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Triruthenium, Hexaruthenium, and Triosmium Carbonyl Derivatives of 2-Amino-6-phenylpyridine[†]

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The triruthenium cluster complexes [$Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HapyPh\text{-}N,N)(CO)_9$] (**1**) and [$Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^3\text{-}HapyC_6H_4\text{-}N,N,C)_2(CO)_6$] (**2**) and the hexaruthenium ones [$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}apyPh\text{-}N,N)(\mu\text{-}CO)_2(CO)_{14}$] (**3**) and [$Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\eta^3\text{-}apyC_6H_4\text{-}N,N,C)(\mu\text{-}CO)_3(CO)_{13}$] (**4**) have been prepared from [$Ru_3(CO)_{12}$] and 2-amino-6-phenylpyridine (H_2apyPh). Compound **1** contains a deprotonated HapyPh ligand capping a face of the metal triangle. Compound **2** contains two cyclometalated HapyC_6H_4 ligands, each spanning a Ru−Ru edge through the N atom of the amido fragment and chelating the remaining Ru atom through both the pyridine N atom and the C atom of the cyclometalated ring. The hexanuclear derivatives **3** and **4** have an uncommon basal edge-bridged square pyramidal metallic skeleton. The bridging ligand of **3** is a doubly deprotonated apyPh ligand which caps the metallic square through the exocyclic N atom, while is attached to the Ru atom that bridges the edge of the square pyramid through the pyridine N atom. Complex **4** is structurally related to **3** but has a cyclometalated phenyl ring. It has been established that compound **2** is formed by reaction of **1** with H_2apyPh and that complex **3** is formed by reaction of **1** with [$Ru_3(CO)_{12}$]. While the hydrogenation of **4** gives **3**, the thermolysis of **3** gives **4** among other unidentified products. The reaction of the osmium cluster [$Os_3(CO)_{10}(MeCN)_2$] with H_2apyPh gives a 1:5 mixture of the edge-bridged decacarbonyl derivatives [$Os_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}HapyPh\text{-}N)(CO)_{10}$] (**5**) and [$Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}HapyPh\text{-}N,N)(CO)_{10}$] (**6**). Both compounds give the face-capped nonacarbonyl derivative [$Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HapyPh\text{-}N,N)(CO)_9$] (**7**) upon irradiation with UV light. Curiously, while complexes **5** and **7** are stable in refluxing toluene, the thermolysis of **6** gives a mixture of **5**, **7**, and the cyclometalated dihydride [$Os_3(\mu\text{-}H)_2(\mu\text{-}\eta^3\text{-}HapyC_6H_4\text{-}N,N,C)(CO)_9$] (**8**).

Introduction

We have previously carried out a thorough study of the synthesis and reactivity of carbonyl metal clusters derived from 2-aminopyridines.[1,2] Most of these clusters are trinuclear and contain a face-capping apy ligand (H_2apy = a generic 2-aminopyridine) that results from the coordination of the pyridine N atom and the activation of an N−H bond to give a bridging amido fragment and a hydride ligand, e.g., [$Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}Hapy\text{-}N,N)(CO)_9$] (Chart 1). Some of these complexes have been recognized as catalytic precursors for the hydrogenation,[3,4] dimerization,[5] polymerization,[5] and hydroformylation[6] of selected alkynes.

In a recent article, we have reported the reactivity of a particular member of the 2-aminopyridine family, 2-amino-7,8-benzoquinoline (H_2abqH), with triruthenium and triosmium carbonyls.[7] In ruthenium complexes, the coordination of the quinoline N atom triggers the cyclometalation of the benzo ring, e.g., [$Ru_3(\mu_3\text{-}\eta^3\text{-}Habq\text{-}N,N,C)(CO)_9$] (Chart 1). However, for osmium, the benzo ring in the 7,8-position hampers the coordination of the quinoline N atom and only a simple μ-amido derivative was obtained, [$Os_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}HabqH\text{-}N)(CO)_{10}$] (Chart

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[†] Dedicated to Prof. José Vicente, on the occasion of his 60th birthday.

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

(2) For relevant articles in the field, 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.; 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. (c) Cabeza, J. A.; Riera, V.; Trivedi, R.; Grepioni, F. *Organometallics* **2000**, *19*, 2043. (d) Cabeza, J. A.; del Río, I.; Riera, V.; García-Granda, S.; Sanni, S. B. *Organometallics* **1997**, *16*, 1743. (e) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; van der Maelen, J. F. *Organometallics* **1993**, *12*, 2973. (f) Andreu, P. L.; Cabeza, J. A.; Pellinghelli, M. A.; Riera, V.; Tiripicchio, A. *Inorg. Chem.* **1991**, *30*, 4611.

(3) Cabeza, J. A. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby P. R., Eds.; Wiley-VCH: Weinheim, 1999; p 715.

(4) For a review on alkyne hydrogenation mediated by 2-amidopyridine-bridged triruthenium carbonyl cluster complexes, see: Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A. *Synlett* **1995**, 579.

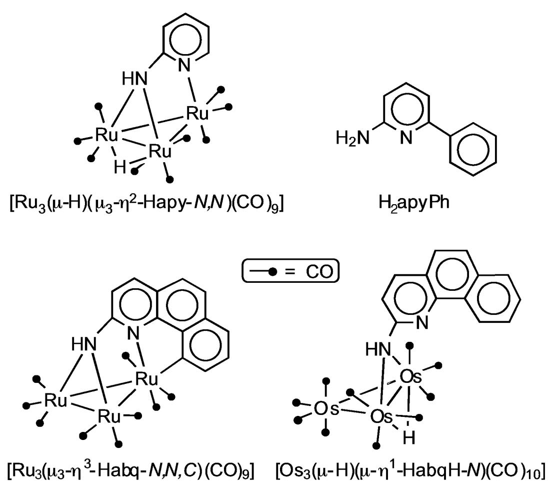
(5) Nombel, P.; Lugan, N.; Mulla, F.; Lavigne, G. *Organometallics* **1994**, *13*, 4673.

(6) Nombel, P.; Lugan, N.; Donnadieu, B.; Lavigne, G. *Organometallics* **1999**, *18*, 187.

(7) Cabeza, J. A.; del Río, I.; García-Granda, S.; Riera, V.; Suárez, M. *Organometallics* **2002**, *21*, 5055.

10.1021/om034040y CCC: $27.50

Chart 1



1). The cyclometalation of H_2abqH has also been observed in mononuclear iridium complexes.[8]

These results prompted us to study the reactivity of triruthenium and triosmium carbonyls with 2-amino-6-phenylpyridine (H_2apyPh, Chart 1). We were interested in knowing whether this ligand might present the same behavior as H_2abqH or behave as a "normal" 2-aminopyridine. In addition, as far as we are aware, no transition metal complexes derived from this ligand have hitherto been reported.

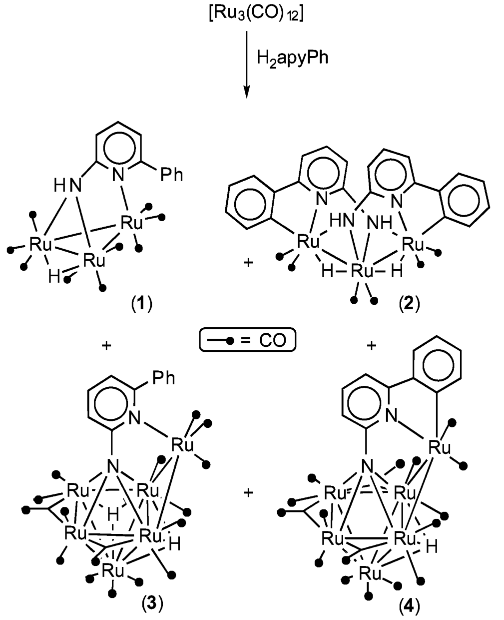
We now report that both cyclometalated and noncyclometalated products have been obtained from the reactions of H_2apyPh with triruthenium and triosmium carbonyl clusters. Interestingly, these reactions have led not only to trinuclear products but also to hexaruthenium derivatives of an uncommon metallic skeleton, basal edge-bridged square pyramid.[9]

Results

Synthesis of H_2apyPh. This compound[10] was prepared in 35% yield by amination of 2-phenylpyridine with sodium amide, following the method previously described for the synthesis of 2-amino-7,8-benzoquinoline,[8c] but using 2-phenylpyridine instead of 7,8-benzoquinoline.

Synthesis of Compounds 1–4. The reactions of $[Ru_3(CO)_{12}]$ with H_2apyPh led to mixtures of the trinuclear complexes $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HapyPh\text{-}N,N)(CO)_9]$ (**1**) and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^3\text{-}HapyC_6H_4\text{-}N,N,C)_2(CO)_6]$ (**2**) and the hexanuclear ones $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}apyPh\text{-}N,N)(\mu\text{-}CO)_2(CO)_{14}]$ (**3**) and $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\eta^3\text{-}apyC_6H_4\text{-}N,N,C)(\mu\text{-}CO)_3(CO)_{13}]$ (**4**) (Scheme 1). The yield of each product depended on the ratio of the reactants and the reaction conditions. Thus, at H_2apyPh to $[Ru_3(CO)_{12}]$ ratios greater than 1, complex **2** was the major product in refluxing toluene, whereas the highest yields of the hexanuclear derivatives **3** and **4** were obtained in refluxing xylene, using a H_2apyPh to $[Ru_3(CO)_{12}]$ ratio of 0.5 and adding the H_2apyPh in two portions, to minimize the formation of complex **2** and $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$.

Scheme 1. New Products Isolated from the Reaction of $[Ru_3(CO)_{12}]$ with H_2apyPh[a]



[a] Yields depend on the ratio of the reactants, reaction temperature, and reaction time.

Additional experiments were carried out with the purpose of establishing relationships between these products. Complex **1** reacted with $[Ru_3(CO)_{12}]$ (1:1 ratio) to give the hexanuclear derivatives **3** and **4**, as well as some **2** and $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$. Complex **1** also reacted with H_2apyPh to give **2** quantitatively. This indicates that in the reactions where $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ is observed, this complex is formed from $[Ru_3(CO)_{12}]$ and the dihydrogen that should be released when **1** reacts with H_2apyPh to give **2**. In addition, it was ascertained that complex **1** is thermally unstable, since it underwent decomposition into a mixture of products that contained complex **2** when its solutions were heated at temperatures higher than 70 °C.

These latter experiments explain why compound **1** was always a minor product in the reactions of $[Ru_3(CO)_{12}]$ with H_2apyPh. Even using a 1:1 $[Ru_3(CO)_{12}]$ to H_2apyPh ratio, the yield of **1** was never higher than 15%. With the aim to obtain compound **1** in higher yield, the activated complex $[Ru_3(CO)_{10}(MeCN)_2]$ was treated with H_2apyPh (1:1 ratio) in THF. Unfortunately, the reaction was very slow. After 2 h at room temperature, most of the $[Ru_3(CO)_{10}(MeCN)_2]$ decomposed into $[Ru_3(CO)_{12}]$ and only a 15% yield of compound **1** was obtained.

The thermolysis of the hexanuclear complex **3** in refluxing xylene gave a small amount of the cyclometalated derivative **4** and two unidentified products, of which at least one seemed to contain coordinated xylene (NMR), but it could not be characterized. To avoid the interference of xylene, the thermolysis was also carried out in diglime (140 °C, 3 h). In this case, the products

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[8] (a) Patel, B. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 13105. (b) Lee, D.-H.; Patel, B. P.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *Chem. Commun.* **1999**, 297. (c) Lee, D.-H.; Kwon, H. J.; Patel, B. P.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H. *Organometallics* **1999**, *18*, 1615. (d) Gruet, K.; Crabtree, R. H.; Lee, D.-H.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2000**, *19*, 2228.

[9] The synthesis of the hexaruthenium derivatives has been briefly communicated in a preliminary form: Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Riera, V.; Suárez, M.; García-Granda, S. *Dalton Trans.* **2003**, 2808.

[10] Goshaev, M.; Otroshchenko, O. S.; Sadykov, A. S.; Azimova, M. P. *Khim. Geterotsikl. Soedin.* **1972**, *12*, 1642; *Chem. Abstr.* **1973**, *78*, 58201t.

were **3**, **4**, and one of the unidentified complexes observed in the thermolysis in xylene, in a ratio of 1:0.5: 0.8, respectively.

The hexanuclear cyclometalated complex **4** observed in the reactions of $[Ru_3(CO)_{12}]$ with H_2apyPh seems to arise from more than one source, since in these reactions, complex **4** is formed after short reaction times, in yields only a bit lower than those of **3**. In addition, the thermal transformation of **3** into **4** is rather inefficient, even after long reaction times (see above). Therefore, complex **4** may also be formed by condensation of $[Ru_3(CO)_{12}]$ with a trinuclear cyclometalated species that would arise from complex **1** under the reaction conditions. Although such a cyclometalated species (that would contain either none or two hydride ligands) has not been detected, an orthometalated monohydride species was spectroscopically detected (NMR) as the major product of the thermolysis of compound **1** in 1,2-dichloroethane. Unfortunately, this species has not been fully characterized because it could not be isolated as a pure product (it decomposed on chromatographic supports). Most probably, the original orthometalated intermediate evolves to the observed monohydride species under the reaction conditions.

In addition, although it is clear that, in the reactions of $[Ru_3(CO)_{12}]$ with H_2apyPh, most of the hexanuclear complex **3** is formed by condensation of compound **1** with $[Ru_3(CO)_{12}]$ (this has been checked by condensing $[Ru_3(CO)_{12}]$ with trinuclear complexes analogous to **1** but derived from 2-aminopyridines without phenyl substituents[9]), a small amount of **3** can also arise from the hydrogenation of the cyclometalated complex **4**, since we checked that this reaction does take place and the release of hydrogen parallels the formation of compounds **2** and **4**. This argument also agrees with the proposal that, in the reactions of $[Ru_3(CO)_{12}]$ with H_2apyPh, complex **4** does not arise from complex **3**.

Characterization of Compounds 1−4. The composition and trinuclear nature of **1** was suggested by its microanalysis and mass spectrum. The presence of NH and hydride groups was indicated by its ^1H NMR spectrum, which contains singlets at 4.68 and −11.25 ppm, respectively. DEPT ^{13}C NMR spectra show five *C*O, six *C*H, and three *C* resonances, confirming the C_s symmetry of the compound. Its IR and NMR spectra are related to those of other μ_3-apy-bridged hydride nonacarbonyl triruthenium complexes.[11]

Although the microanalysis and mass spectrum of compound **2** indicated the presence of two $HapyC_6H_4$ ligands per Ru_3 unit, its ^1H and DEPT ^{13}C NMR spectra display only the resonances of one hydride, one metalated $HapyC_6H_4$ ligand, and three CO groups. The CO region of its IR spectrum is also very simple, showing three ν(CO) absorptions. The structure depicted for this complex in Scheme 1 is based on a comparison of its spectroscopic data with those of the 50-electron complex $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^3\text{-}Habq\text{-}N,N,C)_2(CO)_6]$, which was characterized by X-ray diffraction methods and has C_2 symmetry (the 2-fold axis passes through the central Ru atom).[7]

The structures of compounds **3** and **4** in solid state were determined by X-ray diffraction methods (Figures 1 and 2). As far as possible, a common atomic numbering scheme was used for both compounds to facilitate comparisons between related structural parameters (Table 1). Both compounds have a basal edge-bridged square pyramidal metallic skeleton (88 valence electrons). While the pyridine nitrogen N(2) of the bridging ligand is attached to the metal atom that spans the base of the square pyramid, Ru(3), the exocyclic nitrogen atom N(1), which now bears no hydrogen atoms, caps the metallic square, being ca. 0.06 Å closer to the metal atoms of the bridged edge, Ru(1) and Ru(2), than to Ru(4) and Ru(5). The Ru−Ru distances between the apex metal atom Ru(6) and the four basal ruthenium atoms are 0.1−0.2 Å longer than the remaining Ru−Ru distances. While the phenyl ring of **3** is uncoordinated and perpendicular to the pyridine plane, that of complex **4** is cyclometalated and coplanar with the pyridine ring,

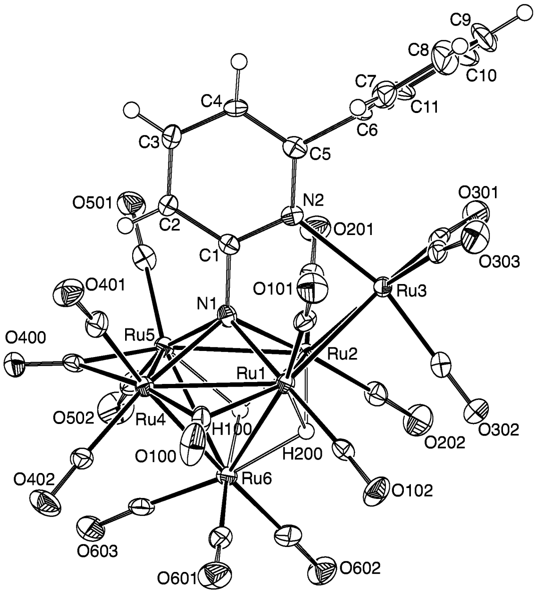

Figure 1. Molecular structure of compound **3**. Thermal ellipsoids are drawn at the 50% probability level. Both C and O atoms of the same carbonyl ligand bear the same number.

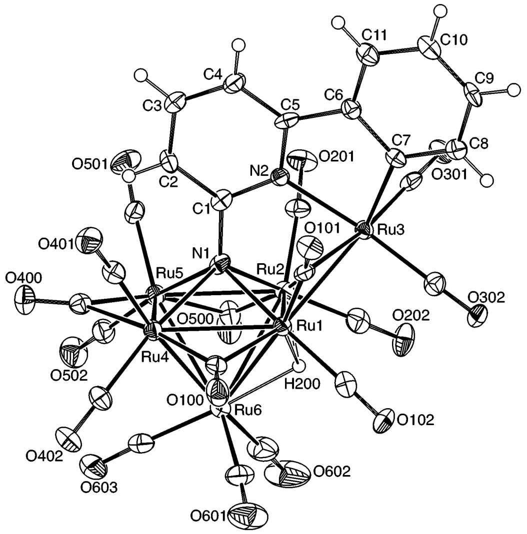

Figure 2. Molecular structure of compound **4**. Thermal ellipsoids are drawn at the 40% probability level. Both C and O atoms of the same carbonyl ligand bear the same number.

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[11] Andreu, P. L.; Cabeza, J. A.; Riera, V.; Jeannin, Y.; Miguel, D. *J. Chem. Soc., Dalton Trans.* **1990**, 2201.

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

	3	**4**
Ru(1)−Ru(2)	2.7724(5)	2.7713(9)
Ru(1)−Ru(3)	2.7763(5)	2.7532(9)
Ru(1)−Ru(4)	2.7513(5)	2.7334(9)
Ru(1)−Ru(6)	2.9791(6)	2.9059(9)
Ru(2)−Ru(3)	2.6841(6)	2.9018(8)
Ru(2)−Ru(5)	2.7648(5)	2.7176(9)
Ru(2)−Ru(6)	2.8761(5)	2.9035(9)
Ru(4)−Ru(5)	2.7381(5)	2.7300(9)
Ru(4)−Ru(6)	2.8470(5)	2.8431(9)
Ru(5)−Ru(6)	2.9307(5)	2.8558(9)
Ru(1)−N(1)	2.166(4)	2.168(7)
Ru(2)−N(1)	2.164(4)	2.139(7)
Ru(3)−N(2)	2.226(4)	2.121(7)
Ru(4)−N(1)	2.253(4)	2.225(7)
Ru(5)−N(1)	2.222(4)	2.215(7)
Ru(1)−C(100)	2.104(5)	2.080(10)
Ru(1)−C(101)	1.895(6)	1.900(9)
Ru(1)−C(102)	1.895(5)	1.889(10)
Ru(2)−C(201)	1.862(5)	1.895(9)
Ru(2)−C(202)	1.859(5)	1.886(10)
Ru(2)−C(500)		2.010(9)
Ru(3)−C(301)	1.906(5)	1.855(10)
Ru(3)−C(302)	1.883(6)	1.884(9)
Ru(3)−C(303)	1.953(6)	
Ru(4)−C(100)	2.064(5)	2.083(9)
Ru(4)−C(400)	2.183(5)	2.107(9)
Ru(4)−C(401)	1.992(6)	1.946(9)
Ru(4)−C(402)	1.882(5)	1.883(9)
Ru(5)−C(400)	2.008(5)	2.048(9)
Ru(5)−C(500)		2.207(10)
Ru(5)−C(501)	1.886(5)	1.910(10)
Ru(5)−C(502)	1.880(6)	1.895(9)
Ru(6)−C(601)	1.897(6)	1.914(11)
Ru(6)−C(602)	1.952(6)	1.920(11)
Ru(6)−C(603)	1.896(6)	1.885(10)
Ru(3)−C(7)		2.078(8)

being attached to Ru(3) through C(7). Such an interaction induces a lengthening of the Ru(2)−Ru(3) distance from 2.6841(6) Å in **3** to 2.9018(8) Å in **4**, as a consequence of the higher *trans* influence of the phenyl group with respect to that of the carbonyl ligand. While both compounds have a hydride ligand capping the Ru(1)−Ru(2)−Ru(6) face, complex **3** has an additional hydride capping the Ru(2)−Ru(5)−Ru(6) face. Both compounds contain 16 CO ligands, but they differ in the number of bridging carbonyls, since **3** has two, whereas **4** has three bridging CO ligands. In both cases, these carbonyl ligands span the edges of the metallic square that are not bridged by hydride ligands. The structure of **3** is comparable with that reported for $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}NCO_2Me\text{-}N,O)(\mu\text{-}CO)_2(CO)_{14}]$, in which the N atom caps the metallic square and the carbonyl oxygen atom is attached to the Ru atom that bridges the base of the square pyramid.[12]

The IR and ^1H NMR spectra of compounds **3** and **4** are in agreement with their solid-state structures. Thus, the absorptions of two and three bridging CO ligands are clearly observed in the IR spectra of **3** and **4**, respectively. In their ^1H NMR spectra, the hydride ligands of **3** are observed as two doublets at −11.46 and −15.87 ppm ($J = 2.4$ Hz), whereas that of **4** appears as a singlet at −16.62 ppm. The ^{13}C NMR spectra of ^{13}CO-enriched samples of these compounds indicate that their CO ligands are fluxional at room temperature (Figures 3 and 4). At −80 °C, compound **3** is rigid (the peak at 199.1 ppm contains two coincident resonances). However, fluxional processes are still active in compound **4** at −80 °C.

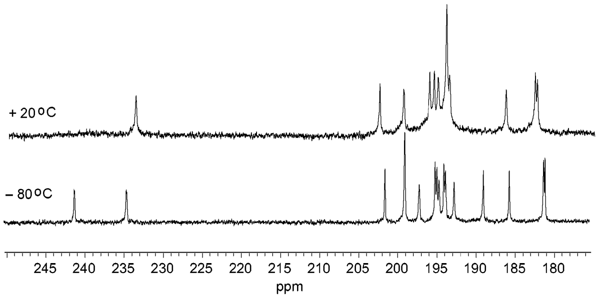


Figure 3. Carbonyl region of $^{13}C\{^1H\}$ NMR spectra (CD_2Cl_2, 75 MHz) of a ^{13}CO-enriched sample of compound **3** at two different temperatures.

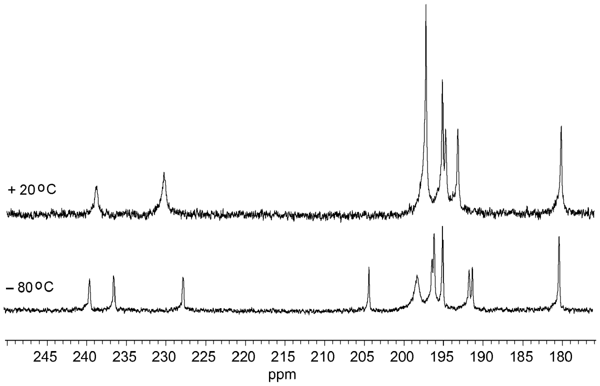
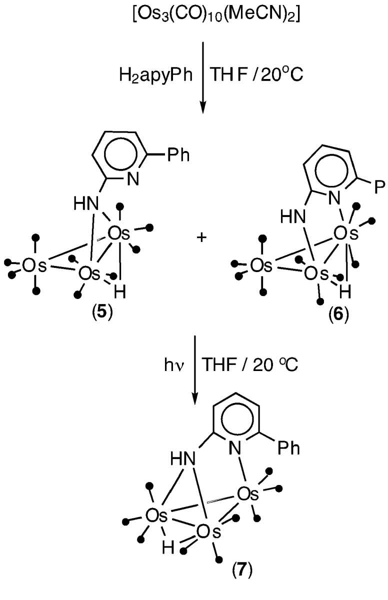


Figure 4. Carbonyl region of $^{13}C\{^1H\}$ NMR spectra (CD_2Cl_2, 75 MHz) of a ^{13}CO-enriched sample of compound **4** at two different temperatures.

Scheme 2



Synthesis of Compounds 5−8. H_2apyPh reacted with $[Os_3(CO)_{10}(MeCN)_2]$ in THF at room temperature to give a 1:5 mixture of the edge-bridged decacarbonyl derivatives $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}HapyPh\text{-}N)(CO)_{10}]$ (**5**) and $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}HapyPh\text{-}N,N)(CO)_{10}]$ (**6**), respectively (Scheme 2). Both compounds underwent decarbonylation upon irradiation with UV light to give the face-capped nonacarbonyl derivative $[Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HapyPh\text{-}N,N)(CO)_9]$ (**7**) in quantitative yield (Scheme 2).

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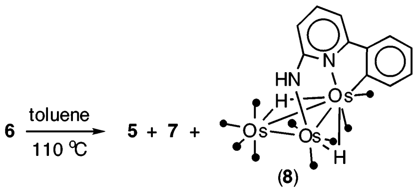
[12] Lee, K. K. H.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1996**, 1707.

Scheme 3



All attempts to transform these complexes into derivatives analogous to the ruthenium complexes **2**−**4**, described above, were unsuccessful.

Attempts were also made to transform compounds **5**−**7** into cyclometalated derivatives via thermal activation. While complexes **5** and **7** remained unaltered when they were heated in refluxing toluene for 5 h, complex **6** gave a 2:1:4 mixture of **5**, **7**, and the cyclometalated derivative $[Os_3(\mu\text{-}H)_2(\mu\text{-}\eta^3\text{-}HapyC_6H_4\text{-}N,N,C)(CO)_9]$ (**8**), respectively, after a short thermolysis (25 min) in refluxing toluene (Scheme 3).

Attempting the crystallization of complex **8** by slow diffusion of pentane into a solution of the complex in dichloromethane, we always obtained crystals of compound **7** after several days at room temperature. We subsequently checked that complex **8** undergoes a slow isomerization into complex **7** under visible light.

Characterization of Compounds 5−8. The osmium clusters **5** and **6** were characterized by analytical and spectroscopic methods. Their microanalyses and mass spectra confirmed their trinuclear nature and the presence of a HapyPh ligand and 10 CO groups. The presence of NH and hydride groups was indicated by their ^{1}H NMR spectra, which contain signals at 5.94 and −14.03 ppm, respectively, for **5**, and at 4.52 and −11.82 ppm, respectively, for **6**. Their DEPT ^{13}C NMR spectra show eight *C*H and three *C* resonances for the bridging ligand, indicating that it is not metalated. Five lines, corresponding to six carbonyl resonances, with intensities 1:1:2:2:4 (the latter contains two overlapping resonances) are also observed in the ^{13}C NMR spectrum of **5**, confirming a C_s symmetry for the complex. The asymmetry of **6** was indicated by its ^{13}C NMR spectrum, which shows 10 carbonyl resonances.

All these data are in agreement with the structures depicted in Scheme 2 for these complexes. For complex **5**, although an *endo* arrangement of the pendant 6-phenylpyrid-2-yl fragment would also be compatible with the analytical and spectroscopic data, the *exo* arrangement minimizes any steric interaction between the organic fragment and the axial carbonyl ligand on the unbridged Os atom. This structure is related to those of other amido-bridged decacarbonyl triosmium complexes,[13] including a derivative of H_2abqH (Chart 1),[7] but none of these amido ligands arise from 2-aminopyridines. On the contrary, the structure of compound **6** has been previously found for triosmium complexes derived from 2-aminopyridine,[14] di-(2-pyridyl)amine,[2a] and 7-azaindole.[15]

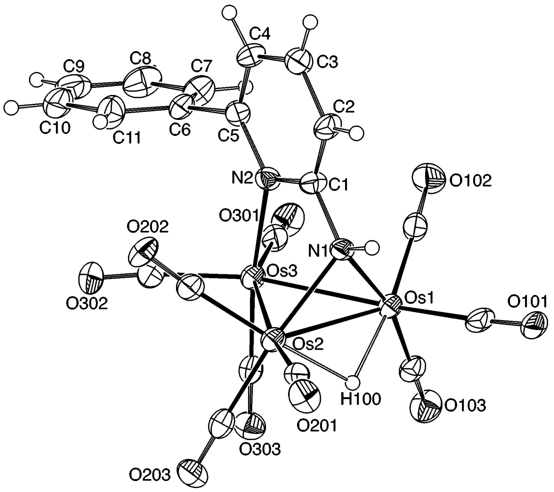


Figure 5. Molecular structure of compound **7**. Thermal ellipsoids are drawn at the 40% probability level. Both C and O atoms of the same carbonyl ligand bear the same number.

Table 2. Selected Interatomic Distances (Å) in Compound 7

Os(1)−Os(2)	2.8141(6)	Os(1)−Os(3)	2.7873(6)
Os(2)−Os(3)	2.7765(6)	Os(1)−N(1)	2.138(9)
Os(2)−N(1)	2.148(8)	Os(3)−N(2)	2.219(8)
Os(1)−C(101)	1.96(1)	Os(1)−C(102)	1.90(1)
Os(1)−C(103)	1.89(1)	Os(2)−C(201)	1.93(1)
Os(2)−C(202)	1.91(1)	Os(2)−C(203)	1.91(1)
Os(3)−C(301)	1.93(1)	Os(3)−C(302)	1.93(1)
Os(3)−C(303)	1.88(1)		

The solid-state structure of **7** was determined by X-ray diffraction methods (Figure 5, Table 2). The compound has C_s symmetry, with the 2-amidopyridine ligand capping the metal triangle and the hydride spanning the same Os−Os edge as the amido fragment. The phenyl ring is perpendicular to the pyridine plane. Overall, this structure is similar to those of analogous triosmium complexes derived from 2-aminopyridine,[14] di(2-pyridyl)amine,[2a] and 7-azaindole,[15] which also have related spectroscopic data in solution.

Compound **8** was characterized by analytical and spectroscopic methods. Their microanalyses and mass spectra confirmed its trinuclear nature, the presence of all the atoms of H_2apyPh, and nine CO groups. One NH and two hydride groups are observed in its ^{1}H NMR spectrum, which contains signals at 4.35, −13.02, and −13.32 ppm, respectively. Its DEPT ^{13}C NMR spectra show seven *C*H and four *C* resonances for the bridging ligand, indicating cyclometalation. Its asymmetry was confirmed by its ^{13}C NMR spectrum, which shows nine carbonyl resonances. These data strongly support the structure proposed for this complex in Scheme 3.

Discussion

A different behavior has been observed for triruthenium and triosmium clusters in their reactions with H_2apyPh. Triruthenium complexes analogous to the osmium derivatives **5** and **6** may be intermediates in the synthesis of **1**. However, they have not been detected. While complex **1** is the first product observed in the

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[13] See, for example: (a) Cabeza, J. A.; del Río, I.; Grepioni, F.; Riera, V. *Organometallics* **2000**, *19*, 4643. (b) Kong, F. S.; Kong, W. T. *J. Organomet. Chem.* **1999**, *589*, 180. (c) Hui, B. K. M.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1998**, 3977. (d) Dawoodi, Z.; Mays, M. J.; Hendrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 433.

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[15] Kong, F. S.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1997**, 1237.

reactions of $[Ru_3(CO)_{12}]$ and $[Ru_3(CO)_{10}(MeCN)_2]$ with H_2apyPh, the analogous triosmium cluster **7** is only formed forcing the elimination of CO ligands from the decacarbonyls **5** or **6** (irradiation with UV light). These findings should be related with the well-known fact that it is more difficult to substitute CO ligands in osmium than in ruthenium carbonyls.

The phenyl group of H_2apyPh rotates freely about the C−C bond that connects it with the pyridine fragment. This accounts for the fact that the chemistry described herein for H_2apyPh is considerably different from that reported for H_2abqH, which is planar and rigid, for which only two ruthenium and one osmium derivatives are known, namely, $[Ru_3(\mu_3\text{-}\eta^3\text{-Habq-}N,N,C)(CO)_9]$ (Chart 1), $[Ru_3(\mu\text{-H})_2(\mu_3\text{-}\eta^3\text{-Habq-}N,N,C)_2(CO)_6]$, and $[Os_3(\mu\text{-H})(\mu\text{-}\eta^1\text{-HabqH-}N)(CO)_{10}]$ (Chart 1).[7] The latter two compounds are structurally analogous to the H_2apyPh derivatives **2** and **5**, respectively. Steric reasons explain why no species derived from H_2abqH analogous to compounds **1**, **3**, **6**, and **7** are known (if the benzo ring is not metalated, it hampers the coordination of the pyridine N atom). Curiously, the metalated complex $[Ru_3(\mu_3\text{-}\eta^3\text{-Habq-}N,N,C)(CO)_9]$ is unique in that no related species derived from H_2apyPh is known.

The hexanuclear complexes **3** and **4** are noteworthy because of their uncommon metallic skeleton, basal edge-bridged square pyramid. To date, very few hexaruthenium cluster complexes of this type that have been reported, and they have been prepared in several steps from $[Ru_3(CO)_{12}]$ in low overall yields.[12,16,17] In fact, no efficient syntheses of hexanuclear complexes containing a basal edge-bridged square pyramidal metallic skeleton have hitherto been reported. It is interesting that the herein reported synthesis of compound **3** represents the first one-pot preparation of clusters of this type directly from $[Ru_3(CO)_{12}]$. Although the yields of compounds **3** and **4** are not high, these results led us to extend this synthetic method to no cyclometalable 2-aminopyridines. In this case, high yields of hexaruthenium derivatives have been obtained,[9] and this has allowed the study of their reactivity.[18]

The low tendency of osmium carbonyls to substitute their CO ligands may also explain why all attempts to make hexaosmium derivatives analogous to compound **3**, by treating complex **7** with $[Os_3(CO)_{10}(MeCN)_2]$, were unsuccessful. Attempts to prepare mixed-metal Os_3Ru_3 complexes, by treating either **1** with $[Os_3(CO)_{10}(MeCN)_2]$ or complex **7** with $[Ru_3(CO)_{10}(MeCN)_2]$, also failed.

Experimental Section

General Data. Solvents were dried over $Na[Ph_2CO]$ (THF, diethyl ether, hydrocarbons) or CaH_2 (dichloromethane, 1,2-dichloroethane, acetonitrile) and distilled under nitrogen prior to use. The term "xylene" refers to the commercial mixture of ortho, meta, and para isomers. The reactions were carried out under nitrogen, using Schlenk−vacuum line techniques, and were routinely monitored by solution IR spectroscopy and by spot TLC on silica gel. Photolytic reactions were carried out in Pyrex glass water-refrigerated jacketed Schlenk tubes, using a 400 W mercury lamp. $[Os_3(CO)_{10}(MeCN)_2]$[19] and ^{13}CO-enriched $[Ru_3(CO)_{12}]$ (ca. 20% enrichment)[20] were prepared as described elsewhere. Anhydrous Me_3NO was obtained by azeotropic distillation of $Me_3NO\cdot 2H_2O$ in toluene. Instrumentation was as previously reported.[7] Unless otherwise stated, NMR spectra were run at room temperature using internal $SiMe_4$ as standard ($\delta = 0$). MS data refer to the most abundant molecular ion isotopomer.

2-Amino-6-phenylpyridine. A suspension containing 2-phenylpyridine (5 mL, 0.035 mol), $NaNH_2$ (6.76 g, 0.173 mol), and *N*,*N*-dimethylaniline (15 mL) was heated at 160 °C for 3.5 h. The color changed from yellow to green and finally to dark violet. The solvent was removed under reduced pressure, and the oily red residue was hydrolyzed with water (10 mL). The aqueous phase was extracted with diethyl ether (3 × 15 mL), and the combined extracts were dried with anhydrous Na_2SO_4. The dried solution was evaporated to dryness to give a red-orange oil, which was washed with hexane (3 × 10 mL) to give the product as a yellow solid (2.09 g, 35%). Anal. Calcd for $C_{11}H_{10}N_2$ (fw = 170.21): C, 72.62; H, 5.92; N, 16.46. Found: C, 72.91; H, 6.01; N, 16.37. EI-MS (*m*/*z*): 171 [(M + 1)$^+$]. ^{1}H NMR ($CDCl_3$): δ 7.94 (d, br, *J* = 8.0 Hz, 2 H), 7.53−7.38 (m, 4 H), 7.09 (d, *J* = 7.4 Hz, 1 H), 6.45 (d, *J* = 8.0 Hz, 1 H), 4.54 (s, br, 2 H, NH_2). $^{13}C\{^1H\}$ NMR, DEPT ($CDCl_3$): δ 158.6 (C), 158.4 (C), 140.0 (C), 138.6 (CH), 128.9 (CH), 128.8 (2 CH), 127.1 (2 CH), 111.2 (CH), 107.4 (CH).

$[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HapyPh-}N,N)(CO)_9]$ (1). A solution of Me_3NO (39 mg, 0.520 mmol) in dichloromethane (10 mL) was slowly added to a cold (−78 °C) solution of $[Ru_3(CO)_{12}]$ (150 mg, 0.235 mmol) in 10:1 dichloromethane−acetonitrile (110 mL). After stirring for 10 min, solid H_2apyPh (48 mg, 0.282 mmol) was added. The solution was allowed to warm to room temperature, and the solvent was removed under reduced pressure. THF (40 mL) was added, and the resulting solution was stirred for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane (2 mL). This solution was separated by column chromatography on silica gel (2 × 10 cm). Hexane eluted some $[Ru_3(CO)_{12}]$. Hexane−dichloromethane (1:1) eluted an orange band that afforded compound **1** upon solvent removal (25 mg, 15%). Anal. Calcd for $C_{20}H_{10}N_2O_9Ru_3$ (fw = 725.55): C, 33.11; H, 1.39; N, 3.86. Found: C, 33.21; H, 1.25; N, 3.75. FAB-MS (*m*/*z*): 727 [M$^+$]. IR (CH_2Cl_2): ν_{CO} 2079 (m), 2050 (s), 2026 (vs), 1997 (s), 1987 (m), 1961 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.60−7.49 (m, 3 H), 7.51 (t, *J* = 7.7 Hz, 1 H), 7.34−7.30 (m, 2 H), 6.79 (dd, *J* = 7.7, 1.2 Hz, 1 H), 6.61 (dd, *J* = 7.7, 1.2 Hz, 1 H), 4.68 (s, br, 1 H, NH), −11.25 (s, 1 H). $^{13}C\{^1H\}$ NMR, DEPT ($Me_2CO\text{-}d_6$): δ 204.3 (CO), 203.5 (2 CO), 200.9 (2 CO), 199.9 (2 CO), 186.2 (2 CO), 180.9 (C), 165.2 (C), 143.5 (C), 140.8 (CH), 130.7 (CH), 130.5 (2 CH), 130.0 (2 CH), 121.9 (CH), 112.6 (CH).

$[Ru_3(\mu\text{-H})_2(\mu_3\text{-}\eta^3\text{-HapyC}_6H_4\text{-}N,N,C)_2(CO)_6]$ (2). A solution of compound **1** (70 mg, 0.097 mmol) and H_2apyPh (16 mg, 0.094 mmol) in toluene (25 mL) was stirred at reflux temperature for 135 min. The color changed from orange to deep red. The solvent was removed under reduced pressure and the residue washed with hexane (2 × 5 mL) to give compound **2** as an orange-yellow solid (75 mg, 96%). Anal. Calcd for $C_{28}H_{18}N_4O_6Ru_3$ (fw = 809.69): C, 41.54; H, 2.24; N, 6.92. Found: C, 41.63; H, 2.26; N, 6.85. FAB-MS (*m*/*z*): 811 [M$^+$]. IR (CH_2Cl_2): ν_{CO} 2051 (vs), 2030 (s), 1976 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.06 (d, *J* = 7.5 Hz, 1 H), 7.32 (t, *J* = 7.9 Hz, 1 H), 7.18 (d, *J* = 7.5, Hz, 1 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.85 (d, *J* = 7.9 Hz, 1 H), 6.77 (d, *J* = 7.5 Hz, 1 H), 6.01 (d, *J* = 7.9 Hz, 1 H), 4.32 (s, br, 1 H, NH), −9.40 (s, 1 H). $^{13}C\{^1H\}$ NMR, DEPT (CD_2Cl_2): δ 199.3 (CO), 199.2 (CO), 197.9 (CO), 168.2 (C), 164.6 (C), 161.9 (C),

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144.4(C), 139.5 (CH), 136.3 (CH), 129.2 (CH), 125.6 (CH), 123.3 (CH), 118.6 (CH), 111.2 (CH).

[Ru$_6$(μ_3-H)$_2$(μ_5-η^2-apyPh-*N,N*)(μ-CO)$_2$(CO)$_{14}$] (3) and [Ru$_6$(μ_3-H)(μ_5-η^3-apyC$_6$H$_4$-*N,N,C*)(μ-CO)$_3$(CO)$_{13}$] (4). A solution of [Ru$_3$(CO)$_{12}$] (100 mg, 0.157 mmol) and H$_2$apyPh (6 mg, 0.035 mmol) in xylene (7 mL) was heated at reflux temperature for 15 min. Then, an additional amount of H$_2$apyPh (7 mg, 0.041 mmol) was added, and the solution was heated further for 15 min. The color changed from orange to dark brown. The solvent was removed under high vacuum, and the residue was dissolved in dichloromethane (5 mL). This solution was placed onto of a silica gel column (2 × 15 cm) packed in hexane. Hexane eluted a small amount of [Ru$_4$(μ-H)$_4$(CO)$_{12}$]. Hexane−diethyl ether (50:1) eluted three bands. The first, dark brown, led to compound **3** after solvent removal (33 mg, 35%). The second, dark green, led to compound **4** after solvent removal (10 mg, 11%). The third band, yellow, contained compound **2** (10 mg, 32%).

Data for 3. Anal. Calcd for $C_{27}H_{10}N_2O_{16}Ru_6$ (fw = 1224.86): C, 26.48; H, 0.82; N, 2.29. Found: C, 26.44; H, 0.75; N, 2.32. FAB-MS (*m*/*z*): 1198 [(M − CO)$^+$]. IR (CH$_2$Cl$_2$): ν_{CO} 2094 (m), 2069 (s), 2048 (s), 2032 (vs), 2013 (m, sh), 1994 (w, sh), 1972 (m), 1951 (w, sh), 1859 (m, br), 1827 (m, br) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.57−7.48 (m, 3 H), 7.32 (dd, *J* = 8.3, 7.5 Hz, 1 H), 7.20 (d, br, *J* = 7.1 Hz, 1 H), 7.11 (d, br, *J* = 7.5 Hz, 1 H), 6.62 (dd, *J* = 7.1, 1.2 Hz, 1 H), 5.90 (dd, *J* = 8.3, 1.2 Hz, 1 H), −11.46 (d, *J* = 2.4 Hz, 1 H), −15.87 (d, *J* = 2.4 Hz, 1 H). ^{13}C{^{1}H} NMR, DEPT (CD$_2$Cl$_2$): δ 233.6 (CO), 202.3 (CO), 199.2 (CO), 195.9 (CO), 195.3 (CO), 194.8 (CO), 193.7 (CO), 193.3 (CO), 188.3 (C), 186.1 (CO), 182.3 (CO), 182.0 (CO), 161.2 (C), 140.3 (C), 139.3 (CH), 130.0 (CH), 129.2 (3 CH), 128.5 (CH), 121.1 (CH), 116.5 (CH).

Data for 4. Anal. Calcd for $C_{27}H_8N_2O_{16}Ru_6$ (fw = 1222.86): C, 26.52; H, 0.66; N, 2.29. Found: C, 26.41; H, 0.57; N, 2.22. FAB-MS (*m*/*z*): 1224 [M$^+$]. IR (CH$_2$Cl$_2$): ν_{CO} 2088 (m), 2050 (vs), 2028 (m), 2014 (m), 1997 (w, sh), 1961 (w, sh), 1880 (w), 1860 (m), 1841 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.85 (dd, *J* = 7.5, 0.8 Hz 1 H), 7.64 (dd, *J* = 7.9, 1.6 Hz, 1 H), 7.39 (td, *J* = 7.5, 1.6 Hz, 1 H), 7.24−7.13 (m, 3 H), 5.15 (d, *J* = 7.1 Hz, 1 H), −16.62 (s, br, 1 H). ^{13}C{^{1}H} NMR, DEPT (CD$_2$Cl$_2$): δ 238.6 (CO), 230.2 (br, CO), 197.2 (CO), 195.1 (CO), 194.7 (CO), 193.1 (CO), 186.3 (C), 180.1 (CO), 162.8 (C), 161.6 (C), 142.2 (C), 139.1 (CH), 137.9 (CH), 132.6 (CH), 126.0 (CH), 124.7 (CH), 115.6 (CH), 111.6 (CH).

Reaction of [Ru$_3$(CO)$_{12}$] with 2.2 Equiv of H$_2$apyPh. A solution of [Ru$_3$(CO)$_{12}$] (100 mg, 0.156 mmol) and H$_2$apyPh (58 mg, 0.341 mmol) in toluene (20 mL) was heated at reflux temperature for 3 h. The color changed from orange to dark brown. The solvent was removed under high vacuum. A ^{1}H NMR spectrum of the residue showed the presence of compounds **1**, **2**, **3**, and [Ru$_4$(μ-H)$_4$CO)$_{12}$] in 6:100:12:1.5 molar ratio.

Reaction of Compound 1 with [Ru$_3$(CO)$_{12}$]. A solution of compound **1** (50 mg, 0.069 mmol) and [Ru$_3$(CO)$_{12}$] (44 mg, 0.069 mmol) in toluene (25 mL) was stirred at reflux temperature until the complete disappearance of [Ru$_3$(CO)$_{12}$] was observed by IR spectroscopy (ca. 105 min). The color changed from orange to dark brown. The solvent was removed under high vacuum, and the residue was dissolved in dichloromethane (3 mL). This solution was placed onto a silica gel column (2 × 15 cm) packed in hexane. Hexane eluted some [Ru$_4$(μ-H)$_4$(CO)$_{12}$]. Hexane−diethyl ether (50:1) eluted three bands. The first, dark brown, led to compound **3** after solvent removal (6 mg, 7%). The second, dark green, led to compound **4** after solvent removal (4 mg, 5%). The third band, yellow, contained compound **2** (12 mg, 21%).

Thermolysis of Compound 1. Compound **1** (50 mg, 0.069 mmol) was heated in 1,2-dichloroethane at reflux temperature for 5 h. The solvent was removed under vacuum. The ^{1}H NMR spectrum of the crude residue indicated the presence of two hydrido derivatives, with hydride integrals in a 1:4 ratio, corresponding to compound **2** and an as yet unidentified product that contains a metalated HapyC$_6$H$_4$ ligand (an intact NH fragment was observed in the ^{1}H NMR spectrum, and the resonances of all seven CH and the three C groups of HapyC$_6$H$_4$ were observed in the DEPT ^{13}C spectra). This compound could not be fully characterized, because it was never obtained pure and underwent decomposition upon all attempted chromatographic separations (it decomposed on the chromatographic supports). Thermolysis of **1** in refluxing toluene led to compound **2** and extensive untractable decomposition.

Thermolysis of Compound 3. A solution of compound **3** (20 mg, 0.016 mmol) in xylene (3 mL) was heated at reflux temperature for 45 min. The color changed from dark brown to very dark green. The solvent was removed under vacuum. The ^{1}H NMR spectrum of the crude residue indicated the presence of complexes **3**, **4**, and two as yet unidentified dihydrido derivatives **X** and **Y**, in a 1:1:1:5 ratio, respectively. The latter two show hydride ligands at −12.70 and −13.30 (**X**) and −16.32 and −16.34 (**Y**) ppm. Compound **X** underwent decomposition upon all attempted chromatographic separations (it decomposed on the chromatographic supports). Compound **Y**, dark green, was successfully separated. Its analysis and ^{1}H NMR spectrum suggested the presence of coordinated xylene, but its structure has not yet been determined. Themolysis of **1** in diglime (140 °C, 3 h) led to a 1:0.5:0.8 mixture of **3**, **4**, and **X**.

Hydrogenation of Compound 4. Hydrogen was slowly bubbled for 1 h through a solution of complex **4** (10 mg, 0.008 mmol) in THF (20 mL) at reflux temperature. The color changed from dark green to dark brown. The IR spectrum of this solution indicated the quantitative transformation of complex **4** into **3**.

[Os$_3$(μ-H)(μ-η^1-HapyPh-*N*)(CO)$_{10}$] (5) and [Os$_3$(μ-H)(μ-η^2-HapyPh-*N,N*)(CO)$_{10}$] (6). A THF solution (20 mL) of H$_2$apyPh (25 mg, 0.147 mmol) and [Os$_3$(CO)$_{10}$(MeCN)$_2$] (100 mg, 0.107 mmol) was stirred at room temperature for 4 h and 30 min. The color changed from lime yellow to yellow. The solvent was removed under reduced pressure, the residue was dissolved in dichloromethane (1 mL), and the resulting solution was separated by TLC on silica gel. Hexane−dichloromethane (2:1) eluted five yellow bands that were extracted with dichloromethane and afforded, in order of elution, a trace amount of [Os$_3$(CO)$_{12}$], [Os$_3$(μ-H)(μ-η^1-HapyPh-*N*)(CO)$_{10}$] (**5**) (12 mg, 11%), [Os$_3$(μ-H)(μ-η^2-HapyPh-*N,N*)(CO)$_{10}$] (**6**) (60 mg, 55%), [Os$_3$(μ-H)(μ_3-η^2-HapyPh-*N,N*)(CO)$_9$] (**7**) (5 mg, 5%), and a trace amount of an as yet unidentified compound.

Data for 5. Anal. Calcd for $C_{21}H_{10}N_2O_{10}Os_3$ (fw = 1020.92): C, 24.71; H, 0.99; N, 2.74. Found: C, 24.77; H, 1.06; N, 2.71. FAB-MS (*m*/*z*): 1022 [M$^+$]. IR (CH$_2$Cl$_2$): ν_{CO} 2103 (w), 2067 (s), 2051 (m), 2015 (m), 1994 (m, br), 1977 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.08 (d, *J* = 8.1 Hz, 1 H), 8.08 (d, *J* = 7.7 Hz, 1 H), 7.63 (t, *J* = 7.7 Hz, 1 H), 7.54−7.47 (m, 4 H), 6.88 (d, *J* = 7.7 Hz, 1 H), 5.94 (s, br, 1 H, NH), −14.03 (d, *J* = 2.6 Hz, 1 H). ^{13}C{^{1}H} NMR, DEPT (CD$_2$Cl$_2$): δ 190.1 (CO), 181.6 (CO), 177.5 (2 CO), 176.5 (2 CO), 172.5 (4 CO), 170.0 (C), 155.3 (C), 138.7 (CH), 137.3 (C), 129.5 (CH), 128.6 (2 CH), 126.7 (2 CH), 116.8 (CH), 110.8 (CH).

Data for 6. Anal. Calcd for $C_{21}H_{10}N_2O_{10}Os_3$ (fw = 1020.92): C, 24.71; H, 0.99; N, 2.74. Found: C, 24.81; H, 1.04; N, 2.69. FAB-MS (*m*/*z*): 1022 [M$^+$]. IR (CH$_2$Cl$_2$): ν_{CO} 2104 (m), 2064 (vs), 2054 (s), 2015 (s, br), 1993 (m), 1979 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): 7.60−7.43 (m, 4 H), 6.90 (d, br, *J* = 8.0 Hz, 1 H), 6.83 (dd, *J* = 8.7, 6.8 Hz, 1 H), 6.22 (dd, *J* = 8.7, 1.2 Hz, 1 H), 5.91 (dd, *J* = 6.8, 1.2 Hz, 1 H), 4.52 (s, br, 1 H, NH), −11.82 (s, 1 H). ^{13}C{^{1}H} NMR, DEPT (CD$_2$Cl$_2$): δ 183.7 (CO), 182.4 (CO), 178.0 (CO), 177.4 (CO), 176.1 (CO), 175.1 (CO), 174.2 (CO), 173.9 (CO), 172.7 (CO), 172.6 (CO), 170.2 (C), 160.7 (C), 145.4 (C), 134.7(CH), 129.9 (CH), 129.3 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 117.0 (CH), 109.9 (CH).

Table 3. Crystal, Measurement, and Refinement Data for $3\cdot(CH_2Cl_2)_{0.5}$, 4, and 7

	$\mathbf{3}\cdot(CH_2Cl_2)_{0.5}$	**4**	**7**
formula	$C_{27.5}H_{11}ClN_2O_{16}Ru_6$	$C_{27}H_8N_2O_{16}Ru_6$	$C_{20}H_{10}N_2O_9Os_3$
fw	1267.25	1222.77	992.90
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/a$
a, Å	11.8240(3)	10.1497(3)	16.0037(5)
b, Å	15.0404(4)	10.6673(3)	8.2977(3)
c, Å	19.4733(5)	30.1217(9)	17.6828(6)
β, deg	95.778(2)	92.410(2)	101.808(2)
vol, Å^3	3445.5(1)	3258.4(1)	2298.5(1)
Z	4	4	4
$F(000)$	2396	2304	1776
D_{calcd}, g cm^{-3}	2.443	2.493	2.869
radiation (λ, Å)	Cu Kα (1.54180)	Cu Kα (1.54180)	Cu Kα (1.54180)
μ, mm^{-1}	22.166	22.667	31.131
cryst size, mm	0.12 × 0.10 × 0.10	0.10 × 0.08 × 0.05	0.15 × 0.10 × 0.07
temp, K	120(2)	120(2)	120(2)
θ limits, deg	3.72 to 68.37	2.94 to 68.28	2.55 to 68.35
min./max. h, k, l	0/14, 0/18, −23/22	0/12, 0/12, −36/36	−19/18, 0/10, 0/21
no. of reflns collected	33 790	65 586	39 106
no. of unique reflns	6283	5973	4219
no. of reflns with $I > 2\sigma(I)$	5557	4727	3706
absorp corr	XABS	SORTAV	SORTAV
max./min. transmn	0.112/0.080	0.320/0.164	0.095/0.062
no. of params/restraints	495/0	460/0	310/7
GOF on F^2	1.056	1.017	1.048
final R_1 (on F, $I > 2\sigma(I)$)	0.0304	0.0450	0.0524
final wR_2 (on F^2, all data)	0.1012	0.1452	0.1357
max./min. $\Delta\rho$, e Å^{-3}	1.598/−1.009	1.999/−1.319	2.851/−2.925

$[Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HapyPh\text{-}N,N)(CO)_9]$ (7). A THF solution (20 mL) of compound **6** (30 mg, 0.029 mmol) was irradiated with UV light for 5 min, maintaining a gentle bubbling of dinitrogen through the solution. No color change was observed, but the IR spectrum showed the complete disappearance of the starting material. The solvent was removed under reduced pressure, and the residue was washed with hexane (2 × 5 mL) to give complex **7** as a yellow solid (26 mg, 90%). Similar results were obtained using compound **5** as starting material. Anal. Calcd for $C_{20}H_{10}N_2O_9Os_3$ (fw = 992.91): C, 24.19; H, 1.02; N, 2.82. Found: C, 24.33; H, 1.08; N, 2.80. FAB-MS (m/z): 994 [M$^+$]. IR (CH_2Cl_2): ν_{CO} 2081 (w), 2051 (vs), 2022 (s), 1991 (s), 1978 (m), 1954 (w), 1943 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): 7.65 (t, J = 7.8 Hz, 1 H), 7.57−7.30 (m, 5 H), 6.80 (dd, J = 7.8, 1.2 Hz, 1 H), 6.60 (dd, J = 7.8, 1.2 Hz, 1 H), 5.05 (s, br, 1 H, NH), −12.82 (s, 1 H). ^{13}C{^{1}H} NMR, DEPT (CD_2Cl_2): δ 188.8 (2 CO), 179.9 (2 CO), 177.3 (3 CO), 174.8 (2 CO), 171.4 (C), 164.9 (C), 142.0 (C), 137.8 (CH), 129.3 (CH), 128.9 (2 CH), 128.2 (2 CH), 121.2 (CH), 112.5 (CH).

Thermolysis of Compounds 5 and 7. A solution of **5** (20 mg, 0.020 mmol) in toluene (20 mL) was heated at reflux temperature for 5 h. The IR spectrum of the solution showed only the presence of the starting material. Identical results were obtained using **7** as starting material.

$[Os_3(\mu\text{-}H)_2(\mu\text{-}\eta^3\text{-}HapyC_6H_4\text{-}N,N,C)(CO)_9]$ (8). A solution of compound **6** (45 mg, 0.044 mmol) in toluene was heated at reflux temperature for 25 min. No color change was observed. The solvent was removed under reduced pressure, the residue was dissolved in THF (5 mL), and the resulting solution was separated by TLC on silica gel. Hexane−dichloromethane (2:1) eluted three yellow bands. The first one, in order of elution, contained complex **5** (7 mg, 16%). The second band yielded complex **8** (15 mg, 34%). The third one gave complex **7** (4 mg, 8%). Compound **8** is unstable in solution at room temperature, being transformed into complex **7** over a period of several days under visible light. Anal. Calcd for $C_{20}H_{10}N_2O_9Os_3$ (fw = 992.91): C, 24.19; H, 1.02; N, 2.82. Found: C, 24.26; H, 1.10; N, 2.77. FAB-MS (m/z): 994 [M$^+$]. IR (CH_2Cl_2): ν_{CO} 2127 (w), 2075 (m), 2048 (s), 2032 (m), 1995 (w), 1986 (w), 1953 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): 8.16 (d, J = 7.2 Hz, 1 H), 7.72 (d, J = 8.5 Hz, 1 H), 7.27 (td, J = 7.2 1.2 Hz, 1 H), 7.18 (td, J = 7.2 1.2 Hz, 1 H), 7.02 (t, J = 8.5 Hz, 1 H), 6.85 (d, J = 7.2 Hz, 1 H), 6.36 (d, J = 8.5 Hz, 1 H), 4.35 (s, br, 1 H, NH), −13.02 (s, 1 H), −13.32 (s, 1 H). ^{13}C{^{1}H} NMR, DEPT (CD_2Cl_2): δ 181.8 (CO), 175.0 (CO), 174.7 (CO), 174.5 (CO), 174.3 (CO), 173.3 (CO), 172.2 (CO), 171.1 (CO), 169.9 (CO), 166.6 (C), 162.2 (C), 146.6 (C), 144.5 (C), 139.4 (CH), 134.7 (CH), 129.8 (CH), 124.0 (CH), 123.3 (CH), 114.4 (CH), 101.9 (CH).

X-ray Structures of Compounds $3\cdot(CH_2Cl_2)_{0.5}$, 4, and 7. A selection of crystal, measurement, and refinement data are given in Table 3. Diffraction data were collected on a Nonius Kappa-CCD diffractometer equipped with a 95 mm CCD camera on a κ-goniostat, using graphite-monochromated Cu Kα radiation. Data were reduced to F_o^2 values. Empirical absorption corrections were applied using XABS2[21] for $\mathbf{3}\cdot(CH_2Cl_2)_{0.5}$ or SORTAV[22] for **4** and **7**. The structures were solved by Patterson interpretation using the program DIRDIF-96.[23] Isotropic and full matrix anisotropic least-squares refinements were carried out using SHELXL-97.[24] The dichloromethane solvent molecule of $\mathbf{3}\cdot(CH_2Cl_2)_{0.5}$ was disordered over two equally populated positions. All non H atoms were refined anisotropically. Hydrogen atoms H100 and H200 of $\mathbf{3}\cdot(CH_2Cl_2)_{0.5}$ were located in the corresponding Fourier maps, and their coordinates and thermal parameters were refined. The positions of the hydrides H100 of **4** and **7** were calculated using the program XHYDEX,[25] and their coordinates and thermal parameters were fixed. All the remaining hydrogen atom positions were geometrically calculated and were refined riding on their parent atoms, except for H1 of compound **7**, which was refined with fixed N−H bond distance and fixed thermal parameter. The molecular plots were made with the EUCLID program package.[26] The WINGX program system[27] was used throughout the structure determinations.

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Supporting Information Available: Crystallographic data in CIF format for **3**·$(CH_2Cl_2)_{0.5}$, **4**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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