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Novel Osmium *N*-Oxide Complexes from the Reaction of Triosmium Clusters with 1-Hydroxybenzotriazole

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Reaction of $Os_3(CO)_{10}(NCMe)_2$ (**1**) with 1-hydroxybenzotriazole (**2**) gave the hydrido complex $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-NNN(O)}C_6H_4)$ (**3**) in 60% yield; reaction of isocyanide complexes $Os_3(CO)_{10}(CNR)(NCMe)$ (**4**: R = *n*-Pr, CH_2Ph) with **2** gave the bridging aminocarbyne products $Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-NNN(O)}C_6H_4)(\mu_2\text{-}\eta^1\text{-C=NHR})$ (**5** and **6**). The O–H bond of the hydroxybenzotriazole ligand was cleaved in these reactions to afford complexes **3**, **5**, and **6**, which contained an *N*-oxide moiety. Complexes **5a** and **6a** as well as **5b** and **6b** were regioisomers because of the restricted rotation about the C=N double bond in the bridging aminocarbyne. These isomers exhibited different polarities and were separated by chromatography. Results from single-crystal X-ray diffraction analyses for **3**, **5a**, and **6b** revealed the following data. **3**: $P2_1/c$; $a = 8.629(1)$ Å, $b = 9.919(1)$ Å, $c = 25.446(2)$ Å; $\beta = 95.447(9)°$, $V = 2168.1(3)$ Å^3, $Z = 4$, $R = 2.7\%$, $R_w = 3.0\%$. **5a**: $P2_1/c$; $a = 10.4824(6)$ Å, $b = 15.765(2)$ Å, $c = 16.001(3)$ Å; $\beta = 97.981(9)°$, $V = 2618.6(6)$ Å^3, $Z = 4$, $R = 3.0\%$, $R_w = 3.7\%$. **6b**: $P2_1/c$; $a = 9.997(2)$ Å, $b = 23.639(4)$ Å, $c = 12.636(2)$ Å; $\beta = 111.37(1)°$, $V = 2780.8(8)$ Å^3, $Z = 4$, $R = 2.9\%$, $R_w = 3.1\%$. Studies on the structures of **5a** and **6b** by X-ray methods provided the first evidence indicating the existence of regioisomers with different orientations of the coordinated aminocarbyne group.

Introduction

Some *N*-oxides possess important antibacterial activity on certain gram-positive and gram-negative species.[1] *N*-Oxides are also used as growth promoters in poultry, pigs, and calves for increasing their live weights.[2] 2,3-Dihydroxymethylquinoxaline 1,4-di-*N*-oxide,[1d] myxin (1-hydroxy-6-methoxyphenazine 5,10-di-*N*-oxide),[3] and 2-[(3-aminopropyl)amino]phenazine 5,10-di-*N*-oxide[4] are recognized as potential DNA cleaving agents. We considered the possibility that *N*-oxides may interact with osmium clusters, in which the metal could play a role in mediating the biological activity resulting from the oxide ligand.

Herein we report our findings on the formation of *N*-oxide complexes by reacting triosmium clusters with 1-hydroxybenzotriazole. A comparison was made to understand the reactivity difference resulting from the carbonyl and the isocyanide ligands by reaction of $Os_3(CO)_{10}(NCMe)_2$ and $Os_3(CO)_{10}(CNR)(NCMe)$ with 1-hydroxybenzotriazole. We also found that stabilization offered by metal centers facilitated the conversion of the *N*-hydroxyl moiety in 1-hydroxybenzotriazole to *N*-oxide in the complexes under mild conditions. The conversion of an *N*-hydroxyl moiety to an *N*-oxide functional group has been reported;[5] nevertheless, the same conversion facilitated by a metal center has been less explored. Furthermore, we generated an aminocarbyne bridge in the complexes from the isocyanide ligand in triosmium clusters, which were separated as two regioisomers. Their structures were determined by the single-crystal X-ray diffraction method.

Results and Discussion

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1-Hydroxybenzotriazole. We treated the labile complex $Os_3(CO)_{10}(NCMe)_2$ (**1**) with 1-hydroxybenzotriazole (**2**) in CH_2Cl_2 at −50 °C to room temperature to give the hydrido complex $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-NNN(O)}C_6H_4)$ (**3**) in 60% yield (eq 1). Performance of the same reaction at room temperature gave a complex mixture, from which **3** was isolated in 20% yield only. The ^{1}H NMR spectrum of **3** showed a hydride signal at δ −13.72, which came from the proton of the hydroxyl group in the activated 1-hydroxybenzotriazole (**2**). The FAB mass spectrum of **3** showed the molecular ion peak at *m/z* 988 and peaks corresponding to subsequent CO-loss fragments.

By use of the single-crystal X-ray diffraction method, we obtained solid evidence to support the structure of complex **3**. An ORTEP drawing of **3** is shown in Figure 1, and its pertinent crystallographic data are given in

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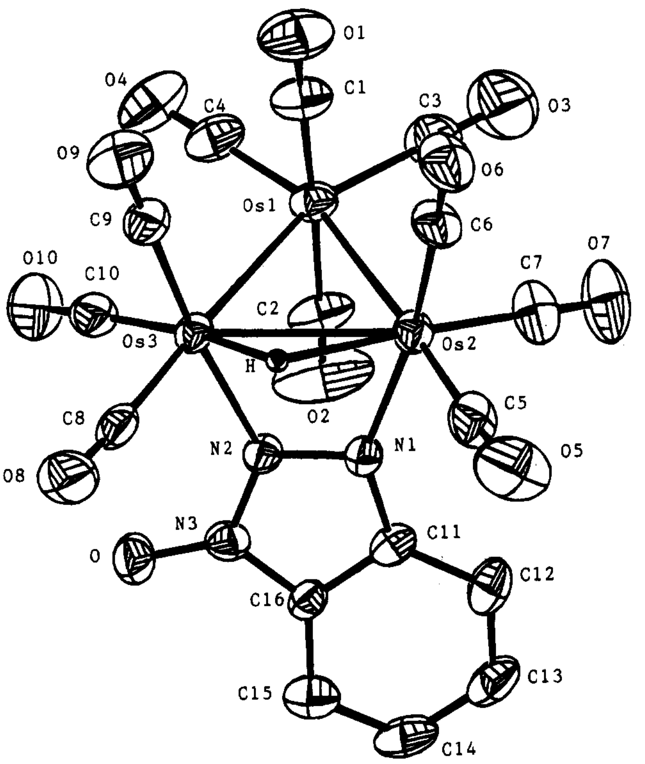
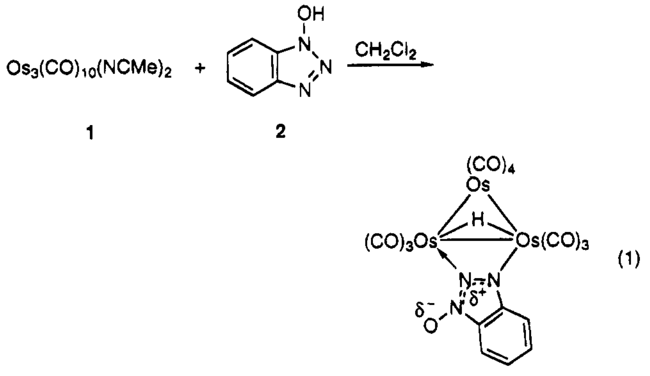


Figure 1. ORTEP diagram of (μ-H)$Os_3(CO)_{10}(\mu_2$-(2,3-η^2)-$NNN(O)C_6H_4$) (**3**).



Tables 1−3. This complex consists of a triangular cluster of osmium atoms with distances Os(1)−Os(2) = 2.8674(5) Å, Os(1)−Os(3) = 2.8667(5) Å, and Os(2)−Os(3) = 2.9262(5) Å. A hydride ligand (located and refined) and the benzotriazole group mutually bridge the Os(2) and the Os(3) atoms and lengthen the distance between them. Two contiguous nitrogen atoms adjacent to the N−O moiety in the benzotriazole coordinate at two axial sites of the Os(2)−Os(3) vector. The N(1), N(2), Os(3), and Os(2) atoms are nearly coplanar. The plane defined by these four atoms is almost orthogonal to that defined by the triosmium atoms with an N(2)−Os(3)−Os(2)−Os(1) dihedral angle of 102.5(2)° and an N(1)−Os(2)−Os(3)−Os(1) dihedral angle of −101.2(2)°. This novel *N*-oxide-containing compound possesses a molecular architecture similar to that of the related complex (μ-H)$Os_3(CO)_{10}(\mu_2$-(3,4-η^2)-$N_2C_3H_3$), which is prepared from $Os_3(CO)_{10}(NCMe)_2$ and imidazole.[6] In complex **3**, a partial double-bond character exists between N(1)−N(2) and N(2)−N(3), which have the same bond length (1.35(1) Å). These results indicate that three canonical forms exist in structure **3** (see Scheme 1). This is corroborated by the slightly shorter distance of N(3)−O bond (1.27(1) Å) in the *N*-oxide moiety than the average value (1.30(2) Å) reported.[7] Aime et al.[8]

Table 1. Crystal and Intensity Collection Data for 3, 5a, and 6b

	3	5a	6b
formula	$C_{16}H_5N_3O_{11}Os_3$	$C_{20}H_{12}N_4O_{11}Os_3$	$C_{24}H_{12}N_4O_{11}Os_3$
fw	985.83	1054.93	1102.98
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	8.62940(10)	10.4824(6)	9.9966(20)
b, Å	9.9190(10)	15.7646(21)	23.639(4)
c, Å	25.4456(20)	16.001(3)	12.6364(18)
β, deg	95.477(9)	97.981(9)	111.371(14)
V, Å^3	2168.1(3)	2618.6(6)	2780.8(8)
D_{calc}, g cm^{-3}	3.020	2.676	2.635
Z	4	4	4
μ(Mo Kα), cm^{-1}	176.2	146.0	137.5
temp	room temp	room temp	room temp
radiation	Mo Kα	Mo Kα	Mo Kα
2θ (max)	49.8	49.8	44.8
scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
total no. of rflns	7896	4774	3805
no. of obsd rflns, $F_o > 2.5\sigma(F_o)$	2922	3404	2761
no. of obsd variables	299	343	379
R	0.027	0.030	0.029
R_w	0.030	0.037	0.031
$\Delta(\varrho)$, e Å^{-3}	1.040	0.960	1.180
Δ/σ_{max}	0.001	0.012	0.001
GOF	1.65	1.42	1.38

Table 2. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for (μ-H)$Os_3(CO)_{10}(\mu_2$-(2,3-η^2)-$NNN(O)C_6H_4$) (3)

atom	*x*	*y*	*z*	B_{iso}[a]
Os(1)	0.80762(5)	0.49733(3)	0.15101(1)	2.79(2)
Os(2)	0.89988(4)	0.23996(3)	0.11321(1)	2.49(2)
Os(3)	0.63411(4)	0.26323(3)	0.17597(1)	2.23(1)
N(1)	0.6872(8)	0.2329(6)	0.0642(3)	2.5(3)
N(2)	0.5703(8)	0.2396(6)	0.0956(3)	2.3(3)
N(3)	0.4341(9)	0.2082(7)	0.0676(3)	2.6(3)
O	0.3068(8)	0.2028(7)	0.0888(3)	3.8(3)
O(1)	1.0229(10)	0.4608(8)	0.2535(3)	5.8(4)
O(2)	0.5813(13)	0.5177(7)	0.0504(3)	7.4(5)
O(3)	1.0516(13)	0.6644(9)	0.1022(4)	7.9(6)
O(4)	0.6224(11)	0.7219(8)	0.1997(3)	5.5(4)
O(5)	0.9942(10)	−0.0367(8)	0.0766(4)	7.2(5)
O(6)	1.1683(9)	0.2238(8)	0.1974(3)	5.0(4)
O(7)	1.0738(10)	0.3881(9)	0.0323(3)	6.0(4)
O(8)	0.4475(10)	0.0125(7)	0.1993(3)	5.0(4)
O(9)	0.7709(10)	0.2721(8)	0.2895(3)	5.5(4)
O(10)	0.3725(9)	0.4618(7)	0.1910(3)	5.2(4)
C(1)	0.9434(13)	0.4706(9)	0.2161(4)	3.9(5)
C(2)	0.6659(14)	0.5065(9)	0.0870(4)	4.0(5)
C(3)	0.9630(15)	0.6024(11)	0.1205(4)	4.7(6)
C(4)	0.6964(14)	0.6364(10)	0.1821(4)	3.8(5)
C(5)	0.9536(12)	0.0657(10)	0.0901(4)	3.8(5)
C(6)	1.0700(11)	0.2351(9)	0.1647(4)	3.4(4)
C(7)	1.0104(12)	0.3344(11)	0.0620(4)	3.9(5)
C(8)	0.5176(12)	0.1026(9)	0.1893(3)	3.0(4)
C(9)	0.7189(12)	0.2728(9)	0.2479(4)	3.3(4)
C(10)	0.4711(12)	0.3882(9)	0.1864(4)	3.4(4)
C(11)	0.6227(11)	0.2008(8)	0.0152(3)	2.4(4)
C(12)	0.6890(12)	0.1819(10)	−0.0325(4)	3.6(5)
C(13)	0.5901(14)	0.1490(10)	−0.0759(4)	3.9(5)
C(14)	0.4293(14)	0.1333(9)	−0.0739(4)	3.8(5)
C(15)	0.3617(12)	0.1528(9)	−0.0280(4)	3.5(4)
C(16)	0.4625(10)	0.1870(8)	0.0163(3)	2.3(3)
H	0.767	0.138	0.166	2.9(19)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

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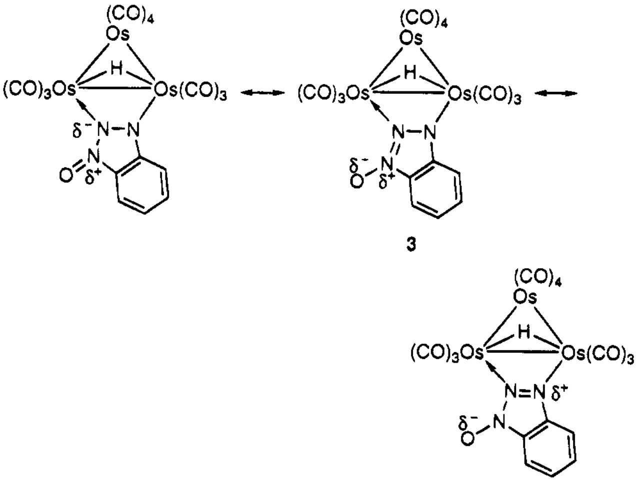
Table 3. Selected Bond Distances and Angles for (μ-H)$Os_3(CO)_{10}(\mu_2$-(2,3-η^2)-NNN(O)C_6H_4) (3)

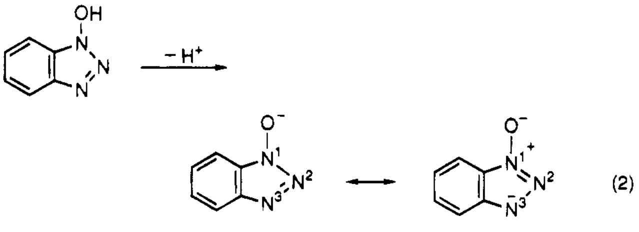
(a) Bond Distances (Å)			
Os(1)−Os(2)	2.8674(5)	N(1)−N(2)	1.347(10)
Os(1)−Os(3)	2.8667(5)	N(1)−C(11)	1.354(11)
Os(2)−Os(3)	2.9262(5)	N(2)−N(3)	1.351(10)
Os(2)−N(1)	2.120(7)	N(3)−O	1.271(10)
Os(2)−H	2.1051(4)	N(3)−C(16)	1.367(11)
Os(3)−N(2)	2.080(6)	C(11)−C(12)	1.401(13)
Os(3)−H	1.7308(3)	C(11)−C(16)	1.392(13)
(b) Bond Angles (deg)			
Os(2)−Os(1)−Os(3)	61.368(13)	Os(2)−N(1)−N(2)	107.7(5)
Os(1)−Os(2)−Os(3)	59.305(12)	Os(2)−N(1)−C(11)	143.7(6)
Os(1)−Os(2)−N(1)	88.53(17)	N(2)−N(1)−C(11)	107.1(7)
Os(3)−Os(2)−N(1)	69.15(19)	Os(3)−N(2)−N(1)	116.5(5)
N(1)−Os(2)−C(5)	90.6(4)	Os(3)−N(2)−N(3)	132.8(5)
N(1)−Os(2)−C(6)	171.1(4)	N(1)−N(2)−N(3)	109.8(6)
N(1)−Os(2)−C(7)	94.3(4)	N(2)−N(3)−O	122.0(7)
C(7)−Os(2)−H	176.5(3)	N(2)−N(3)−C(16)	108.2(7)
Os(1)−Os(3)−Os(2)	59.327(13)	O−N(3)−C(16)	129.8(7)
Os(1)−Os(3)−N(2)	88.18(19)	N(1)−C(11)−C(12)	131.5(9)
Os(2)−Os(3)−N(2)	66.56(19)	N(1)−C(11)−C(16)	109.0(7)
N(2)−Os(3)−C(8)	89.2(3)	C(12)−C(11)−C(16)	119.5(8)
N(2)−Os(3)−C(9)	172.1(4)	N(3)−C(16)−C(11)	105.9(7)
N(2)−Os(3)−C(10)	94.6(3)	N(3)−C(16)−C(15)	130.7(8)
C(10)−Os(3)−H	174.1(3)		

Scheme 1



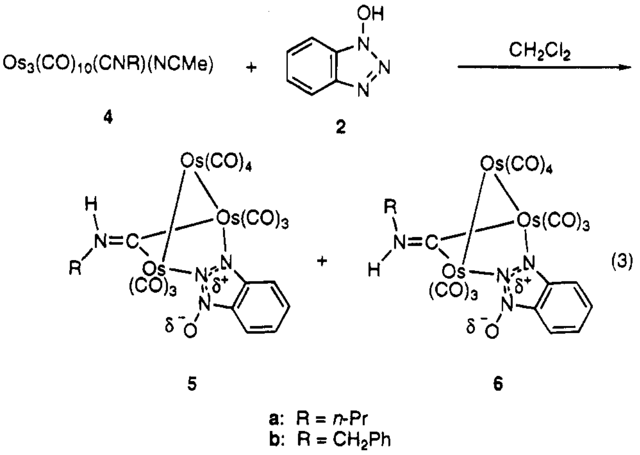
carried out a related reaction, in which $Os_3(CO)_{10}(NCMe)_2$ was treated with benzotriazole to give (μ-H)$Os_3(CO)_{10}(C_6H_4N_3)$. This complex possesses the μ_2-η^2-*N*,*N*-coordinated mode of the ligand to two osmium centers. The structural characteristics of our newly synthesized complex **3** provide further evidence to support the proposed configuration of the complex (μ-H)$Os_3(CO)_{10}(C_6H_4N_3)$.

Oxygen-coordinated complexes were not obtained when we activated the *N*-hydroxyl group in 1-hydroxybenzotriazole to form the *N*-oxide-containing osmium complex **3**. The reaction may proceed initially through protonation, which was followed by successive displacements of the two coordinated acetonitriles by ionized benzotriazole at the nitrogen centers. The ionized benzotriazole can exist as a hybridized species,[9] as shown in eq 2. The nucleophilicity of the oxide center in the NO moiety was relatively weaker than that of the N^3 atom because of the partial positive charge on the N^1 atom. Consequently, the N^3 atom in benzotriazole reacted preferentially with osmium to form complex **3** and the *N*-oxide was left uncoordinated.



Furthermore, we found that the existence of two acetonitrile ligands in an osmium carbonyl complex was necessary for allowing it to react with 1-hydroxybenzotriazole. $Os_3(CO)_{11}(NCMe)$ did not react with 1-hydroxybenzotriazole under similar conditions or at elevated temperature; in addition, $Os_3(CO)_{12}$ remained intact in toluene at reflux.

Reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with 1-Hydroxybenzotriazole. Upon treatment with 1-hydroxybenzotriazole in CH_2Cl_2, isocyanide derivatives $Os_3(CO)_{10}(CNR)(NCMe)$ (**4a**, R = *n*-Pr; **4b**, R = CH_2Ph) were converted to the bridging aminocarbyne complexes $Os_3(CO)_{10}(\mu_2$-(2,3-η^2)-NNN(O)$C_6H_5)(\mu_2$-η^1-C=NHR) (**5**, R = *n*-Pr; **6**, R = CH_2Ph; eq 3). These *N*-oxide-containing complexes were obtained as a mixture of two regioisomers, which came from the restricted rotation about the C=N double bond in the bridging aminocarbyne.[10] These complexes with different polarities were separated successfully by chromatography.



Each pair of regioisomers **5a**/**6a** and **5b**/**6b** showed near-identical ^{1}H NMR (300 MHz) spectra with a subtle difference in their ^{13}C NMR spectra. In comparison with **3**, complex **5b** did not exhibit any bridging hydride peak in its ^{1}H NMR spectrum; instead, a peak at δ 9.25 appeared for the bridging aminocarbyne proton (=NH).[10a,b] The FAB mass spectrum of **5b** presented a molecular ion peak at *m/z* 1105 and peaks related to subsequent loss of carbonyls. Complex **6b** was obtained by elution on a TLC plate as a yellow powder, which was followed behind a faint yellow band of **5b**. The chromatographic results indicate that **6b** bore higher polarity than **5b**. Similarly to **5b**, complex **6b** also exhibited a characteristic bridging aminocarbyne peak

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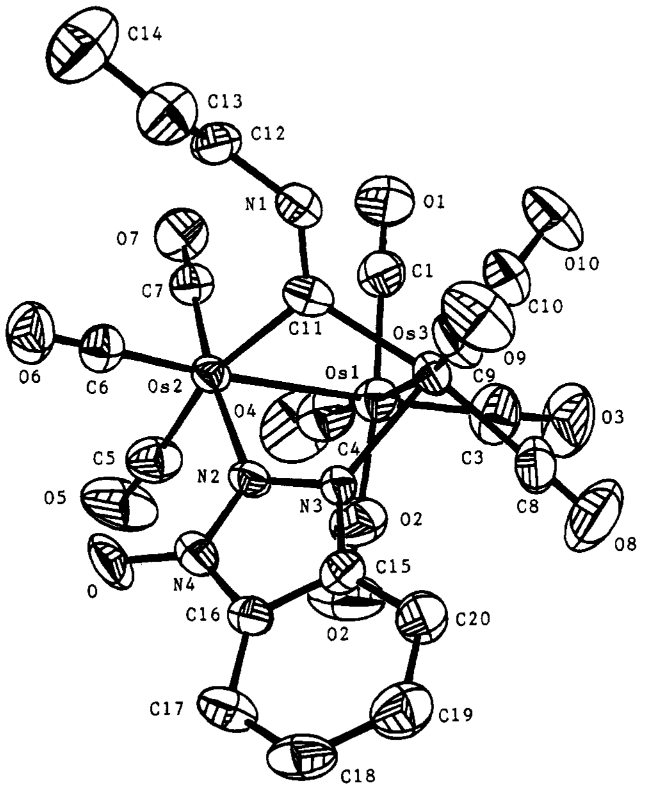

Figure 2. ORTEP diagram of $Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-}NNN(O)C_6H_4)(\mu_2\text{-}\eta^1\text{-}C{=}NHPr)$ (**5a**).

(=NH) at δ 9.22 and a molecular ion at *m/z* 1105. These results provide evidence to support the regioisomeric relationship between complexes **5b** and **6b**.

An ORTEP diagram of $Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}NNN(O)C_6H_4)(\mu_2\text{-}\eta^1\text{-}C{=}NHPr)$ (**5a**) from X-ray analysis is shown in Figure 2; relevant crystallographic details are listed in Tables 4 and 5. The three Os atoms define an isosceles triangle, in which the Os(2) and the Os(3) atoms are bridged at the semiaxial sites by an aminocarbyne group and an *N*-oxide-containing benzotriazole ligand. Pseudooctahedral geometry is observed around the three metals. The doubly bridged Os(2)–Os(3) vector (3.4417(6) Å) is longer than the nonbridged bonds (Os(1)–Os(2) = 2.8906(6) Å and Os(1)–Os(3) = 2.9007(7) Å). Thus, we believe that the Os(2)–Os(3) bond has been cleaved. The bond distances and angles within the coordinated benzotriazole ring are nearly identical with those of complex **3**. The bond length N(2)–N(3) is the same as N(2)–N(4) (1.35(1) Å). The aminocarbyne ligand with the C(11)–N(1) bond length of 1.32(1) Å is structurally similar to those found in the cluster $Os_3(CO)_{10}(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$,[10a,b] $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHR)$,[11] $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}CNMe_2)$,[12] and $(\mu\text{-}H)Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}H_2CNMe_2)(\mu\text{-}SPh)$.[13] The NH of the aminocarbyne moiety is anti to the *N*-oxide group.

Furthermore, we determined the structure of complex **6b** by the X-ray method (Figure 3). The atomic positional parameters are listed in Table 6 and selected interatomic distances and angles in Table 7. The three Os atoms define an isosceles triangle. Both the aminocarbyne group and the benzotriazole unit occupy the "semiaxial" positions on the nonbonding Os(2)–Os(3) vector (3.4292(7) Å). Pseudooctahedral geometry is

Table 4. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for $Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-}NNN(O)C_6H_4)(\mu_2\text{-}\eta^1\text{-}C{=}NHPr)$ (5a)

atom	*x*	*y*	*z*	B_{iso}[a]
Os(1)	0.11028(4)	0.06549(3)	0.28003(3)	3.73(2)
Os(2)	0.37222(4)	0.00330(2)	0.30370(2)	2.67(2)
Os(3)	0.25368(4)	0.16839(2)	0.17504(3)	3.10(2)
N(1)	0.4685(8)	0.1873(5)	0.3215(5)	3.3(4)
N(2)	0.3613(8)	−0.0060(5)	0.1729(5)	2.8(3)
N(3)	0.3115(8)	0.0560(5)	0.1195(5)	2.7(3)
N(4)	0.3996(8)	−0.0711(5)	0.1271(6)	3.4(4)
O	0.4530(8)	−0.1372(4)	0.1637(5)	4.9(4)
O(1)	0.1973(10)	0.1925(6)	0.4222(6)	6.4(5)
O(2)	0.0793(11)	−0.0611(7)	0.1325(7)	7.9(6)
O(3)	−0.1252(9)	0.1710(8)	0.2141(7)	8.2(7)
O(4)	−0.0036(12)	−0.0615(9)	0.3955(8)	9.6(7)
O(5)	0.2787(11)	−0.1818(6)	0.3203(7)	8.0(6)
O(6)	0.6566(8)	−0.0474(6)	0.3254(5)	5.3(4)
O(7)	0.3596(8)	0.0286(5)	0.4900(5)	5.2(5)
O(8)	0.0133(11)	0.1797(8)	0.0398(7)	8.4(6)
O(9)	0.4330(9)	0.2767(6)	0.0863(6)	6.3(5)
O(10)	0.1636(10)	0.3216(5)	0.2653(6)	6.6(5)
C(1)	0.1666(11)	0.1458(8)	0.3695(8)	4.3(5)
C(2)	0.0897(13)	−0.0137(9)	0.1883(9)	5.3(6)
C(3)	−0.0396(12)	0.1289(9)	0.2402(9)	5.6(7)
C(4)	0.0421(13)	−0.0126(10)	0.3528(9)	6.0(8)
C(5)	0.3115(12)	−0.1133(8)	0.3115(7)	4.7(6)
C(6)	0.5503(11)	−0.0269(7)	0.3161(6)	3.3(4)
C(7)	0.3667(10)	0.0201(7)	0.4196(7)	3.4(4)
C(8)	0.1022(13)	0.1764(8)	0.0867(8)	5.0(6)
C(9)	0.3687(12)	0.2347(7)	0.1187(7)	4.2(5)
C(10)	0.1982(11)	0.2626(7)	0.2305(8)	4.3(5)
C(11)	0.3902(10)	0.1333(6)	0.2765(6)	3.1(4)
C(12)	0.5671(10)	0.1711(7)	0.3953(7)	3.7(5)
C(13)	0.6977(12)	0.1808(8)	0.3740(8)	5.1(6)
C(14)	0.8014(15)	0.1668(12)	0.4470(11)	8.1(9)
C(15)	0.3147(9)	0.0258(7)	0.0383(6)	3.1(4)
C(16)	0.3703(10)	−0.0543(6)	0.0436(6)	3.0(4)
C(17)	0.3876(11)	−0.1022(7)	−0.0271(7)	4.0(5)
C(18)	0.3489(12)	−0.0663(8)	−0.1014(7)	4.7(6)
C(19)	0.2949(12)	0.0177(8)	−0.1094(8)	4.8(6)
C(20)	0.2757(11)	0.0638(7)	−0.0404(7)	3.9(5)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 5. Selected Bond Distances and Angles for $Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-}NNN(O)C_6H_4)(\mu_2\text{-}\eta^1\text{-}C{=}NHPr)$ (5a)

	(a) Bond Distances (Å)		
Os(1)–Os(2)	2.8906(6)	N(1)–C(12)	1.480(14)
Os(1)–Os(3)	2.9007(7)	N(2)–N(3)	1.354(11)
Os(2)–Os(3)	3.4417(6)	N(2)–N(4)	1.354(11)
Os(2)–N(2)	2.085(8)	N(3)–C(15)	1.388(12)
Os(2)–C(11)	2.109(10)	N(4)–O	1.285(11)
Os(3)–N(3)	2.108(7)	N(4)–C(16)	1.355(13)
Os(3)–C(11)	2.084(11)	C(15)–C(16)	1.388(14)
N(1)–C(11)	1.324(13)		
	(b) Bond Angles (deg)		
Os(2)–Os(1)–Os(3)	72.923(16)	Os(3)–N(3)–N(2)	116.6(5)
Os(1)–Os(2)–Os(3)	53.674(14)	Os(3)–N(3)–C(15)	136.7(6)
Os(1)–Os(2)–N(2)	88.49(22)	N(2)–N(3)–C(15)	106.6(7)
Os(1)–Os(2)–C(11)	75.8(3)	N(2)–N(4)–O	120.7(8)
N(2)–Os(2)–C(7)	173.6(4)	N(2)–N(4)–C(16)	110.0(8)
N(2)–Os(2)–C(11)	81.6(3)	O–N(4)–C(16)	129.2(8)
C(5)–Os(2)–C(11)	165.0(5)	Os(2)–C(11)–Os(3)	110.3(4)
Os(1)–Os(3)–Os(2)	53.403(14)	Os(2)–C(11)–N(1)	125.4(7)
Os(1)–Os(3)–N(3)	88.67(21)	Os(3)–C(11)–N(1)	124.0(7)
Os(1)–Os(3)–C(11)	75.9(3)	N(3)–C(15)–C(16)	108.6(8)
N(3)–Os(3)–C(10)	175.6(4)	N(3)–C(15)–C(20)	130.7(9)
C(8)–Os(3)–C(11)	165.9(5)	C(16)–C(15)–C(20)	120.7(9)
C(11)–N(1)–C(12)	129.3(8)	N(4)–C(16)–C(15)	105.9(8)
Os(2)–N(2)–N(3)	123.1(5)	N(4)–C(16)–C(17)	131.1(9)
Os(2)–N(2)–N(4)	128.1(6)	C(15)–C(16)–C(17)	123.0(10)
N(3)–N(2)–N(4)	108.8(7)		

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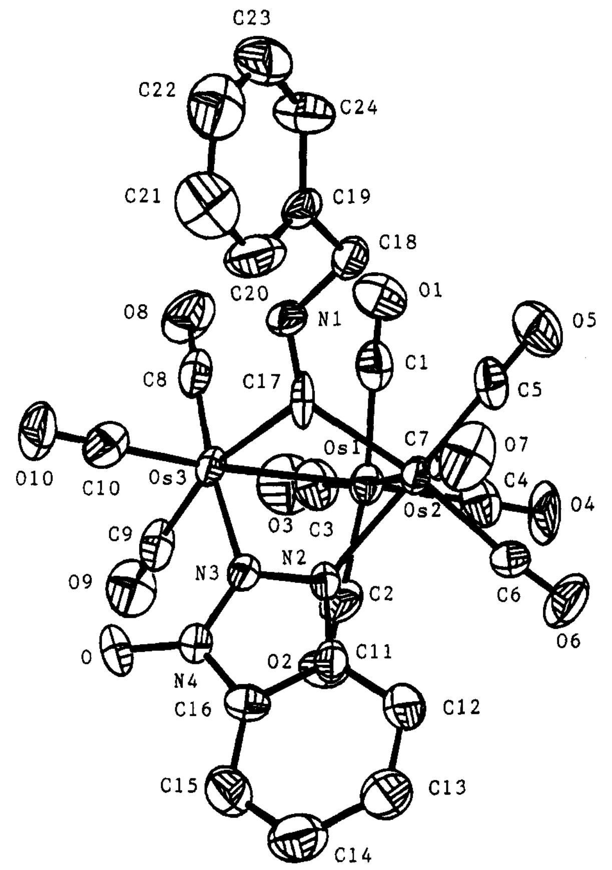

Figure 3. ORTEP diagram of $Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-}NNN(O)C_6H_4)(\mu_2\text{-}\eta^1\text{-}C{=}NHCH_2Ph$ (**6b**).

observed around the three metals. The aminocarbyne ligand with C(16)−N = 1.29(3) Å is structurally similar to those found in the related cluster.[10−13] The structure parameters of **6b** are similar to those of **5a**, except that the aminocarbyne (=NH) moiety is syn to the *N*-oxide group. The aminocarbyne and the *N*-oxide groups reside far away from each other in the crystal structures of **5a** and **6b**. The aminocarbyne unit in either complex **5** or **6** is near to two $Os(CO)_3$ groups; such a configuration may allow them to show almost identical NMR characteristics. On the other hand, the arrangement of the two ligands in the molecule introduces significantly different polarities.

After separation by chromatography, compounds **5** and **6** retained their identity as shown by TLC. Nevertheless, about 10% of **5a** in CH_2Cl_2 was estimated to isomerize to **6a** at 28 °C in 24 h, as monitored by TLC. Reversion of complex **6a** to **5a** was also found to be slow at this temperature. Complexes **5b** and **6b** exhibited similar isomerization behavior. We were able to separate these isomers with different polarities by chromatography because of their slow isomerization rate. In our previous studies, some related aminocarbyne derivatives, such as $Os_3(CO)_{10}(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$[10a,b] and $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHR)$,[11] also exist as two isomeric forms in equilibrium in solution at ambient temperature; nevertheless, separation of those isomers is not successful. We believe that the orientation of the aminocarbyne group accompanied by the polar character of the *N*-oxide moiety played a role in mediating the polarity of the complexes **5** and **6**.

Table 6. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for $Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-}NNN(O)C_6H_4)(\mu_2\text{-}\eta^1\text{-}C{=}NHCH_2Ph)$ (6b)

atom	*x*	*y*	*z*	B_{iso}[a]
Os(1)	0.58845(5)	0.06569(2)	0.28597(4)	2.86(3)
Os(2)	0.27809(4)	0.07455(2)	0.20011(4)	2.39(2)
Os(3)	0.51553(4)	0.18090(2)	0.20976(4)	2.50(2)
N(1)	0.3072(9)	0.1872(4)	0.3318(8)	2.8(4)
N(2)	0.2845(9)	0.1077(4)	0.0445(7)	2.5(5)
N(3)	0.3745(9)	0.1502(4)	0.0518(8)	2.7(5)
N(4)	0.3633(9)	0.1658(4)	−0.0524(8)	2.7(5)
O	0.4369(8)	0.2068(3)	−0.0707(7)	3.7(4)
O(1)	0.5801(11)	0.1026(5)	0.5158(9)	6.2(7)
O(2)	0.5673(10)	0.0528(4)	0.0383(8)	5.0(5)
O(3)	0.9140(11)	0.0830(5)	0.3704(10)	7.4(7)
O(4)	0.5702(11)	−0.0618(4)	0.3280(10)	6.4(7)
O(5)	0.2798(10)	0.0287(4)	0.4230(8)	5.6(6)
O(6)	0.2659(10)	−0.0497(4)	0.1188(9)	5.6(6)
O(7)	−0.0460(9)	0.0901(4)	0.1159(9)	5.5(6)
O(8)	0.7040(10)	0.2136(4)	0.4512(9)	5.9(6)
O(9)	0.7583(9)	0.1814(4)	0.1119(9)	5.7(6)
O(10)	0.4453(11)	0.3046(4)	0.1486(9)	5.8(6)
C(1)	0.5818(13)	0.0895(5)	0.4306(12)	4.2(7)
C(2)	0.5733(13)	0.0569(5)	0.1280(13)	4.0(7)
C(3)	0.7885(15)	0.0769(6)	0.3372(13)	5.1(8)
C(4)	0.5766(12)	−0.0153(6)	0.3130(12)	4.2(7)
C(5)	0.2813(12)	0.0461(5)	0.3403(11)	3.7(6)
C(6)	0.2688(12)	−0.0040(5)	0.1429(10)	3.3(6)
C(7)	0.0764(14)	0.0863(4)	0.1488(10)	3.1(6)
C(8)	0.6340(13)	0.2016(5)	0.3586(13)	3.8(7)
C(9)	0.6715(13)	0.1823(5)	0.1479(12)	4.0(7)
C(10)	0.4628(12)	0.2578(6)	0.1683(11)	3.9(7)
C(11)	0.2160(11)	0.0947(5)	−0.0655(10)	2.8(6)
C(12)	0.1094(13)	0.0540(5)	−0.1216(11)	3.9(7)
C(13)	0.0625(13)	0.0526(6)	−0.2362(11)	4.4(7)
C(14)	0.1131(14)	0.0903(6)	−0.3007(11)	5.1(8)
C(15)	0.2130(14)	0.1297(6)	−0.2489(12)	4.3(7)
C(16)	0.2645(11)	0.1315(5)	−0.1295(10)	3.0(6)
C(17)	0.3466(11)	0.1549(4)	0.2629(10)	3.0(6)
C(18)	0.1949(13)	0.1733(5)	0.3802(11)	4.1(7)
C(19)	0.1026(11)	0.2228(5)	0.3715(10)	2.9(6)
C(20)	0.0285(15)	0.2473(6)	0.2687(12)	4.9(8)
C(21)	−0.0660(14)	0.2933(7)	0.2600(13)	5.5(8)
C(22)	−0.0906(14)	0.3100(6)	0.3524(16)	5.3(10)
C(23)	−0.0181(15)	0.2872(6)	0.4544(13)	5.0(9)
C(24)	0.0781(13)	0.2438(6)	0.4636(11)	4.3(7)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

In comparison with $Os_3(CO)_{10}(NCMe)_2$, the isocyanide species $Os_3(CO)_{10}(CNR)(NCMe)$ (**4**) possessed the following features by reacting with 1-hydroxybenzotriazole. (1) The isocyanide ligand reacted with a proton to form a bridging aminocarbyne complex without offering a chance for the formation of a hydrido species. (2) Cleavage of the doubly bridged Os−Os bond occurred. (3) Separation of the two regioisomers, which were formed as a result of restricted rotation around the C=N double bond of the aminocarbyne group, was successful.

Conclusion

Synthesis of *N*-oxide-containing osmium complexes has been accomplished in good yield by reaction of $Os_3(CO)_{10}(NCMe)_2$ and $Os_3(CO)_{10}(CNR)(NCMe)$, respectively, with 1-hydroxybenzotriazole under mild reaction conditions. The structures of the hydrido complex **3** and aminocarbyne-bridged complexes **5a** and **6b** were characterized by the X-ray method. Restricted rotation about the C=N double bond of the bridging aminocarbyne along with the polar character of the *N*-oxide moiety in **5** and **6** allowed them to exist as regioisomers at room temperature and to be separated by chromatography.

Table 7. Selected Bond Distances and Angles for $Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-}NNN(O)C_6H_4)(\mu_2\text{-}\eta^1\text{-}C{=}NHCH_2Ph)$ (6b)

(a) Bond Distances (Å)

Os(1)–Os(2)	2.8972(9)	N(1)–C(18)	1.497(14)
Os(1)–Os(3)	2.8923(7)	N(2)–N(3)	1.330(12)
Os(2)–Os(3)	3.4292(7)	N(2)–C(11)	1.342(15)
Os(2)–N(2)	2.139(8)	N(3)–N(4)	1.332(13)
Os(2)–C(17)	2.077(11)	N(4)–O	1.288(11)
Os(3)–N(3)	2.109(9)	N(4)–C(16)	1.372(15)
Os(3)–C(17)	2.123(11)	C(11)–C(16)	1.389(16)
N(1)–C(17)	1.321(15)		

(b) Bond Angles (deg)

Os(2)–Os(1)–Os(3)	72.643(16)	Os(3)–N(3)–N(2)	121.8(7)
Os(1)–Os(2)–Os(3)	53.613(16)	Os(3)–N(3)–N(4)	128.8(7)
Os(1)–Os(2)–N(2)	89.07(22)	N(2)–N(3)–N(4)	109.2(8)
Os(3)–Os(2)–C(17)	35.7(3)	N(3)–N(4)–O	122.6(9)
N(2)–Os(2)–C(5)	177.4(4)	N(3)–N(4)–C(16)	108.5(9)
N(2)–Os(2)–C(17)	84.3(4)	O–N(4)–C(16)	128.9(10)
C(5)–Os(2)–C(17)	94.4(5)	N(2)–C(11)–C(12)	132.8(10)
Os(1)–Os(3)–Os(2)	53.745(17)	N(2)–C(11)–C(16)	107.8(9)
Os(1)–Os(3)–N(3)	89.52(23)	C(12)–C(11)–C(16)	119.4(11)
N(3)–Os(3)–C(8)	173.5(4)	N(4)–C(16)–C(11)	105.6(10)
N(3)–Os(3)–C(17)	82.3(4)	N(4)–C(16)–C(15)	131.9(11)
C(9)–Os(3)–C(17)	163.7(5)	C(11)–C(16)–C(15)	122.5(11)
C(17)–N(1)–C(18)	126.2(9)	Os(2)–C(17)–Os(3)	109.5(6)
Os(2)–N(2)–N(3)	117.3(7)	Os(2)–C(17)–N(1)	130.1(8)
Os(2)–N(2)–C(11)	133.9(7)	Os(3)–C(17)–N(1)	120.3(7)
N(3)–N(2)–C(11)	108.7(8)		

Experimental Section

General Data. The complexes $Os_3(CO)_{11}(CNPr)$ and $Os_3(CO)_{11}(CNCH_2Ph)$ were prepared previously.[14] Other reagents were purchased from commercial sources and were used as received except that 1-hydroxybenzotriazole hydrate (Aldrich) was made anhydrous in dry benzene at reflux for 12 h by use of a Dean–Stark water trap. All manipulations were performed with standard Schlenk techniques. Solvents were dried over Na/benzophenone (tetrahydrofuran and ether), CaH_2 (hexanes, CH_2Cl_2, and CH_3CN), or $CaCl_2$ (acetone) and were freshly distilled before use. Infrared spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. NMR spectra were obtained on a Bruker AC-200, an ACP-300, or an AMX-500 FT-NMR spectrometer, and mass spectra were recorded on a VG 70-250S mass spectrometer. Elemental analyses were carried out by use of a Perkin-Elmer 2400 CHN elemental analyzer.

Formation of $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-}NNN(O)C_6H_4)$ (3). To a solution of $Os_3(CO)_{12}$ (202 mg, 0.22 mmol) in CH_2Cl_2 (200 mL) and acetonitrile (10 mL) was added a solution of Me_3NO (36 mg, 0.48 mmol) in a mixture of CH_3CN and CH_2Cl_2 (1:5, 8.0 mL). The mixture was stirred at room temperature for 1 h and filtered through a short column of silica gel. The solvent was removed under vacuum and the residue, $Os_3(CO)_{10}(NCMe)_2$, was redissolved in CH_2Cl_2 (200 mL) precooled to −50 °C. To the resultant solution at −50 °C was added a solution of 1-hydroxybenzotriazole (30 mg, 0.22 mmol) in dry acetone (15 mL). After the addition, the cooling bath was removed and the mixture was warmed to room temperature. Stirring was continued for an additional 1 h. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate (2-mm thickness) by use of a mixture of CH_2Cl_2 and hexanes (3:1) as eluent to furnish the compound $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}(2,3\text{-}\eta^2)\text{-}NNN(O)C_6H_4)$ (**3**; 131 mg, 0.133 mmol) as a yellow solid in 60% yield. Anal. Calcd for $C_{16}H_5N_3O_{11}Os_3$: C, 19.49; H, 0.51; N, 4.26. Found: C, 19.94; H, 0.47; N, 4.00. IR (CH_2Cl_2): ν_{CO} 2114, 2080, 2065, 2031, 2019 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.06–7.76 (m, 4 H, aromatic), −13.72 (hydride). ^{13}C NMR ($CDCl_3$): δ 181.8, 181.1, 176.9, 175.9, 173.9, 173.3, 172.6, 171.6, 170.3, 169.0 (CO), 143.9, 129.6, 129.2, 124.7, 114.0, 113.1 (aromatic). MS (FAB): *m/z* 988 (M^+), 904 (M^+ − 3CO), 876 (M^+ − 4CO), 848 (M^+ − 5CO), 820 (M^+ − 6CO), 792 (M^+ − 7CO), 764 (M^+ − 8CO).

Reaction of $Os_3(CO)_{10}(CNPr)(NCMe)$ with 1-Hydroxybenzotriazole. A mixture of $Os_3(CO)_{11}(CNPr)$ (201 mg, 0.21 mmol), CH_2Cl_2 (150 mL), and acetonitrile (3.0 mL) was treated with a solution of Me_3NO (19 mg, 0.25 mmol) in a mixture of CH_3CN and CH_2Cl_2 (1:5, 5.0 mL). It was stirred at room temperature for 30 min and filtered through a short column of silica gel. After removal of the solvent under vacuum, the residue was redissolved in CH_2Cl_2 (200 mL) precooled to −50 °C. The resultant solution of $Os_3(CO)_{10}(CNPr)(NCMe)$ was treated with 1-hydroxybenzotriazole (29 mg, 0.21 mmol) in dry acetone (5.0 mL). The cooling bath was removed, and the mixture was stirred for 1 h. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate (2-mm thickness) with a mixture of THF and CH_2Cl_2 (3:97) as eluent to give the compounds $Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}NNN(O)C_6H_5)(\mu_2\text{-}\eta^1\text{-}C{=}NHPr)$ (**5a**; 43 mg, 0.041 mmol) as a pale yellow solid in 19% yield and **6a** (7.0 mg, 0.0066 mmol) in 3% yield. For **5a**: Anal. Calcd for $C_{20}H_{12}N_4O_{11}Os_3$: C, 22.75; H, 1.14; N, 5.31. Found: C, 23.50; H, 0.99; N, 5.20. IR (CH_2Cl_2): ν_{CO} 2098, 2067, 2048, 2016, 2005, 1990, 1971 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 9.37 (s, b, 1 H, NH), 7.24–7.79 (m, 4 H, aromatic), 3.65–3.84 (m, 2 H, $CH_2CH_2CH_3$), 1.90 (m, 2 H, $CH_2CH_2CH_3$), 1.05 (t, *J* = 7.5 Hz, 3 H, CH_3). ^{13}C NMR (acetone-d_6): δ 258.9 (CNH), 182.9, 182.1, 181.4, 179.8, 177.4, 177.2, 170.2, 169.7, 169.5 (CO), 145.1, 129.7, 128.3, 124.6, 117.0, 114.4 (aromatic), 64.7 ($CH_2CH_2CH_3$), 22.4 ($CH_2CH_2CH_3$), 11.3 (CH_3). MS (FAB): *m/z* 1057 (M^+), 1029 (M^+ − CO), 1014 (M^+ − Pr), 1001 (M^+ − 2CO), 986 (M^+ − Pr − CO), 973 (M^+ − 3CO), 945 (M^+ − 4CO), 917 (M^+ − 5CO), 889 (M^+ − 6CO), 861 (M^+ − 7CO), 833 (M^+ − 8CO), 805 (M^+ − 9CO), and 777 (M^+ − 10CO). For **6a**: IR (CH_2Cl_2): ν_{CO} 2098, 2067, 2048, 2016, 2004, 1989, 1971 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.21 (s, b, 1 H, NH), 7.19–7.81 (m, 4 H, aromatic), 3.59–3.80 (m, 2 H, $CH_2CH_2CH_3$), 1.89 (m, 2 H, $CH_2CH_2CH_3$), 1.08 (t, *J* = 7.4 Hz, 3 H, CH_3). MS (FAB): *m/z* 1057 (M^+), 1029 (M^+ − CO), 1014 (M^+ − Pr), 986 (M^+ − Pr − CO), 958 (M^+ − Pr − 2CO), 945 (M^+ − 4CO), 930 (M^+ − Pr − 3CO), 917 (M^+ − 5CO).

Reaction of $Os_3(CO)_{10}(CNCH_2Ph)(NCMe)$ with 1-Hydroxybenzotriazole. A solution of $Os_3(CO)_{11}(CNCH_2Ph)$ (204 mg, 0.20 mmol) in CH_2Cl_2 (150 mL) and acetonitrile (3.0 mL) was treated with a solution of Me_3NO (18 mg, 0.24 mmol) in a mixture of CH_3CN and CH_2Cl_2 (1:5, 5.0 mL). The mixture was stirred at ambient temperature for 2 h and filtered through a short column of silica gel. The solvent was removed under vacuum and the residue, $Os_3(CO)_{10}(CNCH_2Ph)(NCMe)$, was redissolved in CH_2Cl_2 (100 mL). To this solution was added 1-hydroxybenzotriazole (27 mg, 0.20 mmol) in dry acetone (5.0 mL), and the mixture was stirred for 2 h. After removal of the solvent under vacuum, the residue was chromatographed on a silica gel TLC plate (2-mm thickness) with a mixture of CH_2Cl_2 and Et_2O (19:1) as eluent to afford $Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}NNN(O)C_6H_5)(\mu_2\text{-}\eta^1\text{-}C{=}NHCH_2Ph)$ (**5b**; 52 mg, 0.047 mmol) in 24% yield as a faint yellow solid and **6b** (65 mg, 0.059 mmol) in 29% yield as a yellow solid. For **5b**: Anal. Calcd for $C_{24}H_{12}N_4O_{11}Os_3$: C, 26.13; H, 1.09; N, 5.08. Found: C, 26.21; H, 1.10; N, 4.83. IR (CH_2Cl_2): ν_{CO} 2098, 2068, 2049, 2016, 2004, 1991, 1971 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.25 (s, b, 1 H, NH), 7.05–7.67 (m, 9 H, aromatic), 4.71 (m, 2 H, CH_2Ph). ^{13}C NMR ($CDCl_3$): δ 267.6 (CNH), 183.4, 182.0, 180.8, 180.6, 180.1, 178.0, 175.1, 169.3, 168.4 (CO), 144.6, 134.3, 129.5, 129.1, 128.6, 128.0, 124.2, 116.1, 114.4 (aromatic), 66.1 (CH_2Ph). MS (FAB): *m/z* 1105 (M^+), 1077 (M^+ − CO), 1049 (M^+ − 2CO), 1028 (M^+ − Ph). For **6b**: Anal. Calcd for $C_{24}H_{12}N_4O_{11}Os_3$: C, 26.13; H, 1.09; N, 5.08. Found: C, 26.16; H, 0.80; N, 4.85. IR (CH_2Cl_2): ν_{CO} 2098, 2068, 2049, 2016, 2005, 1990, 1972 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.22 (s, b, 1 H, NH), 7.04–7.65 (m, 9 H, aromatic), 4.69 (m, 2 H, CH_2Ph). ^{13}C NMR ($CDCl_3$): δ 267.6 (CNH), 183.4, 182.0, 181.8, 180.3, 180.2,

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178.0, 175.2, 174.9, 169.1, 168.6 (CO), 144.5, 134.2, 129.5, 129.1, 128.6, 128.0, 124.2, 116.0, 114.4 (aromatic), 66.1 (CH_2-Ph). MS (FAB): *m/z* 1105 (M^+), 1077 ($M^+ - CO$), 1049 ($M^+ - 2CO$), 1028 ($M^+ - Ph$), 1000 ($M^+ - Ph - CO$), 972 ($M^+ - Ph - 2CO$).

Crystallographic Structure Determination. Crystals of (μ-H)$Os_3(CO)_{10}$(μ_2-(2,3-η^2)-NNN(O)C_6H_4) (**3**), $Os_3(CO)_{10}$(μ_2-η^2-NNN(O)C_6H_5)(μ_2-η^1-C=NHPr) (**5a**), and $Os_3(CO)_{10}$(μ_2-η^2-NNN(O)C_6H_5)(μ_2-η^1-C=NHCH$_2$Ph) (**6b**) were grown from a mixture of CH_2Cl_2 and hexanes at −5 °C. Specimens of suitable quality were mounted in a glass capillary and used for measurement of precise cell constants and intensity data collection. All diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer by use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.709\,30$ Å) with the $\theta-2\theta$ scan mode. Unit cells were determined and refined by use of 25 randomly selected reflections obtained with the CAD-4 automatic search, center, index, and least-squares routines. The space group was determined from the systematic absences observed during data collection. The systematic absences in the diffraction data of **3**, **5a**, and **6b** established the space group as $P2_1/c$ unambiguously. An empirical absorption correction was applied to each of the data sets. The structures were solved by the heavy-atom method. All remaining nonhydrogen atoms were located from the difference Fourier map, and they were included in the final refinement cycle and refined by full-matrix least squares. All the data processing was carried out on a Microvax 3600 by use of the NRCC SDP program.[15]

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Supplementary Material Available: Tables of atomic coordinates, crystal and intensity collection data, anisotropic thermal parameters, and bond lengths and angles for **3**, **5a**, and **6b** (15 pages). Ordering information is given on any current masthead page.

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