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High-Nuclearity Ruthenium Carbonyl Cluster Complexes Derived from 2-Amino-6-methylpyridine: Synthesis of Nonanuclear Derivatives Containing μ_4- and μ_5-Oxo Ligands

Javier A. Cabeza,*,[†] Ignacio del Río,[†] Pablo García-Álvarez,[†] and Daniel Miguel[‡]

Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica "Enrique Moles", Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain, and Área de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47071 Valladolid, Spain

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Nonanuclear cluster complexes $[Ru_9(\mu_3\text{-}H)_2(\mu\text{-}H)(\mu_5\text{-}O)(\mu_4\text{-ampy})(\mu_3\text{-Hampy})(CO)_{21}]$ (**4**) (H_2ampy = 2-amino-6-methylpyridine), $[Ru_9(\mu_5\text{-}O)_2(\mu_4\text{-ampy})(\mu_3\text{-Hampy})_2(\mu\text{-CO})(CO)_{20}]$ (**5**), $[Ru_9(\mu_5\text{-}O)_2(\mu_4\text{-ampy})(\mu_3\text{-Hampy})_2(\mu\text{-CO})_2(CO)_{19}]$ (**6**), and $[Ru_9(\mu_4\text{-}O)(\mu_5\text{-}O)(\mu_4\text{-ampy})(\mu_3\text{-Hampy})(\mu\text{-Hampy})(\mu\text{-CO})(CO)_{19}]$ (**7**), together with the known hexanuclear $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-ampy})(\mu\text{-CO})_2(CO)_{14}]$ (**2**) and the novel pentanuclear $[Ru_5(\mu_4\text{-ampy})_2(\mu\text{-CO})(CO)_{12}]$ (**3**) complexes, are products of the thermolysis of $[Ru_3(\mu\text{-}H)(\mu_3\text{-Hampy})(CO)_9]$ (**1**) in decane at 150 °C. Two different and very unusual quadruply bridging coordination modes have been observed for the ampy ligand. Compounds **4**–**7** also feature one (**4**) or two (**5**–**7**) bridging oxo ligands. With the exception of one of the oxo ligands of **7**, which is in a distorted tetrahedral environment, the remaining oxo ligands of **4**–**7** are surrounded by five metal atoms. In carbonyl metal clusters, quadruply bridging oxo ligands are very unusual, whereas quintuply bridging oxo ligands are unprecedented. By using ^{18}O-labeled water, we have unambiguously established that these oxo ligands arise from water.

Introduction

The derivative chemistry of triruthenium carbonyl clusters containing 2-amidopyridine ligands has been extensively studied during the past decade.[1,2] These studies have demonstrated that such ligands act as strong anchors that hold the three metal atoms in close proximity, preventing cluster fragmentations and aggregations, at least at temperatures up to 110 °C.

As far as higher-nuclearity ruthenium carbonyl clusters derived from 2-aminopyridines are concerned, we have recently reported that the trinuclear cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-Hampy})(CO)_9]$ (**1**) (H_2ampy = 2-amino-6-methylpyridine)[3] reacts with $[Ru_3(CO)_{12}]$ at 110−140 °C to give the hexanuclear derivative $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-ampy})(\mu\text{-CO})_2(CO)_{14}]$ (**2**) in high yield (Scheme 1).[4] 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 compound **2** as the 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 penta- and heptanuclear products in some reactions.[5] Recently, we have also reported that compound **2** reacts with 2-amino-6-methylpyridine at high temperature (160 °C) to give a hexanuclear cluster complex and an octanuclear derivative that contain the imido N atoms of their

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* To whom correspondence should be addressed. E-mail: jac@fq.uniovi.es.

[†] Universidad de Oviedo.

[‡] Universidad de Valladolid.

(1) (a) For a review on the reactivity of triruthenium carbonyl clusters derived from 2-aminopyridines, see: Cabeza, J. A. *Eur. J. Inorg. Chem.* **2002**, 1559.

(2) For recent articles uncovered by ref 1, see: (a) Cabeza, J. A.; del Río, I.; García-Granda, S.; Riera, V.; Suárez, M. *Organometallics* **2002**, *21*, 2540. (b) Cabeza, J. A.; del Río, I.; García-Granda, S.; Riera, V.; Suárez, M. *Organometallics* **2002**, *21*, 5055. (c) Cabeza, J. A.; del Río, I.; Moreno, M.; García-Granda, S.; Pérez-Priede, M.; Riera, V. *Eur. J. Inorg. Chem.* **2002**, 3204. (d) Cabeza, J. A.; del Río, I.; García-Granda, S.; Martínez-Méndez, L.; Moreno, M.; Riera, V. *Organometallics* **2003**, *22*, 1164. (e) Cabeza, J. A.; del Río, I.; Riera, V.; Suárez, M.; García-Granda, S. *Organometallics* **2004**, *23*, 1107. (f) Cabeza, J. A.; del Río, I.; García-Granda, S.; Moreno, M.; Pérez-Carreño, E.; Suárez, M.; *Organometallics* **2004**, *23*, 5839.

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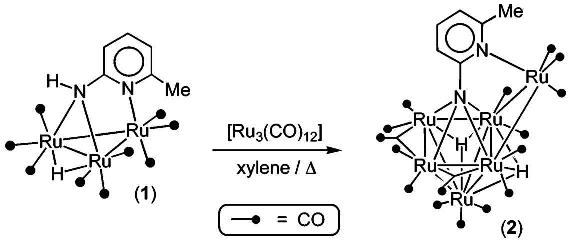
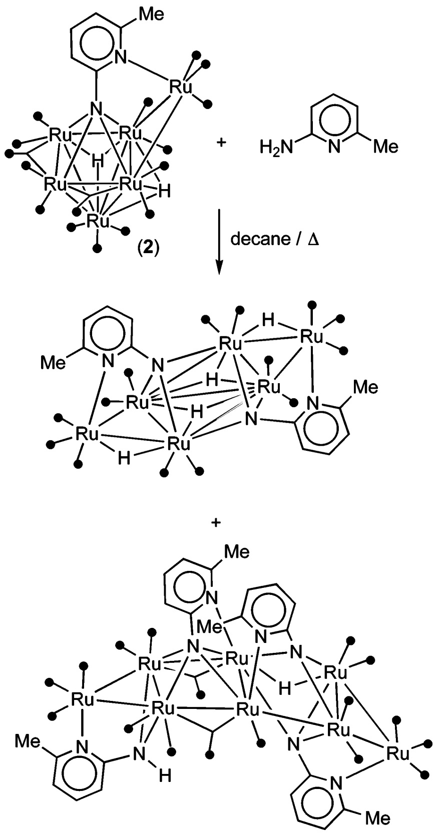
10.1021/ic060433o CCC: $33.50

Scheme 1



Scheme 2



2-imidopyridine ligands capping metallic triangles and squares (Scheme 2).[6]

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[3−8] and keeping in mind the ability of 2-aminopyridines to undergo N−H bond-cleavage processes in the presence of ruthenium carbonyl clusters under appropriate thermal conditions,[3,4,6,9] we decided to study the thermolysis of compound **1** at high temperature (150 °C), attempting the synthesis of novel high-nuclearity ruthenium carbonyl clusters containing ligands derived from 2-aminopyridines. 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 not only the synthesis of a few novel 2-aminopyridine-derived penta- and nonaruthenium carbonyl clusters, but also that some of these compounds contain μ_4- and μ_5-oxo ligands. Oxo ligands are very unusual in transition-metal carbonyl chemistry. For ruthenium, no carbonyl derivatives with terminal or bridging (μ_2) oxo ligands are known, and only a few of such complexes containing μ_3-oxo[10] and μ_4-oxo[11] ligands have been reported. This article reports the first examples of carbonyl complexes containing μ_5-oxo ligands.

Results and Discussion

Synthesis. The thermolysis of compound **1** was carried out in a nitrogen-filled Schlenk tube attached to a reflux condenser covered by a silicone-oil bubbler. Decane was used as the solvent, and the mixture was stirred at 150 °C. Heating was stopped when all of starting material **1** was consumed (IR and/or TLC monitoring). The reaction was repeated several times, and we observed that the reaction time varied considerably from one reaction to another, depending on how many times the reactor was opened to take aliquots for IR and/or TLC monitoring. To avoid exposing the reaction mixture to air when aliquots were taken, we passed a flow of nitrogen gas through (using the Schlenk gas manifold) for the time the system was opened (2−3 s). This vented off the gases contained within the system and replaced them by nitrogen. Without opening the system, most of **1** (>85%) remained unchanged after 3 h. The complete consumption of **1** was observed after 4 h when the gases were vented at 1 h intervals. Some black solid, insoluble in dichloromethane, accompanied a mixture of dichloromethane-soluble compounds. When a continuous flow of nitrogen was passed through the system (ca. one bubble per second) for 3 h, the amount of insoluble black material increased considerably, decreasing the amount of soluble compounds. Therefore, the presence of carbon monoxide (that is released during the thermolysis) in the atmosphere of the reaction vessel, although it decreases the reaction rate, protects the final

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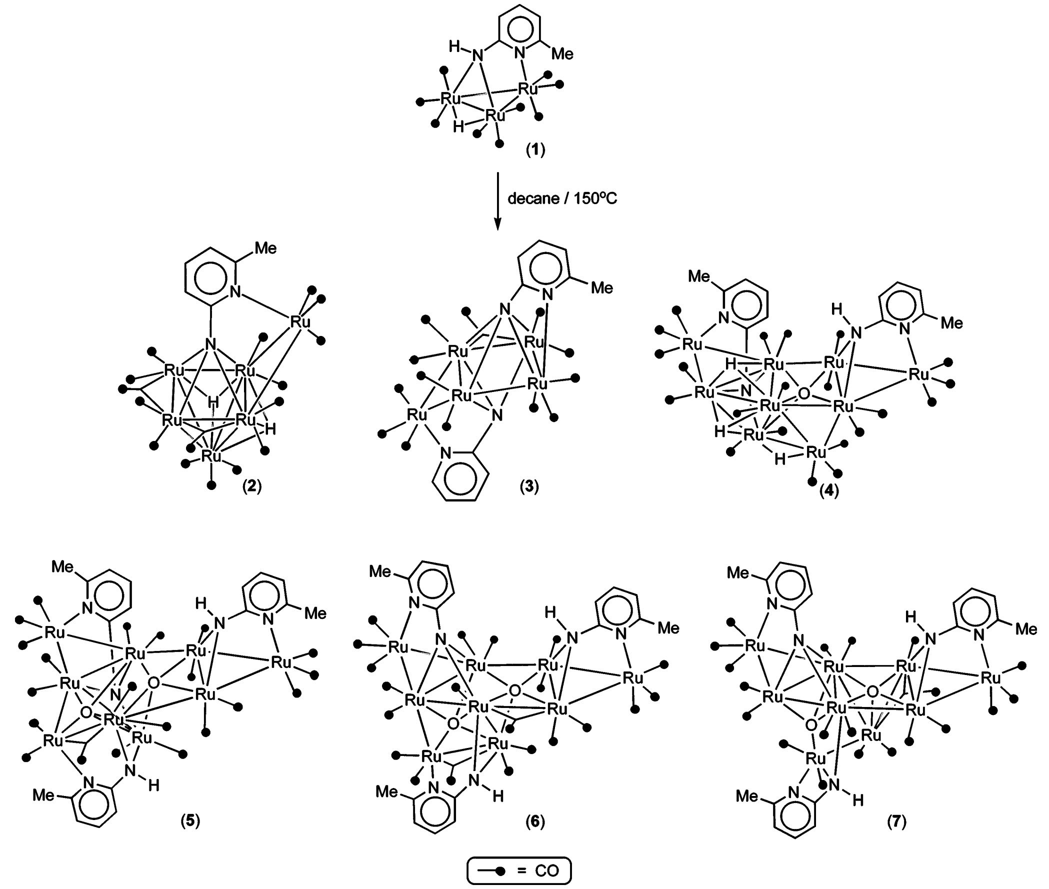
Scheme 3



products from thermal decomposition, lowering the final amount of black insoluble solid. Only an intractable black solid was obtained from a 30 min reaction carried out under air. This indicates that the final products decompose rapidly under air at the working temperature. At lower temperatures (e.g., 120 °C), the thermolysis of **1** was very slow.

The dichloromethane-soluble products were separated by chromatographic methods and were subsequently identified as the known complex $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ (**2**)[4] and the novel derivatives $[Ru_5(\mu_4\text{-ampy})_2(\mu\text{-}CO)(CO)_{12}]$ (**3**), $[Ru_9(\mu_3\text{-}H)_2(\mu\text{-}H)(\mu_5\text{-}O)(\mu_4\text{-ampy})(\mu_3\text{-Hampy})(CO)_{21}]$ (**4**), $[Ru_9(\mu_5\text{-}O)_2(\mu_4\text{-ampy})(\mu_3\text{-Hampy})_2(\mu\text{-}CO)(CO)_{20}]$ (**5**), $[Ru_9(\mu_5\text{-}O)_2(\mu_4\text{-ampy})(\mu_3\text{-Hampy})_2(\mu\text{-}CO)_2(CO)_{19}]$ (**6**), and $[Ru_9(\mu_4\text{-}O)(\mu_5\text{-}O)(\mu_4\text{-ampy})(\mu_3\text{-Hampy})(\mu\text{-Hampy})(\mu\text{-}CO)(CO)_{19}]$ (**7**) (Scheme 3).

The observation of compounds **2**−**4** as reaction products indicates that upon thermolysis, complex **1** releases not only carbon monoxide but also metallic $Ru(CO)_n$ fragments (compound **3** has two ampy ligands but only five metal atoms), which subsequently condense with other metallic complexes to give some of the final products (compound **2** has six metal atoms and only one ampy ligand and compound **4** has one ampy, one Hampy, and nine metal atoms). Therefore, although Hampy[1] and ampy[5] ligands act as anchors that prevent cluster fragmentation at temperatures below 120 °C, their anchoring efficiency is lower at 150 °C.

It is clear that nonanuclear derivatives **5**−**7** arise from three molecules of **1**. Although it cannot be ruled out that these complexes may form independently, the reaction sequence **5** → **6** → **7** does occur at high temperature. This was confirmed by an experiment in which compound **5** was heated in THF at reflux temperature. The percentages of **5**−**7** in the reaction solution at different reaction times were 29, 57, and 14%, respectively, after 2 h; 10, 54, and 36% after 4 h; and 0, 33, and 67% after 7 h.

Structural Characterization. The atom connectivity of compounds **3**−**7** was determined by X-ray diffraction. When we first saw the bridging atoms of **4**−**7** in difference Fourier maps, we thought they were carbide ligands. In fact, it is well-known that on some occasions, the thermolysis of ruthenium carbonyl clusters may lead to carbide derivatives of higher nuclearity,[12] whereas, as commented in the Introduction, bridging oxygen atoms (oxo ligands) are very rare in ruthenium carbonyl chemistry.[10,11] However, anisotropic refinement of these atoms resulted in nonpositive definite thermal ellipsoids when they were treated as carbon atoms, whereas they behaved correctly when they were treated as oxygen atoms.

The positive FAB mass spectra of **4**−**7** are also in agreement with the proposal that the bridging atoms are oxygen, because they display the correct molecular ions (carbon and oxygen differ by 4 amu). In addition, no resonances above 250 ppm are observed in the $^{13}C\{^1H\}$ NMR

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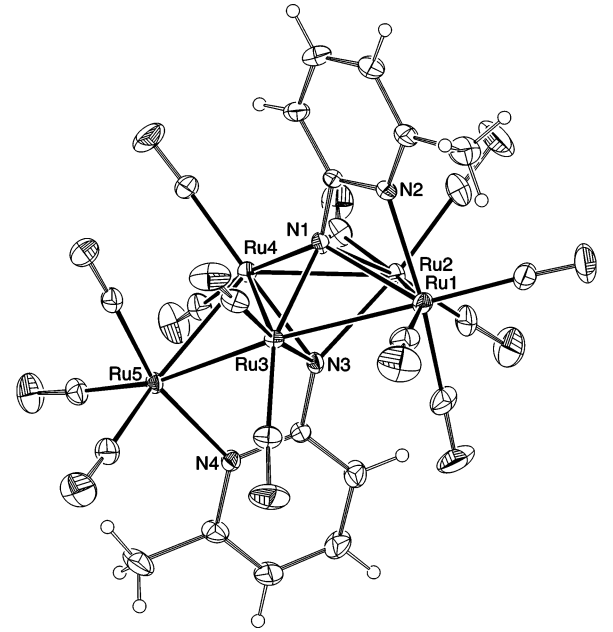

Figure 1. Molecular structure of **3**. Thermal ellipsoids are drawn at the 20% probability level.

Table 1. Selected Interatomic Distances (Å) in Compound **3**

Ru(1)−Ru(2)	2.8299(5)	Ru(1)−Ru(3)	2.8363(5)
Ru(2)−Ru(4)	2.7234(5)	Ru(3)−Ru(4)	2.7047(4)
Ru(3)−Ru(5)	2.7216(5)	Ru(4)−Ru(5)	2.8077(5)
N(1)−Ru(1)	2.511(4)	N(1)−Ru(2)	2.105(4)
N(1)−Ru(3)	2.102(4)	N(1)−Ru(4)	2.140(4)
N(2)−Ru(1)	2.208(4)	N(3)−Ru(2)	2.203(4)
N(3)−Ru(3)	2.116(4)	N(3)−Ru(4)	2.121(4)
N(4)−Ru(5)	2.207(4)		

spectra of ^{13}CO-enriched samples of **5**−**7** (made from ^{13}CO-enriched **1**). As carbide ligands of carbonyl clusters arise from carbonyl ligands (2 CO → C + CO$_2$),[12] these ^{13}C{^{1}H} NMR spectra clearly indicate that **5**−**7** do not contain carbide ligands. The ^{13}C{^{1}H} NMR spectrum of compound **4** was not obtained because it was prepared in a very small yield.

The molecular structure of compound **3** is shown in Figure 1. Important interatomic distances are given in Table 1. The compound is pentanuclear with a metallic skeleton that can be described as being an edge-bridged distorted square. Its most relevant features are the coordination modes of the two ampy ligands. One is attached to the edge-bridging Ru(5) atom through the pyridine N atom while it bridges three metal atoms of the square, Ru(2), Ru(3), and Ru(4), through its imido N atom. The other one caps the four Ru atoms of the square with its imido N atom while the pyridine N atom is attached to one of these metal atoms, Ru(1). Although triply[13] and quadruply bridging[4,5,13d,13f,14] imido ligands are well-known in carbonyl metal cluster chemistry, the coordination modes displayed by the ampy ligands in complex **3** are very rare for 2-imidopyridine ligands. In fact, each coordination mode has only one precedent.[6] When the ampy ligands are considered to be 6-electron donors, the cluster obeys the EAN rule, because it has six M−M bonds, two ampy ligands, 13 CO ligands, and an electron count of 78 electrons.

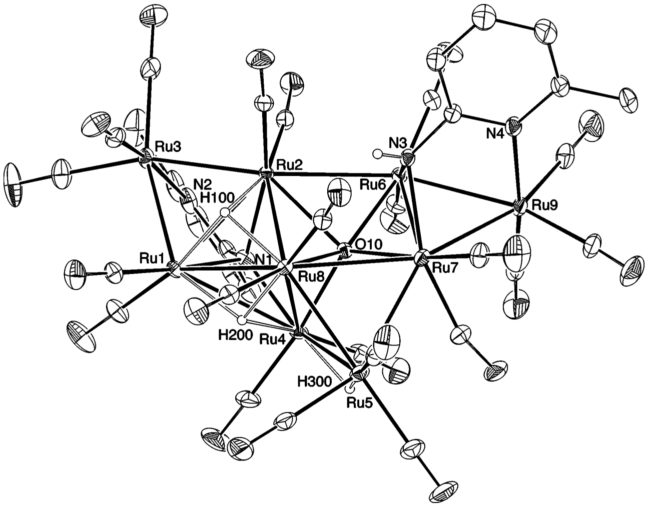

Figure 2. Molecular structure of **4**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms attached to carbon atoms have been omitted for clarity.

Table 2. Selected Interatomic Distances (Å) in Compound **4**

Ru(1)−Ru(2)	2.7940(5)	Ru(1)−Ru(3)	2.7061(6)
Ru(1)−Ru(4)	2.9642(6)	Ru(1)−Ru(8)	2.9886(5)
Ru(2)−Ru(3)	2.7003(5)	Ru(2)−Ru(6)	2.8333(5)
Ru(2)−Ru(8)	2.9802(5)	Ru(4)−Ru(5)	3.0513(6)
Ru(4)−Ru(8)	2.8287(5)	Ru(5)−Ru(7)	2.8207(6)
Ru(5)−Ru(8)	2.7283(6)	Ru(6)−Ru(7)	2.9015(5)
Ru(6)−Ru(9)	2.7113(5)	Ru(7)−Ru(8)	2.9123(5)
Ru(7)−Ru(9)	2.7739(6)	N(1)−Ru(1)	2.079(4)
N(1)−Ru(2)	2.160(4)	N(1)−Ru(4)	2.095(5)
N(2)−Ru(3)	2.208(5)	N(3)−Ru(6)	2.124(4)
N(3)−Ru(7)	2.131(4)	N(4)−Ru(9)	2.202(5)
O(10)−Ru(2)	2.360(3)	O(10)−Ru(4)	2.108(3)
O(10)−Ru(6)	2.182(3)	O(10)−Ru(7)	2.086(3)
O(10)−Ru(8)	2.145(3)		

Figure 2 shows the molecular structure of compound **4**. Table 2 contains a selection of interatomic distances. The compound is nonanuclear and contains a μ_4-ampy, a μ_3-Hampy, three hydrides (one edge-bridging, H(300), and two face-capping, H(100) and H(200)), 21 CO ligands, and a μ_5-oxo ligand. Its most-relevant feature is the presence of the oxo ligand, O(10), which is surrounded by a distorted square pyramid of Ru atoms. The coordination mode of the μ_4-ampy ligand is the same as that of one of ampy ligands of **3** (see above). The triangular face-capping coordination of the μ_3-Hampy ligand is well-represented in trinuclear complexes.[1] With its 15 M−M bonds, complex **4** obeys the EAN rule (132 electrons) if the oxo ligand contributes four electrons. As commented in the Introduction, quintuply bridging oxo ligands have no precedent in carbonyl metal chemistry.

The metallic skeletons of compounds **5** (Figure 3) and **6** (Figure 4) are very similar, comprising nine ruthenium atoms

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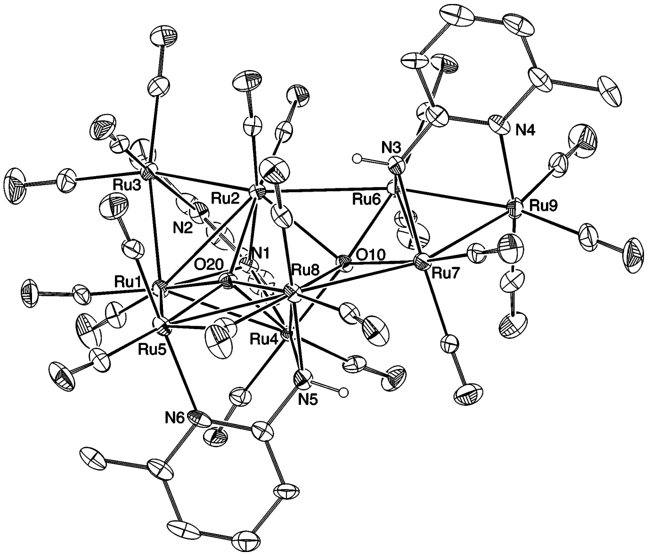

Figure 3. Molecular structure of **5**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms attached to carbon atoms have been omitted for clarity.

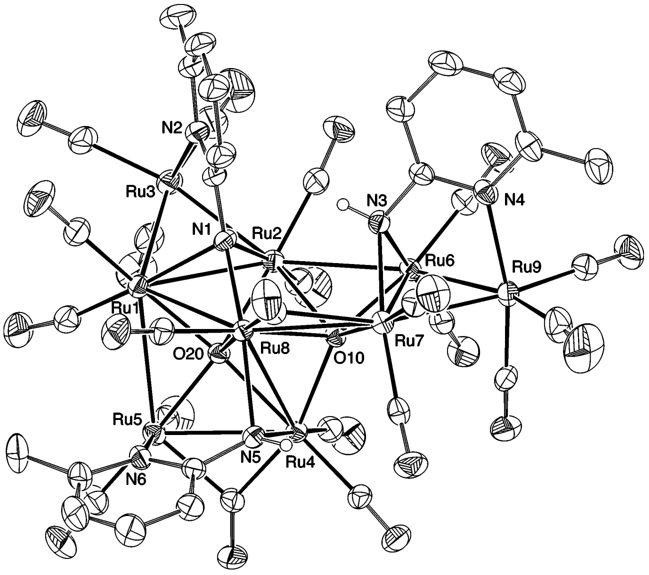

Figure 4. Molecular structure of **6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms attached to carbon atoms have been omitted for clarity.

interconnected by 12 Ru−Ru bonds (Table 3). Both are supported by two μ_3-Hampy ligands, one μ_4-ampy ligand, and two μ_5-oxo ligands. Both complexes contain 21 carbonyl ligands. Their electron count is 138, for which the EAN rule predicts 12 M−M bonds. Their most remarkable difference is that the imido fragment of the ampy ligand of **5** caps the Ru(1), Ru(2), and Ru(4) metal atoms, whereas the same fragment of **6** caps the Ru(1), Ru(2), and Ru(8) metal atoms. The coordination modes of the μ_3-Hampy and μ_4-ampy ligands in **5** and **6** are similar to those displayed by the same ligands in the preceding structures. In both compounds, the oxo ligand O(10) is in a very distorted square pyramidal environment, whereas the oxo ligand O(20) is in an approximate trigonal bipyramidal environment.

Table 3. Selected Interatomic Distances (Å) in Compounds **5**−**7**

	5	**6**	**7**
Ru(1)−Ru(2)	2.955(2)	2.8990(6)	3.004(2)
Ru(1)−Ru(3)	2.703(2)	2.7046(7)	2.699(2)
Ru(1)−Ru(4)	2.927(2)		
Ru(1)−Ru(5)	2.939(2)	3.0818(6)	
Ru(1)−Ru(8)		2.8847(6)	2.847(2)
Ru(2)−Ru(3)	2.714(2)	2.6941(7)	2.732(2)
Ru(2)−Ru(4)			2.842(2)
Ru(2)−Ru(6)	2.959(2)	2.9312(6)	2.976(2)
Ru(2)−Ru(8)			3.037(2)
Ru(4)−Ru(5)		2.9267(7)	2.700(2)
Ru(4)−Ru(6)			2.876(2)
Ru(4)−Ru(8)	3.085(2)	3.0379(6)	
Ru(5)−Ru(8)	2.911(2)		
Ru(6)−Ru(7)	2.837(2)	2.8284(6)	2.877(2)
Ru(6)−Ru(9)	2.723(2)	2.7134(6)	2.739(2)
Ru(7)−Ru(8)	2.935(2)	2.9203(6)	3.020(2)
Ru(7)−Ru(9)	2.693(2)	2.6979(6)	2.724(2)
N(1)−Ru(1)	2.175(8)	2.140(5)	2.14(1)
N(1)−Ru(2)	2.069(8)	2.089(5)	2.10(1)
N(1)−Ru(4)	2.079(8)		
N(1)−Ru(8)		2.068(5)	2.101(9)
N(2)−Ru(3)	2.206(9)	2.209(5)	2.23(1)
N(3)−Ru(6)	2.126(10)	2.150(5)	2.14(1)
N(3)−Ru(7)	2.142(9)	2.147(5)	2.18(1)
N(4)−Ru(9)	2.219(10)	2.208(5)	2.20(1)
N(5)−Ru(4)	2.167(9)	2.148(5)	
N(5)−Ru(5)			2.22(1)
N(5)−Ru(8)	2.133(10)	2.150(5)	2.16(1)
N(6)−Ru(5)	2.228(10)	2.223(5)	2.15(1)
O(10)−Ru(2)	2.534(7)	2.562(4)	2.399(8)
O(10)−Ru(4)	2.098(6)	2.256(3)	2.072(8)
O(10)−Ru(6)	2.155(6)	2.131(3)	2.168(8)
O(10)−Ru(7)	2.160(7)	2.119(3)	2.140(8)
O(10)−Ru(8)	2.423(6)	2.160(3)	2.220(8)
O(20)−Ru(1)	2.089(7)	2.118(4)	2.084(9)
O(20)−Ru(2)	2.306(7)	2.240(3)	2.159(8)
O(20)−Ru(4)	2.142(6)	2.224(4)	
O(20)−Ru(5)	2.162(7)	2.131(3)	2.117(8)
O(20)−Ru(8)	2.210(7)	2.190(3)	2.111(8)

The structure of compound **7** (Figure 5, Table 3) can be described as being derived from that of **6**, the former having one CO ligand less than the latter. The electron count of **7** is therefore 136, for which the EAN rule predicts 13 M−M bonds. Whereas the Ru(1)−Ru(5) and Ru(4)−Ru(8) bonds of **6** do not exist in **7**, three new Ru−Ru bonds are observed in **7**, namely Ru(2)−Ru(8), Ru(2)−Ru(4), and Ru(4)−Ru(6). As in compound **6**, the metallic environment

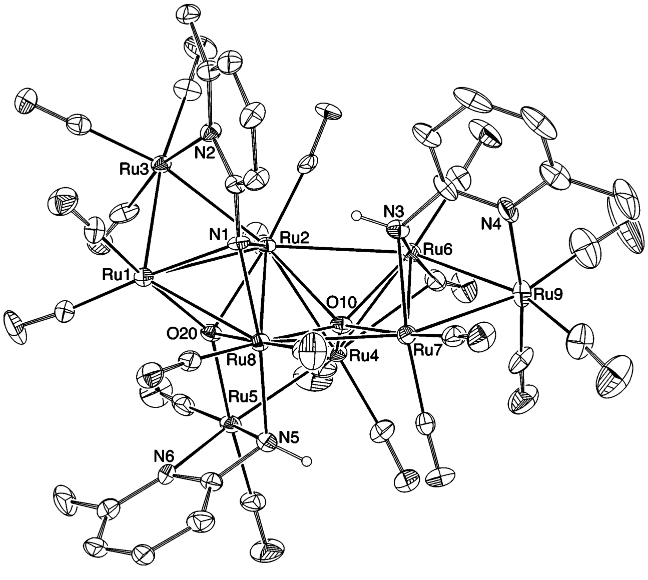

Figure 5. Molecular structure of **7**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms attached to carbon atoms have been omitted for clarity.

of oxo ligand O(10) of compound **7** is distorted square pyramidal; however, that of oxo ligand O(20) has changed from distorted square pyramidal (in **6**) to distorted tetrahedral (in **7**). An additional interesting feature of complex **7** is that one of the Hampy ligands is attached to only two metal atoms, Ru(5) and Ru(8), with its amidic nitrogen atom N(5) spanning both metal atoms and its pyridine nitrogen N(6) bonded to Ru(5). As far as we know, there is only one previous report describing 2-amidopyridine ligands acting as a 5-electron donor attached to only two metal atoms.[15]

On the Origin of the Oxo Ligands. The best results (minimum decomposition) were obtained when the thermolysis of **1** was carefully carried out in the absence of air (we used 99.999% dinitrogen as a protecting atmosphere), because as commented upon above, the reaction products are not stable under air at the working temperature (150 °C). In addition, no differences were observed when the decane solvent was deoxygenated prior to use. These results indicate that the oxo ligands of compounds **4**−**7** do not arise from air.

Supposing that the transformation of a CO ligand into an oxo ligand on a carbonyl metal complex was possible, the thermolysis of complex **1** should have also afforded carbide derivatives as reaction products. Carbide ruthenium carbonyl clusters should be stable at high temperatures.[12] As we have not observed any such products, we exclude carbon monoxide as the source of the oxo ligands. Moreover, there is no precedent for such a transformation of a CO ligand on a carbonyl metal complex.

Considering the possibility that water could be the source of the oxo ligands of compounds **4**−**7**, we carried out the thermolysis of **1** in the presence of a small amount of ^{18}O-enriched water (100 μL, 97.9 atom % ^{18}O, in 15 mL of decane). In this case, the FAB MS of the obtained products reflected an increase of 2 or 4 amu in the molecular weights, depending on the number of oxo ligands in each particular product (1 or 2, respectively). Therefore, the oxo ligands of compounds **4**−**7** arise from water.

Concerning the mechanism by which ^{18}O is introduced into the clusters, the molecular weights of the products prepared in the presence of ^{18}O-enriched water indicate that water should directly attack the metal atoms. If water could also attack the CO ligands of these complexes, according to the water−gas−shift reaction equilibrium $CO + H_2O = CO_2 + H_2$, many ^{18}O-labeled CO ligands would be formed and the molecular weights of the obtained products would be much higher than those observed because there are many CO ligands available and an excess of ^{18}O-enriched water.

However, no particular difference (same products and analogous yields within similar periods of time) was observed when the thermolysis of compound **1** was performed using commercial decane, very wet decane (100 μL of water was added to 15 mL of decane), or dry decane (2 h of reflux over sodium under nitrogen and subsequent distillation under nitrogen directly into the thermolysis Schlenk tube) as the solvent. These results indicate that, working on a small scale, residual water from dry solvent and/or from the surface of the glassware is enough to allow the preparation of small amounts of compounds **4**−**7**. In fact, the calculated amount of water necessary to make 20 mg (0.011 mmol) of compound **5** is only 0.39 μL. These results also demonstrate that the final products are stable in the presence of moisture under the thermolysis conditions and that the amount of water present in solution does not affect the reaction rate, which, as commented upon above, seems to be associated with the activation of compound **1** by CO elimination.

Concluding Remarks

The thermolysis of complex **1** in commercial decane is slow at temperatures below 150 °C. Even at this temperature, the evolved carbon monoxide should be removed a few times during the reaction in order to observe an acceptable reaction rate. However, the reaction products rapidly decompose at this temperature unless a protecting atmosphere of carbon monoxide is present in the reactor. This contradictory situation has been solved by purging the reactor with nitrogen for 2−3 s every hour over a period of 4 h. Under these conditions, the reaction affords a black, insoluble, and uncharacterized material and a fraction soluble in dichloromethane that contains compounds **2**−**7**. Although compound **2** is a previously reported complex, compounds **3**−**7** are novel. Complex **3** is pentanuclear and complexes **4**−**7** are nonanuclear.

The metal atoms of these compounds are supported by bridging 2-amido- and 2-imidopyridine ligands (Hampy and ampy, respectively). Two different and very unusual quadruply bridging coordination modes have been observed for the ampy ligand.

Compounds **4**−**7** also contain one (**4**) or two (**5**−**7**) bridging oxo ligands. With the exception of one of the oxo ligands of **7**, which is in a distorted tetrahedral environment, the remaining oxo ligands of **4**−**7** are surrounded by five metal atoms. Quintuply bridging oxo ligands are unprecedented in carbonyl metal clusters. By using ^{18}O-labeled water, we have unambiguously established that these oxo ligands arise from water (from the solvent and/or the surface of the glassware).

An important key feature of the synthesis of the oxo clusters **4**−**7** is not only the presence of water during the reaction but also the high reaction temperature (150 °C). The fact that oxo ligands have so far been very rare in carbonyl cluster chemistry may be a consequence of the fact that the

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(14) For additional examples of clusters with μ_4-imido ligands, see: (a) Link, H.; Fenske, D. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1878. (b) Reiss, P.; Fenske, D. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2245. (c) Blohm, M. L.; Gladfelter, W. L. *Organometallics* **1986**, *5*, 1049. (d) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *J. Chem. Res.* **1979**, *334*, 3943. (e) Ho, E. N. M.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1998**, 4215. (f) Ho, E. N. M.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1998**, 513. (g) Ho, E. N. M.; Lin, Z.; Wong, W. T. *Eur. J. Inorg. Chem.* **2001**, 1321. (h) Han, S. W. H.; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2034. (i) Scoles, L.; Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Chem. Commun.* **2002**, 320. (j) Cabeza, J. A.; del Río, I.; García-Granda, S.; Moreno, M.; Riera, V.; Rosales-Hoz, M. J.; Suárez, M. *Eur. J. Inorg. Chem.* **2001**, 2899. (k) Yeh, W. Y.; Stern, C.; Shriver, D. F. *Inorg. Chem.* **1996**, *35*, 7857. (l) Hansert, B.; Powell, A. K.; Vahrenkamp, H. *Chem. Ber.* **1991**, *124*, 2697.

(15) Cabeza, J. A.; del Río, I.; García-Granda, S.; Lavigne, G.; Lugan, N.; Moreno, M.; Nombel, P.; Pérez-Priede, M.; Riera, V.; Rodríguez, A.; Suárez, M.; van der Maelen, J. F. *Chem.—Eur. J.* **2001**, *7*, 2370.

reactions of carbonyl cluster complexes are generally carried out at lower temperatures.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, diethyl ether), sodium (hydrocarbons), or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. The reactions were monitored by solution IR spectroscopy (carbonyl stretching region) and spot TLC. ^{18}O-enriched water (97.9 atom % ^{18}O) was purchased from Cambridge Isotope Laboratories, Inc. ^{13}C-enriched carbon monoxide (99.1% atom ^{13}C) was purchased from Isotec Inc. Compound **1**[3] and ^{13}CO-enriched $[Ru_3(CO)_{12}]$[16] were prepared as previously reported. IR spectra were recorded in solution on a Perkin−Elmer Paragon 1000 FT spectrophotometer. ^1H NMR spectra were run on a Bruker DPX-300 instrument at room temperature, using the dichloromethane solvent resonance as an internal standard ($\delta = 5.30$). Microanalyses were obtained from the University of Oviedo Analytical Service. Positive FAB-MS 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 below have been estimated by taking into account the ruthenium content of each product.

Thermolysis of Compound 1 in Decane. Compound **1** (150 mg, 0.226 mmol) and a Teflon-coated stirring bar were added to a Schlenk tube containing decane (15 mL). The tube was attached to a reflux condenser that was stopped with a silicone-oil bubbler. The air was flushed out from the system by gently introducing nitrogen gas into the system through the Schlenk sidearm for 30 s. With the nitrogen inlet closed, the Schlenk was introduced into an oil bath that was thermostated at 150 °C. The complete consumption of **1** was observed after 4 h when the gases were vented with nitrogen (for 2−3 s) every hour. The color changed from yellow-orange to dark greenish gray. A considerable amount of black solid also formed. The solvent was removed under vacuum, and the solid residue was extracted into dichloromethane (10 mL). Silica gel (6 g) was added to this solution, and the mixture was evaporated to dryness. The solid was transferred to the top of a silica gel chromatographic column (2 × 20 cm) packed in hexane. Hexane−dichloromethane (4:1) eluted two brown fractions, corresponding to compound **3** (10 mg, 8%) and the known cluster **2** (7 mg, 5%). Hexane−dichloromethane (3:1) eluted a violet band that contained compound **4** (3 mg, 2%) and a very weak band (green), which was discarded. Hexane−diethyl ether (2:1) eluted two bands. The first one (violet) was very weak and was discarded. The following band (dark green) contained compound **5** (35 mg, 25%). Further elution of the column with hexane−dichloromethane (2:1) eluted a dark gray band, which contained a mixture of compounds **6** and **7**. A dark residue remained uneluted at the top of the column. Compounds **6** and **7** were separated by TLC on silica gel, eluting the plates repeatedly with hexane−dichloromethane (2:1). The first band (dark gray) contained compound **7** (15 mg, 11%). The second band (dark greenish gray) afforded compound **6** (10 mg, 7%).

Thermolysis of Compound 5 in THF. A solution of compound **5** (6 mg, 0.003 mmol) in THF (4 mL) was stirred under nitrogen at reflux temperature for 2 h. The solvent was removed under vacuum, and the residue was analyzed by ^1H NMR. The composition of this solution was 29% **5**, 57% **6**, and 14% **7**. The NMR solvent was evaporated, and the residue was dissolved in THF (4 mL). This solution was stirred under nitrogen at reflux temperature for 2 h. The solvent was removed under vacuum, and the residue was analyzed by ^1H NMR. The composition of this solution was 10% **5**, 54% **6**, and 36% **7**. The NMR solvent was evaporated, and the residue was dissolved in THF (4 mL). This solution was stirred under nitrogen at reflux temperature for 3 h. The composition of this solution was 0% **5**, 33% **6**, and 67% **7**.

$[Ru_5(\mu_4\text{-ampy})_2(\mu\text{-CO})(CO)_{12}]$ (3). Anal. Calcd for $C_{25}H_{12}N_4O_{13}Ru_5$ (fw = 1081.73): C, 27.76; H, 1.12; N, 5.18. Found: C, 27.91; H, 1.22; N, 5.06. MS (+FAB): m/z 1082 [M^+]. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2077 (w), 2047 (vs), 2021 (vs), 2006 (s), 1990 (m, br), 1962 (w, sh), 1935 (w, br), 1882 (vw, br). ^1H RMN ($CDCl_3$, 20 °C): δ 7.3−7.0 (m, 2 H), 6.50 (d, $J = 7.6$ Hz, 2 H), 6.0−5.0 (m, br, 2 H), 2.9−2.1 (s, br, 6 H). ^1H NMR (CD_2Cl_2, −40 °C): 7.19 (t, $J = 7.7$ Hz, 1 H), 7.09 (t, $J = 7.7$ Hz, 1 H), 6.51 (d, $J = 7.7$ Hz, 1 H), 6.48 (d, $J = 7.7$ Hz, 1 H), 5.75 (d, $J = 7.7$ Hz, 1 H), 5.29 (d, $J = 7.7$ Hz, 1 H), 2.61 (s, 3 H), 2.20 (s, 3 H).

$[Ru_9(\mu_3\text{-H})_2(\mu\text{-H})(\mu_5\text{-O})(\mu_4\text{-ampy})(\mu_3\text{-Hampy})(CO)_{21}]$ (4). Anal. Calcd for $C_{33}H_{16}N_4O_{22}Ru_9$ (fw = 1730.12): C, 22.91; H, 0.93; N, 3.24. Found: C, 23.07; H, 1.05; N, 3.19. MS (+FAB): m/z 1731 [M^+]. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2098 (m), 2075 (s), 2065 (vs), 2048 (s), 2008 (s, br), 1980 (w, sh), 1968 (vw, sh), 1935 (m, br), 1903 (vw, br). ^1H NMR ($CDCl_3$, 20 °C): δ 7.49 (t, $J = 7.9$ Hz, 1 H), 7.48 (t, $J = 7.9$ Hz, 1 H), 7.14 (d, $J = 7.9$ Hz, 1 H), 6.91 (d, $J = 7.9$ Hz, 1 H), 6.73 (d, $J = 7.9$ Hz, 1 H), 6.32 (d, $J = 7.9$ Hz, 1 H), 2.86 (s, 3 H, Me), 2.69 (s, 3 H, Me), −12.90 (d, $J = 1.8$ Hz, 1 H), −13.11 (t, $J = 1.8$ Hz, 1 H), −17.40 (d, $J = 1.8$ Hz, 1 H) (the NH proton was not observed).

$[Ru_9(\mu_5\text{-O})_2(\mu_4\text{-ampy})(\mu_3\text{-Hampy})_2(\mu\text{-CO})(CO)_{20}]$ (5). Anal. Calcd for $C_{39}H_{20}N_6O_{23}Ru_9$ (fw = 1850.23): C, 25.32; H, 1.09; N, 4.54. Found: C, 25.35; H, 1.13; N, 4.51. MS (+FAB): m/z 1823 [$M^+ - CO$]. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2082 (w), 2067 (vs), 2052 (s), 2026 (s), 1998 (s, br), 1980 (m, br), 1962 (w), 1914 (m, br), 1774 (w, br). ^1H NMR (acetone-d_6, 20 °C): δ 7.77 (t, $J = 7.8$ Hz, 1 H), 7.76 (t, $J = 7.8$ Hz, 1 H), 7.67 (t, $J = 7.8$ Hz, 1 H), 7.21 (d, $J = 7.8$ Hz, 1 H), 7.13 (d, $J = 7.8$ Hz, 1 H), 7.10 (d, $J = 7.8$ Hz, 1 H), 6.91 (d, $J = 7.8$ Hz, 1 H), 6.80 (d, $J = 7.8$ Hz, 1 H), 6.33 (d, $J = 7.8$ Hz, 1 H), 4.15 (s, 1 H), 3.70 (s, 1 H), 3.25 (s, 3 H), 2.90 (s, 3 H), 2.78 (s, 3 H). $^{13}C\{^1H\}$ NMR (DEPT, CD_2Cl_2, 20 °C): δ 232.8 (μ-CO), 201.8, 201.4, 200.7, 200.3, 200.1, 199.8, 199.7, 199.0, 198.9, 198.3, 197.9, 196.3, 195.1, 193.7, 192.2, 189.8, 188.2, 186.5, 186.3, 184.3 (20 COs), 179.1 (C), 175.3 (C), 174.2 (C), 161.3 (C), 159.6 (C), 158.3 (C), 140.8 (CH), 140.3 (CH), 140.1 (CH), 120.8 (CH), 118.4 (CH), 117.5 (CH), 113.2 (CH), 111.6 (CH), 110.1 (CH), 29.6 (CH_3), 28.5 (CH_3), 27.7 (CH_3).

$[Ru_9(\mu_5\text{-O})_2(\mu_4\text{-ampy})(\mu_3\text{-Hampy})_2(\mu\text{-CO})_2(CO)_{19}]$ (6). Anal. Calcd for $C_{39}H_{20}N_6O_{23}Ru_9$ (fw = 1850.23): C, 25.32; H, 1.09; N, 4.54. Found: C, 25.39; H, 1.18; N, 4.47. MS (+FAB): m/z 1823 [$M^+ - CO$]. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2084 (s), 2070 (vs), 2059 (m, sh), 2032 (w), 2011 (vs), 1983 (m, br), 1971 (m, sh), 1937 (m, sh), 1913 (w, br), 1764 (w, br). ^1H NMR (CD_2Cl_2, 20 °C): δ 7.56 (t, $J = 7.8$ Hz, 1 H), 7.46 (t, $J = 7.8$ Hz, 1 H), 7.34 (t, $J = 7.8$ Hz, 1 H), 6.91 (d, $J = 7.8$ Hz, 1 H), 6.79 (d, $J = 7.8$ Hz, 1 H), 6.74 (d, $J = 7.8$ Hz, 1 H), 6.60 (d, $J = 7.8$ Hz, 1 H), 6.07 (d, $J = 7.8$ Hz, 1 H), 5.60 (d, $J = 7.8$ Hz, 1 H), 3.17 (s, 3 H), 2.95 (s, 1 H), 2.80 (s, 3 H), 2.72 (s, 1 H), 2.70 (s, 3 H). $^{13}C\{^1H\}$ NMR (DEPT, $CDCl_3$, 20 °C): δ 235.9 (μ-CO), 203.0, 202.8, 200.6, 200.3, 200.1, 199.9, 199.4, 198.1, 197.9, 197.4, 197.2, 197.1, 196.9, 195.0, 191.2, 191.1, 189.8, 186.0, 184.1, 183.9 (20 COs), 180.1 (C), 176.4 (C), 174.5 (C), 161.6 (C), 160.3 (C), 160.0 (C), 141.7 (CH), 140.4 (CH), 140.1 (CH), 120.6 (CH), 118.2 (CH), 117.4 (CH), 113.3 (CH), 110.9 (CH), 109.6 (CH), 29.8 (CH_3), 29.7 (CH_3), 28.4 (CH_3).

$[Ru_9(\mu_4\text{-O})(\mu_5\text{-O})(\mu_4\text{-ampy})(\mu_3\text{-Hampy})(\mu\text{-Hampy})(\mu\text{-CO})(CO)_{19}]$ (7). Anal. Calcd for $C_{38}H_{20}N_6O_{22}Ru_9$ (fw = 1822.22): C, 25.05; H, 1.11; N, 4.61. Found: C, 25.11; H, 1.17; N, 4.56. MS

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Table 4. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-ray Diffraction

	3	**4**·CH_2Cl_2	**5**	**6**	**7**·0.25(C_7H_8)
formula	$C_{25}H_{12}N_4O_{13}Ru_5$	$C_{33}H_{16}N_4O_{22}Ru_9$·$CH_2Cl_2$	$C_{39}H_{20}N_6O_{23}Ru_9$	$C_{39}H_{20}N_6O_{23}Ru_9$	$C_{38}H_{20}N_6O_{22}Ru_9$·0.25($C_7H_8$)
cryst syst	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	15.5476(2)	10.3849(2)	15.632(7)	12.6444(3)	11.049(5)
b (Å)	10.2437(1)	11.0108(1)	14.108(6)	13.3104(2)	14.805(7)
c (Å)	20.8661(2)	21.9664(3)	24.727(11)	18.7836(3)	17.931(9)
α (deg)	90	86.577(1)	90	87.741(1)	94.583(10)
β (deg)	90.212(1)	87.122(1)	106.252(7)	87.401(1)	97.112(9)
γ (deg)	90	85.863(1)	90	75.315(1)	94.107(9)
V (Å^3)	3323.22(6)	2498.10(6)	5235(4)	3053.6(1)	2891(2)
Z	4	2	4	2	2
radiation (λ, Å)	Cu Kα (1.54180)	Cu Kα (1.54180)	Mo Kα (0.71073)	Cu Kα (1.54180)	Mo Kα (0.71073)
μ (mm^{-1})	18.584	23.092	2.601	18.146	2.355
T (K)	293(2)	150(2)	296(2)	200(2)	296(2)
index ranges	$0 \leq h \leq 18$, $0 \leq k \leq 12$, $-23 \leq l \leq 24$	$0 \leq h \leq 12$, $-13 \leq k \leq 13$, $-26 \leq l \leq 26$	$-17 \leq h \leq 17$, $-12 \leq k \leq 15$, $-25 \leq l \leq 27$	$0 \leq h \leq 15$, $-15 \leq k \leq 16$, $-22 \leq l \leq 22$	$-12 \leq h \leq 12$ $-16 \leq k \leq 16$, $-19 \leq l \leq 11$
no. of collected reflns	11 332	16 875	22 670	18 221	12 695
no. of unique reflns	5871	9221	7509	11112	8142
no. of reflns with $I > 2\sigma(I)$	5636	8284	6133	9636	6422
no. of params/restraints	424/0	656/1	698/0	702/0	696/0
GOF on F^2	1.099	1.036	1.009	1.040	0.995
R_1 (on F, $I > 2\sigma(I)$)	0.0376	0.0385	0.0468	0.0394	0.0626
wR_2 (on F^2, all data)	0.0967	0.0921	0.1252	0.1128	0.1814

(+FAB): m/z 1823 [M$^+$]. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2081 (m), 2069 (vs), 2034 (s), 2011 (vs), 1987 (m, sh), 1976 (m), 1965 (m), 1954 (w), 1932 (m, br), 1920 (w, br). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.69 (t, J = 7.8 Hz, 1 H), 7.55 (t, J = 7.8 Hz, 1 H), 7.34 (t, J = 7.8 Hz, 1 H), 7.06 (d, J = 7.8 Hz, 1 H), 6.81 (d, J = 7.8 Hz, 1 H), 6.71 (d, J = 7.8 Hz, 1 H), 6.45 (d, J = 7.8 Hz, 1 H), 5.98 (d, J = 7.8 Hz, 1 H), 5.65 (d, J = 7.8 Hz, 1 H), 3.34 (s, 1 H), 2.77 (s, 3 H), 2.63 (s, 6 H), 1.87 (s, 1 H). ^{13}C{^{1}H} NMR (DEPT, $CDCl_3$ 20 °C): δ 203.2, 201.5, 200.9, 200.6, 199.9, 199.8, 199.4 (7 COs), 198.6 (2 COs), 198.5 (2 COs), 197.6, 197.1, 195.5, 192.5, 190.5, 189.1, 188.9, 186.8, 186.1 (9 COs), 178.5 (C), 175.3 (C), 174.4 (C), 160.8 (C), 160.0 (C), 156.8 (C), 141.8 (CH), 140.6 (CH), 140.5 (CH), 120.2 (CH), 119.3 (CH), 117.3 (CH), 113.9 (CH), 110.3 (CH), 107.6 (CH), 29.1 (CH_3), 27.8 (CH_3), 23.7 (CH_3).

X-ray Structures of 3, 4·CH_2Cl_2, and 6. A selection of crystal, measurement, and refinement data is given in Table 4. Diffraction data were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromatized Cu−Kα radiation. Raw frame data were integrated with DENZO and SCALEPACK.[17] Empirical absorption corrections were applied using XABS2.[18] The structures were solved by Patterson interpretation using the program DIRDIF-96.[19] Isotropic and full matrix anisotropic least-squares refinements against F^2 were carried out using SHELXL-97.[20] The positions of the hydride atoms H(100), H(200), and H(300) of **4** were calculated using the program XHYDEX[21] and were freely refined except for the thermal parameter of H200, which was fixed. The NH hydrogen atoms H(3) of **4** and H(30) and H(50) of **6** were located in Fourier maps. The N−H(3) distance of **4** was fixed, and the rest of parameters were freely refined. The remaining hydrogen atoms were set in calculated positions and refined as riding atoms All non-H atoms were refined anisotropically. The molecular plots were made with the PLATON program package.[22] The WINGX program system[23] was used throughout the structure determination. CCDC deposition numbers: 601370 (**3**), 601371 (**4**·CH_2Cl_2), and 601373 (**6**).

X-ray Structures of 5 and 7·0.25(C_7H_8). A selection of crystal, measurement, and refinement data is given in Table 4. Diffraction data were measured at room temperature on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromatized Mo−Kα radiation. Raw frame data were integrated with SAINT.[24] Absorption corrections were applied with SADABS.[25] Structures were solved by direct methods and refined by full matrix least-squares against F^2 with SHELXTL.[26] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. The molecular plots were made with the PLATON program package.[22] The WINGX program system[23] was used throughout the structure determinations. CCDC deposition numbers: 601372 (**5**) and 601374 (**7**·0.25(C_7H_8)).

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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.

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