Organometallics **2002,** *21,* 5055−5059 5055

Triruthenium and Triosmium Carbonyl Cluster Complexes Containing Bridging Ligands Derived from 2-Amino-7,8-benzoquinoline

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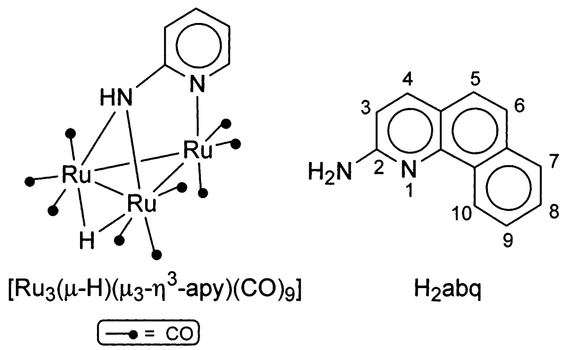
Received July 16, 2002

The ruthenium cluster complexes [$Ru_3(\mu_3$-η^3-abq-*C,N,N*)$(CO)_9$] (**1**) and [$Ru_3(\mu$-$H)_2(\mu_3$-η^3-abq-*C,N,N*)$_2(CO)_6$] (**2**) (H_2abq = 2-amino-7,8-benzoquinoline) have been stepwise prepared from [$Ru_3(CO)_{10}(MeCN)_2$]. Both compounds contain cyclometalated abq ligands which span a Ru−Ru edge through the N atom of an amido fragment and chelate the remaining Ru atom through both the quinolinic N atom and the C atom of the cyclometalated ring. For steric reasons, the cyclometalation is responsible for the observation of short Ru−N_{amido} bond lengths. The reaction of the osmium cluster [$Os_3(CO)_{10}(MeCN)_2$] with H_2abq gives the amido-bridged decacarbonyl derivative [$Os_3(\mu$-H$)(\mu$-η^1-Habq-*N*)$(CO)_{10}$] (**3**). Curiously, while complex **3** is stable in refluxing toluene, the ruthenium analogue of **3** has not been detected. Compounds **1**−**3** represent the first trinuclear carbonyl clusters containing ligands derived from 2-amino-7,8-benzoquinoline.

Introduction

We have previously carried out a thorough study of the synthesis and reactivity of carbonylmetal clusters derived from 2-aminopyridines.[1,2] Most of these clusters are trinuclear and contain a face-capping apy ligand (Hapy = a generic 2-aminopyridine) that results from the coordination of the pyridinic N atom and the activation of an N−H bond to give a bridging amido fragment and a hydride ligand, e.g., [$Ru_3(\mu$-H$)(\mu_3$-η^2-apy-*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.

Chart 1



[$Ru_3(\mu$-H$)(\mu_3$-η^3-apy$)(CO)_9$]

H_2abq

2-Amino-7,8-benzoquinoline (H_2abq) can be considered as a member of the 2-aminopyridine family. However, its carbonyl cluster chemistry was expected to be quite different from that of "normal" 2-aminopyridines, because the coordination of the quinolinic N atom should either (a) be hampered by the presence of the benzo ring in the 7,8-position, in particular the hydrogen atom on C^{10} (Chart 1), or (b) trigger the cyclometalation of the benzo ring by activating the C^{10}−H bond. The latter case was very tempting to us because it was expected to lead to trinuclear dihydrido derivatives (with a different reactivity from that of monohydrido apy derivatives) and it could be the first stage of a pathway leading to C^{10}-functionalized 2-amino-7,8-benzoquinolines. The cyclometalation of 2-amino-7,8-benzoquinoline has already been observed in mononuclear iridium complexes,[7] which, to our knowledge, are the only transition metal derivatives of this ligand reported to date.

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(1) 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 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.

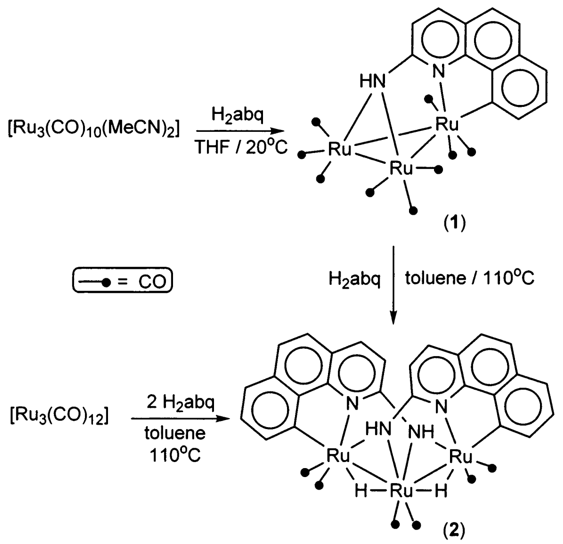
(4) For a review on alkyne hydrogenation mediated by 2-amidopyridine-bridged triruthenium carbonyl cluster complexes, see: Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A. *Synlett* **1995**, 579.

(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.

10.1021/om0205647 CCC: $22.00
Publication on Web 10/09/2002

Scheme 1



We now report the reactions of H_2abq with triruthenium and triosmium carbonyl clusters. Interestingly, cyclometalated products have been obtained for ruthenium, but not for osmium.

Results

Synthesis of Compounds 1−3. The reaction of $[Ru_3(CO)_{10}(MeCN)_2]$ with 1 equiv of H_2abq, in THF at room temperature, led to the cyclometalated complex $[Ru_3(\mu_3\text{-}\eta^3\text{-abq-}C,N,N)(CO)_9]$ (**1**, Scheme 1) in moderate yield (20−25%). $[Ru_4(\mu_3\text{-}H)_4(CO)_{12}]$ was a byproduct of this reaction. Although complex **1** did not react with more H_2abq at room temperature, it led to the dihydrido derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^3\text{-abq-}C,N,N)_2(CO)_6]$ (**2**, Scheme 1) when it was treated with H_2abq in refluxing toluene.

All attempts to make compound **1** from $[Ru_3(CO)_{12}]$ and H_2abq were unsuccessful. No reaction was observed in refluxing THF. In refluxing toluene, complex **2** and $[Ru_4(\mu_3\text{-}H)_4(CO)_{12}]$ were the only isolated products, regardless of the ratio of the reactants. The best yield of **2** (32%) was obtained using a $[Ru_3(CO)_{12}]$ to H_2abq ratio of 2.2 in a 3 h reaction in refluxing toluene.

Treatment of $[Os_3(CO)_{10}(MeCN)_2]$ with H_2abq in THF at room temperature led to the amido-bridged derivative $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{-Habq-}N)(CO)_{10}]$ (**3**) in 40% yield (Scheme 2). This compound contains a pendant 7,8-benzoquinol-2-yl fragment. All attempts to transform this complex into a derivative analogous to the ruthenium complexes mentioned above were unsuccessful. No changes were observed when it was irradiated with UV light for 2 h or when it was heated in toluene at reflux temperature for 2 h.

Characterization of Compound 1. The composition and trinuclear nature of **1** was suggested by its microanalysis and mass spectrum. The presence of an NH group was indicated by its ^1H NMR spectrum, which contains a broad singlet at 5.39 ppm and shows no signals attributable to hydride ligands. DEPT ^{13}C NMR spectra show seven *C*H and six *C* resonances, indicating the metalation of the bridging ligand. The carbonyl ligands are fluxional at room temperature, since they all appear as a broad singlet in the ^{13}C NMR spectrum.

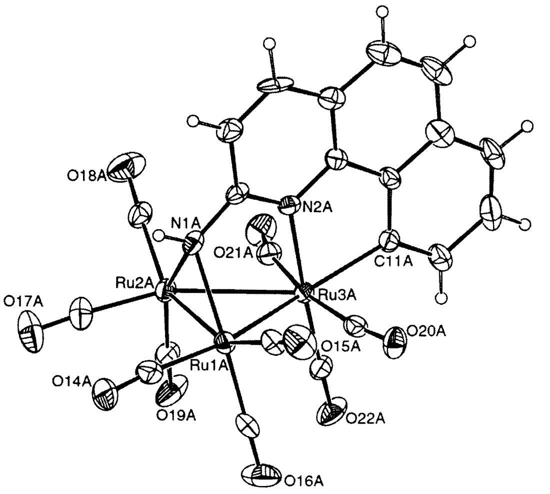
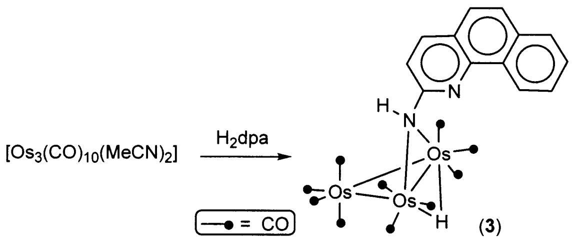


Figure 1. Molecular structure of compound **1** (only one of the two crystallographically independent molecules is shown). Thermal ellipsoids are drawn at the 30% probability level. Selected interatomic distances (Å): Ru(1A)−Ru(2A) 2.609(1), Ru(1A)−Ru(3A) 2.893(1), Ru(2A)−Ru(3A) 2.871(1), Ru(1A)−N(1A) 2.163(6), Ru(2A)−N(1A) 2.139(7), Ru(3A)−N(2A) 2.112(6), Ru(3A)−C(11A) 2.116(8).

Scheme 2



The structure of this cluster was unambiguously determined by X-ray diffraction methods. Figure 1 shows a view of one of the two independent but chemically equivalent molecules found in the asymmetric unit. Its caption contains a selection of structural parameters. The cluster is a closed 48-electron species of C_s symmetry (noncrystallographic), in which the planar abq ligand spans a Ru−Ru edge through the N atom of the amido fragment and chelates the remaining Ru atom through both the quinolinic N atom and the C atom of the cyclometalated ring. The cluster shell is completed with nine CO ligands.

Although the N atoms of the ligand are attached to the Ru_3 triangle in an analogous way as that found in many triruthenium clusters containing apy ligands,[1,2,5,6] a comparison of the Ru−C and Ru−N bond distances involving the abq ligand in **1** with analogous bond distances in related cluster complexes indicates that, as a consequence of the structure and the rigidity of the bridging ligand, the cluster is rather constrained. Thus, while the $Ru-C_{metalated}$ distance, 2.116(8) Å, is similar to other Ru−C distances involving metalated rings,[2a,8,9] the $Ru-N_{amido}$ distances are ca. 0.04−0.10 Å shorter than those of μ_3-apy-bridged Ru_3 clusters.[2,9,10]

Characterization of Compound 2. The structure of this cluster was unambiguously determined by X-ray

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(7) (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.

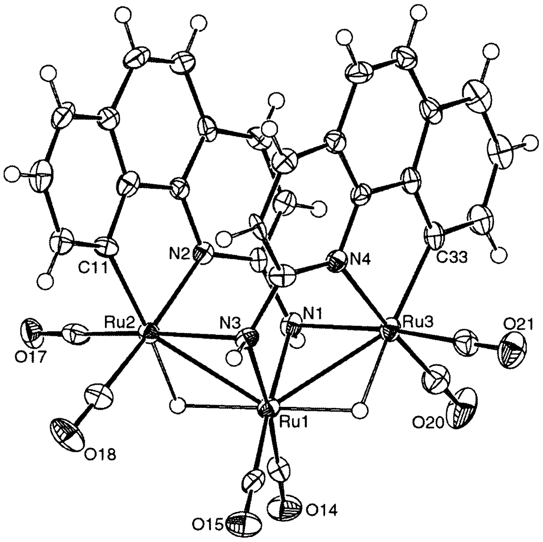

Figure 2. Molecular structure of compound **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å): Ru(1)−Ru(2) 2.7823(6), Ru(1)−Ru(3) 2.8012(6), Ru(2)−Ru(3) 4.7101(6), Ru(1)−N(1) 2.146(5), Ru(1)−N(3) 2.161(5), Ru(2)−N(2) 2.127(5), Ru(2)−N(3) 2.183(5), Ru(2)−C(11) 2.072(6), Ru(3)−N(1) 2.171(5), Ru(3)−N(4) 2.155(5), Ru(3)−C(33) 2.074(6).

diffraction methods (Figure 2). The cluster is an open 50-electron trinuclear species with a very long Ru−Ru edge, Ru(2)−Ru(3) 4.7101(6) Å. Two nearly parallel abq ligands (Figure 3) are attached to the Ru_3 triangle in such a way that each abq ligand spans a metal−metal bonded Ru−Ru edge through the N atom of the amido fragment and chelates the other Ru atom through both the quinolinic N atom and the C atom of the cyclometalated ring. The cluster shell is completed with six CO ligands (a pair attached to each Ru atom) and two hydrides (each spanning a metal−metal bonded Ru−Ru edge). Overall, the cluster can be considered as having C_2 symmetry (noncrystallographic), with the 2-fold axis passing through the unique Ru(1) atom (Figure 3). Compound **2** seems to be a bit more constrained than **1**. Although its $Ru-N_{amido}$ distances are short and similar to those of complex **1**, its $Ru-C_{metalated}$ distances, 2.072(6) and 2.074(6) Å, are ca. 0.05 Å shorter than that of **1**.

In solution, cluster **2** has C_2 symmetry, since its ^1H and DEPT ^{13}C NMR spectra display only the resonances of one metalated abq ligand, three CO groups, and one hydride. Its IR spectrum in the CO region is also very simple, showing three ν(CO) absorptions.

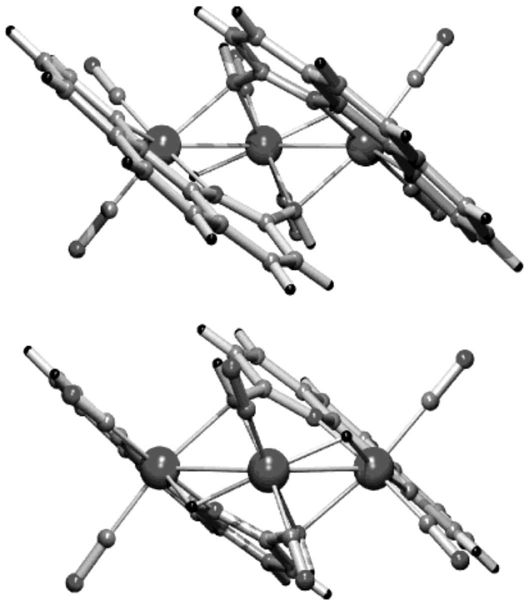

Figure 3. Views of compound **2** approximately along the C_2 axis (noncrystallographic), from the side of the abq ligands (top) and from the side of the carbonyl ligands (bottom).

Characterization of Compound 3. The osmium cluster **3** was characterized by analytical and spectroscopic methods. Its microanalysis and mass spectrum confirmed its trinuclear nature and the presence of an Habq ligand and ten CO groups. The presence of an NH group was indicated by its ^1H NMR spectrum, which contains a broad singlet at 5.97 ppm, and shows a singlet at −13.77 ppm attributable to a hydride ligand. DEPT ^{13}C NMR spectra show eight *C*H and five *C* resonances for the bridging ligand, indicating that on this occasion it is not metalated. Six carbonyl resonances, with intensities 1:1:2:2:2:2, are also observed in the ^{13}C NMR spectrum, confirming a C_s symmetry for the complex.

All these data are in agreement with the structure depicted in Scheme 2 for this complex. Although an *endo* arrangement of the pendant 7,8-benzoquinol-2-yl fragment would also be compatible with the analytical and spectroscopic data, taking into account that the complex is stable in refluxing toluene, we feel inclined to propose an *exo* arrangement of the pendant fragment. In addition, this arrangement also minimizes any steric interaction between the organic fragment and the axial carbonyl ligand on the unbridged Ru atom. This structure is related to those of other amido-bridged decacarbonyl triosmium complexes.[11]

Discussion

It is interesting that **1** contains no hydride ligands. We expected a dihydride derivative as the product of the reaction of H_2abq with $[Ru_3(CO)_{10}(MeCN)_2]$. In contrast, the dihydride intermediate resulting from the cyclometalation prefers to release dihydrogen, leading to a 48-electron nonacarbonyl species (**1**), instead of

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(8) For examples of metalation of pyridine rings by triruthenium clusters, see: (a) Ellis, D.; Farrugia, L. J. *J. Cluster Sci.* **1996**, *7*, 71. (b) Cifuentes, M. P.; Humphrey, M. G.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1994**, *466*, 211. (c) Cifuentes, M. P.; Humphrey, M. G.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *513*, 201. (d) Wong, W. Y.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1996**, 3209. (e) Deeming, A. J.; Smith, M. B. *J. Chem. Soc., Dalton Trans.* **1993**, 2041. (f) Eisenstadt, A.; Giandomenico, C. M.; Frederick, M. F.; Laine, R. M. *Organometallics* **1985**, *4*, 2033.

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(11) See, for example: (a) Cabeza, J. A.; del Río, I.; Grepioni, F.; Riera, V. *Organometallics* **2000**, *19*, 4643. (b) Kong, F. S.; Wong, 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. *Chem. Soc., Dalton Trans.* **1984**, 433.

releasing CO or ending in a 50-electron dihydride species. The dihydrogen released is taken by unreacted [$Ru_3(CO)_{10}(MeCN)_2$] to give [$Ru_4(\mu_3\text{-}H)_4(CO)_{12}$]. This latter process is responsible for the moderate yields obtained for compounds **1** and **2**.

Compounds **1** and **2** are unique, not only because they are the first polynuclear derivatives of H_2abq but also because of their structures. Metalated heterocyclic ligands tend to occupy axial positions in trinuclear clusters;[8,12−14] in other words, they are positioned on one side of the metal triangle. However, the particular structure of the abq ligand and its coordination through three atoms (two nitrogens and one carbon) forces the occupation of both axial and equatorial positions in complex **1** and a completely new type of structure for complex **2**. In the reported cases where two cyclometalated pyridine or quinoline ligands have been incorporated into a trinuclear cluster, both ligands occupy axial positions on either sides of the metal triangle.[8f,14b] However, in complex **2**, both abq ligands are cut by the Ru_3 plane, resulting in an uncommon structure for which no axial or equatorial sites can be proposed.

In the present work, a different behavior has been observed for triruthenium and triosmium clusters in their reactions with H_2abq. A trinuclear ruthenium complex analogous to the osmium derivative **3** has to be an early intermediate in the synthesis of **1** and **2**. However, while complex **3** is stable in refluxing toluene, the ruthenium analogue of **3** has not been detected.

No metalations of 2-aminopyridines and 2-aminoquinolines have hitherto been reported, but the metalation of pyridine[8,12] and quinoline[8f,13,14] rings by triruthenium and triosmium clusters has been reported on a few occasions. It is noteworthy that pyridines behave similarly to triruthenium and triosmium carbonyls,[8f] but this is not the case for quinolines, which behave as pyridines with ruthenium, giving cyclometalated 48-electron species containing $\mu\text{-}\eta^2\text{-}N,C$ ligands,[13] but give unsaturated cyclometalated 46-electron triosmium derivatives containing $\mu_3\text{-}\eta^2\text{-}N,C$ ligands.[14b] Di-(2-pyridyl)amine also gives different products when treated with analogous ruthenium and osmium carbonyls, since it behaves as a “normal” Hapy ligand with osmium but gives a cyclometalated product with ruthenium.[2a]

Although the higher difficulty to substitute CO ligands in osmium carbonyls has to be related with the different reactivity observed for some ligands in their reactions with analogous osmium and ruthenium carbonyl clusters, more work is necessary to rationalize the situation.

The metalated ligand and the absence of hydrides in **1** make this complex an attractive starting material for reactivity studies, because it should present a different reactivity from that of monohydrido apy derivatives, and it could be the first stage of a pathway leading to C^{10}-functionalized 2-amino-7,8-benzoquinolines. We have already started such studies.

Experimental Section

General Data. Solvents were dried over Na[Ph_2CO] (THF, hydrocarbons) or CaH_2 (dichloromethane, acetonitrile) and distilled under nitrogen prior to use. 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. 2-Amino-7,8-benzoquinoline[7c] and [$Os_3(CO)_{10}(MeCN)_2$][15] were prepared as described elsewhere. Anhydrous Me_3NO was obtained by azeotropic distillation of $Me_3NO{\cdot}2H_2O$ in toluene. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run at room temperature on Bruker DPX-300, AC-200, and AC-300 instruments, using internal $SiMe_4$ as standard ($\delta = 0$). Microanalyses were obtained from the University of Oviedo Analytical Service. FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

[$Ru_3(\mu_3\text{-}\eta^3\text{-abq-}C,N,N)(CO)_9$] (1). A solution of Me_3NO (91 mg, 1.212 mmol) in dichloromethane (10 mL) was slowly added to a cold (−78 °C) solution of [$Ru_3(CO)_{12}$] (350 mg, 0.548 mmol) in 10:1 dichloromethane−acetonitrile (110 mL). After stirring for 10 min, solid H_2abq (107 mg, 0.551 mmol) was added. The solution was allowed to warm to room temperature, and the solvent was removed under reduced pressure. THF (30 mL) wad added, and the resulting solution was stirred until the complete disappearance of [$Ru_3(CO)_{10}(MeCN)_2$] (IR monitoring, ca. 90 min). The solvent was removed under reduced pressure, and the resulting residue was dissolved in dichloromethane (1 mL). This solution was separated by column chromatography on neutral alumina (2 × 10 cm, activity III). Hexane eluted some [$Ru_3(CO)_{12}$] and [$Ru_4(\mu_3\text{-}H)_4(CO)_{12}$]. Hexane−dichloromethane (2:1) eluted a yellow-orange band, which afforded compound **1** upon solvent removal (90 mg, 22%). Anal. Calcd for $C_{22}H_8N_2O_9Ru_3$ ($M = 747.57$): C, 35.35; H, 1.08; N, 3.75. Found: C, 35.53; H, 1.14; N, 3.59. MS (m/z): 749 [M^+]. IR (CH_2Cl_2): ν_{CO} 2079 (m), 2037 (vs), 2025 (s), 2001 (m), 1982 (m), 1937 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.28 (dd, $J = 7.0$, 0.7 Hz, 1 H), 8.00 (d, $J = 8.8$ Hz, 1 H), 7.80 (dd, $J = 8.4$, 0.7 Hz, 1 H), 7.73−7.28 (m, 2 H), 7.53 (d, $J = 8.8$ Hz, 1 H), 6.98 (d, $J = 8.4$ Hz, 1 H), 5.39 (s, br, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR, DEPT (CD_2Cl_2): δ 195.7 (br, COs), 173.4 (C), 159.9 (C), 152.7 (C), 141.0 (C), 140.1 (CH), 138.3 (CH), 135.1 (C), 130.7 (CH), 126.7 (CH), 123.2 (CH), 123.1 (CH), 122.0 (C), 111.4 (CH) ppm.

[$Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^3\text{-abq-}C,N,N)_2(CO)_6$] (2). Method a. A solution of H_2abq (134 mg, 0.690 mmol) and [$Ru_3(CO)_{12}$] (200 mg, 0.313 mmol) in toluene (15 mL) was stirred at reflux temperature for 3 h. The color changed from orange to dark brown. The solvent was removed under reduced pressure. The residue was dissolved in THF (2 mL) and was mixed with silica gel (ca.1 g). After solvent removal, the solid was poured onto a silica gel column (2 × 10 cm) packed in hexane. Hexane eluted some [$Ru_4(\mu_3\text{-}H)_4(CO)_{12}$]. Hexane−dichloromethane (3:2) eluted a yellow band, which afforded compound **2** upon solvent removal (85 mg, 32%).

Method b. A solution of compound **1** (20 mg, 0.027) and H_2abq (6 mg, 0.081) in toluene (10 mL) was stirred at reflux temperature for 25 min. After removing the solvent at reduced pressure, a ^1H NMR spectrum of the crude reaction mixture

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(12) For examples of metalation of pyridine rings by triosmium clusters, see: (a) Ref 8f. (b) Deeming, A. J.; Stchedroff, M. J.; Whittaker, C.; Arce, A. J.; de Sanctis, Y.; Steed, J. W. *J. Chem. Soc., Dalton Trans.* **1999**, 3289. (c) Darling, S. L.; Goh, P. K. Y.; Bampos, N.; Freeder, N.; Montalti, M.; Prodi, L.; Johnson, B. F. G.; Sanders, J. K. M. *Chem. Commun.* **1998**, 2031. (d) Wong, W. Y.; Cheung, S. H.; Lee, S. M.; Leung, S. Y. *J. Organomet. Chem.* **2000**, *596*, 36.

(13) For examples of metalation of quinoline rings by triruthenium clusters, see: (a) Ref 8f. (b) Kabir, S. E.; Siddiquee, T. A.; Rosenberg, E.; Smith, R.; Hursthouse, M. B.; Malik, K. M. A.; Hardcastle, K. I. *J. Cluster Sci.* **1998**, *9*, 185. (c) Fish, R. H.; Kim, T. J.; Stewart, J. L.; Bushweller, J. H.; Rosen, R. K.; Dupont, J. W. *Organometallics* **1986**, *5*, 2193.

(14) For examples of metalation of quinoline rings by triosmium clusters, see: (a) Ref 8f. (b) Abedin, M. J.; Bergman, B.; Holmquist, R.; Smith, R.; Rosenberg, E.; Ciurash, J.; Hardcastle, K. I.; Roe, J.; Vázquez, V.; Roe, C.; Kabir, S. E.; Roy, B.; Azam, K. A. *Coord. Chem. Rev.* **1999**, *190−192*, 975, and references therein.

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showed only the resonances of residual toluene, compound **2**, and free H_2abq. Anal. Calcd for $C_{32}H_{18}N_4O_6Ru_3$ ($M = 857.76$): C, 44.81; H, 2.12; N, 6.53. Found: C, 44.93; H, 2.22; N, 6.45. MS (*m*/*z*): 859 [M^+]. IR (CH_2Cl_2): ν_{CO} 2052 (vs), 2032 (s), 1977 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.24 (t, $J = 4.4$ Hz, 1 H), 7.54 (d, $J = 4.4$ Hz, 1 H), 7.40 (d, $J = 8.4$, Hz, 1 H), 6.81 (d, $J = 8.4$ Hz, 1 H), 6.58 (d, $J = 8.9$ Hz, 1 H), 6.10 (d, $J = 8.9$ Hz, 1 H), 4.70 (s, br, 1 H, NH) −9.29 (s, 1 H, μ-H) ppm. ^{13}C{^{1}H} NMR, DEPT (CD_2Cl_2): δ 199.9 (2 CO), 199.6 (2 CO), 198.0 (2 CO), 165.8 (C), 164.1 (C), 151.1 (C), 139.8 (C), 136.4 (CH), 135.5 (C), 134.4 (CH), 128.7 (CH), 126.7 (CH), 122.5 (CH), 122.0 (CH), 121.4 (C), 119.9 (CH) ppm.

[Os_3(μ-H)(μ-η^1-Habq-*N*)$(CO)_{10}$] (3). A THF solution (20 mL) of H_2abq (45 mg, 0.232 mmol) and [$Os_3(CO)_{10}(MeCN)_2$] (180 mg, 0.193 mmol) was stirred at room temperature for 2 h. 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 eluting with hexane−dichloromethane (2:1). The first band contained a small amount of an unidentified yellow compound. The second band, yellow, afforded compound **3** upon extraction with dichloromethane and solvent removal (80 mg, 40%). Anal. Calcd for $C_{23}H_{10}N_2O_{10}Os_3$ ($M = 1044.94$): C, 26.44; H, 0.95; N, 2.68. Found: C, 26.57; H, 1.05; N, 2.53. MS (*m*/*z*): 1046 [M^+]. IR (CH_2Cl_2): ν_{CO} 2103 (w), 2066 (vs), 2052 (s), 2016 (s), 1994 (s), 1975 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 9.09 (dd, $J = 5.9, 3.5$ Hz, 1 H), 8.04 (d, $J = 8.4$ Hz, 1 H), 7.91 (dd, $J = 5.9, 2.5$ Hz, 1 H), 7.73−7.69 (m, 4 H), 7.18 (d, $J = 8.4$ Hz, 1 H), 5.97 (s, br, 1 H, NH), −13.77 (d, $J = 2.5$ Hz, 1 H, μ-H). ^{13}C{^{1}H} NMR, DEPT (CD_2Cl_2): δ 189.6 (CO), 181.1 (CO), 176.9 (2 CO), 176.1 (2 CO), 172.0 (2 CO), 171.9 (2 CO), 169.0 (C), 143.7 (C), 137.3 (CH), 133.6 (C), 129.5 (C), 127.9 (CH), 127.3 (CH), 126.1 (CH), 126.0 (CH), 124.3 (CH), 124.2 (CH), 124.1 (C), 112.0 (CH) ppm.

X-ray Structures of Compounds 1 and 2·CH_2Cl_2. Suitable crystals were obtained by slow diffusion of hexane into an acetone−dichloromethane (1:4) solution of complex **1** and by slow diffusion of hexane into a dichloromethane solution of complex **2**. Diffraction data for **1** were collected on a Nonius CAD-4 diffractometer, with the $\omega-2\theta$ scan technique and a variable scan rate, using graphite-monochromated Mo Kα radiation. Lorentz and polarization corrections were applied and data were reduced to F_o^2 values. Diffraction data for **2**·CH_2Cl_2 were collected on a Kappa-CCD diffractometer equipped with a 95 mm CCD camera and a κ-goniostat, using graphite-monochromated Cu Kα radiation. Data were reduced to F_o^2 values. For both compounds, empirical absorption corrections were applied using XABS2,[16] with transmission factors in the ranges 0.907−0.728 for **1** and 0.176−0.103 for **2**·CH_2Cl_2. The structures were solved by Patterson interpretation using the program DIRDIF-96.[17] Two crystallographically independent molecules were found in the asymmetric unit of compound **1**. Isotropic and full matrix anisotropic least-squares refinements were carried out using SHELXL-97.[18] All non H atoms were refined anisotropically. Hydrogen atom positions were geometrically calculated and refined riding on their parent atoms, except the hydrides of **2**·CH_2Cl_2, which were located and refined with free coordinates and thermal parameters, and the NH hydrogen atoms of **2**·CH_2Cl_2, which were located and refined with free coordinates and fixed thermal parameters. The disorder of a chlorine atom of the solvent molecule of **2**·CH_2Cl_2 was treated with a mixture of constraints and restraints as described elsewhere.[19] Plots were made with the EUCLID program package.[20] The WINGX program system[21] was used throughout the structure determinations. Selected crystal and refinement data are given as footnotes.[22,23] Relevant molecular parameters are given in the captions of Figures 1 and 2.

Acknowledgment. This work has been supported by the Spanish DGESIC (grant PB98-1555 to J.A.C.) and CICYT (grants BQU2000-2019 to S.G.-G. and BQU2000-0220 to V.R.).

Supporting Information Available: Tables of bond distances and angles, atomic coordinates, and anisotropic thermal parameters in CIF format for **1** and **2**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0205647

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[22] Crystal and selected refinement data for **1**: $C_{22}H_8N_2O_9Ru_3$; fw = 747.51; cryst size = 0.20 × 0.20 × 0.07 mm; cryst syst = monoclinic; space group = $P2_1/n$; $a = 16.012(6)$ Å; $b = 16.902(7)$ Å; $c = 17.920(6)$ Å; $\beta = 103.23(3)°$; $V = 4721(3)$ Å^3; $Z = 8$; $\rho_{calcd} = 2.103$ g/cm^3; $\lambda = 0.71073$ Å; $\mu = 1.950$ mm^{-1}; $F(000) = 2864$; index range $-19 < h < 19$, $0 < k < 20$, $0 < l < 22$; θ range = 1.54−25.97°; temp = 293(2) K; collected reflns = 9985; unique reflns = 9254; $R_{Int} = 0.0444$; reflns with $I < 2\sigma(I) = 5010$; no. of variables = 657; weighting scheme $w^{-1} = \sigma^2F_o^2 + (0.0535P)^2$, $P = (F_o^2 + 2F_c^2)/3$; GoF = 0.988; final $R_{2\sigma(I)} = 0.0396$; final $wR_{2\text{all data}} = 0.1167$; largest diff peak and hole = 0.630 and −0.804 e/Å^3.

[23] Crystal and selected refinement data for **2**·CH_2Cl_2: $C_{32}H_{18}N_4O_6Ru_3\cdot CH_2Cl_2$; fw = 942.64; cryst size = 0.23 × 0.18 × 0.13 mm; cryst syst = monoclinic; space group = $P2_1/c$; $a = 13.2841(3)$ Å; $b = 10.6019(3)$ Å; $c = 22.6787(5)$ Å; $\beta = 91.985(2)°$; $V = 3192.1(1)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.961$ g/cm^3; $\lambda = 1.54180$ Å; $\mu = 13.343$ mm^{-1}; $F(000) = 1840$; index range: $0 < h < 15$, $0 < k < 12$, $-27 < l < 27$; θ range = 3.33 to 68.38°; temp = 200(2) K; collected reflns = 17646; unique reflns = 5854; $R_{int} = 0.039$; reflns with $I < 2\sigma(I) = 5478$; no. of variables = 456; weighting scheme $w^{-1} = \sigma^2F_o^2 + (0.0951P)^2 + 12.5933P$, $P = (F_o^2 + 2F_c^2)/3$; GoF = 1.199; final $R_{2\sigma(I)} = 0.0442$; final $wR_{2\text{all data}} = 0.1593$; largest diff peak and hole = 1.685 and −1.115 e/Å^3.