

**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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Amides, NH_2COR ($\text{R} = \text{CF}_3, \text{Ph}$), 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,¹ the corresponding reactions of N–H bonds are much less familiar.^{2,3} However, as others have noted,³ 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

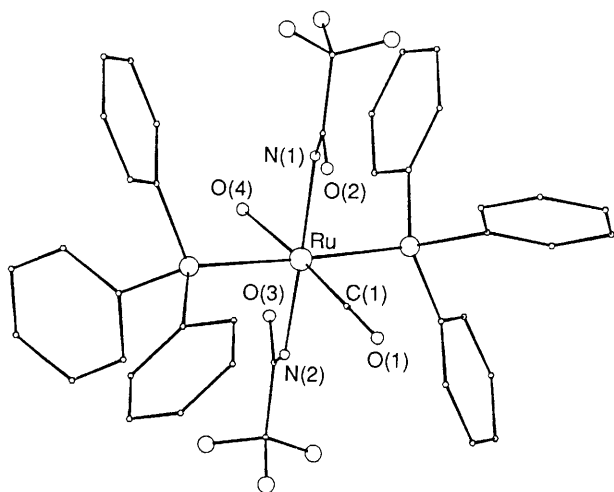


Fig. 1 Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): P(1)–Ru(1) 2.379(3), P(2)–Ru(1) 2.445(3), O(4)–Ru(1) 2.160(5), N(1)–Ru(1) 2.069(5), N(2)–Ru(1) 2.101(5), C(1)–Ru(1) 1.813(6).

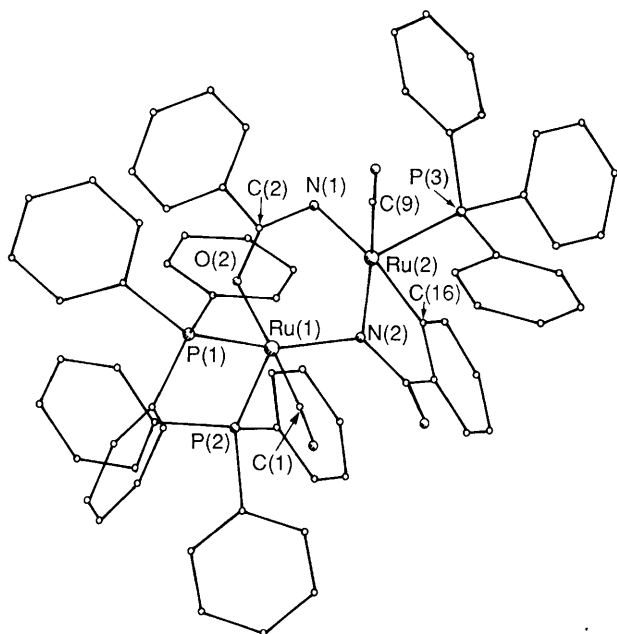


Fig. 2 Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ru(2)–Ru(1) 2.842(4), P(1)–Ru(1) 2.329(5), P(2)–Ru(1) 2.395(5), C(1)–Ru(1) 1.825(13), O(2)–Ru(1) 2.128(10), N(2)–Ru(1) 2.178(11), P(3)–Ru(2) 2.293(5), N(1)–Ru(2) 2.142(12), C(9)–Ru(2) 1.815(12), 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(1) centre.⁴

We now report reactions between amides NH_2COR ($\text{R} = \text{CF}_3$, 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 CF_3CONH^- 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 $[(\text{Ph}_3\text{P})(\text{OC})\text{Ru}(\mu\text{-NHCOCH}_2\text{C}_6\text{H}_4\text{-o})(\mu\text{-NHCOCH}_2\text{C}_6\text{H}_4\text{-o})\text{Ru}(\text{CO})(\text{PPh}_3)_2]$ **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 NH_2COCF_3 , by attack on the second hydride ligand (2), and in the case of the less acidic NH_2COPh , by cyclometallation (3), condensation with a second molecule of the intermediate $\text{RuH}(\text{NHCOCH}_2\text{C}_6\text{H}_4\text{-o})(\text{CO})-$

[†] Selected spectroscopic data for **1**: IR (Nujol mull) $\nu(\text{CO})$ 1945 cm^{-1} ; NMR (CD_2Cl_2) ^1H δ 4.4 (s), NH; ^{31}P $\{^1\text{H}\}$ δ 31.5(s).

For **2**: IR (Nujol mull) $\nu(\text{CO})$ 1912, 1953 cm^{-1} ; $\nu(\text{RuHRu})$ masked; NMR (CD_2Cl_2) ^1H δ –11.43 (d of d of d, $^2J_{\text{HP}}$ 63.5, 27.5 and 22.7 Hz), RuHRu; ^{31}P $\{^1\text{H}\}$ δ 52.55 (d of d, J_{PP} 17 and 4 Hz), 50.08 (d or d, J_{PP} 40 and 4 Hz), 22.70 (d or d, J_{PP} 40 and 17 Hz).

For **3**: IR (Nujol mull) $\nu(\text{RuHRu})$ masked; NMR (CD_2Cl_2) ^1H δ –7.52 (t of t, $^2J_{\text{HP}}$ 49.8 and 15.5 Hz), RuHRu; ^{31}P $\{^1\text{H}\}$ δ 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**: $\text{C}_{41}\text{H}_{54}\text{N}_2\text{O}_4\text{F}_6\text{P}_2\text{Ru}(\text{CH}_3\text{OH})_2$ (CH_2Cl_2), $M = 1044.75$, Triclinic, $a = 18.624(2)$, $b = 12.484(2)$, $c = 10.137(1)$ Å, $\alpha = 92.29(1)^\circ$, $\beta = 92.04(1)^\circ$, $\gamma = 92.91(1)^\circ$, $U = 2350.28$ Å³, $D_c = 1.39$ g cm^{-3} , $Z = 2$, space group $P\bar{1}$ Mo-K α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 5.079$ 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.⁵ 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, $\beta = 106.78(2)^\circ$, $U = 12576.46$ Å³, $D_c = 1.354$ g cm^{-3} , $Z = 8$, space group $I2/a$, Mo-K α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 6.04$ cm^{-1} , $F(000) = 5224$. Intensity data were collected with a detector swing angle of 18° and a crystal-to-detector distance of 45 mm. This corresponds to a minimum θ_{max} value of 24° ; 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**: $\text{C}_{76}\text{H}_{63}\text{N}_2\text{O}_2\text{F}_6\text{P}_4\text{ClRu}_2$ ($0.5\text{CH}_2\text{Cl}_2$, H_2O), $M = 1572.31$, Orthorhombic, $a = 12.542(3)$, $b = 24.069(4)$, $c = 25.081(4)$ Å, $U = 7571.29$ Å³, $D_c = 1.376$ g cm^{-3} , $Z = 4$, space group $P2_12_12_1$, Mo-K α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 6.04$ 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.⁵ 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.

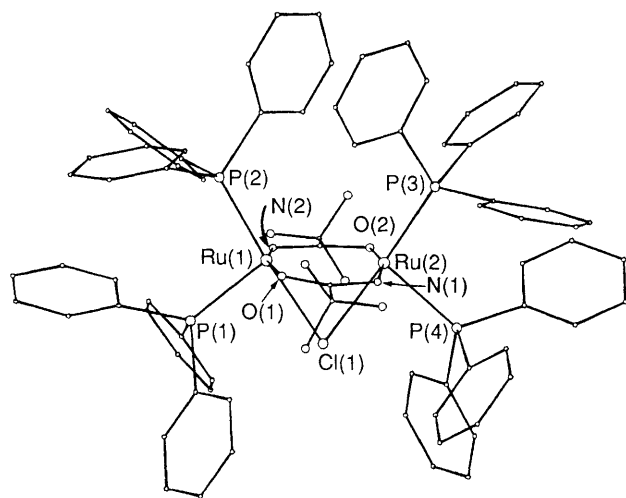
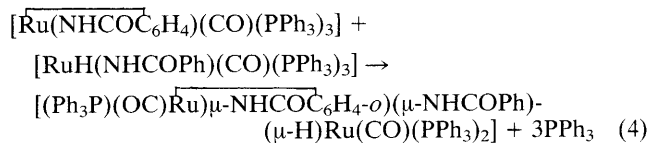
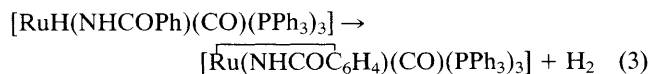
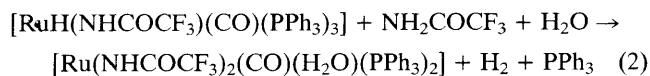
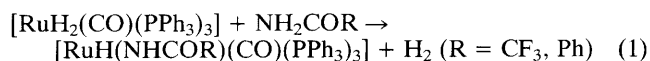
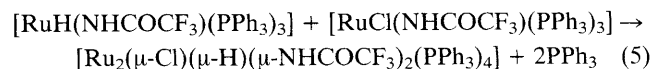


Fig. 3 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ru(2)–Ru(1) 2.811(4), Cl(1)–Ru(1) 2.427(4), P(1)–Ru(1) 2.339(4), P(2)–Ru(1) 2.281(4), O(1)–Ru(1) 2.162(7), N(2)–Ru(1) 2.061(8), Cl(1)–Ru(2) 2.429(4), P(3)–Ru(2) 2.298(4), P(4)–Ru(2) 2.336(4), 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).

(PPh₃)₂ and finally elimination of triphenylphosphine ligands (4).



Finally trifluoroacetamide reacts with RuCl₂(PPh₃)₃ in refluxing toluene in the presence of triethylamine to afford the quadruply bridged species [Ru₂(μ-Cl)(μ-H)(μ-NHCOCF₃)₂(PPh₃)₄] **3**[†] as air-stable orange crystals. The X-ray crystal structure of **3**[†] has been determined and is shown in Fig. 3 together with salient bond lengths and angles. Partial conversion of [RuCl₂(PPh₃)₃] to [RuCl(NHCOCF₃)(PPh₃)₃] and, via [RuHCl(PPh₃)₃] to [RuH(NHCOCF₃)(PPh₃)₃], 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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References

- 1 R. G. Bergman, *Science*, 1984, **223**, 902; R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245; A. H. Janowicz, R. A. Periana, J. M. Buchanan, C. A. Kovac, J. M. Stryker, M. J. Wax and R. G. Bergman, *Pure Appl. Chem.*, 1984, **56**, 13; W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1986, **108**, 4814; C. K. Ghosh and W. A. G. Graham, *J. Am. Chem. Soc.*, 1987, **109**, 4726; M. Hackett and G. M. Whitesides, *J. Am. Chem. Soc.*, 1988, **110**, 1449; W. D. Jones and F. J. Feher, *Acc. Chem. Res.*, 1989, **22**, 91.
- 2 D. R. Schaad and C. R. Landis, *J. Am. Chem. Soc.*, 1990, **112**, 1628 and references therein.
- 3 F. T. Lapido and J. S. Merola, *Inorg. Chem.*, 1990, **29**, 4172.
- 4 A. L. Casalnuovo, J. C. Calabrese and D. Milstein, *Inorg. Chem.*, 1987, **26**, 971; A. L. Casalnuovo, J. C. Calabrese and D. Milstein, *J. Am. Chem. Soc.*, 1988, **110**, 6738.
- 5 R. A. Jones, M. B. Hursthouse, K. M. A. Malik and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.