Derivative Chemistry of Cationic Triruthenium Carbonyl Cluster Compounds. Reactions Leading to a Neutral Hexanuclear Complex Consisting of Two Vertex-Linked Metal Triangles

Javier A. Cabeza,*,† Ignacio del Río, and Víctor Riera

Instituto de Química Organometálica "Enrique Moles", Facultad de Química, Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain

Fabrizia Grepioni*

Dipartimento di Chimica "G. Ciamician", Universitá degli Studi di Bologna, via Selmi 2, I-40126 Bologna, Italy

Summary: [Ru₆(µ₃-ampy)₂(CO)₁₈] (1; Hampy = 2-amino-6-methylpyridine), the first neutral hexanuclear carbonyl cluster complex consisting of two closed trimetal units connected by only one metal−metal bond (X-ray structure), has been prepared by (a) reaction of the cationic precursor [Ru₃(µ₃-ampy)(CO)₁₀]⁺ (2) with aqueous NaOH, (b) reaction of complex 2 with the anion [Ru₃(µ₃-ampy)(CO)₉]⁻, and (c) zinc reduction of complex 2.

Recent reviews on structural and bonding aspects of metal cluster chemistry[1,2] report examples for 22 different structural types corresponding to hexanuclear carbonyl cluster compounds, the most representative ones being those consisting of two closed metal triangles connected by six (octahedron (**A**), bicapped tetrahedron (**B**)), five (capped square pyramid (**C**), edge-sharing bitetrahedron (**D**)), four (basal edge-bridged square pyramid (**E**), bi-semicapped square (**F**)), three (trigonal prism (**G**), rhombic raft (**H**)), or two (bi-edge-bridged square (**I**)) metal−metal bonds (Chart 1).[1] However, only one carbonyl cluster compound corresponding to the simplest structure depicted in Chart 1 (**J**), consisting of two metal triangles connected to each other by only one metal−metal bond, has been reported so far, namely, the mixed-metal anionic cluster [Re₄Ir₂(µ-H)₂(CO)₂₂]²⁻.[3] We now describe different synthetic approaches to the first neutral carbonyl compound of type **J**, the ruthenium complex [Ru₆(µ₃-ampy)₂(CO)₁₈] (**1**, Chart 2; Hampy = 2-amino-6-methylpyridine), as well as its X-ray structure. Rational approaches to the preparation of high-nuclearity cluster compounds are now being actively investigated.[4]

The hexanuclear compound **1** was made during the course of a reactivity study of the cationic precursor
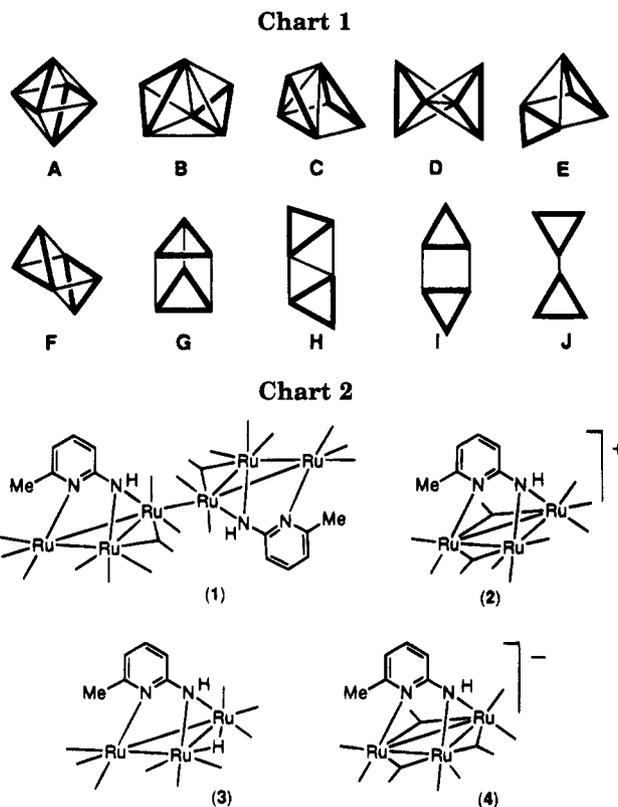
Chart 1

Chart 2

[Ru₃(µ₃-ampy)(CO)₁₀][BF₄] (**2**; Chart 2).[5] This compound is the only non-hydridic 48-electron cationic cluster compound reported to date and was expected to have an enhanced reactivity toward nucleophilic reagents due to its cationic nature.

Complex **2** reacts with an excess of aqueous NaOH in 1,2-dichloroethane (**2** is unstable in donor solvents such as alcohols, THF, or acetone) to give a mixture of the known [Ru₃(µ-H)(µ₃-ampy)(CO)₉][6] (**3**; Chart 2) and complex **1**.[7] A possible mechanism for this transformation is sketched in Scheme 1. It involves the nucleophilic attack of the hydroxide anion on a coordinated CO ligand of complex **2** to give an unstable hydroxycarbonyl derivative which rapidly releases CO_2, rendering **3**.[8] Before all complex **2** has been consumed,

(1) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapter 2, p 11.

(2) (a) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice-Hall International: Englewood Cliffs, NJ, 1990. (b) Farrar, D. H.; Goudsmit, R. J. In *Metal Clusters*; Moskovits, M., Ed.; Wiley: New York, 1986; Chapter 3, p 29.

(3) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Garlaschelli, L.; Moret, M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1992**, 1865.

(4) For a review on the types of reactions that have been useful in preparing cluster complexes in a rational and systematic way, see: Adams, R. D. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapter 3, p 121.

(5) Cabeza, J. A.; del Río, I.; Llamazares, A.; Riera, V.; García-Granda, S.; Van der Maelen, J. F. *Inorg. Chem.* **1995**, *34*, 1620.

(6) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Jeannin, Y.; Miguel, D. *J. Chem. Soc., Dalton Trans.* **1990**, 2201.

Scheme 1
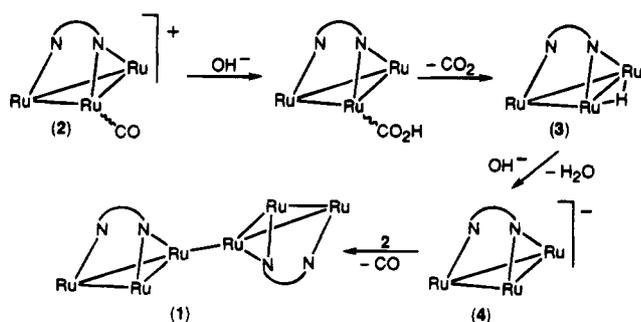
complex **3** deprotonates with more OH⁻ to give the anionic derivative [Ru₃(μ₃-ampy)(CO)₉]⁻ (**4**).[9] Finally, complex **4** reacts with the remaining complex **2** to give CO and the hexanuclear cluster **1**.

This reaction sequence is supported by the fact that the reaction of complex **2** with complex **4** does yield the expected hexanuclear cluster **1**.[10] It is interesting to point out that complexes **2** and **3** are insoluble in water and that no anionic complex **4** was formed (IR evidence) when a 1,2-dichloroethane solution of the neutral hydrido complex **3** was treated with an aqueous solution of NaOH unless [Et₄N][BF₄] was added to the mixture. This confirms that the [BF₄]⁻ anion is necessary to promote the phase transfer of the OH⁻ groups from the aqueous to the organic phase. It should also be noted that, in the reaction of complex **2** with aqueous NaOH, the organic phase contains initially only 1 equiv of the [BF₄]⁻ anion; therefore, only 1 equiv of OH⁻ anion can be transferred to the organic phase. This and the observation of **1** and **3** (but not **2** and **4**) in the product mixture imply that at least ¹/₂ equiv of OH⁻ reacts with complex **2** to give **3**; the remaining OH⁻ reacts with **3** to form the anion **4**, which finally couples with the unreacted **2** to give **1**.

The dimeric structure of the 94-electron cluster **1** (Figure 1) suggested that it could also be prepared by a

Figure 1. (a) Molecular structure of complex **1** viewed along the pseudo-2-fold axis. Relevant bond distances (Å): Ru(1)–Ru(2), 2.734(4); Ru(1)–Ru(3), 2.778(4); Ru(2)–Ru(3), 2.732(4); Ru(4)–Ru(5), 2.726(4); Ru(4)–Ru(6), 2.777(4); Ru(5)–Ru(6), 2.726(4); Ru(1)–Ru(4), 2.855(4); N(1)–Ru(1), 2.18(2); N(1)–Ru(2), 2.10(2); N(2)–Ru(3), 2.21(2); N(3)–Ru(4), 2.18(2); N(3)–Ru(5), 2.09(2); N(4)–Ru(6), 2.22(2). (b) Projection in the metal frame main plane, showing the *cis* configuration of the two Ru₃ triangles. The two ampy ligands have been omitted for clarity.

1-electron reduction reaction of the cationic complex **2**, since this should lead to the 49-electron radical [Ru₃(μ₃-ampy)(CO)₁₀] which would lose CO and undergo dimerization to give **1**. In fact, complex **1** was also made by reacting complex **2** with zinc dust in 1,2-dichloroethane.[11] So far, we have been unable to prepare complex **1** by chemical oxidation of the anionic complex **4**.

The synthetic methods reported herein are significantly different from that used in the preparation of [Re₄Ir₂(μ-H)₂(CO)₂₂]²⁻, the only previously known hexanuclear carbonyl cluster of type **J**, which involves treatment of [Re₂(μ-H)₂(CO)₈] with [Ir(CO)₄]⁻ to give [Re₂IrH(μ-H)(CO)₁₂]⁻; subsequently, this trinuclear adduct releases CO and H₂ and undergoes dimerization, rendering the hexanuclear dianion.[3]

As the analytical and spectroscopic data of complex **1**[7] were insufficient to unequivocally assign a structure, an X-ray diffraction study was carried out.[12] The solid-state molecular structure of compound **1** is shown in Figure 1. The metal frame consists of two Ru₃ triangular units linked by one Ru–Ru bond. The intertriangle Ru(1)–Ru(4) bond is appreciably longer than the average value of the remaining metal–metal bonds

(7) Aqueous NaOH (0.2 mL, 10 M) was added to a solution of complex **2** (100 mg, 0.129 mmol) in 1,2-dichloroethane (20 mL). The color changed from dark red to brown. After it was stirred for 20 min, the solution was concentrated in vacuo to ca. 2 mL and chromatographed in a short column (10 × 3 cm) of neutral alumina (activity IV). Elution with hexane–dichloromethane (3:1) afforded two bands. The second band (orange) contained complex **3** (IR, ¹H NMR).[6] The first band (brown), which partially decomposed within the column to give **3**, afforded complex **1** as a very dark brown, nearly black, solid (16 mg, 24%). Anal. Found: C, 32.42; H, 1.23; N, 5.31. Calcd for C₃₀H₁₄N₄O₁₈Ru₆: C, 32.25; H, 1.37; N, 5.48. IR (CH₂Cl₂), *ν*(CO): 2079 (w), 2061 (s), 2039 (vs), 1996 (s), 1975 (sh), 1853 (w, br) cm⁻¹. ¹H NMR (CDCl₃): 7.31 (t, *J* = 7.8 Hz, 1 H), 6.79 (d, *J* = 7.8 Hz, 1 H), 6.40 (d, *J* = 7.8 Hz, 1 H), 4.34 (s, br, 1 H, NH), 2.77 (s, 3 H, Me) ppm. ¹³C{¹H} NMR (CD₂Cl₂): 240.7, 218.3, 203.1, 202.8, 202.4, 197.9, 196.8, 196.6, 188.1 (CO ligands), 174.9, 160.4, 138.9, 120.3, 111.2, 30.0 (ampy ligand) ppm.

(8) The nucleophilic attack of OH⁻ groups on coordinated CO ligands is well documented. See, for example: Schatz, W.; Neumann, H.-P.; Nuber, B.; Kanellakopulos, B.; Ziegler, M. L. *Chem. Ber.* **1991**, *124*, 453.

(9) (a) The deprotonation of neutral hydrido carbonyl cluster complexes with alcoholic solutions of KOH to give anionic derivatives has been reported. See, for example: Barner-Thorsen, C.; Hardcastle, K. I.; Rosenberg, E.; Siegel, J.; Manotti-Lanfredi, A. M.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Inorg. Chem.* **1981**, *20*, 4306. (b) Complex **4** (PPN salt), as the analogous [PPN][Ru₃(μ₃-anpy)(CO)₉] (Hanpy = 2-anilinopyridine), can also be made by reaction of its neutral precursor (**3**) with [PPN][BH₄]. See: Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimata, E. W.; Bonnet, J.-J. *J. Am. Chem. Soc.* **1990**, *112*, 8607.

(10) Equivalent amounts (0.076 mmol) of [Ru₃(μ₃-ampy)(CO)₁₀][BF₄] (**2**) and [PPN][Ru₃(μ₃-ampy)(CO)₉] (**4**)[9b] were dissolved in 1,2-dichloroethane (10 mL) to give a dark brown solution which was worked up as in ref 7 to give complex **1** in 32% yield.
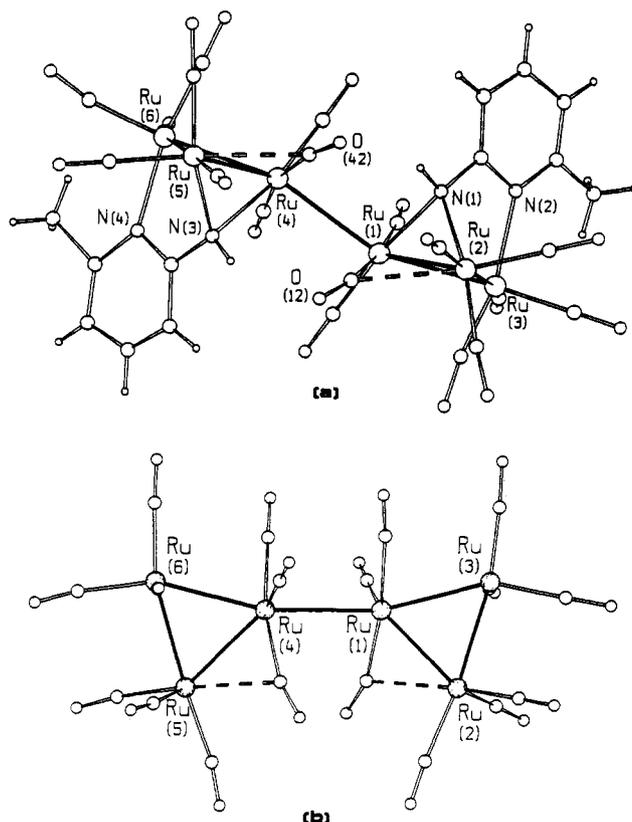
(11) A mixture of complex **2** (50 mg, 0.065 mmol) and zinc dust (0.3 g) in 1,2-dichloroethane (15 mL) was stirred at reflux temperature for 45 min. The solids were filtered off, and the brown solution was worked up as in ref 7 to give complex **1** in 30% yield.

(2.855(4) *vs* 2.744(4) Å), as previously observed in the rhenium non-carbonyl cluster [Re$_6$(μ-Cl)$_6$(μ-H)(CH$_2$-SiMe$_3$)$_9$] (intertriangle Re−Re distance 2.993(1) Å *vs* an average intratriangle distance of 2.405(1) Å).[13] In **1**, the two triangles are almost coplanar (maximum deviation from the mean plane of the six atoms 0.37 Å). The idealized molecular symmetry is C_2, with the pseudo 2-fold axis bisecting the Ru(1)−Ru(4) bond and parallel to the plane defined by the two triangles. The two Ru$_3$ triangles adopt a *cis* configuration with respect to the Ru(1)−Ru(4) bond, as shown in Figure 1. In this aspect, the molecular geometry is different from that of the rhenium cluster previously mentioned,[13] where the two coplanar Re$_3$ triangles conform to the geometry shown for structure **J** in Chart 1 and that of the anionic cluster [Re$_4$Ir$_2$(μ-H)$_2$(CO)$_{22}$]$^{2-}$, where the two Re$_2$Ir triangles adopt a staggered *trans* configuration.[3] Two CO ligands asymmetrically bridge two Ru−Ru bonds (Ru(1)−C(12) = 1.95(4), Ru(2)−C(12) = 2.56(3) Å; Ru(4)−C(42) = 1.99-(3), Ru(5)−C(42) = 2.57(3) Å), while the remaining CO ligands are all terminally bound. The two ampy ligands bind to the two triangles on opposite sites and contribute five electrons each to the cluster. In both ligands, the two N−Ru bond distances associated with the bridging amido moiety are appreciably different (N(1)−Ru(1) = 2.18(2), N(1)−Ru(2) = 2.10(2) Å; N(3)−Ru(4) = 2.18(2), N(3)−Ru(5) = 2.09(2) Å). All N−Ru bond distances fall

within the range observed for other Ru$_3$[5,14] and Ru$_6$[15] clusters containing the ampy ligand in the same coordination mode.

The observation of nine carbonyl resonances in the solution ^{13}C NMR spectrum of complex **1**[7] supports either a static C_2 structure, as in the solid state, or free rotation around the Ru(1)−Ru(4) bond. However, the X-ray diffraction study reveals that the proximity of the semibridging carbonyl ligands impedes such rotation. The proximity of these ligands may also account for their high ^{13}C NMR chemical shift (240.7 ppm).

In conclusion, this communication reports the synthesis of a hexanuclear ruthenium cluster complex of a novel structural type using three different synthetic methods: (a) the reaction of a cluster cation with aqueous NaOH, (b) the reaction of a cluster anion with a cluster cation,[16] and (c) the reduction of a cluster cation. These methods have never been used before for the synthesis of high-nuclearity clusters, and it is anticipated that they will be useful to many other cluster chemists. Further studies on the reactivity of the cationic complex **2** are in progress.

Supporting Information Available: An ORTEP plot and tables of crystal data, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H-atom coordinates for complex **1** (11 pages). Ordering information is given on any current masthead page.

OM950303F

(12) (a) Crystal and selected refinement data for **1**: C$_{30}$H$_{14}$N$_4$O$_{18}$-Ru$_6$, M_r = 1324.87, monoclinic, space group $P2_1/c$, a = 13.192(7) Å, b = 20.32(1) Å, c = 17.876(4) Å, β = 107.64(3)°, V = 4567(4) Å^3, Z = 4, D_c =1.927 g cm^{-3}, $F(000)$ = 2520, μ(Mo Kα) = 20.02 cm^{-1}, 2.5 < θ < 25°, final $R1$ value (on F, $I > 2\sigma(I)$) = 0.077, $wR2$ (on F^2, all data) = 0.281 for 7661 unique reflections. Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer, equipped with a graphite monochromator (Mo Kα radiation, λ = 0.710 69 Å), by the $\omega-2\theta$ scan method. The structure was solved by direct methods[12b] followed by difference Fourier syntheses and subsequent least-squares refinement on F^2 using SHELX93.[12c] All non-H atoms were treated anisotropically. The H atoms were added in calculated positions and refined riding on their respective C atoms. Residual electron density (<1.00 e Å^{-3}) was found in the proximity of the molecules, indicating the presence of a disordered solvent. A detailed analysis of the crystal packing also revealed small cavities among the molecules in correspondence with the residual peaks. However, neither the nature nor the amount of this solvent could be unambiguously determined. The impossibility of locating and refining the solvent is partially responsible for the not quite satisfactory refinement result. (b) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. (c) Sheldrick, G. M. SHELX93, Program for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1993.

(13) Mertis, K.; Edwards, P. G.; Wilkinson, G.; Malik, K. M. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 705.

(14) See, for example: (a) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Bois, C.; Jeannin, Y. *J. Chem. Soc., Dalton Trans.* **1990**, 3347. (b) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 157. (c) Briard, P.; Cabeza, J. A.; Llamazares, A.; Ouahab, L.; Riera, V. *Organometallics* **1993**, *12*, 1006. (d) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V.; García-Granda, S.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 4352.

(15) Cabeza, J. A.; Fernández-Colinas, J. M.; García-Granda, S.; Llamazares, A.; López-Ortiz, F.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 426.

(16) Treatment of anionic clusters with cationic mononuclear complexes has been used for the synthesis of "large" clusters. See, for example: (a) Reference 4. (b) Voss, E. J.; Stern, C. L.; Shriver, D. W. *Inorg. Chem.* **1994**, *33*, 1087 and references therein. (c) Lewis, J.; Li, C.-K.; Al-Mandhary, M. R. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1993**, 1915 and references therein. (d) Evans, J.; Stroud, P. M.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1991**, 2027.