Reactions of Tertiary Amines with Trinuclear Clusters. 3.[†]
Reactions of *N*-Methylpyrrolidine with Ru₃(CO)₁₂ and Os₃(CO)₁₀(CH₃CN)₂

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The reaction of N-methylpyrrolidine with $Ru_3(CO)_{12}$ in the presence of the three reaction promoters $Fe_2(CO)_4(\mu\text{-}SCH_2CH_3)_2(P(C_6H_5)_3)_2$ (iron dimer), $(CH_3)_3NO$, and $(C_6H_5)_2C\dot{=}O^-Na^+$ was studied in the temperature range 65–80 °C. In the presence of the iron dimer catalyst, in hexane at 68 °C, one major trinuclear product isolated in 15–20% yield proved to be $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CH\text{-}\overline{N\!=\!CCH_2CH_2CH_2})$ (1). In the presence of trimethylamine N-oxide or sodium benzophenone ketyl in benzene at 80 °C a different trinuclear product isolated in 30% yield, $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\overline{N\!=\!CCH_2CH_2CH_2})$ (2), is a structural analogue of the major product obtained from the reaction of triethylamine with $Ru_3(CO)_{12}$ in the presence of the above mentioned diiron reaction promoter. A minor product isolated in the reaction of $Ru_3(CO)_{12}$ with N-methylpyrrolidine in the presence of $(CH_3)_3NO$ is the tetranuclear η^1-carbene species $(\mu\text{-}H)_4Ru_4\text{-}(CO)_{11}(\eta^1\text{-}\overline{C\!=\!N(CH_3)CH_2CH_2CH_2})$ (3). Thermolysis of 1 in heptane at 100 °C gave moderate yields of the compound $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}\overline{CH_3N\text{-}CH\!=\!CHCH_2CH_2})$ (4), in which two hydrogens have been transferred to the methyne carbon and further rearrangement of the ligand has occurred. The lightly stabilized cluster $Os_3(CO)_{10}(CH_3CN)_2$ was reacted with N-methylpyrrolidine in refluxing benzene to give $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{CH_3N\!=\!CC(H)CH_2CH_2})$ (5) and $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}\overline{CH_3N\!=\!C(H)CCH_2CH_2})$ (6). Compounds 1–5 were characterized by X-ray diffraction methods in the solid state, and 1–6, by ^1H NMR and infrared spectroscopy in solution. Compound 1 crystallizes in the monoclinic space group $P2_1/n$, with $a = 9.015$ (2) Å, $b = 16.759$ (4) Å, $c = 13.266$ (3) Å, and $\beta = 95.98$ (2)°. Least-squares refinement of 3822 observed reflections gave a final agreement factor of $R = 0.048$ ($R_w = 0.055$). Compound 2 crystallizes in the monoclinic space group $P2_1/m$, with $a = 7.657$ (1) Å, $b = 14.910$ (3) Å, $c = 8.172$ (2) Å, and $\beta = 106.32$ (2)°. Least-squares refinement of 1938 observed reflections gave a final agreement factor of $R = 0.026$ ($R_w = 0.031$). Compound 3 crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.198$ (1) Å, $b = 14.229$ (2) Å, $c = 16.512$ (3) Å, and $\beta = 102.34$ (1)°. Least-squares refinement of 2033 observed reflections gave a final $R = 0.025$ ($R_w = 0.036$). Compound 4 crystallizes in the monoclinic space group $P2_1/c$, with $a = 8.858$ (2) Å, $b = 13.455$ (5) Å, $c = 18.400$ (4) Å, and $\beta = 118.70$ (2)°. Least-squares refinement of 2254 observed reflections gave a final $R = 0.043$ ($R_w = 0.045$). Compound 5 crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 11.567$ (2) Å, $b = 17.653$ (6) Å, and $c = 9.900$ (2) Å. Least-squares refinement of 2600 observed reflections gave a final $R = 0.074$ ($R_w = 0.065$).

Introduction

In our recent reports of the reactions of tertiary amines with $Ru_3(CO)_{12}$ in the presence of the substitution promoter $Fe_2(CO)_4(\mu\text{-}SCH_2CH_3)_2(P(C_6H_5)_3)_2$ we found that products resulting from alkyl cleavage as well as alkyl coupling to the amine are formed (eq 1).[1,2] We and others formulated the hypothesis that initial carbon–nitrogen bond cleavage proceeds via amine coordination, carbon–hydrogen bond activation followed by H–N reductive elimination, and homolytic rupture of the C–N bond to form a carbene–secondary amine complex.[2,3] The subsequent formation of alkyl cleavage products could then arise via carbene dissociation, while the coupling products could result via secondary amine dissociation followed by coordination of a second molecule of tertiary amine. In order to test this hypothesis we decided to study the reaction of a cyclic amine with $Ru_3(CO)_{12}$ reasoning that carbon–nitrogen cleavage of an endocyclic C–N bond could

result in a chelate-stabilized carbene–amine complex. We report here the results of our studies on the reaction of N-methylpyrrolidine with $Ru_3(CO)_{12}$ and with $Os_3(C\text{-}O)_{10}(CH_3CN)_2$. Although we did not observe a chelate-stabilized carbene–amine complex, we did observe the formation of trinuclear complexes with the amine, prior to and after C–N bond cleavage. Even more interesting we observed a marked shift in the product distribution depending on the type of the reaction promoter used (i.e. iron dimer, trimethylamine N-oxide or sodium benzophenone ketyl). Other workers have studied the reactions of cyclic unsaturated amines such as quinolines,[4] phenanthridine,[4] pyrrole,[5a] indoles,[5b] and imidazoles[5c] with the lightly stabilized clusters $M_3(CO)_{10}(CH_3CN)_2$ (M = Ru,
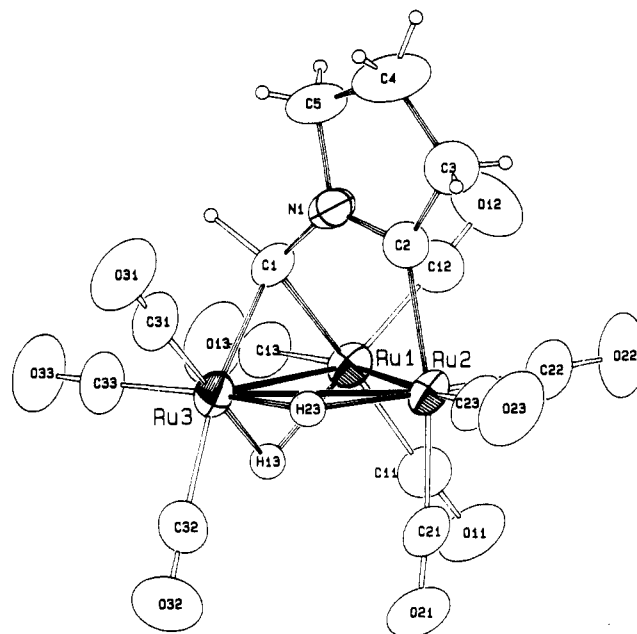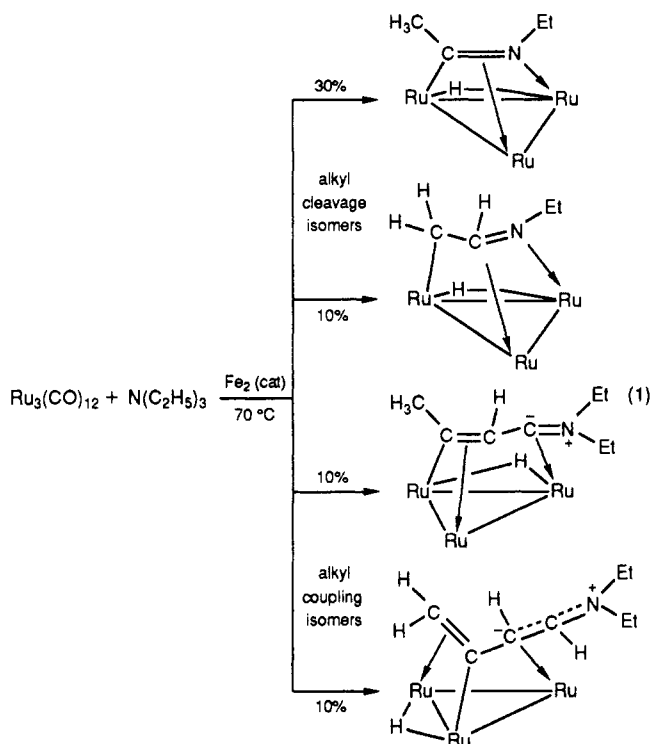
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Figure 1. Solid-state structure of compound 1. All hydrogen positions shown are calculated.

Os); however, only C–H activation of the sp^2 carbons was observed. More recently Adams et al. have reported facile carbon–nitrogen bond cleavage in the reactions of bis-(dimethylamino)methane with a variety of osmium clusters.[6] The C–N bond activation process observed for ordinary tertiary aliphatic amines under relatively mild reaction conditions seems unique to ruthenium so far, as the results reported previously and here illustrate.

Results and Discussion

A. Reaction of Ru$_3$(CO)$_{12}$ and *N*-Methylpyrrolidine in the Presence of Fe$_2$(CO)$_4$(*μ*-SCH$_2$CH$_3$)$_2$(P(C$_6$H$_5$)$_3$)$_2$. When *N*-methylpyrrolidine is refluxed with Ru$_3$(CO)$_{12}$ for 12 h in hexane in the presence of a catalytic amount of Fe$_2$(CO)$_4$(*μ*-SCH$_2$CH$_3$)$_2$(P(C$_6$H$_5$)$_3$)$_2$, only one band containing trinuclear ruthenium products is obtained. The ^{1}H NMR spectrum in CDCl$_3$ of this band showed it to contain one major product (90% of the total 15–20% obtained) with two slightly broadened singlet hydride resonances at –12.16 (1) and –16.44 (1) ppm, a series of three multiplets at 2.92 (2, t, J_{HH} = 7.7 Hz), 1.76 (2, t, J_{HH} = 7.7 Hz), and 0.96 ppm (2, quintuplet), and a singlet at 5.94 (1) ppm. There were two impurities in the band, as evidenced by the presence of two singlet hydrides at –14.89 and –18.36 ppm, each integrating about 1:20 with one of the two hydride signals of the major product. The –18.36 ppm signal is due to the compound (*μ*-H)Ru$_3$(CO)$_9$($μ_3$-$η^2$-$\overline{\text{C=NCH}_2\text{CH}_2\text{CH}_2}$) (2) (vide infra). The other peak at –14.89 ppm belongs to an as yet unidentified hydride product. Repeated attempts to separate these two impurities from the major product by chromatographic methods failed. However recrystallization of the major

product band from hexane gave analytically pure (*μ*-H)$_2$Ru$_3$(CO)$_9$($μ_3$-$η^2$-$\overline{\text{CHN=CCH}_2\text{CH}_2\text{CH}_2}$) (1), whose structure was subsequently elucidated by single-crystal X-ray diffraction methods and is entirely consistent with the solution ^{1}H NMR data given above. The solid-state structure of 1 is shown in Figure 1, the crystal data are given in Table I, and selected distances and bond angles are given in Table II. The structure consists of a trimetallic core with two almost equivalent metal–metal bonds (Ru(1)–Ru(2) = 2.806 (1) Å and Ru(1)–Ru(3) = 2.796 (1) Å) and one elongated metal–metal bond (Ru-(2)–Ru(3) = 3.000 (1) Å). The locations of the two hydrides were calculated by using the potential energy minimum program Hydex.[7] The location of H(23) as almost in the plane of the ruthenium triangle is consistent with the long Ru(2)–Ru(3) distance and its location trans to CO(33) and CO(22) to fill out the approximately octahedral geometry around Ru(2) and Ru(3). Similarly, the location of H(13) is tucked down below the ruthenium triangle, placing it trans to CO(31) and CO(12), and is consistent with the shorter Ru(1)–Ru(3) distance expected for a hydride sharing the same edge as another single atom bridge.[2,8] The organic ligand must donate four electrons to the metal core in order to make 1 a saturated 48e$^-$ cluster. The bridging methyne carbon, C(1), donates two electrons via two fairly symmetric metal–carbon $σ$ bonds to Ru(1) and Ru(3) (Ru(1)–C(1) = 2.13 (1) Å and Ru(3)–C(1) = 2.12 (1) Å). Two additional electrons are donated by the quaternary zwitterionic carbon, C(2), to Ru(2) (Ru(2)–C(2) = 2.07 (1) Å). The long nitrogen to metal distances (N(1)–Ru(1) = 3.04 Å, N(1)–Ru(2) = 2.90 Å, N(1)–Ru(3) = 3.04 Å) seem to preclude any direct nitrogen–ruthenium bonding. Similarly, the short carbon–nitrogen double bond (C(2)–N(1) = 1.31 (1) Å) seems to preclude any significant $π$-bonding interaction between this bond and the metal triangle. Overall this bonding scheme, with the nonbonding heteroatom suspended over the face of a metal triangle, is unique in cluster chemistry but is reminiscent

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Table I. Crystal Data and Collection and Refinement Parameters

| compd	1	2	3	4	5
formula	$C_{14}H_9NO_9Ru_3$	$C_{12}H_7NO_9Ru_3$	$C_{16}H_{13}NO_{11}Ru_4$	$C_{13}H_9NO_9Ru_3$	$C_{15}H_93NO_{10}Os_3$
fw	638.44	624.41	800.57	638.44	933.84
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/m$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a, Å	9.015 (2)	7.657 (1)	10.198 (1)	9.858 (2)	11.567 (2)
b, Å	16.759 (4)	14.910 (3)	14.229 (2)	13.455 (2)	17.653 (6)
c, Å	13.266 (3)	8.172 (2)	16.512 (3)	18.400 (4)	9.900 (2)
α, deg	90	90	90	90	90
β, deg	95.98 (2)	106.32 (2)	102.34 (1)	118.70 (2)	90
γ, deg	90	90	90	90	90
V, Å^3	1993	895	2341	1923	2021
Z	4	2	4	4	4
D_{calc}, g/cm^3	2.13	2.31	2.27	2.17	3.07
abs coeff μ, cm^{-1}	22.5	24.9	25.4	23.3	188.9
data collect temp, °C	25 ± 1	25 ± 1	25 ± 1	25 ± 1	25 ± 1
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan limits, deg	$2 < 2\theta < 54$	$2 < 2\theta < 68$	$2 < 2\theta < 40$	$2 < 2\theta < 50$	$2 < 2\theta < 62$
scan speed, deg/min	1.2–8.3	3.0–5.5	2.5–8.2	0.8–5.5	2.5–8.2
scan range, deg	0.8	1.0	0.9	0.8	0.9
no. of data	4492	3833	2301	3473	3490
no. of data obsd	3822	1938	2033	2254	2600
no. of variables	245	124	289	244	263
R^a	0.048	0.026	0.025	0.043	0.074
R_w^b	0.055	0.031	0.036	0.045	0.065
largest shift/esd	0.0	0.0	0.0	0.0	0.25
weighting scheme	unit	$1/\sigma^2$	$1/\sigma^2$	unit	$1/\sigma^2$
highest peak in final diff map, e Å^{-3}	0.82 (18)	0.56 (10)	0.39 (14)	1.47 (14)	3.76 (51)
rel transm coeff	0.85–0.99	0.94–0.99	0.76–0.99	0.95–0.99	0.54–0.99

$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $^b R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Bond Distances (Å) and Angles (deg) for $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\overline{CHN=CCH_2CH_2CH_2})$ (1)^a

Distances

Ru1–Ru2	2.8061 (5)	N1–C1	1.441 (6)
Ru1–Ru3	2.7955 (6)	N1–C2	1.307 (6)
Ru2–Ru3	3.0005 (5)	N1–C5	1.484 (6)
Ru1–C1	2.128 (5)	C2–C3	1.473 (7)
Ru3–C1	2.123 (5)	C3–C4	1.510 (9)
Ru2–C2	2.072 (5)	C4–C5	1.473 (9)
Ru1–H13	1.85	Ru3–H13	1.85
Ru2–H23	1.85	Ru3–H23	1.85
Ru–C(CO)	1.92 (3)^b	C–O(CO)	1.13 (1)^b

Angles

Ru1–Ru2–Ru3	57.44 (1)	N1–C2–C3	109.2 (4)
Ru1–Ru3–Ru2	57.78 (1)	N1–C5–C4	103.8 (5)
Ru2–Ru1–Ru3	64.77 (1)	C2–C3–C4	105.9 (5)
C1–N1–C2	122.9 (4)	C2–N1–C5	114.1 (4)
C1–N1–C5	122.9 (4)	C3–C4–C5	106.9 (5)
		Ru–C–O(CO)	177 (2)^b

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits. ^{b} Average values.

in the way the carbons are bound to the metal of the structure of $(\mu\text{-H})_2M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CH\text{—}C=N(R)_2)$ (M = Ru, Os, R = n-Pr, i-Pr; see structure A).[2,9] It should be


A
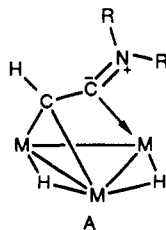
noted that the solid-state structure of 1 reveals that the ring hydrogens are magnetically inequivalent. However the ^{1}H NMR pattern for these protons shows no evidence of this. This is undoubtedly due to an edge hopping of

H(23) between the Ru(2)–Ru(3) and Ru(1)–Ru(2) edges, which is rapid on the NMR time scale at room temperature as has been previously observed for many other dihydride complexes of this type.[2,10,11]

B. Reaction of Ru₃(CO)₁₂ with N-Methylpyrrolidine in the Presence of (CH₃)₃NO and Sodium Benzophenone Ketyl. The reaction of N-methylpyrrolidine with $Ru_3(CO)_{12}$ in the presence of 1 molar equiv (with respect to $Ru_3(CO)_{12}$) of trimethylamine N-oxide in refluxing benzene for 5–6 h led to the formation of only one product $(\mu\text{-H})Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\overline{N=CCH_2CH_2CH_2})$ (2) in moderate yield (30%). The ^{1}H NMR spectrum in CDCl₃ of this product showed a singlet hydride at –18.36 (1) ppm and a set of three multiplets at 3.55 (2, t, J_{HH} = 6.6 Hz), 2.98 (2, t, J_{HH} = 7.0 Hz) and 1.85 ppm (2, m). On the basis of these ^{1}H NMR data, we assigned a structure analogous to the major product obtained from the reaction of triethylamine with $Ru_3(CO)_{12}$ (see structure B).[1] Here

B
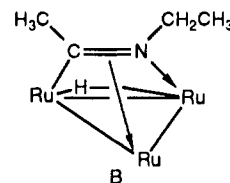
again, the apparent equivalence of the methylene protons in 2 on each ring carbon can be rationalized by invoking a windshield-wiper motion of the organic ligand over the face of the cluster coupled with an edge-hopping motion of the bridging hydride, which is rapid on the ^{1}H NMR time scale at room temperature as has been shown for structure B.[1] An analogous triruthenium complex, $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\overline{N=CCH_2CH_2CHCH_2OCH_3})$, has been

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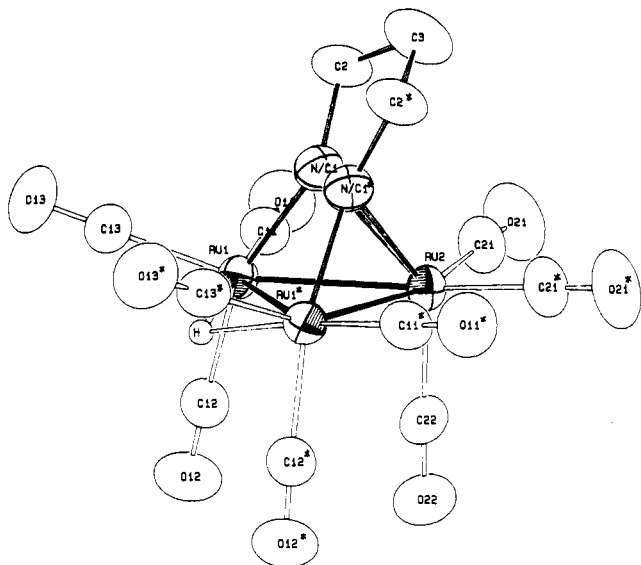(11) Evans, J.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Organomet. Chem.* 1979, 97, C16.

Figure 2. Solid-state structure of 2.

Table III. Bond Distances (Å) and Angles (deg) for
(μ-H)Ru₃(CO)₉(μ₃-η²-N̄=CCH₂CH₂C̄H₂) (2)[a]

Distances			
Ru1–Ru2	2.709 (1)	Ru1–Ru1*	3.018 (1)
Ru1–N/C1	2.07 (1)	Ru2–N/C1	2.26 (1)
Ru3–H	1.85	N/C1–C2	1.50 (1)
N/C1–N/C1*	1.34 (1)	Ru–C(CO)	1.91 (3)[b]
C2–C2	1.54 (2)	C–O(CO)	1.13 (1)[b]

Angles			
Ru1–Ru2–Ru1*	67.7 (2)	N/C1–C2–C3	103.4 (4)
Ru2–Ru1–Ru1*	56.1 (2)	C2–N/C1–N/C1*	111.2 (5)
C2–C3–C2*	103.7 (5)	Ru–C–O(CO)	178.6 (6)[b]

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Average values.

obtained from the reaction of 2-(methoxymethyl)-pyrrolidine and ruthenium carbonyl by using sodium benzophenone ketyl as the reaction promoter.[12] Variable-temperature ¹H NMR studies at 400 MHz in CD₂Cl₂ (−80 to +25 °C) did reveal the expected inequivalence of the ring protons, and from this data we were able to estimate a $\Delta G^{\ddagger}$ = 43 ± 2 kJ/mol at −50 °C for the windshield-wiper motion in 2.

In order to verify this structural assignment for 2, we undertook a single-crystal X-ray diffraction study. The structure of 2 is shown in Figure 2, the crystal data are summarized in Table I, and selected distances and bond angles are given in Table III. The molecule lies on a crystallographic mirror plane but cannot possess mirror symmetry. Molecular enantiomers in approximately equal amounts are present in the crystal, and our results represent disordered pyrrolidine moieties with refinement based on equal populations of N and C(1) in each of the ring positions bonded to Ru(1). Compound 2 consists of an isosceles triangle of ruthenium atoms (Ru(2)–Ru(1) = Ru(2)–Ru(1*) = 2.709 (1) Å) with one elongated metal–metal bond (Ru(1)–Ru(1*) = 3.018 (1) Å) where the hydride is located (Hydex[7]). The location of the hydride is very similar to the corresponding hydride in structure B, which was actually located by Fourier difference mapping.[1] The overall disposition of the organic ligand on the face of the cluster in 2 is the same as found for B with the only differences being a slightly shorter ring–metal bond (Ru-

(1)–N/C(1) = 2.07 (1) Å in 2 and Ru–N = 2.09 (1) Å in B) and slightly longer Ru–Ru distance (Ru(1)Ru(1*) = 3.018 (1) Å in 2 and Ru(1)–Ru(3) = 2.92 (1) Å in B).[1] It is interesting to note that the pyrrolidine ring in 2 is distinctly puckered, while this ring in 1 is virtually planar.

The yields reported here for 2 have been optimized, and many reactions were performed by using different ratios of trimethylamine N-oxide to cluster (0.5 to 2), different amine to cluster ratios (2 to 20), different temperatures (40–80 °C), different reaction times (1–6 h), and different solvents (CH₂Cl₂, THF, and C₆H₆). In none of these reactions was any of 1 or any other product but 2 detected. As mentioned above, trace amounts of 2 were observed in the iron dimer reaction, but 1 was always the dominant product under shorter or longer reaction times (6–24 h). Additionally, 2 was the only product obtained in approximately 30% yield when the reaction of N-methylpyrrolidine with Ru₃(CO)₁₂ was performed in benzene by using a THF solution of sodium benzophenone ketyl as a substitution promoter. Reactions performed in refluxing THF with sodium benzophenone ketyl or trimethylamine N-oxide gave only red intractable gums and no isolable products.

When N-methylpyrrolidine is reacted with Ru₃(CO)₁₂, with (CH₃)₃NO as a promoter for shorter periods in refluxing dry benzene (3–4 h), an additional compound, (μ-H)₄Ru₄(CO)₁₁(η¹-C̄=N(CH₃)CH₂CH₂C̄H₂) (3), was obtained as a minor product in ~5% yield. The ¹H NMR spectrum (80 MHz) of 3 at room temperature shows a sharp singlet in the hydride region at −17.76 (4) ppm, a singlet at 3.58 (3) ppm, two triplets at 3.84 (2, J_{H-H} = 6.9 Hz) and 3.26 ppm (2, J_{H-H} = 7.0 Hz), and a quintet at 2.00 ppm (2, J_{H-H} = 7.0 Hz). The ¹H NMR spectrum (400 MHz) of 3 at −90 °C shows three broadened singlet hydride resonances at −16.48 (1), −17.20 (1), and −18.29 (2) ppm. The hydrides in this analogue of H₄Ru₄(CO)₁₂ are remarkably rigid compared with the parent compound.[13a] The only cases reported where hydride mobility has been frozen out on the NMR time scale are the phosphine-substituted derivatives of H₄Ru₄(CO)₁₂.[13b] Apparently even relatively minor changes in charge distribution and/or symmetry are enough to significantly change hydride mobility in polynuclear complexes.

In order to elucidate the structure in 3, a single-crystal X-ray diffraction study was done. The structure of 3 is shown in Figure 3, the crystal data are given in Table I, and selected bond distances and angles are given in Table IV. Compound 3 exists as a tetrahedron of ruthenium atoms with four elongated metal–metal bonds (Ru(1)–Ru(2) = 3.02 (1) Å, Ru(1)–Ru(3) = 2.98 (1) Å, Ru(1)–Ru(4) = 2.99 (1) Å, and Ru(2)–Ru(3) = 2.91 (1) Å) and two nearly equal shorter metal–metal bonds (Ru(2)–Ru(4) = Ru(3)–Ru(4) = 2.78 (1) Å). The locations of the hydrides were calculated with the program Hydex.[7] The position of the hydride ligands is consistent with the elongated metal–metal bonds, and their location trans to either carbonyl ligands or the N-methylpyrrolidine ligand maintain approximate octahedral geometry around the ruthenium atoms. The organic ligand must donate two electrons to the metal core in order to make 3 a saturated 60e⁻ cluster. The two electrons are donated by a carbenoid carbon, C(1), to Ru(1) (C(1)–Ru(1) = 2.04 (1) Å). All nitrogen–carbon and carbon–carbon bond distances are normal single bonds

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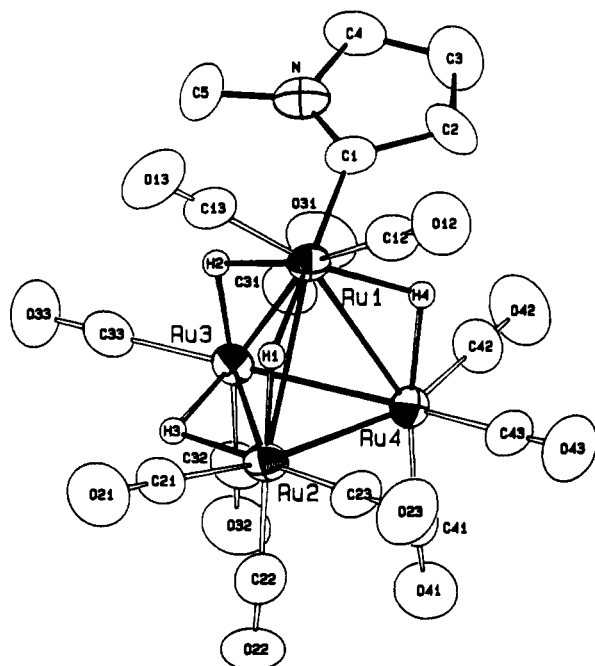
Figure 3. Solid-state structure of 3. All hydrogen positions shown are calculated.

Table IV. Bond Distances (Å) and Angles (deg) for
$(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{11}(\eta^1\text{-}\overline{\text{C}\!=\!\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2})$ **(3)**[a]

	Distances		
Ru1–Ru2	3.0146 (5)	N–C4	1.494 (6)
Ru1–Ru3	2.9756 (6)	N–C5	1.478 (7)
Ru1–Ru4	2.9177 (5)	C1–C2	1.525 (8)
Ru2–Ru3	2.9177 (5)	C2–C3	1.517 (9)
Ru2–Ru4	2.7815 (6)	C3–C4	1.541 (9)
Ru3–Ru4	2.7828 (6)	Ru3–H2	1.85
Ru1–H1	1.85	Ru3–H3	1.85
Ru1–H2	1.85	Ru4–H4	1.85
Ru1–H4	1.85	Ru4–H4	1.85
Ru2–H1	1.85	Ru–C(CO)	1.89 (2)[b]
Ru1–C1	2.049 (4)	C–O(CO)	1.13 (2)[b]
N–C1	1.320 (6)		

	Angles		
Ru1–Ru2–Ru3	60.18 (1)	Ru1–Ru2–Ru4	61.98 (1)
Ru1–Ru3–Ru2	61.52 (1)	Ru1–Ru3–Ru4	62.48 (1)
Ru1–Ru4–Ru2	62.84 (1)	Ru1–Ru4–Ru3	61.92 (1)
Ru2–Ru1–Ru3	58.29 (1)	Ru2–Ru1–Ru4	55.18 (1)
Ru2–Ru3–Ru4	58.35 (1)	Ru2–Ru4–Ru3	63.25 (1)
Ru3–Ru1–Ru4	55.60 (1)	Ru3–Ru2–Ru4	58.40 (1)
C1–C2–C3	107.0 (5)	C2–C3–C4	105.7 (5)
C1–N–C4	116.1 (4)	C1–N–C5	127.6 (4)
C4–N–C5	116.2 (4)	N–C1–C2	107.3 (4)
N–C4–C3	103.1 (4)	Ru–C–O(CO)	177 (2)[b]

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Average values.

with the exception of the bond between N and C(1), which shows considerable double-bond character (N–C(1) = 1.32 (1) Å). The overall structure of **3** is remarkably similar to other $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ derivatives with one carbonyl group replaced by the η^1-carbene ligand.[13c] This η^1-carbene complex is unique in tetranuclear clusters, but amine-stabilized η^1-carbene complexes of hexanuclear and trinuclear osmium clusters have recently been reported.[14]

It appeared to us at first that **1** could be a precursor to **2** with **1** being isolated only under the more mild conditions (68 °C) used with the diiron reaction promoter. However, thermolysis of **1** at 80–100 °C in hydrocarbon solvents
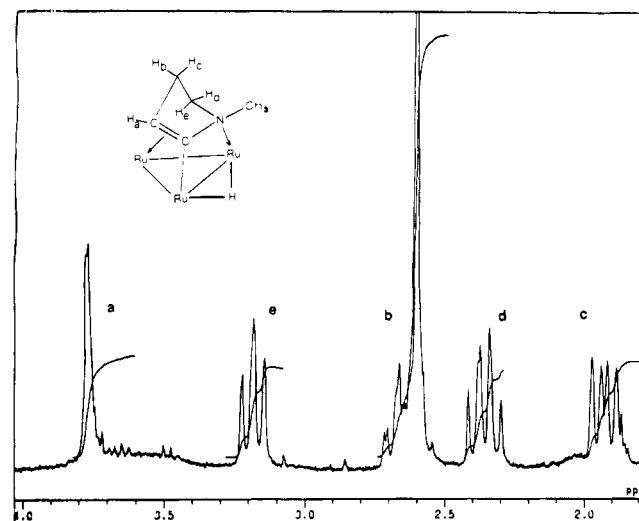
(14) (a) Adams, R. D.; Babin, J. E.; Kim, H. *Inorg. Chem.* **1986**, *25*, 4319. (b) Adams, R. D.; Babin, J. E.; Kim, H.; Tanner, J. T.; Wolfe, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 3426.

Figure 4. 270-MHz ^{1}H NMR spectrum of compound 4 in CDCl$_3$ at 22 °C.
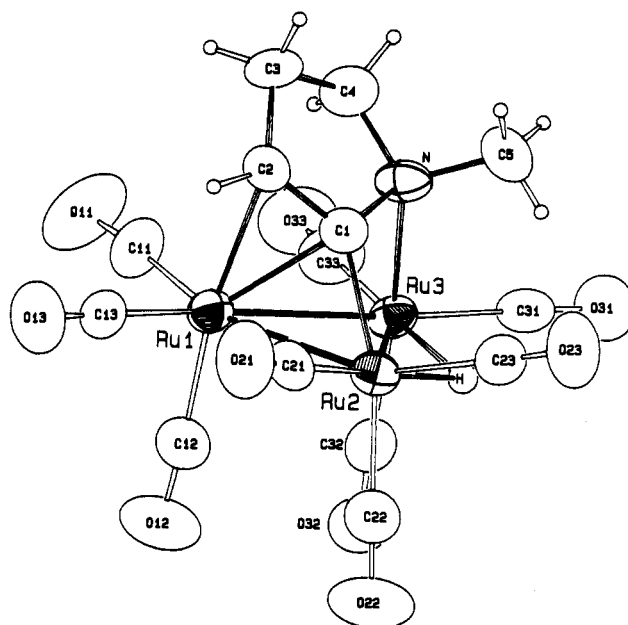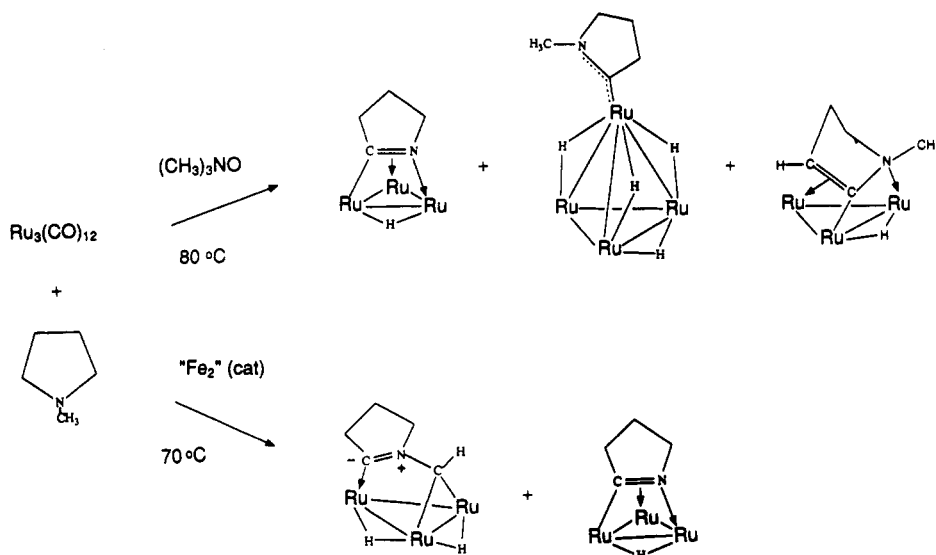

Figure 5. Solid-state structure of 4. All hydrogen positions shown are calculated.

yielded a new compound in moderate yield (40%) in addition to nonspecific decomposition. This compound shows an ^{1}H NMR spectrum at 270 MHz in CDCl$_3$ consisting of a hydride singlet at −14.20 (1) ppm, an N-methyl singlet at 2.60 (3) ppm, a doublet at 3.76 ppm (H$_a$, 1, $J_{\text{H}_a\text{H}_b}$ = 3.4 Hz), and a series of multiplets at 3.18 (H$_e$, 1, $J_{\text{H}_b\text{H}_e}$ = $J_{\text{H}_d\text{H}_e}$ = 10.4 Hz), 2.64 (H$_b$, 1, superimposed on the methyl singlet), 2.35 (H$_d$, 1, $J_{\text{H}_d\text{H}_c}$ = 14.3 Hz), and 1.93 ppm (H$_c$, 1, $J_{\text{H}_d\text{H}_c}$ = 9.9 Hz) (see Figure 4 for letter assignments). On the basis of decoupling experiments, we were able to make tentative assignments for all of these resonances, and these assignments suggested that the compound be formulated as $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-}\overline{\text{HC}\!=\!\text{CN}(\text{CH}_3)\text{CH}_2\text{CH}_2})$ **(4)** with the structure shown in Figure 5.

A single-crystal X-ray diffraction study of compound **4** confirmed our tentative structural assignment. The solid-state structure of **4** is shown in Figure 5, the crystal data are summarized in Table I, and selected bond distances and bond angles are given in Table V. Compound **4** consists of a triangular metal core with three distinct metal–metal bond lengths (Ru(1)–Ru(2) = 2.733 (1) Å,

Scheme I

Table V. Bond Distances (Å) and Angles (deg) for
(μ-H)Ru$_3$(CO)$_9$(μ_3-η^2-CH=C-N(CH$_3$)CH$_2$CH$_2$) (4)^a

Distances			
Ru1–Ru2	2.733 (1)	N–C1	1.48 (1)
Ru1–Ru3	2.814 (1)	N–C4	1.50 (1)
Ru2–Ru3	2.907 (1)	N–C5	1.49 (2)
Ru1–C1	2.28 (1)	C1–C2	1.37 (1)
Ru1–C2	2.38 (1)	C2–C3	1.51 (2)
Ru3–N	2.19 (1)	C3–C4	1.53 (1)
Ru2–C1	2.03 (1)	Ru–C(CO)	1.90 (2)^b
Ru2–H	1.85	C–O(CO)	1.13 (2)^b
Ru3–H	1.85		

Angles			
Ru1–Ru2–Ru3	59.76 (3)	C2–C3–C4	102.0 (8)
Ru2–Ru1–Ru3	63.20 (3)	N–C4–C3	106.1 (9)
Ru1–Ru3–Ru2	57.04 (3)	C1–N–C5	111.8 (8)
C1–N–C4	107.2 (7)	N–C1–C2	108.5 (9)
C4–N–C5	109.5 (8)	Ru–C–O(CO)	177 (2)^b
C1–C2–C3	112.6 (9)		

^{a} Numbers in parentheses are estimated standard deviationsi in the least significant digits. ^{b} Average values.

Ru(1)–Ru(3) = 2.814 (1) Å, and Ru(2)–Ru(3) = 2.907 (1) Å). The bridging hydride ligand was located on the longest edge of the triangle (Ru(2)–Ru(3)) by using the Hydex program[7] and is approximately trans to CO(21) and CO-(33). It should be pointed out that all of the ruthenium and osmium clusters with σ-π-vinyl bonding frameworks reported to date have the bridging hydride located on the same edge as that bridged by the σ-π-vinyl moiety.[2,15] This is not the case for 4, where the hydride bridges the edge common to the σ-bound carbon atom and the coordinated nitrogen. This may reflect a greater electron density along the Ru(2)–Ru(3) edge due to the fact that both Ru(2) and Ru(3) are bound to the ligand by strictly donor σ bonds as opposed to donor–acceptor π bonds.

The thermolysis of 1 to give 4 is in sharp contrast with the thermolysis of the related complex (μ-H)$_2$Ru$_3$(CO)$_9$-(μ_3-η^2-HC—C=N(CH(CH$_3$)$_2$)$_2$) (A, M = Ru, R = *i*-Pr), which loses molecular hydrogen and undergoes C–H oxidative addition to the cluster under identical reaction conditions (eqs 2 and 3).[2] This may be due to the overall greater steteochemical rigidity of 1 compared with A. The hydrides in A are in fact much more mobile than those in 1 coalescing at ~0 °C ($\Delta G^{\ddagger}$ = 47.2 kJ/mol)[2], while those
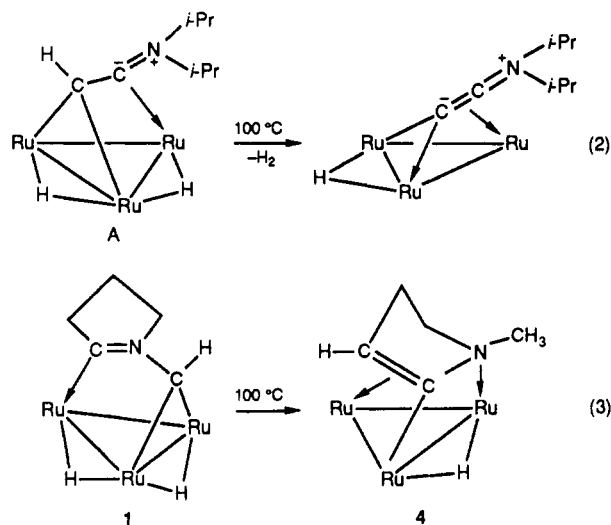
in 1 are only slightly broadened up at 25 °C ($\Delta G^{\ddagger}$ = 64 ± 2 kJ/mol estimated from VT (variable temperature) ^{1}H NMR data at 80 MHz in CDCl$_3$, coalescence at +60 °C). This greater rigidity for 1 may be a reflection of a more rigid metal core-ligand framework. On heating, opening of the methyne bridge may be the lowest energy pathway to relieve strain, thus making transfer of hydrogen back to the ligand the most accessible reaction pathway.

Compound 4 is also isolated (<5%) in larger scale reactions (500 mg of Ru$_3$(CO)$_{12}$) by using (CH$_3$)$_3$NO, suggesting that 1 is also formed with this promoter as well as with the diiron promoter. In this connection it is relevant to note that the general level of decomposition is much higher with (CH$_3$)$_3$NO than with the diiron promoter. A summary of the reactions of Ru$_3$(CO)$_{12}$ with these two different promoters is shown in Scheme I. Unreacted Ru$_3$(CO)$_{12}$ is always recovered from reactions with diiron promoter, while maximum yields of 2 are obtained after complete consumption of Ru$_3$(CO)$_{12}$ with (CH$_3$)$_3$NO. The isolation of the tetranuclear product 3 in the early stages of this reaction suggests that cluster fragmentation may play an important role in determining the products formed in a reaction of tertiary amines with Ru$_3$(CO)$_{12}$. Thermolysis of 3 does not lead to 1 or 2 but to a mixture of yet to be identified products. However, the formation of carbon nitrogen bond cleavage products such as 2 and structure B (and the alkyl-coupling products shown in eq
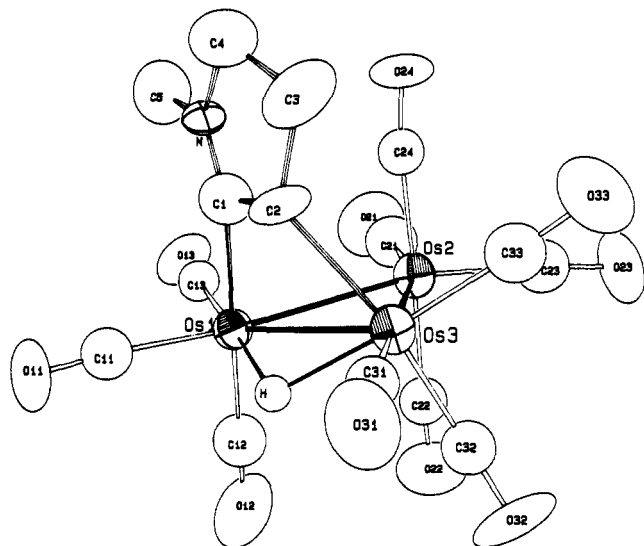
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Figure 6. Solid-state structure of **5**. All hydrogen positions shown are calculated.

1) may well be the result of facile cluster degradation-agglomeration processes instead of the ligand-dissociation processes previously proposed.[2] Consistent with this idea is the fact that the reactions of tertiary amines with $Os_3(CO)_{12}$ give alkyl cleavage products only at much higher temperatures (140–150 °C), where cluster fragmentation is an accessible process.[16] At lower temperatures (80 °C) the reaction of triethylamine with $Os_3(CO)_{10}(CH_3CN)_2$ gives a major product in which only carbon–hydrogen bonds have been activated (eq 4).[17,18] In light of these previous results we decided to investigate the reaction of *N*-methylpyrrolidine with $Os_3(CO)_{10}(CH_3CN)_2$.

(4)
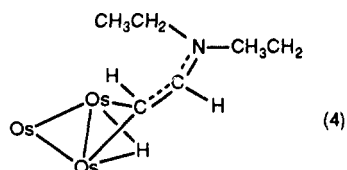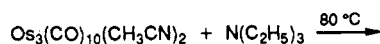
C. Reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with *N*-Methylpyrrolidine. When *N*-methylpyrrolidine is reacted with $Os_3(CO)_{10}(CH_3CN)_2$ for 1 h in refluxing benzene, four triosmium products are obtained (eq 5). Two

$$Os_3(CO)_{10}(CH_3CN)_2 + \text{N-methylpyrrolidine} \longrightarrow$$

$$(\mu\text{-H})_2Os_3(CO)_{10} + (\mu\text{-H})Os_3(\mu\text{-OH})(CO)_{10} \quad (5)$$
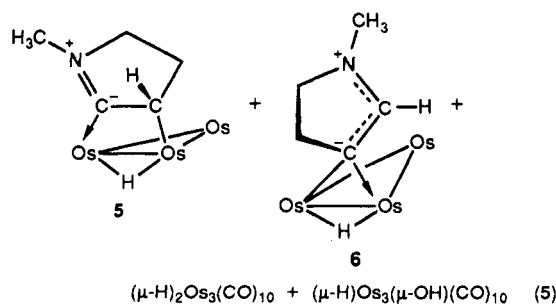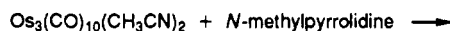
products, obtained in 2.5% yield each, were identified by IR $\nu(CO)$ bands as $(\mu\text{-H})_2Os_3(CO)_{10}$ and $(\mu\text{-H})Os_3(\mu\text{-OH})(CO)_{10}$. The ^1H NMR spectrum of one of the re-

maining products, obtained in 6% yield, shows a singlet hydride at −17.04 (1) ppm, a singlet methyl resonance at 3.26 (3) ppm, and a series of four multiplets at 4.22 (1, m), 3.38 (2, m), 2.23 (1, m), and 1.94 ppm (1, m). On the basis of these ^1H NMR data, we assign the structure of this compound as $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-CH}_3\overline{N\!=\!CCHCH_2CH_2})$ (**5**). Although the carbon skeleton of the ligand was clear from the ^1H NMR data, the ligand–metal cluster bonding framework was not.

In order to ascertain the exact structure of **5**, we undertook a single-crystal X-ray diffraction study. The structure of **5** is shown in Figure 6, the crystal data are summarized in Table I, and selected bond distances and angles are given in Table VI. Compound **5** exists as an approximate isosceles triangle of osmium atoms (Os(1)–Os(2) = 2.885 (2) Å, Os(2)–Os(3) = 2.893 (2) Å) with one elongated metal–metal bond (Os(1)–Os(3) = 2.957 (2) Å) where the hydride is located. The location of the hydride was calculated by using the program Hydex.[7] Its position as 0.6 Å below the plane of the metal atoms is consistent with the elongated Os(1)–Os(3) distance, and its position as trans to CO(12) and CO(32) maintains approximate octahedral geometry around Os(1) and Os(3). The organic ligand must donate three electrons to the metal core in order to make **5** a saturated 48e⁻ cluster. Two electrons are donated by the quaternary carbenoid carbon, C(1), to Os(1) (C(1)–Os(1) = 2.11 (4) Å). An additional electron is donated by a conventional σ bond from C(2) to Os(3) (C(2)–Os(3) = 2.24 (3) Å). The short N to C(1) distance (N–C(1) = 1.20 (5) Å), the single-bond character of the C(1)–C(2) bond (C(1)–C(2) = 1.59 (5) Å), and the geometry around C(2) (see Table VI for angles) indicate that the resonance at 4.22 ppm in the ^1H NMR spectrum is assignable to a proton on C(2). The *N*-methylpyrrolidine ring is puckered with C(3) lying 0.33 Å out of the plane defined by all the other non-hydrogen atoms of the organic ligand. Compound **5** apparently exists as two isomers in solution, as evidenced by the observation of a second hydride resonance (in 0.2 to 1 ratio relative to the major isomer) at −16.73 ppm. We propose that the two isomers differ by the disposition of the vinylic proton, over or off the face of the cluster (Chart I). Location of the methyne hydrogen in the solid state by using the program Hydro[19]

Table VI. Bond Distances (Å) and Angles (deg) for $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-CH}_3N\!=\!CC(H)CH_2CH_2)$ (5)[a]

Distances			
Os1–Os2	2.885 (2)	N–C4	1.55 (5)
Os1–Os3	2.957 (2)	N–C5	1.45 (5)
Os2–Os3	2.893 (2)	C1–C2	1.59 (5)
Os1–C1	2.11 (4)	C2–C3	1.45 (5)
Os3–C2	2.24 (3)	C3–C4	1.52 (6)
Os1–H	1.85	Os–C(CO)	1.92 (5)[b]
Os3–H	1.85	C–O(CO)	1.16 (5)[b]
N1–C1	1.20 (5)		

Angles			
Os1–Os2–Os3	61.57 (3)	C2–C3–C4	104 (3)
Os1–Os3–Os2	59.09 (4)	N–C4–C3	104 (3)
Os2–Os1–Os3	59.35 (4)	C1–N–C5	126 (3)
C1–N–C4	111 (3)	N–C1–C2	112 (3)
C4–N–C5	123 (3)	Os–C–O(CO)	174 (3)[b]
C1–C2–C3	105 (3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Average values.

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Chart I

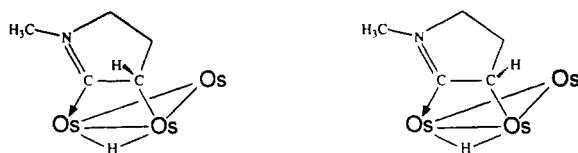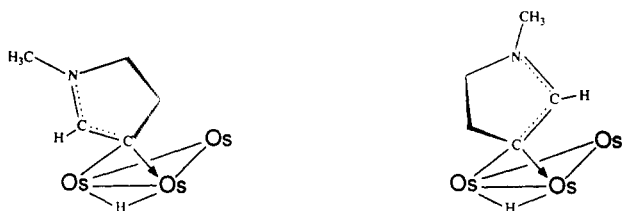**Chart II**

places it off the cluster, suggesting that this is the major isomer in solution.

The ^{1}H NMR spectrum of the major product, obtained in 16% yield, shows a singlet hydride at -15.83 (1) ppm a singlet methyl resonance at 2.96 (3) ppm, a singlet at 8.33 (1) ppm, and two triplets at 3.17 (2, J_{HH} = 8.3 Hz) and 2.1 (2) ppm. On the basis of these ^{1}H NMR data, we assign the structure of this compound as (μ-H)Os$_3$(CO)$_{10}$(μ-η^1-CH$_3$N=CHCCH$_2$CH$_2$) (6). Compound 6 also exists as two isomers in solution, as evidenced by the observation of a second CH singlet at 7.06 ppm (in 0.2 to 1 ratio with the CH singlet of the major isomer) and a corresponding hydride at -16.23 ppm. We were unable to obtain crystals of 6 suitable for a solid-state structural analysis, but we propose a structure analogous to the major product obtained from the reaction of triethylamine with Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$ (eq 4) on the basis of the ^{1}H NMR data and the similarity of the infrared spectrum of 6 to that of this compound.[17] We propose that the two isomers observed for 6 differ in the relative orientation of the methyl groups with respect to the cluster as shown in Chart II The two sets of isomers observed for 5 and 6 do not interconvert on the ^{1}H NMR time scale up to +80 °C, illustrating the stereochemically rigid nature of the metal-ligand bonding framework in these clusters.

There are thus very significant differences in the reactions of Ru$_3$(CO)$_{12}$ (in the presence of reaction promotors) and Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$ with tertiary amines in the same temperature range. First, no carbon hydrogen bond activation of the methyl group is observed in the osmium case, and second, as for triethylamine, no alkyl cleavage products are isolated. Additionally, in the ruthenium case only products that are the result of initial α-carbon-hydrogen bond activation are isolated, while for osmium compounds resulting from both α- and β-carbon-hydrogen bond activation are observed (2α and 1β for 5 and 1α and 2β for 6). It is difficult to adequately explain these observed differences without a knowledge of the earlier intermediates in these reactions. There is the possibility that β-carbon-hydrogen bond activation requires the presence of an adjacent vacant metal atom site after initial nitrogen coordination and that in the ruthenium case rapid cluster fragmentation-agglomeration precludes this process. Alternatively, the known large differences in the activation energy for radial to axial migration of the ligands[20] may play a critical role in directing the course of the reactions of these clusters with tertiary amines, as we previously proposed.[2] Further studies with osmium clusters that are

more stable toward fragmentation and with the more reactive secondary amines[21] are underway in our laboratories to further elucidate the factors controlling these reactions.

Experimental Section

Synthesis of (μ-H)$_2$Ru$_3$(CO)$_9$(μ_3-η^2-CH-N=CCH$_2$CH$_2$CH$_2$) (1). In a 500-mL three-neck flask fitted with a reflux condenser and gas inlet adaptor connected to a nitrogen line and a bubbler were combined 300 mg (0.45 mmol) of Ru$_3$(CO)$_{12}$, 50 mg (0.057 mmol) of Fe$_2$(CO)$_4$(μ-SCH$_2$CH$_3$)$_2$(P(C$_6$H$_5$)$_3$)$_2$, 2.0 mL (19 mmol) of *N*-methylpyrrolidine, and 250 mL of hexane. The reaction mixture was heated for a total of 12 h; a detectable product band (by analytical thin-layer chromatography, silica gel) was observed after 6 h. Longer reaction times did not improve the product yield. After cooling, the reaction mixture was rotary evaporated and the residue extracted with 2-4 mL of CH$_2$Cl$_2$ and then separated on silica gel preparative thin-layer chromatography plates using 1:4 CH$_2$Cl$_2$/hexane as eluent. This procedure resolved four major bands; the top band was Ru$_3$(CO)$_{12}$ (50 mg recovered) followed by a yellow product band and two slower moving bands, which proved to be Fe$_2$(CO)$_5$(μ-SCH$_2$CH$_3$)$_2$P(C$_6$H$_5$)$_3$ (~10 mg) and Fe$_2$(CO)$_4$(μ-SCH$_2$CH$_3$)$_2$(P(C$_6$H$_5$)$_3$)$_2$ (20 mg). The yellow product band was recrystallized from hexane to yield 45 mg (15%, based on Ru$_3$(CO)$_{12}$) of compound 1. Anal. Calcd for C$_{14}$H$_9$NO$_9$Ru$_3$: 26.31, C; 1.42, H. Found: 26.32, C; 1.35, H. Infrared (hexane): ν(CO) 2091 m, 2062 s, 2053 m, 2040 vs, 2013 m, 2004 m, 1983 br, 1969 cm^{-1} br, w.

Synthesis of (μ-H)Ru$_3$(CO)$_9$(μ_3-η^2-N=CCH$_2$CH$_2$CH$_2$) (2). In a three-necked 500-mL round-bottom flask fitted with a reflux condenser and a gas inlet adapter connected to a nitrogen line and a bubbler were combined 100 mg (0.157 mmol) of Ru$_3$(CO)$_{12}$, 17.4 mg (0.157 mmol) of (CH$_3$)$_3$NO·2H$_2$O, 0.10 mL (0.94 mmol) of *N*-methylpyrrolidine, and 50 mL of benzene. After the solvent was degassed and the system was flushed with nitrogen, the mixture was refluxed for 5-6 h, at which time all of the Ru$_3$(CO)$_{12}$ was consumed (analytical thin-layer chromatography). The reaction mixture was filtered and rotary evaporated, the residue was taken up in 2 mL of CH$_2$Cl$_2$, and the mixture was chromatographed on two 20 × 20 cm silica gel preparative thin-layer chromatography plates. One major band was eluted with 1:4 CH$_2$Cl$_2$/hexane yielding 33 mg of 2 (30%). Anal. Calcd for C$_{13}$H$_7$NO$_9$Ru$_3$: 25.00, C; 1.13, H. Found: 24.76, C; 1.14, H. Infrared (hexane): ν(CO) 2092 m, 2066 s, 2061 m, 2037 s, 2022 s, 2010 m, 2006 m, 1999 m, 1981 w, 1975 cm^{-1} w.

In a separate experiment 100 mg (0.157 mmol) of Ru$_3$(CO)$_{12}$ was combined with (0.10 mL, 0.94 mmol) of *N*-methylpyrrolidine

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in 50 mL of benzene, and 1.0 mL of a 0.025 M solution of sodium benzophenone ketyl in THF was added. Immediate discoloration of the purple solution was noted, but no product formation was seen until the solution was refluxed. After 4.5 h of reflux all the $Ru_3(CO)_{12}$ was consumed (by analytical TLC) and the reaction was worked up as above to yield 30 mg of **2** (~30%).

Synthesis of $(\mu\text{-}H)_4Ru_4(CO)_{11}(\eta^1\text{-}C=N(CH_3)CH_2CH_2CH_2)$ (3). In a three-necked 500-mL round-bottom flask fitted with a reflux condenser, a gas inlet adapter connected to a nitrogen line, and a bubbler were combined 500 mg (0.782 mmol) of $Ru_3(CO)_{12}$, 70.9 mg (0.638 mmol) of $(CH_3)_3NO\cdot 2H_2O$, 0.50 mL (4.69 mmol) of *N*-methylpyrrolidine, and 250 mL of dry benzene. The solution was refluxed for 4 h. The reaction mixture was rotary evaporated to dryness, the residue was taken up in a minimum amount of CH_2Cl_2, and the mixture was chromatographed on four 20×20 cm silica gel preparative thin-layer chromatography plates. Six bands were eluted. The top band was $Ru_3(CO)_{12}$ (100 mg), the second band was 50 mg (10%) (**2**), and band three gave 15 mg (<5%) (**4**). The fourth band was collected giving 31 mg (5%) of $(\mu\text{-}H)_4Ru_4(CO)_{11}(\eta^1\text{-}C=N(CH_3)CH_2CH_2CH_2)$ (**3**). Anal. Calcd for $C_{16}H_{13}NO_{11}Ru_4$ 27.51, C; 1.87, H. Found: 27.30, C; 2.01, H. Infrared (hexanes): $\nu(CO)$ 2082 m, 2049 s, 2027 s, 2002 m, 1982 cm^{-1} w. Unfortunately, we were unable to obtain the other two slower moving bands in sufficient quantity to allow characterization.

Thermolysis of 1 To Give $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}HC=CN\text{-}(CH_3)CH_2CH_2)$ (4). In a round-bottom flask 100 mg of **1** was dissolved in 25 mL of heptane and the solution refluxed under a nitrogen atmosphere for 7 h. After rotary evaporation the reaction residue was taken up in CH_2Cl_2 and the components separated on two 20×20 cm silica gel preparative thin-layer chromatography plates using 1:9 CH_2Cl_2/hexane as eluent. One major band eluted in addition to two slower moving minor bands, which were present in too small an amount to characterize (<5 mg). The major band proved to be **4** and was recrystallized from hexane at -20 °C to give 41 mg (41% yield). Anal. Calcd for $C_{14}H_9NO_9Ru_3$: 26.31, C; 1.42, H. Found: 26.05, C; 1.63, H. Infrared (hexane): $\nu(CO)$ 2084 m, 2055 s, 2044 m, 2028 vs, 2012 s, 2002 br, m, 1984 br, w, 1962 cm^{-1} w.

Synthesis of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}(H_3C)N=CC(H)CH_2CH_2)$ (5) and $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}(H_3C)N=C(H)CCH_2CH_2)$ (6). In a 200-mL Schlenk tube fitted with a reflux condenser were combined 450 mg (0.482 mmol) of $Os_3(CO)_{10}(CH_3CN)_2$, 0.250 mL (2.41 mmol) of *N*-methylpyrrolidine, and 100 mL of benzene. The solution was refluxed for 1 h. The color changed from yellow to red. The solvent was rotary evaporated to dryness, and the residue was chromatographed on silica gel thin-layer chromatography plates eluting with 5:1 hexane/dichloromethane. Four bands were eluted in the following order: $(\mu\text{-}H)_2Os_3(CO)_{10}^{20}$ (10 mg, 2.4%), $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH_3N=CCHCH_2CH_2)$ (**5**) (27 mg, 6%), $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}CH_3N=CHCCH_2CH_2)$ (**6**) (72 mg, 16%), and $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OH)^{20}$ (10 mg, 2.4%). Anal. Calcd for **5**, $C_{15}H_9NO_{10}Os_3$: 19.3, C; 1.0, H; 1.5, N. Found: 19.5, C; 0.9, H; 1.6, N. IR $(\nu(CO)$, cyclohexane): 2095 w, 2055 s, 2042 s, 2016 s, 1989 s, 1977 m, 1967 cm^{-1} w. Anal. Calcd for **6**, $C_{15}H_9NO_{10}Os_3$: 19.3, C; 1.0, H; 1.5, N. Found: 19.4, C; 0.9, H; 1.5, N. IR $(\nu(CO)$, cyclohexane): 2091 m, 2057 sh, 2047 vs, 2038 s, 2011 s, 1922 s, 1985 m, 1975 s, 1963 cm^{-1} w.

X-ray Crystallography. Crystal Structure Determinations of 1–5. Crystals of **1–5** for X-ray studies were obtained from saturated hexane solutions cooled to -20 °C. Crystals having approximate dimensions of $0.50 \times 0.10 \times 0.05$ mm for **1**, $0.25 \times 0.20 \times 0.20$ mm for **2**, $0.30 \times 0.30 \times 0.50$ mm for **3**, $0.08 \times 0.08 \times 0.15$ mm for **4**, and $0.20 \times 0.13 \times 0.08$ mm for **5** were examined by using similar procedures, as follows. 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 from 22 reflections with $12° < 2\theta < 40°$ for **1**, 23 re-

flections with $10° < 2\theta < 38°$ for **2**, 25 reflections with $8° < 2\theta < 34°$ for **3**, 25 reflections with $16° < 2\theta < 22°$ for **4**, and 25 reflections with $14° < 2\theta < 38°$ for **5** by using the centering program in the CAD4 system. Details of the crystal data are given in Table I. Systematic absences of $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$ for 1 uniquely define the monoclinic space group $P2_1/n$, systematic absences of $0k0$, $k = 2n + 1$ for **2** indicate the monoclinic space group $P2_1/m$, systematic absences of $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ for **3** uniquely define the monoclinic space group $P2_1/c$, systematic absences of $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ for **4** indicate the monoclinic space group $P2_1/c$, and systematic absences of $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$, $l = 2n + 1$ for **5** indicate the orthorhombic space group $P2_12_12_1$. These were verified by successful least-squares refinement of the structures. For each crystal the actual scan range was calculated by using scan width = scan range + $0.35 \tan \theta$ and backgrounds were measured by using the moving crystal–moving counter techique, at the beginning and end of each scan. As a check on instrument and crystal stability, three 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 ψ scans. The number of data observed and used for least-squares refinement $(F \geq 3\sigma(F))$ for each crystal are listed in Table I. All other reflections were considered to be unobserved.

Each of the structures was solved by the Patterson method with SHELXS-86,[27] which revealed the positions of the metal atoms. All other non-hydrogen atoms were found by successive difference Fourier syntheses. The hydride positions were calculated with the program Hydex,[7] and all other hydrogens were calculated with the program Hydro.[18] Hydrogen atom positions were included but not refined in the final least-squares cycles. All non-hydrogen atoms were refined anisotropically except in compound **5**, in which the carbonyl carbon atoms were refined isotropically because of poor crystal quality and resulting lack of sufficient data. Also, no improvement in the structural results for compound **5** were obtained when the enantiomeric molecular form of **5** (the space group is acentric) was refined. Selected bond distances and angles are given in Tables II–VI, and the residual electron densities in the final structures are listed in Table I.

Scattering factors were taken from Cromer and Waber.[28] Anomalous dispersion corrections were those of Cromer.[29] All calculations were carried out on a DEC MicroVAX II computer using the SDP/VAX system of programs.

Supplementary Material Available: For 1–5, Tables VII–XVI, listing atomic positional and thermal parameters, anisotropic displacement factors, and distances and angles (33 pages); Tables XVII–XXI, listing observed and calculated structure factors (118 pages). Ordering information is given on any current masthead page.

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

(29) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.