# Hexaruthenium and octaruthenium carbonyl cluster complexes derived from 2-amino-6-methylpyridine — Novel coordination modes for 2-imidopyridines[1]

Javier A. Cabeza, Ignacio del Río, Pablo García-Álvarez, and Daniel Miguel

**Abstract:** The hexanuclear ruthenium cluster $[Ru_6(\mu_3\text{-}H)_2(\mu\text{-}H)_2(\mu_4\text{-}\kappa^2\text{-ampy})_2(CO)_{14}]$ (**1**) and the octanuclear one $[Ru_8(\mu\text{-}H)(\mu_4\text{-}\kappa^2\text{-ampy})_3(\mu_3\text{-}\kappa^2\text{-Hampy})(\mu\text{-}CO)_2(CO)_{15}]$ (**2**) have been prepared by treating $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ with 2-amino-6-methylpyridine ($H_2$ampy) in decane at reflux temperature. Their metal atoms are supported by ligands that derive from the activation of one (complex **2**) or both N—H bonds (complexes **1** and **2**) of the $H_2$ampy amino fragment. Both contain at least one ampy ligand featuring an unprecedented coordination type: the imido N atom caps a triangle of metal atoms while the pyridine nitrogen is attached to an additional metal atom. One of the ampy ligands of cluster **2** also displays another unprecedented coordination type: it caps a distorted square of metal atoms through the imido N atom while the pyridine nitrogen is attached to one of the atoms included in that square.

*Key words:* ruthenium, cluster compounds, amido ligands, imido ligands.

**Résumé :** En faisant réagir du $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ avec de la 2-amino-6-méthylpyridine ($H_2$ampy), dans du décane au reflux, on obtenu les agrégats de ruthénium hexanucléaire $[Ru_6(\mu_3\text{-}H)_2(\mu\text{-}H)_2(\mu_4\text{-}\kappa^2\text{-ampy})_2(CO)_{14}]$ (**1**) et octanucléaire $[Ru_8(\mu\text{-}H)(\mu_4\text{-}\kappa^2\text{-ampy})_3(\mu_3\text{-}\kappa^2\text{-Hampy})(\mu\text{-}CO)_2(CO)_{15}]$ (**2**). Les atomes métalliques sont supportés par les ligands qui dérivent de l'activation d'une (complexe **2**) ou des deux liaisons N—H (complexes **1** et **2**) du fragment aminé $H_2$ampy. Les deux contiennent chacun au moins un ligand ampy comportant un type jusque là inconnu de coordination: les atomes d'azote imido recouvrent un triangle d'atomes métalliques alors que l'azote de la pyridine est attaché à un atome métallique additionnel. Un des ligands ampy de l'agrégat **2** présente en plus un autre type jusque là inconnu de coordination: l'atome d'azote imido recouvre un carré déformé d'atomes métalliques alors que l'azote de la pyridine est attaché à un des atomes inclus dans le carré.

*Mots clés :* ruthénium, agrégats, ligands amido, ligands imido.

[Traduit par la Rédaction]

## Introduction

An extensive derivative chemistry of triruthenium carbonyl clusters containing 2-amidopyridine ligands has been developed during the last decade. These studies have demonstrated that such ligands help maintain the cluster integrity because they act as strong anchors that hold the three metal atoms in close proximity, preventing cluster fragmentations (1).

We have recently reported that the trinuclear cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-Hampy})(CO)_9]$ ($H_2$ampy = 2-amino-6-methylpyridine) undergoes condensation with $[Ru_3(CO)_{12}]$ at 110–140 °C to give the hexanuclear derivative $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ in high yield (2, 3) (Scheme 1). This reaction afforded the first example of a 2-imidopyridine ligand in which the imido N atom caps a metallic square. Subsequent reactivity studies using $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ as starting material have shown that its apical $Ru(CO)_3$ fragment, which is not anchored by the N atoms, is labile and that this fact is responsible for the observation of pentanuclear and heptanuclear derivatives on some occasions (4).

Prompted by the fact that the number of known ruthenium carbonyl cluster complexes of nuclearity greater than five that contain N-donor ligands is as yet small (2–6), and having in mind the ability of 2-aminopyridines to undergo N—H bond cleavage processes under thermal conditions when treated with $[Ru_3(CO)_{12}]$ (2, 7, 8), we decided to attempt the

Received 26 May 2005. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 17 February 2006.

*Dedicated to Professor Arthur J. Carty, for his outstanding contributions to organometallic cluster chemisty.*

**J.A. Cabeza,[2] I. del Río, and P. García-Álvarez.** Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica "Enrique Moles", Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain.
**D. Miguel.** Área de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain.

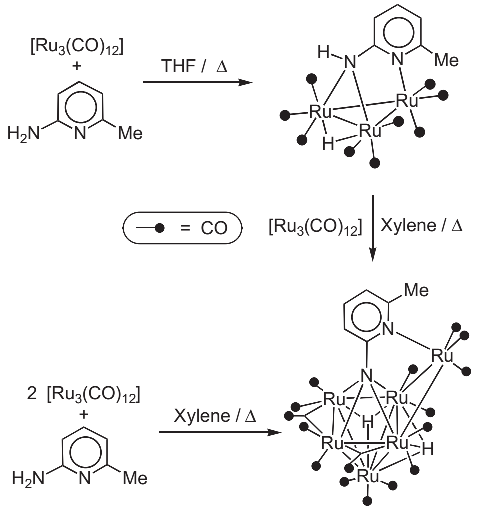
---

[1] This article is part of a Special Issue dedicated to Professor Arthur Carty.

[2] Corresponding author (e-mail: jac@fq.uniovi.es).

doi:10.1139/V05-228

**Scheme 1.**



synthesis of new high nuclearity ruthenium carbonyl clusters containing ligands derived from 2-amino-6-methylpyridine. The reason for using a methyl-substituted 2-aminopyridine is that the methyl group facilitates the monitoring of the reactions by $^1$H NMR spectroscopy (1).

We now report that the treatment of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu\text{-}CO)_2(CO)_{14}]$ with $H_2$ampy at high temperature has provided two new high-nuclearity ruthenium carbonyl cluster complexes featuring two novel coordination modes for 2-imidopyridine ligands.

## Results and discussion

The reaction of the hexanuclear complex $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu\text{-}CO)_2(CO)_{14}]$ with $H_2$ampy (1:3 molar ratio) in refluxing decane for 50 min afforded a mixture of carbonyl products along with some intractable black solid. Shorter reaction times resulted in the observation of considerable amounts of unreacted hexanuclear starting complex. A chromatographic workup revealed the presence of trace amounts of several complexes accompanying two major products, which were subsequently identified as the hexanuclear and octanuclear derivatives $[Ru_6(\mu_3\text{-}H)_2(\mu\text{-}H)_2(\mu_4\text{-}\kappa^2\text{-}ampy)_2(CO)_{14}]$ (**1**) and $[Ru_8(\mu\text{-}H)(\mu_4\text{-}\kappa^2\text{-}ampy)_3(\mu_3\text{-}\kappa^2\text{-}Hampy)(\mu\text{-}CO)_2(CO)_{15}]$ (**2**), respectively (Scheme 2).

The X-ray diffraction structure of compound **1** is shown in Fig. 1. A selection of interatomic distances is given in Table 1. The molecule can be described as being formed by two trinuclear moieties related to each other by a noncrystallographic twofold axis. The metal atoms of each trinuclear fragment are capped by an ampy ligand that is also attached to one of the metal atoms of the other trinuclear fragment through the N atom of its imido fragment. The cluster shell is completed by four hydrides (two edge-bridging and two face-capping) and 14 terminal CO ligands. The electron count for this cluster is 92 for which the 18-electron rule predicts eight M—M bonds. However, nine Ru—Ru bonding interactions between the atoms of a double wing edge-bridged butterfly metallic skeleton are clearly observed, two of them are shorter than 2.70 Å and four are longer than 2.95 Å (9). These long distances suggest that a considerable amount of electron density is residing in Ru—Ru antibonding orbitals.

**Scheme 2.**

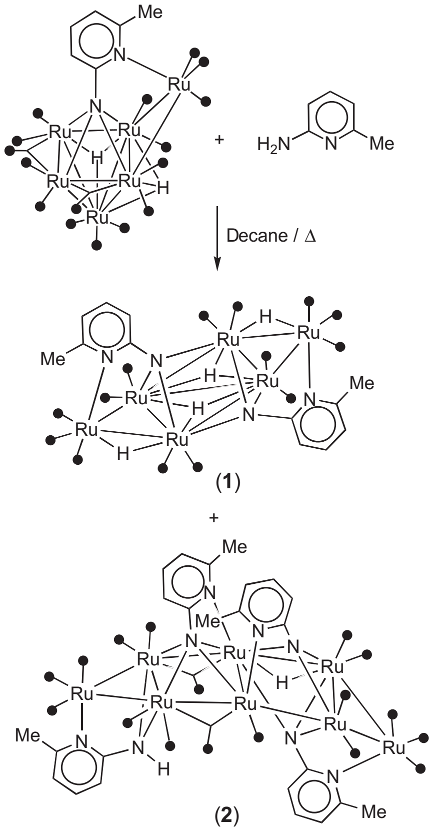
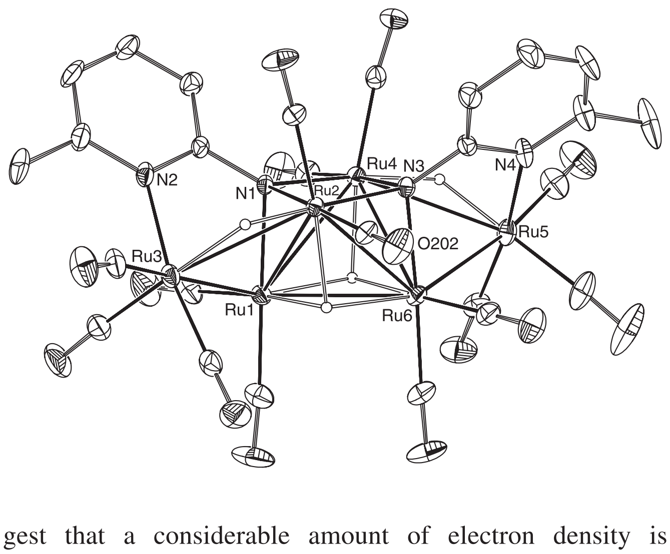


**Fig. 1.** Molecular structure of compound **1** (H atoms, except hydrides, omitted for clarity).



A remarkable feature of the structure of compound **1** is that its ampy ligands bridge four metal atoms, being attached to one Ru atom through their pyridine N atom and to three additional Ru atoms through the imido N atom. Although triply bridging imido ligands are well-known in cluster chemistry (10), this coordination mode displayed by the ampy ligands in complex **1** is unprecedented for 2-imidopyridine ligands.

**Table 1.** Selected interatomic distances (Å) in compound **1**.

| Interatomic distances (Å) | |
|---|---|
| Ru(1)—Ru(2) | 2.8795(8) |
| Ru(1)—Ru(3) | 2.6961(8) |
| Ru(1)—Ru(4) | 2.9559(8) |
| Ru(1)—Ru(6) | 2.9164(8) |
| Ru(2)—Ru(3) | 2.9598(9) |
| Ru(2)—Ru(6) | 2.9701(8) |
| Ru(4)—Ru(5) | 2.9808(8) |
| Ru(4)—Ru(6) | 2.8731(8) |
| Ru(5)—Ru(6) | 2.6946(8) |
| Ru(1)—N(1) | 2.067(5) |
| Ru(2)—N(1) | 2.102(5) |
| Ru(2)—N(3) | 2.088(5) |
| Ru(3)—N(2) | 2.182(5) |
| Ru(4)—N(1) | 2.087(4) |
| Ru(4)—N(3) | 2.109(5) |
| Ru(5)—N(4) | 2.197(5) |
| Ru(6)—N(3) | 2.064(5) |

The solution $^{1}$H NMR spectrum of complex **1** corroborates that the symmetric molecular structure found in the solid state is maintained in solution because it only shows the resonances of one ampy ligand and two hydrides (–14.27 and –17.89 ppm, $J$ = 1.7 Hz).

The X-ray diffraction structure of the octanuclear cluster **2** is shown in Fig. 2. A selection of interatomic distances is given in Table 2. Its metallic skeleton can be described as formed by two distorted edge-sharing squares having their most distant edges spanned by two additional metal atoms. Three metal atoms of one of the squares (Ru(1), Ru(2), and Ru(3)) are doubly capped by the imido N atoms of two ampy ligands, one of which has the pyridyl fragment attached to the remaining Ru atom of that square (Ru(4)), while the other has its pyridyl group bonded to the edge-bridging atom Ru(8). An additional ampy ligand is attached to the remaining square in such a way that it caps the four metal atoms with the imido N atom, while the pyridyl fragment is attached to one of these atoms (Ru(1)). The unique Hampy ligand caps the remaining metal triangle, since its amido N atom spans the Ru(5)—Ru(6) edge and its pyridine N atom is attached to Ru(7). The cluster shell is completed with one hydride ligand, which spans the Ru(1)—Ru(3) edge, and 17 carbonyl ligands, two of which asymmetrically span two edges of the imido-capped square. It can be considered that the cluster obeys the 18-electron rule, since its electron count is 122 and has 11 M—M bonds. The long Ru(1)—Ru(4) distance (3.178(1) Å) seems to be compensated for with four distances shorter than 2.72 Å.

The way by which the unique ampy ligand of compound **2** coordinates to the square of metal atoms Ru(1), Ru(4), Ru(5), and Ru(6) is remarkable because, although a few examples of quadruply bridging imido ligands are already known in cluster chemistry (2–4, 6*d*–6*f*, 11), it represents an unprecedented coordination mode for 2-imidopyridine ligands.

The $^{1}$H NMR spectrum of cluster **2** is in agreement with its solid state structure, since it shows the resonances of four different 6-methylpyrid-2-yl fragments, along with those of one NH proton (–0.20 ppm) and one hydride ligand (–10.18 ppm).

**Fig. 2.** Molecular structure of compound **2** (H atoms, except hydride and NH, omitted for clarity).

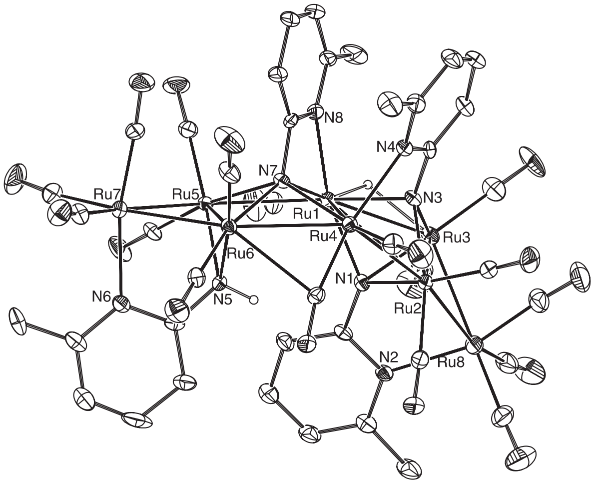


**Table 2.** Selected interatomic distances (Å) in compound **2**.

| Interatomic distances (Å) | |
|---|---|
| Ru(1)—Ru(3) | 2.703(1) |
| Ru(1)—Ru(4) | 3.178(1) |
| Ru(1)—Ru(5) | 2.897(1) |
| Ru(2)—Ru(3) | 2.656(1) |
| Ru(2)—Ru(4) | 2.771(1) |
| Ru(2)—Ru(8) | 2.741(1) |
| Ru(3)—Ru(8) | 2.754(1) |
| Ru(4)—Ru(6) | 2.805(1) |
| Ru(5)—Ru(6) | 2.846(1) |
| Ru(5)—Ru(7) | 2.711(1) |
| Ru(6)—Ru(7) | 2.711(1) |
| Ru(1)—N(1) | 2.081(6) |
| Ru(1)—N(3) | 2.122(6) |
| Ru(1)—N(8) | 2.100(7) |
| Ru(1)—N(7) | 2.213(6) |
| Ru(2)—N(1) | 2.118(7) |
| Ru(2)—N(3) | 2.042(6) |
| Ru(3)—N(1) | 2.113(6) |
| Ru(3)—N(3) | 2.062(6) |
| Ru(4)—N(4) | 2.193(6) |
| Ru(4)—N(7) | 2.210(7) |
| Ru(5)—N(5) | 2.123(6) |
| Ru(5)—N(7) | 2.230(6) |
| Ru(6)—N(5) | 2.175(6) |
| Ru(6)—N(7) | 2.192(6) |
| Ru(7)—N(6) | 2.217(7) |
| Ru(8)—N(2) | 2.210(7) |

## Concluding remarks

The reaction of the hexanuclear complex $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ with $H_2$ampy has provided two

**Table 3.** Selected crystal, measurement, and refinement data for the X-ray structures of **1** and **2**·0.25($CH_2Cl_2$).

| Compound | **1** | **2**·0.25($CH_2Cl_2$) |
|---|---|---|
| Empirical formula | $C_{26}H_{16}N_4O_{14}Ru_6$ | $C_{41}H_{26}N_8O_{17}Ru_8\cdot 0.25(CH_2Cl_2)$ |
| Formula mass | 1 214.85 | 1 732.49 |
| Color, habit | Dark red, block | Black, block |
| Crystal dimensions (mm) | 0.12 × 0.09 × 0.08 | 0.18 × 0.10 × 0.08 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P$–1 |
| $Z$ | 4 | 2 |
| $a$ (Å) | 22.545(4) | 11.219(3) |
| $b$ (Å) | 9.051 6(16) | 13.020(3 |
| $c$ (Å) | 17.678(3) | 19.787(5) |
| α (°) | 90 | 74.711(4) |
| β (°) | 90.600(4) | 86.421(6) |
| γ (°) | 90 | 72.977(5) |
| Collection ranges | $-21 < h < 25$,<br>$-10 < k < 10$,<br>$-19 < l < 19$ | $-11 < h < 12$,<br>$-14 < k < 14$,<br>$-21 < l < 17$ |
| Temperature (K) | 293(2) | 296(2) |
| Volume (Å$^3$) | 3 607.4(11) | 2 665.6(12) |
| $D_{calcd}$ (Mg m$^{-3}$) | 2.237 | 2.159 |
| Radiation (λ, Å) | Mo Kα (0.710 73) | Mo Kα (0.710 73) |
| Absorption coeff. (μ) (mm$^{-1}$) | 2.515 | 2.300 |
| Absorption correction | SADABS | SADABS |
| $F$(000) | 2 304 | 1 653 |
| θ Range for data collection (°) | 0.90 to 23.27 | 1.07 to 23.29 |
| Observed reflns | 15 464 | 11 953 |
| Independent reflns | 5 170 ($R_{int}$ = 0.040 7) | 7 588 ($R_{int}$ = 0.026) |
| Data/restraints/parameters | 5 170 / 0 / 463 | 7 588 / 0 / 699 |
| Maximum shift/error | 0.001 | 0.001 |
| Goodness-of-fit on $F^2$ | 0.993 | 0.998 |
| Final $R$ indices ($I > 2\sigma(I)$) | $R_1$ = 0.028 0, $wR_2$ = 0.052 1 | $R_1$ = 0.038 2, $wR_2$ = 0.100 9 |
| $R$ indices (all data) | $R_1$ = 0.046 8, $wR_2$ = 0.062 3 | $R_1$ = 0.059 4, $wR_2$ = 0.112 2 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.474 and –0.479 | 1.156 and –0.640 |

new high-nuclearity ruthenium carbonyl clusters and has allowed us to observe two new coordination types for 2-imidopyridine ligands.

In the reaction, once coordinated, the $H_2$ampy ligand undergoes one or two N—H bond activation processes that results in the formation of new ligands containing amido (as in **2**) or imido fragments (as in **1** and **2**). As these new ligands are excellent donors, they easily replace carbonyl ligands of the same metallic fragment (as in **1**) or bind to other metallic fragments that are present in solution (as in **2**).

## Experimental

### General

Solvents were dried over sodium (hydrocarbons) or $CaH_2$ (dichloromethane) and distilled under nitrogen prior to use. The hexanuclear cluster $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ was prepared as described elsewhere (3). $H_2$ampy was purchased from Aldrich. Instrumentation: IR: PerkinElmer FT Paragon 1000X; NMR: Bruker DPX-300, with $SiMe_4$ as internal standard (δ 0); microanalyses: PerkinElmer 2400.

### Synthesis of $[Ru_6(\mu_3\text{-}H)_2(\mu\text{-}H)_2(\mu_4\text{-}\kappa^2\text{-ampy})_2(CO)_{14}]$ (1) and $[Ru_8(\mu\text{-}H)(\mu_4\text{-}\kappa^2\text{-ampy})_3(\mu_3\text{-}\kappa^2\text{-Hampy})(\mu\text{-}CO)_2(CO)_{15}]$ (2)

A solution of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ (150 mg, 0.129 mmol) and $H_2$ampy (42 mg, 0.387 mmol) in decane (20 mL) was stirred under nitrogen at reflux temperature for 50 min. At this time, the IR spectrum of the solution did not show any starting material. A change in the color of the solution from dark brown to reddish brown was accompanied by the formation of some black solid. The solvent was removed under vacuum. The solid residue was extracted into dichloromethane (10 mL) and the solution was supported on silica gel (ca. 6 g). The resulting solid was placed onto a silica gel chromatographic column (2 cm × 20 cm) packed in hexane. Three bands, A (brown), B (brown), and C (red-brown), were eluted with hexane–dichloromethane (10:1). Subsequent elution of the column with hexane–dichloromethane (5:1) afforded band D (greenish yellow). Further elution of the column with hexane–dichloromethane (3:1) afforded band E (violet-brown). Bands A and D contained trace amounts of compounds that were not characterized. Band B contained 5 mg of the starting material, $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$. Band C afforded 10 mg of compound **1** (6.4%). Band E gave 7 mg of compound **2** (4.2%).

### *Data for compound 1*

IR ($CH_2Cl_2$) $\nu_{CO}$: 2089 (m), 2075 (vs), 2038 (s, sh), 2031 (vs), 2013 (vs), 1983 (m), 1944 (w), 1929 (w). $^1H$ NMR ($CDCl_3$, 293 K, 300 MHz) $\delta$: 7.45 (t, $J$ = 7.8 Hz, 1H), 7.28 (d, $J$ = 7.8 Hz, 1H), 6.65 (d, $J$ = 7.8 Hz, 1H), 2.56 (s, 3H), –14.27 (d, $J$ = 1.7 Hz, 1H), –17.89 (d, $J$ = 1.7 Hz, 1H). Anal. calcd. for $C_{26}H_{16}N_4O_{14}Ru_6$: C 25.71, H 1.33, N 4.61; found: C 25.54, H 1.35, N 4.55.

### *Data for compound 2*

IR ($CH_2Cl_2$) $\nu_{CO}$: 2070 (w), 2054 (vs), 2009 (vs), 2000 (s, sh), 1987 (m, sh), 1948 (w, br), 1924 (w, sh), 1869 (w, br). $^1H$ NMR ($CDCl_3$, 293 K, 300 MHz) $\delta$: 7.15–6.95 (m, 4H), 6.70 (d, $J$ = 7.8 Hz, 1H), 6.57 (d, $J$ = 7.8 Hz, 1H), 6.42 (d, $J$ = 7.8 Hz, 1H), 6.25 (d, $J$ = 7.8 Hz, 1H), 6.05 (d, $J$ = 7.8 Hz, 1H), 5.93 (d, $J$ = 7.8 Hz, 1H), 5.79 (d, $J$ = 7.8 Hz, 1H), 5.06 (d, $J$ = 7.8 Hz, 1H), 2.82 (s, 3H), 2.72 (s, 3H), 2.31 (s, 3H), 2.01 (s, 3H), –0.20 (s, 1H, NH), –10.18 (s, 1H). Anal. calcd. for $C_{41}H_{26}N_8O_{17}Ru_8$: C 28.78, H 1.53, N 6.55; found: C 28.56, H 1.66, N 6.38.

### X-ray diffraction studies

A selection of crystal, measurement, and refinement data for **1** and **2**·0.25($CH_2Cl_2$) is given in Table 3. Diffraction data were collected at room temperature on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromated Mo K$\alpha$ radiation. Absorption corrections were applied with SADABS (12). The structures were solved by direct methods and refined by full matrix least-squares against $F^2$ with SHELXTL (13). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The edge-bridging hydrides of **1** were located on difference Fourier maps and were freely refined. The positions of the face-capping hydrides of **1** and the hydride of **2**·0.25($CH_2Cl_2$) were calculated with XHYDEX (14) and were freely refined. The molecular plots were made with the PLATON program package (15). The WINGX program system (16) was used throughout the structure determinations.[3]

## Acknowledgements

This work has been supported by the Spanish Ministry of Education and Science through grants BQU2002-2623 (to JAC) and BQU2002-3414 (to DM). PG-A is also grateful to the FPI program (Programa de Formación de Personal Investigador) for a doctoral fellowship.

## References

1. For a review on the reactivity of triruthenium carbonyl clusters containing 2-amidopyridine ligands, see: J.A. Cabeza. Eur. J. Inorg. Chem. 1559 (2002).
2. J.A. Cabeza, I. del Río, P. García-Álvarez, V. Riera, M. Suárez, and S. García-Granda. Dalton Trans. 2808 (2003).
3. J.A. Cabeza, I. del Río, P. García-Álvarez, D. Miguel, and V. Riera. Inorg. Chem. **43**, 5450 (2004).
4. J.A. Cabeza, I. del Río, P. García-Álvarez, and D. Miguel. Organometallics, **24**, 665 (2005).
5. For a review on medium- and high-nuclearity clusters of ruthenium, see: M.P. Cifuentes and M.G. Humphrey. *In* Comprehensive organometallic chemistry II. Vol. 7. *Edited by* D.F. Shriver and M.I. Bruce. Pergamon, Oxford. 1995. Chap. 16. p. 907.
6. For additional examples of ruthenium cluster complexes of nuclearity greater than five containing N-donor ligands, see: (*a*) L. Hoferkamp, G. Rheinwald, H. Stoeckli-Evans, and G. Süss-Fink. Inorg. Chem. **34**, 5786 (1995); (*b*) L. Hoferkamp, G. Rheinwald, H. Stoeckli-Evans, and G. Süss-Fink. Organometallics, **15**, 1122 (1996); (*c*) U. Bodensieck, L. Hoferkamp, H. Stoeckli-Evans, and G. Süss-Fink. J. Chem. Soc. Dalton Trans. 127 (1993); (*d*) S.W. Han, S.T. Nguyen, G.L. Geoffroy, and A.L. Rheingold. Organometallics, **7**, 2034 (1988); (*e*) K.K.H. Lee and W.T. Wong. J. Organomet. Chem. **503**, C43 (1995); (*f*) K.K.H. Lee and W.T. Wong. J. Chem. Soc. Dalton Trans. 1707 (1996); (*g*) J.A. Cabeza, J.M. Fernández-Colinas, S. García-Granda, A. Llamazares, F. López-Ortiz, V. Riera, and J.F. Van der Maelen. Organometallics, **14**, 3342 (1995); (*h*) J.A. Cabeza, I. del Río, V. Riera, and F. Grepioni. Organometallics, **14**, 3124 (1995); (*i*) J.A. Cabeza, I. da Silva, I. del Río, L. Martínez-Méndez, D. Miguel, and V. Riera. Angew. Chem. Int. Ed. **43**, 3464 (2004).
7. P.L. Andreu, J.A. Cabeza, V. Riera, Y. Jeannin, and D. Miguel. J. Chem. Soc. Dalton Trans. 2201 (1990).
8. N. Lugan, F. Laurent, G. Lavigne, T.P. Newcomb, E.W. Liimatta, and J.J. Bonnet. Organometallics, **11**, 1351 (1992).
9. The Ru—Ru distances in $[Ru_3(CO)_{12}]$ are in the range 2.8595 to 2.8515 Å: M.R. Churchill, F.J. Hollander, and J.P. Hutchinson. Inorg. Chem. **16**, 2655 (1977).
10. For examples of clusters having $\mu_3$-imido ligands, see: (*a*) M.I. Bruce, M.P. Cifuentes, and M.G. Humphrey. Polyhedron, **10**, 277 (1991), and refs. cited therein; (*b*) J.S. Song, S.H. Han, S.T. Nguyen, G.L. Geoffroy, and A.L. Rheingold. Organometallics, **9**, 2386 (1990), and refs. cited therein; (*c*) D.M. Ramage, G.L. Geoffroy, A.L. Rheingold, and B.S. Haggerty. Organometallics, **11**, 1242 (1992); (*d*) A.J. Deeming. *In* Comprehensive organometallic chemistry II. Vol. 7. *Edited by* D.F. Shriver and M.I. Bruce. Pergamon, Oxford. 1995. Chap. 12. p. 683; (*e*) L.A. Oro, M.A. Ciriano, C. Tejel, Y.M. Shi, and F. Modrego. *In* Metal clusters in chemistry. *Edited by* P. Braunstein, L.A. Oro, and P.R. Raithby. Wiley-VCH, Weinheim. 1999. p. 381.
11. For additional examples of clusters having $\mu_4$-imido ligands, see: (*a*) H. Link and D.Z. Fenske. Anorg. Allg. Chem. **625**, 1878 (1999); (*b*) P. Reiβ and D. Fenske. Z. Anorg. Allg. Chem. **626**, 2245 (2000); (*c*) M.L. Blohm and W.L. Gladfelter. Organometallics, **5**, 1049 (1986); (*d*) G. Gervasio, R. Rossetti, and P.L. Stanghellini. J. Chem. Res. **334**, 3943 (1979); (*e*) E.N.M. Ho and W.T. Wong. J. Chem. Soc. Dalton Trans.

---

[3] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 4083. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 272943 (**1**) and 272944 (**2**) contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

4215 (1998); (*f*) E.N.M. Ho and W.T. Wong. J. Chem. Soc. Dalton Trans. 513 (1998); (*g*) E.N.M. Ho, Z. Lin, and W.T. Wong. J. Eur. J. Inorg. Chem. 1321 (2001); (*h*) S.W.H. Han, S.T. Nguyen, G.L. Geoffroy, and A.L. Rheingold. Organometallics, **7**, 2034 (1988); (*i*) L. Scoles, B.T. Sterenberg, K.A. Udachin, and A.J. Carty. Chem. Commun. (Cambridge), 320 (2002); (*j*) J.A. Cabeza, I. del Río, S. García-Granda, M. Moreno, V. Riera, M.J. Rosales-Hoz, and M. Suárez. Eur. J. Inorg. Chem. 2899 (2001); (*k*) W.Y. Yeh, C. Stern, and D.F. Shriver. Inorg. Chem. **35**, 7857 (1996); (*l*) B. Hansert, A.K. Powell, and H. Vahrenkamp. Chem. Ber. **124**, 2697 (1991).

12. G.M. Sheldrick. SADABS [computer program]. University of Göttingen, Göttingen, Germany. 1997.
13. G.M. Sheldrick. SHELXTL. Version 5.1 [computer program]. Bruker AXS Inc., Madison, Wis. 1998.
14. A.G. Orpen. J. Chem. Soc. Dalton Trans. 2509 (1980).
15. A.L. Spek. PLATON [computer program]. University of Göttingen, Göttingen, Germany. 1997.
16. L.J. Farrugia. J. Appl. Crystallogr. **32**, 837 (1999).