Nonanuclear Ruthenium Carbonyl Cluster Complexes with a Novel Metallic Skeleton: Pentagonal Bipyramid with Two Equatorial Edges Spanned by Metal Atoms

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Summary: The nonanuclear cluster complexes [$Ru_9(\mu$-$H)_2(\mu_4$-κ^2-ampy)$_4$(CO)$_{17}$] and [$Ru_9(\mu_3$-$H)(\mu$-$H)(\mu_4$-κ^2-ampy)$_3$(CO)$_{18}$] (ampy = 2-imido-6-methylpyridine) have been prepared by heating [$Ru_6(\mu_3$-$H)_2(\mu_5$-κ^2-ampy)(μ-CO)$_2$(CO)$_{14}$] in undecane at reflux temperature. Both compounds feature a novel metallic skeleton that can be described as a pentagonal bipyramid with two equatorial edges spanned by metal atoms. In both cases, the ampy ligands are attached to edge-bridging Ru atoms through the pyridine N atoms, while their imido N atoms cap metallic triangles formed by the metal atoms of one of the metal-bridged edges and one of the apical metal atoms.

Introduction

The trinuclear cluster [$Ru_3(\mu$-$H)(\mu_3$-κ^2-Hampy)(CO)$_9$][1] (**1**) (H$_2$ampy = 2-amino-6-methylpyridine) reacts with [Ru_3(CO)$_{12}$] at 110−140 °C to give the hexanuclear derivative [$Ru_6(\mu_3$-$H)_2$-(μ_5-κ^2-ampy)(μ-CO)$_2$(CO)$_{14}$] (**2**) in high yield (Scheme 1).[2] This reaction afforded the first example of a 2-imidopyridine ligand in which the imido N atom caps a metallic square. Reactivity studies using compound **2** as starting material have revealed that its apical Ru(CO)$_3$ fragment, which is not anchored by the N atoms, is labile at temperatures in the range 110−140 °C and that this fact is responsible for the observation of penta- and heptanuclear products in some reactions.[3]

As far as high-nuclearity ruthenium carbonyl clusters derived from 2-aminopyridines are concerned, we have also reported that the hexanuclear compound **2** reacts with 2-amino-6-methylpyridine at high temperature (160 °C) to give the hexanuclear cluster complex [$Ru_6(\mu_3$-$H)_2(\mu$-$H)_2(\mu_4$-κ^2-ampy)$_2$-(CO)$_{14}$] and the octanuclear one [$Ru_8(\mu$-$H)(\mu_4$-κ^2-ampy)$_3(\mu_3$-κ^2-Hampy)(μ-CO)$_2$(CO)$_{15}$], which contain the imido N atoms of their μ_4-ampy ligands capping metallic triangles and squares (Scheme 2).[4] Recently, we have also reported that the thermolysis of the trinuclear compound **1** at 150 °C gives penta-, hexa-, hepta-, and nonaruthenium carbonyl cluster derivatives that contain ampy and Hampy ligands and also μ_4- and μ_5-oxo ligands.[5]

Scheme 1

Scheme 2
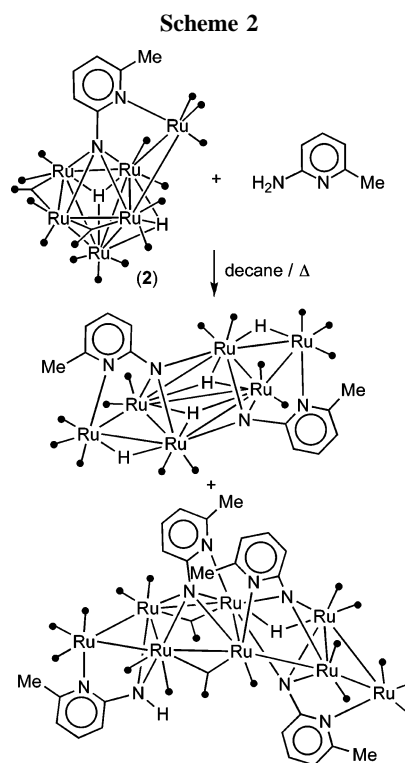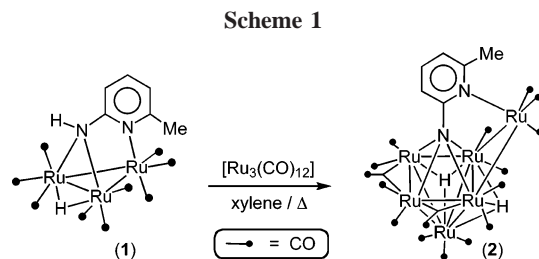
Prompted by the fact that the number of known ruthenium carbonyl cluster complexes of nuclearity greater than five that contain N-donor ligands is still small,[2−7] and having in mind the ability of ruthenium carbonyl clusters to undergo aggregation processes under appropriate thermal conditions,[2,4−7] we decided to study the thermolysis of the hexanuclear cluster **2** at high temperature (>180 °C, since this compound is stable up to 150

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(1) Andreu, P. L.; Cabeza. J. A.; Riera, V.; Jeannin, Y.; Miguel, D. *J. Chem. Soc. Dalton Trans.* **1990**, 2201.
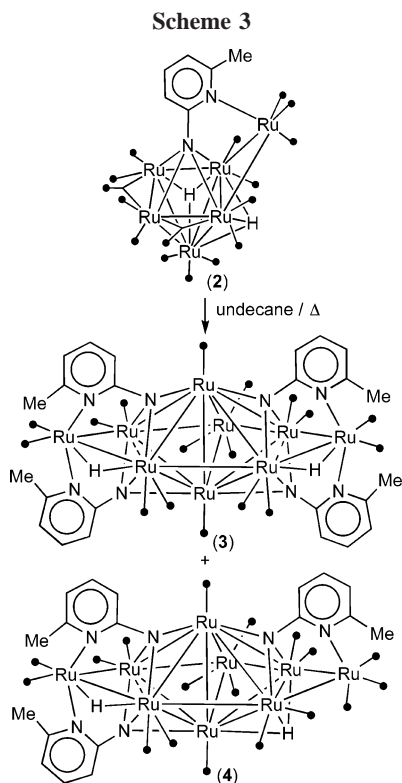
(2) (a) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Riera, V.; Suárez, M.; García-Granda, S. *Dalton Trans.* **2003**, 2808. (b) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D.; Riera, V. *Inorg. Chem.* **2004**, *43*, 5450.

(3) (a) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Organometallics* **2005**, *24*, 665. (b) Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; García-Álvarez, P.; Miguel, D. *Organometallics* **2006**, *25*, 1492. (c) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Organometallics* **2006**, *25*, 2683.

(4) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Can. J. Chem.* **2006**, *84*, 105.

(5) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Inorg. Chem.* **2006**, *45*, 6020.

(6) For a review on medium- and high-nuclearity clusters of ruthenium, see: Cifuentes, M. P.; Humphrey, M. G. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson G., Eds.; Vol. 7 (Shriver D. F., Bruce M. I., Vol. Eds.); Pergamon: Oxford, 1995; Chapter 16, p 907.

Scheme 3

Table 1. Selected Interatomic Distances (Å) in Compounds 3 and 4

	3	4
Ru(1)−Ru(2)	3.194(3)	3.182(2)
Ru(1)−Ru(3)	2.927(4)	2.951(2)
Ru(1)−Ru(4)	3.067(3)	2.919(2)
Ru(1)−Ru(5)	3.120(4)	3.042(2)
Ru(1)−Ru(6)	3.064(3)	2.907(2)
Ru(2)−Ru(3)	2.708(4)	2.782(2)
Ru(2)−Ru(4)	2.916(4)	2.757(2)
Ru(2)−Ru(6)	2.940(3)	2.990(2)
Ru(2)−Ru(9)	2.849(4)	2.832(2)
Ru(4)−Ru(5)	3.088(4)	2.698(2)
Ru(4)−Ru(6)	2.770(3)	2.757(2)
Ru(4)−Ru(7)	2.885(4)	3.058(2)
Ru(4)−Ru(9)	2.719(4)	2.692(2)
Ru(5)−Ru(6)	3.093(3)	3.082(2)
Ru(5)−Ru(7)	3.211(4)	2.827(2)
Ru(5)−Ru(8)	2.932(4)	2.733(2)
Ru(6)−Ru(7)	2.915(3)	2.887(2)
Ru(6)−Ru(9)	2.670(4)	2.638(2)
Ru(7)−Ru(8)	2.722(4)	2.733(2)
Ru(7)−Ru(9)	2.857(4)	2.942(3)
N(1)−Ru(1)	2.10(3)	2.10(1)
N(1)−Ru(2)	2.17(3)	2.08 (1)
N(1)−Ru(4)	1.96(3)	1.98(1)
N(2)−Ru(3)	2.12(3)	2.13(1)
N(3)−Ru(1)	2.11(3)	2.11(1)
N(3)−Ru(2)	2.09(3)	2.17(1)
N(3)−Ru(6)	1.97(2)	1.94(1)
N(4)−Ru(3)	2.16(3)	2.12(1)
N(5)−Ru(5)	2.08(3)	2.07(1)
N(5)−Ru(6)	2.01(2)	1.95(1)
N(5)−Ru(7)	2.19(3)	2.12(1)
N(6)−Ru(8)	2.09(3)	2.20(1)
N(7)−Ru(4)	1.97(2)	
N(7)−Ru(5)	2.07(3)	
N(7)−Ru(7)	2.11(2)	
N(8)−Ru(8)	2.15(2)	

°C), attempting the synthesis of novel high-nuclearity ruthenium carbonyl clusters containing 2-imidopyridine ligands.

We now report the synthesis of two nonaruthenium carbonyl clusters that contain three and four μ_4-ampy ligands and that have in common an unprecedented metallic skeleton that can be described as a pentagonal bipyramid with two equatorial edges spanned by metal atoms.

Results and Discussion

The thermolysis of compound **2** was carried out by stirring the complex in undecane at reflux temperature (196 °C). IR and TLC monitoring of the reaction indicated the complete consumption of the starting material after 2 h. A dark greenish-brown dichloromethane-soluble fraction and an insoluble black solid were obtained. A TLC separation of the soluble fraction allowed the isolation of [Ru$_9$(μ-H)$_2$(μ_4-κ^2-ampy)$_4$(CO)$_{17}$] (**3**, 15% yield) and [Ru$_9$(μ_3-H)(μ-H)(μ_4-κ^2-ampy)$_3$(CO)$_{18}$] (**4**, 28% yield) as green and brown solids, respectively (Scheme 3).

The atom connectivity of compounds **3** and **4** was determined by X-ray diffraction. Their molecular structures are shown in Figure 1. Important interatomic distances are given in Table 1. Both compounds are nonanuclear and have a common metallic skeleton that can be described as a distorted pentagonal bipyramid with two equatorial edges, Ru(1)−Ru(2) and Ru(5)−

(7) For additional examples of ruthenium carbonyl cluster complexes of nuclearity greater than five containing N-donor ligands, see: (a) Hoferkamp, L.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *Inorg. Chem.* **1995**, *34*, 5786. (b) Hoferkamp, L.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *Organometallics* **1996**, *15*, 1122. (c) Bodensieck, U.; Hoferkamp, L.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Chem. Soc. Dalton Trans.* **1993**, 127. (d) Han, S. W.; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2034. (e) Lee, K. K. H.; Wong, W. T. *J. Organomet. Chem.* **1995**, *503*, C43. (f) Lee, K. K. H.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1996**, 1707. (g) Cabeza, J. A.; Fernández-Colinas, J. M.; García-Granda, S.; Llamazares, A.; López-Ortiz, F.; Riera, V.; Van, der Maelen, J. F. *Organometallics* **1995**, *14*, 3342. (h) Cabeza, J. A.; del Río, I.; Riera, V.; Grepioni, F. *Organometallics* **1995**, *14*, 3124. (i) Cabeza, J. A.; da Silva, I.; del Río, I.; Martínez-Méndez, L.; Miguel, D.; Riera, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 3464.

Ru(7), spanned by the Ru(3) and Ru(8) atoms, respectively. Such an unprecedented metallic framework is supported by four (in **3**) or three (in **4**) μ_4-ampy ligands, each of which caps a face of the pentagonal bipyramid through the imido N atom, while it is also attached to one of the edge-bridging Ru atoms through the pyridine N atom. While compound **3** has two edge-bridging hydride ligands, H(100) and H(200), that span the Ru(1)−Ru(3) and Ru(5)−Ru(8) edges, respectively, the hydrides of compound **4** are one edge-bridging, H(200), on the Ru(1)−Ru(3) edge, and the other face-capping, H(100), on the Ru(4)−Ru(5)−Ru(7) face. The cluster shells are completed with 17 (in **3**) and 18 (in **4**) terminal CO ligands. The lack of the fourth ampy ligand in compound **4** not only reduces the symmetry of the cluster (ca. C_{2v} in **3**, C_1 in **4**) but provokes a considerable distortion of the equatorial pentagon, in which the Ru(5) atom is not coplanar with the remaining four Ru atoms, since it lies 0.620(1) Å below the plane defined by Ru(1), Ru(2), Ru(7), and Ru(9).

Considering the ampy ligand as a six-electron donor, the electron counts of compounds **3** and **4** are 132 and 128 electrons, respectively, for which the EAN rule predicts 15 and 17 Ru−Ru single bonds, respectively. However, a doubly edge-bridged pentagonal bipyramidal metallic skeleton with interconnected apical atoms contains 20 M−M interactions (122 electrons). In addition, the PSEP theory also fails to justify the structures of these compounds. They are just too electron-rich. A detailed analysis of the Ru−Ru distances in compounds **3** and **4** reveals that the former has seven distances longer than 3.0 Å, while four of such distances are present in the latter. In both cases, the longest distances (ca. 3.2 Å) correspond to edges that are doubly bridged by imido N atoms, Ru(1)−Ru(2) and Ru(5)−
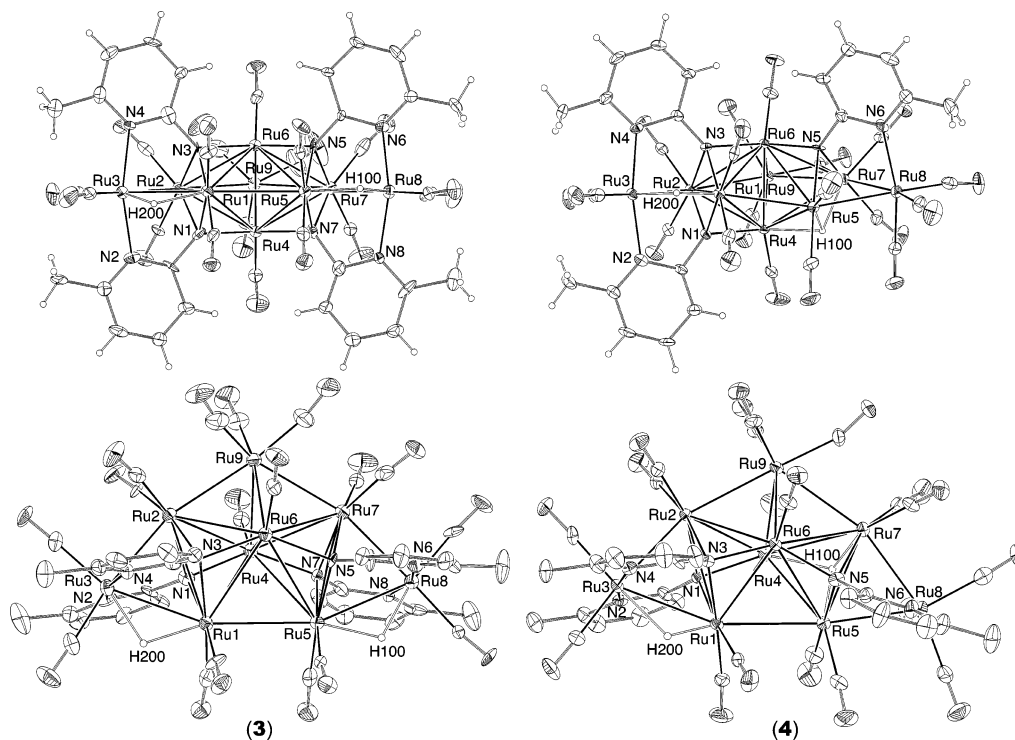
Figure 1. Two views of the molecular structures of **3** (left) and **4** (right). In the bottom views, the hydrogen atoms attached to carbon atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Ru(7) of **3** and Ru(1)−Ru(2) of **4**. Therefore, the observed metal−metal distances are strongly influenced by the presence of the bridging ligands, which, for species with more electrons than those expected for closed situations, such as **3** and **4**, are responsible for maintaining many of the metal atoms at distances a bit longer than those expected for normal single metal−metal bonds,[8] but short enough to allow some metal−metal interaction. A similar situation has previously been observed for some ligand-bridged 50-electron trinuclear clusters, that, instead of having an open edge (as predicted by the EAN rule), have three elongated metal−metal bonds.[9] For instance, the Ru−Ru distances in $[Ru_3(\mu\text{-Cl})(\mu\text{-PPh}_2)_3(CO)_7]$ are 2.9293(8), 3.2222(7), and 3.1288(8) Å[9b] and in $[Ru_3(\mu_3\text{-PPhpy})(\mu\text{-PPh}_2)_3(CO)_6]$ are 3.112(1), 3.084(1), and 3.112(1) Å.[9c]

The FAB mass spectra and the ^{1}H NMR spectra of **3** and **4** are in accordance with the solid-state structures described above. The ^{1}H NMR spectrum of **3** displays the resonances of only one ampy ligand and one hydride with a 2:1 integral ratio, confirming that the complex has C_{2v} symmetry in solution. The lack of symmetry of **4** is reflected by its ^{1}H NMR spectrum, which shows the resonances of three different ampy ligands and two hydrides.

Although triply bridging imido ligands are well known in carbonyl metal cluster chemistry,[10] the coordination mode displayed by the ampy ligands in complexes **3** and **4** is very rare for 2-imidopyridine ligands. In fact, only two previous reports have described such a coordination mode. One deals with the reactivity of compound **2** with 2-amino-6-methyl-

pyridine,[4] and the other one describes the thermolysis of the trinuclear complex **1** in refluxing decane.[5]

The thermolysis of **2** in refluxing undecane produces compounds **3** and **4** as well as a considerable amount of a black insoluble solid with a small content of carbon monoxide (IR identification). As the ampy to ruthenium ratio in **3** and **4** is greater than in the starting material **2**, the obtained black solid should arise from the decomposition, via thermal decarbonyl-ation, of transient $Ru_n(CO)_m$ species released from **2** or from other ampy-containing species during the thermolysis reaction. Therefore, an additional remarkable feature of the results described in this report is that they make clear that the bridging ampy ligands increase the thermal stability of the products that contain them. In fact, compounds **3** and **4** survive at temperatures as high as 196 °C.

Compound **4** does not react with H_2ampy in refluxing undecane to give **3**. Therefore, in the thermolysis of complex **2**, these compounds should be formed through different reaction pathways by aggregation of ampy-containing species.

In conclusion, the present paper describes the synthesis and structural characterization of two nonanuclear ruthenium clusters with an unprecedented metallic skeleton, a pentagonal bipyramid with two equatorial edges spanned by metal atoms. The metal atoms of these cluster complexes are anchored to quadruply bridging 2-imidopyridine ligands that confer the clusters an exceptional thermal stability.

(8) The Ru−Ru distances in $[Ru_3(CO)_{12}]$ are in the range 2.8595 to 2.8515 Å: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(9) For examples of electron-rich trinuclear clusters with closed but expanded frameworks, see: (a) Cherkas, A. A.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 385. (b) Cabeza, J. A.; Lahoz, F. J.; Martín, A. *Organometallics* **1992**, *11*, 2754. (c) Lugan, N.; Fabre, P. L.; de Montauzon, D.; Lavigne, G.; Bonnet, J. J.; Saillard, J. Y.; Halet, J. F. *Inorg. Chem.* **1994**, *33*, 434.

(10) For examples of clusters having μ_3-imido ligands, see: (a) Bruce, M. I.; Cifuentes, M. P.; Humphrey, M. G. *Polyhedron* **1991**, *10*, 277, and references therein. (b) Song, J. S.; Han, S. H.; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2386, and references therein. (c) Ramage, D. M.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1992**, *11*, 1242. (d) Deeming, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Vol. 7 (Shriver, D. F., Bruce, M. I., Vol. Eds.); Pergamon: Oxford, UK, 1995; Chapter 12, p 683. (e) Oro, L. A.; Ciriano, M. A.; Tejel, C.; Shi, Y. M.; Modrego F. J. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, Germany, 1999; p 381.

Experimental Section

General Data. Solvents were dried over sodium (hydrocarbons) or CaH_2 (dichloromethane, 1,2-dichloroethene) and distilled under nitrogen prior to use. Compound **2** was prepared as previously reported.[2] IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^{1}H NMR spectra were run on a Bruker DPX-300 instrument, at room temperature, using the dichloromethane solvent resonance as internal standard ($\delta = 5.30$). Microanalyses were obtained from the University of Oviedo Analytical Service. Positive FAB mass spectra were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer. The yields (%) given have been estimated taking into account the ampy content of each product.

Thermolysis of Compound 2. Compound **2** (50 mg, 0.043 mmol) was stirred in undecane at reflux temperature for 2 h. The reaction was monitored by solution IR spectroscopy (carbonyl stretching region) and spot TLC. The solution changed from dark brown to greenish brown. A considerable amount of black solid precipitated. The solvent was removed under reduced pressure, and the residue was extracted into dichloromethane (2 mL). The black solid remained undissolved. The dichloromethane solution was supported on silica gel TLC plates. Repeated elution with hexane−dichloromethane (2:1) separated various weak bands followed by two major bands. The first major band, green, afforded compound **3** (3 mg, 15%). The second major band, brown, afforded compound **4** (7 mg, 28%).

Data for [Ru_9(μ-H)_2(μ_4-κ^2-ampy)_4(CO)_17] (3). Anal. Calcd for $C_{41}H_{26}N_8O_{17}Ru_9$ (1812.33): C, 27.17; H, 1.45; N, 6.18. Found: C, 27.31; H, 1.52; N 6.07. FAB-MS: *m/z* 1813 [M]$^+$. IR (CH_2Cl_2): ν_{CO} 2054 (m), 2026 (vs), 2017 (s), 1984 (m, br), 1966 (s), 1954 (m, sh), 1932 (w, sh), 1902 (w, br), 1723 (w, br). ^{1}H NMR (CDCl_3, 293 K): δ 6.98 (t, $J = 7.9$ Hz, 2 H), 6.63 (d, $J = 7.9$ Hz, 2 H), 5.93 (d, $J = 7.9$ Hz, 2 H), 3.02 (s, 6 H, 2 Me), −5.70 (s, 1 H, μ-H).

Data for [Ru_9(μ_3-H)(μ-H)(μ_4-κ^2-ampy)_3(CO)_18] (4). Anal. Calcd for $C_{36}H_{20}N_6O_{18}Ru_9$ (1734.21): C, 24.93; H, 1.16; N, 4.85. Found: C, 24.98; H, 1.20; N 4.77. FAB-MS: *m/z* 1735 [M]$^+$. IR (CH_2Cl_2): ν_{CO} 2069 (m), 2042 (vs), 2022 (vs), 2011 (s, sh), 1998 (s), 1960 (m, br), 1914 (w, br). ^{1}H NMR (CDCl_3, 293 K): δ 7.51 (t, $J = 7.7$ Hz, 1 H), 7.12−6.99 (m, 3 H), 6.77 (d, $J = 7.7$ Hz, 1 H), 6.73 (d, $J = 7.7$ Hz, 1 H), 6.67 (d, $J = 7.7$ Hz, 1 H), 6.07 (d, $J = 7.7$ Hz, 1 H), 5.91 (d, $J = 7.7$ Hz, 1 H), 3.09 (s, 3 H), 2.93 (s, 3 H), 2.92 (s, 3 H), −5.22 (s, 1 H, μ-H), −16.87 (s, 1 H, μ_3-H).

X-ray Diffraction Analyses. A selection of crystal, measurement, and refinement data is given in Table 2. *Data for 3:* Only poor-quality plate-shaped crystals could be obtained. Diffraction data were collected on a Nonius Kappa-CCD diffractometer, using graphite-monochromatized Cu Kα radiation. A empirical absorption correction was applied using XABS2.[11] Despite the low intensity of the reflections, the structure was solved by Patterson interpretation using the program DIRDIF-96.[12] Isotropic and full-matrix anisotropic least-squares refinements were carried out using SHELXL-97.[13] Various $2\theta_{max}$ values were tested. With $2\theta_{max} < 50°$, although the final *R* values decreased slightly, too many non-H atoms resulted nonpositive definite upon anisotropic refinement. With $2\theta_{max} = 50°$, only the carbon atoms C(25), C(401), and C(701) were nonpositive definite and were refined isotropically. All other non-H atoms were refined anisotropically. The H(100) and H(200) atom positions were

Table 2. Crystal, Measurement, and Refinement Data for 3 and 4·0.5($C_2H_4Cl_2$)

	3	**4·0.5($C_2H_4Cl_2$)**
formula	$C_{41}H_{26}N_8O_{17}Ru_9$	$C_{36}H_{20}N_6O_{18}Ru_9$·0.5($C_2H_4Cl_2$)
fw	1812.33	1783.69
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a, Å	10.5436(4)	42.29(3)
b, Å	15.2685(6)	9.933(7)
c, Å	16.1872(6)	26.91(2)
α, deg	97.046(2)	90
β, deg	97.423(3)	112.35(2)
γ, deg	95.284(3)	90
vol, Å^3	2549.1(2)	10 455(12)
Z	2	8
F(000)	1720	6744
D_{calcd}, g cm^{-3}	2.361	2.266
μ, mm^{-1}	21.636	2.646
cryst size, mm	0.12 × 0.10 × 0.02	0.25 × 0.09 × 0.06
temp, K	293(2)	296(2)
θ limits, deg	2.78 to 57.50	1.04 to 23.43
min./max. *h, k, l*	0/11, −16/16, −17/17	−44/47, −11/8, −26/29
no. of collected rflns	24 597	22 937
no. of unique rflns	6996	7526
no. of reflns with $I > 2\sigma(I)$	5836	5316
no. of params/restraints	661/0	648/0
GOF on F^2	1.036	1.055
R_1 (on *F*, $I > 2\sigma(I)$)	0.1224	0.0563
wR_2 (on F^2, all data)	0.3430	0.1633
max./min. $\Delta\rho$, e Å^{-3}	3.124/−2.818	2.320/−1.193

calculated using the program XHYDEX.[14] The remaining H atom positions were geometrically calculated and refined riding on their parent atoms. The refinement of this model converged with a high discrepancy index ($R_1 = 0.1224$) because, due to the low-intensity data set, many essentially "unobserved" reflections were used in the refinement. The highest residual peak is located at 1.08 Å from N(3). *Data for 4·0.5($C_2H_4Cl_2$):* Diffraction data were measured at room temperature on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromatized Mo Kα radiation. An absorption correction was applied with SADABS.[15] The structure was solved by direct methods and refined by full-matrix least-squares against F^2 with SHELXTL.[16] The hydride ligand H(100) was located in Fourier maps, and its parameters were refined. The position of hydride H(200) was calculated with XHYDEX.[14] The remaining H atom positions were geometrically calculated and refined riding on their parent atoms. The highest residual peak is located at 1.23 Å from the solvent atom C(91). The molecular plots were made with the PLATON program package.[17] The WINGX program system[18] was used throughout the structure determinations.

Supporting Information Available: Crystallographic data in CIF format for the compounds studied by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060655U

(11) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

(12) Beurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; García-Granda, S.; Gould, R. O.; Israël, R.; Smits, J. M. M. *The DIRDIF-96 Program System*; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1996.

(13) Sheldrick, G. M. *SHELXL97*, Version 97-2; University of Göttingen: Göttingen, Germany, 1997.

(14) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

(15) Sheldrick, G. M. *SADABS, Empirical Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

(16) Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, Version 5.1; Bruker AXS, Inc.: Madison, WI, 1998.

(17) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; University of Utrecht: Utrecht, The Netherlands, 2003.

(18) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.