

Reactions of Electron-Deficient Triosmium Clusters with Diazomethane: Electrochemical Properties and Computational Studies of Charge Distribution

Md. Abdul Mottalib, Noorjahan Begum, S. M. Tareque Abedin, Tahmina Akter, Shariff E. Kabir,* and Md. Arzu Miah

Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh

Dalia Rokhsana and Edward Rosenberg*

Department of Chemistry, University of Montana, Missoula, Montana 59812

G. M. Golzar Hossain

Department of Chemistry, University of Wales Cardiff, P.O. Box 912, Park Place, Cardiff CF1 3TB, U.K.

Kenneth I. Hardcastle

Department of Chemistry, Emory University, Atlanta, Georgia 30322

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The 46-electron quinoline triosmium clusters $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_9\text{H}_5(\text{R})\text{N})$ (**6**, R = 4-CH₃; **7**, R = H) react with excess CH₂N₂ at 0 to 25 °C to give $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CHC}_9\text{H}_5(\text{R})\text{N})$ (**10**, R = 4-CH₃; **11**, R = H), formed by insertion and subsequent C–H oxidative addition of a CH₂ moiety into the ring C(8)–Os bond. In contrast, the related 46-electron quinoxaline compound $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_5\text{N}_2)$ (**8**) reacts with excess CH₂N₂ at 0 to 25 °C to give $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CHC}_8\text{H}_4(5\text{-CH}_3)\text{N}_2)$ (**12**), where two CH₂ groups have inserted into the C(5)–H bond as well as the C(8)–Os bond, and $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CHC}_8\text{H}_5\text{N}_2)$ (**13**), the analogue of **11**. The 5-methylquinoxaline compound $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_4(5\text{-CH}_3)\text{N}_2)$ (**9**) reacts with diazomethane at 0 to 25 °C to give **12** and $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_4(5\text{-CH}_3)\text{N}_2)\text{-}(\mu\text{-CH}_2)(\text{CH}_3)$ (**14**), containing an edge-bridging methylene group and a σ -bound methyl group. Thermolysis of **10** and **11** at 98 °C yields $(\mu\text{-H})_3\text{Os}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-C}(\text{C}_9\text{H}_5)(\text{R})\text{N})$ (**15**, R = 4-CH₃; **16**, R = H), $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}(\text{C}_9\text{H}_5)(\text{R})\text{N})$ (**17**, R = 4-CH₃; **18**, R = H), and $(\mu\text{-H})\text{Os}_4(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{-C}(\text{C}_9\text{H}_5)(\text{R})\text{N})$ (**19**, R = 4-CH₃; **20**, R = H). The trihydrides **15** and **16** are formed by a further C–H activation of the coordinated methyldiene group of **10** and **11**, respectively. Thermolysis of **10** and **11** in the presence of H₂ at 1 atm at 80 °C gives **15** and **16** in high yields. The solid-state structure of **17** reveals that the methyldiene carbon atom has a significant bonding interaction with the osmium atom coordinated to nitrogen. Thermolysis of **12** and **13** at 98 °C gives $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CC}_8\text{H}_4(\text{R})\text{N}_2)$ (**21**, R = 5-CH₃; **22**, R = H), whereas a similar thermolysis in the presence of H₂ (1 atm) at 80 °C gives $(\mu\text{-H})_3\text{Os}_3(\text{CO})_8\text{-}(\mu_3\text{-}\eta^2\text{-CC}_8\text{H}_4(5\text{-CH}_3)\text{N}_2)$ (**23**, R = 5-CH₃; **24**, R = H). The compounds **12**, **13**, **23**, and **24** all show one-electron reversible reductions, and the reduction potentials are similar to previously studied quinoxaline clusters. DFT calculations show that most of the spin density is confined to the heterocyclic ligand, and this explains the similarity between the observed reduction potentials for the products with different bonding modes to cluster but containing the same heterocycle. The qualitative correlation between the calculated natural charges and the distribution of unpaired spin densities in **12** and **13** corroborate this conclusion. The molecular structures of **10**, **12**, **13**, **17**, and **20** have been determined by single-crystal X-ray diffraction studies.

Introduction

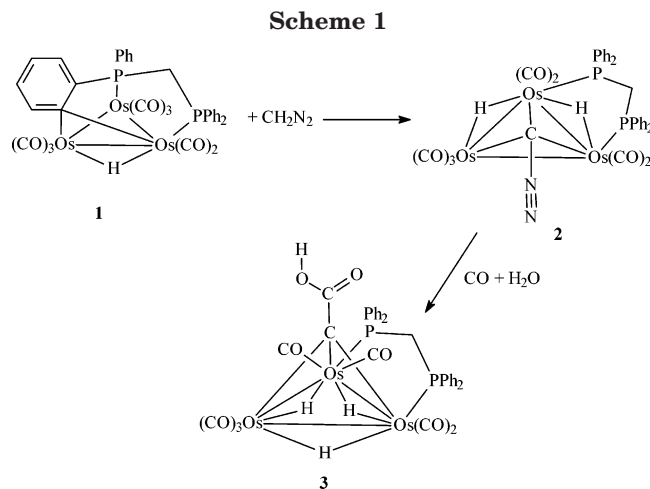
Organic diazo compounds are highly reactive substrates having several reaction centers in one molecule.^{1,2} This makes them promising reagents for the synthesis of functionalized organometallic complexes. Reactions of diazoalkanes with transition metal complexes often result in the formation of carbene complexes

with concurrent liberation of N₂.^{3,4} This is a key reaction in catalytic processes such as carbene insertion into C–H bonds, cyclopropanation of olefins, Fischer–Trop-

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sch synthesis, and alkyne isomerization.⁵ The reactions of diazoalkanes with both coordinatively unsaturated and saturated trimetallic complexes of osmium, ruthenium, and iron have been investigated by several groups and have been found to give many interesting compounds with various coordination modes.^{6–21} For example, the saturated triosmium acetonitrile compound $\text{Os}_3(\text{CO})_{11}(\text{MeCN})$ reacts with CH_2N_2 to yield $\text{Os}_3(\mu\text{-CO})(\text{CO})_{10}(\mu\text{-CH}_2)$,^{6,7} whereas the coordinatively unsaturated cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ gives $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)$, which exists in equilibrium with $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_3)$.⁸ The parent iron compound, $\text{Fe}_3(\text{CO})_{12}$, reacts with diphenyldiazomethane to give $\text{Fe}_3(\text{CO})_9(\text{NNCPh}_2)_2$, containing the $\mu_3\text{-}\eta^1$ -diazoalkane ligand.⁹ On the contrary, the ruthenium analogue, $\text{Ru}_3(\text{CO})_{12}$, reacts with diazomethane to give $\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}(\mu\text{-CH}_2)$, which rearranges to the hydrido ketenylidene compound $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu\text{-CCO})$ at 45 °C. The latter reacts further with CH_2N_2 to give the C–C coupling product, $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\text{CCH}_2)$.¹⁰ The dppm-substituted compound, $\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})$, reacts with CH_2N_2 to afford the μ -methylene compound, $\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^3\text{-C}(\text{O})\text{CH}_2)(\mu\text{-CH}_2)(\mu\text{-dppm})$, which readily reacts with CO to give the dinuclear complex, $\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^4\text{-CH}_2\text{C}(\text{O})\text{CH}_2)(\mu\text{-dppm})$.¹¹ There have been several reports on the coupling of μ_3 -imidoyls¹⁹ or μ_3 -alkynes^{14,18} with μ -methylenes or η^1 -carbenes²² in trinuclear clusters of osmium and ruthenium. For example, the μ_3 -imidoyl clusters $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}=\text{NCH}_2\text{CH}_2\text{CH}_2\text{-})$ react with CH_2N_2 to afford $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CH}=\text{C}=\text{NCH}_2\text{CH}_2\text{CH}_2\text{-})$, in which a methylene fragment has inserted into the



carbon–metal σ -bond of the imidoyl ligand and undergone a C–H oxidative addition.¹⁹

We have been investigating the reactivity of a novel class of electron-deficient complexes of the general formula $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-L-H})$ (L = benzoheterocycle) where the electron deficiency arises from the presence of a three-center two-electron bond β to the coordinated pyridinyl nitrogen.²³ The reactions of these complexes with neutral nucleophiles such as phosphines and amines result in ligand addition at the metal core,^{23a,b} while with anionic nucleophiles such as hydride or carbanions nucleophilic addition is at the carbocyclic ring.^{23c,24} Most recently, we have demonstrated that despite their structural similarities, the reactivity of these complexes is sensitive to the nature of the heterocyclic ring.^{24,25}

In a preliminary communication we reported²⁰ that the coordinatively unsaturated compound $(\mu\text{-H})\text{Os}_3(\text{CO})_8(\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4)$ (**1**) reacts with CH_2N_2 to give the novel compound $(\mu\text{-H})_2\text{Os}_3(\text{CO})_7(\mu_3\text{-CN}_2)(\mu\text{-dppm})$ (**2**), which reacts with CO and H_2O to give $(\mu\text{-H})_3\text{Os}_3(\text{CO})_7(\mu_3\text{-CCOOH})(\mu\text{-dppm})$ (**3**) (Scheme 1). We have also reported²¹ that in the case of the unsaturated cluster $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_7\text{H}_3(2\text{-CH}_3)\text{NS})$ (**4**) the reaction with diazomethane proceeds in a completely different way to give $\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^2\text{-C}_7\text{H}_3(2\text{-CH}_3)\text{NS})(\mu\text{-CH}_2)\text{CH}_3$ (**5**), containing an edge-bridging methylene group and

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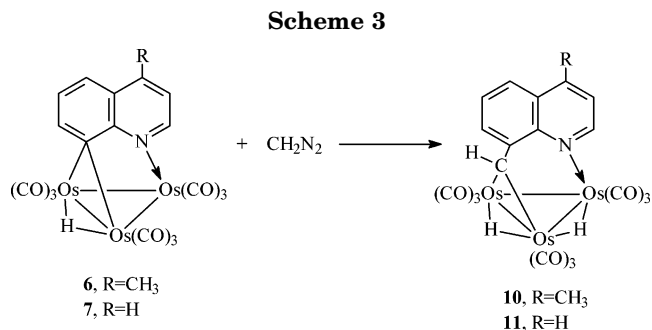
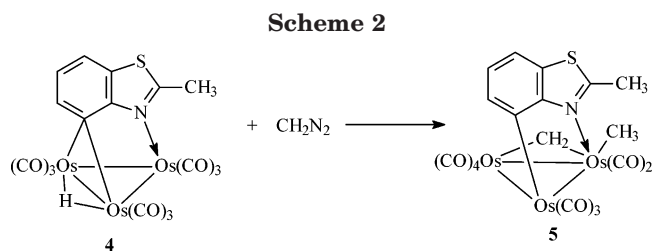
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a σ -bound methyl group²¹ (Scheme 2). The above observations suggested remarkable sensitivity of the regiochemistry of methylene addition toward the structure of the heterocycle and prompted us to examine the reactivity of the related 46-electron triosmium compounds (μ -H)Os₃(CO)₉(μ_3 - η^2 -C₉H₅(R)N) (**6**, R = 4-CH₃; **7**, R = H) and (μ -H)Os₃(CO)₉(μ_3 - η^2 -C₈H₄(R)N₂) (**8**, R = H; **9**, R = 5-CH₃) with diazomethane. We were particularly interested to see how the reactivity of these aza and diaza heterocycles with diazomethane compared with the previously reported thioaza heterocycles. We report here an examination of these reactions as well as an investigation of the electrochemical properties of the products in an attempt to gain a further understanding of how changes in the bonding mode of a complex organic molecule to a trimetallic core impacts its electron acceptor properties and the stability of the resulting radical anion. For the radical anions that were found to be stable on the cyclic voltammetry (CV) time scale we have performed *ab initio* density functional theory (DFT) calculations in order to elucidate the electron distribution in these systems.

Results and Discussion

In sharp contrast to the reaction of the 2-methylbenzothiazole triosmium compound **4** with CH₂N₂, which afforded the μ -methylidene σ -methyl compound **5**,²¹ the reactions of the electron-deficient clusters **6** and **7** with excess CH₂N₂ at 0 to 25 °C give (μ -H)₂Os₃(CO)₉(μ_3 - η^2 -CHC₉H₅(R)N) (**10**, R = 4-CH₃; **11**, R = H) in 80 and 85% yields, respectively (Scheme 3).

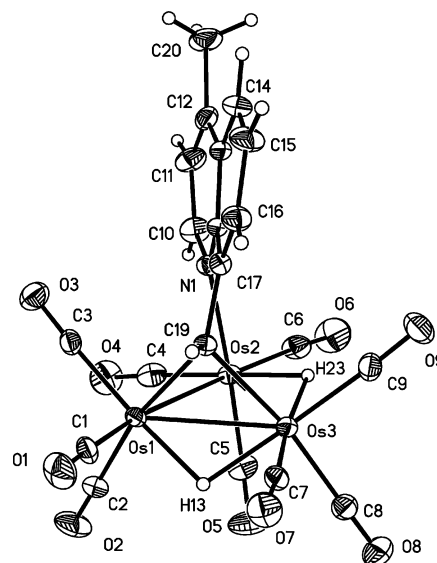
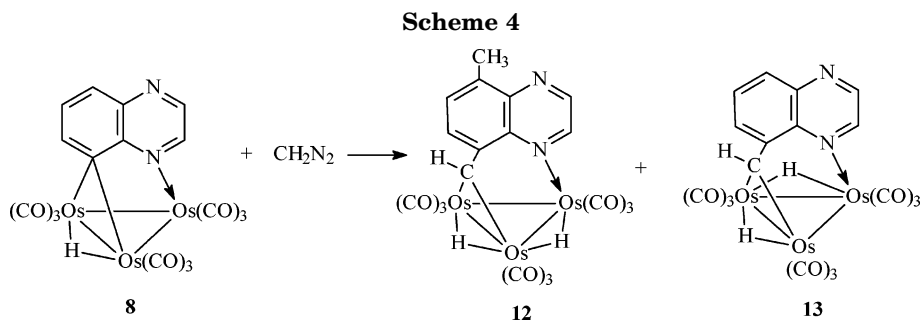


Figure 1. Molecular geometry of (μ -H)₂Os₃(CO)₉(μ_3 - η^2 -CHC₉H₅(4-CH₃)N), **10**, showing the calculated position of the hydrides. Thermal ellipsoids are drawn at the 50% probability level.

These compounds are presumably formed by insertion of the methylene group into the metal–carbon σ -bond of the quinoline ligands followed by C–H oxidative addition. In contrast, addition of excess ethereal diazomethane to a dichloromethane solution of the quinoline unsaturated compound **8** at 0 to 25 °C affords two new compounds, (μ -H)₂Os₃(CO)₉(μ_3 - η^2 -CHC₈H₄(5-CH₃)N₂) (**12**) and (μ -H)₂Os₃(CO)₉(μ_3 - η^2 -CHC₈H₅N₂) (**13**), in 20 and 35% yields, respectively (Scheme 4). All the compounds have been characterized by spectroscopic data together with single-crystal X-ray diffraction analyses for **10**, **12**, and **13**.

The solid-state structures of **10** and **12** are shown in Figures 1 and 2, respectively, crystal data are given in Table 1, and selected bond distances and angles are summarized in Tables 2 and 3, respectively. The basic cores of both the molecules are the same, having a triangular metal framework of osmium atoms with three distinctly different osmium–osmium bond lengths (Os(1)–Os(2) = 2.7919(4), Os(2)–Os(3) = 2.9913(4), and Os(1)–Os(3) = 2.8323(4) Å for **10** and Os(1)–Os(2) = 2.9959(7), Os(2)–Os(3) = 2.8070(7), and Os(1)–Os(3) = 2.8283(7) Å for **12**) and nine terminal carbonyl ligands, three on each metal atom. The hydride ligands for both **10** and **12** were located using the program WinGX.²⁶ In case of **10**, the hydride ligand H(23) is located at the elongated Os(2)–Os(3) edge, which is also bridged by the heterocyclic ligand, μ_3 - η^2 -CHC₉H₅(4-CH₃)N, while the other hydride H(13) shares the same shortest



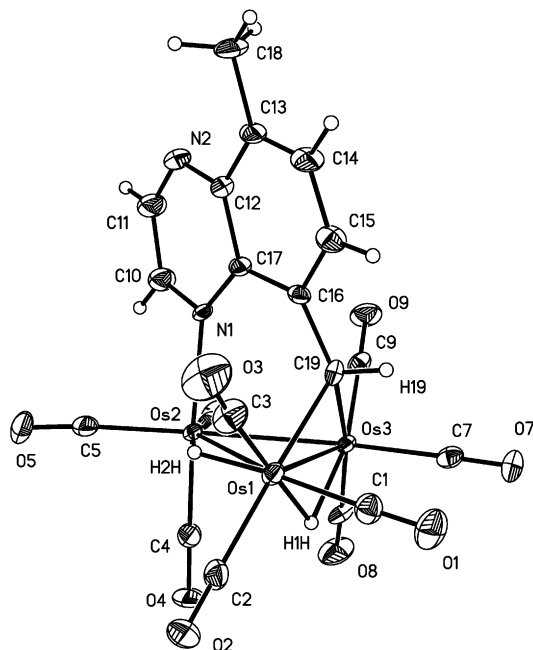


Figure 2. Molecular geometry of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CHC}_8\text{H}_4(5\text{-CH}_3)\text{N}_2)$, **12**, showing the calculated position of the hydrides. Thermal ellipsoids are drawn at the 50% probability level.

$\text{Os}(1)\text{-Os}(2)$ edge as the alkylidene carbon and is well-tucked well below the Os_3 triangle. Similarly, for **12**, the hydrides are found to bridge the $\text{Os}(1)\text{-Os}(2)$ and $\text{Os}(1)\text{-Os}(3)$ edges of the Os triangle in which the $\text{Os}(1)\text{-Os}(2)$ edge is bridged by the N atom of the heterocyclic ligand, $\mu_3\text{-}\eta^2\text{-CHC}_8\text{H}_4(5\text{-CH}_3)\text{N}_2$, while the $\text{Os}(1)\text{-Os}(3)$ edge is bridged by the methylidene carbon of the ligand. These observations are analogous to that reported for $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CHC}=\text{NCH}_2\text{CH}_2\text{CH}_2\text{-})$, in which metal-metal bonds bridged by heterocyclic and hydride ligands are significantly longer than the other bridging metal-metal bonds.¹⁹ The bridging positions of the hydrides in **10** are further supported by the orientation of carbonyl groups CO(3), CO(9), CO(4), and CO(7), which were essentially *trans* to the metal hydrogen bond vectors, maintaining approximately octahedral geometry. The μ -alkylidene carbon bridges Os(1) and Os(3) almost symmetrically ($\text{Os}(1)\text{-C}(19) = 2.159(4)$, $\text{Os}(3)\text{-C}(19) = 2.151(4)$ Å for **10** and $\text{Os}(1)\text{-C}(19) = 2.158(5)$, $\text{Os}(3)\text{-C}(19) = 2.151(5)$ Å), and the nitrogen is coordinated to Os(2) with $\text{Os}(2)\text{-N}(1)$ bond lengths of 2.203(4) Å for **10** and 2.191(4) Å for **12**, which are significantly longer than the corresponding bond length in **6** (2.13(2) Å)^{23a} but is comparable to the Os-N bond length in $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}1,8\text{-}\eta^2\text{-C}_9\text{H}_6\text{N})$.²⁷ An intriguing feature of **12** is the presence of the 5-methyl group on the quinoxaline ring that most probably has been formed by insertion of a second methylene group into the C(5)-H bond of the quinoxaline ligand. Both clusters **10** and **12** contain 48 valence electrons, as expected for an electron-precise trinuclear cluster containing three metal-metal bonds, and each metal atom achieves an 18-electron configuration. The spectroscopic data for **10** and **12** are in

accord with the solid-state structure, and the spectroscopic data for **11** indicate that it is a direct analogue of **10** and **12**.

The solid-state structure of **13** is shown in Figure 3, crystal data are given in Table 1, and selected bond distances and angles are collected in Table 4. Compound **13** crystallizes in the triclinic space group with two crystallographically independent and enantiomeric molecules in the unit cell. Each molecule consists of an Os_3 triangle with three different metal-metal bonds and nine terminal carbonyl ligands, three bonded to each osmium atom. The molecules differ in the relative location of the cluster-bound hydride ligands. In molecule 1 (Figure 3), one of the hydrides bridges the unbridged $\text{Os}(3)\text{-Os}(2)$ edge, which is supported by the observation that this edge is significantly elongated (3.0059(7) Å) compared to the methylidene carbon-bridged $\text{Os}(3)\text{-Os}(1)$ edge (2.8365(7) Å). This edge is also spanned by the other hydride ligand. The heterocyclic ligand bridges the $\text{Os}(2)\text{-Os}(1)$ edge (2.7986(7) Å). However, in molecule 2, one of the hydrides bridges the $\text{Os}(2)\text{-Os}(1)$ edge, which is simultaneously bridged by the heterocyclic ligand and is also consistent with substantially elongated bond (2.9981(7) Å) compared to the other two Os-Os distances ($\text{Os}(3)\text{-Os}(1) = 2.8365(7)$, $\text{Os}(2)\text{-Os}(3) = 2.8013(7)$ Å). As in molecule 1, the remaining hydride bridges the $\text{Os}(3)\text{-Os}(1)$ edge, which is simultaneously bridged by the methylidene carbon atom, and the $\text{Os}(3)\text{-Os}(1)$ distances in the two molecules are exactly the same (2.8365(7) Å in molecule 1 and 2.8365(7) Å in molecule 2). The dimensions of heterocyclic ligands in the two molecules are similar. Thus C(16)-N(2), C(17)-N(1), C(13)-C(14), and C(11)-C(12) bond distances in molecule 1 are 1.32(2), 1.357(17), 1.34(2), and 1.401(18) Å, respectively, while the corresponding distances in molecule 2 are 1.30(3), 1.321(2), 1.31(3), and 1.360(18) Å, respectively. The spectroscopic data of **13** are consistent with the solid-state structures.

The unusual formation of **12** from the above reaction was further substantiated by synthesizing the 5-methyl quinoxaline electron-deficient compound $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_4(5\text{-CH}_3)\text{N})$ (**9**) followed by reaction with CH_2N_2 . The reaction of **9** with excess diazomethane gives **12** and $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_4(5\text{-CH}_3)\text{N}_2)(\mu\text{-CH}_2\text{-}(\text{CH}_3)$ (**14**) (Scheme 5) in 49 and 11% yields, respectively. Compound **14** has been characterized by elemental analysis and infrared and ^1H NMR spectroscopic data. The formation of **14** can be viewed as resulting from the insertion of a methylene group into one of the metal-metal bonds followed by the interaction of the second methylene with the cluster-bound bridging hydride. The reverse sequence, formation of a methyl group followed by reaction with a second methylene, is also possible. To our knowledge compound **14** provides the second example of a triosmium cluster containing both bridging methylene and σ -bonded methyl groups, the first being **5**.²¹

Thermolysis of **10** and **11** at 98 °C affords two trinuclear compounds, $(\mu\text{-H})_3\text{Os}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-C}(\text{C}_9\text{H}_5)(\text{R})\text{N})$ (**15**, R = 4-CH₃, 17%; **16**, R = H, 15%) and $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}(\text{C}_9\text{H}_5)(\text{R})\text{N})$ (**17**, R = 4-CH₃, 30%; **18**, R = H, 36%), and one tetranuclear compound, $(\mu\text{-H})\text{Os}_4(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{-C}(\text{C}_9\text{H}_5)(\text{R})\text{N})$ (**19**, R = 4-CH₃, 15%; **20**,

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Table 1. Crystal Data and Structure Refinement for **10**, **12**, **13**, **17**, and **20**

	10	12	13
empirical formula	C ₂₀ H ₁₁ NO ₉ Os ₃	C ₁₉ H ₁₀ N ₂ O ₉ Os ₃	C ₁₈ H ₈ N ₂ O ₉ Os ₃
fw	979.90	980.89	966.88
temperature (K)	173(2)	173(2)	150(2)
wavelength Å	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	triclinic
space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1
unit cell dimens			
<i>a</i> (Å)	9.6788(12)	9.487(2)	11.2089(4)
<i>b</i> (Å)	10.4164(14)	10.269(3)	12.7527(5)
<i>c</i> (Å)	11.5639(15)	11.790(3)	15.4816(7)
α (deg)	100.764(3)	98.686(7)	85.582(2)
β (deg)	90.929(3)	90.684(9)	89.192(2)
γ (deg)	100.978(3)	99.636(7)	84.136(2)
<i>V</i> (Å ³)	1122.8(3)	1118.6(5)	2194.83(15)
<i>Z</i>	2	2	4
density _{calc} (mg/m ³)	2.899	2.912	2.923
abs coeff (cm ⁻¹)	16.985	17.049	17.376
<i>F</i> (000)	876	876	1710
cryst size (mm)	0.22 × 0.20 × 0.16	0.40 × 0.36 × 0.22	0.25 × 0.22 × 0.18
θ range for data	1.80 to 28.33	1.75 to 28.29	2.16 to 26.38
collection (deg)			
limiting indices	-12 ≤ <i>h</i> ≤ 12 -13 ≤ <i>k</i> ≤ 13 -15 ≤ <i>l</i> ≤ 15	-12 ≤ <i>h</i> ≤ 12 -13 ≤ <i>k</i> ≤ 13 -15 ≤ <i>l</i> ≤ 15	-14 ≤ <i>h</i> ≤ 14 -15 ≤ <i>k</i> ≤ 15 -19 ≤ <i>l</i> ≤ 19
no. of reflns collected	11 751	15 327	22 944
no. of indep reflns	5571 [<i>R</i> _{int} = 0.025]	5533 [<i>R</i> _{int} = 0.0418]	8855 [<i>R</i> _{int} = 0.1045]
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
no. of data/restraints/params	5571/0/299	5533/0/299	8855/0/577
goodness-of-fit on <i>F</i> ²	1.035	1.024	1.014
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0243, <i>wR</i> ₂ = 0.0578	<i>R</i> ₁ = 0.0265, <i>wR</i> ₂ = 0.0674	<i>R</i> ₁ = 0.0566, <i>wR</i> ₂ = 0.1362
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0270, <i>wR</i> ₂ = 0.0589	<i>R</i> ₁ = 0.0292, <i>wR</i> ₂ = 0.0688	<i>R</i> ₁ = 0.0750, <i>wR</i> ₂ = 0.1479
largest diff peak and hole (e Å ⁻³)	1.693 and -2.272	1.637 and -2.324	3.362 and -3.901
	17		20
empirical formula	C ₂₀ H ₉ NO ₉ Os ₃	C ₂₁ H ₇ NO ₁₁ Os ₄	
fw	977.90	1210.07	
temperature (K)	150(2)	293(2)	
wavelength Å	0.71069	0.71073	
cryst syst	monoclinic	monoclinic	
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	
unit cell dimens			
<i>a</i> (Å)	15.731(4)	12.4821(2)	
<i>b</i> (Å)	8.900(2)	12.4363(2)	
<i>c</i> (Å)	16.263(3)	16.2496(2)	
α (deg)			
β (deg)	100.16(2)	104.0791(8)	
γ (deg)			
volume (Å ³)	2241.2(9)	2446.67(6)	
<i>Z</i>	4	4	
density _{calc} (mg/m ³)	2.901	3.282	
abs coefficient (cm ⁻¹)	17.017	20.767	
<i>F</i> (000)	1748	2124	
cryst size (mm)	0.25 × 0.22 × 0.15	0.22 × 0.15 × 0.12	
θ range for data	1.98 to 25.06	1.68 to 27.51	
collection (deg)			
limiting indices	-10 ≤ <i>h</i> ≤ 17 -8 ≤ <i>k</i> ≤ 10 -18 ≤ <i>l</i> ≤ 18	-16 ≤ <i>h</i> ≤ 16 -16 ≤ <i>k</i> ≤ 16 -21 ≤ <i>l</i> ≤ 21	
no. of reflns collected	8001	54 059	
no. of indep reflns	3355 [<i>R</i> _{int} = 0.0684]	5626 [<i>R</i> _{int} = 0.0914]	
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	
no. of data/restraints/params	3355/48/299	5626/0/334	
goodness-of-fit on <i>F</i> ²	0.962	1.116	
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0332, <i>wR</i> ₂ = 0.0845	<i>R</i> ₁ = 0.0312, <i>wR</i> ₂ = 0.0729	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0446, <i>wR</i> ₂ = 0.0863	<i>R</i> ₁ = 0.0462, <i>wR</i> ₂ = 0.082	
largest diff peak and hole (e Å ⁻³)	1.542 and -1.620	1.584 and -3.644	

R = H, 18%), in addition to a trace amount of the parent compounds **6** and **7**, respectively (Scheme 6).

The structural assignments of **15** and **16** have been made on the basis of spectroscopic analysis (IR, NMR, and mass) and by comparing the spectroscopic data with those reported for (μ -H)₃Os₃(CO)₈(μ_3 - η^2 -CC₇H₃(Me)NS),

whose structure has been determined by single-crystal X-ray diffraction study.²¹ The carbonyl stretching frequencies of **15** and **16** are very similar to those of (μ -H)₃Os₃(CO)₈(μ_3 - η^2 -CHC₇H₃(Me)NS), indicating that they have similar structures.²¹ The aromatic region of the ¹H NMR spectrum of **15** shows three doublets at δ

Table 2. Selected Bond Distances (Å) and Angles (deg) for 10

Bond Distances			
Os(1)–Os(2)	2.7919(4)	C(11)–C(12)	1.362(8)
Os(2)–Os(3)	2.9913(4)	C(12)–C(13)	1.442(7)
Os(1)–Os(3)	2.8323(4)	C(12)–C(20)	1.515(7)
Os(3)–C(19)	2.151(4)	C(13)–C(14)	1.418(7)
Os(1)–C(19)	2.159(4)	C(13)–C(18)	1.428(6)
C(14)–C(15)	1.354(7)	C(18)–N(1)	1.397(6)
C(15)–C(16)	1.393(7)	Os(2)–N(1)	2.203(4)
C(16)–C(17)	1.392(6)	C(10)–C(11)	1.397(7)
C(17)–C(18)	1.438(6)	C(10)–N(1)	1.337(6)
C(17)–C(19)	1.495(6)	C(10)–C(11)	1.397(7)

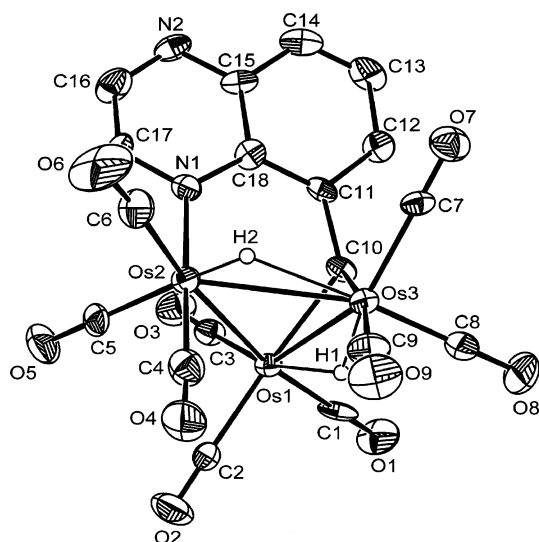
Bond Angles			
Os(2)–Os(1)–Os(3)	64.258(8)	C(19)–Os(1)–Os(3)	48.80(11)
Os(1)–Os(2)–Os(3)	58.526(11)	C(19)–Os(3)–Os(1)	49.03(12)
Os(1)–Os(3)–Os(2)	57.216(7)	N(1)–Os(2)–Os(1)	88.72(10)
C(19)–Os(1)–Os(2)	81.06(12)	Os(1)–C(19)–Os(3)	82.17(15)
Os(3)–Os(2)–C(6)	115.38(16)	Os(3)–Os(1)–C(2)	119.61(15)
Os(2)–Os(3)–C(9)	110.18(14)	Os(1)–Os(3)–C(7)	95.39(14)

Table 3. Selected Bond Distances (Å) and Angles (deg) for 12

Bond Distances			
Os(1)–Os(2)	2.9959(7)	C(12)–C(17)	1.449(7)
Os(2)–Os(3)	2.8070(7)	C(13)–C(14)	1.359(8)
Os(1)–Os(3)	2.8283(7)	C(13)–C(18)	1.515(7)
Os(1)–C(19)	2.158(5)	C(14)–C(15)	1.401(7)
Os(3)–C(19)	2.151(5)	C(15)–C(16)	1.401(7)
Os(2)–N(1)	2.191(4)	C(16)–C(17)	1.438(7)
C(10)–C(11)	1.392(8)	C(16)–C(19)	1.489(6)
C(11)–N(2)	1.291(8)	C(17)–N(1)	1.394(6)
C(12)–N(2)	1.359(7)	C(12)–C(13)	1.425(7)
C(10)–N(1)	1.331(7)		

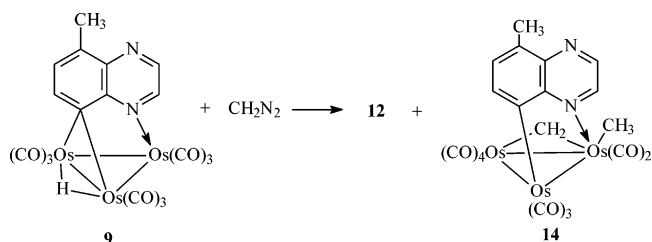
Bond Angles			
Os(3)–Os(2)–Os(1)	58.230(18)	C(1)–Os(1)–Os(3)	94.41(17)
Os(2)–Os(3)–Os(1)	64.229(12)	C(8)–Os(3)–Os(1)	120.10(17)
Os(3)–Os(1)–Os(2)	57.541(12)	C(3)–Os(1)–Os(2)	111.23(19)
C(5)–Os(2)–Os(1)	114.02(19)	C(19)–Os(3)–Os(1)	49.09(13)
N(1)–Os(2)–Os(3)	89.56(11)	C(19)–Os(1)–Os(3)	44.88(13)
		Os(3)–C(19)–Os(1)	82.03(17)

8.96, 7.82, and 7.08, a triplet at δ 7.52, and a doublet of doublets at δ 7.25, each integrating for one hydrogen atom, while **16** gives two doublets of doublets at δ 7.12 and 8.14, a multiplet at δ 7.48, a triplet at δ 7.30, and a doublet at δ 9.12 in a relative intensity of 1:1:2:1:1. The high-field triplets at δ –17.11, –18.08, and –18.81

**Figure 3.** ORTEP drawing of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CHC}_8\text{H}_5\text{N}_2)$, **13** (molecule A). Thermal ellipsoids are drawn at the 35% probability level.**Table 4. Selected Bond Distances (Å) and Angles (deg) for 13**

	Bond Distances	
	molecule 1	molecule 2
Os(1)–Os(2)	2.7986(7)	2.9981(7)
Os(2)–Os(3)	3.0059(7)	2.8013(7)
Os(1)–Os(3)	2.8366(7)	2.8365(7)
Os(2)–N(1)	2.189(11)	2.214(10)
Os(1)–C(10)	2.146(12)	2.176(12)
Os(3)–C(10)	2.179(11)	2.152(12)
N(1)–C(17)	1.357(17)	1.321(17)
N(2)–C(16)	1.32(2)	1.30(3)
N(1)–C(18)	1.390(17)	1.392(16)
N(2)–C(15)	1.352(17)	1.33(2)
C(10)–C(11)	1.498(17)	1.502(16)
C(11)–C(18)	1.422(19)	1.421(18)
C(13)–C(14)	1.34(2)	1.31(3)
C(15)–C(18)	1.456(18)	1.444(17)
C(11)–C(12)	1.404(18)	1.360(18)
C(12)–C(13)	1.41(2)	1.39(2)
C(14)–C(15)	1.42(2)	1.42(3)
C(16)–C(17)	1.34(2)	1.38(2)

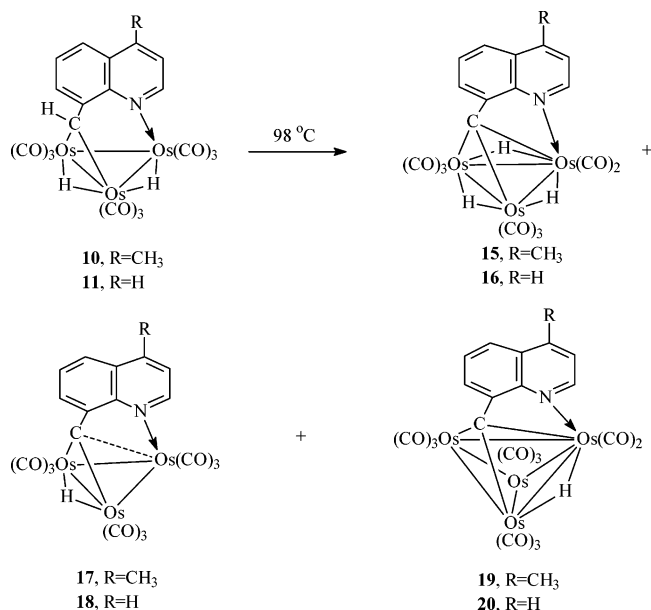
Bond Angles		
	molecule 1	molecule 2
Os(1)–Os(2)–Os(3)	58.378(17)	58.446(17)
Os(2)–Os(1)–Os(3)	64.468(18)	57.306(17)
Os(1)–Os(3)–Os(2)	57.153(17)	64.248(18)
C(3)–Os(1)–Os(2)	93.6(5)	108.9(4)
C(2)–Os(1)–Os(2)	92.5(4)	96.3(5)
C(2)–Os(1)–Os(3)	120.3(4)	122.0(5)
N(1)–Os(2)–Os(1)	88.3(3)	97.5(3)
Os(1)–C(10)–Os(3)	82.0(4)	81.9(4)
C(1)–Os(1)–Os(2)	168.3(5)	154.1(4)
C(10)–Os(1)–Os(2)	82.6(3)	77.6(3)
C(1)–Os(1)–Os(3)	103.9(5)	97.0(4)
C(10)–Os(1)–Os(3)	49.5(3)	48.7(3)
C(5)–Os(2)–N(1)	88.8(5)	90.4(5)
C(6)–Os(2)–Os(1)	172.9(5)	144.4(5)
C(10)–Os(3)–Os(1)	48.5(3)	49.3(3)
C(10)–Os(3)–Os(2)	77.2(4)	82.6(3)

Scheme 5

($J = 2.2$ Hz) for **15** and δ –16.98, –18.10, and –18.65 ($J = 2.0$ Hz) for **16**, each integrating for one hydrogen atom, are consistent with the presence of three non-equivalent bridging hydride ligands. All the spectroscopic features of **15** and **16** are very similar to those of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-CHC}_7\text{H}_3(\text{Me})\text{NS})$.²¹ The mass spectra contain molecular ion peaks at m/z 951 for **15** and 937 for **16**. The formation of compounds **15** and **16** from **10** and **11** involves activation of the methylidene C–H bond followed by loss of one carbonyl ligand.

Compounds **17** and **18** have been characterized by elemental analysis, infrared, ¹H NMR, and mass spectroscopic data together with a single-crystal X-ray structure analysis for **17**. The molecular structure of **17** is depicted in Figure 4, crystal data are given in Table 1, and selected bond distances and angles are summarized in Table 5. The structure is based upon a triangular array of osmium atoms in which the

Scheme 6

Table 5. Selected Bond Distances (Å) and Angles (deg) for **17**

Bond Distances			
Os(1)–Os(2)	2.9077(9)	C(15)–C(19)	1.431(18)
Os(2)–Os(3)	2.8484(11)	C(16)–C(20)	1.505(18)
Os(1)–Os(3)	2.8230(10)	C(10)–C(11)	1.462(18)
Os(1)–C(10)	2.004(13)	C(11)–C(19)	1.44(2)
Os(2)–C(10)	2.038(13)	C(13)–C(14)	1.38(2)
Os(3)–C(10)	2.222(13)	C(15)–C(16)	1.399(19)
Os(3)–N(1)	2.199(10)	C(16)–C(17)	1.308(18)
C(11)–C(12)	1.357(17)	C(17)–C(18)	1.411(19)
C(12)–C(13)	1.407(18)	N(1)–C(19)	1.363(16)
C(14)–C(15)	1.452(18)	N(1)–C(18)	1.280(18)
Bond Angles			
Os(3)–Os(1)–Os(2)	59.59(2)	C(10)–Os(1)–Os(3)	51.5(4)
Os(3)–Os(2)–Os(1)	58.72(2)	C(10)–Os(3)–Os(2)	45.3(3)
Os(1)–Os(3)–Os(2)	61.68(3)	Os(1)–C(10)–Os(2)	92.0(5)
C(10)–Os(2)–Os(1)	43.5(4)	Os(1)–C(10)–Os(3)	83.6(5)
C(10)–Os(3)–Os(1)	44.9(3)	Os(2)–C(10)–Os(3)	83.8(5)
C(1)–Os(1)–Os(2)	117.6(4)	C(4)–Os(2)–Os(1)	117.9(4)

hydride-bridged Os(1)–Os(2) distance of 2.9077(9) Å is significantly longer than the other two Os–Os edges

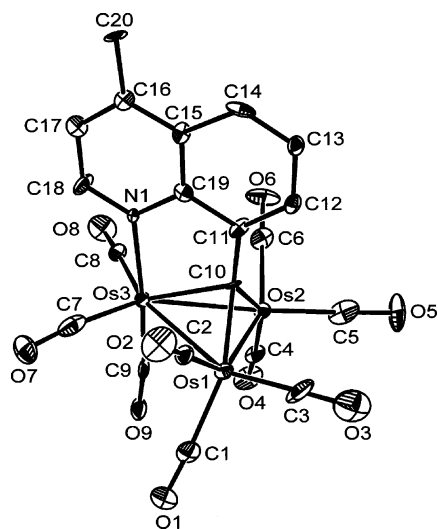


Figure 4. ORTEP drawing of $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}(\text{C}_9\text{H}_5)\text{-4-CH}_3\text{N})$, **17**. Thermal ellipsoids are drawn at the 50% probability level.

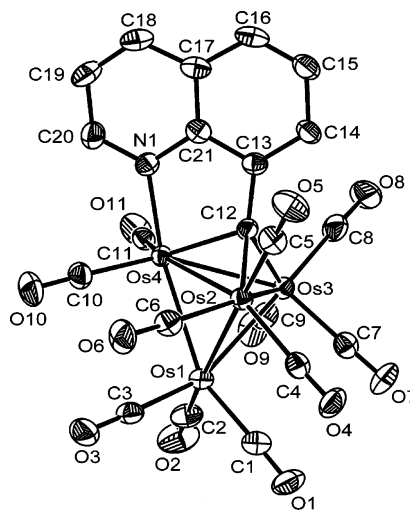


Figure 5. ORTEP drawing of $(\mu\text{-H})\text{Os}_4(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{-C}(\text{C}_9\text{H}_6)\text{N})$, **20**. Thermal ellipsoids are drawn at the 35% probability level.

(Os(1)–Os(3) = 2.8230(10) and Os(2)–Os(3) = 2.8484(11) Å). The bridging hydride in **17** was not located crystallographically but geometrically assigned to bridge the Os(1)–Os(2) edge according to the lengthening of the metal–metal vector. The most interesting feature of the structure of **17** is that the bridging heterocyclic ligand lies over the triosmium plane as reported for $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CR})$ (R = H, Ph, CH₂CHMe₂).^{28–30} In the complex $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CH})$ the CH ligand is closer to μ_3 and with the three Os–C distances being 2.35(1), 2.01(1), and 2.00(1) Å. In **17** the corresponding osmium–carbon distances are 2.222(13), 2.004(13), and 2.039(13) Å. These distances are indicative of some direct interaction between Os(3) and C(10), and hence this bonding mode may be termed as “semi-triply” bridging. Two additional electrons are donated by the N atom of the heterocyclic ligand to Os(3) (Os(3)–N(1) = 2.199(10) Å), indicating a significant and direct bonding interaction between these two atoms. The spectroscopic data of **17** are consistent with its crystal structure. The close similarities of the IR and ¹H NMR spectra of **17** and **18** indicate that they have analogous structures.

The change in metal nuclearity associated with the formation of **19** and **20** indicates that cluster fragmentation and reaggregation processes are occurring. Crystals of **19** suitable for X-ray diffraction analysis could not be obtained, but suitable crystals of **20** have been obtained. The molecular structure of **20** is depicted in Figure 5, crystal data are given in Table 1, and selected bond lengths and angles are given in Table 6. The metal framework of **20** consists of a distorted Os₄ tetrahedron with Os–Os distances of Os(1)–Os(2) = 2.8199(4), Os(1)–Os(3) = 2.8148(4), Os(1)–Os(4) = 2.9011(4), Os(2)–Os(4) = 2.8549(4), Os(2)–Os(3) = 2.8435(4), and Os(3)–Os(4) = 2.8616(4) Å. The long Os(1)–Os(4) bond of 2.9011(4) Å is believed to contain the bridging hydride ligand which resonates at δ –21.50 but was not located crystallographically. This is sup-

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Table 6. Selected Bond Distances (Å) and Angles (deg) for **20**

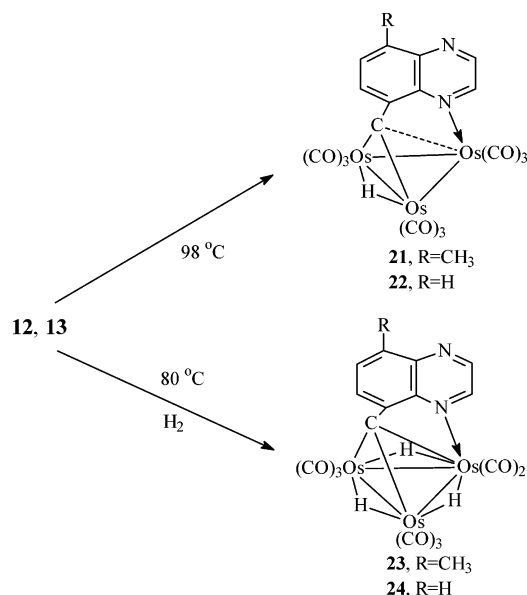
Bond Distances			
Os(1)–Os(2)	2.8199(4)	C(18)–C(19)	1.363(14)
Os(2)–Os(3)	2.8435(4)	C(13)–C(14)	1.373(10)
Os(3)–Os(4)	2.8616(4)	C(14)–C(15)	1.432(11)
Os(2)–Os(4)	2.8549(4)	C(16)–C(17)	1.398(12)
Os(1)–Os(3)	2.8148(4)	C(17)–C(21)	1.417(11)
Os(1)–Os(4)	2.9011(4)	C(19)–C(20)	1.386(12)
Os(4)–N(1)	2.140(6)	N(1)–C(20)	1.341(10)
C(12)–C(13)	1.468(10)	N(1)–C(21)	1.375(10)
C(13)–C(21)	1.410(10)	C(13)–C(21)	1.410(10)
C(15)–C(16)	1.333(13)	C(15)–C(16)	1.333(13)
C(17)–C(18)	1.408(12)	C(17)–C(18)	1.408(12)

Bond Angles			
Os(2)–Os(1)–Os(4)	59.851(9)	C(12)–Os(2)–Os(3)	45.43(18)
Os(1)–Os(2)–Os(4)	61.486(9)	C(12)–Os(2)–Os(4)	46.70(19)
Os(1)–Os(3)–Os(2)	59.782(10)	C(12)–Os(3)–Os(1)	92.9(2)
Os(2)–Os(3)–Os(4)	60.054(9)	C(12)–Os(3)–Os(2)	46.54(19)
Os(3)–Os(1)–Os(2)	60.614(10)	C(12)–Os(3)–Os(4)	46.62(19)
Os(3)–Os(1)–Os(4)	60.063(10)	C(12)–Os(2)–Os(4)	46.7(2)
Os(1)–Os(2)–Os(3)	59.604(10)	C(12)–Os(4)–Os(2)	46.25(19)
Os(3)–Os(2)–Os(4)	60.288(9)	C(12)–Os(4)–Os(3)	45.07(18)
Os(1)–Os(3)–Os(4)	61.464(10)	Os(3)–C(12)–Os(2)	88.0(3)
Os(2)–Os(4)–Os(1)	58.663(10)	Os(3)–C(12)–Os(4)	88.3(3)
Os(2)–Os(4)–Os(3)	59.658(9)	Os(2)–C(12)–Os(4)	87.0(3)
Os(3)–Os(4)–Os(1)	58.473(10)	C(12)–Os(4)–N(1)	76.6(2)
C(12)–Os(2)–Os(1)	91.95(19)		

ported by the CO ligand displacements observed around these coordination sites. The bridging tertiary carbon C(12) donates three electrons to the metal core through similar metal–carbon σ -bonds to Os(2), Os(3), and Os(4) (C(12)–Os(2) = 2.065(7), C(12)–Os(3) = 2.027(6), and C(12)–Os(4) = 2.081(7) Å). This is in sharp contrast to **17**, and when taken together with the almost equal Os–Os bond lengths of the carbon-capped face, suggests a much more symmetrical bonding interaction resulting from capping the opposite face with the fourth osmium atom. The metal atoms Os(1), Os(2), and Os(3) each contain three linear carbonyl ligands, and the other metal atom Os(4) has only two. Two additional electrons are donated by the lone pair on nitrogen via a two-electron donor σ -bond from N(1) to Os(4). The Os(4)–N(1) bond length in **20** (2.140(6) Å) is very similar to the Os(2)–N(1) bond lengths in **6** (2.13(2) Å).^{23a} As far as electron counting is concerned, cluster **20** contains 60 cluster valence electrons (CVE) and is consistent with the six metal–metal bonds observed in the structure in accord with the effective atomic number (EAN) rule. The spectroscopic properties of **20** are consistent with the solid-state structure. The infrared and ¹H NMR spectroscopic data of **20** are very similar to those of **19**, indicating that they have analogous structures.

A similar thermolysis of **10** and **11** but at 80 °C and in the presence of H₂ (1 atm) gives the trihydrides **15** and **16** in 72 and 77% yields, respectively, in addition to trace amounts of the parent clusters **6** and **7**. The spectroscopic properties of **20** are consistent with the solid-state structure. The infrared and ¹H NMR spectroscopic data of **20** are very similar to those of **19**, indicating that they have analogous structures.

In contrast to the thermolysis of **10** and **11**, which afforded a mixture of two trinuclear complexes and one tetranuclear complex, the thermolysis of **12** and **13** proceeds smoothly to yield (μ -H)Os₃(CO)₉(μ_3 - η^2 -CC₈H₄(5-CH₃)N₂) (**21**) and (μ -H)Os₃(CO)₉(μ_3 - η^2 -C(C₈H₅)N₂) (**22**), respectively (Scheme 7). The infrared and ¹H NMR

Scheme 7**Table 7. Reduction Potential of Compounds in CH₂Cl₂ Relative to Fc/Fc⁺**

compound	reduction in volts
10	–2.24 (<i>E</i> _{IRR})
12	–1.60 (<i>E</i> _{REV})
13	–1.64 (<i>E</i> _{REV})
23	–1.74 (<i>E</i> _{REV})
24	–1.65 (<i>E</i> _{REV})
25	–1.63 (<i>E</i> _{REV})

spectra and of **21** and **22** are virtually identical to those observed for **17** and **18**, indicating that they are structurally similar. The formulations of **21** and **22** are clear from their mass spectra, which show molecular ion peaks at *m/z* 978 for **21** and 964 for **22**.

The thermolysis of **12** and **13** in the presence of molecular hydrogen (1 atm) at 80 °C gives the trihydrides (μ -H)₃Os₃(CO)₈(μ_3 - η^2 -CC₈H₄(5-CH₃)N₂) (**23**) and (μ -H)₃Os₃(CO)₈(μ_3 - η^2 -CC₈H₅N₂) (**24**), respectively, in high yields. Both compounds have been characterized by elemental analysis, infrared, and ¹H NMR spectroscopy. The infrared spectra of **23** and **24** are very similar to those of **15** and **16** and (μ -H)₃Os₃(CO)₈(μ_3 - η^2 -CHC₇H₃(Me)NS), indicating that they are isostructural.

Electrochemical studies of the methyldene insertion cluster containing the quinoxaline ligand are of interest due to the interesting electrochemical behavior observed from our previous studies of the quinoxaline ligand and quinoxaline triosmium clusters.²⁵ The quinoxaline containing a 48-electron precise cluster, (μ -H)Os₃(CO)₁₀(μ - η^2 -C₈H₅N₂), showed a one-electron reversible reduction potential at –1.63 V vs Fc/Fc⁺. This reduction potential is significantly less negative than the free ligand, and the latter is also irreversible.²⁵ Very similar electrochemical behavior is observed for the diazomethane reaction products. The electrochemical reduction potentials of the complexes are provided in Table 7. The quinoxaline-containing complexes **12**, **13**, **23**, and **24** all show reversible one-electron reduction potentials at –1.70, –1.64, –1.74, and –1.65 V in CH₂Cl₂ vs Fc/Fc⁺, respectively, whereas the quinoline derivative **10** shows an irreversible reduction at –2.24 V. The reversibility of the CVs for **12**, **13**, **23**, and **24** was gauged on the

Table 8. Selected Calculated Bond Angles and Bond Lengths for **12** and **13**

Bond Distances			
12		13	
Os(1)–Os(2)	3.08	C(12)–C(17)	1.45
Os(2)–Os(3)	2.90	C(13)–C(14)	1.38
Os(1)–Os(3)	2.85	C(13)–C(18)	1.50
Os(1)–C(19)	2.17	C(14)–C(15)	1.40
Os(3)–C(19)	2.18	C(15)–C(16)	1.40
Os(2)–N(1)	2.23	C(16)–C(17)	1.43
C(10)–C(11)	1.40	C(16)–C(19)	1.48
C(11)–N(2)	1.32	C(17)–N(1)	1.39
C(12)–N(2)	1.36	C(12)–C(13)	1.42
C(10)–N(1)	1.34		
Os(1)–Os(2)	2.855	Os(1)–Os(2)	2.855
Os(2)–Os(3)	3.080	Os(2)–Os(3)	3.080
Os(1)–Os(3)	2.90	Os(1)–Os(3)	2.90
Os(1)–C(10)	2.170	Os(1)–C(10)	2.170
Os(3)–C(10)	2.180	Os(3)–C(10)	2.180
N(1)–C(17)	1.340	N(1)–C(17)	1.340
N(2)–C(16)	1.320	N(2)–C(16)	1.320
N(1)–C(18)	1.390	N(1)–C(18)	1.390
N(2)–C(15)	1.37	N(2)–C(15)	1.37
C(10)–C(11)	1.480	C(10)–C(11)	1.480
C(11)–C(18)	1.440	C(11)–C(18)	1.440
C(13)–C(14)	1.370	C(13)–C(14)	1.370
C(15)–C(18)	1.45	C(15)–C(18)	1.45
C(11)–C(12)	1.40	C(11)–C(12)	1.40
C(12)–C(13)	1.40	C(12)–C(13)	1.40
C(14)–C(15)	1.41	C(14)–C(15)	1.41
C(16)–C(17)	1.40	C(16)–C(17)	1.40
Bond Angles			
12		13	
Os(3)–Os(2)–Os(1)	58.32	Os(1)–Os(2)–Os(3)	58.37
Os(2)–Os(3)–Os(1)	64.81	Os(2)–Os(1)–Os(3)	64.81
Os(3)–Os(1)–Os(2)	56.85	Os(1)–Os(3)–Os(2)	56.80
C(5)–Os(2)–Os(1)	113.67	C(3)–Os(1)–Os(2)	92.85
N(1)–Os(2)–Os(3)	90.46	C(2)–Os(1)–Os(2)	93.11
C(1)–Os(1)–Os(3)	94.73	C(2)–Os(1)–Os(3)	120.34
C(8)–Os(3)–Os(1)	120.31	N(1)–Os(2)–Os(1)	90.36
C(3)–Os(1)–Os(2)	110.78	Os(1)–C(10)–Os(3)	83.50
C(19)–Os(3)–Os(1)	48.17	C(1)–Os(1)–Os(2)	167.61
C(19)–Os(1)–Os(3)	46.33	C(10)–Os(1)–Os(2)	81.29
Os(3)–C(19)–Os(1)	83.49	C(1)–Os(1)–Os(3)	102.88
		C(10)–Os(1)–Os(3)	48.31
		C(5)–Os(2)–N(1)	88.38
		C(6)–Os(2)–Os(1)	171.53
		C(10)–Os(3)–Os(1)	48.17
		C(10)–Os(3)–Os(2)	75.89

criteria that the half-wave potentials of the reductive and oxidative scans were separated by less than 80 mV at scan rates of 200 mV/s. The similar reduction potentials of the quinoxaline-containing 48-electron cluster, $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-C}_8\text{H}_5\text{N}_2)$ (**25**), **13**, and **24** suggest that the binding mode of the heterocycle to the metal cluster has little effect on their reduction potentials. This is in agreement with our previously reported DFT calculations, which showed that the LUMO is predominantly ligand based for the previously studied $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-C}_8\text{H}_5\text{N}_2)$.²⁵ The methyl substituent on the quinoxaline ring shifts the reduction potential about 60–90 mV toward more negative potential due to the expected electron-donating effect of the methyl group. It would appear that the cluster acts as an electron sink for the bonding electrons of the heterocycle, delocalizing them onto the core and the carbonyl ligands, and that this delocalization takes place whether the C(8) carbon of the quinoxaline ring is directly bound to the metal or connected through a methylidene or methylidyne carbon with concomitant stabilization of the LUMO. The relatively short C–C distances between C(8) and these carbons implies some conjugation with the ring in these systems (1.489 and 1.497 Å). This effect is large enough to sufficiently stabilize the radical anions of the more electron-poor heterocycle quinoxaline and makes the reductions reversible. This is not the case for the relatively more electron-rich quinolines.

Density functional theory calculations were carried out on complexes **12** and **13**. The optimized geometries gave bond lengths and angles that are in good agreement with the experimentally determined bond lengths for **12** and **13** (Tables 4, 5, and 8). Spin density calculations on the corresponding radical anions reveal that most of the spin density is distributed within the ring at the two nitrogen atoms and at positions 2, 3, and 5 of the ring (scaled to 1000 for $1e^-$, Figure 7). The

net natural charge population analysis (NPA) of the C–H groups on the heterocyclic ring of **12** and **13** reveals localization of the most positive charges at the C-2 and C-3 position (Figure 7). There is also a significant amount of positive charge distributed on the carbonyl of Os(1) and particularly at the axial carbonyl of Os(2) for **12**. Similar charge distribution patterns were also found for compound **13**. The charge distributions at the C-2 and C-3 position are very similar. However, the spin density calculation shows that more spin density is localized at C-2 rather than at C-3 position. Another interesting feature is found at the C-5 position, which has a net charge very similar to the C-6 or C-7 positions but where significant spin density is found, suggesting particular stabilization of the resulting radical anion probably due to its *para*-relationship to the cluster-bound carbon atom which can delocalize bonded electrons to the cluster. Most importantly, in general the higher the positive charge at a particular position, the higher the calculated spin density at that

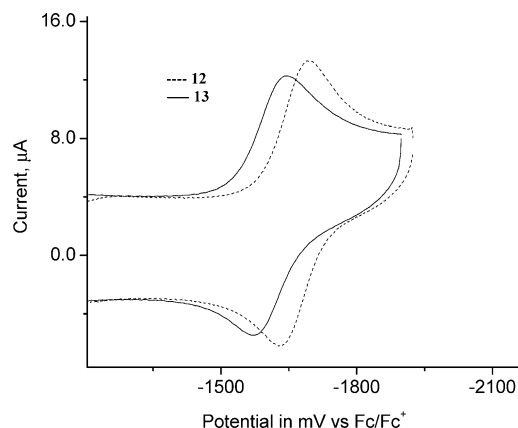


Figure 6. Cyclic voltammogram of **12** and **13** at 400 mV/s vs Fc/Fc⁺.

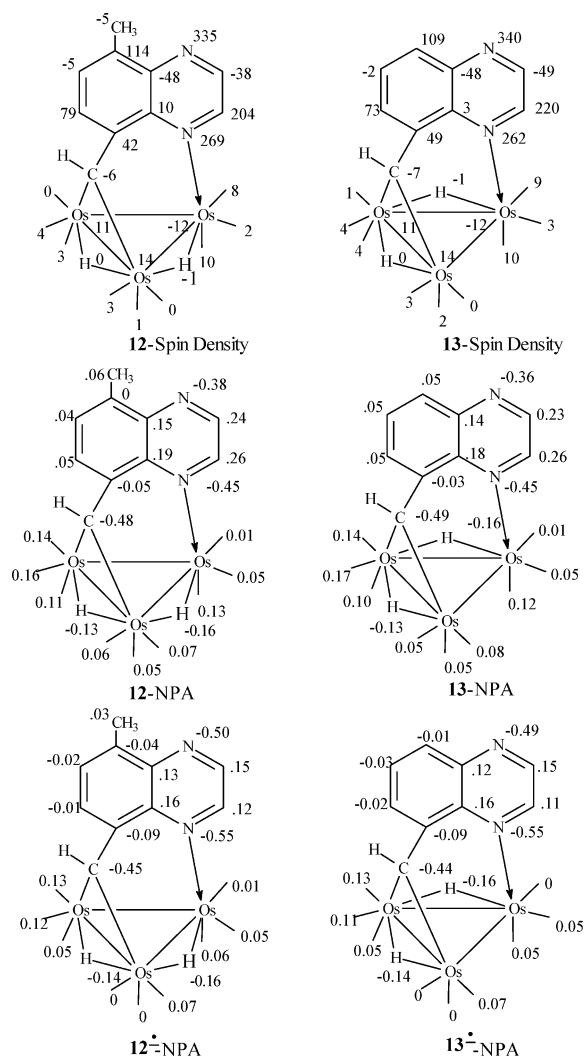


Figure 7. Distribution of spin density and natural charge in **12** and **13**. Sum of the natural charges of C and O and C and H are shown on the CO groups and on the benzo-heterocycle, respectively.

position (Figure 7). The natural charge analysis of radicals **12** and **13** shows that the natural charges at C-2 and on the nitrogen atoms are shifted significantly toward more negative values than on any other atoms. Notably the carbonyl carbons do not show nearly the same change in net charge consistent with the idea that most of the charge due to the added electron remains in the heterocycle. The stabilities of the radicals of these complexes on the cyclic voltammetry time scale are thus mainly due to the distribution of unpaired spin density into the heterocyclic ring, and this explains the difference in behavior between quinoline and quinoxaline. The rather narrow range in measured reduction potentials observed for **12**, **13**, and **23–25** relative to the diversity in bonding modes of **12** and **13** versus **23**, **24**, and **25** is surprising and is not reflected in the NPA analyses.

Conclusions

The reaction of the quinoxaline triosmium cluster **8** with diazomethane represents a novel example of insertion of one methylene group into the Os–C σ -bond of the cluster and another to the C(5)–H bond of the

carbocyclic ring, resulting in modification of the heterocyclic ligand and affording compound **12** (Scheme 4). Thus, the now well-known attack of nucleophiles at the C(5) of quinoline in these electron-deficient clusters is paralleled by diazomethane (commonly viewed as an electrophile), but only in the case of the more electron-deficient quinoxaline system does substitution of methyl for hydrogen at the 5 position redirect the reaction toward the Os–C and Os–H bonds to give **12** and **14**. The latter provides a second interesting example of a triosmium cluster containing an edge-bridging methylene group and a σ -bound methyl group.²¹

Compounds **10** and **11**, on thermolysis, produce one tetranuclear and two trinuclear complexes (Scheme 6), while **12** and **13** give only a single monohydrido triosmium compound which corresponds to only one of the three compounds obtained from **10** and **11**. This may also be related to the more electron-poor quinoxaline ring system.

In summary, the reactivity of diazomethane toward unsaturated triosmium clusters containing heterocyclic ligands is markedly influenced by the structure of the ligand. To explore the effect of the structure of the diazoalkane on product formation, investigations of the reactivity of **1**, **4**, and **6–9** with diphenyldiazomethane, dimethyldiazomethane, and diazoacetate are currently underway in our laboratories. Finally, it is interesting to note that the binding of the electron-poor quinoxaline ring to the cluster in a variety of bonding modes gives clusters capable of one-electron reversible reduction, whereas the free ligand shows irreversible reduction at more negative potentials. It would appear that coordination of the heterocycle to the osmium core in almost any bonding arrangement is sufficient to stabilize radical anions on the cyclic voltammetry time scale relative to the free ligand. This is only true, however, for electron-precise clusters with relatively electron-poor heterocycles. The natural charge population analysis and spin density calculations also demonstrate that charge localization in the heterocyclic ring is the primary origin of the radical stabilities of compounds **12** and **13**.

Experimental Section

General Procedures. Although the reaction products are air stable, all of the reactions were performed under an atmosphere of nitrogen. Reagent grade solvents were freshly distilled from appropriate drying agents. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on Varian Unity Plus 400 and Bruker DPX 400 instruments. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. The compounds $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_9\text{H}_5(4\text{-CH}_3\text{N}))$ (**6**), $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_9\text{H}_6\text{N})$ (**7**), $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_5\text{N}_2)$ (**8**), and $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_4(5\text{-CH}_3\text{N}_2))$ (**9**) were prepared according to the published procedures.^{23a,d} Diazomethane was prepared from diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) using an Aldrich mini diazald apparatus.

Reaction of $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_9\text{H}_5(4\text{-CH}_3\text{N}))$ (6**) with CH_2N_2 .** An ethereal solution of freshly prepared diazomethane (~0.700 g, ~16.6 mmol) was added to a dichloromethane solution (10 mL) of **3** (0.155 g, 0.160 mmol) at 0 °C, and the reaction mixture was warmed to room temperature. Immediate formation of insoluble polymethylene was observed. The reaction mixture was stirred at room temperature for 1 h, during which time the color changed from green to yellow. The

polymer was separated by filtration, and the solvent from the filtrate was removed under reduced pressure. The residue was chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (5:1, v/v) gave one major band, which afforded (μ -H)₂Os₃(CO)₉(μ_3 - η^2 -CH(C₉H₅)(4-CH₃)N) (**10**) (0.125 g, 80%) as yellow crystals after recrystallization from hexane/CH₂Cl₂ at -20 °C. Anal. Calcd for C₂₀H₁₁NO₉Os₃: C, 24.51; H, 1.13; N, 1.43. Found: C, 24.65; H, 1.24; N, 1.45. IR (ν CO, hexane): 2092s, 2066vs, 2036vs, 2005m, 1986m, 1963w, 1939w cm⁻¹. ¹H NMR (CDCl₃): δ 2.68 (s, 3H), 6.62 (d, 1H, J = 2.0 Hz), 6.99 (d, 1H, J = 5.2 Hz), 7.29 (dd, 1H, J = 7.4, 1.6 Hz), 7.66 (d, 1H, J = 7.6 Hz), 7.84 (d, 1H, J = 6.8 Hz), 9.53 (d, 1H, J = 5.2 Hz) -14.76 (d, 1H, J = 2.0 Hz) -15.16 (t, 1H, J = 2.0 Hz). ¹³C{¹H} NMR (CDCl₃), carbonyl region: δ 166.4 (s, 1C), 171.4 (s, 1C), 171.8 (s, 1C), 173.0 (s, 1C), 173.8 (s, 1C), 174.5 (s, 1C), 177.2 (s, 1C), 179.9 (s, 1C), and 184.1 (s, 1C); hydrocarbon region: δ 20.3 (s, 1C), 41.0 (s, 1C), 119.9 (s, 1C), 122.3 (s, 1C), 127.5 (s, 1C), 131.0 (s, 1C), 131.8 (s, 1C), 146.2 (s, 1C), 149.7 (s, 1C), 158.4 (s, 1C), and 162.6 (s, 1C). MS: (m/z) 979 [M]⁺.

Reaction of (μ -H)Os₃(CO)₉(μ_3 - η^2 -C₉H₆)N (**7**) with CH₂N₂.

A reaction similar to that above of an ethereal solution of freshly prepared CH₂N₂ (~0.700 g, ~16.6 mmol) with **7** (0.145 g, 0.150 mmol) followed by similar chromatographic workup gave one major band, which afforded (μ -H)₂Os₃(CO)₉(μ_3 - η^2 -CH(C₉H₆)N) (**11**) (0.125 g, 85%) as yellow crystals after recrystallization from hexane/CH₂Cl₂ at -20 °C. Anal. Calcd for C₁₉H₉NO₉Os₃: C, 23.62; H, 0.94; N, 1.45. Found: C, 23.83; H, 1.05; N, 1.54. IR (ν CO, hexane): 2094m, 2067s, 2044vs, 2010vs, 1993m, 1988m, 1974w, 1968m cm⁻¹. ¹H NMR (CDCl₃): δ 6.58 (d, 1H, J = 2.0 Hz), 7.14 (dd, 1H, J = 5.2, 8.4 Hz), 7.31 (t, 1H, J = 7.0 Hz), 7.49 (dd, 1H, J = 1.4, 7.0 Hz), 7.87 (d, 1H, J = 7.6 Hz), 8.28 (dd, 1H, J = 1.4, 8.0 Hz), 9.68 (dd, 1H, J = 1.4, 5.2 Hz), -14.74 (d, 1H, J = 2.0 Hz), -15.21 (t, 1H, J = 2.0 Hz). MS: (m/z) 965 [M]⁺.

Reaction of (μ -H)Os₃(CO)₉(μ_3 - η^2 -C₈H₅N₂) (**8**) with CH₂N₂.

A treatment similar to that above of **8** (0.095 g, 0.098 mmol) with CH₂N₂ (~0.700 g, ~16.6 mmol) at 0 to 25 °C for 1.5 h followed by similar chromatographic separation gave the following compounds in order of elution. (μ -H)₂Os₃(CO)₉(μ_3 - η^2 -CH(C₈H₄)(5-CH₃)N₂) (**12**) (0.019 g, 20%) as red crystals from hexane/CH₂Cl₂ at -20 °C: Anal. Calcd for C₁₉H₁₀N₂O₉Os₃: C, 23.26; H, 1.03; N, 2.86. Found: C, 23.38; H, 1.15; N, 2.92. IR (ν CO, CH₂Cl₂): 2094m, 2969vs, 2042vs, 2004s, 1992m, 1967m, cm⁻¹. ¹H NMR (CD₂Cl₂): δ 9.56 (d, 1H, J = 2.8 Hz), 8.59 (d, 1H, J = 2.8 Hz), 7.87 (d, 1H, J = 7.6 Hz), 7.44 (d, 1H, J = 7.6 Hz), 6.54 (d, 1H, J = 1.6 Hz), 2.58 (s, 3H), -14.69 (d, 1H, J = 1.6 Hz), -15.19 (t, 1H, J = 1.6 Hz). ¹³C{¹H} NMR (CD₂Cl₂), carbonyl region: δ 171.8 (s, 1C), 171.9 (s, 1C), 173.3 (s, 1C), 173.9 (s, 1C), 174.5 (s, 1C), 177.5 (s, 1C), 180.3 (s, 1C), 182.8 (s, 1C), 183.6 (s, 1C); hydrocarbon region: δ 17.8 (s, 1C), 39.8 (s, 1C), 130.9 (s, 1C), 132.2 (s, 1C), 133.6 (s, 1C), 143.2 (s, 1C), 150.3 (s, 1C), 157.7 (s, 1C), 160.9 (s, 1C), 166.5 (s, 1C). MS: m/z 980. (μ -H)₂Os₃(CO)₈(μ_3 - η^2 -CHC₈H₅N₂) (**13**) (0.033 g, 35%), as red crystals after recrystallization from hexane/CH₂Cl₂ -20 °C: Anal. Calcd for C₁₈H₈N₂O₉Os₃: C, 22.36; H, 0.84; N, 2.90. Found: C, 22.48; H, 0.97; N, 2.96. IR (ν CO, CH₂Cl₂): 2096m, 2070vs, 2042vs, 2010s, 1992s, 1967m cm⁻¹. ¹H NMR (CD₂-Cl₂): δ 9.51 (d, 1H, J = 3.2 Hz), 8.57 (d, 1H, J = 3.2 Hz), 7.95 (dd, 1H, J = 7.6, 1.2 Hz), 7.85 (dd, 1H, J = 7.6, 1.2 Hz), 7.54 (t, 1H, J = 7.6 Hz), 6.47 (d, 1H, J = 1.6 Hz), -14.70 (d, 1H, J = 1.6 Hz), -15.24 (t, 1H, J = 1.6 Hz). MS: m/z 966.

Reaction of (μ -H)Os₃(CO)₉(μ_3 - η^2 -C₈H₄(5-CH₃)N₂) (9**) with CH₂N₂.** A similar reaction of **9** (0.095 g, 0.098 mmol) with diazomethane (0.700 g, 16.6 mmol) at 0 to 25 °C followed by similar chromatographic separation afforded **12** (0.047 g, 49%) and Os₃(CO)₉(μ - η^2 -C₈H₄(5-CH₃)N₂)(μ -CH₂)CH₃ (**14**) (0.011 g, 11%) as orange crystals from hexane/CH₂Cl₂ at -5 °C. Anal. Calcd for C₂₀H₁₂N₂O₉Os₃: C, 24.14; H, 1.22; N, 2.82. Found: C, 24.48; H, 1.34; N, 2.88. IR (ν CO, CH₂Cl₂): 2095m, 2068vs, 2041vs, 2009s, 1988s, 1962w cm⁻¹. ¹H NMR (CD₂Cl₂): δ 8.80

(d, 1H, J = 2.4 Hz), 8.61 (d, 1H, J = 2.4 Hz), 8.57 (d, 1H, J = 7.2 Hz), 7.50 (d, 1H, J = 7.2 Hz), 7.40 (d, 1H, J = 6.8 Hz), 6.27 (d, 1H, J = 6.8 Hz), 2.66 (s, 3H), 0.76 (s, 3H).

Thermolysis of 10. A heptane solution (2.0 mL) of **10** (0.100 g, 0.102 mmol) was heated to reflux for 2.5 h. The solvent was removed in vacuo and the residue subjected to TLC on silica gel. Elution with hexane/CH₂Cl₂ (5:1, v/v) gave four bands. The fast band gave (μ -H)₃Os₃(CO)₈(μ_3 - η^2 -C(C₉H₅)(4-CH₃)N) (**15**) (0.016 g, 17%) as pale yellow crystals after recrystallization from hexane/CH₂Cl₂ at -20 °C. Anal. Calcd for C₁₉H₁₁NO₈Os₃: C, 23.97; H, 1.17; N, 1.47. Found: C, 23.75; H, 1.08; N, 1.28. IR (ν CO, CH₂Cl₂): 2093m, 2074s, 2018m, 2014vs, 1987w, 1954m cm⁻¹. ¹H NMR (CDCl₃): δ 8.96 (d, 1H, J = 4.8 Hz), 7.82 (d, 1H, J = 6.6 Hz), 7.25 (dd, 1H, J = 6.6, 4.8 Hz), 7.52 (t, 1H, J = 4.8 Hz), -17.11 (t, 1H, J = 2.2 Hz), -18.08 (t, 1H, J = 2.2 Hz), -18.81 (t, 1H, J = 2.2 Hz). MS: (m/z) 951 [M]⁺. The second band afforded (μ -H)Os₃(CO)₉{ μ_3 - η^2 -C(C₉H₅)(4-CH₃)N} (**17**) (0.030 g, 30%) as orange crystals from hexane/CH₂Cl₂ at -20 °C. Anal. Calcd for C₂₀H₉NO₉Os₃: C, 24.56; H, 0.93; N, 1.43. Found: C, 24.62; H, 1.02; N, 1.58. IR (ν CO, hexane): 2085m, 2058vs, 2029vs, 2008s, 1987m, 1979w, 1962w cm⁻¹. ¹H NMR (CDCl₃): δ 2.65 (s, 3H), 7.06 (d, 1H, J = 4.8 Hz), 7.43 (d, 1H, J = 6.4 Hz), 7.52 (dd, 1H, J = 7.6, 1.4 Hz), 7.79 (d, 1H, J = 6.0 Hz), 9.30 (d, 1H, J = 4.8 Hz), -16.66 (s, 1H). MS: (m/z) 977 [M]⁺. The third band gave a trace amount of an uncharacterized compound. The fourth band gave (μ -H)-Os₄(CO)₁₁(μ_3 - η^2 -C(C₉H₅)(4-CH₃)N) (**19**) (0.019 g, 15%) as red crystals after recrystallization from hexane/CH₂Cl₂ at -20 °C. Anal. Calcd for C₂₀H₉NO₉Os₃: C, 24.56; H, 0.93; N, 1.43. Found: C, 21.65; H, 0.92; N, 1.28. IR (ν CO, hexane): 2085m, 2081s, 2056m, 2039vs, 2025s, 1980m cm⁻¹. ¹H NMR (CDCl₃): δ 2.69 (s, 3H), 7.15 (d, 1H, J = 4.8 Hz), 7.81 (t, 1H, J = 7.6), 8.06 (d, 1H, J = 7.4 Hz), 8.56 (d, 1H, J = 7.2 Hz), 9.22 (d, 1H, J = 5.2 Hz), -21.46 (s, 1H). MS: (m/z) 1224 [M]⁺.

Thermolysis of 11. A heptane solution (20 mL) of **11** (0.075 g, 0.078 mmol) was heated to reflux for 2.5 h. The solvent was removed in vacuo, and the residue was subjected to TLC on silica gel. Elution with hexane/CH₂Cl₂ (5:1, v/v) gave four bands. The fast band gave (μ -H)₃Os₃(CO)₈(μ_3 - η^2 -C(C₉H₆)N) (**16**) (0.011 g, 15%) as pale yellow crystals after recrystallization from hexane/CH₂Cl₂ at -20 °C. Anal. Calcd for C₁₈H₉NO₈Os₃: C, 23.05; H, 0.97; N, 1.49. Found: C, 23.27; H, 1.15; N, 1.51. IR (ν CO, CH₂Cl₂): 2094m, 2074vs, 2019s, 2013vs, 2007w, 1986w, 1955m, cm⁻¹. ¹H NMR (CDCl₃): δ 7.12 (dd, 1H, J = 7.2, 1.2 Hz), 7.30 (t, 1H, J = 7.2 Hz), 7.48 (m, 2H), 8.14 (dd, 1H, J = 7.8, 1.2 Hz), 9.12 (d, 1H, J = 5.8 Hz), -16.98 (t, 1H, J = 2.0 Hz), -18.10 (t, 1H, J = 2.0 Hz), -18.65 (t, 1H, J = 2.0 Hz). MS: (m/z) 937 [M]⁺. The second band afforded (μ -H)Os₃(CO)₉(μ_3 - η^2 -C(C₉H₆)N) (**18**) (0.027 g, 36%) as orange crystals from hexane/CH₂Cl₂ at -20 °C. Anal. Found: C, 23.78; H, 0.89; N, 1.57. C₁₉H₇NO₉Os₃: C, 23.67; H, 0.73; N, 1.45. IR (ν CO, hexane): 2085m, 2057vs, 2029vs, 2009s, 1988m, 1979w, 1963w, cm⁻¹. ¹H NMR (CDCl₃): δ 7.22 (m, 2H), 7.44 (t, 1H, J = 8.0 Hz), 7.49 (t, 1H, J = 7.6 Hz), 8.26 (dd, 1H, J = 8.4, 1.2 Hz), 9.22 (d, 1H, J = 6.4 Hz), -16.61 (s, 1H). MS (m/z) 963 [M]⁺. The third band was too small for complete characterization, while the fourth band gave (μ -H)Os₄(CO)₁₁(μ_3 - η^2 -C(C₉H₆)N) (**20**) (0.017 g, 18%) as red crystals after recrystallization from hexane/CH₂Cl₂ at -20 °C. Anal. Found: C, 20.96; H, 0.69; N, 1.29. C₂₁H₇NO₁₁Os₄: C, 20.84; H, 0.58; N, 1.16. IR (ν CO, CH₂Cl₂): 2080s, 2060vs, 2037m, 2022s, 1989s, cm⁻¹. ¹H NMR (CDCl₃): δ 2.69 (s, 3H), 7.15 (d, 1H, J = 4.8 Hz), 7.81 (t, 1H, J = 7.6 Hz), 8.06 (d, 1H, J = 7.4 Hz), 8.56 (d, 1H, J = 7.2 Hz), 9.22 (d, 1H, J = 5.2 Hz), -21.46 (s, 1H). MS: (m/z) 1210 [M]⁺.

Thermolysis of 10 in the Presence of H₂. A cyclohexane solution (50 mL) of **10** (0.105 g, 0.109 mmol) was heated to reflux under hydrogen (1 atm) for 8 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (10:

3, v/v) gave, in order of elution, **15** (0.073 g, 72%) and **6** (0.011 g, 11%).

Thermolysis of 11 in the Presence of H₂. A similar thermolysis of **11** (0.075 g, 0.078 mmol) followed by similar chromatographic separation gave **16** (0.056 g, 77%) and **7** (0.008 g, 11%).

Thermolysis of 13. A heptane solution (20 mL) of **13** (0.033 g, 0.034 mmol) was heated to reflux for 2 h. The solvent was removed under reduced pressure, and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (3:2, v/v) developed two bands. The first band gave (*μ*-H)Os₃(CO)₉(*μ*₃-η²-C(C₈H₅N₂)) (**22**) (0.012 g, 36%) as red crystals from hexane/CH₂Cl₂ at -20 °C. Anal. Calcd for C₁₈H₆N₂O₉Os₃: C, 22.41; H, 0.63; N, 2.90. Found: C, 22.68; H, 0.45, N, 2.96. IR (νCO, CH₂Cl₂): 2087m, 2058vs, 2031s, 2004m, 1992m, 1983w cm⁻¹. ¹H NMR (CDCl₃): δ 9.18 (d, 1H, *J* = 2.4 Hz), 8.76 (dd, 1H, *J* = 6.6, 1.4 Hz), 8.70 (dd, 1H, *J* = 8.4, 1.4 Hz), 8.57 (d, 1H, *J* = 2.4 Hz), 7.48 (t, 1H, *J* = 6.8 Hz), -16.45 (s, 1H). MS: (*m/z*) 964 [M]⁺. The second band was too small for complete characterization.

Thermolysis of 12. A similar thermolysis of **12** (0.033 g, 0.034 mmol) in heptane (20 mL) for 2 h followed by similar workup gave (*μ*-H)Os₃(CO)₉(*μ*₃-η²-CC₈H₄(5-CH₃)N₂) (**21**) (0.014 g, 42%) as red crystals after recrystallization from hexane/CH₂Cl₂ at 0 °C. Anal. Calcd for C₁₉H₁₀N₂O₉Os₃: C, 23.26; H, 1.03; N, 2.86. Found: C, 23.35; H, 1.15; N, 2.92. IR (νCO, CH₂Cl₂): 2085m, 2058vs, 2031vs, 2006s, 1981s cm⁻¹. ¹H (NMR, CD₂Cl₂): δ 9.21 (d, 1H, *J* = 2.4 Hz), 8.69 (d, 1H, *J* = 2.4 Hz), 7.62 (d, 1H, *J* = 7.2 Hz), 7.43 (d, 1H, *J* = 7.2 Hz), 2.65 (s, 3H), -16.43 (s, 1H). MS: (*m/z*) 978 [M]⁺.

Thermolysis of 12 in the Presence of H₂. A cyclohexane solution (50 mL) of **12** (0.085 g, 0.087 mmol) was refluxed under hydrogen (1 atm) for 8 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (1:1, v/v) gave one major band, which afforded (*μ*-H)₃Os₃(CO)₈(*μ*₃-η²-CC₈H₄(5-CH₃)N₂) (**23**) (0.072 g, 87%) as red crystals after recrystallization from hexane/CH₂Cl₂ at -20 °C. Anal. Calcd for C₁₈H₁₀N₂O₈Os₃: C, 22.69; H, 1.06; N, 2.94. Found: C, 22.89; H, 1.18; N, 2.98. IR (νCO, CH₂Cl₂): 2090m, 2072vs, 2017m, 2013s, 1985s, 1951m cm⁻¹. ¹H (NMR, CDCl₃): δ 9.05 (d, 1H, *J* = 2.4 Hz), 8.75 (d, 1H, *J* = 2.4 Hz), 7.77 (d, 1H, *J* = 7.2 Hz), 7.55 (d, 1H, *J* = 7.2 Hz), 2.68 (s, 3H), -16.90 (t, 1H, *J* = 2.0 Hz), -18.02 (t, 1H, *J* = 2.0 Hz), -18.65 (t, 1H, *J* = 2.0 Hz).

Thermolysis of 13 in the Presence of H₂. A thermolysis similar to that above of **13** (0.045 g, 0.047 mmol) under hydrogen followed by similar chromatographic separation gave (*μ*-H)₃Os₃(CO)₈(*μ*₃-η²-CC₈H₅N₂) (**24**) (0.037 g, 84%) as red crystals after recrystallization from hexane/CH₂Cl₂ at -20 °C. Anal. Calcd for C₁₇H₈N₂O₈Os₃: C, 21.75; H, 0.86; N, 2.98. Found: C, 21.98; H, 0.95; N, 3.05. IR (νCO, CH₂Cl₂): 2090m, 2073vs, 2018m, 2012s, 1984s, 1950m cm⁻¹. ¹H (NMR, CD₂Cl₂): δ 9.06 (d, 1H, *J* = 2.4 Hz), 9.76 (d, 1H, *J* = 2.4 Hz), 7.88 (t, 1H, *J* = 4.4 Hz), 7.73 (d, 2H, *J* = 4.4 Hz), 2.66 (s, 3H), -16.93 (t, 1H, *J* = 2.0 Hz), -18.04 (t, 1H, *J* = 2.0 Hz), -18.65 (t, 1H, *J* = 2.0 Hz).

X-ray Structure Analysis of 10 and 12. Suitable crystals of **10** and **12** were coated with Paratone N oil, suspended in a small fiber loop, and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite-monochromated Mo Kα (0.71073 Å) radiation. A hemisphere of data was measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3 frame widths. Data collection, indexing, and initial cell refinements were all carried out using SMART³¹ software. Frame integration and final cell refinements were done using SAINT³² software. The final cell parameters were determined from least-squares refinement on 3077 and 4205

reflections, respectively, for **10** and **12**. The SADABS³³ program was used to carry out absorption corrections.

The structures were solved using direct methods and difference Fourier techniques (SHELXTL, V6.12).³⁴ Hydrogen atoms were placed in their expected chemical position using the HFIX command and were included in the final cycles of least squares with isotropic *U*_{*i*}'s related to the atoms ridden on. The hydrides were positioned by using the XHYDEX program in the WinGX suite of programs.²⁶ All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from *International Tables for X-ray Crystallography*.³⁵ Structure solution, refinement, graphics, and generation of publication materials were performed by using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Table 1.

X-ray Structure Analysis of 13, 17, and 20. Crystals of **13**, **17**, and **20** suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution at -4 °C. Crystallographic data were collected at 120 K, using a Bruker-Nonius CCD area detector diffractometer and Mo Kα radiation (λ = 0.71073 Å). Data collection and processing were carried out using the programs COLLECT³⁶ and DENZO.³⁷ Empirical absorption corrections were applied to the data set using multiple and symmetry-related data measurements via the program SORTAV.^{38,39} The unit cell parameters were indexed from all observed reflections in a θ range of 10° and refined using the entire data set. The structures were solved by direct methods (SHELXS-97)⁴⁰ and refined on *F*² by full matrix least-squares (SHELXL-97)⁴¹ using all unique data. The bridging hydrides in **13** were located from a difference map but not refined. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions (riding model) with *U*_{iso} set at 1.2 times the *U*_{eq} of the parent atom.

Electrochemistry. Electrochemical measurements were performed using a BAS CV-50W analyzer equipped with a standard three-electrode cell. This cell was designed to allow the tip of the reference electrode to approach closely to the working electrode. Voltammetric experiments were performed using aqueous Ag/AgCl as a reference electrode, a glossy carbon as a working electrode, and platinum wire as the auxiliary electrode. Potential data are referred to the ferrocene (0/+) couple, which is oxidized in CH₂Cl₂ at +0.48 V vs Ag/AgCl. Typically, a solution containing 1 mM of the cluster and 0.1 M supporting electrolyte (tetrabutylammonium hexafluorophosphate, Bu₄NPF₆) was prepared using freshly distilled dichloromethane. The solution was degassed prior to introducing the sample and also between runs. Positive feedback *iR* compensation was routinely applied.

Computational Details. DFT calculations were performed using the Gaussian 98 and 03 programs.⁴² The molecular structures from single-crystal X-ray structure determinations were used for geometry optimization. We used restricted Becke's three-parameter hybrid functional⁴³ and Lee-Yang-Parr's gradient-corrected correlation function (B3LYP) through-

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out.⁴⁴ The basis sets employed were LanL2dz for the osmium atoms, using the relativistic effective core potential (ECP), which replaces the inner core electrons, and 6-31G for the other atoms in all the calculations. No symmetry restrictions were placed on the optimizations. Stationary points were determined by performing normal-mode analyses on the optimized structures.

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Supporting Information Available: Text and tables giving details of the X-ray crystallographic structure determination for **10**, **12**, **13**, **17**, and **20**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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