz,  $^4J_{\text{PP}}$  13 Hz), 31.77 (d of d,  $^2J_{\text{PP}}$  20 Hz,  $^4J_{\text{PP}}$  13 Hz).

‡ Crystal data for **1**:  $\text{C}_{41}\text{H}_{54}\text{N}_2\text{O}_4\text{F}_6\text{P}_2\text{Ru}(\text{CH}_2\text{OH})_2$  ( $\text{CH}_2\text{Cl}_2$ ),  $M = 1044.75$ , Triclinic,  $a = 18.624(2)$ ,  $b = 12.484(2)$ ,  $c = 10.137(1)$  Å,  $\alpha = 92.29(1)$ ,  $\beta = 92.04(1)$ ,  $\gamma = 92.91(1)^\circ$ ,  $U = 2350.28$  Å<sup>3</sup>,  $D_c = 1.39$  g  $\text{cm}^{-3}$ ,  $Z = 2$ , space group  $P\bar{1}$  Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\mu(\text{Mo-K}\alpha) = 5.079$   $\text{cm}^{-1}$ ,  $F(000) = 1004$ . Intensity data were collected in the range  $1.5 < \theta < 23.0$  on a CAD4 diffractometer by the method described previously.<sup>5</sup> The structure was solved by Patterson and Fourier techniques and refined by blocked full-matrix least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the parent atoms, and refined in a riding mode. Final  $R = 0.038$  and  $R_w = 0.060$  for 5223 unique reflections with  $|F_o| > 3\sigma(|F_o|)$ .

For **2**:  $\text{C}_{70}\text{H}_{57}\text{N}_2\text{O}_4\text{P}_3\text{Ru}_2$ ,  $M = 1285.29$ , Monoclinic,  $a = 21.433(5)$ ,  $b = 26.271(9)$ ,  $c = 23.329(3)$  Å,  $\beta = 106.78(2)^\circ$ ,  $U = 12576.46$  Å<sup>3</sup>,  $D_c = 1.354$  g  $\text{cm}^{-3}$ ,  $Z = 8$ , space group  $I2/a$ , Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\mu(\text{Mo-K}\alpha) = 6.04$   $\text{cm}^{-1}$ ,  $F(000) = 5224$ . Intensity data were collected on a FAST diffractometer. One hemisphere of data were collected with a detector swing angle of  $18^\circ$  and a crystal-to-detector distance of 45 mm. This corresponds to a minimum  $\theta_{\text{max}}$  value of  $24^\circ$ ; additional data with a non-spherical distribution, owing to the geometry of this 'flat plate' system were also collected and included. The structure was solved by Patterson and Fourier techniques and refined by blocked full-matrix least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the parent atoms, and refined in a riding mode. Final  $R = 0.058$  and  $R_w = 0.071$  for 5260 unique reflections with  $|F_o| > \sigma(|F_o|)$ .

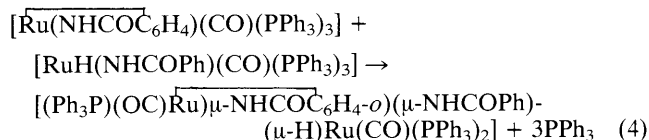
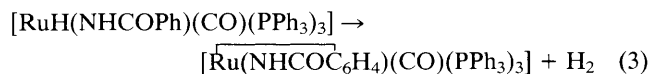
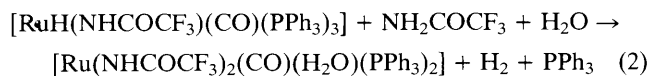
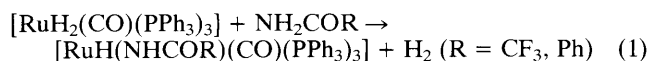
For **3**:  $\text{C}_{76}\text{H}_{63}\text{N}_2\text{O}_2\text{F}_6\text{P}_4\text{ClRu}_2$  ( $0.5\text{CH}_2\text{Cl}_2, \text{H}_2\text{O}$ ),  $M = 1572.31$ , Orthorhombic,  $a = 12.542(3)$ ,  $b = 24.069(4)$ ,  $c = 25.081(4)$  Å,  $U = 7571.29$  Å<sup>3</sup>,  $D_c = 1.376$  g  $\text{cm}^{-3}$ ,  $Z = 4$ , space group  $P2_12_12_1$ , Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\mu(\text{Mo-K}\alpha) = 6.04$   $\text{cm}^{-1}$ ,  $F(000) = 1004$ . Intensity data were collected in the range  $1.5 < \theta < 23.0$  on a CAD4 diffractometer by the method described previously.<sup>5</sup> The structure was solved by Patterson and Fourier techniques and refined by blocked full-matrix least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the parent atoms, and refined in a riding mode. Final  $R = 0.038$  and  $R_w = 0.058$  for 6664 unique reflections with  $|F_o| > 6\sigma(|F_o|)$ .

All three sets of data were corrected for absorption using the DIFABS® procedure. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

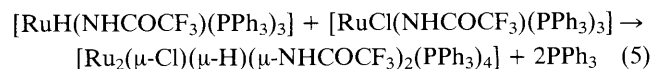


**Fig. 3** Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ru(2)–Ru(1) 2.811(4), Cl(1)–Ru(1) 2.427(4), P(1)–Ru(1) 2.339(4), P(2)–Ru(1) 2.281(4), O(1)–Ru(1) 2.162(7), N(2)–Ru(1) 2.061(8), Cl(1)–Ru(2) 2.429(4), P(3)–Ru(2) 2.298(4), P(4)–Ru(2) 2.336(4), N(1)–Ru(2) 2.041(8), O(2)–Ru(2) 2.153(7), Cl(1)–Ru(1)–Ru(2) 54.7(1), P(1)–Ru(1)–Ru(2) 139.8(1), P(2)–Ru(1)–Ru(2) 120.6(2), O(1)–Ru(1)–Ru(2) 82.0(2), N(2)–Ru(1)–Ru(2) 83.4(3), Cl(1)–Ru(2)–Ru(1) 54.6(1), P(3)–Ru(2)–Ru(1) 121.1(2), P(4)–Ru(2)–Ru(1) 139.9(1), N(1)–Ru(2)–Ru(1) 84.3(3), O(2)–Ru(2)–Ru(1) 82.7(2).

(PPh<sub>3</sub>)<sub>2</sub> and finally elimination of triphenylphosphine ligands (4).



Finally trifluoroacetamide reacts with RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> in refluxing toluene in the presence of triethylamine to afford the quadruply bridged species [Ru<sub>2</sub>(μ-Cl)(μ-H)(μ-NHCOCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] **3**<sup>†</sup> as air-stable orange crystals. The X-ray crystal structure of **3**<sup>†</sup> has been determined and is shown in Fig. 3 together with salient bond lengths and angles. Partial conversion of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] to [RuCl(NHCOCF<sub>3</sub>)(PPh<sub>3</sub>)<sub>3</sub>] and, via [RuHCl(PPh<sub>3</sub>)<sub>3</sub>] to [RuH(NHCOCF<sub>3</sub>)(PPh<sub>3</sub>)<sub>3</sub>], followed by condensation of these two intermediates with elimination of two molecules of triphenylphosphine [eqn. (5)] offers a feasible route to **3**.



Preliminary studies indicate that osmium and iridium precursors undergo similar reactions with amides.

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