imines.[11] The harsher conditions which were required with $Os_3(CO)_{12}$ are probably due to the need to activate $Os_3(CO)_{12}$ through loss of CO.

From the stoichiometry of the reactions it seems unlikely that A is produced from B or vice versa and we have shown explicitly that these reactions do not occur by simple thermolysis. It thus appears that the conditions which promote hydrogen addition to or abstraction from various unsaturated small molecules are not vastly different. In fact, one might be able to exercise a great degree of control over which reaction prevails by introducing small changes in the substituents of the substrate molecule or the ligand structure of the cluster complex.

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Reactions of α,β-Unsaturated Imines with (μ-H)₂Os₃(CO)₁₀ Including the Dehydrogenation of an Isopropyl Group

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The unsaturated imine $(CH_3)_2C=CHC(CH_3)=NC_6H_5$ was found to react with $(\mu-H)_2Os_3(CO)_{10}$ to produce the compounds $(\mu-H)_2(\mu_3-\eta^2-(CH_3)_2CHCC(CH_3)=NC_6H_5)Os_3(CO)_9$, A, and $(\mu-H)_2(\mu_3-\eta^4-CH_2C(CH_3)CC(CH_3)=NC_6H_5)Os_3(CO)_8$, B. Both products have been characterized crystallographically by using diffractometer data. For A, the space group is $P2_1/c$ (C_{2h}^5), No. 14, with $a = 14.818$ (5) Å, $b = 9.051$ (5) Å, $c = 20.098$ (6) Å, $\beta = 108.45$ (3)°, $Z = 4$, and $\rho_{calcd} = 2.59$ g/cm³. The structure was solved by the heavy-atom method and refined to the final residuals $R_1 = 0.058$ and $R_2 = 0.067$. For B, the space group is $P2_1/c$ (C_{2h}^5), No. 14, with $a = 16.060$ (5) Å, $b = 8.820$ (4) Å, $c = 16.809$ (4) Å, $\beta = 93.83$ (2)°, $Z = 4$, and $\rho_{calcd} = 2.703$ g/cm³. This structure was also solved by the heavy-atom method and refined to the final residuals $R_1 = 0.037$ and $R_2 = 0.041$. A contains a $\mu_3-\eta^2-(CH_3)_2CHCC(CH_3)=NC_6H_5$ ligand bridging one face of a triangular cluster of osmium atoms. The nitrogen atom is terminally bonded to one osmium atom while the α-carbon serves as a bridge across the two remaining osmium atoms. The hydrogen atom on the α-carbon has been removed, and one has been added to the β-carbon, thus forming an isopropyl group. B contains a $\mu_3-\eta^4-CH_2C(CH_3)CC(CH_3)=NC_6H_5$ ligand bridging one face of a triangular cluster of osmium atoms. A terminally coordinated nitrogen atom is again bonded to one osmium atom. The α-carbon bridges the two remaining osmium atoms. The α- and γ-carbon atoms have each lost one hydrogen atom. Together with the β-carbon atom they are bonded in the form of a π-allyl group to one osmium atom. A has been independently converted into B through the dehydrogenation of the isopropyl group.

Introduction

In the preceding paper we examined the reactivity of the cluster complex $(\mu-H)_2Os_3(CO)_{10}$ toward an aliphatic imine.[2] We found that the cluster reacts with imine groups on a 1:1 basis and can either add or abstract a hydrogen atom to or from the iminyl carbon atom. In further studies we have examined the reactivity of α,β-unsaturated imines with the cluster $(\mu-H)_2Os_3(CO)_{10}$. With these imines the olefinic group could significantly influence the reactivity of the iminyl group and even participate in the reaction itself. The results of our studies of the reaction of $(\mu-H)_2Os_3(CO)_{10}$ with $(CH_3)_2C=CHC(CH_3)=NC_6H_5$ are reported here.

Experimental Section

$Os_3(CO)_{12}$ was purchased from Strem Chemicals Inc., Newburyport, Mass., and used without further purification. The imine $C_6H_5N=C(CH_3)CH=C(CH_3)_2$[3a] was prepared from mesityl oxide

(1) Fellow of the Alfred P. Sloan Foundation 1979–1981.
(2) See: Adams, R. D.; Selegue, J. P. *Inorg. Chem.*, preceding paper in this issue.
(3) (a) Tung, C. C. *Tetrahedron* **1963**, *19*, 1685. (b) Tsuchimoto, M.; Nishimura, S.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 675. (c) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

and aniline in the presence of 4A molecular sieves.[3b] $(\mu-H)_2Os_3(CO)_{10}$ was prepared by the method of Kaesz.[3c] All reactions were performed under an atmosphere of dry nitrogen. Hexanes solvent was dried by distilling from sodium–benzophenone. Infrared spectra were recorded on a Perkin-Elmer 237 spectrometer and were calibrated with polystyrene. ^{1}H NMR spectra were recorded on the Southern New England High-Field NMR Facility operating at 270 MHz.

Reaction of $H_2Os_3(CO)_{10}$ with $C_6H_5N=C(CH_3)CH=C(CH_3)_2$. $H_2Os_3(CO)_{10}$ (90 mg, 0.11 mmol), hexanes (25 mL), and $PhN=C(CH_3)CH=C(CH_3)_2$ (0.20 mL, 1.2 mmol) were heated to reflux for 70 h. The yellow supernatant and a 5-mL CH_2Cl_2 washing of a small amount of yellow-brown precipitate were transferred to a grade II neutral alumina column. Elution with hexanes gave a mixture of $Os_3(CO)_{12}$ and $(\mu-H)_2(\mu_3-\eta^2-(CH_3)_2CHCC(CH_3)=NC_6H_5)Os_3(CO)_{10}$, A. Extraction of this mixture with hexanes gave 29.0 mg (27.6%) of pure A, mp 169–740 °C. IR (hexanes): 2100 (m), 2070 (s), 2045 (s), 2010 (s), 2005 (sh), 1995 (m), 1990 (m), 1965 (m), 1960 (sh) cm⁻¹.

Elution of the column with benzene gave a mixture of $Os_3(CO)_{12}$ and $(\mu-H)_2(\mu_3-\eta^4-CH_2C(CH_3)CC(CH_3)=NC_6H_5)Os_3(CO)_8$, B. Extraction of this mixture with 3:1 hexanes–CH_2Cl_2 gave 43.4 mg (42.5%) of B as yellow crystals, mp 142–143.5 °C. IR (hexanes): 2100 (ms), 2050 (s), 2020 (s), 2000 (s), 1995 (sh), 1980 (ms), 1972 (sh), 1970 (s) cm⁻¹.

Pyrolysis of $(\mu-H)_2(\mu_3-\eta^2-(CH_3)_2CHC(CH_3)=NC_6H_5)Os_3(CO)_{10}$, A. Complex A (31.6 mg, 0.032 mmol) in 25 mL of hexanes was

refluxed for ca. 5 days, with no change in its infrared spectrum. The hexanes were removed in vacuo and replaced with 25 mL of octane. After 22 h at reflux, an infrared spectrum showed that no A remained. The product was chromatographed twice over silica gel. Elution with 1:1 benzene–hexanes and subsequent crystallization from pentane afforded 29.9 mg (97.6%) of complex B as yellow crystals.

Crystallographic Analyses

Crystals of $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}(CH_3)_2CHCC(CH_3)=NC_6H_5)Os_3(CO)_9$, A, and $(\mu\text{-H})_2(\mu_3\text{-}\eta^4\text{-}CH_2C(CH_3)CC(CH_3)=NC_6H_5)Os_3(CO)_8$, B, were grown from solutions in hexanes by cooling. All diffraction measurements were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Unit cells were determined from 25 randomly selected reflections by using the CAD-4 automatic search, center, index, and least-squares routines. Space groups were determined from the systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, observed for both structures during data collection.

All calculations were performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. Both structures were solved by the heavy-atom method. Anomalous dispersion corrections[4a] were added to the neutral-atom scattering factors[4b] used for all nonhydrogen atoms. Full-matrix least-squares refinements minimized the function $\sum w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (pF_o^2)^2]^{1/2}/Lp$. Crystallographic data for both structures are listed in Table I.

$(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}(CH_3)_2CHCC(CH_3)=NC_6H_5)Os_3(CO)_9$, A. A thick crystalline plate of dimensions 0.10 mm × 0.18 mm × 0.28 mm was selected and mounted in a thin-walled glass capillary. The crystal faces were identified as $2\bar{1}4$, $\bar{2}1\bar{4}$, $\bar{2}\bar{1}4$, $21\bar{4}$, $1\bar{2}2$, 014, $\bar{1}11$, 111, and $02\bar{1}$. ω-Scan peak widths at half peak height were in the range 0.1–0.2°. The crystal was mounted with the normal to the 011 planes oriented 9.09° from the diffractometer ϕ axis. From a total of 5461 reflections, 3026 ($F^2 \geq 3.0\sigma(F^2)$) were used in the structure solution and refinement. Standard reflections monitored periodically showed only a random (±2%) fluctuation during data collection. Full-matrix least-squares refinement using anisotropic thermal parameters for the osmium atoms and isotropic thermal parameters for the remaining atoms converted to the final residuals $R_1 = 0.058$ and $R_2 = 0.067$. The hydrogen atom positions were calculated on the basis of idealized tetrahedral or planar C_6H_6 geometry. Hydrogen atom positions on the methyl groups were calculated by using threefold symmetry and staggered rotational conformations with respect to the substituents on the adjacent atom. Hydrogen atoms were included in structure factor calculations but were not refined. The largest peaks in the final difference Fourier synthesis were 2.8–3.1 e/Å^3 and were clustered about the metal atoms. The largest value of the shift/error parameter on the final cycle of refinement was 0.03. The error in an observation of unit weight was 3.66. Final atomic coordinates and thermal parameters are listed in Table II. Bond distances and angles with errors from the inverse matrix obtained on the final cycle of least-squares refinement are listed in Tables III and IV.

$(\mu\text{-H})_2(\mu_3\text{-}\eta^4\text{-}CH_2C(CH_3)CC(CH_3)=NC_6H_5)Os_3(CO)_8$, B. A thick crystalline plate with dimensions 0.171 mm × 0.040 mm × 0.42 mm was mounted in a thin-walled glass capillary. The faces were identified as 100, $\bar{1}00$, 001, $00\bar{1}$, 021, $01\bar{2}$, and $1\bar{1}\bar{1}$. The crystal was mounted with the [010] direction oriented 6.5° from the diffractometer ϕ axis. Of 5096 reflections which were collected 3237 ($F^2 \geq 3.0\sigma(F^2)$) were used in the structure solution and refinement. Least-squares refinement using anisotropic thermal parameters for the osmium atoms and isotropic thermal parameters for all remaining atoms converged to the final residuals $R_1 = 0.037$ and $R_2 = 0.041$. The hydrocarbon hydrogen atom positions were calculated on the basis of idealized geometry (vide supra) employing located positions when possible. Their contributions were included in structure factor calculations, but they were not refined. Seven reflections were suspected of serious extinction effects and were deleted from the data set. The largest value of the shift/error parameter on the final cycle was 0.01. The error in an observation of unit weight was 3.61. The largest peaks in the final difference Fourier synthesis were 1.4–1.6 e/Å^3 and were in the vicinity of the osmium atoms. Final atomic coordinates and thermal pa-

(4) "International Tables for X-ray Crystallography"; Kynoch Press: Brimingham, England, 1975; Vol. IV: (a) Table 2.3.1, pp 149–50; (b) Table 2.2B, pp 99–101.

Table I. Crystallographic Data for X-ray Diffraction Studies of $(\mu\text{-H})_2(\mu\text{-}\eta^2\text{-}(CH_3)_2CHCC(CH_3)=NC_6H_5)Os_3(CO)_9$, A, and $(\mu\text{-H})_2(\mu\text{-}\eta^4\text{-}CH_2C(CH_3)CC(CH_3)=NC_6H_5)Os_3(CO)_8$, B

	A	B
(A) Crystal Parameters at 23 °C		
space group	$P2_1/c$ (C_{2h}^5), No. 14	$P2_1/c$ (C_{2h}^5), No. 14
a, Å	14.818 (5)	16.060 (5)
b, Å	9.051 (5)	8.820 (4)
c, Å	20.098 (6)	16.809 (4)
β, deg	108.45 (3)	93.83 (2)
V, Å^3	2557 (4)	2376 (2)
Z	4	4
mol wt	997.97	966.94
ρ_{calcd}, g/cm^3	2.59	2.70
(B) Measurement of Intensity Data		
radiation	Mo $K\bar{\alpha}$ (0.710 73 A)	Mo $K\bar{\alpha}$ (0.710 73 A)
monochromator	graphite	graphite
detector aperture, mm		
horizontal: $A + B \tan \theta$	$A = 3.0$	2.6
	$B = 1.0$	1.2
vertical	4.0	4.0
rflctns measd	$+h,+k,\pm l$	$+h,+k,\pm l$
max 2θ, deg	52	52
scan type	moving crystal-stationary counter	moving crystal-stationary counter
ω scan width, deg	0.8	0.8
background	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan
ω scan rate, deg/min: max, min	10, 1.25	10, 1.33
no. rflctns measd	5461	5096
data used ($F^2 > 3.0\sigma(F^2)$)	3292	3237
(C) Treatment of Data		
abs coeff μ, cm^{-1}	158.6	170.6
grid	8 × 12 × 8	6 × 14 × 10
transmission coeff: max, min	0.201, 0.059	0.098, 0.008
p factor	0.02	0.01
final residuals: R_1, R_2	0.058, 0.067	0.037, 0.041
esd of unit wt	3.658	3.606
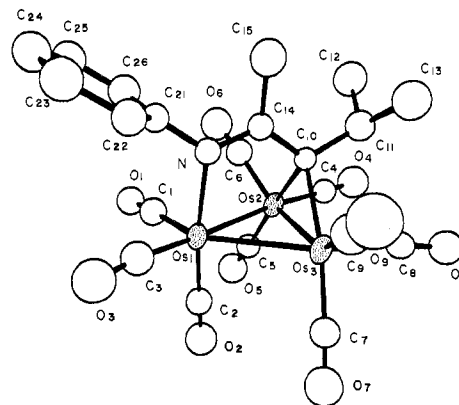
Figure 1. A perspective ORTEP diagram of A showing 50% probability ellipsoids.

rameters are listed in Table V. Bond distances and angles are listed in Tables VI and VII. Structure factor amplitudes for both structures are available (see supplementary material).

Results

Two products, A and B, have been isolated from the reaction of $(CH_3)_2C=CHC(CH_3)=NC_6H_5$ with $(\mu\text{-H})_2Os_3(CO)_{10}$. Both products have been characterized crystallograpically.

Description of the Structures. $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}(CH_3)_2CHCC-(CH_3)=NC_6H_5)Os_3(CO)_9$, A. The molecular structure of A

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}(CH_3)_2CHCC(CH_3)_2=NC_6H_5)Os_3(CO)_9$, A

atom	x/a	y/b	z/c	B, Å²	atom	x/a	y/b	z/c	B, Å²
Os(1)	0.30866 (5)	0.6689 (1)	0.18048 (4)	a	C(13)	0.237 (2)	0.835 (3)	−0.1038 (13)	5.5 (6)
Os(2)	0.28437 (5)	0.4787 (1)	0.06620 (4)	a	C(14)	0.183 (1)	0.776 (2)	0.0402 (10)	2.9 (4)
Os(3)	0.40117 (5)	0.7281 (1)	0.07172 (4)	a	C(15)	0.105 (2)	0.877 (3)	−0.0048 (12)	4.8 (5)
O(1)	0.177 (1)	0.457 (2)	0.2272 (8)	5.0 (4)	C(21)	0.129 (1)	0.861 (2)	0.1358 (10)	3.0 (4)
O(2)	0.482 (1)	0.499 (2)	0.2637 (2)	5.9 (4)	C(22)	0.149 (1)	1.003 (3)	0.1612 (11)	4.0 (5)
O(3)	0.340 (1)	0.904 (2)	0.2976 (9)	6.9 (5)	C(23)	0.086 (2)	1.076 (3)	0.1913 (13)	5.3 (6)
O(4)	0.280 (1)	0.307 (2)	−0.0662 (10)	7.1 (5)	C(24)	0.007 (2)	1.002 (3)	0.1995 (12)	4.9 (5)
O(5)	0.365 (1)	0.220 (2)	0.1667 (10)	6.7 (5)	C(25)	−0.010 (2)	0.868 (3)	0.1729 (12)	4.6 (5)
O(6)	0.079 (1)	0.414 (2)	0.0523 (9)	6.8 (5)	C(26)	0.048 (2)	0.782 (3)	0.1431 (12)	4.6 (5)
O(7)	0.606 (1)	0.733 (2)	0.1696 (9)	5.9 (4)	H(22)[b]	0.207	1.050	0.159	
O(8)	0.466 (1)	0.659 (2)	−0.0553 (8)	5.1 (4)	H(23)	0.099	1.179	0.206	
O(9)	0.397 (1)	1.056 (3)	0.0432 (10)	7.7 (5)	H(24)	−0.034	1.047	0.223	
N	0.194 (1)	0.787 (2)	0.1085 (8)	3.0 (3)	H(25)	−0.069	0.821	0.172	
C(1)	0.225 (1)	0.542 (3)	0.2085 (11)	4.3 (5)	H(26)	0.033	0.674	0.127	
C(2)	0.415 (1)	0.562 (3)	0.2323 (11)	3.9 (5)	H(11)	0.275	0.621	−0.069	
C(3)	0.322 (2)	0.814 (3)	0.2505 (12)	4.5 (5)	H(151)	0.097	0.868	−0.053	
C(4)	0.284 (1)	0.379 (3)	−0.0137 (11)	3.7 (5)	H(152)	0.045	0.860	0.001	
C(5)	0.335 (1)	0.313 (3)	0.1263 (11)	4.1 (5)	H(153)	0.122	0.980	0.007	
C(6)	0.156 (1)	0.439 (3)	0.0543 (12)	4.6 (5)	H(121)	0.119	0.613	−0.156	
C(7)	0.528 (1)	0.731 (3)	0.1299 (15)	3.7 (4)	H(122)	0.122	0.521	−0.090	
C(8)	0.436 (1)	0.685 (3)	−0.0102 (10)	3.4 (4)	H(123)	0.077	0.678	−0.101	
C(9)	0.399 (2)	0.927 (3)	0.0531 (13)	5.3 (6)	H(131)	0.224	0.819	−0.152	
C(10)	0.249 (1)	0.702 (2)	0.0145 (9)	2.2 (3)	H(132)	0.194	0.907	−0.096	
C(11)	0.225 (1)	0.690 (3)	−0.0661 (11)	4.1 (5)	H(133)	0.301	0.872	−0.084	
C(12)	0.129 (2)	0.623 (3)	−0.1077 (13)	5.7 (6)					

	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Os(1)	3.08 (3)	3.19 (4)	2.73 (3)	0.15 (3)	1.51 (2)	0.04 (3)
Os(2)	3.05 (2)	2.89 (4)	3.29 (3)	0.27 (3)	1.65 (2)	−0.19 (3)
Os(3)	3.11 (2)	2.89 (4)	3.50 (3)	0.35 (3)	2.03 (2)	0.20 (3)

[a] Anisotropic thermal parameters are listed in the second half of the table. The form of the anisotropic thermal parameter is $\exp[-1/4 \cdot (B(1,1)h^2a^{*2} + B(2,2)k^2b^{*2} + B(3,3)l^2c^{*2} + B(1,2)hka^*b^* + B(1,3)hla^*c^* + B(2,3)klb^*c^*)]$. [b] Hydrogen atom positions were calculated and not refined. Isotropic thermal parameters of 5.0 Å² were used.

Table III. Bond Distances (Å) with Estimated Standard Deviations for $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}(CH_3)_2CHCC(CH_3)=NC_6H_5)Os_3(CO)_9$, A

Os(1)-Os(2)	2.801 (1)	C(14)-C(15)	1.529 (17)
Os(1)-Os(3)	2.974 (1)	C(14)-N	1.336 (13)
Os(2)-Os(3)	2.825 (1)	N-C(21)	1.417 (13)
Os(1)-C(1)	1.903 (13)	C(21)-C(22)	1.376 (16)
Os(1)-C(2)	1.857 (13)	C(22)-C(23)	1.429 (17)
Os(1)-C(3)	1.888 (14)	C(23)-C(24)	1.411 (18)
Os(1)-N	2.139 (9)	C(24)-C(25)	1.317 (18)
Os(2)-C(4)	1.841 (12)	C(25)-C(26)	1.429 (17)
Os(2)-C(5)	1.922 (14)	C(26)-C(21)	1.446 (16)
Os(2)-C(6)	1.882 (13)	C(1)-O(1)	1.187 (14)
Os(2)-C(10)	2.256 (10)	C(2)-O(2)	1.149 (14)
Os(3)-C(7)	1.877 (12)	C(3)-O(3)	1.214 (15)
Os(3)-C(8)	1.918 (11)	C(4)-O(4)	1.223 (15)
Os(3)-C(9)	1.833 (17)	C(5)-O(5)	1.156 (15)
Os(3)-C(10)	2.201 (10)	C(6)-O(6)	1.152 (13)
C(10)-C(11)	1.550 (15)	C(7)-O(7)	1.180 (13)
C(10)-C(14)	1.400 (14)	C(8)-O(8)	1.147 (12)
C(11)-C(12)	1.536 (18)	C(9)-O(9)	1.188 (18)
C(11)-C(13)	1.553 (19)		

is shown in Figure 1. The molecule contains a triangular cluster of mutually bonded osmium atoms Os(1)-Os(2) = 2.801 (1) Å, Os(1)-Os(3) = 2.974 (1) Å, and Os(2)-Os(3) = 2.825 (1) Å. Two of these distances are slightly shorter than the average Os-Os bond distance of 2.877 (3) Å found in $Os_3(CO)_{12}$[5] while one is substantially longer. Nine linear terminal carbonyl ligands are arranged such that each osmium atom has three. Three of these ligands lie on one side more or less perpendicular to the plane of the Os_3 triangle while the remaining six lie more or less in the plane of the triangle.

One entire face of the Os_3 triangle is occupied by a μ_3-η^2-$(CH_3)_2CHCC(CH_3)=NC_6H_5$ ligand. It is bonded to the cluster through the atoms N and C(10). The nitrogen atom

Table IV. Bond Angles (Deg) with Estimated Standard Deviations for $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}(CH_3)_2CHCC(CH_3)=NC_6H_5)Os_3(CO)_9$, A

Os(1)-Os(2)-Os(3)	63.82 (2)	Os(2)-Os(3)-C(10)	51.5 (3)
Os(1)-Os(3)-Os(2)	57.69 (2)	C(7)-Os(3)-C(8)	92.6 (5)
Os(2)-Os(1)-Os(3)	58.50 (2)	C(7)-Os(3)-C(9)	93.3 (6)
Os(2)-Os(1)-C(1)	86.8 (4)	C(7)-Os(3)-C(10)	171.7 (4)
Os(2)-Os(1)-C(2)	90.4 (4)	C(8)-Os(3)-C(9)	90.8 (6)
Os(2)-Os(1)-C(3)	173.9 (4)	C(8)-Os(3)-C(10)	92.5 (4)
Os(2)-Os(1)-N	83.4 (2)	C(9)-Os(3)-C(10)	93.1 (5)
Os(3)-Os(1)-C(1)	145.3 (4)	Os(2)-C(10)-C(13)	78.7 (3)
Os(3)-Os(1)-C(2)	90.1 (3)	Os(2)-C(10)-C(11)	111.1 (7)
Os(3)-Os(1)-C(3)	117.3 (4)	Os(3)-C(10)-C(11)	113.8 (6)
Os(3)-Os(1)-N	82.2 (2)	C(11)-C(10)-C(14)	117.9 (9)
C(1)-Os(1)-C(2)	92.0 (5)	C(10)-C(11)-C(12)	117.1 (10)
C(1)-Os(1)-C(3)	97.1 (5)	C(10)-C(11)-C(13)	115.4 (11)
C(1)-Os(1)-N	92.9 (5)	C(12)-C(11)-C(13)	107.0 (11)
C(2)-Os(1)-C(3)	94.1 (6)	C(10)-C(14)-C(15)	123.4 (10)
C(2)-Os(1)-N	171.9 (4)	C(10)-C(14)-N	123.1 (10)
C(3)-Os(1)-N	91.7 (5)	N-C(14)-C(15)	112.4 (10)
Os(1)-Os(2)-C(4)	169.0 (4)	C(14)-N-C(21)	124.2 (10)
Os(1)-Os(2)-C(5)	92.3 (4)	Os(1)-N-C(14)	117.7 (7)
Os(1)-Os(2)-C(6)	94.8 (4)	Os(1)-N-C(21)	117.7 (7)
Os(1)-Os(2)-C(10)	77.2 (2)	N-C(21)-C(22)	119.1 (10)
Os(3)-Os(2)-C(4)	105.2 (4)	N-C(21)-C(26)	119.6 (11)
Os(3)-Os(2)-C(5)	119.2 (4)	C(21)-C(22)-C(23)	119.8 (11)
Os(3)-Os(2)-C(6)	137.8 (4)	C(22)-C(23)-C(24)	120.5 (14)
Os(3)-Os(2)-C(10)	49.8 (2)	C(23)-C(24)-C(25)	117.1 (13)
C(4)-Os(2)-C(5)	93.4 (5)	C(24)-C(25)-C(26)	127.3 (13)
C(4)-Os(2)-C(6)	94.0 (5)	C(25)-C(26)-C(21)	113.9 (13)
C(4)-Os(2)-C(10)	95.3 (5)	C(26)-C(21)-C(22)	121.0 (11)
C(5)-Os(2)-C(6)	96.2 (5)	Os(1)-C(1)-O(1)	176 (1)
C(5)-Os(2)-C(10)	167.3 (5)	Os(1)-C(2)-O(2)	178 (1)
C(6)-Os(2)-C(10)	97.1 (5)	Os(1)-C(3)-O(3)	174 (1)
Os(1)-Os(3)-C(7)	98.6 (3)	Os(2)-C(4)-O(4)	177 (1)
Os(1)-Os(3)-C(8)	155.2 (4)	Os(2)-C(5)-O(5)	175 (1)
Os(1)-Os(3)-C(9)	110.3 (4)	Os(2)-C(6)-O(6)	175 (1)
Os(1)-Os(3)-C(10)	74.2 (2)	Os(3)-C(7)-O(7)	176 (1)
Os(2)-Os(3)-C(7)	121.2 (4)	Os(3)-C(8)-O(8)	174 (1)
Os(2)-Os(3)-C(8)	97.6 (4)	Os(3)-C(9)-O(9)	178 (1)
Os(2)-Os(3)-C(9)	143.7 (4)		

(5) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations for
$(\mu\text{-}H)_2(\mu_3\text{-}\eta^4\text{-}CH_2C(CH_3)CC(CH_3)=NC_6H_5)Os_3(CO)_8$, B

atom	x/a	y/b	z/c	B	atom	x/a	y/b	z/c	B, Å²
Os(1)	0.29739 (4)	0.28199 (7)	0.10200 (3)	a	C(12)	0.4682 (11)	0.701 (2)	0.0797 (9)	5.9 (4)
Os(2)	0.33967 (3)	0.54112 (7)	0.19940 (3)	a	C(13)	0.4702 (9)	0.488 (2)	0.1733 (8)	4.6 (3)
Os(3)	0.17098 (3)	0.50070 (7)	0.12085 (3)	a	C(14)	0.3043 (8)	0.577 (2)	0.0074 (7)	3.6 (3)
O(1)	0.4558 (8)	0.091 (2)	0.0907 (7)	8.0 (3)	C(15)	0.3417 (10)	0.613 (2)	−0.0697 (8)	5.1 (4)
O(2)	0.1942 (8)	0.029 (1)	0.1752 (7)	7.4 (3)	C(21)	0.1717 (8)	0.675 (2)	−0.0419 (7)	3.3 (3)
O(3)	0.2298 (8)	0.231 (1)	−0.0700 (6)	7.0 (3)	C(22)	0.1378 (9)	0.597 (2)	−0.1078 (8)	4.2 (3)
O(4)	0.3632 (7)	0.878 (1)	0.2270 (6)	5.7 (3)	C(23)	0.0843 (10)	0.672 (2)	−0.1637 (8)	5.1 (3)
O(5)	0.3520 (8)	0.490 (1)	0.3760 (6)	7.0 (3)	C(24)	0.0656 (10)	0.822 (2)	−0.1545 (8)	4.8 (3)
O(6)	0.0529 (7)	0.317 (1)	0.0086 (6)	5.5 (2)	C(25)	0.0994 (10)	0.901 (2)	−0.0895 (8)	5.1 (4)
O(7)	0.1185 (6)	0.328 (1)	0.2649 (5)	5.1 (2)	C(26)	0.1519 (9)	0.832 (2)	−0.0322 (8)	4.3 (3)
O(8)	0.0492 (6)	0.766 (1)	0.1438 (5)	5.1 (2)	H(121)[b]	0.482	0.765	0.125	
N	0.2252 (7)	0.604 (1)	0.0194 (6)	3.3 (2)	H(122)	0.430	0.759	0.044	
C(1)	0.3934 (10)	0.159 (2)	0.0953 (9)	5.6 (4)	H(123)	0.519	0.689	0.052	
C(2)	0.2359 (10)	0.123 (2)	0.1486 (8)	5.3 (4)	H(151)	0.408	0.634	−0.070	
C(3)	0.2564 (10)	0.246 (2)	−0.0034 (8)	4.8 (3)	H(152)	0.314	0.698	−0.094	
C(4)	0.3549 (9)	0.747 (2)	0.2171 (7)	3.9 (3)	H(153)	0.332	0.527	−0.106	
C(5)	0.3458 (10)	0.514 (2)	0.3071 (8)	4.7 (3)	H(131)	0.449	0.392	0.192	
C(6)	0.0982 (9)	0.385 (2)	0.0506 (7)	4.1 (3)	H(132)	0.516	0.533	0.203	
C(7)	0.1367 (9)	0.392 (2)	0.2104 (7)	3.8 (3)	H(22)	0.154	0.490	−0.114	
C(8)	0.0951 (9)	0.668 (2)	0.1362 (7)	3.9 (3)	H(23)	0.062	0.615	−0.209	
C(10)	0.3556 (8)	0.499 (2)	0.0736 (7)	3.4 (3)	H(24)	0.028	0.870	−0.194	
C(11)	0.4328 (9)	0.553 (2)	0.1041 (8)	4.3 (3)	H(25)	0.086	1.004	−0.083	
					H(26)	0.177	0.890	0.013	

	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Os(1)	3.97 (2)	2.77 (2)	4.22 (2)	0.15 (2)	0.50 (2)	0.14 (2)
Os(2)	2.78 (2)	3.31 (2)	3.62 (2)	−0.13 (2)	−0.25 (2)	0.31 (2)
Os(3)	2.69 (2)	3.62 (2)	2.51 (2)	−0.10 (2)	0.08 (2)	−0.02 (2)

a Anisotropic thermal parameters are listed in the second half of the table. The form of the anisotropic thermal parameter is $\exp[-^1/_4 \cdot (B(1,1)h^2a^{*2} + B(2,2)k^2b^{*2} + B(3,3)l^2c^{*2} + B(1,2)hka^*b^* + B(1,3)hla^*c^* + B(2,3)klb^*c^*)]$. b Hydrogen atom positions were calculated and not refined. An isotropic thermal parameter of 6.0 was used for each.

Table VI. Bond Distances (Å) with Estimated Standard Deviations for $(\mu\text{-}H)_2[\mu_3\text{-}\eta^4\text{-}CH_2C(CH_3)CC(CH_3)=NC_6H_5]Os_3(CO)_8$, B

Os(1)–Os(2)	2.834 (1)	C(11)–C(13)	1.395 (10)
Os(1)–Os(3)	2.955 (1)	C(14)–C(15)	1.498 (10)
Os(2)–Os(3)	2.866 (1)	C(14)–N	1.321 (9)
Os(1)–C(6)	1.893 (10)	N–C(21)	1.438 (8)
Os(1)–C(7)	1.912 (10)	C(21)–C(22)	1.386 (9)
Os(1)–C(8)	1.875 (8)	C(22)–C(23)	1.397 (10)
Os(1)–N	2.193 (7)	C(23)–C(24)	1.369 (11)
Os(2)–C(1)	1.854 (8)	C(24)–C(25)	1.375 (10)
Os(2)–C(2)	1.822 (8)	C(25)–C(26)	1.382 (10)
Os(2)–C(3)	2.180 (6)	C(26)–C(21)	1.427 (10)
Os(2)–C(10)	2.266 (8)	C(1)–O(1)	1.175 (10)
Os(3)–C(4)	2.220 (8)	C(2)–O(2)	1.173 (10)
Os(3)–C(5)	1.902 (8)	C(3)–O(3)	1.179 (8)
Os(3)–C(10)	1.899 (8)	C(4)–O(4)	1.169 (9)
Os(3)–C(11)	1.942 (8)	C(5)–O(5)	1.176 (8)
Os(3)–C(13)	2.169 (5)	C(6)–O(6)	1.150 (8)
C(10)–C(11)	1.394 (10)	C(7)–O(7)	1.131 (8)
C(10)–C(14)	1.509 (9)	C(8)–O(8)	1.146 (8)
C(11)–C(12)	1.495 (12)		

Figure 2. A perspective ORTEP diagram of B showing 50% probability ellipsoids.

atoms were not observed crystallographically, their presence was confirmed by the ${}^1H$ NMR spectrum. The spread of bond distances and angles within the phenyl ring is rather large, but we do not feel that this is chemically or structurally significant.

The ${}^1H$ NMR spectrum showed the presence of two hydride ligands. They were not observed crystallographically but their structural imprints are apparent in the molecule. One hydride ligand evidently bridges the Os(2)–Os(3) bond in a large cavity circumscribed by the carbonyl ligands C(4)–O(4), C(5)–O(5), C(7)–O(7), and C(8)–O(8). The other hydride probably bridges the Os(1)–Os(3) bond. This is indicated by the long metal–metal bond length and the bending of the carbonyl ligand C(3)–O(3) away from that bond.[8] This bending is shown by the large bond angle Os(3)–Os(1)–C(3) = 117.3 (4)° compared to the corresponding angle Os(2)–Os(1)–C(1) which is only 86.8 (4)°. An alternative configuration having hydride bridges along the bonds Os(1)–Os(3) and Os(1)–Os(2)

N is bonded solely to Os(1), Os(1)–N = 2.139 (9) Å, while carbon atom C(10) serves as a fairly symmetrical bridge between Os(2) and Os(3), Os(2)–C(10) = 2.256 (10) Å and Os(3)–C(10) = 2.201 (10) Å, and could be described as a bridging carbenoid carbon. The C(14)–N distance at 1.336 (13) Å is slightly longer than that of a carbon–nitrogen double bond.[6] The C(10)–C(14) distance at 1.400 (14) Å is short and indicates the presence of partial multiple bonding between the iminyl group and the carbenoid carbon. A normal isopropyl group is bonded to C(10), and although the hydrogen

(6) C–N double bond lengths have been reported in the range 1.253–1.306 Å in a variety of oximes.[7]

(7) Wetherington, J. B.; Moncrief, J. W. *Acta Crystallogr., Sect. B* **1973**, *29*, 1520.

(8) (a) Churchill, M. R.; Deboer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843. (b) Churchill, M. R. *Adv. Chem. Ser.* **1978**, *No. 167*, 36–60.

Table VII. Bond Angles (Deg) with Estimated Standard Deviations for $(\mu\text{-H})_2[\mu_3\text{-}\eta^4\text{-CH}_2C(CH_3)CC(CH_3)=NC_6H_5]Os_3(CO)_8$, B

Os(2)–Os(3)–Os(1)	58.23 (1)	Os(3)–Os(1)–C(8)	114.4 (2)
Os(2)–Os(1)–Os(3)	59.32 (1)	Os(3)–Os(1)–N	84.0 (1)
Os(3)–Os(2)–Os(1)	62.45 (1)	C(6)–Os(1)–C(7)	91.3 (3)
Os(3)–Os(2)–C(1)	109.1 (3)	C(6)–Os(1)–C(8)	97.2 (3)
Os(3)–Os(2)–C(2)	117.4 (3)	C(6)–Os(1)–N	90.0 (3)
Os(3)–Os(2)–C(3)	136.7 (3)	C(7)–Os(1)–C(8)	93.6 (3)
Os(3)–Os(2)–C(10)	48.9 (2)	C(7)–Os(1)–N	172.0 (3)
Os(1)–Os(2)–C(1)	171.2 (3)	C(8)–Os(1)–N	94.1 (3)
Os(1)–Os(2)–C(2)	93.4 (3)	Os(2)–C(10)–Os(3)	81.9 (2)
Os(1)–Os(2)–C(3)	90.6 (3)	Os(2)–C(10)–C(11)	126.9 (6)
Os(1)–Os(2)–C(10)	75.6 (2)	Os(2)–C(10)–C(14)	110.0 (5)
C(1)–Os(2)–C(2)	92.9 (4)	Os(3)–C(10)–C(11)	75.1 (4)
C(1)–Os(2)–C(3)	94.8 (3)	Os(3)–C(10)–C(14)	122.8 (5)
C(1)–Os(2)–C(10)	97.1 (3)	C(11)–C(10)–C(14)	122.8 (7)
C(2)–Os(2)–C(3)	96.1 (3)	C(10)–C(11)–C(13)	119.3 (7)
C(2)–Os(2)–C(10)	165.2 (3)	C(10)–C(11)–C(12)	123.0 (7)
C(3)–Os(2)–C(10)	93.9 (3)	C(12)–C(11)–C(13)	115.9 (7)
Os(2)–Os(3)–C(4)	153.7 (2)	Os(3)–C(11)–C(10)	68.4 (4)
Os(2)–Os(3)–C(5)	117.3 (3)	Os(3)–C(11)–C(12)	121.0 (6)
Os(2)–Os(3)–C(10)	49.2 (2)	Os(3)–C(11)–C(13)	70.1 (4)
Os(2)–Os(3)–C(11)	77.0 (2)	Os(3)–C(13)–C(11)	73.7 (5)
Os(2)–Os(3)–C(13)	84.8 (2)	C(10)–C(14)–C(15)	120.2 (7)
Os(1)–Os(3)–C(4)	107.3 (2)	N–C(14)–C(15)	122.6 (6)
Os(1)–Os(3)–C(5)	114.6 (3)	C(14)–N–C(21)	120.3 (6)
Os(1)–Os(3)–C(10)	73.1 (2)	Os(1)–N–C(14)	118.9 (5)
Os(1)–Os(3)–C(11)	108.6 (2)	Os(1)–N–C(21)	119.6 (4)
Os(1)–Os(3)–C(13)	137.4 (2)	N–C(21)–C(22)	122.8 (7)
C(4)–Os(3)–C(5)	88.3 (3)	N–C(21)–C(26)	117.7 (6)
C(4)–Os(3)–C(10)	107.6 (3)	C(26)–C(21)–C(22)	119.5 (7)
C(4)–Os(3)–C(11)	89.0 (3)	C(21)–C(22)–C(23)	119.6 (8)
C(4)–Os(3)–C(13)	97.1 (3)	C(22)–C(23)–C(24)	120.8 (8)
C(5)–Os(3)–C(10)	160.0 (3)	C(23)–C(24)–C(25)	120.1 (8)
C(5)–Os(3)–C(11)	135.5 (3)	C(24)–C(25)–C(26)	121.2 (8)
C(5)–Os(3)–C(13)	100.3 (3)	C(25)–C(26)–C(21)	118.8 (7)
C(10)–Os(3)–C(11)	36.5 (2)	Os(2)–C(1)–O(1)	175.8 (9)
C(10)–Os(3)–C(13)	66.3 (2)	Os(2)–C(2)–O(2)	176.2 (8)
C(11)–Os(3)–C(13)	36.2 (3)	Os(2)–C(3)–O(3)	177.0 (8)
Os(2)–Os(1)–C(6)	88.9 (2)	Os(3)–C(4)–O(4)	178.6 (7)
Os(2)–Os(1)–C(7)	89.5 (2)	Os(3)–C(5)–O(5)	176.7 (8)
Os(2)–Os(1)–C(8)	173.1 (2)	Os(1)–C(6)–O(6)	178.7 (8)
Os(2)–Os(1)–N	82.6 (1)	Os(1)–C(7)–O(7)	178.0 (7)
Os(3)–Os(1)–C(6)	148.1 (2)	Os(1)–C(8)–O(8)	178.4 (7)
Os(3)–Os(1)–C(7)	90.7 (2)		

Table VIII

(A) Unit Weighted Least-Squares Planes for $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-(CH}_3)_2CHCC(CH_3)=NC_6H_5)Os_3(CO)_9$, A

plane	atoms	dist from plane, Å
1	Os(1)	0.00
	Os(2)	0.00
	Os(3)	0.00
	C(10)[a]	1.72 (2)
	C(11)[a]	2.36 (2)
	C(14)[a]	2.56 (2)
	N[a]	2.11 (2)
2	C(11)	0.05 (2)
	C(10)	−0.08 (2)
	C(14)	0.05 (2)
	C(15)	−0.03 (3)
	N	0.02 (2)
	C(12)[a]	1.32 (3)
	C(13)[a]	−1.16 (3)
3	C(21)	0.01 (2)
	C(22)	−0.01 (2)
	C(23)	0.01 (2)
	C(24)	−0.03 (2)
	C(25)	0.03 (2)
	C(26)	−0.02 (2)
	N[a]	−0.06 (2)
	Os(1)[a]	0.99 (2)

(B) Equations of Planes: $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	−0.6671	0.5258	−0.5277	−0.9182
2	−0.6219	−0.7770	−0.0972	−7.1136
3	−0.2729	0.3496	−0.8963	0.1044

(C) Dihedral Angles

planes	angle, deg	planes	angle, deg
1–2	86.7	2–3	89.2
1–3	33.0		

[a] These atoms were not used in the calculation of the plane.

is ruled out because the isopropyl methyl groups are inequivalent in the ^{1}H NMR spectrum.

Overall the structure of A is similar to that of the compound $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-OC}_6H_3CH_2C_6H_5)Os_3(CO)_9$[9] which contains a $\mu_3\text{-}\eta^2\text{-OC}_6H_3CH_2C_6H_5$ ligand bonded to the face of an triosmium cluster with an oxygen atom bonded to one osmium atom and an ortho position of an aromatic ring bridging the two remaining osmium atoms. There are no unusually short intermolecular contacts in the crystal of A. The shortest distances were between carbonyl oxygen atoms (cf. Table X).

$(\mu\text{-H})_2(\mu_3\text{-}\eta^4\text{-CH}_2C(CH_3)CC(CH_3)=NC_6H_5)Os_3(CO)_8$, **B.** The molecular structure of B is shown in Figure 2. A triangular cluster of osmium atoms contains eight linear terminal carbonyl ligands. The molecule is derived from A by the loss of one of the equatorial carbonyl ligands from Os(3), dehydrogenation of the isopropylmethinyl and one of the methyl carbon atoms, and attachment of those carbons to the metal atom Os(3). Except for these changes the gross molecular structure of B is very similar to that of A.

The ^{1}H NMR spectrum shows two hydride resonances. The metal–metal bond distances and disposition of ligands are similar to those of A, and we anticipate a similar arrangement of hydride ligands.

The $\mu_3\text{-}\eta^4\text{-CH}_2C(CH_3)CC(CH_3)=NC_6H_5$ ligand bonds to

(9) Azam, K. A.; Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Chem. Commun.* **1978**, 1086.

one face of the cluster. As in A the nitrogen atom is bonded solely to Os(1), Os(1)–N = 2.169 (5) Å. Atom C(10) bridges Os(2) and Os(3), Os(2)–C(10) = 2.193 (7) Å and Os(3)–C(10) = 2.180 (6) Å. However, in B atoms C(11) and C(13) are now bonded to Os(3), Os(3)–C(11) = 2.266 (8) Å and Os(3)–C(13) = 2.220 (8) Å. In combination the group C(10)–C(11)–C(13) could be viewed as an allyl group π bonded to Os(3) with C(10) σ bonded to Os(2) and C(14). The carbon–carbon distances C(10)–C(11) = 1.394 (10) Å and C(11)–C(13) = 1.395 (10) Å infer a uniform delocalization across these three atoms. The C(10)–C(14) distance at 1.509 (9) Å is significantly longer (0.109 Å) than the corresponding distance in A. Evidently the partial multiple bonding to C(10) has moved from C(14) in A to C(11) in B. The C(14)–N distance at 1.321 (9) Å is slightly but not significantly shorter (based on 3σ) than the C(14)–N distance in A. There were no usually short intermolecular contacts. The shortest distances were between carbonyl oxygen atoms (cf. table XI).

^{1}**H NMR Spectra.** The 270-MHz ^{1}H NMR spectrum of A in CDCl$_3$ showed resonances at δ 7.38 (t, $J = 7$ Hz, 2 H, Ph), 7.12 (d, $J = 7$ Hz, 1H, Ph), 6.63 (d, $J = 7$ Hz, 1 H, Ph), 6.44 (d, $J = 7$ Hz, 1 H, Ph), 2.24 (septet, $J = 6.1$ Hz, CH(CH$_3$)$_2$), 1.42 (s, 3 H, N=CCH$_3$), 1.34 (d, $J = 6.1$ Hz, 3 H, CH(CH_3)$_2$), 1.32 (d, $J = 6.1$ Hz, 3 H, CH(CH_3)$_2$), −12.98 (s, 1 H, OsHOs), and −13.54 (s, 1 H, OsHOs). The isopropyl methyl resonances are inequivalent due to the unsymmetric distribution of hydride ligands around the Os$_3$ triangle. This also indicates that the hydride ligands do not readily move around the cluster. The 270-MHz spectrum of B showed resonances at δ 6.52–7.48 (m, 5 H, Ph), 3.20 (d, $J = 3.3$ Hz, 1 H, C=CH$_2$), 2.42 (dd, $J = 3.3$ Hz, $J = 3.7$ Hz, 1 H,

Table IX

(A) Unit Weighted Least-Squares Planes for
$(\mu\text{-H})_2(\mu_3\text{-}\eta^4\text{-CH}_2\text{C(CH}_3)\text{CC(CH}_3)\text{=NC}_6\text{H}_s)\text{Os}_3(\text{CO})_8$, B

plane	atoms	dist from plane, Å
1	Os(1)	0.00
	Os(2)	0.00
	Os(3)	0.00
	C(10)^a	1.65 (1)
	N^a	2.15 (1)
2	N	0.007 (11)
	C(14)	−0.020 (14)
	C(10)	0.006 (13)
	C(15)	0.007 (17)
3	C(10)	−0.03 (1)
	C(11)	0.08 (1)
	C(12)	−0.03 (1)
	C(13)	−0.03 (2)
	Os(3)^a	−1.776 (1)
4	C(21)	0.000 (13)
	C(22)	0.004 (14)
	C(23)	−0.003 (16)
	C(24)	−0.001 (15)
	C(25)	0.005 (16)
	C(26)	−0.004 (14)
	N^a	−0.035 (10)
	Os(1)^a	−1.946 (1)

(B) Equations of Planes: $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	0.3373	0.4903	−0.8036	1.4168
2	−0.2469	−0.8958	−0.3697	−5.7907
3	0.5717	−0.5386	−0.6190	0.1160
4	0.8210	0.2536	−0.5114	4.1729

(C) Dihedral Angles

planes	angle, deg	planes	angle, deg
1-2	−77.0	2-3	55.2
1-3	64.8	2-4	−76.1
1-4	35.7	3-4	49.5

^{a} These atoms were not used in the calculation of the plane.

Table X. Intermolecular Contacts (Å) for
$(\mu\text{-H})_2[\mu_3\text{-}\eta^2\text{-(CH}_3)_2\text{CHC(CH}_3)\text{=NC}_6\text{H}_s]\text{Os}_3(\text{CO})_9$, A,
Less Than 3.5 Å^a

O(2)–C(3)^I	3.44 (2)	C(4)–O(9)^{IV}	3.39 (2)
O(2)–O(3)^I	3.36 (1)	O(4)–C(7)^V	3.48 (2)
O(2)–O(5)^{II}	3.01 (1)	O(4)–O(7)^V	3.08 (1)
O(2)–C(7)^I	3.27 (2)	O(4)–O(9)^{IV}	3.26 (2)
O(2)–O(7)^I	3.23 (1)	C(5)–O(9)^{IV}	3.17 (2)
O(3)–O(7)^{II}	3.10 (2)	O(5)–O(7)^I	3.18 (1)
O(3)–O(8)^{III}	3.01 (1)	O(5)–O(9)^{IV}	3.06 (2)
		O(6)–O(6)^{VI}	3.03 (2)

^{a} Symmetry transforms: (I) $1 - x$, $y - 1/2$, $1/2 - z$; (II) $1 - x$, $y + 1/2$, $1/2 - z$; (III) x, $3/2 - y$, $1/2 - z$; (IV) x, $y - 1$, z; (V) $1 - x$, $1 - y$, $-z$; (VI) $-x$, $1 - y$, $-z$.

C=CH$_2$), 2.35 (s, 3 H, CH$_3$), 1.61 (s, 3 H, CH$_3$), −13.15 (s, 1 H, OsHOs), and −16.31 (d, J = 3.7 Hz, 1 H, OsHOs). Interestingly one of the hydrogen atoms of the alkenyl group was coupled to one of the hydride ligands.

Discussion

$(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ reacted with $(\text{CH}_3)_2\text{C=CHC(CH}_3)\text{=N-}C_6H_5$ on a 1:1 basis, lost 1 mol of carbon monoxide, and formed the complex $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-(CH}_3)_2\text{CHCC(CH}_3)\text{=}NC_6H_5$)Os$_3(CO)_9$, A. Unlike the reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ with aliphatic imines where a hydrogen atom can be either added to or removed from the iminyl carbon,[2] in the present case there was no net transfer of hydrogen between the cluster to the iminyl group. Although the iminyl nitrogen atom did become coordinated to the cluster, the most important reaction

Table XI. Intermolecular Contacts (Å) for
$(\mu\text{-H})_2[\mu_3\text{-}\eta^4\text{-CH}_2\text{C(CH}_3)\text{CC(CH}_3)\text{=NC}_6\text{H}_s]\text{Os}_3(\text{CO})_8$, B,
Less Than 3.5 Å^a

C(1)–O(4)^I	3.38	O(4)–C(13)^{IV}	3.21
O(1)–O(4)^I	3.39	O(4)–C(15)^V	3.46
O(1)–O(5)^{II}	3.23	O(6)–C(8)^{VI}	3.29
O(1)–C(12)^I	3.45	O(6)–O(8)^{VI}	3.03
C(2)–O(4)^I	3.20	O(6)–C(24)^{VI}	3.43
O(2)–O(4)^I	3.10	O(6)–C(25)^{VI}	3.46
O(2)–O(8)^I	3.31	O(7)–O(8)^{VII}	3.23
C(3)–O(5)^{III}	3.35	O(7)–C(24)^V	3.50
O(3)–O(5)^{III}	2.95	O(7)–C(25)^V	3.45
O(3)–O(7)^{III}	3.24	O(8)–C(23)^V	3.29
		O(8)–C(24)^V	3.47

^{a} Symmetry transforms: (I) x, $y - 1$, z; (II) $1 - x$, $y - 1/2$, $1/2 - z$; (III) x, $1/2 - y$, $z - 1/2$; (IV) $1 - x$, $1/2 + y$, $1/2 - z$; (V) x, $3/2 - y$, $1/2 + z$; (VI) $-x$, $y - 1/2$, $1/2 - z$. All esd's ±0.01 Å.

Scheme I
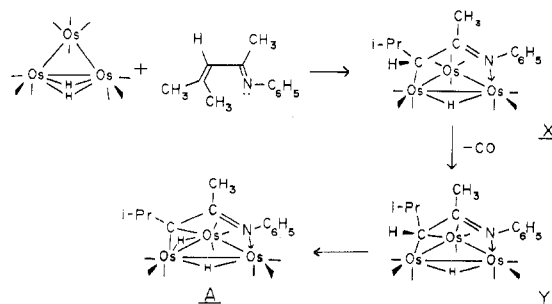
occurred at the olefinic group where a 1,2 shift moved the hydrogen atom from the α- to the β-carbon atom. This produced an isopropyl group and the α-carbon assumed a bridging position across two metal atoms. We do not currently know the mechanism of the 1,2 shift, or whether or not the shifted hydrogen atom has scrambled with the original cluster hydride ligands. Our efforts to carry out a labeling study have not been successful.

It is interesting, however, to compare our results with those of Shapley[10] who studied the reaction of H$_2$Os$_3$(CO)$_{10}$ with α,β-unsaturated esters. In those reactions he observed facile transfer of one hydrogen atom from the cluster to the β-carbon of the olefinic unit. It was proposed that the alkylcarboxylate ligand which formed bridged an edge of the cluster via the ketonic oxygen atom of the carboxylate group and the α-carbon atom. These complexes readily eliminated alkane via transfer of the second hydrogen atom to the ligand.

Interestingly, these reactions do suggest a plausible mechanism for the formation of A. Hydrogen transfer to the olefinic unit of the unsaturated imine could produce an intermediate, X (see Scheme I), containing an *edge*-bridging alkyliminyl ligand. Decarbonylation might yield a complex, Y, containing a *face*-bridging alkyliminyl ligand. The bridging alkyl carbon in Y is not without precedent and could be structurally similar to that of the bridging methyl group in $(\mu\text{-H})(\mu\text{-CH}_3)\text{Os}_3$-(CO)$_{10}$.[11] Transfer of the α-hydrogen atom in Y to the metal atoms could produce A. That rearrangement might be very similar to the known interconversion between $(\mu\text{-H})(\mu$-CH$_3$)Os$_3$(CO)$_{10}$ and $(\mu\text{-H})_2(\mu\text{-CH}_2)\text{Os}_3(\text{CO})_{10}$.[12]

The second product isolated from the reaction was the compound $(\mu\text{-H})_2(\mu_3\text{-}\eta^4\text{-CH}_2\text{C(CH}_3)\text{CC(CH}_3)\text{=NC}_6\text{H}_5)$-Os$_3(CO)_8$, B. B was formed by the loss of 2 mol of carbon monoxide from the original cluster and two hydrogen atoms, one from the α-carbon and one from a γ-carbon atom of the

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imine. It occurred to us that B might have been formed from A through removal of hydrogen atoms from the methinyl and a methyl carbon of the isopropyl group. Complex A was not converted to B in refluxing hexanes solution in the absence of imine. However, under slightly more vigorous conditions, namely, refluxing octane solution, A was converted to B in high (97%) yield. The ability of triosmium clusters to abstract hydrogen from alkyl groups has been observed on several previous occasions.[12–14] The fate of the hydrogen atoms is not known. At present we can only assume that they were expelled from the cluster as H_2.

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Notes

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Synthesis and Structure of a 12-Crown-4 Sandwich Complex of Manganese(II), Bis(1,4,7,10-tetraoxacyclododecane)manganese(II) Tribromide

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The coordination chemistry of crown ether ligands has drawn considerable interest. Natural macrocyclic antibiotics display unique selectivity for binding simple cationic metal ions, and much effort has been devoted to the design and preparation of synthetic chelating agents which demonstrate similar specificity.[2] While the primary focus of this research has concerned coordination complexes of alkali and alkaline metal ions, a large and growing compendium of transition-metal complexes exists.[3] The crown ether oxygen donors show a much weaker affinity for transition-metal ions than for A group metal ions. Structural investigations carried out on presumed crown ether complexes of transition metals isolated from aqueous solution have shown a stronger tendency for hydrogen bond formation to coordinated aquo ligands than direct bonding to the metal. This has been found to be the result for $[Co(H_2O)_6][CoCl_4]\cdot18$-crown-6·$(CH_3)_2CO^4$, $[Mn(H_2O)_6](ClO_4)_2\cdot18$-crown-6,[5] and $[Mn(NO_3)(H_2O)_5]$-$(NO_3)\cdot18$-crown-6·H_2O^6 and should prove to be the case in similar complexes. In the absence of a better ligating agent, crown ether complexes of transition-metal ions can be isolated. In this note we report the preparation of the bis(12-crown-4)manganese(II) cation isolated as its tribromide salt and the results of a crystallographic molecular structure determination carried out on the compound.

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Experimental Section

Synthesis of $[Mn(C_8H_{16}O_4)_2](Br_3)_2$. A solution containing 1.23 g (7 mmol) of 12-crown-4 and 1.72 g (8 mmol) of anhydrous $MnBr_2$ dissolved in 40 mL of dry methanol was refluxed for 4 h. After the solution was cooled in an ice bath, an excess (6 mL) of bromine was added. The yellow precipitate which immediately formed was filtered and washed with methanol and absolute ether. The crude yield was 84% on the basis of 12-crown-4. Crystals suitable for X-ray analysis were grown by recrystallization from dry methanol. They were observed to slowly decompose to a white powder during prolonged exposure to air.

Crystallography. A yellow-orange crystal of $[Mn(C_8H_{16}O_4)_2](Br_3)_2$ was mounted and coated with an amorphous resin to retard surface decomposition during data collection. Preliminary photographs indicated the monoclinic crystal system with extinctions of hkl, $h + k = 2n + 1$, consistent with the centric space group $C2/m$ and acentric space groups $C2$ and Cm. The crystal was aligned on a Syntex $P\bar{1}$ automated diffractometer equipped with a graphite crystal monochromator by using Mo Kα radiation ($\lambda = 0.71069$ Å). The following cell constants were calculated from the refined settings of 22 independent high-angle reflections: $a = 18.585$ (2) Å, $b = 8.513$ (1) Å, $c = 9.693$ (1) Å, and $\beta = 116.33$ (1)°. An experimental density of 2.16 (3) g cm^{-3} agrees with a calculated value of 2.143 g cm^{-3} for *two* formula weights per unit cell.

Intensity data were collected at room temperature by using the $\theta/2\theta$ scan technique. A total of 1355 independent reflections with 2θ values less than 50° were measured. Of this number 707 were found to have $F_o^2 > 3\sigma(F_o^2)$ and were used in the refinement. Data were processed in the usual manner. Corrections were applied for Lorentz, polarization, and absorption effects. With $\mu = 97.8$ cm^{-1} transmission coefficients ranged from 0.18 to 0.26. The crystal was a parallelepiped of dimensions 0.17 × 0.23 × 0.51 mm with bounding planes of {001}, {110}, and {1$\bar{1}$0}.

The crystal structure was solved by using both a sharpened Patterson map and direct methods. Initial refinement was carried out in space group $C2/m$ with the half tribromide ion located on the mirror plane (special position *i*) and the manganese ion at a position of $2/m$ symmetry (special position *d*). These positions were consistent with the solutions obtained from the Patterson and refined to a conventional R_F of 0.122. The $2/m$ site symmetry imposed on the complex molecule in the centric space group requires substantial disorder of the crown ether ligands, and at this point the two acentric space groups were considered. In space group $C2$ the complex cation is required to have twofold symmetry with one independent tribromide anion. Space group Cm requires mirror symmetry for the complex molecule with two half tribromide anions also lying on the mirror plane. The conformational structure of the ethylene bridges of the 12-crown-4 ligand precludes a structure in which the ligands are bisected by the mirror plane without complete disorder of the carbon atoms. Also, the orientation of the complex molecule in $C2$ and Cm is different. In $C2$ the coordination geometry would be rotated approximately 22.5° from its orientation in Cm. Patterson vectors and the results obtained by