# Reactions of Bis(acetonitrile)triosmium Decacarbonyl with Secondary Mixed Amines NHRR′ (R = $CH_2CH_3$, R′ = $CH_3$ or *n*-$CH_2CH_2CH_3$)

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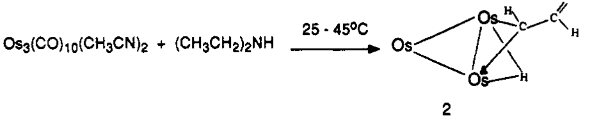
The reactions of the mixed secondary amines methylethylamine and *n*-propylethylamine with $(CH_3CN)_2Os_3(CO)_{10}$ (1) in benzene or dichloromethane at 25–45 °C have been studied. In the case of methylethylamine five trinuclear products containing amine-derived ligands are obtained: $(\mu\text{-H})(\mu\text{-}\eta^1\text{-CHCHN}(CH_3)CH_2CH_3)Os_3(CO)_{10}$ (4), $(\mu\text{-H})(\mu\text{-}\eta^1\text{-N(H)}CH_3)Os_3(CO)_{10}$ (5), $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}CH_3C{=}NCH_3)Os_3(CO)_{10}$ (6), $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}CH_3CH_2N(H)CH_2)Os_3(CO)_{10}$ (7), and $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}CH_3N{=}CHCH_2)Os_3(CO)_{10}$ (8). With *n*-propylethylamine only two trinuclear products containing amine-derived ligands are isolated: $(\mu\text{-H})(\mu\text{-}\eta^1\text{-N(H)}CH_2CH_2CH_3)Os_3(CO)_{10}$ (9) and $(\mu\text{-H})(\mu\text{-}\eta^1\text{-CHCHN}(CH_2CH_3)CH_2CH_2CH_3)Os_3(CO)_{10}$ (10). Thermolysis of 7 at 68 °C, containing the least activated amine ligand, in the presence of excess methylethylamine yields only 4 while in the absence of amine thermolysis at 98 °C yields the dihydrido cluster $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-CHCH}{=}NCH_3)Os_3(CO)_9$ (11), which is also formed from 8 at similar temperatures. Compound 6 decarbonylates at 125 °C to yield $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}CH_3C{=}NCH_3)Os_3(CO)_9$. All compounds were characterized by $^1H$ NMR, infrared, and elemental analysis. For compounds 6, 7, and 10, solid-state structural investigations by X-ray diffraction techniques are reported. Compound 6 crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.605$ (3) Å, $b = 12.096$ (3) Å, $c = 16.572$ (3) Å, and $V = 1925$ (1) $Å^3$ for $Z = 4$. Least-squares refinement of 2454 observed reflections gave $R = 0.030$ ($R_w = 0.034$). Compound 7 crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.516$ (2) Å, $b = 12.975$ (2) Å, $c = 16.260$ (3) Å, $\beta = 103.85$ (2)°, $V = 1949$ (1) $Å^3$ for $Z = 4$. Least-squares refinement of 2918 observed reflections gave a final agreement factor of $R = 0.046$ ($R_w = 0.045$). Compound 10 crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.679$ (2) Å, $b = 19.250$ (5) Å, $c = 17.091$ (5) Å, $\beta = 112.63$ (3)°, $V = 2332$ (2) $Å^3$, for $Z = 4$. Least-squares refinement of 3594 observed reflections gave $R = 0.061$ ($R_w = 0.061$).

## Introduction

An understanding of the sequence and the factors controlling the rates of activation of carbon–nitrogen and carbon–hydrogen bonds by transition metals is critical to our understanding of the industrially and environmentally important hydrodenitrification (HDN) process.[1-4] Trinuclear clusters of ruthenium and osmium have proved to be useful systems for modeling HDN chemistry.[5-7] Recently, it has been shown that additions of $Ru_3(CO)_{12}$ to heterogeneous HDN catalysts greatly improve their performance but it is not clear exactly why or how this improved performance arises.[6,7] Since it has also been shown that reduction of nitrogen-containing aromatic heterocycles to cyclic aliphatic amines is the first step in the HDN process,[8,9] it is particularly important to elucidate the factors controlling the early stages of the activation of aliphatic amines by transition-metal centers. Until recently, there were relatively few examples in the literature of low-temperature activation of aliphatic C–H bonds in nitrogen-containing ligands by trinuclear clusters.[10,11]

We have reported, in preliminary form, the reactions of a range of secondary amines with $(CH_3CN)_2Os_3(CO)_{10}$ (1) and noted that the reaction products obtained were extremely sensitive to the structure of the amine used.[10] Using diethylamine at 25–45 °C the carbon–nitrogen coupling product $(\mu\text{-H})(\mu\text{-}\eta^1\text{-CHCHN}(CH_2CH_3)_2)Os_3(CO)_{10}$ (2, eq 1) is obtained, identical with the major product observed for the reaction of triethylamine with 1 at 80 °C.[12] This apparent carbon–nitrogen coupling is quenched when the bulky diisopropylamine is reacted with 1 and the secondary-amine derivative $(\mu\text{-H})(\mu\text{-}\eta^1\text{-CHC}(CH_3)NHCH(CH_3)_2)Os_3(CO)_{10}$ (3) is the only product isolated. With pyrrolidine or di-*n*-propylamine carbon–nitrogen coupling is also not observed but moderate to good yields of μ-imidoyl cluster derivatives are formed in which only α-carbon–hydrogen bonds have been activated (eqs 2 and 3).[10] At that time we also examined the reaction of methylethylamine with 1 and obtained the expected cross-coupling product (eq 4) in addition to several other products that were not characterized at that time. We report here characterization of these coproducts and the results of our investigation of the reaction of 1 with *n*-propylethylamine which shed further light on the mechanism of formation of the coupling products (eqs 1 and 4) and on the factors



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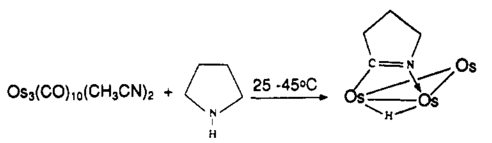

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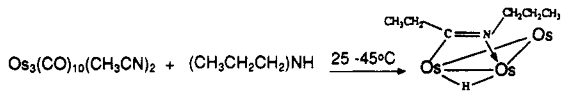

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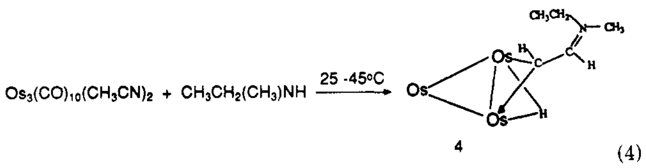

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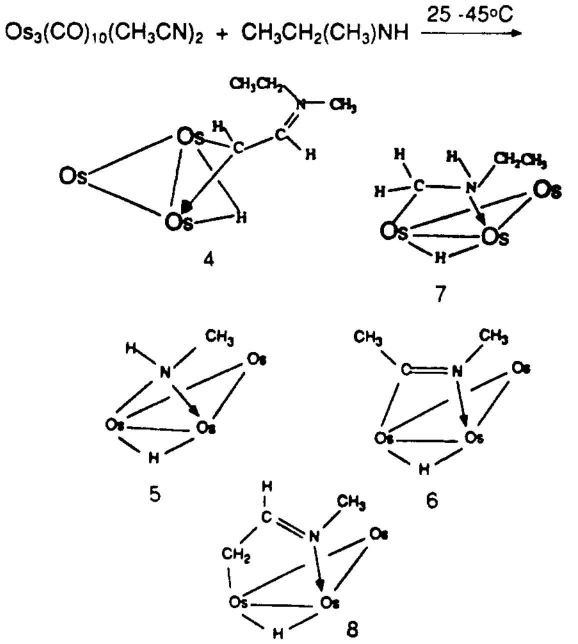
controlling the reaction of a particular secondary amine with 1.

## Results

The reaction of 1 with methylethylamine at 25 °C in $CH_2Cl_2$ yields five triosmium clusters containing ligands derived from the amine as well as $(\mu\text{-H})_2Os_3(CO)_{10}$[13] and $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$[14] (eq 5). In addition to the previously reported cross coupling product $(\mu\text{-H})(\mu\text{-}\eta^1\text{-}CHCHN(CH_3)CH_2CH_3)Os_3(CO)_{10}$ (4),[10] $(\mu\text{-H})(\mu\text{-}\eta^1\text{-}N(H)CH_3)Os_3(CO)_{10}$ (5), $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}CH_3C{=}NCH_3)Os_3(CO)_{10}$ (6), $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}CH_3CH_2N(H)CH_2)Os_3(CO)_{10}$ (7), and $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}CH_3N{=}CHCH_2)Os_3(CO)_{10}$ (8) are obtained. Compound 5 obtained in 8% yield has been reported previously from the reaction of methylamine with $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$[15] or by thermolysis of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}CON(H)CH_3)Os_3(CO)_{10}$[16] and was characterized here by comparison of its $^1H$ NMR and infrared spectra with those reported in the literature. Compounds 4 and 8 obtained in 15 and 2% yields, respectively, were characterized by $^1H$ NMR, infrared, and elemental analysis. We were unable to obtain suitable crystals of 8 for solid-state structural analysis, and direct analogues of 4 have been studied by X-ray diffraction techniques (see below). Compounds 6 and 7 obtained in 2 and 4% yields, respectively, were characterized by $^1H$ NMR, infrared, and elemental analysis, and their solid-state structures were determined by X-ray diffraction techniques (see below). Including $(\mu\text{-H})_2Os_3(CO)_{10}$[13] and $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$[14] obtained in 5 and 11% yields, respectively, we can account for ~50% of the osmium used. At 40–45 °C in benzene the reaction of 1 with methylethylamine yields the same products in slightly different relative yields with products 4–8 being obtained in 20, 2, 10, 6, and 2% yields, respectively. The $(\mu\text{-H})_2Os_3(CO)_{10}$ formed most likely comes from the known reaction of 1 with $H_2$[13c] formed by dehydrogenation of the amine ligand in the formation of 4, 6, and 8. The $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$ is formed by the reaction of 1 with trace $H_2O$ introduced with the $(CH_3)_3NO{\cdot}2H_2O$ used or during chromatographic purification of 1.[10] This compound is always obtained when reaction of 1 with a ligand is slow. We have reacted secondary amines with $(\mu\text{-H})_2Os_3(CO)_{10}$ and found that insoluble adducts form which do not move on preparative thin-layer chromatography plates. Since these reactions were performed in the presence of a 5-fold molar excess of amines, reaction of the $(\mu\text{-H})_2Os_3(CO)_{10}$ formed in situ with amine may account for some of the unrecovered osmium in addition to nonspecific decomposition.



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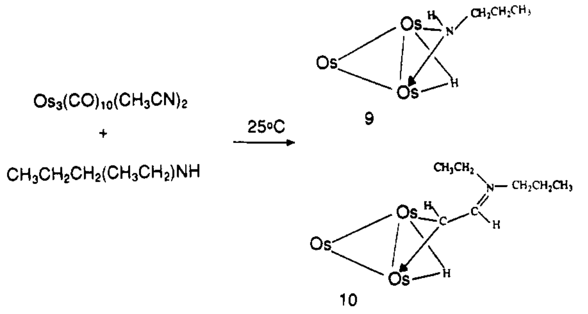
The reaction of $n$-propylethylamine with 1 at 25 °C in $CH_2Cl_2$ yields two triosmium products derived from the amine ligand $(\mu\text{-H})(\mu\text{-}\eta^1\text{-}N(H)CH_2CH_2CH_3)Os_3(CO)_{10}$ (9) and $(\mu\text{-H})(\mu\text{-}\eta^1\text{-}CHCHN(CH_2CH_3)CH_2CH_2CH_3)Os_3(CO)_{10}$ (10) in 13 and 15% yields, respectively, as well as $(\mu\text{-H})_2Os_3(CO)_{10}$[13] and $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$[14] in 5 and 12% yields, respectively (eq 6). Compound 9 was characterized by $^1H$ NMR, infrared, and elemental analysis. The $^1H$ NMR data for 9 are very similar to that for 5. Specifically, a hydride doublet at −14.92 ppm arising from a three-bond coupling to the N–H hydrogen ($^3J_{H-H}$ = 3.3 Hz; −14.82 ppm, $^3J_{H-H}$ = 2.8 Hz in 5) is observed. The N–H proton shows up as a broad signal at 4.13 ppm in 9 and 3.99 ppm in 5. Other analogues of 5 and 9 have been reported.[18,19] Compound 10 was characterized by $^1H$ NMR and infrared spectroscopy and by a solid-state structural investigation (see below).



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We previously reported[10] that compound 4 exists as two isomers in solution, and only one isomer in solution has

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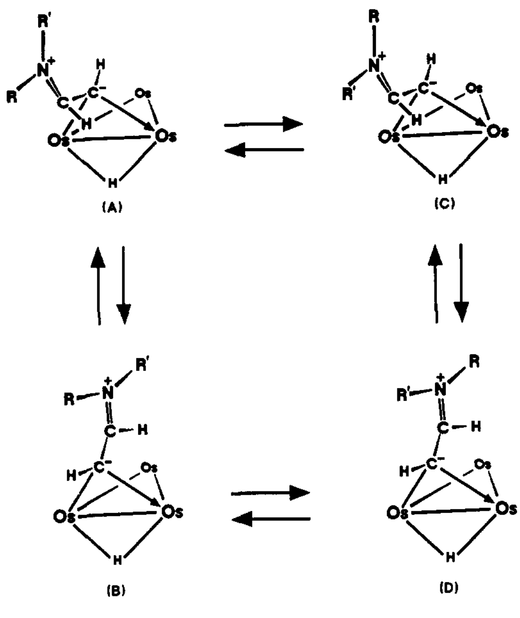
**Scheme I**



2; R = R' = $CH_2CH_3$
4; R = $CH_3$ R' = $CH_2CH_3$
10; R = $CH_2CH_3$ R' = $CH_2CH_2CH_3$

been reported[12] for 2. A reexamination of the $^1H$ NMR data for 2 and 4 and the 400-MHz $^1H$ NMR data for 10 reported here revealed that 2 exists as two isomers whereas 4 and 10 exist as 4 isomers in solution. In the case of 2 one major and one minor isomer are observed in a ratio of 9:1 in $CD_2Cl_2$ and 8:1 in toluene-$d_8$. The $^1H$ NMR spectra of these isomers differ in the magnitude of the $^3J_{H-H}$ between the hydride and hydrogen bound to the metal bridging carbon of the alkylidene ligand ($^3J_{H-H}$ = 2.4 Hz (major) and $^2J_{H-H}$ = 1.2 Hz (minor)) and in the relatively large chemical shift difference between the hydrides (−16.70 ppm (major) and −15.98 ppm (minor)) and the hydrogens on the alkylidene ligand (7.12 and 4.83 ppm (major) and 8.65 and 5.08 ppm (minor)). The vicinal H–H couplings in the two isomers are similar ($^2J_{H-H}$ = 13.9 Hz (major) and 14.7 Hz (minor)), suggesting a similar population of conformers around this formally single carbon–carbon bond in the alkylidene ligand. Considering the known structure of 2 and 10 (vide infra), there are four possible structural isomers for 4 and 10 (Scheme I, A–D) and two for 2, as observed (Scheme I, R′ = R). The isomers observed for 2 must differ by an anti (major) isomer versus syn (minor) orientation between the hydride and the hydrogen on the metal-bound carbon, with the anti orientation being found in the solid state. This type of isomerism has been previously observed in related triosmium clusters.[20] Heating a toluene-$d_8$ solution of 2 to +60 °C and observing the $^1H$ NMR spectrum at 80 MHz leads to averaging of the two isomers on the NMR time scale, as evidenced by the reversible averaging of the hydrides to a single doublet at −16.53 ppm ($^3J_{H-H}$ = 2.3 Hz), in good agreement with the calculated value of −16.59 ppm ($^3J_{H-H}$ = 2.3 Hz) using isomer populations corrected for temperature and the room-temperature 80-MHz $^1H$ NMR data.

The two major isomers for compound 4 observed in a 2:1 ratio in $CD_2Cl_2$ show the same H–H coupling constant between the hydride and hydrogen bound to the metal-bound carbon ($^3J_{H-H}$ = 2.4 Hz) and similar hydride chemical shifts (−16.81 and −16.72 ppm) and are assigned to the anti isomers A and C (Scheme I). The two isomers observed in a ratio of 3:1 to each other and in a 1:24 combined ratio to the major isomer pair show smaller couplings with the hydride ($^3J_{H-H}$ = 1.5 and 1.9 Hz, respectively) and are assigned to the syn isomers B and D (Scheme I). On heating to +60 °C in toluene-$d_8$, the minor isomers average with the major isomers to give two doublet hydride signals in a ratio of 2:1. This shows that for 4 interchange between A and B or C and D is faster than interchange between A and C or B and D (Scheme I). We can tentatively assign the more abundant isomer within each pair to the isomer with the larger alkyl group pointing away from the cluster (A and B, R′ = $CH_2CH_3$).

In the case of 10 there appears to be a crossover in the isomer populations compared with 4. The hydride signals of the major isomer pair, observed in a 1:1 ratio, appear as a singlet at −16.70 ppm and a doublet at −16.69 ppm ($^3J_{H-H}$ = 3.3 Hz). The hydride signals of the minor isomer pair, observed in a ratio of 2:3 to each other and in a combined ratio of 1:4 to a major isomer pair, appear as a singlet at −15.99 ppm and a doublet at −15.98 ppm ($^3J_{H-H}$ = 2.1 Hz). On the basis of these data and the corresponding resonances for the alkylidene hydrogens (see Experimental Section), we can assign the two major isomers in 10 as A and B, a syn–anti pair with the larger *n*-propyl group pointing away from the cluster. At +60 °C in toluene-$d_8$ at 80 MHz all four isomers average to a single doublet at −16.51 ppm ($^3J_{H-H}$ = 2.1 Hz). As expected raising the energy of isomer C relative to A lowers the barrier to interconversion of these two isomers, similarly for B and D. Apparently, the presence of the longer *n*-propyl group in 10 causes sufficient steric crowding with the cluster to stabilize isomer B relative to C.

The large vicinal H–H coupling constants between the hydrogens on the alkylidene ligand suggest that the principal conformation of 2, 4, and 10 in solution is the same as that observed in the solid state for 2 (i.e. with the two hydrogens essentially trans). We have no evidence that there is any hindered rotation around the formal single bond linking these carbon atoms, as it is not possible to distinguish between a single rigid trans conformation and free rotation around this bond but with mainly the trans conformer populated at room temperature.

In order to elucidate the possible relationships between the various products (4–8) obtained from the reaction of 1 and methylethylamine, we studied the thermolysis of 7 and 8. Compound 7 proved to be surprisingly stable, showing no rearrangement in refluxing hexane. However, in refluxing heptane for 6 h partial conversion to a new product, $(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}CHCH{=}NCH_3)Os_3(CO)_9$ (11) is observed, as characterized by $^1H$ NMR and infrared spectroscopy (eq 7). The $^1H$ NMR data for 11 (i.e. the chemical shift of the hydrides, the shift difference between hydrides, and the shift of the bridging alkylidene) are very similar to a compound we have obtained as the only product from the reaction of $(\mu\text{-}H)(C{=}NCH_2CH_2CH_2)Os_3(CO)_9$ with diazomethane, $(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}$

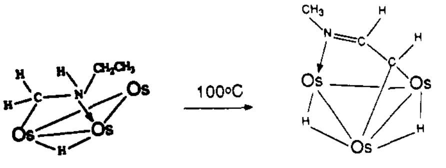


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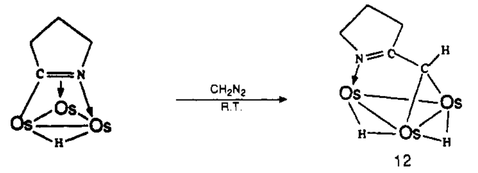
**Table I. Crystal Data and Collection and Refinement Parameters**[a]

| | 6 | 7 | 10 |
|---|---|---|---|
| formula | $C_{13}H_7NO_{10}Os_3$ | $C_{13}H_9NO_{10}Os_3$ | $C_{17}H_{15}NO_{10}Os_3$ |
| fw | 907.80 | 909.82 | 963.91 |
| crystal syst | orthorhombic | monoclinic | monoclinic |
| size, mm$^3$ | 0.10 × 0.13 × 0.32 | 0.10 × 0.15 × 0.40 | 0.13 × 0.38 × 0.40 |
| space group | $P2_12_12_1$ | $P2_1/c$ | $P2_1/c$ |
| $a$, Å | 9.605 (3) | 9.516 (2) | 7.679 (2) |
| $b$, Å | 12.096 (3) | 12.975 (2) | 19.250 (5) |
| $c$, Å | 16.572 (3) | 16.260 (3) | 17.091 (5) |
| $\beta$, deg | | 103.85 (2) | 112.63 (3) |
| $V$, Å$^3$ | 1925 (1) | 1949 (1) | 2332 (2) |
| $Z$ | 4 | 4 | 4 |
| $D_{ca}3l_{c}$, g/cm$^3$ | 3.13 | 3.10 | 2.75 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 198.3 | 195.9 | 163.8 |
| temp, °C | 25 ± 1 | 25 ± 1 | 25 ± 1 |
| no. of orient. reflns 2$\theta$ range, deg | 23; 4–54 | 23; 16–28 | 23; 4–30 |
| 2$\theta$ scan range, deg | 2–62 | 2–50 | 4–56 |
| scan speed, deg/min | 2.40–8.23 | 7.20–8.23 | 5.49 |
| scan range, deg | 0.8 | 0.8 | 0.9 |
| no. of unique data | 3464 | 3584 | 5775 |
| no. obsd detn (>3$\sigma F_o$) | 2454 | 2918 | 3594 |
| no. of variables | 245 | 244 | 275 |
| $R$ | 0.030 | 0.046 | 0.061 |
| $R_w$ | 0.034 | 0.045 | 0.061 |
| largest shift/esd | 0.01 | 0.00 | 0.06 |
| weighting scheme | $1/\sigma^2$ | $1/\sigma^2$ | $1/\sigma^2$ |
| highest peak $\Delta F$, map, e Å$^{-3}$ | 1.02 (22) | 0.90 (31) | 1.87 (39) |
| rel trans coeff | 0.534–0.997 | 0.472–0.997 | 0.456–0.997 |

[a] For each determination: Mo radiation ($\lambda$ = 0.71073 Å), graphite monochromator, $\omega$–2$\theta$ scan mode.

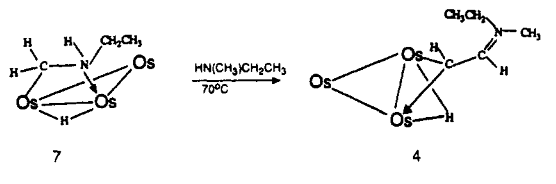
$CHC{=}NCH_2CH_2CH_2)Os_3(CO)_9$ (12), which was characterized by a solid-state structural investigation[21] (eq 8).



(8)

The shifts of the hydrides in 11 are −14.14 and −14.31 ppm and −14.26 and −14.56 ppm in 12, and the shift of the alkylidyne hydrogen is 4.15 ppm in 11 and 4.13 ppm in 12. The infrared spectra of 11 and 12 are virtually identical.

Interestingly, the addition of methylethylamine to a refluxing solution of 7 in hexane yields 4 in 40% yield and recovered 7 in 33% yield (eq 9).



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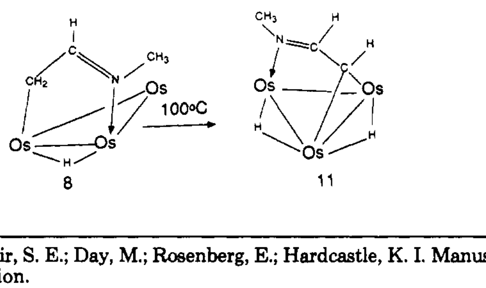
Thermolysis of 8 in refluxing heptane also yields 11 as the only product in 67% yield (eq 10). Compound 4 is thermally stable in refluxing heptane although Adams et al. have reported that an analogous compound rearranges



(10)

to a $\mu_3$-alkylidyne on photolysis.[22] Compound 6 slowly decarbonylates to give $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}CH_3C{=}NCH_3)Os_3(CO)_9$ (13) in refluxing octane, as we have previously demonstrated for related compounds.[10]

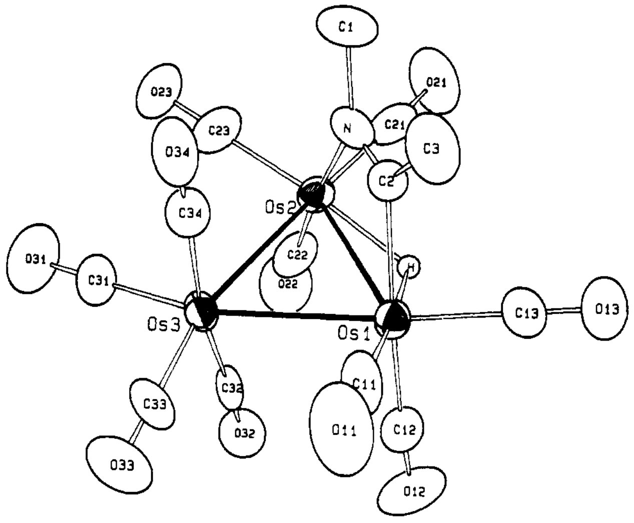


**Figure 1.** ORTEP diagram of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}CH_3C{=}NCH_3)Os_3(CO)_{10}$ (6) showing the calculated position of the hydride. Selected distances (Å) and angles (deg) are Os(1)–Os(2) = 2.900 (1), Os(1)–Os(3) = 2.867 (1), Os(2)–Os(3) = 2.864 (1), Os(1)–C(2) = 2.14 (1), Os(2)–N = 2.12 (1), N–C(2) = 1.28 (2), N–C(2)–C(3) = 125 (1), C(1)–N–C(2) = 121 (1).

**Solid-State Structure of 6.** The solid-state structure of 6 is shown in Figure 1 with relevant bond distances and angles in the caption; crystal data are given in Table I. The structure of 6 consists of an approximate isosceles triangle of osmium atoms, with the longer edge Os(1)–Os(2) = 2.900 (1) Å bearing the $\mu$-imidoyl ligand and the hydride whose position was calculated by using the program Hy-

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[21] Kabir, S. E.; Day, M.; Rosenberg, E.; Hardcastle, K. I. Manuscript in preparation.

[22] Adams, R. D.; Tanner, J. T. *Organometallics* **1988**, *7*, 2241.

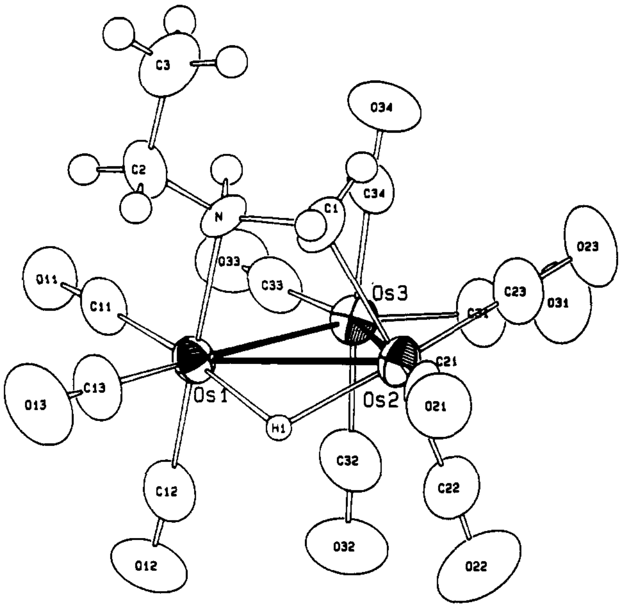

**Figure 2.** ORTEP diagram of $(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH_3CH_2N(H)CH_2)Os_3(CO)_{10}$ (**7**) showing the calculated position of the hydride. Selected distances (Å) and angles (deg) are Os(1)–Os(2) = 2.897 (1), Os(1)–Os(3) = 2.892 (1), Os(2)–Os(3) = 2.887 (1), Os(1)–N = 2.17 (1), Os(2)–C(1) = 2.21 (1), N–C(1) = 1.48 (2), C(1)–N–C(2) = 114 (1), N–C(2)–C(3) = 114 (1).

dex.[23] The Os(1)–C(2) distance of 2.14 (1) Å and the Os(2)–N distance of 2.12 (1) Å are very similar to those found in the structurally analogous $(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C{=}NCH_2CH_2CH_2)Os_3(CO)_{10}$ (2.14 (1) and 2.12 (1) Å, respectively).[10] The overall structure including the disposition of the carbonyl groups and the calculated position of the hydride is virtually identical with the previously reported $(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}PhC{=}NMe)Os_3(CO)_{10}$[24] and the cyclic analogue.[10]

**Solid-State Structure of 7.** The solid-state structure of **7** is shown in Figure 2 with relevant bond distances and angles in the caption; crystal data are given in Table I. Compound **7** consists of an isosceles triangle of osmium atoms, with the slightly shorter Os(2)–Os(3) bond bearing the bridging amino ligand. The N–C(2) bond length of 1.48 (2) Å clearly designates this bond as a carbon–nitrogen single bond. The C(1)–Os(2) and N–Os(1) distances of 2.21 (1) and 2.17 (1) Å are significantly longer than the corresponding ligand–metal distances in **6** (2.14 (1) and 2.12 (1) Å), suggesting weaker metal–ligand bonding interactions in **7** relative to the μ-imidoyl species. The positions of the hydrogen atoms on C(1)–C(3) and on nitrogen are calculated by using the program Hydro[25] and are entirely consistent with the $^1H$ NMR data obtained. The dispositions of the carbonyl groups and the calculated position of the hydride (using Hydex) are very similar to those found in **6** and in related decacarbonyl derivatives of triosmium clusters containing two-atom bridging ligands.[10] The structure of compound **7** is unique, to our knowledge, in that it contains a μ-secondary aliphatic amine in which only carbon–hydrogen bond has been activated. A direct analogue of **7** has been reported for a tertiary amine.[26]

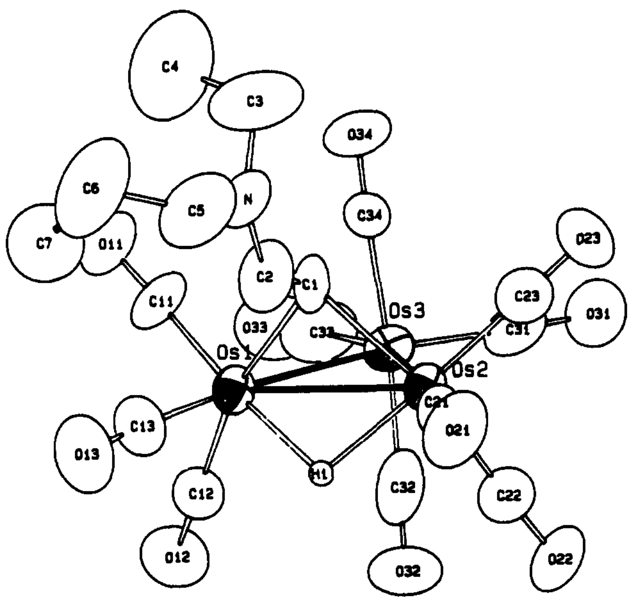

**Figure 3.** ORTEP diagram of $(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}CHCHN(CH_2CH_3)CH_2CH_2CH_3)Os_3(CO)_{10}$ (**10**) showing calculated position of the hydride. Selected distances (Å) and angles (deg) are Os(1)–Os(2) = 2.783 (1), Os(1)–Os(3) = 2.859 (1), Os(2)–Os(3) = 2.868 (1), Os(1)–C(1) = 2.23 (2), Os(2)–C(1) = 2.14 (2), N–C(2) = 1.29 (2), N–C(3) = 1.45 (3), C(1)–C(2) = 1.38 (2), N–C(5) = 1.52 (2), N–C(2)–C(1) = 130 (2), N–C(3)–C(4) = 115 (2), N–C(5)–C(6) = 114 (1), C(3)–N–C(5) = 117 (2), C(5)–C(6)–C(7) = 111 (3).

**Solid-State Structure of 10.** The solid structure of **10** is shown in Figure 3 with relevant bond distances and angles in the caption; crystal data are given in Table I. The overall structure of **10** is very similar to the previously reported $(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}CHCHN(CH_2CH_3)_2)Os_3(CO)_{10}$ (**2**)[12] and $(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}CHC(CH_3)N(H)CH(CH_3)_2)Os_3(CO)_{10}$ (**3**).[10] The osmium atoms form an isosceles triangle with one relatively short Os(1)–Os(2) bond of 2.783 (1) Å, which is almost identical with the previously reported diethyl[12] (2.785 (1) Å) and isopropyl[10] (2.787 (3) Å) analogues for the edge bridged by the organic ligand and the hydride. In contrast to the previously reported analogues there a significant asymmetry in the C(1)–Os(1) and C(1)–Os(2) bond lengths (2.23 (2) and 2.14 (2) Å, respectively, 2.15 (3) and 2.16 (3) Å in the diethyl analogue[12]; 2.10 (2) and 2.13 (2) Å in the isopropyl analogue[10]). This asymmetry may be the result of steric crowding induced by the bending back of the *n*-propyl group (Figure 3), resulting in the apparent crossover in isomer population observed for **10** and the small hydride–hydrogen couplings in the syn isomers, since this coupling should be very sensitive to the angle between the C(1)–H bond vector and the Os(1)–Os(2)–H(1) plane. The C(1)–C(2) bond length of 1.38 (2) Å (1.42 (3) Å in the diethyl analogue[12] and 1.45 (3) Å in the isopropyl analogue[10]) implies some double-bond character consistent with a fixed trans orientation of the hydrogens on C(1) and C(2). It is possible that in solution that is hindered rotation around this bond giving rise to the large vicinal coupling between these hydrogens (~14 Hz) in the $^1H$ NMR spectrum. The effective atomic number rule requires the ligand in **10** to be a three-electron donor, thus requiring one metal–carbon σ bond and one metal–carbon carbenoid bond with the metal-bound carbon bearing a formal negative charge. Alternatively, the metal ligand bonding framework can be viewed as two metal–carbon σ bonds with the triosmium cluster bearing a formal negative charge. The latter description seems to

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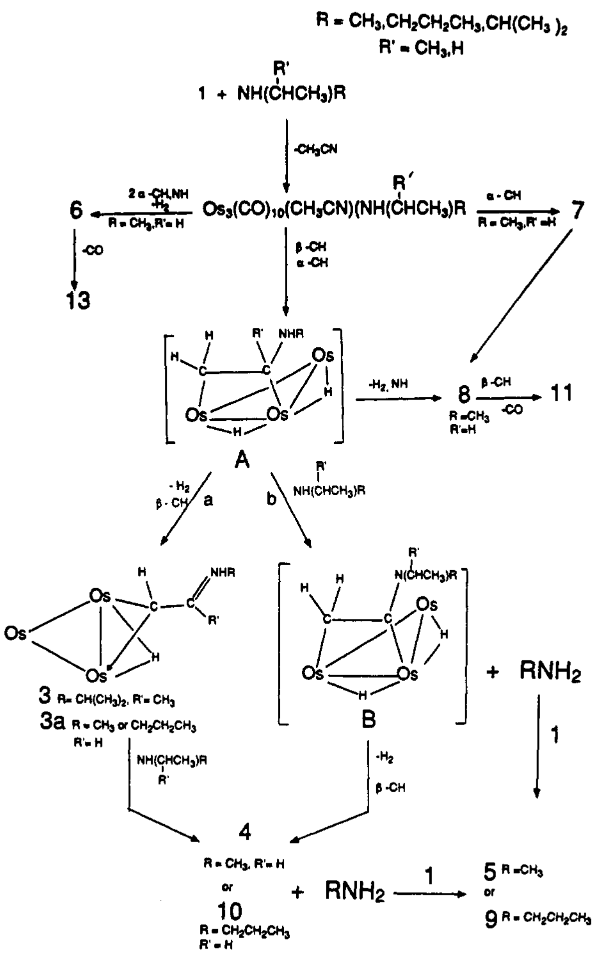
(23) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, *2509*.

(24) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1978**, *17*, 1969.

(25) Frenz, B. A. The Enraf-Nonius CAD4 SDP—A Real-time System for Concurrent X-Ray Data Collection and Crystal Structure Determination. In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R., vanKonigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

(26) Adams, R. D.; Babin, J. E. *Organometallics* **1988**, *7*, 963.

**Scheme II**



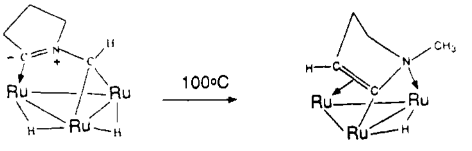
be born out by the relatively low values of the carbonyl stretching frequencies in **10** and related compounds[27] compared with other decacarbonyl triosmium clusters (about 5–15 cm$^{-1}$ lower). The expected position of the hydride ligand (Figure 3) was calculated by using Hydex,[23] a potential energy minimum positioning program, and the hydride position is virtually identical with that found in the diethyl analogue, which was actually located.[12] The N–C(2) bond length of 1.29 (2) Å is consistent with a high degree of double-bond character for this bond while the N–C(3) and N–C(5) bond lengths of 1.45 (3) and 1.52 (2) Å are consistent with these being single bonds.

## Discussion

By using the mixed amines, certain aspects of the previously observed reactivity patterns of secondary aliphatic amines with **1** have been further elucidated. First of all, the isolation of primary-amine N–H oxidative addition products **5** and **9** clearly points to the fact that the C–N coupling products **4** and **10** arise from disproportionation of a secondary amine into a primary and tertiary amine. Although we do not know the exact structure of the intermediate from which this disproportionation takes place, the isolation of ($\mu$-H)($\mu$-$\eta^1$-CHC(CH$_3$)N(H)CH(CH$_3$)$_2$)-Os$_3$(CO)$_{10}$ (**3**) from the reaction of **1** with diisopropylamine[10] suggests that nucleophilic attack at a more sterically accessible secondary-amine triosmium derivative such as **3a** (Scheme II, pathway a) could lead to **4** and **10** plus primary amine, which then reacts with **1** to give **5** and **9**. Alternatively, amine disproportionation could take place earlier in the reaction from an intermediate such as A (Scheme II, pathway b), with **3** being formed only when transamination is blocked by steric encumbrance in A. Although we do not know the sequence of carbon–hydrogen and carbon–nitrogen activation processes leading to **3a**, as yet it is significant that only C$_2$-vinylidenes such as those in **4** and **10** are found in the coupling products **4** and **10**. This points to the possible importance of $\beta$-activation in the early stages of the reaction. Thus, it is not possible in the case of methylethylamine to form a coupling product by activation of the methyl group alone. In the *n*-propylethylamine it is possible that $\beta$-activation is sterically precluded on the *n*-propyl group by the presence of the $\gamma$-methyl. This is supported by the fact that with di-*n*-propylamine, **1** reacts to give only $\alpha$-carbon activation, leading to products structurally analogous to **6**.[10] Furthermore, the reaction of pyrrolidine with **1** where the $\beta$-carbon–hydrogen bonds are tied back also leads to only $\alpha$-carbon–hydrogen bond activation products related to **6** and no carbon–nitrogen coupling.[10]

The formation of an intermediate such as **3a** (which could lead to **4**, **5**, **9**, and **10** (Scheme II, pathway a)) is the result of two $\beta$- and one $\alpha$-carbon–hydrogen bond activations. The formation of **6** is the result of two $\alpha$-carbon–hydrogen and one nitrogen–hydrogen bond activations, while formation of **8** is the result of one $\beta$-, one $\alpha$-, and one nitrogen–hydrogen bond activation. All of these compounds (i.e. **3a**, **6**, **8**) have in common the loss of 1 mol of H$_2$ from the amine and formation of a hydride ligand. It seems reasonable therefore to propose that these different products or intermediates are differentiated in the early stages of the reaction by the sequence and/or efficacy of carbon–hydrogen and nitrogen–hydrogen bond activation.

The isolation of compound **7**, which is the result of only one $\alpha$-carbon–hydrogen bond activation on a methyl, is unique in all the amine reactions with **1** investigated so far and points to kinetic stability of species containing primary hydrogens on metal-bound carbons. Similar results were observed in reactions of tertiary amines with Ru$_3$(CO)$_{12}$.[20] Although we do not understand the reasons for this kinetic stability toward further carbon–hydrogen or carbon–nitrogen bond activation, the thermolysis of **7** supports this idea. Thus we propose that the lowest energy process in the thermolysis of **7** is reductive elimination of the carbon hydrogen bond similar to that observed in a related ruthenium system[20] (eq 11). In the absence of excess amine the coordinatively unsaturated amine complex gives **8**, which under the elevated temperature required for the reductive elimination goes on to form **11**. In the presence of excess amine reductive elimination to give an amine complex leads to the coupling product **4**. This in turn implies that perhaps a common intermediate resulting from the activation of one $\beta$- and one $\alpha$-carbon–hydrogen bond such as A is formed (Scheme II, pathway b), which then goes on to form **4** or **8** depending on whether a second molecule of amine is available, rather than the amine disproportionation proceeding through **3a** as proposed above. We cannot, at present, delineate between these possibilities, but investigations of these reactions at



(11)

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(27) Deeming, A. J.; Nuel, D.; Powell, N. I.; Whittaker, C. *J. Chem. Soc., Chem. Commun.* **1990**, *68*. Deeming, A. J.; Kabir, S. E.; Nuel, D.; Powell, N. I. *Organometallics* **1989**, *8*, 717. Henrick, K.; McPartlin, M.; Deeming, A. J.; Hasso, S.; Manning, P. J. *J. Chem. Soc., Dalton Trans.* **1982**, *899*.

lower temperatures to detect earlier intermediates are underway in our laboratories.

The sequence of reactions in Scheme II should be considered schematic rather than mechanistic at present, but the chemistry reported here is distinctly different from the carbene-based catalytic transalkylations observed for tertiary amines with complexes such as $(\mu\text{-H})_2(\mu_3\text{-S})(\eta^1\text{-C(H)N(CH}_3)_2)Os_3(CO)_8$ at 145 °C by Adams et al.[28] The chemistry reported here is best understood in terms of binuclear interactions of the triosmium cluster with the amine ligand and results in disproportionation of the secondary amine. The chemistry observed by Adams et al.[28] is best understood in terms of interactions of the incoming amine with only the carbene-bound osmium atom and results in transalkylation rather than disproportionation.

## Experimental Section

**General Considerations.** Reactions were performed under a dry nitrogen atmosphere. Dichloromethane was distilled from $CaH_2$ and benzene from sodium benzophenone ketyl prior to use. Methylethylamine (Aldrich) and *n*-propylethylamine (Alfa) were dried over molecular sieves. Water from $(CH_3)_3NO\cdot 2H_2O$ was removed by using a Dean-Stark apparatus with benzene as a solvent. The starting cluster $(CH_3CN)_2Os_3(CO)_{10}$ was prepared according to published procedures.[29] Infrared spectra were recorded on a PE-1420 spectrophotometer. $^1H$ NMR spectra were recorded on an IBM-NR80, a JOEL-GX270/89, or a Bruker-AM400 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, New York, NY.

**Reaction of $(CH_3CN)_2Os_3(CO)_{10}$ with $CH_3CH_2N(H)CH_3$ in $CH_2Cl_2$ at 25 °C: Synthesis of Clusters 4–8.** Methylethylamine (0.184 $\mu$L, 2.15 mmol) was added to a dichloromethane (50 mL) solution of $(CH_3CN)_2Os_3(CO)_{10}$ (0.400 g, 0.429 mmol), and the reaction mixture was allowed to stir at 25 °C in the dark for 24 h. The solvent was rotary evaporated, and the residue was dissolved in a minimum volume of $CH_2Cl_2$ and chromatographed on silica gel TLC plates. Elution with a hexane/$CH_2Cl_2$ mixture (5:1, v/v) gave five bands. The fastest and the slowest moving bands gave $(\mu\text{-H})_2Os_3(CO)_{10}$ (0.018 g, 5%) and $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$ (0.040 g, 11%). The $^1H$ NMR spectrum of the second and third band showed each to be a mixture of two compounds. The fourth (orange) band gave $(\mu\text{-H})(\mu\text{-}\eta^1\text{-CHCHN(CH}_3)\text{CH}_2\text{CH}_3)Os_3(CO)_{10}$ (**4**) (0.060 g, 15%) as orange crystals from hexane/$CH_2Cl_2$ at −20 °C. Rechromatography of the second band eluting several times with hexane, gave two bands from which the clusters $(\mu\text{-H})(\mu\text{-}\eta^1\text{-HNCH}_3)Os_3(CO)_{10}$ (**5**) (0.031 g, 8%) and $(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH}_3\text{C}{=}\text{NCH}_3)Os_3(CO)_{10}$ (**6**) (0.007 g, 2%) were isolated as yellow crystals from hexane/$CH_2Cl_2$ at −20 °C. The third band on recrystallization from hexane/$CH_2Cl_2$ at −20 °C gave $(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH}_3\text{CH}_2\text{N(H)CH}_2)Os_3(CO)_{10}$ (**7**) (0.020 g, 5%) as yellow crystals. Repeated recrystallization of the crystals obtained from the mother liquor gave $(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH}_3\text{N}{=}\text{CHCH}_2)Os_3(CO)_{10}$ (**8**) (0.008 g, 2%) as yellow crystals.

**Analytical Data. Compound 4.** IR ($\nu$(CO), cyclohexane): 2090 (w), 2057 (2), 2045 (s), 2035 (m), 2009 (s), 1992 (s), 1986 (m), 1977 (w), 1963 (s) cm$^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): four isomers (isomer A or C, 64%) 7.14 (d, 1 H, $J_{H-H}$ = 13.7 Hz), 4.74 (dd, 1 H, $J_{H-H}$ = 13.7 Hz, $J_{H-H}$ = 2.4 Hz), 3.35 (q, 2 H, $J_{H-H}$ = 7.3 Hz), 2.95 (s, 3 H), 1.28 (t, 3 H, $J_{H-H}$ = 7.3 Hz), −16.81 (d, 1 H, $J_{H-H}$ = 2.4 Hz) ppm; (isomer A or C, 32%) 7.08 (d, 1 H, $J_{H-H}$ = 13.7 Hz), 4.81 (dd, 1 H, $J_{H-H}$ = 13.7 Hz, $J_{H-H}$ = 2.4 Hz), 3.35 (q, 2 H, $J_{H-H}$ = 7.3 Hz), 3.03 (s, 3 H), 1.29 (t, 3 H, $J_{H-H}$ = 7.3 Hz), −16.72 (d, 1 H, $J$ = 2.4 Hz) ppm; (isomer B or D, 3%) 8.67 (d, 1 H, $J_{H-H}$ = 14.4 Hz), 5.03 (dd, 1 H, $J_{H-H}$ = 14.4 Hz, $J_{H-H}$ = 1.9 Hz), −16.00 (d, 1 H, $J_{H-H}$ = 1.9 Hz) ppm; (isomer B or D, 1%) 8.61 (d, 1 H, $J_{H-H}$ = 14.3 Hz), 5.01 (dd, 1 H, $J_{H-H}$ = 14.3, $J_{H-H}$ = 14.3 Hz, $J_{H-H}$ = 1.5 Hz), −16.07 (d, 1 H, $J_{H-H}$ = 1.5 Hz). The methyl and ethyl resonances of the minor pair overlap with the methyl and ethyl resonances of the major isomer pair. Anal. Calcd for $C_{15}H_{11}NO_{10}Os_3$: C, 19.25; H, 1.19; N, 1.50. Found: C, 19.62; H, 1.19; N, 1.51.

**Compound 5.** See ref 15.

**Compound 6.** IR ($\nu$(CO), cyclohexane): 2100 (w), 2058 (vs), 2047 (s), 2019 (vs), 2000 (vs), 1998 (sh), 1986 (s), 1973 (w) cm$^{-1}$. $^1H$ NMR ($CDCl_3$, 80 MHz): 3.27 (s, 3 H), 2.15 (s, 3 H), −15.16 (s, 1 H) ppm. Anal. Calcd for $C_{13}H_7NO_{10}Os_3$: C, 17.20; H, 0.78; N, 1.54. Found: C, 17.58; H, 0.74; N, 1.57.

**Compound 7.** IR ($\nu$(CO), cyclohexane): 2098 (w), 2059 (vs), 2043 (s), 2018 (s), 1988 (s), 1982 (s), 1969 (w) cm$^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): 3.04 (m, 1 H), 2.27 (m, 1 H), 2.24 (s, br, 1 H), 1.70 (m, 2 H), 0.12 (t, 3 H, $J_{H-H}$ = 7.2 Hz), −15.93 (d, 1 H, $J_{H-H}$ = 3.7 Hz) ppm. Anal. Calcd for $C_{13}H_9NO_{10}Os_3$: C, 17.16; H, 1.00; N, 1.54. Found: C, 16.93; 0.091; N, 1.48.

**Compound 8.** IR ($\nu$(CO), cyclohexane): 2098 (w), 2057 (vs), 2045 (vs), 2081 (vs), 1997 (m), 1991 (s), 1985 (sh), 1969 (w) cm$^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): 9.07 (s, 1 H), 3.63 (s, 3 H), 2.32 (d, 1 H, $J_{H-H}$ = 20.5 Hz), 1.68 (d, 1 H, $J_{H-H}$ = 20.5 Hz), −14.22 (s, 1 H) ppm. Anal. Calcd for $C_{13}H_7NO_{10}Os_3$: C, 17.20; H, 0.78; N, 1.54. Found: C, 17.35; H, 0.85; N, 1.58.

**Reaction of $(CH_3CN)_2Os_3(CO)_{10}$ (1) with Methylethylamine at 40–45 °C in Benzene.** In a three-necked, round-bottom flask equipped with a reflux condenser were combined $(CH_3CN)_2Os_3(CO)_{10}$ (0.400 g, 0.429 mmol), methylethylamine (0.184 $\mu$L, 2.15 mmol), and 150 mL of benzene. The reaction solution was heated at 40–45 °C for 6 h. The color changed from yellow to orange. A workup similar to that above followed by similar chromatographic separations and recrystallization procedures gave the following compounds: $(\mu\text{-H})_2Os_3(CO)_{10}$ (0.018 g, 5%), **4** (0.080 g, 20%), **5** (0.007 g, 2%), **6** (0.038 g, 10%), **7** (0.025 g, 6%), **8** (0.007 g, 2%), and $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$ (0.047 g, 10%).

**Reaction of $(CH_3CN)_2Os_3(CO)_{10}$ (1) with *n*-Propylethylamine at 25 °C.** A solution of $(CH_3CN)_2Os_3(CO)_{10}$ (0.220 g, 0.236 mmol) and $CH_3CH_2N(H)CH_2CH_2CH_3$ (0.103 g, 1.18 mmol) in dichloromethane (50 mL) was stirred at 25 °C for 24 h. After removal of solvent and excess ligand under reduced pressure, the residue was chromatographed on silica TLC plates, eluting with hexane/$CH_2Cl_2$ (10:3, v/v) to give four bands. The first and the fourth bands gave $(\mu\text{-H})_2Os_3(CO)_{10}$ (0.010 g, 5%) and $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$ (0.025 g, 15%). The third (orange) band gave $(\mu\text{-H})(\mu\text{-}\eta^1\text{-CHCHN(CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3)Os_3(CO)_{10}$ (**10**) (0.034 g, 15%) as red crystals from hexane/$CH_2Cl_2$ at −20 °C and the second (yellow) band gave $(\mu\text{-H})(\mu\text{-}\eta^1\text{-N(H)CH}_2\text{CH}_2\text{CH}_3)Os_3(CO)_{10}$ (**9**) (0.028 g, 13%) as yellow crystals from hexane/$CH_2Cl_2$ at −20 °C.

**Analytical Data. Compound 10.** IR ($\nu$(CO), hexanes): 2090 (m), 2046 (vs), 2036 (s), 2010 (vs), 1993 (s), 1978 (w), 1964 (s) cm$^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): four isomers (isomer A or B, 40%) 7.14 (d, 1 H, $J_{H-H}$ = 14.03 Hz), 4.82 (d, 1 H, $J_{H-H}$ = 14.3 Hz), 3.45 (m, 1 H), 3.34 (m, 1 H), 3.27 (m, 1 H), 3.22 (m, 1 H), 1.77 (m, 1 H), 1.69 (m, 1 H), 1.29 (m, 3 H), 0.98 (m, 3 H), −16.70 (s, 1 H) ppm; (isomer A or B, 40%) 7.11 (d, $J_{H-H}$ = 14.2 Hz), 4.80 (dd, 1 H, $J_{H-H}$ = 14.2 Hz, $J_{H-H}$ = 3.3 Hz) 3.45 (m, 1 H), 3.34 (m, 1 H), 3.27 (m, 1 H), 3.22 (m, 1 H), 1.77 (m, 1 H), 1.69 (m, 1 H), 1.29 (m, 3 H), 0.98 (m, 3 H), −16.69 (d, 1 H, $J_{H-H}$ = 3.3 Hz) ppm; (isomer C or D, 8%) 8.69 (d, 1 H, $J_{H-H}$ = 14.5 Hz), 5.08 (d, 1 H, $J_{H-H}$ = 14.5 Hz), 3.45 (m, 1 H), 3.34 (m, 1 H), 3.27 (m, 1 H), 3.22 (m, 1 H), 1.77 (m, 1 H), 1.69 (m, 1 H), 1.29 (m, 3 H), 0.98 (m, 3 H), −15.99 (s, 1 H) ppm; (isomer C or D, 12%) 8.62 (d, 1 H, $J_{H-H}$ = 14.6 Hz), 5.07 (dd, 1 H, $J_{H-H}$ = 14.6 Hz, $J_{H-H}$ = 2.1 Hz), 3.45 (m, 1 H), 3.34 (m, 1 H), 3.27 (m, 1 H), 3.22 (m, 1 H), 1.77 (m, 1 H), 1.69 (m, 1 H), 1.29 (m, 3 H), 0.98 (m, 3 H), −15.98 (d, 1 H, $J_{H-H}$ = 2.1 Hz) ppm. Anal. Calcd for $C_{17}H_{15}NO_{10}Os_3$: C, 21.18; H, 1.57; N, 1.45. Found: C, 21.45; H, 1.65; N, 1.57.

**Compound 9.** IR ($\nu$(CO), hexane): 2100 (w), 2062 (vs), 2048 (s), 2019 (vs), 2000 (s), 1998 (sh), 1988 (s), 1976 (w) cm$^{-1}$. $^1H$ NMR ($CDCl_3$, 270 MHz): 4.13 (s, br, 1 H), 2.80 (m, 2 H), 1.58 (m, 2 H), 0.95 (t, 3 H, $J_{H-H}$ = 3.3 Hz), −14.92 (d, 1 H, $J_{H-H}$ = 3.3 Hz) ppm. Anal. Calcd for $C_{13}H_9NO_{10}Os_3$: C, 17.15; H, 1.08; N, 1.54. Found: C, 17.36; H, 1.25; N, 1.50.

**Thermolysis of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH}_3\text{CH}_2\text{N(H)CH}_2)Os_3(CO)_{10}$ (7).** A solution of compound **7** (0.025 g) in heptane (15 mL) was heated

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under reflux for 6 h. The solvent was removed under reduced pressure and the residue chromatographed on silica TLC plates, eluting with hexane/$CH_2Cl_2$ (5:1, v/v) to give two bands. The fast moving band gave $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-CHCH=NCH}_3)Os_3(CO)_9$ (**11**) (0.006 g, 40% based on consumed **7**). The second base gave unreacted **7** (0.010 g).

**Analytical Data. Compound 11.** IR ($\nu$(CO), hexane): 2099 (w), 2071 (s), 2044 (vs), 2015 (vs), 2000 (m), 1989 (m), 1972 (m) $cm^{-1}$. $^1$H NMR ($CDCl_3$, 80 MHz): 10.31 (d, 1 H, $J_{H-H}$ = 4.9 Hz), 4.15 (d, 1 H, $J_{H-H}$ = 4.9 Hz), 3.18 (s, 3 H), −14.14 (s, 1 H), −14.31 (s, 1 H) ppm.

**Thermolysis of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH}_3\text{N=CHCH}_2)Os_3(CO)_{10}$ (8).** A solution of compound **8** (0.009 g) in heptane (10 mL) was refluxed for 2 h. TLC workup as above gave $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-CHCH=NCH}_3)Os_3(CO)_9$ (**11**) (0.004 g, 67% based on the amount of **8** consumed) and unreacted **8** (0.003 g).

**Attempted Thermolysis of $(\mu\text{-H})(\mu\text{-}\eta^1\text{-CHCHN(CH}_3)\text{CH}_2\text{CH}_3)Os_3(CO)_{10}$ (4).** A solution of compound **4** (0.100 g) in heptane (100 mL) was heated to reflux for 4 h. TLC separation as above gave only **4**.

**Reaction of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH}_3\text{CH}_2\text{N(H)CH}_2)Os_3(CO)_{10}$ (7) with $CH_3CH_2N(H)CH_3$.** A solution of **7** (0.015 g, 0.016 mmol) and $CH_3CH_2N(H)CH_3$ (6 $\mu$L, 0.068 mmol) in cyclohexane was refluxed for 1 h. The solvent was removed under reduced pressure and the residue chromatographed on silica TLC plates. Elution with hexane/$CH_2Cl_2$ (10:3, v/v) gave two main bands from which the clusters $(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH}_3\text{CH}_2\text{N(H)CH}_2)Os_3(CO)_{10}$ (**7**) (0.006 g) and $(\mu\text{-H})(\mu\text{-}\eta^1\text{-CHCHN(CH}_3)\text{CH}_2\text{CH}_3)Os_3(CO)_{10}$ (**4**) (0.005 g, 67% based on the amount of **7** consumed) were isolated.

**Thermolysis of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH}_3\text{C=NCH}_3)Os_3(CO)_{10}$ (6).** A solution of compound **6** (0.030 g) in octane (15 mL) was refluxed for 12 h. The solvent was removed under reduced pressure, and the residue was chromatographed as above to give two bands. The fast moving band gave unreacted **6** (0.005 g), while the second band gave $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-CH}_3\text{C=NCH}_3)Os_3(CO)_9$ (**13**) (0.021 g, 88% based on consumed **6**) as yellow crystals from hexane/$CH_2Cl_2$ at −20 °C.

**Analytical Data. Compound 13.** IR ($\nu$(CO), hexane): 2089 (m), 2062 (vs), 2037 (vs), 2011 (vs), 1997 (m), 1990 (s), 1978 (sh), 1965 (w) $cm^{-1}$. $^1$H NMR ($CDCl_3$, 80 MHz): 3.64 (s, 3 H), 2.75 (s, 3 H), −17.63 (s, 1 H) ppm. Anal. Calcd for $C_{12}H_7NO_9Os_3$: C, 16.38; H, 0.80; N, 1.59. Found: C, 16.45; H, 0.95; N, 1.65.

**X-ray Structure Determination of 6, 7, and 10.** Crystals of **6**, **7**, and **10** for X-ray examination were obtained from saturated solutions of each in dichloromethane/hexane solvent systems at −20 °C. Suitable crystals of each were mounted on glass fibers, placed in a goniometer head on an Enraf-Nonius CAD4 diffractometer, and centered optically. Unit cell parameters and an orientation matrix for data collection were obtained by using the centering program in the CAD4 system. Details of the crystal data are given in Table I. For each crystal the actual scan range was calculated by scan width = scan range + 0.35 tan $\theta$ and backgrounds were measured by using the moving crystal–moving counter technique at the beginning and end of each scan. As a check on instrument and crystal stability, two representative reflections were measured every 2 h. Lorentz, polarization, and decay corrections were applied as was an empirical absorption correction based on a series of $\psi$ scans.

Each of the structures was solved by the Patterson method using SHELXS-86,[30] which revealed the positions of the metal atoms. All other non-hydrogen atoms were found by successive difference Fourier syntheses. The expected hydride positions were calculated by using the program Hydex;[23] all other hydrogens were calculated by using the program Hydro.[25] Hydrogen atom positions were included in the structure factor calculations but not refined in the final least-squares cycles. All non-hydrogen atoms were refined anisotropically except for C(7) in structure **10**, which was refined isotropically. The position of this atom could not be determined unambiguously due to apparent disorder in the *n*-propyl group, the final configuration reported being that of the most populated conformation. Final refinement parameters for each crystal are listed in Table I.

Scattering factors were taken from Cromer and Waber.[31] Anomalous dispersion corrections were those of Cromer.[32] All calculation were carried out on a DEC MicroVAX II computer using the SDP/VAX system of programs.

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**Registry No.** 4 (isomer A), 136779-32-3; 4 (isomer B), 136779-34-5; 4 (isomer C), 136779-33-4; 4 (isomer D), 136779-35-6; **5**, 76581-50-5; **6**, 136706-80-4; **7**, 136706-82-6; **8**, 136706-83-7; **9**, 136706-84-8; **10** (isomer A), 136706-79-1; **10** (isomer B), 136779-36-7; **10** (isomer C), 136779-37-8; **10** (isomer D), 136779-38-9; **11**, 136706-85-9; **13**, 136706-81-5; $(CH_3CN)_2Os_3(CO)_{10}$, 61817-93-4; $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$, 63373-90-0; $(\mu\text{-H})_2Os_3(CO)_{10}$, 41766-80-7; methylethylamine, 624-78-2; *n*-propylethylamine, 20193-20-8.

**Supplementary Material Available:** Tables of atomic positions for **6**, **7**, and **10** (Tables 2–4), anisotropic displacement factors (Tables 5–7), and complete bond distances and angles (Tables 8–10) (21 pages); listings of observed and calculated structure factors (Tables 11–13) (91 pages). Ordering information is given on any current masthead page.

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[31] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

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