Reactivity of Triosmium Carbonyl Clusters with 1,8-Diaminonaphthalene − Synthesis and Structural Characterization of Amido, Diamido, and *C*-Metalated Trinuclear Derivatives

Javier A. Cabeza,*[a] Heinrich Nöth,[b] María de Jesús Rosales-Hoz,[c] and Gloria Sánchez-Cabrera[c]

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The compounds $[Os_3(CO)_{12}]$ and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ do not react with 1,8-diaminonaphthalene (H_2dan) under thermal conditions (110 °C, 30 min). However, $[Os_3(CO)_{10}(MeCN)_2]$ reacts with H_2dan (THF, reflux temperature) to give two isomers of $[Os_3(\mu\text{-}H)(\mu\text{-}Hdan)(CO)_9]$ (**1** and **2**). In toluene at reflux temperature, these reagents afford $[Os_3(\mu\text{-}dan)(CO)_{10}]$ (**3**). Compound **2** can be converted into **3** under thermal conditions, but no interconversion between **1** and **2** has been observed. The three compounds have been characterized by X-ray diffraction methods. Compound **1** arises from the *C*-metalation of H_2dan in a position adjacent to an NH_2 group; this generates a hydride and a ligand that interacts with the three metal atoms through one of the NH_2 groups, through the metalated carbon atom (which spans an Os–Os edge), and through one of the C=C bonds of the metalated ring. In compound **2**, the hydride arises from the oxidative addition of an N–H bond of H_2dan; the resulting ligand interacts with two of the three metal atoms through the amido NH fragment (bridging position) and through the remaining NH_2 group. Compound **3** is derived from the transformation of both NH_2 groups of H_2dan into amido NH groups and consists of a 50-electron trinuclear cluster with the longest edge doubly-bridged by both amido groups.

Introduction

The last fifteen years have witnessed the renaissance of amido-metal chemistry, particularly that of the early transition metals.[1] The inert nature of the $R_2N{-}M$ bond in these complexes has allowed the design of reactive metal centers specifically tailored to allow reactions in areas such as the activation of poorly reactive molecules, homogeneous catalysis, and organic synthesis.[1] The amido-metal chemistry of the late transition metals has received much less attention[2−11] as a consequence of the thermodynamically less favorable combination of "soft" metals with "hard" ligands. However, the relative lability of the $R_2N{-}M$ bonds in these complexes has recently been shown to be useful in facilitating reactions such as the formation of C−N bonds through the insertion of unsaturated organic molecules into the $R_2N{-}M$ bonds.[11]

The chemistry of ruthenium carbonyl amido complexes is rather well documented in the literature,[2−4] whereas in the case of osmium only a few carbonyl amido derivatives have been reported. Pentafluoroaniline reacts with $[Os_3(CO)_{12}]$ to give $[Os_3(\mu\text{-}H)(\mu\text{-}NHC_6F_5)(CO)_{10}]$.[5] *ortho*-Functionalized anilines, such as 2-diphenylphosphanylaniline,[3d,6] 1,2-diaminobenzene,[7] and 2-aminophenol[7] react with $[Os_3(CO)_{10}(MeCN)_2]$ to give $[Os_3(\mu\text{-}H)(\mu\text{-}ZC_6H_4X)(CO)_9]$ (Scheme 1). However, the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2-aminothiophenol gives $[Os_3(\mu\text{-}H)(\mu\text{-}SC_6H_4NH_2)(CO)_{10}]$ (Scheme 1) as a consequence of the "softer" character of the sulfur atom.[7] Some 2-amino heterocycles, such as 2-aminopyridine, give amido derivatives when treated with osmium clusters (Scheme 1).[8,9a] The reactivities of other primary and secondary amines towards trinuclear osmium clusters have also been studied.[9]

As far as amido complexes of the late transition metals derived from 1,8-diaminonaphthalene (H_2dan) are concerned, a rich derivative chemistry has been reported for binuclear compounds of ruthenium,[4] rhodium, and iridium[10] incorporating the diamido ligand dan (which is formed by the loss of two NH protons from H_2dan). In these complexes, the basicity of the diamido ligand increases the nucleophilic character of the metal atoms, enhancing their reactivity towards electrophiles (protons, metal fragments, etc.).[4c,4d,4e,10e] In addition, the *cis*-labilizing effect of the "hard" amido fragment promotes regioselective carbonyl substitution processes in positions *cis* to the amido ligand.[4a]

The hitherto obtained results summarized above prompted us to study the reactivity of osmium carbonyl clusters towards 1,8-diaminonaphthalene. We now report that this study has led to the synthesis of amido, diamido, and *C*-metalated triosmium derivatives.

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[a] Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica "Enrique Moles", Universidad de Oviedo-CSIC,
E-33071 Oviedo, Spain
Fax: (internat.) +34-98/510-3446
E-mail: jac@sauron.quimica.uniovi.es
[b] Institut für Anorganische Chemie, Universität München,
Butenandtstraße 5−13, Haus D, D-81377 München, Germany
[c] Departamento de Química, CINVESTAV-IPN,
Apartado Postal 14−740, 07000 México D.F., México

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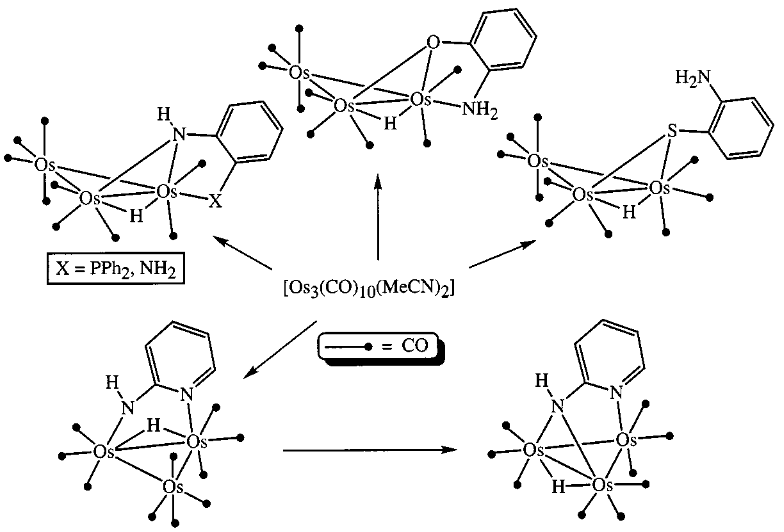


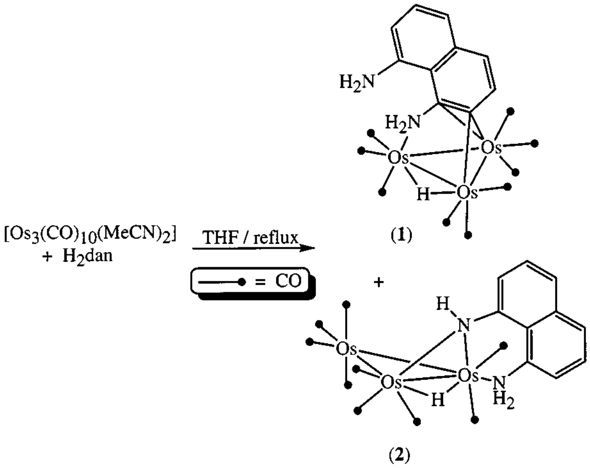
Scheme 1

Results

Synthesis of Compounds 1−3

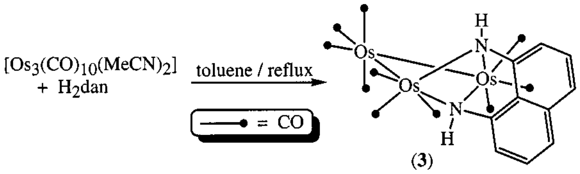
The compounds $[Os_3(CO)_{12}]$ and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ do not react with 1,8-diaminonaphthalene (H_2dan) under thermal conditions (toluene, reflux temperature, 30 min).

However, the activated[12a] cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts with H_2dan in THF (reflux temperature, 30 min) to give two isomers of $[Os_3(\mu\text{-}H)(\mu\text{-}Hdan)(CO)_9]$ (compounds **1** and **2** in Scheme 2), in a 1:4 mol ratio, which may be separated by chromatographic methods. The product ratio remains unchanged after longer reaction times.



Scheme 2

In an attempt to induce the reaction of two H_2dan molecules with $[Os_3(CO)_{10}(MeCN)_2]$, the latter was treated with an excess of H_2dan in refluxing toluene. A new compound, subsequently identified as $[Os_3(\mu\text{-}dan)(CO)_{10}]$ (**3**) was isolated in 58% yield (Scheme 3). We later found that the excess of H_2dan is unnecessary and that the reaction temperature is the crucial factor for the formation of **3**. In fact, this compound could also be prepared, albeit in lower yield (42%), by thermolysis of **2** in refluxing toluene.



Scheme 3

Structural Characterization of Compounds 1−3

The trinuclear nature of **1**−**3** and the isomeric character of **1** and **2** were indicated by their microanalyses and mass spectra, but the information obtained from their IR and NMR spectroscopic data was insufficient to assign their molecular structures, which were determined by X-ray diffraction methods.

The structure of complex **1** is depicted in Figure 1. Selected structural parameters are listed in Table 1. The compound is formed by *C*-metalation of H_2dan in a position adjacent to an NH_2 group. This generates a hydride ligand, which spans the Os(1)−Os(2) edge, and a ligand that interacts with the three metal atoms through one of the NH_2 groups [Os(1)−N(1) = 2.12(1) Å], through the metalated carbon atom C(2), which spans an Os−Os edge, and through the carbon atom C(1). Analysis of the Os−C distances indicates a σ-type interaction with Os(2) [Os(2)−C(2) = 2.13(2) Å] and a π-type interaction with Os(3) [Os(3)−C(1) = 2.35(1); Os(3)−C(2) = 2.30(1) Å]. The ligand shell is completed by nine carbonyl ligands, three on each metal atom.

Figure 2 shows the molecular structure of complex **2**. Selected bond lengths and angles are listed in Table 1. In this compound, an Os−Os edge is doubly-bridged by a hydride ligand and by the amido fragment of an *N*-monodeprotonated H_2dan ligand [Os(1)−N(1) = 2.176(9); Os(2)−N(1) = 2.119(8) Å], of which the NH_2 group is also attached to one

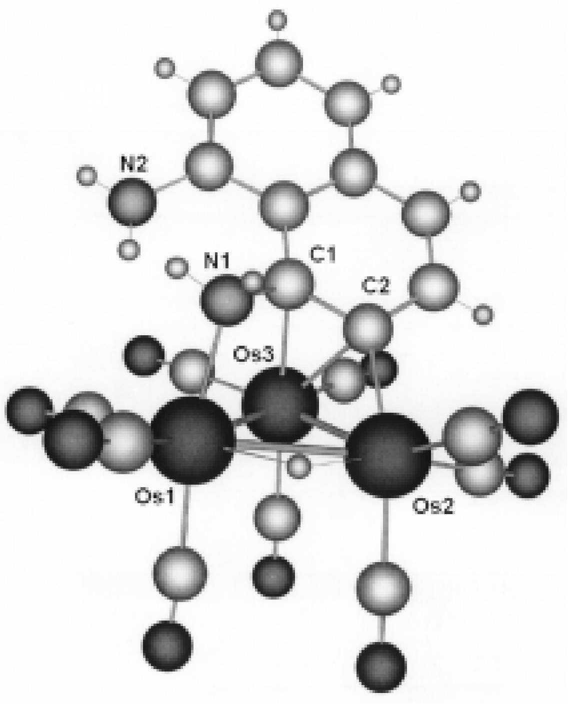


Figure 1. Molecular structure of compound **1**

Table 1. Selected distances [Å] and angles [°] in compounds **1−3**

	1	**2**	**3**
Os(1)−Os(2)	2.957(2)	2.7846(9)	3.088(1)
Os(1)−Os(3)	2.816(1)	2.8510(8)	2.878(1)
Os(2)−Os(3)	2.776(1)	2.7974(8)	2.869(1)
Os(1)−N(1)	2.12(1)	2.176(9)	2.18(1)
Os(1)−N(2)			2.16(1)
Os(2)−N(1)		2.119(8)	2.16(1)
Os(2)−N(2)		2.18(1)	2.17(1)
Os(2)−C(2)	2.13(2)		
Os(3)−C(1)	2.35(2)		
Os(3)−C(2)	2.30(1)		
Os(1)−Os(2)−Os(3)	58.74(3)	61.43(2)	57.63(3)
Os(1)−Os(3)−Os(2)	63.83(3)	59.07(2)	65.02(3)
Os(2)−Os(1)−Os(3)	57.42(3)	59.51(2)	75.35(2)
Os(1)−N(1)−Os(2)		80.8(3)	90.6(4)
Os(1)−N(2)−Os(2)			90.9(4)
Os(2)−C(2)−Os(3)	77.5(7)		

of the metal atoms of the same edge [Os(2)−N(2) = 2.18(1) Å] in a position approximately *trans* to the Os(2)−Os(3) edge. The ligand shell is completed by nine carbonyl ligands, of which four are attached to Os(3), three to Os(1), and two to Os(2).

Figure 3 shows the molecular structure of complex **3**. Selected bond lengths and angles are collected in Table 1. This compound is formed by the transformation of both NH_2 groups of H_2dan into NH groups and consists of a 50-electron trinuclear cluster in which the longest (open?) edge [Os(1)−Os(2) = 3.088(1) Å] is doubly-bridged by both NH groups [av. Os−N = 2.17(1) Å]. The ligand shell of the cluster is completed by ten carbonyl ligands, of which four are attached to Os(3), three to Os(1), and three to Os(2). The naphthalene plane lies perpendicular to the Os(1)−Os(2) edge, resulting in an overall (not crystallographic) C_{2v} symmetry. This symmetry is maintained in solution, as indicated by the ^1H NMR spectrum, which shows only four resonances for the naphthalene and NH protons.

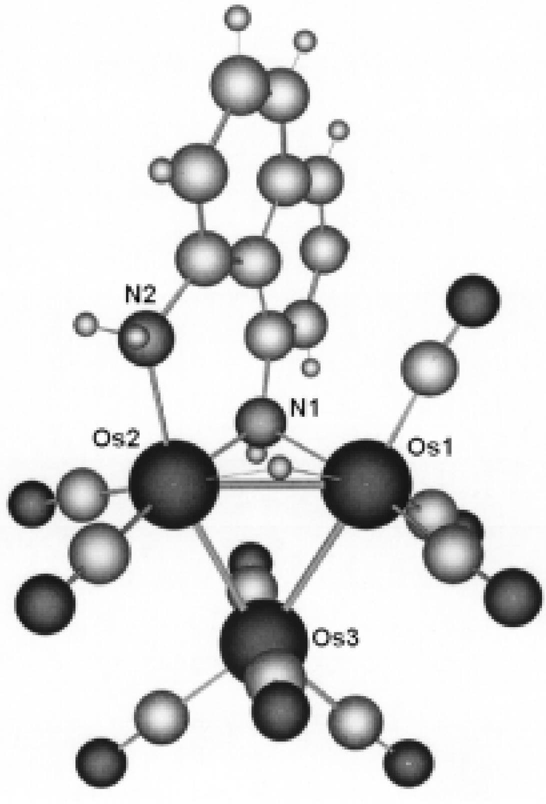


Figure 2. Molecular structure of compound **2**

Discussion

The compound $[Os_3(CO)_{12}]$ is kinetically very stable and generally requires very high temperatures to initiate its reactions, particularly those involving CO substitution.[12b] However, the fact that $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ does not react with H_2dan under thermal conditions seems somewhat surprising as this unsaturated cluster is very reactive.[12c] Indeed, it has been reported that the saturated adducts $[Os_3H(\mu\text{-}H)(CO)_{10}(L)]$ (L = NH_3, NH_2R, NHR_2) can be prepared at room temperature by treating $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with ammonia gas either in the solid state[13] or in solution,[14] or with primary and secondary amines in solution.[15] In the case of H_2dan, the existence of intramolecular hydrogen bonding involving both NH_2 groups may account for its lower reactivity as compared with that of other amines.

The fact that the isomeric compounds **1** and **2** do not mutually interconvert under thermal conditions indicates that neither is an intermediate in the synthesis of the other, although they may be formed from a common intermediate {probably the product of substitution of the acetonitrile ligands in $[Os_3(CO)_{10}(MeCN)_2]$ by H_2dan}. The fact that compound **3** can be prepared by thermolysis of **2** does not necessarily imply that **2** is an intermediate in the synthesis

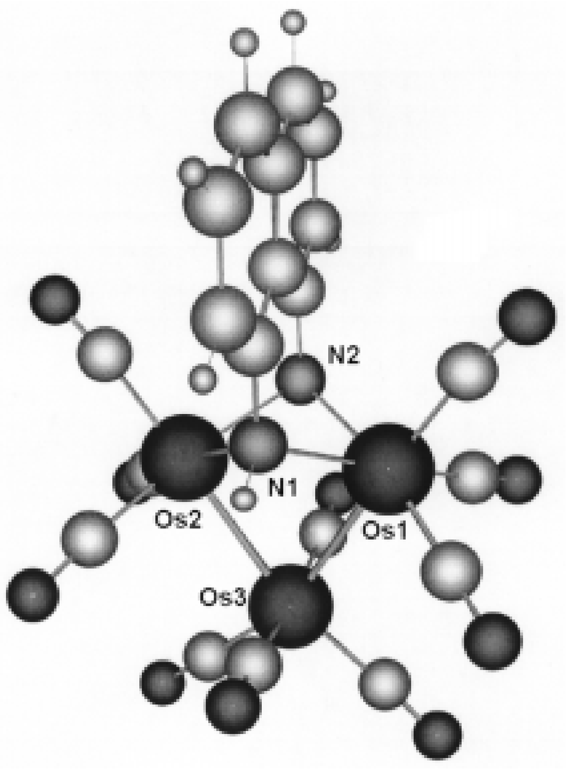


Figure 3. Molecular structure of compound **3**

of **3** from $[Os_3(CO)_{10}(MeCN)_2]$ and H_2dan. It should be noted that **3** has ten CO ligands, whereas **2** has only nine, and that some cluster decomposition occurs in refluxing toluene, since some minor products, including $[Os_4(\mu\text{-}H)_2(CO)_{13}]$, are also formed.

As far as we are aware, the *C*-metalation (as in complex **1**) and the mono *N*-metalation (as in complex **2**) of H_2dan have no precedents in the coordination chemistry of this diamine, although the structure of **2** is reminiscent of those of the ruthenium and osmium cluster complexes $[M_3(\mu\text{-}H)(\mu\text{-}HNC_6H_4X)(CO)_{10}]$ derived from 1,2-diaminobenzene (X = NH_2; M = Ru,[16] Os[7]) and 2-diphenylphosphanylaniline (X = PPh_2; M = Ru,[3d] Os[6]) (Scheme 1). The coordination mode of the dan ligand in complex **3** (symmetric, doubly-bridging six-electron donor) has previously been observed in binuclear complexes of ruthenium,[3c,4a,4b] rhodium, and iridium,[10] and in some trinuclear derivatives resulting from the addition of metallic electrophiles to these binuclear compounds;[4c,4d,10e] however, no homometallic trinuclear complexes incorporating the dan ligand as a doubly-bridging six-electron donor (as in complex **3**) have previously been reported.

It is also interesting to remark that in ruthenium carbonyl cluster chemistry, the binuclear complex $[Ru_2(\mu\text{-}dan)(CO)_6]$ is the sole product of the reaction of $[Ru_3(CO)_{12}]$ with H_2dan.[4a,16] Thus, the osmium chemistry described in this article has no parallel in ruthenium chemistry. This can be rationalized by considering the low reactivity of H_2dan (as mentioned above) and the stronger metal−metal bonds of osmium as compared with those of ruthenium.[12b] Thus, H_2dan requires a high temperature for reaction with $[Ru_3(CO)_{12}]$ (toluene under reflux) and Os−Os bonds withstand this temperature whereas Ru−Ru bonds are more easily cleaved.

Experimental Section

General Remarks: Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or calcium hydride (dichloromethane) 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 (carbonyl stretching region) and by spot TLC (silica gel). − All reagents were purchased as analytically pure samples, except for anhydrous Me_3NO, which was obtained by azeotropic distillation of $Me_3NO\cdot 2H_2O$ in toluene. − IR: Perkin−Elmer FT 1720-X. − ^1H NMR: Bruker AC-200 and AC-300 spectrometers, room temperature, $SiMe_4$ as internal standard. − Microanalyses: Perkin−Elmer 2400. − MS: VG Autospec double-focusing mass spectrometer operating in the FAB+ mode; ions were produced with a standard Cs^+ gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix; data quoted refer to the most abundant molecular ion isotopomer.

$[Os_3(\mu\text{-}H)(\mu\text{-}Hdan)(CO)_9]$ (Isomers 1 and 2): A solution of Me_3NO (9.5 mg, 0.127 mmol) in acetonitrile (2 mL) was added dropwise to a solution of $[Os_3(CO)_{12}]$ (50 mg, 0.055 mmol) in dichloromethane (15 mL) over a period of 15 min. After stirring for 1 h, complete conversion of $[Os_3(CO)_{12}]$ into $[Os_3(CO)_{10}(MeCN)_2]$ had occurred (IR control). The excess Me_3NO was removed by passing the solution through a short column (1 × 5 cm) of neutral alumina (activity I). The solvent was removed under reduced pressure and the solid residue was redissolved in THF (20 mL). Freshly sublimed 1,8-diaminonaphthalene (13 mg, 0.082 mmol) was added and the resulting solution was stirred at reflux temperature for 30 min. The solvent was then removed under reduced pressure and the residue was separated by preparative TLC on silica gel. Elution with hexane/dichloromethane (1:1) afforded three bands. The first band (pale yellow) was found to contain a small amount of an unidentified compound and was discarded. Workup of the second (yellow-orange) and third (yellow) bands afforded compounds **1** (6 mg, 11%) and **2** (25 mg, 46%), respectively.

Analytical and Spectroscopic Data for Compound 1: $C_{19}H_{10}N_2O_9Os_3$ (980.89): calcd. C 23.27, H 1.03, N 2.86; found C 23.52, H 1.28, N 2.75. − FAB-MS: *m*/*z* = 982 [M^+]. − IR (CH_2Cl_2): ν(CO) = 2085 (m), 2056 (s), 2024 (vs), 2002 (m), 1985 (m), 1966 (w) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 8.86 (br. d, *J* = 9.4 Hz, 1 H), 7.86 (d, *J* = 8.8 Hz, 1 H), 7.4−7.0 (m, 2 H), 6.69 (d, *J* = 8.8 Hz, 1 H), 4.03 (br. s, 2 H, NH_2), 3.75 (br. s, 2 H, NH_2), −14.60 (s, 1 H, μ-H).

Analytical and Spectroscopic Data for Compound 2: $C_{19}H_{10}N_2O_9Os_3$ (980.89): calcd. C 23.27, H 1.03, N 2.86; found C 23.38, H 1.27, N 2.71. − FAB-MS: *m*/*z* = 982 [M^+]. − IR (CH_2Cl_2): ν(CO) = 2089 (m), 2049 (vs), 2007 (m), 1995 (s), 1990 (s), 1978 (sh), 1965 (sh), 1918 (m) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.8−7.0 (m, 6 H), 6.48 (br. s, 1 H, NH), 5.94 (d, *J* = 12.7 Hz, 1 H of NH_2), 5.48 (d, *J* = 12.7 Hz, 1 H of NH_2), −12.31 (s, 1 H, μ-H).

$[Os_3(\mu\text{-}dan)(CO)_{10}]$ (3): A solution of 1,8-diaminonaphthalene (13 mg, 0.082 mmol) and $[Os_3(CO)_{10}(MeCN)_2]$ (0.055 mmol, prepared in situ as described above) in toluene (15 mL) was stirred at reflux temperature for 30 min. The solvent was then removed under reduced pressure and the residue was separated by preparative TLC on silica gel. Multiple elution with hexane/dichloromethane (2:1)

Table 2. Summary of crystal and refinement data for compounds **1−3**

	1	**2**	**3**
Formula	$C_{19}H_{10}N_2O_9Os_3$	$C_{19}H_{10}N_2O_9Os_3$	$C_{20}H_8N_2O_{10}Os_3$
Formula weight	980.89	980.89	1006.88
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	10.521(1)	8.585(2)	8.786(2)
b [Å]	15.165(1)	11.572(2)	10.105(2)
c [Å]	14.043(1)	12.122(2)	14.089(3)
α [°]	90	69.70(1)	82.22(3)
β [°]	94.077(2)	77.09(1)	72.45(3)
γ [°]	90	87.74(1)	82.22(3)
V [Å^3]	2235.1(4)	1100.0(4)	1160.9(4)
Z	4	2	2
F(000)	1752	876	900
D(calcd.) [g cm^{-3}]	2.915	2.961	2.881
Crystal size [mm]	0.22 × 0.11 × 0.05	0.34 × 0.10 × 0.02	0.56 × 0.56 × 0.34
T [K]	193(2)	293(2)	293(2)
Radiation (λ [Å])	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
μ [mm^{-1}]	17.065	17.337	16.436
θ range [°]	1.98 to 28.35	2.44 to 25.05	2.47 to 25.07
Min./max. h, k, l	−12/12, −11/12, −17/17	−9/10, −12/13, 0/14	−9/10, −11/12, 0/16
Reflns. collected	12872	3870	4079
Unique reflns. (R_{int})	4033 (0.0606)	3870 (0.0000)	4079 (0.0000)
Reflns. $F > 4\sigma(F)$	2884	3035	3565
Absorption correction	ψ scans	ψ scans	ψ scans
Max./min. trans. factors	0.483/0.095	1.000/0.259	1.000/0.361
Parameters, restraints	298, 0	298, 0	317, 0
GoF (on F^2)	0.991	1.023	1.074
$R1$, $wR2$ [$F > 4\sigma(F)$]	0.0791, 0.1875	0.0403, 0.1001	0.0445, 0.1219
$R1$, $wR2$ (all data)	0.1033, 0.2026	0.0635, 0.1073	0.0536, 0.1261
Max./min. Δρ [e Å^{-3}]	4.563/−7.756	1.594/−3.394	2.396/−2.262

afforded four bands. The first band (yellow) was found to contain a small amount of $[Os_4(\mu\text{-}H)_2(CO)_{13}]$ (IR identification).[17] The third and fourth bands contained very small amounts of unidentified products. Workup of the second band (yellow) afforded compound **3** (32 mg, 58%). − $C_{20}H_8N_2O_{10}Os_3$ (1006.88): calcd. C 23.86, H 0.80, N 2.78; found C 24.01, H 1.02, N 2.73. − FAB-MS: m/z = 1008 [M$^+$]. − IR (CH_2Cl_2): ν(CO) = 2095 (w), 2066 (vs), 2038 (m), 2002 (s), 1982 (m), 1969 (sh) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.55 (d, J = 8.1 Hz, 1 H), 7.26 (d, J = 8.1 Hz, 1 H), 7.18 (d, J = 8.1 Hz, 1 H), 3.89 (br. s, 1 H, NH).

X-ray Crystallographic Studies: Crystal data and details of the structures of compounds **1−3** are listed in Table 2. The selected crystal of compound **1** was covered with perfluoropolyether oil, attached to the tip of a glass fibre, and then mounted on the Euler cradle of a Siemens P4 four-circle diffractometer equipped with a CCD area detector and an LT2 low-temperature device. Unit cell dimensions were calculated from four sets of data collected at 193 K with different crystal orientations over 15 frames, each with Δψ = 0.3°. Data collection was carried out in the hemisphere mode at 193 K, at two different χ settings with Δψ = 0.3° for each series, over a total of 100 frames. Structure solution was performed by the Patterson method, followed by successive difference Fourier cycles.[18] Non-hydrogen atoms were refined anisotropically, while hydrogen positions were calculated with the exception of those bonded to the nitrogen atoms. An absorption correction was applied by empirical methods.

Crystals of complexes **2** and **3** were mounted on glass fibres and their unit cell dimensions were determined from the angular settings of 25 reflections with 10 < θ < 12° on a Nonius CAD4 diffractometer. Both structures were solved by direct methods followed by successive difference Fourier cycles using SHELXL.[19] In both cases, an empirical absorption correction was applied. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were geometrically positioned and included in the refinement with fixed isotropic values.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-142357 (**1**), CCDC-142356 (**2**), and CCDC-142355 (**3**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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