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# Reactivity of $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$ with Aminotributylstannane and Aminotrimethylstannane Derivatives

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The reaction of aminotributylstannane or aminotrimethylstannane derivatives with the dihydride of decacarbonyltriosmium in ether−hexane solution (5:1) at room temperature affords the heterometallic clusters $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{HE})(\text{SnR}_3)]$ (**1**−**8**) (HE = dimethylamine (**1**, **5**), pyrrolidine (**2**, **6**), piperidine (**3**, **7**), and morpholine (**4**, **8**)) and the α-carbon−hydrogen bond activation of the secondary amine moiety of (**2**) $[(\mu\text{-H})\text{-Os}_3(\text{CO})_{10}(\overline{\text{N=CHCH}_2\text{CH}_2\text{C}}\text{H}_2)\text{-}(\text{SnBu}_3)]$ (**2a**) in low yield. In all these heterometallic clusters the secondary amine ligand occupies a weak axial coordination site on the osmium triangle, eventually stabilized through the formation of intramolecular hydrogen-bonding interaction between the N−H and the axial carbonyl ligands. The stannyl ligand ($\text{SnBu}_3$ or $\text{SnMe}_3$) occupies an equatorial position on the osmium triangle, as expected for a bulky substituent. The metal carbonyl angles open out and the Os−C−O axes deviate from linearity so as to bring the carbonyl moieties closer to the tin atom in an "umbrella effect", for **3**, **5**, **6**, **7**, **7′**, **8**, and **2a**. We were unable to grow single crystals for the compounds **1**, **2**, and **4**. However, the spectroscopic information ($^1$H, $^{13}$C, and $^{119}$Sn NMR) is similar for compounds **1**−**8** and **2a**. Thus, it is assumed that they should present similar interactions in the triosmium cluster. All the compounds were characterized by IR, $^1$H, $^{13}$C, and $^{119}$Sn NMR, mass spectra, and elemental analysis. Solid-state structures of **3**, **5**, **6**, **7**, **7′**, **8**, and **2a** were established by single-crystal X-ray diffraction analyses.

## Introduction

There has been considerable interest in the synthesis, characterization, and chemistry of transition metal clusters, including the reactivity modifications of organic ligands, unusual binding of organic substrates to several atoms, and recently the exploitation of the catalytic activity of heterometallic particles.[1] Over the years, metal−tin compounds have attracted attention because tin is often used as one component in many bimetallic catalysts, showing an increase of the selectivity in a variety of chemical transformations.[1b,c,2] Although ruthenium−tin clusters have been used for this purpose, the triosmium clusters have proved to be useful systems for modeling heterogeneous catalytic processes such as HDN[3a] or HDS.[3b,c] Osmium clusters also contribute to the understanding of the factors involved in the different stages of activation of organic molecules by transition metals. In this sense, clusters having metal−tin bonds have been studied, showing that the synthesis of transition metal−tin clusters depends on both the tin reagent and the transition metal clusters.[4−6] For example, main-group metals can be incorporated into transition metal clusters (Os, Ru, Fe, Ir) via low-valent derivatives $\text{M}'\text{R}_2$ ($\text{M}'$ = Ge, Sn) in a controlled reaction under mild conditions and with good yield.[4,5] The displacement reaction of the ($\text{CH}_3\text{CN}$) ligand from the compounds $[\text{M}_3(\text{CO})_{12-n}(\text{CH}_3\text{CN})_n]$ ($n$ = 1 or 2) by organogermanes and stannanes is a useful method for the preparation of triosmium and triruthenium−main-group metal clusters of the type $[\text{M}_3(\text{H})(\text{CO})_{11}(\text{M}'\text{R}_3)]$ and $[\text{Os}_3(\text{H})(\text{CO})_{10}\text{-}(\text{CH}_3\text{CN})(\text{M}'\text{R}_3)]$ (M = Ru, Os; $\text{M}'$ = Ge, Sn).[6] The oxidative addition of $\text{HM}'\text{R}_3$ ($\text{M}'$ = Si, Sn, or Ge and R = Et, Bu, or Ph) to the unsaturated cluster $[(\mu\text{-H})_2\text{Os}_3\text{-}$

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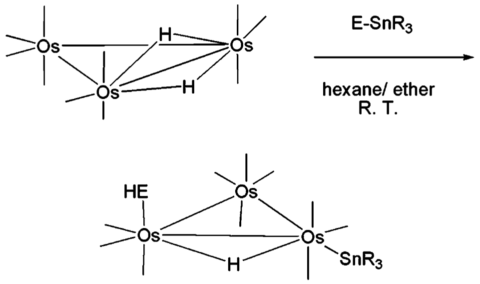
$(CO)_{10}]$ has been previously described,[7] and its kinetics and mechanism showed that the product $[H_3Os_3(CO)_{10}(ER_3)]$ is obtained for most of these reactions, where the hydrogen of $HM'R_3$ remains in the cluster.[7a] Similar to the hydridostannanes, the aminostannanes react with hydride metal compounds to afford metal−metal bonds and a liberated amine.[8] This fact is documented for monometallic centers,[8b] but the reaction with a trinuclear cluster provides the opportunity to explore the chemistry of heterometallic clusters in which the amino moiety remains in the cluster compound after the reaction just like the hydrogen of the hydridostannane remains in the reaction for $[H_3Os_3(CO)_{10}(ER_3)]$.[7] Most of the interest in nitrogen−metal cluster bonds stems from the comparison of their reactivity to that of nitrogen atoms bound to metal surfaces, because adsorbed nitrogen atoms are believed to be key intermediates in several industrial chemical processes such as the Haber process and the oxidation of ammonia.[9] Examples of transition metal carbonyl clusters containing nitrogen-donor ligands have been described for amino,[10] imine,[11] amido,[12] and nitrene[9] compounds in the literature. Nevertheless, only a few clusters containing nitrogen−ruthenium and tin−ruthenium bonds in the same compound have been reported. Some examples are $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(SnR_3)_2(CO)_8]$ (Hampy = 2-amino-6-methylpyridine, R = Bu, Ph)[13a] and $[Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-dmpz})(SnR_3)_2(CO)_8]^-$ (hdmpz = 3,5-dimethylaminopyrazole), R = Bu, Ph).[13b] As far as we are informed, no similar complexes with osmium clusters have been reported. The principal interest in the reaction between aminotrialkylstannanes and the unsaturated cluster $[H_2Os_3(CO)_{10}]$ stems from the idea that it affords a new class of stable compounds where the secondary amine and the stannyl group are tied together through an $Os_3$ unit. This would allow us to determine whether the stannyl group influences the stability of aliphatic secondary amines bonding in the heterometallic clusters or not.

Herein, the preparation and characterization of a series of novel osmium−tin clusters containing a secondary amine, N−Os bond and the trialkylstannyl ligands within the same cluster framework are reported.

## Results and Discussion

**Synthesis.** The oxidative-addition reaction of $[(\mu\text{-}H)_2Os_3(CO)_{10}]$ in the presence of aminostannanes generated a pale yellow, air stable, trinuclear cluster $[(\mu\text{-}H)Os_3(CO)_{10}(HE)(SnR_3)]$ (**1**−**8**) as the major product (Scheme 1). In addition, the α-carbon−hydrogen bond activation of the pyrrolidine ligand in $[(\mu\text{-}H)Os_3(CO)_{10}(N{=}CHCH_2CH_2CH_2)(SnBu_3)]$ (**2a**) was obtained in low yield.[14] It has been reported that the reaction of secondary amines with $[Os_3(CO)_{12}]$ or $[Os_3(CO)_{10}(CH_3CN)_2]$ yields trinuclear products that result from the transalkylation[15a] and/or carbon−hydrogen bond activation[3,15] of the alkyl groups of the secondary amine; the nature of the products obtained is remarkably sensitive to the structure and steric requirements of the amine employed.[15] For example, the α-carbon−hydrogen bond activation of pyrrolidine was obtained in the reaction with $[Os_3(CO)_{10}(CH_3CN)_2]$ as principal product,[15b] while the reaction of azetidine and the osmium cluster generated $[Os_3(CO)_{10}(\mu\text{-}NCH_2CH_2CH_2)(\mu\text{-}H)]$, which contains a four-membered heterocycle that bridges two of the metal atoms through its nitrogen atom.[15c]

**Scheme 1**



| E \ R | Bu | Me |
|---|---|---|
| $(CH_3)_2N$ | 1 | 5 |
| $CH_2CH_2CH_2CH_2N$ | 2 | 6 |
| $CH_2CH_2CH_2CH_2CH_2N$ | 3 | 7 |
| $CH_2CH_2OCH_2CH_2N$ | 4 | 8 |

In this work, the use of the unsaturated cluster $[(\mu\text{-}H)_2Os_3(CO)_{10}]$ and the aminostannanes allowed us to obtain clusters **1**−**8**, where the amino ligand bonds one osmium on the cluster in a weak axial coordination site. This fact is interesting because it had been documented that the reaction with the osmium cluster and heterocyclic amines (including secondary amines) yields iminoyl clusters as principal products.[3,15b] The bulky stannyl groups are tied in the same cluster in the expected equatorial position.

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(14) A subproduct (probably the α-carbon−hydrogen bond activation of the secondary amine) was observed in all the reactions. The IR spectra for those subproducts are similar to the spectrum of **2a**. However, the quantity of product did not allow complete spectroscopic analysis. Compound **2a** was obtained in enough quantity after repeating several times the reaction between (pyrrolidinyl)tributylstannane and the triosmium cluster.

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**Table 1. Selected Spectroscopic Information for 1−8, and 2a**

| compd | hydride $^1$H NMR[a] | CO groups $^{13}$C NMR[b] | $^{119}$Sn NMR[b] |
|---|---|---|---|
| **1** | −16.01, (30.06) | 196.69, 192.36, 191.24, 185.12, 177.65, 175.52, 174.40, 173.88, 173.78 | −49.92 |
| **2** | −16.31, (30.09) | 196.89, 192.54, 191.38, 185.18, 177.50, 174.89, 174.32, 174.22, 174.93, 173.85 | −48.90 |
| **2a** | −16.40, (31.53) | 196.52, 191.27, 189.78, 185.61, 177.93, 175.55, 174.66, 174.45, 173.01 | −51.97 |
| **3** | −16.15, (30.81) | 196.77, 192.39, 191.30, 185.19, 177.69, 175.29, 174.59, 174.21, 173.21 | −50.05 |
| **4** | −16.11, (29.88) | 197.49, 193.15, 191.00, 184.86, 177.39, 175.03, 174.22, 174.07, 173.64 | −49.75 |
| **5** | −15.98, (33.00) | 196.14, 192.37, 190.89, 185.18, 177.42, 175.29, 174.63, 174.23, 173.68 | −68.19 |
| **6** | −16.24, (33.00) | 196.31, 192.58, 191.09, 185.23, 177.32, 174.69, 174.07, 173.81 | −67.54 |
| **7** | −16.12, (32.97) | 196.20, 192.40, 191.03, 185.44, 177.45, 175.03, 174.42, 173.81 | −68.22 |
| **8** | −16.06, (33.00) | 196.91, 190.55, 184.81, 177.10, 174.72, 174.20, 173.99, 173.39 | −67.82 |

[a] $\delta$ ppm/($J_{^1H-^{187}Os}$ Hz), in $CDCl_3$. [b] $\delta$ ppm in $CDCl_3$.

**Table 2. Crystallographic Data of 3, 2a, 5, 6, 7, 7′, and 8**

| | **3** | **2a** | **5** | **6** | **7** | **7′** | **8** |
|---|---|---|---|---|---|---|---|
| formula | $C_{27}H_{39}NO_{10}$-$Os_3Sn$ | $C_{26}H_{35}NO_{10}$-$Os_3Sn$ | $C_{15}H_{17}NO_{10}$-$Os_3Sn$ | $C_{16}H_{19}NO_{10}$-$Os_3Sn$ | $C_{18}H_{21}NO_{10}$-$Os_3Sn$ | $C_{19}H_{22}Cl_3NO_{10}$-$Os_3Sn$ | $C_{19}H_{19}NO_{11}$-$Os_3Sn$ |
| fw | 1226.88 | 1210.84 | 1060.59 | 1086.62 | 1100.65 | 1220.22 | 1102.62 |
| cryst syst | monoclinic | monoclinic | triclinic | monoclinic | monoclinic | orthorhombic | triclinic |
| space group | $P2_1/c$ | $C2/c$ | $P\bar{1}$ | $P2_1/n$ | $P2_1/c$ | $Pbca$ | $P\bar{1}$ |
| $a$/Å | 17.794(1) | 38.345(13) | 9.405(1) | 10.652(1) | 10.717(1) | 14.185(1) | 10.417(1) |
| $b$/Å | 11.656(1) | 11.269(4) | 10.557(1) | 17.897(1) | 17.096(1) | 20.369(2) | 11.093(1) |
| $c$/Å | 17.483(1) | 17.707(6) | 12.768(1) | 13.304(1) | 15.517(1) | 21.522(2) | 12.765(1) |
| $\alpha$/deg | 90 | 90 | 83.848(1) | 90 | 90 | 90 | 104.043(1) |
| $\beta$/deg | 93.850(1) | 114.094(8) | 84.707(1) | 101.656(1) | 110.004(1 | 90 | 107.687(1) |
| $\gamma$/deg | 90 | 90 | 77.250(1) | 90 | 90 | 90 | 95.052(1) |
| $Z$ | 4 | 8 | 2 | 4 | 4 | 8 | 2 |
| $F(000)$ | 2264 | 4448 | 944 | 1944 | 1976 | 4416 | 988 |
| $D_{calc.}$/g cm$^{-3}$ | 2.252 | 2.303 | 2.872 | 2.906 | 2.737 | 2.606 | 2.728 |
| color/shape | yellow/plates | yellow/plates | yellow/prisms | yellow/prisms | yellow/ parallelepipeds | orange/prisms | yellow/needles |
| $\theta$ range/deg | 2.09 to 25.00 | 1.16 to 25.13 | 1.61 to 25.00 | 1.93 to 32.52 | 1.84 to 32.51 | 1.89 to 25.00 | 1.75 to 24.99 |
| $\mu$/mm$^{-1}$ | 11.232 | 11.634 | 16.544 | 16.339 | 15.194 | 13.318 | 15.123 |
| $R_1/R_{w2}$[a] | 0.0743/0.1039 | 0.0643/0.0934 | 0.0478/0.0862 | 0.0464/0.0432 | 0.0831/0.0548 | 0.0588/0.0983 | 0.0540/0.0566 |
| GOF on $F^2$ | 0.998 | 0.941 | 1.041 | 0.940 | 0.948 | 0.936 | 0.997 |

[a] $R$ indices (all data).

**Spectroscopic Information.** The IR spectra of **1**−**8** exhibit eight carbonyl stretching frequency bands in the range 2090−1930, and the shape and intensity of the spectrum are similar in all the compounds, indicating that all share a similar local symmetry around the osmium triangle. No bands in the bridge carbonyl region were found. The $^1$H NMR spectra of compounds **1**−**8** show the signal assigned for one hydride around −16.00 ppm, as expected for a bridging hydride ligand[6] (Table 1), and no significant changes are observed in the shielding for the hydride in **1**−**8** or **2a**. The coupling constant $J(^{187}Os-^1H)$ at natural abundance ($^{187}Os = 1.64\%$) for compounds **1**−**4** and **5**−**8** appears as a single set with values around 30 and 33 Hz, respectively (Table 1). These values are in the range previously observed for hydrides in triosmium clusters.[16] The broad singlets in the range 2.40−2.79 are assignable to the hydrogen of the HN groups of the secondary amines coordinated to the osmium clusters **1**−**8**. The $^1$H NMR spectrum of the compound **2a** shows a single resonance at $\delta = 7.48$ ppm, which can be assigned to a hydrogen atom of the imino group. The $^{13}C\{^1H\}$NMR spectra at natural abundance ($^{13}C = 1.1\%$) for **1**−**8** show from 8 to 10 signals in the range 197.49−173.01 ppm (Table 1). For similar compounds $[(\mu\text{-}H)Os_3(CO)_9(NMe_3)(\mu\text{-}COC_4H_4N)]$,[10a] $[H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}CPh_2]$,[11a] and $[(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C{=}NCH_2CH_2CH_2)Os_3(CO)_{10}]$[15b] the higher resonances appear in the range between 186.01 and 183.50 ppm, which are assignable to the two mutually trans-axial carbonyl groups of the $Os(CO)_4$ fragment of the triosmium clusters. In comparison the resonances in this range, 185−174 (Table 1), should correspond to the $Os(CO)_4$ fragment in compounds **1**−**8** and **2a**, and by a process of elimination the signals in the range 197−190 (Table 1) are assigned to CO groups in the fragment $Os(CO)_3(SnR_3)$ according to the electronic effect that the tin atom has on the CO groups close to it. High chemical shifts (around 200 ppm) of the CO groups in ruthenium cluster compounds where silicon or tin atoms are tied to the cluster have been described.[13a,c] The $^{119}$Sn NMR for **1**−**4** show one signal around −50 and −67 ppm for **5**−**8** (Table 1). It has been reported that the difference in the tin shielding depends not only on electron density on the nuclei but also on the $d_\pi-d_\pi$ interaction between the two metal atoms and the values of $\delta(^{119}Sn)$ defining the region with different coordination numbers of the central tin atom, Thus, the chemical shifts $\delta(^{119}Sn)$ in **1**−**8** are assigned to a quasi-tetrahedral tin four-coordinated compound.[17,18]

**Solid-State Structures of 3, 5, 6, 7, 7′, 8, and 2a.** The solid-state structures of **3**, **5** **6**, **7**, **7′**, **8**, and **2a** were established by single-crystal X-ray diffraction analyses. Crystal data are shown in Table 2, and some selected bond parameters are in Table 3. The molecular structures of **5**, **6**, **7**, and **8** are portrayed in Figures 1, 2, 3, and 4, respectively. The metal framework for **3**, **5**, **6**, **7**, and **8** consists of an osmium scalene triangle with the

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**Table 3. Selected Bond Distances (Å) and Angles (deg) for 2a, 3, 5, 6, 7, 7′, and 8**

| | **2a** | **3** | **5** | **6** | **7** | **7′** | **8** |
|---|---|---|---|---|---|---|---|
| Distances | | | | | | | |
| Os(1)−Os(2) | 3.0401(11) | 3.0159(7) | 3.0212(6) | 3.0148(3) | 3.0179(4) | 3.0025(6) | 3.0053(5) |
| Os(1)−Os(3) | 2.8704(12) | 2.8768(8) | 2.8741(6) | 2.8841(3) | 2.8704(4) | 2.8655(6) | 2.8685(5) |
| Os(2)−Os(3) | 2.8856(10) | 2.9123(8) | 2.9106(6) | 2.9033(4) | 2.9132(4) | 2.9099(6) | 2.9174(6) |
| Os(1)−Sn(1) | 2.6929(14) | 2.6994(11) | 2.7021(8) | 2.6847(4) | 2.6953(5) | 2.6903(9) | 2.6909(8) |
| Os(2)−N(1) | 2.185(10) | 2.226(10) | 2.208(10) | 2.201(4) | 2.214(5) | 2.252(9) | 2.226(6) |
| Angles | | | | | | | |
| Os(3)−Os(1)−Os(2) | 58.364(19) | 59.181(18) | 59.108(14) | 58.917(8) | 59.243(8) | 59.402(14) | 59.507(14) |
| Os(1)−Os(3)−Os(2) | 63.76(3) | 62.790(18) | 62.965(15) | 62.788(7) | 62.901(10) | 62.642(15) | 62.581(14) |
| Os(3)−Os(2)−Os(1) | 57.87(3) | 58.029(18) | 57.927(15) | 58.295(7) | 57.856(8) | 57.956(14) | 57.913(12) |
| C(4)−Os(2)−N(1) | 172.8(4) | 173.5(5) | 176.6(4) | 174.12(18) | 176.5(2) | 175.6(4) | 177.2(4) |
| C(2)−Os(1)−Sn(1) | 86.5(4) | 83.0(5) | 83.8(3) | 86.79(15) | 81.05(18) | 80.5(3) | 84.9(3) |
| C(1)−Os(1)−Sn(1) | 82.7(4) | 85.1(4) | 83.5(3) | 84.73(14) | 85.26(18) | 84.9(9) | 83.3(3) |

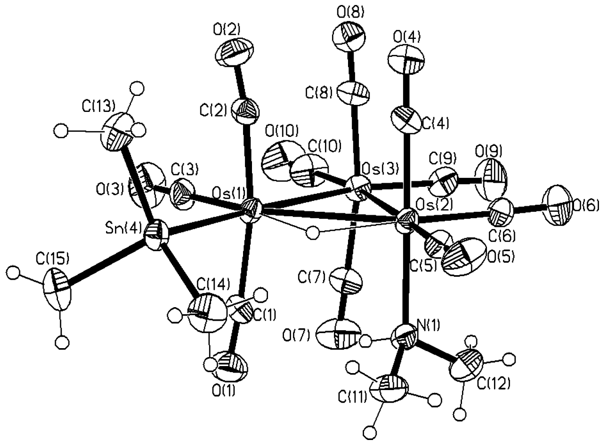

**Figure 1.** Molecular structure of **5** with the atom-numbering scheme.

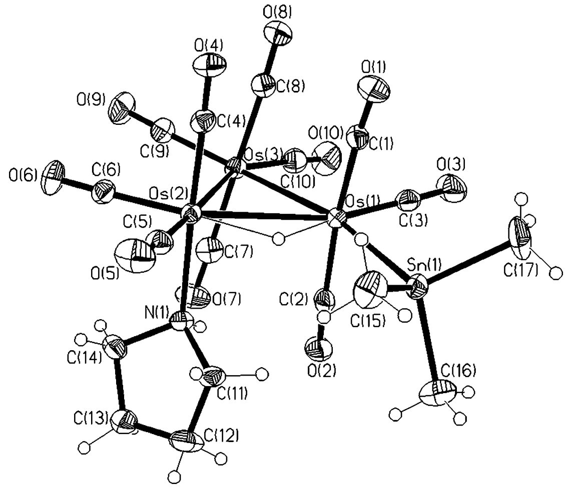

**Figure 2.** Molecular structure of **6** with the atom-numbering scheme.

amine group perpendicular to the $Os_3$ plane. The location of the hydride was determined by diffraction analysis for **6** and **7** and geometrically assigned for **2b**, **3**, **5**, and **8**, and it was located undoubtedly between Os(1)−Os(2) according to the lengthening of the metal−metal vector, which is associated with the bond length distances for **3**, **5**, **6**, **7**, **8**, and **2a** found in the range 3.0212(6)−3.0053(6) Å (Table 3), common for Os−Os bonds bridged by a hydrogen atom.[19] The secondary amine ligand acts as a σ-two-electron donor through a coordination bond, N−Os(2) 2.226(10) Å for **3** and 2.201(4) Å for **6** (Table 3). The distances are relatively long,

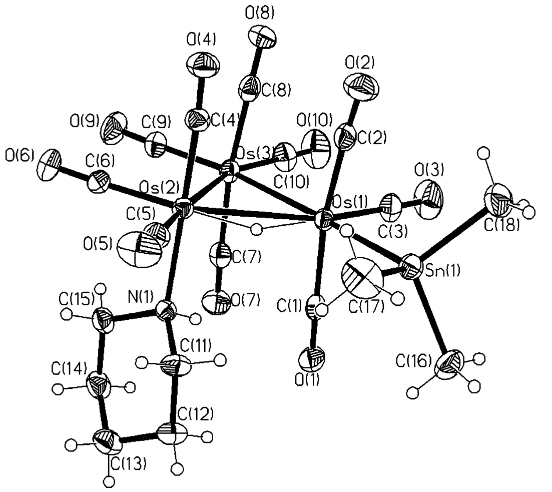

**Figure 3.** Molecular structure of **7** with the atom-numbering scheme.

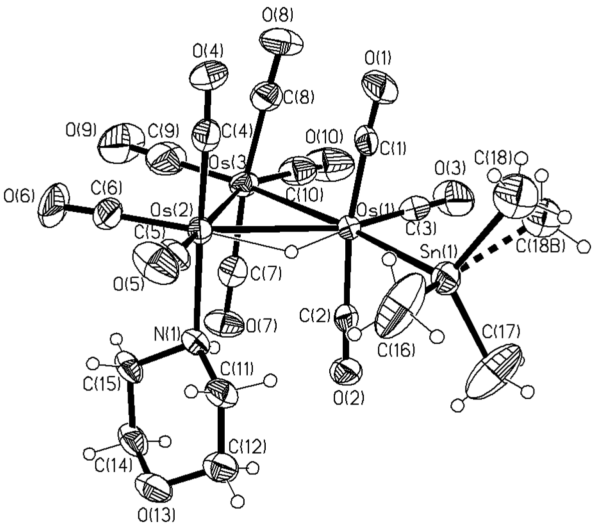

**Figure 4.** Molecular structure of **8** with the atom-numbering scheme.

suggesting that the bond N(1)−Os(2) is weak in the structures **3**, **5**, **6**, **7**, **8**, and **2a** (Figures 1−4). There are just a few cluster compounds tied to an amine in a σ-coordination bond. However, some of these examples have similar Os−N distances: 2.282(13) Å found for the Os−$NMe_3$ equatorial bond in $[Os_3(\mu\text{-H})(CO)_9(NMe_3)(\mu\text{-}$

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**Table 4. Hydrogen Bond Distances (Å) and Angles (deg) for 5, 6, 7, and 8**

| | D−H···A N(1)−H(1)···O(7) | | | | |
|---|---|---|---|---|---|
| | **5** | **6** | **7** | **7′** | **8** |
| *d*(D−H) | 0.78(12) | 0.72(4) | 0.89(4) | 0.93(13) | 0.68(8) |
| *d*(H···A) | 2.71(13) | 2.50(5) | 2.41(4) | 2.48(12) | 2.45(9) |
| *d*(D···A) | 3.177(15) | 3.074(6) | 3.165(6) | 3.148(12) | 3.004(9) |
| ∠(DHA) | 120(11) | 138(5) | 142(4) | 129(10) | 147(11) |

$COC_4H_4N)]$[10a] or 2.22(2) Å for Os−$NMe_3$ in $[Os_3(CO)_9(NO)_2(NMe_3)]$.[10c] The imine bond distance N−Os = 2.185(10) Å in **2a** is slightly bigger than the distances reported for similar coordination modes of the imine $[H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}CPh_2)]$[11a] (2.150(4) Å) or $[Os_3(\mu\text{-}H)(\mu\text{-}HNCHPh_2)(HN{=}CPh_2)(CO)_9]$[12a] (2.167(7) Å). The carbon−nitrogen bond length of 1.277(15) Å in **2a** is typical of carbon−nitrogen double bonds (1.28 Å) in the closely related triosmium cluster $[Os_3(\mu\text{-}H)(\mu\text{-}HNCHPh_2)(HN{=}CPh_2)(CO)_9]$.[12a] The angle C(4)−Os(2)−N(1) in **3**, **5**, **6**, **7**, and **8** is almost linear, for example, 173.5(5)° and 175.6(4)° for **3** and **7**, respectively (Table 3). The distances for the Os(1)−Sn(1) bonds are around 2.69 Å (Table 3) and are similar to the terminal Os−Sn lengths reported in the literature: 2.653(1) Å in $[Os_3(\mu\text{-}H)(\mu_3\text{-}S)(\mu_3\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)]$[20] and 2.711(1) Å in *trans*-$[Os(CO)_4(SnPh_3)_2]$.[21] These lengths are also comparable with Os−Sn distances found for molecules in which the tin ligand bridges two osmium atoms.[4,5] The C(2)−Os(1)−Sn(1) and Os(1)−C(1)−Sn(1) angles for **3**, **5**, **6**, **7**, **7′**, **8**, and **2a** are around 83° (Table 3). Similar angles were found in the cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}(SnMe_3)_2]$ for the carbonyl groups in the fragment $Os(CO)_3(SnMe_3)$[7b] and had been described for mononuclear metal carbonyl derivatives as the "umbrella effect", describing the tendency of the carbonyl system to lean toward the second metal atom to fill space more efficiently.[22] However, in this work, all the structures present the "umbrella effect" in the $Os(CO)_3(SnR_3)$ fragment of the osmium cluster network. In particular two structures, **7** and **7′**, present the same effect in the C(2)−Os(1)−Sn(1) and Os(1)−C(1)−Sn(1) angles (around 83°) even though **7′** is a solvate compound of **7** and consequently the packing effects are different. This suggests that the packing effects are not completely responsible of the "umbrella effect" in the cluster network. The presence of an intramolecular NH···O interaction between the amine proton donor and the oxygen of the carbonyl group was determined for **5**, **6**, **7**, and **8** (Table 4), This is interesting because it has been suggested that similar XH···HM interactions are responsible for driving the stereochemistry of the resulting products.[11] Then, the axial position of the secondary amine is stabilized by the NH···O interaction present in the cluster compounds **5**, **6**, **7**, and **8**.

There is no significant change between the series of Os−N distances in compounds **5** (dimethylamine), **6** (pyrrolidine), **7** (piperidine), and **8** (morpholine) independently of the inherent electronic requirements of each amine.

## Conclusions

Nine triosmium carbonyl cluster complexes containing amino (**1**−**8**) and one (**2a**) containing imino terminal ligands derived from aminostannane compounds have been prepared and characterized. Compounds **1**−**8** have noteworthy structures due to a σ-nitrogen−metal coordination mode that has rarely been observed in the cluster compounds when aliphatic heterocycle-amino ligands are present.[3a,10,15] The secondary amine occupies an axial amino ligand probably stabilized by an intramolecular NH···O interaction. The α-carbon−hydrogen bond activation was not favored in this compound, as it is described for secondary amines.[3a,15] The nature of the products was not sensitive to the structure and steric requirements of the aminostannane employed. Compounds **1**, **2**, and **4** share a similar structure with **2a**, **3**, **5**, **6**, **7**, **7′**, and **8**, in accord with the shielding of signals in the $^{13}C$ and $^{119}Sn$ NMR spectra for the carbonyl groups and tin, respectively (Table 1). In fact the IR spectra in cyclohexane solution show that the local symmetry around the osmium triangle is similar for all these compounds.

## Experimental Section

**General Data.** All the reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were purified and dried according to standard literature procedures.[23] Piperidine, pyrrolidine, and morpholine were dried and were freshly distilled prior to use. The starting materials $[Os_3(CO)_{12}]$[24] and $[(\mu\text{-}H)_2Os_3(CO)_{10}]$[25] were prepared by literature methods. Reactions were monitored by analytical thin-layer chromatography (Merck Kieselgel 60 $F_{254}$), and the products were separated by thin-layer chromatography (Merck Kieselgel 60 $F_{254}$). IR spectra were recorded on a Nicolet-750 spectrometer in cyclohexane solution. $^1H$ (300 MHz), $^{13}C$ (75 MHz), and $^{119}Sn$ (112 MHz) NMR spectra were obtained on an JEOL GX 300 spectrometer, and $SnMe_4$ was used as external reference for $^{119}Sn$ spectra. Positive ionization fast atom bombardment (FAB) mass spectra were recorded on a JEOL JMS-SX-102A mass spectrometer, using *m*-nitrobenzyl alcohol as matrix solvent. The elemental analyses were performed by Galbraith Laboratory, Inc.

**Crystal Structure Determination.** Suitable X-ray quality crystals of **2a**, **3**, **5**, **6**, **7**, and **8** were grown by slow layer diffusion of *n*-pentane−diethyl ether (1:1) into a saturated dichloromethane solution at −4 °C, and **7′** was grown by slow evaporation of the $CDCl_3$ in the resonance tube at −4 °C. The crystals were each mounted on a glass fiber, and diffraction experiments were performed on a Bruker Smart Apend CCD diffractometer with graphite-monocromated Mo Kα radiation. The unit-cell constants were obtained from the least-squares refinements of the observed reflections in the range $1.16° < 2\theta < 32.5°$, using the Bruker SMART program.[26] Data were corrected for crystal decay with the Bruker SAINT Plus program.[26] All data sets were collected using the $\omega$ scan mode. Additional crystallographic data are collected in Table 2.

Structures of the compounds were solved by direct methods using the SHELXS-97 program[27] for **2a**, **3**, **5**, **6**, **7**, **7′**, and **8**, and the refinements were carried out by full matrix least-squares on $F^2$. Weigthed *R*-factors, $R_w$, and all goodness of fit

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(26) *Bruker AXS SMART*, version 5.62; Bruker Inc.: Madison, WI, 2001.

(27) Sheldrick, G. M. *SHELXS-97*, version 97-1; Gottingen University: Gottingen, 1997.

indicators, $S$, were based on $F^2$. The observed criterion of $F^2 > 2\sigma F^2$ was used only for calculating the $R$-factors. The number of observed reflections is presented in Table 2.

**Preparation of Aminotrialkylstannanes Compounds.** The aminotributylstannanes were prepared by transmetalation with lithium salts of secondary amines[28] and the aminotrimethylstannanes by a transamination reaction using (dimethylamino)trimethylstannane according to the Lappert method.[28]

**(Dimethylamino)tributylstannane (i).** $^1$H NMR (CDCl$_3$): $\delta$ 2.34 (s, 6H), 1.57 (m, 6H), 1.27 (m, 12H), 0.84 (t, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 38.66, 28.28 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 29.7$ Hz), 27.27 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 60.5$ Hz), 13.56, 13.07 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 322.7$ Hz). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 58.64.

**(Piperidinyl)tributylstannane (ii).** $^1$H NMR (CDCl$_3$): $\delta$ 2.78 (s, 4H), 1.65 (m, 6H), 1.52 (s, 6H), 1.33 (m, 12H), 0.90 (m, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 47.35, 28.12, 27.19, 25.15, 16.41, 13.63, 13.12 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 329.7$ Hz). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 58.18.

**(Pyrrolidinyl)tributylstannane (iii).** $^1$H NMR (CDCl$_3$): $\delta$ 2.75 (m, 4H), 1.58 (m, 10H), 1.26 (m, 12H), 0.83 (m, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 47.04, 28.26 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 19.4$ Hz), 27.27 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 61.7$ Hz), $\delta$ 25.53, 13.51, 13.07 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} =$ 330.7). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 58.59.

**(Morpholinyl)tributylstannane (iv).** $^1$H NMR (CDCl$_3$): $\delta$ 3.65 (m, 4H), 2.84 (m, 4H), 1.51 (m, 6H), 1.28 (m, 6H), 0.97 (t, 6H,), 0.87 (m, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 68.22, 46.62, 28.25 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 17.2$ Hz), 27.34 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 62.7$ Hz), 16.43 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 348$ Hz), 13.76. $^{119}$Sn NMR (CDCl$_3$): $\delta$ 58.79.

**(Dimethylamino)trimethylstannane (v).** $^1$H NMR (CDCl$_3$): $\delta$ 2.32 (s, 6H), 0.40 (s, 9H, $J_{^{1}\text{H}\ -^{119/117}\text{Sn}} = 52.12/54.39$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 38.64, $-7.13$ ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 366.2/348.0$ Hz). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 127.9, 84.18.

**(Piperidinyl)trimethylstannane (vi).** $^1$H NMR (CDCl$_3$): $\delta$ 2.71 (s, 4H), 1.42 (s, 6H), 0.40 (s, 9H). $^{13}$C NMR (CDCl$_3$) $\delta$ 47.31, 27.16, 25.12, $-7.17$ ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 329.7$ Hz). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 128.1, 87.89.

**(Pyrrolidinyl)trimethylstannane (vii).** $^1$H NMR (CDCl$_3$): $\delta$ 2.76 (m, 4H), 1.57 (m, 4H), 0.22 (s, 9H, $J_{^{1}\text{H}-^{117/119}\text{Sn}} = 55$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 47.15, 25.54, $-2.10$ ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 390.2/370.7$ Hz). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 128.01.

**(Morpholinyl)trimethylstannane (viii).** $^1$H NMR (CDCl$_3$): $\delta$ 3.46 (m, 4H), 2.65 (m, 4H), 0.11 (s, 9H, $J_{^{1}\text{H}-^{117/119}\text{Sn}} = 55.77$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 68.00, 46.46, $-2.19$ ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 361.0$ Hz). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 127.46.

**Reaction of Aminotrialkylstannanes with $[(\mu\text{-H}_2)\text{Os}_3(\text{CO})_{10}]$. Synthesis of $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{HNMe}_2)(\text{SnBu}_3)]$ (1).** A 50 mg (0.058 mmol) amount of $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$ was dissolved in 40 mL of a mixture of diethyl ether−hexane (5:1). To this solution was added ~22 mg (0.058 mmol) of (dimethylamino)tributylstannane, and the mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure, and the principal product was isolated by TLC using *n*-hexane−dichloromethane (3:1 v/v). A procedure analogous to that described for **1** was used for synthesizing compounds **2**−**8**.

**$[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{HNMe}_2)(\text{SnBu}_3)]$ (1).** Yield = 33%. Anal. Calcd for $C_{24}H_{35}NO_{10}Os_3Sn$: C, 24.29; H, 2.97; N, 1.18. Found: C, 24.41; H, 3.02; N, 1.21. Mp: 93−95 °C. FAB-MS *m/z*: 1130 ($M^+ - 2CO$). IR (cyclohexane): $\nu$(CO) 2094 (m), 2053 (s), 2029 (s), 2015 (s), 1999 (s), 1982 (s), 1969 (s) 1935(w). $^1$H NMR (CDCl$_3$): $\delta$ 2.90 (m, 6H), 2.79 (s, 1H), 1.56 (m, 6H), 1.35 (m, 6H), 1.23 (m, 6H), 0.90 (m, 9H), $-16.01$ (s, 1H, $J_{^{1}\text{H}-^{187}\text{Os}} = 30.06$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 196.69, 192.36, 191.24, 185.12, 177.65, 175.52, 174.40, 173.88, 173.78 (CO groups), 53.70, 51.94, 30.35 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 18.2$ Hz), 27.56 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 60.5$ Hz), 13.76, 12.52 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 267.25$ Hz). $^{119}$Sn NMR (CDCl$_3$): $\delta$ $-49.62$.

**$[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{HNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{SnBu}_3)]$ (2).** Yield = 28%. Anal. Calcd for $C_{26}H_{37}NO_{10}Os_3Sn$: C, 25.74; H, 3.07; N, 1.15. Found: C, 25.74; H, 3.26; N, 1.13. Mp: 108−110 °C. FAB-MS *m/z:* 1156 ($M^+ -2CO$). IR (cyclohexane): $\nu$(CO) 2093 (m), 2051 (s), 2028 (s), 2014 (s), 1998 (s), 1979 (s), 1966 (s) 1932(w). $^1$H NMR (CDCl$_3$): $\delta$ 3.08, (m, 2H), 2.72 (m, 2H), 2.48 (m, 1H), 1.84 (m, 2H), 1.53 (m, 8H), 1.37 (m, 6H), 1.23 (m, 6H) 0.89 (m, 9H), $-16.31$ (s, 1H, $J_{^{1}\text{H}-\text{Os}^{187}} = 30.09$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 196.94, 192.57, 191.38, 185.18, 177.52, 174.91, 174.31, 174.23, 173.94, 173.87 (CO groups), 62.63, 60.38, 30.38 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 19.25$ Hz), 27.57 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 60.5$ Hz), 27.67, 12.57. $^{119}$Sn NMR (CDCl$_3$): $\delta$ $-48.90$.

**$[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{N}{=}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{SnBu}_3)]$ (2a).** Yield = 6%. FAB-MS (high resolution) *m/z*: 1211.0057 (calcd for $C_{26}H_{35}O_{10}Os_3NSn$, 1211.0061). Mp: 85−88 °C. IR (cyclohexane): $\nu$(CO) 2093 (m), 2067 (m), 2053 (s), 2028 (s), 2013 (s), 1998 (s), 1989 (s), 1978 (s) 1941(w). $^1$H NMR (CDCl$_3$): $\delta$ 7.54 (s, 1H), 3.76, (m, 2H), 2.85 (m, 2H), 1.99 (m, 2H), 1.55 (m, 10H), 1.38 (m, 7H), 1.26 (m, 6H), 0.89 (m, 9H), $-16.40$ (s, 1H, $J_{^{1}\text{H}-^{187}\text{Os}} = 31.53$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 196.52, 191.27, 189.78, 185.61, 177.93, 175.55, 174.66, 174.45, 174.34, 173.01 (CO groups), 183.23, 71.57, 38.20, 30.43, 27.62, 22.21, 13.80, 12.54. $^{119}$Sn NMR (CDCl$_3$): $\delta$ $-51.97$.

**$[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{HNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{SnBu}_3)]$ (3).** Yield = 56%. Anal. Calcd for $C_{27}H_{39}NO_{10}Os_3Sn$: C, 26.43; H, 3.20; N, 1.14. Found: C, 26.03; H, 3.26; N, 1.13. Mp: 92−95 °C. FAB-MS *m/z*: 1228. IR (cyclohexane): $\nu$(CO) 2093 (m), 2052 (s), 2028 (s), 2014 (s), 1998 (s), 1979 (s), 1968 (s) 1934(w). $^1$H NMR (CDCl$_3$): $\delta$ 3.13 (s, 1H), 3.08 (s, 1H), 2.86 (m, 2H), 2.40 (m, 1H), 1.79 (s, 1H), 1.54 (m, 8H), 1.37 (m, 8H), 1.22 (m, 6H), 0.90 (m, 9H), $-16.15$ (s, 1H, $J_{^{1}\text{H}-^{187}\text{Os}} = 30.81$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 196.77, 192.39, 191.30, 185.19, 177.69, 175.29, 174.59, 174.21, 173.99 (CO groups), 63.36, 61.12, 30.34 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 18.2$ Hz), 29.16, 28.86, 27.57 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 60.5$ Hz), 21.79, 13.76, 12.50 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 259.2$). $^{119}$Sn NMR (CDCl$_3$): $\delta$ $-50.05$.

**$[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{HNCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)(\text{SnBu}_3)]$ (4).** Yield = 70%. Anal. Calcd for $C_{26}H_{37}NO_{11}Os_3Sn$: C, 26.09; H, 3.16; N, 1.13. Found: C, 26.05; H, 3.22; N, 1.19. FAB-MS *m/z*: 1229. Mp: 70−80 °C. IR (cyclohexane): $\nu$(CO) 2094 (m), 2053 (s), 2028 (s), 2015 (s), 1999 (s), 1981 (s), 1965 (s) 1931(w). $^1$H NMR (CDCl$_3$): $\delta$ 3.70 (m, 2H), 3.43 (m, 2H), 3.17 (m, 2H), 2.89 (m, 2H), 2.68 (m, 1H), 1.52 (m, 6H), 1.35 (m, 6H), 1.21 (m, 6H), 0.88 (m, 9H), $-16.11$ (s, 1H, $J_{^{1}\text{H}-^{187}\text{Os}} = 29.88$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 197.49, 193.15, 191.00, 184.86, 177.39, 175.03, 174.22, 174.07, 173.64 (CO groups), 69.16, 69.09, 61.64, 59.41, 30.34 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 18.2$ Hz), 27.54 ($J_{^{13}\text{C}-^{117/119}\text{Sn}} = 59.5$ Hz), 13.76, 12.55. $^{119}$Sn NMR (CDCl$_3$): $\delta$ $-49.75$.

**$[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{HNMe}_2\ )(\text{SnMe}_3)]$ (5).** Yield = 26%. Anal. Calcd for $C_{15}H_{17}NO_{10}Os_3Sn$: C, 16.99; H, 1.62; N, 1.32. Found: C, 17.07; H, 1.72; N, 1.37. FAB-MS *m/z*: 1046. Mp: 113−115 °C. IR (cyclohexane): $\nu$(CO) 2095 (m), 2053 (s), 2031 (s), 2015 (s), 1999 (s), 1984 (s), 1970 (s) 1937 (w). $^1$H NMR (CDCl$_3$): $\delta$ 2.91 (s, 6H), 2.78 (s, 1H), 0.54 (s, 9H, $J_{^{1}\text{H}-^{117/119}\text{Sn}} = 46.71$ Hz), $-15.98$ (s, 1H, $J_{^{1}\text{H}-^{187}\text{Os}} = 33$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 196.14, 192.37, 190.89, 185.18, 177.42, 175.29, 174.63, 174.23, 173.68 (CO groups), 53.59, 51.89, $-5.55$. $^{119}$Sn NMR (CDCl$_3$): $\delta$ $-68.19$.

**$[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{HNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{SnMe}_3)]$ (6).** Yield = 56%. Anal. Calcd for $C_{17}H_{19}NO_{10}Os_3Sn$: C, 18.79; H, 1.76; N, 1.29. Found: C, 18.83; H, 1.86; N, 1.32. FAB-MS *m/z*: 1072. Mp: 125−128 °C. IR (cyclohexane): $\nu$(CO) 2094 (m), 2053 (s), 2031 (s), 2014 (s), 1998 (s), 1981 (s), 1967 (s) 1933 (w). $^1$H NMR (CDCl$_3$): $\delta$ 3.02, (m, 2H), 2.67 (m, 2H), 2.42 (m, 1H), 1.78 (m, 2H), 1.59 (m, 2H), 0.55 (m, 9H, $J_{^{1}\text{H}-^{117/119}\text{Sn}} = 46.74$ Hz), $-16.24$ (s, 1H, $J_{^{1}\text{H}-^{187}\text{Os}} = 33.00$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 196.31,

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192.58, 191.09, 185.23, 177.32, 174.69, 174.07, 173.81 (CO groups), 62.58, 60.34, 25.68, −5.49. $^{119}$Sn NMR (CDCl$_3$): $\delta$ −67.54.

**[($\mu$-H)Os$_3$(CO)$_{10}$(H$\overline{\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}}$H$_2$)(SnMe$_3$)] (7).** Yield = 67%. Anal. Calcd for $C_{18}H_{21}NO_{10}Os_3Sn$: C, 19.69; H, 1.92; N, 1.27. Found: C, 19.69; H, 2.03; N, 1.36. FAB-MS *m*/*z*: 1085 (−1CO). Mp: 146−149 °C. IR (cyclohexane): $\nu$(CO) 2094 (m), 2053 (s), 2030 (s), 2014 (s), 1998 (s), 1982 (s), 1969 (s) 1936 (w). $^1$H NMR (CDCl$_3$): $\delta$ 3.08 (m, 2H), 2.85 (m, 2H), 2.39 (m, 1H), 1.77 (m, 1H), 1.58 (m, 3H), 1.40 (m, 1H), 0.52 (m, 9H, $J_{^1\text{H}-^{117/119}\text{Sn}}$ = 46.74 Hz), −16.12 (s, 1H, $J_{^1\text{H}-^{187}\text{Os}}$ = 32.97 Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 196.22, 192.42, 191.01, 185.26, 177.50, 175.04, 174.42, 173.85 (CO groups), 63.28, 61.06, 29.15, 28.84, 21.77, −5.62. $^{119}$Sn NMR (CDCl$_3$): $\delta$ −68.05.

**[($\mu$-H)Os$_3$(CO)$_{10}$(H$\overline{\text{NCH}_2\text{CH}_2\text{OCH}_2\text{C}}$H$_2$)(SnMe$_3$)] (8).** Yield = 68%. Anal. Calcd for $C_{17}H_{19}NO_{11}Os_3Sn$: C, 18.52; H, 1.74; N, 1.27. Found: C,18.76; H, 1.92; N, 1.36. FAB-MS *m*/*z*: 1086 (−1CO). Mp: 138−140 °C. IR (cyclohexane): $\nu$(CO) 2095 (m), 2054 (s), 2031 (s), 2015 (s), 1999 (s), 1983 (s), 1969 (s) 1937 (w). $^1$H NMR (CDCl$_3$): $\delta$ 3.73 (m, 2H), 3.41 (m, 2H), 3.18 (m, 2H), 2.86 (m, 2H), 2.69 (m, 1H), 0.53 (s, 9H, $J_{^1\text{H}-^{117/119}\text{Sn}}$ = 52.64 Hz), −16.06 (s, 1H, $J_{^1\text{H}-^{187}\text{Os}}$ = 33.00 Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 199.91, 190.55, 184.81, 177.10, 174.72, 174.31, 174.20, 173.99, 173.39 (CO groups), 69.07, 61.41, 59.31, −5.58. $^{119}$Sn NMR (CDCl$_3$): $\delta$ −67.82.

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**Supporting Information Available:** Details of data collection parameters, bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters for **2a**, **3**, **5**, **6**, **7**, **7′**, and **8** are available free of charge via the Internet at http://pubs.acs.org.

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