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# Extensive Substitution, Protonation, and Methoxidation Reactions of Triruthenium Carbonyl Clusters Containing 2-Amino-6-methylpyridinato ($\mu_3$-ampy) as a Face-Bridging Ligand. X-ray Structures of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_7(PPh_3)_2]$ and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO_2Me)(CO)_6(PPh_3)_2]\cdot MeOH$

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The complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_9]$ (**1**) (Hampy = 2-amino-6-methylpyridine) reacts with excess triphenylphosphine to give the disubstituted derivative $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_7(PPh_3)_2]$ (**3**), which has the phosphorus atoms cis to the bridging amido fragment and cis to the hydride. Complex **3** undergoes protonation with $HBF_4\cdot OEt_2$ at one hydride-unbridged Ru–Ru edge to give $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO)_7(PPh_3)_2]BF_4$ (**4a**), in which one $PPh_3$ ligand has moved from cis (in complex **3**) to trans (in complex **4a**) to the hydride that spans the amido-bridged Ru–Ru edge. The cationic complex $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO)_9]BF_4$ (**2**) reacts with 2 equiv of triphenylphosphine to give $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO)_7(PPh_3)_2]BF_4$ (**4b**), in which the $PPh_3$ ligands are cis to the hydrides on the Ru atoms bonded to only one hydride, being therefore an isomer of **4a**. The transformation of **4b** into **4a** can be achieved in refluxing THF. Both **4a** and **4b** react with an excess of triphenylphosphine to give the trisubstituted derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO)_6(PPh_3)_3]BF_4$ (**5**). The reactions of **4a** and **5** with potassium methoxide lead to the neutral derivatives $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO_2Me)(CO)_6(PPh_3)_2]$ (**6a**) and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO_2Me)(CO)_5(PPh_3)_3]$ (**7**), respectively. These complexes contain a methoxycarbonyl group on the Ru atoms attached to two hydrides. A similar reaction with complex **4b** renders a mixture of two isomers (**6b**, **6c**) of **6a**. The molecular structures of **3** and **6a** have been confirmed by X-ray crystallography. Complex **3**: monoclinic, space group $P2_1/c$, $a$ = 16.719 (7) Å, $b$ = 12.263 (5) Å, $c$ = 24.448 (9) Å, $\beta$ = 108.69 (2)°, and $Z$ = 4. Complex **6a**·MeOH: monoclinic, space group $P2_1/n$, $a$ = 18.006 (7) Å, $b$ = 26.118 (8) Å, $c$ = 10.580 (5) Å, $\beta$ = 90.33 (2)°, and $Z$ = 4. The structures were solved by Patterson and Fourier methods and refined to $R$ = 0.0630 (**3**) and 0.0461 (**6a**) and $R'$ = 0.0860 (**3**) and 0.0624 (**6a**) for 4278 (**3**) and 6422 (**6a**) observed reflections with $I > 2\sigma(I)$.

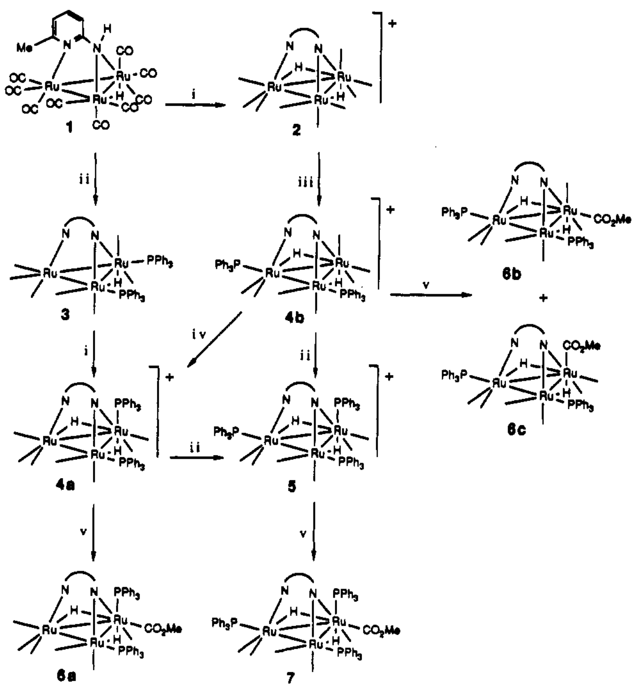
## Introduction

Although the carbonyl substitution chemistry of $[Ru_3(CO)_{12}]$ and of many of its neutral and anionic derivatives has been widely studied, the substitution chemistry of its cationic derivatives remains nearly unexplored.[2] However, a positive charge should enhance the cluster reactivity toward nucleophilic reagents, promoting carbonyl substitutions and nucleophilic additions. In this field, we have recently reported the carbonyl substitution chemistry at room temperature of the complexes $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_9]$[3,4] (**1**) and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO)_9][BF_4]$[3] (**2**) (Hampy = 2-amino-6-methylpyridine[5]), showing that the products of a series of protonation, substitution, and deprotonation reactions could be different from those obtained by direct substitution on the starting material. As a continuation of this work, we now report that up to three carbonyl ligands of the cationic complex **2** can be replaced by P-donor ligands, while only disubstitution can be achieved in the neutral complex **1**. We also describe that these substituted products undergo a series of reactions that lead to the selective synthesis of isomeric clusters.

## Results

The reactions described in this work are summarized in Scheme I. The main analytical tool for the characterization of the compounds was NMR spectroscopy, whose results are collected in Table I. Single-crystal X-ray diffraction studies were undertaken for compounds **3** and **6a**, whose results are presented in Tables II–V. These will be introduced in the appropriate places in the sections that follow.

**Scheme I**[a]



[a] Reagents and conditions: (i) $HBF_4$; (ii) excess $PPh_3$, 67 °C; (iii) 2.2 equiv of $PPh_3$, 67 °C; (iv) 67 °C; (v) $MeO^-$.

## Discussion

As described previously,[3] the reaction of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_9]$ (**1**) with an excess of triphenylphosphine at room temperature gave only the monosubstituted derivative $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_8(PPh_3)]$; however, the disubstituted complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_7(PPh_3)_2]$ (**3**) (Scheme I) could be prepared in high yield by carrying out the reaction in refluxing THF. Its X-ray structure (Figure 1) showed the $PPh_3$ ligands

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(1) (a) University of Oviedo. (b) University of Parma.

(2) See, for example: (a) Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: London, 1982; Vol IV, p 843. (b) Bruce, M. I. *Coord. Chem. Rev.* **1987**, *76*, 1.

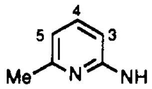
(3) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Bois, C.; Jeannin, Y. *J. Chem. Soc., Dalton Trans.* **1990**, 3347.

(4) Andreu, P. L.; Cabeza, J. A.; Riera, V. *J. Organomet. Chem.* **1990**, *393*, C30.

(5) Our interest in these ligands is related to earlier works on the reactivity of $[Ru_3(CO)_{12}]$ with *N*-donor ligands: (a) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Jeannin, Y.; Miguel, D. *J. Chem. Soc., Dalton Trans.* **1990**, 2201. (b) Andreu, P. L.; Cabeza, J. A.; Fernández-Colinas, J. M.; Riera, V. *J. Chem. Soc., Dalton Trans.* **1990**, 2927. (c) Cabeza, J. A.; Riera, V.; Pellinghelli, M. A.; Tiripicchio, A. *J. Organomet. Chem.* **1989**, *376*, C23. (d) Cabeza, J. A.; Oro, L. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1437.

0020-1669/91/1330-4611$02.50/0

**Table I.** NMR Data[a]



| complex | δ($^1$H) | | | | | | | δ($^{31}$P{$^1$H}) |
|---|---|---|---|---|---|---|---|---|
| | H$^3$ | H$^4$ | H$^5$ | NH | Me | μ-H | other | |
| **3** | 6.42 (d) | 6.92 (t) | 5.12 (d) | 2.02 (s, br) | 2.64 (s) | −9.91 (t) [8.3] | 7.7–7.0 (m, P*Ph*$_3$) | 31.3 (s) |
| **4a**[b] | 6.65 (d) | | 5.74 (d) | 3.25 (d) [5.6] | 2.34 (s) | −12.54 (ddd) [30.3] [5.3] (2.1), −12.64 (dd) [5.8] (2.1) | 7.7–6.8 (m, P*Ph*$_3$) | 35.1 (d) {2.3}, 32.3 (d) {2.3} |
| **4b**[b] | 6.70 (d) | | 6.27 (d) | 4.21 (s, br) | 2.00 (s) | −12.91 (m), −13.33 (m) | 7.8–7.0 (m, P*Ph*$_3$) | 30.2 (d) {49.3}, 26.4 (d) {49.3} |
| **5**[c] | 6.72 (d) | 7.06 (t) | 4.89 (d) | 3.67 (s, br) | 2.10 (s) | −11.22 (m), −11.95 (dm) [47.8] | 8.0–7.1 (m, P*Ph*$_3$) | 31.3 (d) {58.0}, 30.5 (s), 17.7 (d) {58.0} |
| **6a** | 6.19 (d) | 6.43 (t) | 4.84 (d) | 3.09 (d) [6.0] | 2.43 (s) | −11.28 (dd) [34.1] [6.0], −12.13 (dd) [16.8] [5.0] | 7.7–7.1 (m, P*Ph*$_3$), 2.52 (s, CO$_2$*Me*) | 41.2 (d) {3.0}, 36.4 (d) {3.0} |
| **6b**[d] | 6.05 (d) | 7.02 (t) | 5.97 (d) | 3.80 (d) [6.1] | 1.92 (s) | −11.59 (t) [5.4] (5.4), −12.71 (dd) [14.1] (5.4) | 7.6–7.2 (m, P*Ph*$_3$), 2.92 (s, CO$_2$*Me*) | 35.0 (d) {59.5}, 29.1 (d) {59.5} |
| **6c**[d] | 6.05 (d) | 6.68 (t) | 5.84 (d) | 3.43 (s, br) | 1.89 (s) | −11.40 (dd) [13.3] (6.6), −12.21 (t) [6.6] (6.6) | 7.6–7.2 (m, P*Ph*$_3$), 3.16 (s, CO$_2$*Me*) | 36.2 (d) {59.3}, 27.4 (d) {59.3} |
| **7** | 6.02 (d) | 6.34 (t) | 4.56 (d) | 3.06 (d) [7.8] | 1.93 (s) | −11.25 (ddd) [37.1] [4.6] (5.8), −11.56 (ddd) [15.1] [10.7] (5.8) | 7.8–6.8 (m, P*Ph*$_3$), 2.12 (s, CO$_2$*Me*) | 41.6 (s), 33.8 (d) {70.1}, 20.1 (d) {70.1} |

[a] Spectra recorded in CDCl$_3$, at 300 MHz ($^1$H) or 121.7 MHz ($^{31}$P), 25 °C; chemical shifts (δ) relative to SiMe$_4$ (internal, $^1$H) or 85% H$_3$PO$_4$ (external, $^{31}$P); multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad) in parentheses; coupling constants, *J*/Hz, in parentheses ($J_{H-H}$), square brackets [$J_{H-P}$], or braces {$J_{P-P}$}; coupling constants $J_{H-H}$ for H$^3$, H$^4$, and H$^5$ are of ca. 7 Hz in all cases. [b] The resonance of H$^4$ overlaps with those of the phosphine phenyl hydrogens. [c] In acetone-$d_6$. [d] Interchangeable assignments.

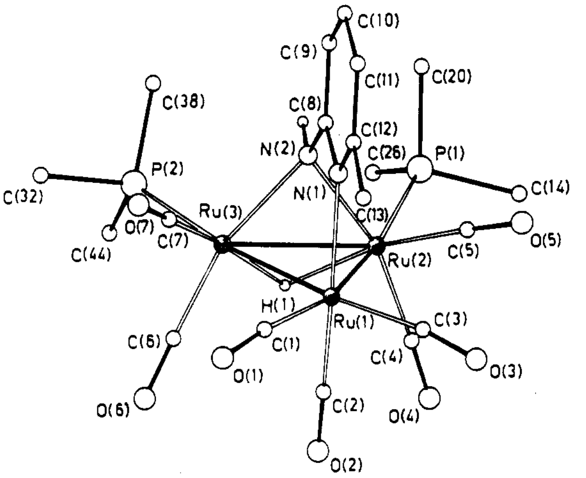


**Figure 1.** Perspective view of the molecular structure of the complex [Ru$_3$(μ-H)(μ$_3$-ampy)(CO)$_7$(PPh$_3$)$_2$] (**3**), showing the atomic numbering scheme (phenyl rings omitted for clarity).

in equatorial positions cis to the bridging hydride, in complete agreement with its NMR data (Table I).

Protonation of complex **3** with HBF$_4$·OEt$_2$ in dichloromethane led to the cationic dihydrido derivative [Ru$_3$(μ-H)$_2$(μ$_3$-ampy)(CO)$_7$(PPh$_3$)$_2$][BF$_4$] (**4a**) (Scheme I). As expected, its IR spectrum showed the ν(CO) absorptions shifted to higher wavenumbers than those of its neutral precursor, indicating a higher formal oxidation state of the metal atoms. The $^1$H and $^{31}$P NMR spectra of **4a** (Table I; Figure 2) indicated that the hydride H$^A$ (see assignments in Figure 2) is coupled to the other hydride [$J$(H$^A$–H$^B$) = 2.1 Hz] and to both phosphorus atoms [$J$(H$^A$–P$^A$) = 30.3 Hz, $J$(H$^A$–P$^B$) = 5.3 Hz]. From the values of the coupling constants it can be inferred that P$^A$ and P$^B$ are trans and cis, respectively, to H$^A$. The hydride H$^B$ is coupled to H$^A$ and to P$^A$ [$J$(H$^B$–P$^A$) = 5.8 Hz, typical of a cis coupling[6]] but is not coupled to P$^B$. The off-resonance $^{31}$P NMR spectrum of **4a** is in complete agreement with the proton spectrum, showing also a small coupling (*J* ca. 5.6 Hz) of P$^B$ to the NH proton. These data clearly indicate that, on protonation, the phosphine ligand attached to the ruthenium atom that bears the two hydrides moves from cis (in complex **3**) to trans (in complex **4a**) to the hydride that spans the amido-bridged Ru–Ru edge. Supposing that the phosphine P$^A$ had remained in its original position, the hydride H$^B$ should couple to P$^A$ with a large coupling constant, as expected for a trans arrangement, remaining uncoupled to P$^B$, and that was not observed. A similar rearrangement of a phosphine ligand was observed previously on protonation of [Ru$_3$(μ-H)(μ$_3$-ampy)(CO)$_8$-

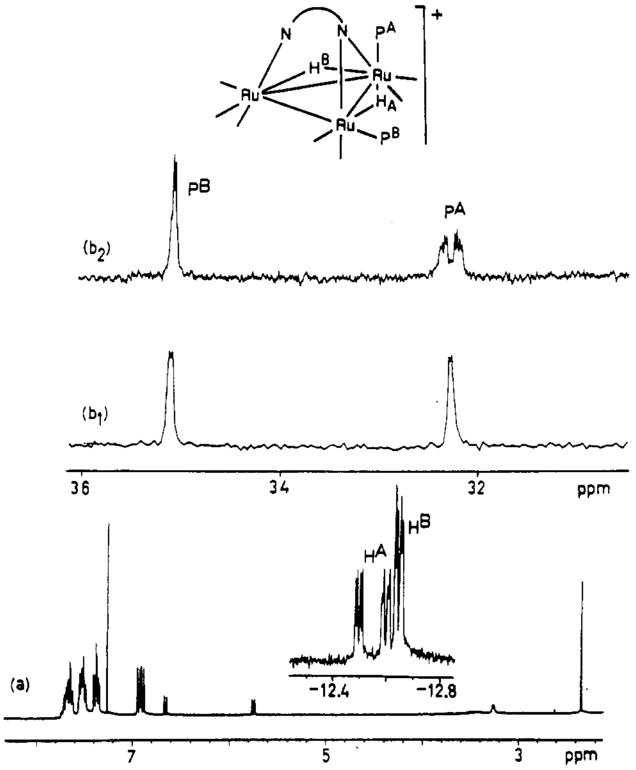


**Figure 2.** NMR spectra of [Ru$_3$(μ-H)$_2$(μ$_3$-ampy)(CO)$_7$(PPh$_3$)$_2$][BF$_4$] (**4a**): (a) $^1$H (CDCl$_3$, 25 °C, 300 MHz); (b$_1$) $^{31}$P{$^1$H}, and (b$_2$) off-resonance $^{31}$P (CDCl$_3$, 25 °C, 121.5 MHz).

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[6] For $J_{cis}$(H–P) couplings in related clusters, see: (a) Deeming, A. J.; Peters, R.; Hursthouse, M. B.; Backer-Dirks, J. D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1205. (b) Lugan, N.; Lavigne, G.; Bonnet, J. J.; Rèau, R.; Neibecker, D.; Tkatchenko, I. *J. Am. Chem. Soc.* **1988**, *110*, 5369. (c) References 3 and 4.

**Table II.** Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations (Esd's) in Parentheses for Compounds **3** and **16a**·MeOH

| | **3** | **6a**·MeOH | | **3** | **6a**·MeOH |
|---|---|---|---|---|---|
| | | Distances | | | |
| Ru(1)–Ru(2) | 2.759 (2) | 2.774 (1) | C(10)–C(11) | 1.38 (2) | 1.368 (14) |
| Ru(1)–Ru(3) | 2.762 (2) | 2.970 (1) | C(11)–C(12) | 1.38 (2) | 1.374 (15) |
| Ru(2)–Ru(3) | 2.819 (2) | 2.815 (1) | N(1)–C(12) | 1.36 (1) | 1.374 (10) |
| Ru(1)–N(1) | 2.212 (10) | 2.181 (6) | N(2)–C(8) | 1.39 (1) | 1.379 (8) |
| Ru(2)–N(2) | 2.153 (11) | 2.144 (5) | C(12)–C(13) | 1.53 (2) | 1.476 (14) |
| Ru(3)–N(2) | 2.150 (10) | 2.162 (5) | C(1)–O(1) | 1.16 (2) | 1.132 (12) |
| Ru(2)–P(1) | 2.368 (5) | 2.366 (2) | C(2)–O(2) | 1.12 (2) | 1.151 (10) |
| Ru(3)–P(2) | 2.382 (3) | 2.314 (2) | C(3)–O(3) | 1.17 (2) | 1.156 (10) |
| Ru(1)–C(1) | 1.91 (2) | 1.928 (9) | C(4)–O(4) | 1.15 (3) | 1.143 (9) |
| Ru(1)–C(2) | 1.87 (2) | 1.851 (8) | C(5)–O(5) | 1.14 (2) | 1.140 (10) |
| Ru(1)–C(3) | 1.89 (1) | 1.897 (8) | C(6)–O(6) | 1.16 (2) | 1.151 (8) |
| Ru(2)–C(4) | 1.89 (2) | 1.863 (7) | C(7)–O(7) | 1.13 (2) | 1.211 (7) |
| Ru(2)–C(5) | 1.89 (1) | 1.887 (8) | C(7)–O(8) | | 1.368 (8) |
| Ru(3)–C(6) | 1.84 (2) | 1.823 (6) | O(8)–C(14) | | 1.454 (11) |
| Ru(3)–C(7) | 1.87 (2) | 2.038 (6) | Ru(2)–H(1) | 1.85 (5) | 1.82 (5) |
| N(1)–C(8) | 1.35 (2) | 1.336 (9) | Ru(3)–H(1) | 1.85 (6) | 1.84 (6) |
| C(8)–C(9) | 1.39 (2) | 1.396 (9) | Ru(1)–H(2) | | 1.80 (5) |
| C(9)–C(10) | 1.34 (2) | 1.353 (12) | Ru(3)–H(2) | | 1.79 (4) |
| | | Angles | | | |
| Ru(2)–Ru(1)–Ru(3) | 61.40 (6) | 58.57 (4) | Ru(1)–Ru(3)–C(6) | 92.7 (5) | 101.0 (2) |
| Ru(1)–Ru(2)–Ru(3) | 59.35 (6) | 64.20 (4) | Ru(1)–Ru(3)–N(2) | 74.0 (3) | 70.1 (1) |
| Ru(1)–Ru(3)–Ru(2) | 59.26 (5) | 57.23 (4) | Ru(1)–Ru(3)–P(2) | 173.4 (1) | 113.4 (1) |
| C(2)–Ru(1)–C(3) | 89.5 (7) | 92.2 (4) | C(6)–Ru(3)–C(7) | 89.2 (6) | 96.0 (3) |
| C(1)–Ru(1)–C(3) | 97.9 (7) | 100.4 (4) | N(2)–Ru(3)–C(7) | 98.7 (5) | 89.1 (2) |
| C(1)–Ru(1)–C(2) | 91.8 (7) | 91.7 (4) | N(2)–Ru(3)–C(6) | 163.5 (5) | 166.5 (3) |
| N(1)–Ru(1)–C(3) | 98.0 (6) | 92.5 (3) | P(2)–Ru(3)–C(7) | 94.0 (4) | 86.4 (2) |
| N(1)–Ru(1)–C(2) | 167.0 (6) | 166.7 (3) | P(2)–Ru(3)–C(6) | 93.7 (4) | 90.7 (2) |
| N(1)–Ru(1)–C(1) | 97.7 (6) | 99.6 (3) | P(2)–Ru(3)–N(2) | 100.1 (3) | 102.2 (1) |
| Ru(3)–Ru(1)–C(3) | 164.0 (5) | 145.7 (3) | Ru(1)–N(1)–C(12) | 128.3 (9) | 126.8 (5) |
| Ru(3)–Ru(1)–C(2) | 86.7 (5) | 84.5 (3) | Ru(1)–N(1)–C(8) | 115.2 (8) | 115.1 (5) |
| Ru(3)–Ru(1)–C(1) | 97.7 (4) | 113.9 (3) | C(8)–N(1)–C(12) | 116.5 (11) | 118.1 (7) |
| Ru(3)–Ru(1)–N(1) | 83.2 (3) | 84.6 (2) | Ru(2)–N(2)–Ru(3) | 81.9 (4) | 81.6 (2) |
| Ru(2)–Ru(1)–C(3) | 102.7 (5) | 87.1 (3) | Ru(3)–N(2)–C(8) | 118.7 (8) | 124.8 (4) |
| Ru(2)–Ru(1)–C(2) | 83.3 (5) | 84.9 (3) | Ru(2)–N(2)–C(8) | 120.2 (8) | 116.3 (4) |
| Ru(2)–Ru(1)–C(1) | 158.7 (4) | 171.9 (3) | Ru(1)–C(1)–O(1) | 171.3 (14) | 170.1 (9) |
| Ru(2)–Ru(1)–N(1) | 84.7 (3) | 82.9 (2) | Ru(1)–C(2)–O(2) | 176.3 (16) | 178.5 (8) |
| Ru(1)–Ru(2)–C(5) | 80.6 (5) | 94.1 (2) | Ru(1)–C(3)–O(3) | 171.1 (14) | 179.2 (8) |
| Ru(1)–Ru(2)–C(4) | 98.1 (7) | 95.4 (2) | Ru(2)–C(4)–O(4) | 175.8 (14) | 177.3 (7) |
| Ru(1)–Ru(2)–N(2) | 74.0 (3) | 74.5 (1) | Ru(2)–C(5)–O(5) | 177.3 (15) | 179.1 (7) |
| Ru(1)–Ru(2)–P(1) | 164.0 (1) | 170.5 (1) | Ru(3)–C(6)–O(6) | 178.0 (12) | 176.8 (6) |
| C(4)–Ru(2)–C(5) | 91.8 (6) | 91.4 (3) | Ru(3)–C(7)–O(7) | 178.1 (12) | 124.5 (5) |
| N(2)–Ru(2)–C(5) | 100.6 (5) | 97.5 (3) | N(1)–C(8)–N(2) | 116.1 (11) | 118.5 (6) |
| N(2)–Ru(2)–C(4) | 163.8 (5) | 167.0 (3) | N(2)–C(8)–C(9) | 121.8 (12) | 120.2 (6) |
| P(1)–Ru(2)–C(5) | 91.7 (5) | 90.5 (3) | N(1)–C(8)–C(9) | 122.1 (12) | 121.2 (6) |
| P(1)–Ru(2)–C(4) | 96.2 (5) | 92.7 (3) | N(1)–C(12)–C(11) | 123.4 (13) | 120.8 (8) |
| P(1)–Ru(2)–N(2) | 93.9 (3) | 96.7 (1) | C(11)–C(12)–C(13) | 118.5 (13) | 119.5 (9) |
| Ru(3)–Ru(2)–C(5) | 133.5 (5) | 143.0 (2) | N(1)–C(12)–C(13) | 118.0 (12) | 119.7 (9) |
| Ru(3)–Ru(2)–C(4) | 114.8 (5) | 118.9 (2) | Ru(2)–H(1)–Ru(3) | 99 (2) | 101 (2) |
| Ru(3)–Ru(2)–P(1) | 120.3 (1) | 107.5 (1) | Ru(1)–H(2)–Ru(3) | | 112 (2) |
| Ru(2)–Ru(3)–C(7) | 134.9 (4) | 96.8 (2) | C(7)–O(8)–C(14) | | 115.5 (6) |
| Ru(2)–Ru(3)–C(6) | 115.9 (5) | 117.9 (2) | O(7)–C(7)–O(8) | | 119.1 (6) |
| Ru(2)–Ru(3)–P(2) | 119.1 (1) | 150.6 (1) | Ru(3)–C(7)–O(8) | | 116.4 (4) |
| Ru(1)–Ru(3)–C(7) | 84.2 (4) | 153.5 (2) | | | |

$(PPh_3)]$ to give $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_3)][BF_4]$.[3]

The reaction of the cationic complex $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**) with an excess of triphenylphosphine at room temperature gave only the monosubstituted derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_3)][BF_4]$;[3] however, in refluxing THF the trisubstituted complex $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_6(PPh_3)_3][BF_4]$ (**5**) was obtained as the final product. Monitoring of the reaction by $^{31}P\{^1H\}$ NMR spectroscopy (Figure 3) showed the progressive substitution of three carbonyl ligands. In fact, the disubstituted derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_7(PPh_3)_2][BF_4]$ (**4b**) could be isolated by using a slight excess of triphenylphosphine in a 30-min reaction. The $^{31}P\{^1H\}$ NMR (Table I) spectrum of **4b** showed two doublets with a large coupling constant (49.3 Hz), while the hydride resonances in the $^1H$ NMR spectrum only showed $J_{cis}(P\text{–}H)$ couplings. These data clearly indicate that the P atoms are in a linear arrangement along a Ru–Ru bond and that the substitutions have therefore taken place at equatorial positions on the Ru atoms bonded to only one hydride. Complex **5** could also be prepared by reaction of **4a** with an excess of triphenylphosphine in refluxing THF; its spectroscopic data are in complete agreement with the structure depicted in the Scheme I.

It is interesting to note that the complex **4b** isomerized into **4a** in refluxing THF, but this reaction was not observed when the solution contained triphenylphosphine. With these data it seems clear that the isomerization takes place through a dissociative mechanism.

The cationic dihydrido complexes **4a**, **4b**, and **5** did not react with triethylamine in dichloromethane at room temperature; however, the compounds **2** and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_3)][BF_4]$ undergo deprotonation under similar conditions.[3] Most probably, the hydrides of **4a**, **4b**, and **5** are not acidic enough to react with triethylamine due to the presence of two or three basic phosphorus atoms in the complexes. However, with a stronger and more nucleophilic base, such as the methoxide ion, the three compounds gave methoxycarbonyl derivatives[7] (Scheme

**Table III.** Crystallographic Data for Compounds **3** and **6a**·MeOH

| | 3 | 6a·MeOH |
|---|---|---|
| chem formula | $C_{49}H_{38}N_2O_7P_2Ru_3$ | $C_{50}H_{42}N_2O_8P_2Ru_3\cdot CH_3OH$ |
| fw | 1132.01 | 1196.09 |
| cryst system | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/n$ |
| $a$/Å | 16.719 (7) | 18.006 (7) |
| $b$/Å | 12.263 (5) | 26.118 (8) |
| $c$/Å | 24.448 (9) | 10.580 (5) |
| $\beta$/deg | 108.69 (2) | 90.33 (2) |
| $V$/Å$^3$ | 4748 (3) | 4975 (3) |
| $Z$ | 4 | 4 |
| $T$/°C | 22 | 22 |
| $\lambda$/Å | 1.541 838 | 0.710 73 |
| $\rho_{calcd}$/g cm$^{-3}$ | 1.584 | 1.597 |
| $\mu$/cm$^{-1}$ | 88.90 (Cu K$\alpha$) | 10.00 (Mo K$\alpha$) |
| $R(F_o)$ | 0.0630 | 0.0461 |
| $R_w(F_o)$ | 0.0860 | 0.0624 |

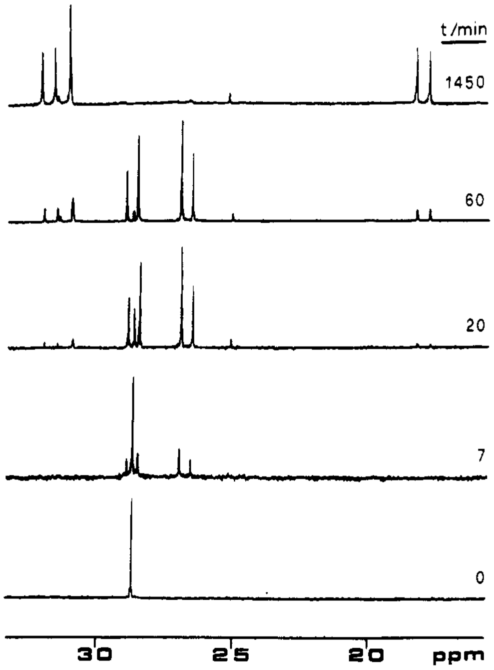

**Figure 3.** Evolution of the reaction of complex **2** with an excess of $PPh_3$ in refluxing THF, showing the progressive formation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_3)][BF_4]$ (0 min), complex **4b** (major species after 60 min), and complex **5** (final product). The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (THF, $D_2O$ capillary lock, 25 °C, 121.5 MHz).

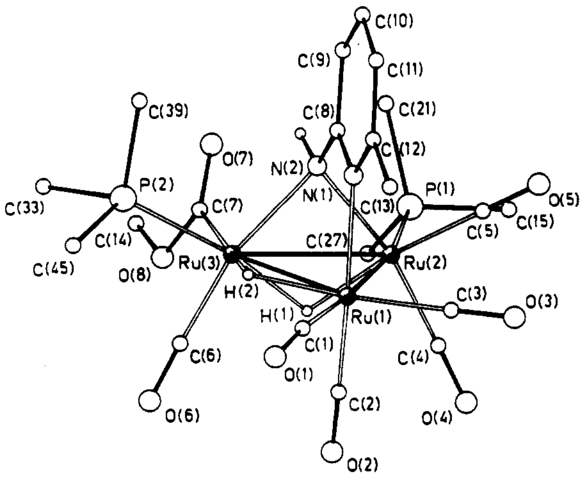

**Figure 4.** Perspective view of the molecular structure of the complex $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO_2Me)(CO)_6(PPh_3)_2]$ (**6a**), showing the atomic numbering scheme (phenyl rings omitted for clarity).

**Table IV.** Fractional Atomic Coordinates ($\times 10^4$) for Selected Atoms of Complex **3**

| atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Ru(1) | 889 (1) | 2650 (1) | 1602 (1) |
| Ru(2) | 2212 (1) | 1530 (1) | 1419 (1) |
| Ru(3) | 1986 (1) | 1518 (1) | 2513 (1) |
| P(1) | 3058 (2) | 182 (4) | 1179 (1) |
| P(2) | 2847 (2) | 357 (3) | 3248 (1) |
| O(1) | −107 (8) | 3798 (11) | 2290 (5) |
| O(2) | 2104 (8) | 4512 (11) | 1915 (5) |
| O(3) | 90 (8) | 3852 (10) | 467 (6) |
| O(4) | 3220 (9) | 3456 (14) | 1219 (5) |
| O(5) | 1005 (7) | 1617 (11) | 194 (4) |
| O(6) | 2527 (7) | 3566 (10) | 3206 (4) |
| O(7) | 476 (7) | 1371 (9) | 2922 (5) |
| N(1) | 224 (6) | 1065 (8) | 1421 (4) |
| N(2) | 1584 (6) | 381 (9) | 1808 (4) |
| C(1) | 220 (9) | 3303 (13) | 2016 (6) |
| C(2) | 1670 (10) | 3792 (15) | 1796 (7) |
| C(3) | 364 (10) | 3316 (12) | 880 (7) |
| C(4) | 2813 (10) | 2740 (19) | 1277 (6) |
| C(5) | 1457 (8) | 1557 (13) | 654 (6) |
| C(6) | 2316 (8) | 2767 (14) | 2947 (6) |
| C(7) | 1053 (8) | 1416 (11) | 2776 (5) |
| C(8) | 726 (7) | 180 (10) | 1559 (5) |
| C(9) | 406 (10) | −873 (12) | 1462 (6) |
| C(10) | −429 (12) | −1041 (14) | 1231 (7) |
| C(11) | −965 (10) | −154 (14) | 1089 (6) |
| C(12) | −618 (7) | 877 (11) | 1191 (5) |
| C(13) | −1211 (9) | 1861 (14) | 1066 (7) |

**Table V.** Fractional Atomic Coordinates ($\times 10^4$) for Selected Atoms of Complex **6a**·MeOH

| atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Ru(1) | 3577 (1) | 434 (1) | 1456 (1) |
| Ru(2) | 3764 (1) | 1446 (1) | 2186 (1) |
| Ru(3) | 2291 (1) | 1085 (1) | 2155 (1) |
| P(1) | 3746 (1) | 2288 (1) | 3012 (2) |
| P(2) | 1333 (1) | 632 (1) | 3081 (1) |
| O(1) | 3125 (4) | −608 (3) | 404 (9) |
| O(2) | 3328 (4) | 860 (3) | −1147 (5) |
| O(3) | 5259 (3) | 389 (3) | 1121 (7) |
| O(4) | 4443 (4) | 1770 (3) | −275 (5) |
| O(5) | 5276 (3) | 1269 (3) | 3373 (7) |
| O(6) | 1486 (3) | 1107 (2) | −305 (4) |
| O(7) | 1901 (3) | 1860 (2) | 3999 (4) |
| O(8) | 1386 (3) | 2011 (2) | 2118 (4) |
| N(1) | 3669 (3) | 295 (2) | 3483 (5) |
| N(2) | 3115 (3) | 1100 (2) | 3649 (4) |
| C(1) | 3305 (4) | −243 (4) | 895 (9) |
| C(2) | 3431 (4) | 702 (3) | −146 (7) |
| C(3) | 4622 (4) | 408 (3) | 1239 (8) |
| C(4) | 4191 (4) | 1658 (3) | 674 (7) |
| C(5) | 4708 (4) | 1332 (3) | 2919 (7) |
| C(6) | 1783 (4) | 1108 (3) | 662 (5) |
| C(7) | 1818 (3) | 1723 (2) | 2914 (6) |
| C(8) | 3417 (3) | 672 (3) | 4218 (6) |
| C(9) | 3472 (4) | 644 (3) | 5533 (6) |
| C(10) | 3766 (5) | 228 (4) | 6107 (8) |
| C(11) | 4003 (5) | −165 (4) | 5355 (10) |
| C(12) | 3971 (4) | −129 (3) | 4060 (10) |
| C(13) | 4242 (6) | −558 (4) | 3282 (12) |
| C(14) | 1020 (5) | 2448 (4) | 2696 (9) |

I). In view of the X-ray structure of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO_2Me)(CO)_6(PPh_3)_2]$ (**6a**) (Figure 4), it seems reasonable that in the complexes **4a**, **4b**, and **5** the equatorial CO ligands attached to the ruthenium atoms which are bonded to the two hydrides bear a higher partial positive charge than the other CO ligands, being therefore more susceptible to nucleophilic attack by the methoxide ion. These arguments also agree with the fact that the reactions

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(7) The formation of methoxycarbonyl groups by attack of methoxide anions to coordinated CO ligands is well-known. See, for example: (a) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627. (b) Isobe, K.; Meanwell, N. J.; Smith, A. J.; Adams, H.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1215.

of **4a** and **5** with methoxide afforded single compounds (**6a**, **7**), while a similar reaction with **4b**, which has two equatorial CO ligands on the Ru atom attached to the two hydrides, gave a mixture of two isomers (**6b**, **6c**).

**Description of the X-ray Structures of Complexes 3 and 6a.** The structures of **3** and **6a** are depicted in Figures 1 and 4, as well as the atomic numbering schemes. Selected bond distances and angles for both complexes are given in Table II. The triangular metal arrangement of complex **3** shows the hydride-bridged Ru(2)–Ru(3) edge slightly longer [2.819 (2) Å] than the other two [2.759 (2) and 2.762 (2) Å]. The hydride bridge [Ru(2)–H(1) = 1.85 (5) Å, Ru(3)–H(1) = 1.85 (6) Å] forms a dihedral angle of 122 (4)° with the metal triangle. Seven terminal carbonyl groups are bonded to the Ru atoms, three to Ru(1) and two to Ru(2) and Ru(3), which are also bonded to the P atoms [Ru(2)–P(1) = 2.368 (5) and Ru(3)–P(2) = 2.382 (3) Å] of two $PPh_3$ ligands, which are in equatorial positions cis to the hydride bridge [P(1)–Ru(2)–H(1) = 105 (2)°, P(2)–Ru(3)–H(1) = 98 (2)°]. The ampy ligand interacts with all three metal atoms, being bonded to Ru(1) through the pyridinic nitrogen N(1) [Ru(1)–N(1) = 2.212 (10) Å] and bridging the Ru(2)–Ru(3) edge through the exocyclic nitrogen N(2) [Ru(2)–N(2) = 2.153 (11) Å, Ru(3)–N(2) = 2.150 (10) Å]. The Ru(2)–N(2)–Ru(3) bridge is nearly perpendicular to the metal triangle [dihedral angle 95.1 (3)°] and forms a dihedral angle of 143 (4)° with the hydride bridge. The pyridine ring is strictly planar and coplanar with the Ru(1), N(2), and C(13) atoms, which deviate by 0.028 (2), −0.03 (1), and −0.09 (2) Å, respectively, from it. The structure and the structural parameters of complex **3** are comparable to those of $[Ru_3(\mu\text{-}H)(\mu_3\text{-anpy})(CO)_9]$ (Hanpy = 2-anilinopyridine).[5a]

In the structure of complex **6a** the two hydride-bridged edges [Ru(1)–Ru(3) = 2.970 (1) Å, Ru(2)–Ru(3) = 2.815 (1) Å] are longer than the third one [Ru(1)–Ru(2) = 2.774 (1) Å]. The Ru(2)–H(1)–Ru(3) bridge [Ru(2)–H(1) = 1.82 (5) Å, Ru(3)–H(1) = 1.84 (6) Å] is nearly perpendicular to the metal triangle, whereas the Ru(1)–H(2)–Ru(3) bridge [Ru(1)–H(2) = 1.80 (5) Å, Ru(3)–H(2) = 1.79 (4) Å] is nearly coplanar with the metal triangle, the dihedral angles being 103 (2) and 10 (4)°, respectively. Six terminal CO groups are bonded to the Ru atoms, three to Ru(1), two to Ru(2), and one to Ru(3). The Ru(2) and Ru(3) atoms are also bonded to the P atoms [Ru(2)–P(1) = 2.366 (2) Å, Ru(3)–P(2) = 2.314 (2) Å] of two $PPh_3$ ligands that are in equatorial positions, but P(1) is cis [P(1)–Ru(2)–H(1) = 98 (2)°] while P(2) is trans [P(2)–Ru(3)–H(1) = 170 (1)°] to the hydride H(1). It is noteworthy that the Ru–P bond trans to a Ru–Ru bond is much longer than the one trans to a hydride. The Ru(3) atom is also bonded to the C(7) carbon atom of a methoxycarbonyl ligand [Ru(3)–C(7) = 2.038 (6) Å], which is planar (apart from the hydrogen atoms) and nearly perpendicular to the metal triangle [dihedral angle 109.4 (2)°]. The ampy ligand is bonded to the Ru(1) atom through the pyridinic nitrogen N(1) [Ru(1)–N(1) = 2.181 (6) Å] and bridging the Ru(2)–Ru(3) edge through the exocyclic nitrogen N(2) [Ru(2)–N(2) = 2.144 (5) Å, Ru(3)–N(2) = 2.162 (5) Å]. The Ru(2)–N(2)–Ru(3) bridge is nearly perpendicular to the metal triangle [dihedral angle 91.4 (2)°] and forms a dihedral angle of 165 (2)° with the H(1) hydride bridge. The pyridine ring is strictly planar and coplanar with the Ru(1), N(2), and C(13) atoms, which deviate by 0.070 (1), −0.010 (5), and −0.004 (11) Å, respectively, from it. A possible hydrogen bond may join the hydrogen atom attached to N(2) to the O(7) atom of the methoxycarbonyl ligand [N(2)···O(7) = 2.979 (7) Å, H(1N2)···O(7) = 2.36 (9) Å; N(2)–H(1N2)–O(7) = 132 (9)°]. Although it is a neutral complex, the structural parameters of **6a** are comparable to those of the cationic complex **2**.[3]

## Concluding Remarks

The results reported herein, coupled with those described earlier by us[3,4] and by other workers,[8,9] present a nearly complete picture of the substitution chemistry of trinuclear ruthenium clusters containing face-bridging N-donor ligands. In this work we have provided synthetic methods and spectroscopic data for trinuclear clusters containing only seven, six, or five CO ligands, and we have crystallographically characterized the clusters **3** and **6a**. We have also showed that cationic clusters undergo substitutions to a higher extent than the neutral ones and that they are easily attacked by nucleophilic reagents, such as the methoxide ion. Throughout this work the ampy ligand has proved to hold the metal atoms firmly, since we have not detected any cluster break down even after long reaction times.

It is anticipated that the results presented herein may prove generally useful to workers studying carbonyl substitution reactions in metal clusters.

## Experimental Section

**General Data.** Solvents were dried and distilled prior to use. All reactions were carried out under nitrogen, using standard Schlenk techniques. The clusters **1**[5a] and **2**[3] were prepared as described previously; all other reagents were obtained from Aldrich and used as received. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer using 0.1-mm $CaF_2$ cells. NMR spectra were run on a Bruker AC-300 instrument, using $SiMe_4$ (internal, $^1H$, $^{13}C$) or 85% $H_3PO_4$ (external, $^{31}P$) as standards ($\delta = 0$ ppm). Microanalyses were obtained with a Perkin-Elmer 240-B microanalyzer.

**Preparation of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_7(PPh_3)_2]$ (3).** Complex **1** (50 mg, 0.075 mmol) and triphenylphosphine (55 mg, 0.21 mmol) were stirred in refluxing THF (10 mL) for 30 min. The deep red solution was evaporated to dryness under reduced pressure and the residue washed with methanol (three 5-mL portions) and recrystallized from dichloromethane–hexane to give complex **3** as red crystals (65 mg, 76%). Anal. Calcd for $C_{49}H_{38}N_2O_7P_2Ru_3$: C, 52.0; H, 3.4; N, 2.45. Found: C, 52.1; H, 3.5; N, 2.5. IR (cm$^{-1}$): $\nu$(CO) (THF) 2030 s, 1992 s, 1974 w, 1958 s, 1939 w, 1926 w; $\nu$(NH) (Nujol) 3292 w.

**Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_7(PPh_3)_2][BF_4]$ (4a).** An excess of $HBF_4 \cdot OEt_2$ (0.5 mL) was added to a solution of complex **3** (58 mg, 0.051 mmol) in dichloromethane (5 mL). The color changed from red to orange. The solvent was removed under reduced pressure and the oily residue washed with diethyl ether (four 4-mL portions) to give **4a** as a yellow-orange solid (39 mg, 59%). Anal. Calcd for $C_{49}H_{39}BF_4N_2O_7P_2Ru_3$: C, 48.25; H, 3.2; N, 2.3. Found: C, 48.0; H, 3.1; N, 2.1. IR (cm$^{-1}$): $\nu$(CO) ($CH_2Cl_2$) 2078 s, 2022 s, 2012 m, 2001 m, 1966 m; $\nu$(NH) 3292 w.

**Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_7(PPh_3)_2][BF_4]$ (4b).** Complex **2** (50 mg, 0.066 mmol) and triphenylphosphine (39 mg, 0.146 mmol) were refluxed in THF (10 mL) for 30 min. The solvent was removed under reduced pressure and the residue washed with hexane (four 5-mL portions) to give complex **4b** as an orange solid (61 mg, 76%). Anal. Calcd for $C_{49}H_{39}BF_4N_2O_7P_2Ru_3$: C, 48.3: H, 3.2; N, 2.3. Found: C, 48.4; H, 3.3; N, 2.3. IR (cm$^{-1}$): $\nu$(CO) ($CH_2Cl_2$) 2122 w, 2058 m, 2033 s, 2002 m, 1970 m, 1950 w; $\nu$(NH) (Nujol) 3266 w.

**Isomerization of 4b into 4a.** A solution of complex **4b** (40 mg, 0.032 mmol) was stirred in THF (10 mL) at reflux temperature. IR and $^{31}P$ NMR monitoring of the reaction showed complete transformation of **4b** into **4a** after 16 h.

**Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_6(PPh_3)_3][BF_4]$ (5).** Complex **2** (150 mg, 0.198 mmol) and triphenylphosphine (312 mg, 1.188 mmol) were stirred in refluxing THF (20 mL) for 26 h. The orange solution was evaporated to dryness and the residue was washed with diethyl ether (seven 5-mL portions) to give complex **5** as an orange solid (147 mg, 51%). This compound could also be prepared by reaction of complex **4a** (40 mg, 0.032 mmol) with triphenylphosphine (13 mg, 0.05 mmol) in refluxing THF (10 mL) for 30 h. Anal. Calcd for $C_{66}H_{54}BF_4N_2O_6P_3Ru_3$: C, 54.6; H, 3.7; N, 1.9. Found: C, 54.9; H, 3.7; N, 1.9. IR (cm$^{-1}$): $\nu$(CO) (THF) 2057 m, 2031 s, 1999 m, 1967 m, 1948 w; $\nu$(NH) (Nujol) 3295 w.

**Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO_2Me)(CO)_6(PPh_3)_2]$ (6a).** A solution of potassium hydroxide in methanol (0.8 cm$^3$, 0.1 M, 0.08 mmol) was added to a solution of complex **4a** (79 mg, 0.065 mmol) in THF (10 mL). The reaction was monitored by IR spectroscopy. After 30 min, only bands of the new product were observed. The solution was stirred for 45 min. The solvent was eliminated under reduced pressure and the residue extracted with dichloromethane (two 5-mL portions) to remove the insoluble $KBF_4$. The combined extracts were evaporated to dryness.

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(8) For a recent review dealing with ruthenium clusters containing *N*-donor ligands, see: Bruce, M. I.; Cifuentes, M. P.; Humphrey, M. G. *Polyhedron* **1991**, *10*, 227.

(9) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimatta, E. W.; Bonnet, J. J. *J. Am. Chem. Soc.* **1990**, *112*, 8607.

Washing of the residue with hexane (two 5-mL portions) gave complex **6a**·MeOH as a yellow solid (50 mg, 64%). Anal. Calcd for $C_{50}H_{42}N_2O_8P_2Ru_3$·MeOH: C, 51.2; H, 3.85; N, 2.35. Found: C, 51.3; H, 3.45; N, 2.3. IR (cm$^{-1}$): $\nu$(CO) ($CH_2Cl_2$) 2078 w, 2054 s, 2022 w, 1996 s, 1985 m, 1972 m, 1937 m; $\nu$(*C*O*O*Me) (Nujol) 1600 s; $\nu$(NH) (Nujol) 3269 m.

**Reaction of Complex 4b with Methoxide Ion.** A solution of KOH in methanol (0.7 mL, 0.1 M, 0.07 mmol) was added to a solution of complex **4b** (72 mg, 0.059 mmol) in THF (5 mL). The reaction was instantaneous. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (15 mL). The extract was evaporated to dryness and the residue washed with hexane (two 5-mL portions) to give a 3.5/1 mixture (by NMR) of the isomers **6b** and **6c** (or **6c** and **6b**) (49 mg, 71%). Anal. Calcd for $C_{50}H_{42}N_2O_8P_2Ru_3$: C, 51.6; H, 3.65; N, 2.4. Found: C, 51.2; H, 3.3; N, 2.2.

**Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO_2Me)(CO)_5(PPh_3)_3]$ (7).** A solution of KOH in methanol (0.5 mL, 0.1 M, 0.05 mmol) was added to a solution of complex **5** (46 mg, 0.031 mmol) in THF (5 mL). The reaction was instantaneous. The yellow solution was evaporated to dryness and the residue extracted with dichloromethane (10 mL). The solvent was removed again and the residue washed with hexane (5 mL) to give complex **7** as a yellow solid (30 mg, 69%). Anal. Calcd for $C_{67}H_{57}N_2O_7P_3Ru_3$: C, 57.55; H, 4.1; N, 2.0. Found: C, 57.8; H, 3.8; N, 1.8. IR (cm$^{-1}$): $\nu$(CO) ($CH_2Cl_2$) 2015 m, 1975 m, 1949 s, 1921 m; $\nu$(NH) (Nujol) 3265 w; $\nu$(*C*O*O*Me) 1598 s.

**Crystal Structures of Complexes 3 and 6a·MeOH.** Crystals of approximate dimensions 0.20 × 0.24 × 0.30 mm (**3**) and 0.18 × 0.22 × 0.25 mm (**6a**·MeOH) were used for the X-ray analyses. Selected crystallographic data for both compounds are collected in Table III.

Data were collected at room temperature on Siemens AED single-crystal diffractometers, using nickel-filtered Cu K$\alpha$ (**3**) and niobium-filtered Mo K$\alpha$ (**6a**) radiations and the $\theta/2\theta$ scan mode. All reflections with $\theta$ in the range 3–70° (**3**) and 3–27° (**6a**) were measured; of 9015 (**3**) and 10918 (**6a**) independent reflections, 4278 (**3**) and 6422 (**6a**), having $I > 2\sigma(I)$, were considered observed and used in the analysis. The individual profiles were analyzed according to Lehmann and Larsen.[10] The intensity of one standard reflection was measured after every 50 reflections as a general check of crystal and instrument stability. No significant changes were observed during the data collection. A correction for absorption effects was applied[11] to the data of **3** (maximum and minimum transmission factors 1.197 and 0.833).

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms excepting those of the phenyl groups of **6a**, the phenyl groups at P(1) of **3**, and the solvent molecule (methanol) of **6a**. The methanol molecule was found disordered and distributed in two positions of equal occupancy. The phenyl groups at P(1) of **3** were treated as rigid groups (C–C = 1.395 Å). The hydrogen atoms, except those of the phenyl groups and the methyl group at C(14) of **6a**, were clearly localized and refined isotropically; the remaining ones, except those of the rigid phenyl groups of **3**, were placed at their calculated positions (C–H = 1.00 Å) and refined riding on the corresponding carbon atoms. A weighting scheme $w = K[\sigma^2(F_0) + gF_0^2]^{-1}$ was used in the last cycles of refinement, with $K = 0.7458$ (**3**) and 0.4367 (**6a**) and $g = 0.0048$ (**3** and **6a**). Final $R$, $R'$ values were 0.0630, 0.0860 (**3**) and 0.0461, 0.0624 (**6a**). The SHELX-76 and SHELXS-86 systems of computer programs were used.[12] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref 13. Selected final atomic coordinates for the non-hydrogen atoms are given in Tables IV (**3**) and V (**6a**). All calculations were carried out on the Cray X-MP/48 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, Italy, and on the Gould Powernode 6040 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

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**Registry No.** **1**, 128477-65-6; **2**, 128477-67-8; **3**, 136537-38-7; **4a**, 136568-80-4; **4b**, 136568-82-6; **5**, 136568-84-8; **6a**, 136568-85-9; **6a**·MeOH, 136656-32-1; **6b**, 136568-86-0; **6c**, 136656-31-0; **7**, 136568-87-1; CO, 630-08-0.

**Supplementary Material Available:** Complete tables of positional parameters, tables of thermal parameters for the non-hydrogen atoms, and tables of hydrogen atom positions with their isotropic thermal parameters for both structures (11 pages); tables of structure factors (60 pages). Ordering information is given on any current masthead page.

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