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High-Nuclearity Osmium Carbonyl Cluster Complexes Containing (6-Methylpyrid-2-yl)imido Ligands. Synthesis of Hepta-, Octa-, and Nonanuclear Derivatives

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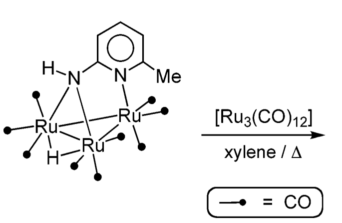
Three high-nuclearity osmium carbonyl cluster complexes, $[Os_7(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-CO})_2(CO)_{17}]$ (**1**), $[Os_8(\mu_3\text{-H})(\mu\text{-H})(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-CO})(CO)_{19}]$ (**2**), and $[Os_9O(\mu_4\text{-}\kappa^2\text{-ampy})_2(CO)_{18}]$ (**3**) (H_2ampy = 2-amino-6-methylpyridine), have been prepared by heating $[Os_3(CO)_{12}]$ with 0.5 equiv of H_2ampy in decane at reflux temperature. The trinuclear complex $[Os_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Hampy})(CO)_9]$ is an intermediate in this reaction. The metallic skeletons of **1** and **2** can be described as mono- (**1**) or bi-face-capped (**2**), basal-edge-bridged, square pyramids, whereas that of compound **3** consists of a pentagonal bipyramid with two equatorial edges spanned by metal atoms. In the three clusters, the ampy ligands are attached to edge-bridging Ru atoms through their pyridine N atoms, while they also cap metallic squares (in **1** and **2**) or triangles (in **3**) through their imido N atom. An additional feature of compound **3** is that it contains a terminal oxo ligand, unprecedented in osmium carbonyl cluster chemistry.

Introduction

We have recently reported that the triruthenium cluster $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Hampy})(CO)_9]$[1] ($H_2ampy$ = 2-amino-6-methylpyridine) reacts with $[Ru_3(CO)_{12}]$ at 110−140 °C to give the hexanuclear derivative $[Ru_6(\mu_3\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-CO})_2(CO)_{14}]$ (Scheme 1).[2,3] A high-yield one-pot synthesis of this compound was achieved by treating $[Ru_3(CO)_{12}]$ with 0.5 equiv of H_2ampy.[3] The unusual metallic skeleton of this cluster, a basal-edge-bridged square pyramid, is supported by a (6-methylpyrid-2-yl)imido ligand (ampy), which caps the metallic square through the imido N atom while its pyridine N atom is attached to the edge-bridging Ru atom. Its efficient synthesis has allowed us to investigate its reactivity with a variety of reagents, such as phosphines,[3] alkynes,[4] unsaturated cyclic hydrocarbons,[5] and H_2ampy.[6] Its thermolysis at high temperature (196 °C) leads to interesting nonanuclear derivatives.[7]

Some triosmium cluster complexes derived from various 2-aminopyridines, similar to $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Hampy})(CO)_9]$, are known.[8−11] However, the polynuclear ruthenium carbonyl chemistry referred to above has no parallel in osmium chemistry. In fact, to date, no examples of osmium carbonyl clusters containing μ_4-imido ligands have been reported and the number of known osmium carbonyl cluster complexes of nuclearity greater than 5 that contain N-donor ligands is very small.[12] These considerations led us to investigate the reactivity of $[Os_3(CO)_{12}]$ with H_2ampy, looking for ampy-bridged cluster derivatives of high nuclearity. The reason for using a methyl-substituted 2-aminopyridine as reagent is that the methyl group facilitates the identification of reaction mixtures by ^1H NMR.[4a,13]

Scheme 1



We now report that, although we have been unable to prepare the osmium analogue of $[Ru_6(\mu_3\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-CO})_2$-

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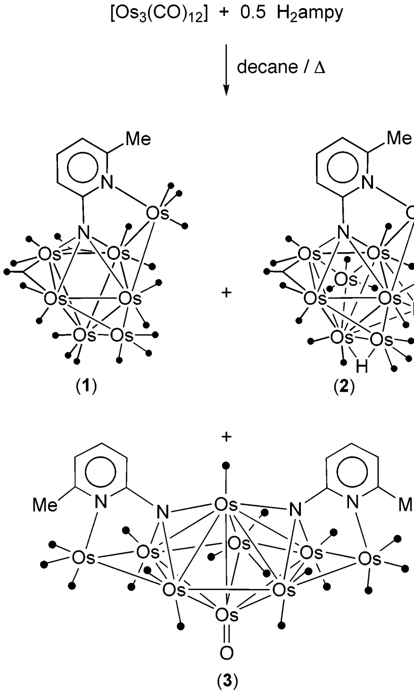
10.1021/om070201c CCC: $37.00

Scheme 2



(CO)$_{14}$], we have isolated and characterized three novel high-nuclearity osmium carbonyl clusters (hepta-, octa-, and nona-nuclear), which have most of their metal atoms attached to (6-methylpyrid-2-yl)imido ligands. The nonanuclear product also features a terminal oxo ligand, unprecedented in osmium carbonyl cluster chemistry.

Results and Discussion

The trinuclear complex [Os$_3$(μ-H)(μ_3-κ^2-Hampy)(CO)$_9$] was prepared in good yield (59%) by treating [Os$_3$(CO)$_{12}$] with an excess of H$_2$ampy (1:5 mole ratio) in decane at reflux temperature for 45 min. Its FAB-MS, IR, and NMR data confirmed that its structure is analogous to those of [Ru$_3$(μ-H)(μ_3-κ^2-Hampy)(CO)$_9$][1] (Scheme 1) and [Os$_3$(μ-H)(μ_3-κ^2-Xpy)(CO)$_9$], where Xpy denotes (pyrid-2-yl)amido ligands derived from 2-aminopyridine,[8] bis(pyrid-2-yl)amine,[9] 7-azaindole,[10] and 2-amino-6-phenylpyridine.[11]

Heating [Os$_3$(CO)$_{12}$] and H$_2$ampy, in a 2:1 mole ratio, in decane at reflux temperature afforded a mixture of compounds that was separated by preparative TLC on silica gel. Three products were isolated and characterized: [Os$_7$(μ_5-κ^2-ampy)(μ-CO)$_2$(CO)$_{17}$] (**1**; 8%), [Os$_8$(μ_3-H)(μ-H)(μ_5-κ^2-ampy)(μ-CO)(CO)$_{19}$] (**2**; 7%), and [Os$_9$O(μ_4-κ^2-ampy)$_2$(CO)$_{18}$] (**3**; 3%) (Scheme 2). Spot TLC, ^{1}H NMR, and IR monitoring of the reaction revealed that the trinuclear complex [Os$_3$(μ-H)(μ_3-κ^2-Hampy)(CO)$_9$] was formed at the initial stages. The reaction was stopped when the starting [Os$_3$(CO)$_{12}$] was no longer observed (9 h). The three products were characterized by IR and NMR spectroscopy, X-ray diffraction, and FAB-MS.

The molecular structures of compounds **1** and **2** are depicted in Figures 1 and 2, respectively. A selection of interatomic distances is given in Table 1. As far as possible, a common atom-numbering scheme has been used for both compounds. The metallic skeleton of compound **1** can be described as a square pyramid with the basal Os(1)−Os(2) edge and the triangular Os(2)−Os(5)−Os(6) face spanned by two additional metal atoms, Os(3) and Os(7), respectively. The imido N(1) atom of the ampy ligand caps the four atoms that define the base of the pyramid, while the pyridine N(2) atom of the ampy ligand is attached to the edge-bridging Os(3) atom. Two edge-bridging and 17 terminal carbonyl ligands complete the cluster shell. With 100 electrons and 13 Os−Os bonds, this cluster adheres to the EAN rule. Only one heptaosmium carbonyl cluster with a metallic framework similar to that of **1** has been previously reported, [Os$_7$(μ-H)$_2$(CO)$_{21}$].[14]

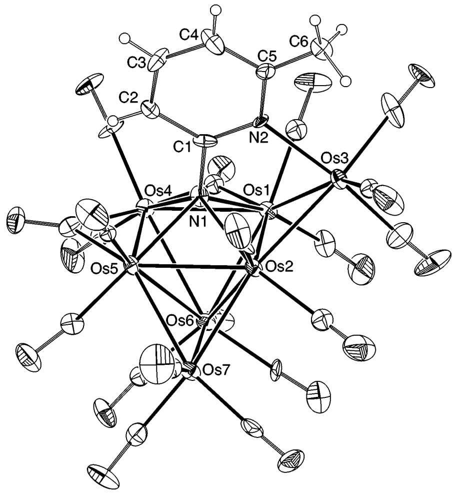


Figure 1. Molecular structure of compound **1**. Ellipsoids are drawn at the 30% probability level.

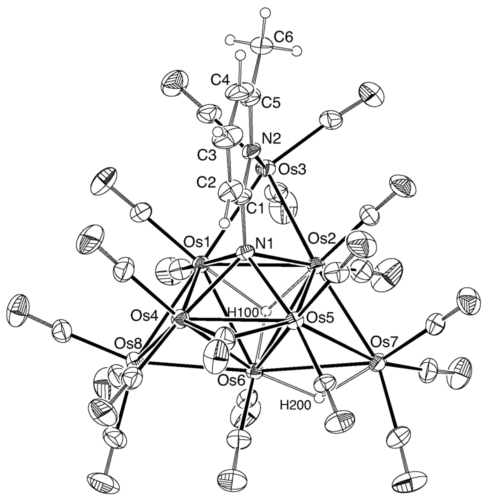


Figure 2. Molecular structure of compound **2**. Ellipsoids are drawn at the 30% probability level.

The structure of the octanuclear cluster **2** can be described as derived from that of **1**. It has the additional osmium atom, Os(8), capping the Os(1)−Os(4)−Os(6) triangular face of the square pyramid. No substantial difference is found in the coordination of the ampy ligand of **2** with respect to that of **1**. While compound **1** has no hydride ligands, compound **2** has two, one spanning the Os(6)−Os(7) edge and the other capping the Os(1)−Os(2)−Os(6) face. The cluster shell of **2** is completed with 1 bridging and 19 terminal CO ligands. With 112 electrons and 16 Os−Os bonds, this cluster also obeys the EAN rule. No previous examples of octaosmium carbonyl clusters with a metallic skeleton similar to that of **2** have been previously reported.

An important feature of compounds **1** and **2** is that their imido N atom caps four osmium atoms. Quite a few osmium clusters

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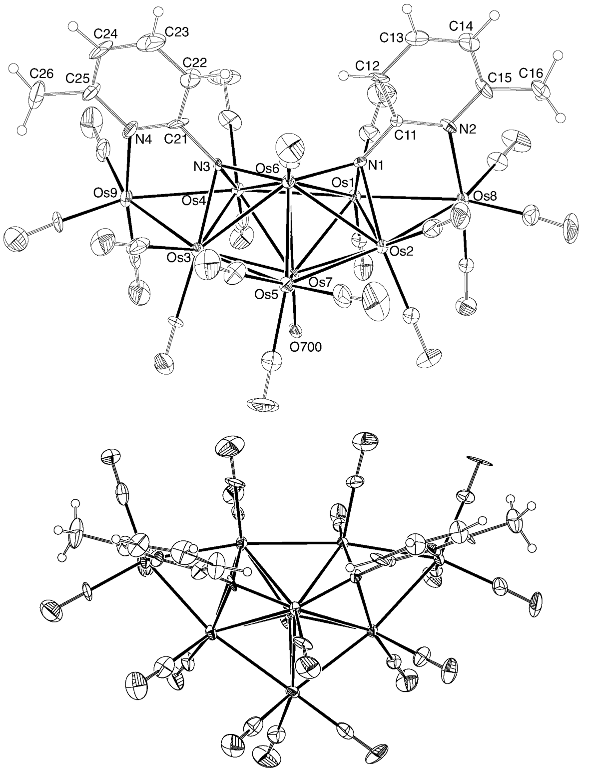

Figure 3. Two views of the molecular structure of compound **3**. Ellipsoids are drawn at the 30% probability level.

having μ_3-imido ligands have been reported,[15] but osmium clusters with μ_4-imido ligands are unprecedented.

The molecular structure of compound **3** is shown in Figure 3. A selection of interatomic distances is given in Table 2. The compound is nonanuclear. Its metallic framework comprises a pentagonal bipyramid with two equatorial edges, Os(1)−Os(2) and Os(3)−Os(4), spanned by the Os(8) and Os(9) atoms, respectively. The two apical atoms, Os(6) and Os(7), are attached to each other. This metallic skeleton is supported by two μ_4-ampy ligands, which have their pyridine N atoms N(2) and N(4) attached to the edge-bridging Os(8) and Os(9) atoms, respectively, and their imido N atoms N(1) and N(3) capping the triangles defined by the apical Os(6) atom and the metal atoms of the metal-bridged equatorial edges. Interestingly, a terminal oxo ligand is attached to the apical Os(7) atom. The cluster shell is completed with 18 terminal carbonyl ligands. With 122 electrons and 20 Os−Os bonds, the cluster obeys the EAN rule.

It is noteworthy that several Os−Os bonds in **3** are exceptionally short (<2.66 Å) and are similar in length to Os−Os bonds in electron-deficient osmium clusters.[16] The bonding between the two apical osmium atoms with a fairly ordinary Os−Os distance, Os(6)−Os(7) = 2.837(1) Å, seems to force the $Os_{ap}-Os_{eq}$ distances to be shorter than expected for normal Os−Os bonds.[16,17] This is clearly the case for the five bonds that connect the apical Os(7) atom to the equatorial osmium atoms. While the bridging ampy ligands do not affect these bonds, the fact that two of the five triangles that share the apical Os(6) are capped by the bridging ligands causes the $Os(6)-Os_{eq}$ and $Os_{eq}-Os_{eq}$ distances to be irregular, being in the range 2.643(1)−3.115(1) Å.

Table 1. Selected Interatomic Distances (Å) in Compounds 1 and 2

	1	2		1	2
Os(1)−Os(2)	2.710(2)	2.7234(4)	Os(4)−Os(8)		2.7673(5)
Os(1)−Os(3)	2.767(2)	2.7542(5)	Os(5)−Os(6)	2.849(2)	2.8450(5)
Os(1)−Os(4)	2.756(2)	2.7587(5)	Os(5)−Os(7)	2.785(2)	2.7639(5)
Os(1)−Os(6)	2.849(2)	2.8478(5)	Os(6)−Os(7)	2.888(2)	2.9580(5)
Os(1)−Os(8)		2.7595(5)	Os(6)−Os(8)		2.8287(4)
Os(2)−Os(3)	2.749(2)	2.7562(5)	N(1)−Os(1)	2.23(2)	2.150(7)
Os(2)−Os(5)	2.740(2)	2.7753(5)	N(1)−Os(2)	2.15(2)	2.165(6)
Os(2)−Os(6)	2.762(2)	2.8652(5)	N(1)−Os(4)	2.27(2)	2.233(7)
Os(2)−Os(7)	2.735(2)	2.7788(5)	N(1)−Os(5)	2.21(2)	2.223(6)
Os(4)−Os(5)	2.716(2)	2.7072(5)	N(2)−Os(3)	2.25(2)	2.208(7)
Os(4)−Os(6)	2.908(2)	2.8528(5)			

Table 2. Selected Interatomic Distances (Å) in Compound 3

Os(1)−Os(2)	2.643(1)	Os(1)−Os(4)	2.884(1)
Os(1)−Os(6)	3.115(1)	Os(1)−Os(7)	2.607(1)
Os(1)−Os(8)	2.751(1)	Os(2)−Os(5)	2.851(1)
Os(2)−Os(6)	2.831(1)	Os(2)−Os(7)	2.640(1)
Os(2)−Os(8)	2.788(1)	Os(3)−Os(4)	2.659(1)
Os(3)−Os(5)	2.845(1)	Os(3)−Os(6)	2.881(1)
Os(3)−Os(7)	2.631(1)	Os(3)−Os(9)	2.765(1)
Os(4)−Os(6)	2.933(1)	Os(4)−Os(7)	2.647(1)
Os(4)−Os(9)	2.763(1)	Os(5)−Os(6)	2.698(1)
Os(5)−Os(7)	2.645(1)	Os(6)−Os(7)	2.837(1)
N(1)−Os(1)	2.13(1)	N(1)−Os(2)	2.17(1)
N(1)−Os(6)	1.95(1)	N(2)−Os(8)	2.18(1)
N(3)−Os(3)	2.16(1)	N(3)−Os(4)	2.12(1)
N(3)−Os(6)	1.92(1)	N(4)−Os(9)	2.18(2)
O(700)−Os(7)	1.69(1)		

No nonaosmium clusters with the metal framework of cluster **3** have been previously reported. The nonaruthenium clusters $[Ru_9(\mu\text{-H})_2(\mu_4\text{-}\kappa^2\text{-ampy})_4(CO)_{17}]$ and $[Ru_9(\mu_3\text{-H})(\mu\text{-H})(\mu_4\text{-}\kappa^2\text{-ampy})_3(CO)_{18}]$, which arise from the thermolysis of $[Ru_6(\mu_3\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-CO})_2(CO)_{14}]$ in refluxing undecane, are the only known clusters with metallic skeletons related to that of **3**.[7] These two ruthenium complexes also have the apical atoms bonded to each other. However, their M−M bond distances cannot be compared with those of complex **3**, because they have bridging ligands on either sides of the equatorial plane and, in contrast to complex **3**, which adheres to the EAN rule, the ruthenium derivatives are electron-rich (132 and 128 electrons, respectively) and, consequently, have several long Ru−Ru distances (>3 Å).[7]

An additional interesting feature of cluster **3** is its terminal oxo ligand. Although a few osmium carbonyl clusters containing μ_3-oxo[18] and μ_4-oxo[19] ligands have been reported, the terminal Os−O bond is unique in carbonyl cluster chemistry. The observed Os(7)−O(700) distance, 1.69(1) Å, is just slightly shorter than those found in mononuclear osmium oxo complexes, such as $[OsO_2(P^iPr_3)_2]$ (1.743 Å)[20] and $[OsO_2Cl_2(py)_2]$ (1.726 Å).[21]

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[15] A literature search at the CSD (version 5.28, Nov 2006) has revealed the existence of 19 X-ray structures of osmium cluster complexes having μ_3-imido ligands.

[16] For example, in $[Os_3(\mu\text{-H})_2(CO)_{10}]$, the Os=Os bond distance is 2.681 Å, whereas the two Os−Os bond distances are 2.812 and 2.817 Å: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2697.

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Table 3. Selected Crystal, Measurement, and Refinement Data for 1, 2, and 3·CH_2Cl_2

	1	**2**	**3**·CH_2Cl_2
formula	$C_{25}H_6N_2O_{19}Os_7$	$C_{26}H_8N_2O_{20}Os_8$	$C_{30}H_{12}N_4O_{19}Os_9 \cdot CH_2Cl_2$
fw	1969.72	2190.18	2529.16
color, habit	dark brown, block	black, plate	dark brown, block
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	10.708(5)	16.9899(1)	10.383(4)
b, Å	10.761(5)	11.8232(8)	11.184(5)
c, Å	17.276(7)	18.9830(1)	20.070(8)
α, deg	101.420(8)	90	97.207(8)
β, deg	94.927(8)	103.280(1)	93.225(8)
γ, deg	114.891(7)	90	91.379(8)
V, Å^3	1738(1)	3711.2(3)	2307(2)
Z	2	4	2
F(000)	1708	3782	2196
D_{calcd}, g cm^{-3}	3.764	3.920	3.640
radiation (λ, Å)	Mo Kα (0.710 73)	Cu Kα (1.5418)	Mo Kα (0.710 73)
μ, mm^{-1}	25.567	50.955	24.860
cryst size, mm	0.22 × 0.11 × 0.05	0.07 × 0.03 × 0.01	0.15 × 0.10 × 0.10
temp, K	296(2)	296(2)	296(2)
θ limits, deg	1.22−23.34	2.67−74.66	1.02−23.29
min/max h, k, l	−11 to +11, −11 to +11, −19 to +19	−20 to +20, −14 to +14, −22 to +23	−10 to +11, −10 to +12, −22 to +22
no. of collected rflns	7867	25 950	10 331
no. of unique rflns	4972	7364	6559
no. of rflns with $I > 2\sigma(I)$	3936	6239	5548
no. of params/restraints	435/1	513/0	563/0
GOF on F^2	1.036	1.101	1.024
R1 (on F, $I > 2\sigma(I)$)	0.0869	0.0282	0.0386
wR2 (on F^2, all data)	0.2411	0.0934	0.1175
max/min $\Delta\rho$, e Å^{-3}	4.439/−5.645	1.385/−2.419	2.003/−3.198

Previous studies have shown that, when work is carried out on a small scale (only a few milligrams of starting carbonyl metal cluster complexes), adventitious water may lead to a significant proportion of products containing oxo ligands.[22]

Concluding Remarks

Three novel high-nuclearity osmium carbonyl cluster complexes have been isolated from the reaction of $[Os_3(CO)_{12}]$ with $^1/_2$ equiv of H_2ampy in refluxing decane. These complexes are remarkable because (a) compounds **1** and **2** are the first examples of osmium carbonyl clusters that contain μ_4-imido ligands, (b) the metallic skeletons of compounds **2** and **3** have never been observed in osmium carbonyl clusters, and (c) compound **3** contains a terminal oxo ligand that is unprecedented in osmium carbonyl chemistry.

An important key feature of the synthesis of clusters **1**−**3** is the high reaction temperature (174 °C). Prior to this work, μ_4-imido ligands had never been observed in osmium carbonyl chemistry; this may be a consequence of the fact the reactions of osmium carbonyl cluster complexes with precursors of imido ligands have generally been performed at lower temperatures.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (hydrocarbons) or CaH_2 (dichloromethane) and were 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 (carbonyl stretching region) and spot TLC. All reagents were purchased from commercial suppliers. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^1H NMR spectra were run on a Bruker DPX-300 instrument, at 293 K, using the dichloromethane solvent resonance as internal standard (δ 5.30). Microanalyses were obtained from the University of Oviedo Analytical Service. Positive FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; the m/z value given for a molecular ion corresponds to that of the most abundant isotopomer.

Reaction of $[Os_3(CO)_{12}]$ with Excess H_2ampy. A mixture of $[Os_3(CO)_{12}]$ (100 mg, 0.110 mmol) and H_2ampy (59.6 mg, 0.551 mmol) was stirred in decane (10 mL) at reflux temperature for 45 min. The color changed from yellow to greenish yellow. The solvent was removed under reduced pressure, and the residue was extracted into dichloromethane (10 mL). Some black solid remained undissolved. The filtered solution was supported onto preparative silica gel (ca. 5 g), and the resulting solid was placed onto a silica gel column (10 × 2 cm) packed in hexane. Hexane−dichloromethane (2:1) eluted a yellow band that yielded $[Os_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Hampy})(CO)_9]$ when it was evaporated to dryness (60 mg, 59%). Anal. Calcd for $C_{15}H_8N_2O_9Os_3$ (930.92): C, 19.35; H, 0.87; N, 3.01. Found: C, 19.44; H, 0.95; N, 2.87. FAB MS: m/z 932 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2082 (m), 2053 (vs), 2021 (vs), 1993 (vs, br), 1983 (m, sh), 1953 (w), 1937 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.53 (t, J = 7.8 Hz, 1 H), 6.77 (d, J = 7.8 Hz, 1 H), 6.35 (d, J = 7.8 Hz, 1 H), 4.80 (s, br, 1 H, NH), 2.75 (s, 3 H, Me), −12.94 (s, 1 H).

Reaction of $[Os_3(CO)_{12}]$ with 0.5 Equiv of H_2ampy. A mixture of $[Os_3(CO)_{12}]$ (100 mg, 0.110 mmol) and H_2ampy (6.4 mg, 0.059 mmol) was stirred in decane (10 mL) at reflux temperature for 9 h. The color changed from yellow to dark brown. The solvent was removed under reduced pressure, and the residue was extracted into dichloromethane (5 mL). A considerable amount of a black solid remained precipitated. The filtered solution was supported onto preparative silica gel TLC plates. Hexane−dichloromethane (2:1) eluted several bands. The major ones were worked up to give, in order of elution, $[Os_8(\mu_3\text{-H})(\mu\text{-H})(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-CO})(CO)_{19}]$ (**2**; violet-brown solid, 6 mg, 7%), $[Os_7(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-CO})_2(CO)_{17}]$ (**1**; brown solid, 7 mg, 8%) ,and $[Os_9O(\mu_4\text{-}\kappa^2\text{-ampy})_2(CO)_{18}]$ (**3**; dark brown solid, 2 mg, 3%). A dark brown residue remained uneluted in the baseline of the TLC plates. It was extracted into dichloromethane, and the solution was evaporated to dryness. A

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^{1}H NMR spectrum of this residue indicated the presence of a complicated mixture of compounds.

Data for 1. Anal. Calcd for $C_{25}H_6N_2O_{19}Os_7$ (1969.72): C, 15.24; H, 0.31; N, 1.42. Found: C, 15.36; H, 0.41; N 1.39. FAB MS: m/z 1970 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2102 (m), 2079 (vs), 2057 (vs), 2035 (vs), 2026 (m), 2013 (s), 1994 (w, sh), 1963 (w, br), 1840 (w, br), 1802 (w, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.35 (t, $J = 7.8$ Hz, 1 H), 6.63 (d, $J = 7.8$ Hz, 1 H), 5.94 (d, $J = 7.8$ Hz, 1 H), 2.49 (s, 3 H).

Data for 2. Anal. Calcd for $C_{26}H_8N_2O_{20}Os_8$ (2190.18): C, 14.26; H, 0.37; N, 1.28. Found: C, 14.37; H, 0.42; N, 1.22. FAB MS: m/z 2191 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2104 (w), 2081 (s), 2073 (s), 2027 (vs), 2007 (m, sh), 1961 (w, br), 1797 (w, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.37 (t, $J = 7.8$ Hz, 1 H), 6.73 (d, $J = 7.8$ Hz, 1 H), 6.00 (d, $J = 7.8$ Hz, 1 H), 2.76 (s, 3 H, Me), -14.59 (s, 1 H), -18.64 (s, 1 H).

Data for 3. Anal. Calcd for $C_{30}H_{12}N_4O_{19}Os_9$ (2444.50): C, 14.74; H, 0.50; N, 2.29. Found: C, 14.91; H, 0.57; N, 2.21. FAB MS: m/z 2445 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2087 (m), 2068 (s), 2053 (m), 2010 (vs), 1961 (w, sh), 1913 (w, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.63 (t, $J = 7.9$ Hz, 1 H), 7.40 (d, $J = 7.9$ Hz, 1 H), 7.14 (d, $J = 7.9$ Hz, 1 H), 3.15 (s, 3 H, Me).

X-ray Structures of 1 and 3·CH_2Cl_2. A selection of crystal, measurement, and refinement data is given in Table 3. Diffraction data were measured at room temperature on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromated Mo Kα radiation. Raw frame data were integrated with SAINT.[23] Absorption corrections were applied with SADABS.[24] Structures were solved by direct methods and refined by full-matrix least squares against F^2 with SHELXTL.[25] Various non-hydrogen atoms of both compounds (9 of **1** and 5 of **3**·CH_2Cl_2) were nonpositive definite upon anisotropic refinement and were refined isotropically. The remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. The molecular plots were made with the PLATON program package.[26] The WINGX program system[27] was used throughout the structure determinations. Cambridge Crystallographic Database files: CCDC 643460 (**1**), CCDC 643462 (**3**·CH_2Cl_2).

X-ray Structure of 2. A selection of crystal, measurement, and refinement data is given in Table 3. Data collection was performed at ambient temperature on an Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using graphite-monochromated Cu Kα radiation. Data reduction and cell refinement were performed with the program CrysAlis-RED.[28] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm, as implemented in CrysAlis-RED. The structure was solved by Patterson interpretation, using the program DIRDIF-96,[29] and was refined by full-matrix least squares against F^2 with SHELXL-97.[30] The positions of the hydride atoms H(100) and H(200) were calculated using the program XHYDEX[31] and were freely refined. The remaining hydrogen atoms were set in calculated positions and refined as riding atoms. All non-H atoms were refined anisotropically. The molecular plots were made with the PLATON program package.[26] The WINGX program system[27] was used throughout the structure determination. Cambridge Crystallographic Database file: CCDC 643461.

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Supporting Information Available: Crystallographic data in CIF format for the compounds studied by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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