

# Triruthenium and Triosmium Carbonyl Cluster Complexes Containing Deprotonated Di(2-pyridyl)amine in Unusual Coordination Modes

Javier A. Cabeza,<sup>\*,†</sup> Ignacio del Río,<sup>†</sup> Santiago García-Granda,<sup>‡</sup>  
 Víctor Riera,<sup>†</sup> and Marta Suárez<sup>†</sup>

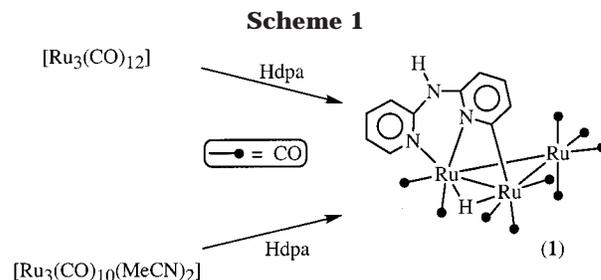
*Instituto de Química Organometálica "Enrique Moles" and Departamento de Química Física y Analítica, Universidad de Oviedo, E-33071 Oviedo, Spain*

Received January 30, 2002

**Summary:** The synthesis of the first trinuclear carbonyl clusters containing ligands derived from di(2-pyridyl)amine (Hdpa) has been achieved. Treatment of  $[\text{Ru}_3(\text{CO})_{12}]$  or  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  with di(2-pyridyl)amine (Hdpa) gives the cluster complex  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-}\eta^3\text{-dpa-C,N,N})(\text{CO})_9]$  (**1**). The dpn ligand in this compound chelates a Ru atom through both pyridinic nitrogens while attached to another Ru atom through the C atom of a metalated pyridine ring, keeping the amino NH fragment uncoordinated. Curiously, the osmium compounds  $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-dpn-N,N})(\text{CO})_{10}]$  (**2**) and  $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-dpn-N,N})(\text{CO})_9]$  (**3**), which have been stepwise prepared from  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  and Hdpa, contain edge-bridging (**2**) and face-capping (**3**) N-deprotonated dpn ligands coordinated through the N atom of a pyridine ring and the N atom of the original amino fragment.

## Introduction

The N-deprotonated form of di(2-pyridyl)amine (dpn) has been widely used as a building block for the synthesis of metal–metal bonded binuclear and linear trinuclear complexes of the types  $[\text{M}_2(\mu\text{-}\eta^2\text{-dpn-N,N})_4\text{L}_2]^1$  and  $[\text{M}_3(\mu_3\text{-}\eta^3\text{-dpn-N,N,N})_4\text{X}_2]^2$ . In these compounds each dpn ligand bridges two or three metal atoms, respectively. A chelating behavior of this ligand has also been observed in quite a few binuclear<sup>3</sup> and mononuclear<sup>4</sup> complexes. Many examples of mononuclear



complexes containing the neutral Hdpa ligand in a chelating form are also known.<sup>5</sup> However, no carbonyl-metal clusters containing either deprotonated or neutral di(2-pyridyl)amine have hitherto been reported.

We have previously carried out a thorough study of the synthesis and reactivity of carbonylmetal clusters derived from 2-aminopyridines.<sup>6,7</sup> As a natural extension of these studies, we now report the reactions of Hdpa with triruthenium and triosmium carbonyl clusters. Interestingly, the products, which represent the first triangular metal clusters having dpn ligands, contain this ligand in different coordination modes depending on the metal used.

## Results

The thermal reaction (refluxing THF) of  $[\text{Ru}_3(\text{CO})_{12}]$  with Hdpa led to the C-metalated complex  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-}\eta^3\text{-dpn-C,N,N})(\text{CO})_9]$  (**1**, Scheme 1) as the major product of a mixture of compounds that was separated

\* Corresponding author. E-mail: jac@sauron.quimica.uniovi.es. Fax: int +34-985103446. URL: <http://www12.uniovi.es/investigacion/jac/>.

<sup>†</sup> Instituto de Química Organometálica "Enrique Moles".

<sup>‡</sup> Departamento de Química Física y Analítica.

(1) See, for example: (a) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Spek, A. L.; Smeets, W. J. J.; Chiang, M. Y. *J. Chem. Soc., Dalton Trans.* **1993**, 789. (b) Suen, M. C.; Wu, Y. Y.; Chem, J. D.; Keng, T. C.; Wang, J. C. *Inorg. Chim. Acta* **1999**, 288, 82. (c) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I. *Inorg. Chem. Commun.* **1998**, 1, 1.

(2) See, for example: (a) Clérac, R.; Cotton, F. A.; Jeffrey, P. S.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2001**, 40, 1265. (b) Cotton, F. A.; Daniels, L. M.; Jordan IV, G. T. *Chem. Commun.* **1997**, 421. (c) Clérac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. M.; Murillo, C. A.; Wang, X. *J. Chem. Soc., Dalton Trans.* **2001**, 386. (d) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I. *J. Am. Chem. Soc.* **1997**, 119, 10223. (e) Clérac, R.; Cotton, F. A.; Dunbar, K. M.; Murillo, C. A.; Pascual, I.; Wang, X. *Inorg. Chem.* **1999**, 38, 2655. (f) Sheu, J. T.; Lin, C. C.; Chao, I.; Wang, C. C.; Peng, S. M. *Chem. Commun.* **1996**, 315. (g) Adulchecha, S.; Hathaway, B. *Chem. Soc., Dalton Trans.* **1991**, 993. (h) Clérac, R.; Cotton, F. A.; Dunbar, K. M.; Lu, T.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2000**, 39, 3065.

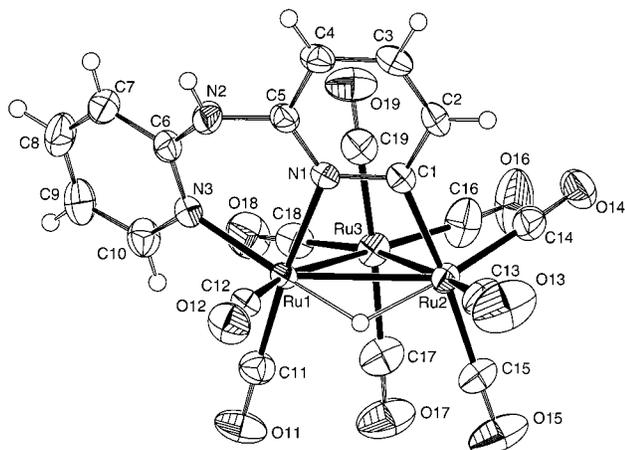
(3) For examples of binuclear compounds in which at least one dpn ligand shows both bridging and chelating behavior, see: (a) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Zhou, H. C. *Inorg. Chim. Acta* **2000**, 305, 69. (b) Gornitzka, H.; Stalke, D. *Eur. J. Inorg. Chem.* **1998**, 311.

(4) (a) Oro, L. A.; Ciriano, M. A.; Viguri, F.; Foces-Foces, C.; Cano, F. H. *Inorg. Chim. Acta* **1986**, 115, 65. (b) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV; Murillo, C. A. *J. Am. Chem. Soc.* **1997**, 119, 10377. (c) Baxter, C. E.; Rodig, O. R.; Schlatzer, R. K.; Sinn, E. *Inorg. Chem.* **1979**, 18, 1918. (d) Freeman, H. C.; Snow, M. R. *Acta Crystallogr.* **1965**, 18, 843. (e) Rodig, O. R.; Brueckner, T.; Hurlburt, B. K.; Schlatzer, R. K.; Venable, T. L.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1981**, 196.

(5) The crystal structures of 129 compounds of this type have been found deposited at the Cambridge Structural Database: CSD v.5.22, Cambridge Crystallographic Data Centre, October 2001.

(6) For a review on triruthenium carbonyl clusters derived from 2-aminopyridines, see: Cabeza, J. A. *Eur. J. Inorg. Chem.* **2002**, in press.

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



**Figure 1.** Molecular structure of compound **1**. Thermal ellipsoids are drawn at 50% probability level. Selected interatomic distances (Å): Ru(1)–Ru(2) 2.8742(8), Ru(2)–Ru(3) 2.8743(8), Ru(1)–Ru(3) 2.8869(9), Ru(1)–N(1) 2.085(3), Ru(1)–N(3) 2.136(3), Ru(2)–C(1) 2.098(3).

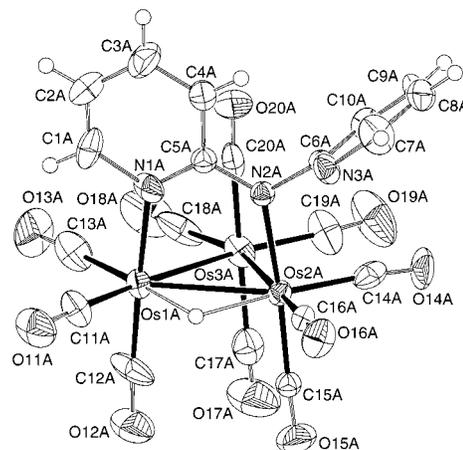
by chromatographic methods. This complex was also obtained using  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  as starting material.

The composition and trinuclear nature of **1** was indicated by its microanalysis and mass spectra. The presence of an NH group was indicated by its  $^1\text{H}$  NMR spectrum, which contains a broad singlet at 7.50 ppm. This spectrum also displays a complex aromatic hydrogen region and a hydride signal at  $-21.07$  ppm. A DEPT  $^{13}\text{C}$  NMR spectrum showed seven CH resonances, indicating that the source of the hydride ligand was a pyridine ring metalation. All these data were not sufficient to precisely assign the position of the metalated dpa ligand on the cluster.

The structure of cluster **1** was unambiguously determined by X-ray diffraction methods. Figure 1 shows a molecular view of complex **1**. Its caption contains a selection of structural parameters. Both pyridinic N atoms of the ligand are attached to the same Ru atom, while the metalated C atom is attached to a different Ru atom. The metalated pyridine ring occupies two axial coordination sites of the cluster, while the N atom of the remaining pyridyl fragment occupies an equatorial site *trans* to the hydride ligand, which spans the same Ru–Ru edge as the metalated pyridine ring.

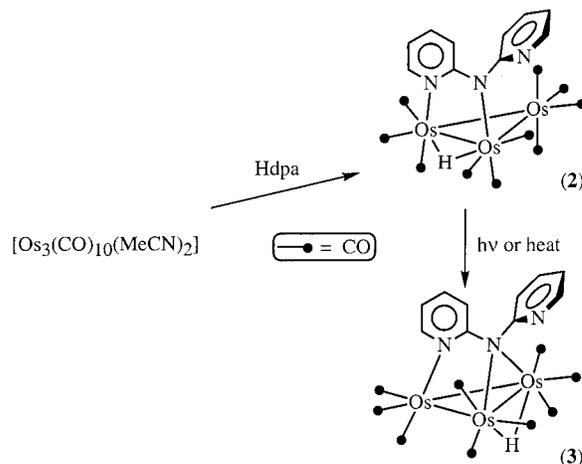
The osmium cluster  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  reacted with Hdpa at room temperature to give  $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-dpa-N,N})(\text{CO})_{10}]$  (**2**, Scheme 2). Under thermal (refluxing 1,2-dichloroethane) or photochemical (UV, mercury lamp) conditions, complex **2** underwent a quantitative decarbonylation reaction to give  $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-dpa-N,N})(\text{CO})_9]$  (**3**, Scheme 2). Both osmium complexes show the corresponding molecular ions in their mass spectra and the presence of a hydride ligand in their  $^1\text{H}$  NMR spectra. No C-metalation was suggested by their DEPT  $^{13}\text{C}$  NMR spectra, which show eight CH resonances. While no symmetry is reflected by the  $^{13}\text{C}$  NMR spectrum of **2** (10 CO resonances), the presence of a mirror plane and the casual overlapping of some CO resonances account for the observation of only three CO signals in the  $^{13}\text{C}$  NMR spectrum of compound **3**.

The analytical and IR and NMR spectroscopic data of compound **3** clearly indicate a face-capping position of the dpa ligand in the cluster, as shown in Scheme 2.



**Figure 2.** Molecular structure of compound **2** (only one of the two crystallographically independent molecules is shown). Thermal ellipsoids are drawn at 50% probability level. Selected interatomic distances (Å): Os(1A)–Os(2A) 2.887(3), Os(2A)–Os(3A) 2.889(3), Os(1A)–Os(3A) 2.896(3), Os(1A)–N(1A) 2.15(1), Os(2A)–N(2A) 2.13(1).

### Scheme 2



However, an X-ray diffraction study was required to assign the positions of the ligands in compound **2**, due to its lack of symmetry. Figure 2 shows a molecular view of this cluster. Its caption contains a selection of structural parameters. The dpa ligand bridges two Ru atoms through two N atoms (a pendant pyridine ring remains uncoordinated), occupying two axial coordination sites. Both the hydride and the dpa ligands span the same Ru–Ru edge of the cluster.

Looking for possible isomerization products, the ruthenium compound **1** and the osmium compound **3** were thermolyzed in refluxing toluene under nitrogen for 30 min. While extensive decomposition was produced in the case of the ruthenium complex, no changes were observed in the osmium complex.

### Discussion

The metalation of pyridine rings has been reported on a few occasions.<sup>8</sup> However, it is noteworthy that the coordination mode of the metalated dpa ligand in complex **1** is very rare. In fact, it has been observed previously only in one instance in a binuclear rhodium complex.<sup>9</sup> It is also intriguing that, although Hdpa can be considered a member of the 2-aminopyridine family,

its reaction with  $[\text{Ru}_3(\text{CO})_{12}]$  follows a completely different pathway from those of "normal" 2-aminopyridines (Hapy) that always give trinuclear products of the type  $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-apy-}N,N)(\text{CO})_9]$ , containing face-capping *N*-deprotonated ligands.<sup>10</sup>

To explain the behavior of Hdpa in its reaction with  $[\text{Ru}_3(\text{CO})_{12}]$ , it could be claimed that Hdpa can act as a chelate (a possibility that is unexpected for "normal" 2-aminopyridines). However, this reasoning is not convincing enough because Hdpa behaves in the osmium reactions as other 2-aminopyridines, for which clusters similar to **2** and **3** (but without the pendant pyridyl fragment) are already known.<sup>11</sup> It can also be tentatively proposed that a binuclear reaction site may be more accessible in isolated  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  than in the case of  $[\text{Ru}_3(\text{CO})_{12}]$  and  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  in the presence of some acetonitrile, for which a single metal atom site may be more probable. In the latter, the initial pyridine *N*- $\eta^1$  coordination followed by *N*- $\eta^1$  to *N*=*C*- $\eta^2$  rearrangement, C–H activation, and *N*-coordination would give complex **1**.<sup>12</sup> The *N*- $\eta^1$  to *N*=*C*- $\eta^2$  rearrangement has been previously proposed to explain the reactivity of quinolines with ruthenium and osmium carbonyls.<sup>13</sup>

Therefore, although tentative proposals can be provided, the explanation for the different chemical behavior of Hdpa with analogous ruthenium and osmium clusters remains unknown. In a few instances, differences in the reactions of these clusters with some heterocyclic ligands have also been observed.<sup>14</sup>

Although the bridging coordination mode of the dpa ligand found in **2** is well known for binuclear complexes,<sup>1</sup> the face-capping behavior found for this ligand in **3** is unprecedented.

### Concluding Remarks

The synthesis of the first trinuclear carbonyl clusters containing ligands derived from di(2-pyridyl)amine (Hdpa) has been achieved. Treatment of  $[\text{Ru}_3(\text{CO})_{12}]$  or  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  with di(2-pyridyl)amine (Hdpa) leads to the cluster complex  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-}\eta^3\text{-dpa-C,N,N})(\text{CO})_9]$  (**1**). The dpa ligand in this compound chelates a Ru atom through both pyridinic nitrogens while is

attached to another Ru atom through the C atom of a metalated pyridine ring, maintaining the amino NH fragment in an uncoordinated state. Curiously, the osmium compounds  $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-dpa-N,N})(\text{CO})_{10}]$  (**2**) and  $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-dpa-N,N})(\text{CO})_9]$  (**3**), which have been stepwise prepared from  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  and Hdpa, contain edge-bridging (**2**) and face-capping (**3**) *N*-deprotonated dpa ligands coordinated through the N atom of a pyridine ring and the N atom of the original amino fragment. The difference between the ruthenium and osmium derivatives of Hdpa still needs to be explained.

### Experimental Section

**General Data.** Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or  $\text{CaH}_2$  (dichloromethane, 1,2-dichloroethane) 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. All reagents were purchased from commercial suppliers, except for anhydrous  $\text{Me}_3\text{NO}$ , which was obtained by azeotropic distillation of  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  in toluene, and  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ , which was prepared as described elsewhere.<sup>15</sup> IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run at room temperature on a Bruker DPX-300 instrument, using internal  $\text{SiMe}_4$  as standard ( $\delta = 0$  ppm). Microanalyses were obtained from the University of Oviedo Analytical Service. FABMS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

**$[\text{Ru}_3(\mu\text{-H})(\mu\text{-}\eta^3\text{-dpa-C,N,N})(\text{CO})_9]$  (**1**). Method a.** Hdpa (60 mg, 0.351 mmol) was added to a solution of  $[\text{Ru}_3(\text{CO})_{12}]$  (200 mg, 0.313 mmol) in THF (30 mL). The solution was heated at reflux temperature until the complete disappearance of the starting complex (ca. 50 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 silica gel ( $2 \times 10$  cm). Hexane–dichloromethane (1:2) eluted three bands. The first two bands, both very pale yellow, were discarded. The third band, orange, afforded compound **1** upon solvent removal (78 mg, 34%).

**Method b.** Hdpa (30 mg, 0.175 mmol) was added to a cold ( $-78$  °C) solution of  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  in dichloromethane–acetonitrile (10:1), prepared in situ from  $[\text{Ru}_3(\text{CO})_{12}]$  (100 mg, 0.156 mmol) and anhydrous  $\text{Me}_3\text{NO}$  (29 mg, 0.387 mmol). The resulting solution was warmed to room temperature, and the solvent was removed in vacuo. THF (20 mL) was added, and the resulting solution was stirred for 1 h. The solvent was removed, and the residue was dissolved in dichloromethane (1 mL) and was added to a silica gel chromatography column ( $2 \times 15$  cm). Hexane eluted some  $[\text{Ru}_3(\text{CO})_{12}]$ . Hexane–dichloromethane (1:2) eluted an orange band that afforded compound **1** upon solvent removal (25 mg, 22%). A dark residue remained uneluted at the top of the column. Calcd for  $\text{C}_{19}\text{H}_9\text{N}_3\text{O}_9\text{Ru}_3$  ( $M = 726.54$ ): C, 31.41; H, 1.25; N, 5.78. Found: C, 31.62; H, 1.22; N, 5.58. MS ( $m/z$ ): 728 [ $M^+$ ]. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  2075 (m), 2032 (s), 2008 (vs), 1966 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.33 (d, br,  $J = 6.1$  Hz, 1 H), 7.65 (td,  $J = 7.3, 1.2$  Hz, 1 H), 7.50 (s, br, 1 H, NH) 7.23–7.09 (m, 2 H), 6.92 (d, br,  $J = 7.9$  Hz, 1 H), 6.75 (ddd,  $J = 7.3, 6.1, 1.2$  Hz, 1 H), 6.46 (dd,  $J = 7.9, 1.2$  Hz, 1 H),  $-21.07$  (s, 1 H,  $\mu\text{-H}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR, DEPT (acetone- $d_6$ ):  $\delta$  208.0, 206.1, 205.6, 203.3, 198.6, 190.8, 189.8 (all COs), 174.4 (C), 156.7 (CH), 154.6 (C), 147.7 (C), 140.4 (CH), 136.2 (CH), 132.4 (CH), 118.1 (CH), 117.1 (CH), 108.0 (CH) ppm.

(8) For examples of metalation of pyridine rings in triruthenium cluster chemistry, 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.

(9) Cotton, F. A.; Murillo, C. A.; Stiriba, S. E. *Inorg. Chem. Commun.* **1999**, 2, 463.

(10) (a) Cabeza, J. A.; Oro, L. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1437. (b) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Jeannin, Y.; Miguel, D. *J. Chem. Soc., Dalton Trans.* **1990**, 2201. (c) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimata, E. W.; Bonnet, J. J. *Organometallics* **1992**, 11, 1351.

(11) Deeming, A. J.; Peters, R.; Hursthouse, M. B.; Backer-Dirks, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1205.

(12) We are very grateful to a reviewer for suggesting this proposal.

(13) Eisenstadt, A.; Giandomenico, C. M.; Frederick, M. F.; Laine, R. *Organometallics* **1995**, 4, 2033.

(14) (a) 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. (b) Abedin, M. J.; Bergman, B.; Holmquist, R.; Smith, R.; Rosenberg, E.; Cjurash, 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.

(15) Nicholls, J. M.; Vargas, M. D. *Inorg. Synth.* **1990**, 28, 232.

**[Os<sub>3</sub>(μ-H)(μ-η<sup>2</sup>-dpa-N,N)(CO)<sub>10</sub>] (2).** A THF solution (20 mL) of Hdpa (33 mg, 0.193 mmol) and [Os<sub>3</sub>(CO)<sub>10</sub>(MeCN)<sub>2</sub>] (154 mg, 0.165 mmol) was stirred at room temperature for 50 min. The solvent was removed under reduced pressure, the residue was dissolved in dichloromethane (1 mL), and the resulting solution was separated by column chromatography on silica gel (2 × 15 cm). Hexane eluted a small amount of an unidentified yellow compound. Hexane–dichloromethane (1:4) eluted a yellow band that afforded compound **2** upon solvent removal (66 mg, 40%). Calcd for C<sub>20</sub>H<sub>9</sub>N<sub>3</sub>O<sub>10</sub>Os<sub>3</sub> (*M* = 1021.91): C, 23.51; H, 0.89; N, 4.11. Found: C, 23.58; H, 1.02; N, 4.08. MS (*m/z*): 1023 [M<sup>+</sup>]. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν<sub>CO</sub> 2106 (m), 2066 (s), 2055 (s), 2018 (vs), 1984 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.63 (dd, *J* = 4.9, 2.0 Hz, 1 H), 8.13 (dd, *J* = 6.4, 1.5 Hz, 1 H), 7.76 (td, *J* = 7.4, 2.0 Hz, 1 H), 7.10 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1 H), 6.78–6.64 (m, 2 H), 5.99 (td, *J* = 6.4, 1.0 Hz, 1 H), 5.65 (dd, *J* = 7.4, 1.0 Hz, 1 H), –11.47 (s, 1 H, μ-H). <sup>13</sup>C{<sup>1</sup>H} NMR, DEPT (CD<sub>2</sub>Cl<sub>2</sub>): δ 183.6 (CO), 178.0 (CO), 177.9 (2 CO), 176.1 (C), 175.9 (CO), 175.7 (2 CO), 174.0 (CO), 169.2 (2 CO), 167.2 (C), 155.5 (CH), 150.1 (CH), 139.5 (CH), 135.6 (CH), 121.2 (2 CH), 116.2 (CH), 110.5 (CH) ppm.

**[Os<sub>3</sub>(μ-H)(μ<sub>3</sub>-η<sup>2</sup>-dpa-N,N)(CO)<sub>9</sub>] (3). Method a.** A solution of complex **2** (30 mg, 0.030 mmol) in THF (25 mL) was irradiated with UV light (Pyrex-filtered mercury lamp). After 5 min, IR monitoring indicated the complete conversion of the starting material. The solvent was removed under reduced pressure and the solid residue washed with hexane to afford complex **3** as a yellow solid (25 mg, 84%).

**Method b.** A solution of complex **2** (30 mg, 0.030 mmol) in 1,2-dichloroethane (25 mL) was stirred at reflux temperature for 75 min. The solvent was removed under reduced pressure and the residue washed with hexane to afford complex **3** as a yellow solid (25 mg, 84%). Calcd for C<sub>19</sub>H<sub>9</sub>N<sub>3</sub>O<sub>9</sub>Os<sub>3</sub> (*M* = 993.90): C, 22.96; H, 0.91; N, 4.23. Found: C, 23.12; H, 1.01; N, 4.21. MS (*m/z*): 995 [M<sup>+</sup>]. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν<sub>CO</sub> 2080 (m), 2052 (vs), 2022 (s), 1991 (s), 1952 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.71 (dd, *J* = 5.9, 2.0 Hz, 1 H), 8.36 (dd, *J* = 4.9, 2.0 Hz, 1 H), 7.66 (ddd, *J* = 8.4, 7.4, 2.0 Hz, 1 H), 7.30 (ddd, *J* = 8.4, 7.4, 2.0 Hz, 1 H), 7.13 (dd, *J* = 7.4, 4.9 Hz, 1 H), 7.04 (d, br, *J* = 8.4 Hz, 1 H), 6.64 (ddd, *J* = 7.4, 6.0, 2.0 Hz, 1 H), 5.54 (d, br, *J* = 8.4 Hz, 1 H), –12.02 (s, 1 H, μ-H). <sup>13</sup>C{<sup>1</sup>H} NMR, DEPT (CD<sub>2</sub>Cl<sub>2</sub>): δ 189.3, 182.6, 178.7 (all CO's), 177.3 (C), 167.8 (C), 157.2 (CH), 146.9 (CH), 138.7 (CH), 136.2 (CH), 123.2 (CH), 122.9 (CH), 119.6 (CH), 115.9 (CH) ppm.

**X-ray Structures of Compounds 1 and 2.** Suitable structures were obtained by slow diffusion of pentane in a THF–CH<sub>2</sub>Cl<sub>2</sub> (1:10) solution of complex **1** and by slow evaporation at room temperature of a diethyl ether solution of complex **2**. Diffraction data were collected on a Nonius CAD-4 diffractometer, with the ω–2θ 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*<sub>o</sub><sup>2</sup> values. Empirical absorption corrections were applied using XABS2,<sup>16</sup> with transmission factors in the ranges 0.703–0.612 for **1** and 0.116–0.134 for **2**. The structures were solved by Patterson interpretation using the program DIRDIF-96.<sup>17</sup> Two crystallographically independent molecules were found

in the asymmetric unit of compound **2**. Isotropic and full matrix anisotropic least-squares refinements were carried out using SHELXL-97.<sup>18</sup> All non H atoms were refined anisotropically, except N(2A), C(5A), C(6A), and C(15A) of compound **2**, which were treated isotropically. Hydrogen atom positions were geometrically calculated and refined riding on their parent atoms, except the hydride and the NH hydrogen atoms of **1**, which were located by Fourier difference maps and their coordinates refined, and the hydride atoms of both independent molecules of **2**, the positions of which were calculated using the program XHYDEX<sup>19</sup> and were refined fixing their coordinates and thermal parameters. The molecular plots were made with the EUCLID program package.<sup>20</sup> The WINGX program system<sup>21</sup> was used throughout the structure determinations. Selected crystal and refinement data are given as footnotes.<sup>22,23</sup> 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 for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020073M

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

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

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

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

(20) Spek, A. L. *The EUCLID Package*, in *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, UK, 1982; p 528.

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

(22) Crystal and selected refinement data for **1**: C<sub>19</sub>H<sub>9</sub>N<sub>3</sub>O<sub>9</sub>Ru<sub>3</sub>; *fw* = 726.5; *cryst size* = 0.23 × 0.23 × 0.17 mm; *cryst system* = triclinic; *space group* = *P1*; *a* = 8.575(4) Å; *b* = 8.811(1) Å; *c* = 15.479(4) Å; α = 87.09(3)°, β = 77.17(3)°, γ = 76.71(2)°; *V* = 1109.9(6) Å<sup>3</sup>; *Z* = 2; ρ<sub>calcd</sub> = 2.174 g/cm<sup>3</sup>; λ = 0.71073 Å; μ = 2.071 mm<sup>-1</sup>; *F*(000) = 696; *index range*: 0 < *h* < 10, –10 < *k* < 10, –18 < *l* < 19; θ range = 1.35–25.98°; *temp* = 293(2) K; *collected reflns* = 4657; *unique reflns* = 4349; *R*<sub>int</sub> = 0.0121; *reflns with I* < 2σ(*I*) = 3620; *no. of variables* = 315; *weighting scheme* *w*<sup>-1</sup> = σ<sup>2</sup>*F*<sub>o</sub><sup>2</sup> + (0.029*P*)<sup>2</sup> + 0.7312*P*, *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3; *GoF* = 1.074; *final R*<sub>2σ(*I*)</sub> = 0.0225; *final wR*<sub>2σ(*I*)</sub> = 0.0591; *largest diff peak and hole* = 0.353 and –0.671 e/Å<sup>3</sup>.

(23) Crystal and selected refinement data for **2**: C<sub>20</sub>H<sub>9</sub>N<sub>3</sub>O<sub>10</sub>Os<sub>3</sub>; *fw* = 1021.9; *cryst size* = 0.13 × 0.13 × 0.13 mm; *cryst system* = monoclinic; *space group* = *P2*<sub>1</sub>/*c*; *a* = 15.595(8) Å; *b* = 25.075(5) Å; *c* = 12.79(1) Å; β = 99.81(6)°; *V* = 4930.5(6) Å<sup>3</sup>; *Z* = 8; ρ<sub>calcd</sub> = 2.753 g/cm<sup>3</sup>; λ = 0.71073 Å; μ = 15.483 mm<sup>-1</sup>; *F*(000) = 3664; *index range*: –19 < *h* < 0, –30 < *k* < 0, –15 < *l* < 15; θ range = 1.33–25.97°; *temp* = 200(2) K; *collected reflns* = 10018; *unique reflns* = 9657; *R*<sub>int</sub> = 0.0732; *reflns with I* < 2σ(*I*) = 5648; *no. of variables* = 629; *weighting scheme* *w*<sup>-1</sup> = σ<sup>2</sup>*F*<sub>o</sub><sup>2</sup> + (0.089*P*)<sup>2</sup>, *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3; *GoF* = 1.009; *final R*<sub>2σ(*I*)</sub> = 0.0478; *final wR*<sub>2σ(*I*)</sub> = 0.1454; *largest diff peak and hole* = 2.181 and –2.409 e/Å<sup>3</sup>.