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Coordination and Activation of Azetidine by a Triosmium Cluster

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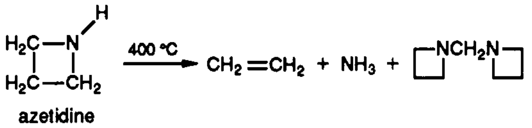
The cluster complex $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2C}H_2)(\mu\text{-}H)$ (1) was obtained in 34% yield from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with azetidine. Complex 1 was characterized crystallographically and shown to contain a four-membered $\overline{NCH_2CH_2C}H_2$ ring bridging two of the metal atoms via the nitrogen atom. When heated to 125 °C, 1 was transformed into two new triosmium complexes $Os_3(CO)_{10}[\mu\text{-}N{=}C(H)Et](\mu\text{-}H)$ (2) (27% yield) and $Os_3(CO)_9(\mu_3\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)$ (3) (15% yield). A small amount of a pentaosmium cluster complex $Os_5(CO)_{14}(\mu\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)_3$ (4) was obtained in 2.4% yield. All three products were characterized by single-crystal X-ray diffraction analysis. Compound 2 was formed by a hydrogen shift and an opening of the four-membered ring of the azetidine ligand. Compound 3 contains a triply bridging heterocyclic ligand $\overline{NCH_2CH_2C}$ formed by a double CH activation at one of the CH_2 groups bonded to the nitrogen atom. Compound 4 contains a capped butterfly cluster of five osmium atoms with the same heterocyclic ligand $\overline{NCH_2CH_2C}$, but it bridges in a different manner between the wing tips of the butterfly. Crystal data: For 1: space group = $P2_1/c$, $a = 8.793(2)$ Å, $b = 16.265(2)$ Å, $c = 13.766(4)$ Å, $\beta = 110.56(1)°$, $Z = 4$, 1872 reflections, $R = 0.039$; for 2: space group = $P\bar{1}$, $a = 14.626(3)$ Å, $b = 22.961(6)$ Å, $c = 9.089(2)$ Å, $\alpha = 92.73(2)°$, $\beta = 99.03(2)°$, $\gamma = 81.52(2)°$, $Z = 6$, 4862 reflections, $R = 0.024$; for 3: space group = $P\bar{1}$, $a = 9.119(1)$ Å, $b = 12.361(3)$ Å, $c = 8.274(2)$ Å, $\alpha = 99.45(2)°$, $\beta = 110.82(1)°$, $\gamma = 81.62(2)°$, $Z = 2$, 1820 reflections, $R = 0.037$; for 4: space group = $P\bar{1}$, $a = 10.774(4)$ Å, $b = 13.722(8)$ Å, $c = 10.102(2)$ Å, $\alpha = 105.46(5)°$, $\beta = 115.60(3)°$, $\gamma = 73.39(4)°$, $Z = 2$, 1902 reflections, $R = 0.034$.

Introduction

The ring opening of nitrogen-containing heterocycles is an integral step in the process of hydrodenitrogenation.[1] The mechanisms by which this step occurs are poorly understood; thus a considerable amount of research has been devoted to modeling this heterogeneous reaction by using homogeneous catalysts.[2,3] Although it has considerable ring strain, the four-membered heterocycle, azetidine, is opened thermally only at temperatures in excess of 400 °C.[4]



(1)

Recently, we have found that thietanes, the saturated four-membered heterocycles containing sulfur, undergo facile ring opening when the molecule is coordinated to osmium cluster complexes.[5] It was shown that a bridging coordination of the sulfur atom promotes this process. Thus, we wondered if it might also be possible to open an azetidine ring in a cluster complex under conditions sufficiently mild that a detailed study of the process might be possible. We have now prepared the cluster complex $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2C}H_2)(\mu\text{-}H)$ (1), in which the nitrogen atom of the azetidine ligand bridges two of the metal atoms, and we have found that the azetidine ring is spontaneously opened when the complex is heated to 125 °C. In addition, two other complexes formed by transformation of the azetidine ligand have been isolated and characterized. The results of this study are reported here. A preliminary report of this work has been reported.[6]

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[1] (a) Flinn, R. A.; Larson, O. A.; Beuther, H. *Hydrocarbon Process. Pet. Refin.* **1963,** *9,* 129. (b) Cocchetto, J. F.; Satterfield, C. N. *Ind. Eng. Chem. Process Des. Dev.* **1976,** *15,* 272. (c) Satterfield, C. N.; Carter, D. L. *Ind. Eng. Chem. Process Des. Dev.* **1981,** *20,* 538. (d) Satterfield, C. N.; Gutekin, S. *Ind. Eng. Chem. Process Des. Dev.* **1981,** *20,* 62. (e) Satterfield, C. N.; Modell, M.; Wikens, J. A. *Ind. Eng. Chem. Process Des. Dev.* **1981,** *19,* 154. (f) Massoth, F. E.; Balusami, K.; Shabtai, J. *J. Catal.* **1990,** *122,* 256. (g) Odebunmi, E. O.; Ollis, D. F. *J. Catal.* **1983,** *80,* 76. (h) Eijsbouts, S.; deBeer, V. H. J.; Prins, R. *J. Catal.* **1990,** *127,* 619. (i) Hirschon, A. S.; Wilson, R. B. *Appl. Organomet. Chem.* **1992,** *6,* 421.

[2] (a) Laine, R. M.; Thomas, D. W.; Cary, L. W. *J. Org. Chem.* **1979,** *44,* 4964. (b) Laine, R. M.; Thomas, D. W.; Cary, L. W. *J. Am. Chem. Soc.* **1982,** *104,* 1763. (c) Laine, R. M. *New J. Chem.* **1987,** *11,* 5113. (d) Laine, R. M. *J. Mol. Catal.* **1983,** *21,* 119. (e) Laine, R. M. *Ann. N.Y. Acad. Sci.* **1983,** *415,* 271. (f) Laine, R. M. *Catal. Rev.—Sci. Eng.* **1983,** *25,* 459.

[3] (a) Fish, R. H. *Ann. N.Y. Acad. Sci.* **1983,** *415,* 292. (b) Fish, R. H.; Thormodesen, A. D.; Tan, J. L. *J. Org. Chem.* **1984,** *49,* 4500. (c) Fish, R. H.; Thormodesen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982,** *104,* 4500. (d) Fish, R. H.; Kim, H. S.; Babin, J. E.; Adams, R. D. *Organometallics* **1988,** *7,* 2250.

[4] Volkova, V. V.; Gusel'nikov, L. E.; Perchenko, V. N.; Zaikin, V. G.; Eremina, E. I.; Nametkin, N. S. *Tetrahedron Lett.* **1978,** 577.

[5] (a) Adams, R. D.; Pompeo, M. P. *Organometallics* **1990,** *9,* 2651. (b) Adams, R. D.; Pompeo, M. P. *Organometallics* **1990,** *9,* 1718. (c) Adams, R. D.; Pompeo, M. P. *J. Am. Chem. Soc.* **1991,** *113,* 1619. (d) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics,* **1991,** *10,* 2539. (e) Adams, R. D.; Pompeo, M. P. *Organometallics,* **1992,** *11,* 103. (f) Adams, R. D.; Belinski, J. A. *Organometallics,* **1992,** *11,* 2488. (g) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1992,** *11,* 2016.

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Table I. Crystallographic Data for Compounds 1–4

	1	2	3	4
formula	$Os_3O_{10}NC_{13}H_7$	$Os_3O_{10}NC_{13}H_7$	$Os_3O_9NC_{12}H_5$	$Os_5O_{14}NC_{17}H_7$
formula wt	907.80	907.80	877.77	1400.24
cryst syst	monoclinic	triclinic	triclinic	triclinic
lattice parameters				
a (Å)	8.793(2)	14.626(3)	9.119(1)	10.774(4)
b (Å)	16.265(2)	22.961(6)	12.361(3)	13.722(8)
c (Å)	13.766(4)	9.089(2)	8.274(2)	10.102(2)
α (deg)		92.73(2)	99.45(2)	105.46(5)
β (deg)	110.56(1)	99.03(2)	110.82(1)	115.60(3)
γ (deg)		81.52(2)	81.62(2)	73.39(4)
V (Å^3)	1901.1(7)	2980(2)	856.1(3)	1273(3)
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	4	6	2	2
D_{calc} (g/cm^3)	3.17	3.03	3.40	3.65
μ(Mo Kα) (cm^{-1})	200.71	192.04	222.75	249.62
temp (°C)	20	20	20	20
$2\theta_{max}$ (deg)	44.0	41.0	44.0	40.0
no. of obs data ($I > 3\sigma(I)$)	1872	4862	1820	1902
no. of variables	247	766	181	244
residuals: R, R_w	0.039, 0.042	0.024, 0.025	0.037, 0.045	0.034, 0.035
goodness of fit indicator	2.02	1.32	2.73	1.74
max shift in final cycle	0.02	0.12	0.01	0.01
largest peak in final diff map (e$^-$/Å^3)	2.78	0.66	2.19	1.56
abs corr	empirical	empirical	empirical	empirical
max/min	1.00/0.23	1.00/0.60	1.00/0.13	1.00/0.23

Table II. Positional Parameters and B(eq) Values (Å^2) for $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2C}H_2)(\mu\text{-}H)$ (1)

atom	x	y	z	B(eq)	atom	x	y	z	B(eq)
Os(1)	0.32163(09)	0.06622(04)	0.66901(06)	2.42(3)	C(2A)	0.538(06)	0.277(03)	0.798(04)	5(1)
Os(2)	0.12717(10)	0.18703(04)	0.71385(07)	2.76(4)	C(2B)	0.621(05)	0.233(03)	0.810(04)	4(1)
Os(3)	0.14268(10)	0.03124(05)	0.81121(07)	2.79(4)	C(3)	0.468(03)	0.2467(11)	0.706(02)	4(1)
O(11)	0.1749(20)	–0.0900(09)	0.5593(13)	5.5(8)	C(11)	0.226(03)	–0.0321(13)	0.5987(19)	4(1)
O(12)	0.604(02)	–0.0294(10)	0.7809(16)	7(1)	C(12)	0.495(02)	0.0073(11)	0.7372(19)	4(1)
O(13)	0.453(02)	0.1075(10)	0.4914(14)	6(1)	C(13)	0.407(02)	0.0944(13)	0.560(02)	4(1)
O(21)	–0.226(02)	0.1594(11)	0.6403(17)	8(1)	C(21)	–0.092(03)	0.1703(13)	0.669(02)	5(1)
O(22)	0.101(02)	0.3440(10)	0.5913(14)	7(1)	C(22)	0.116(03)	0.2850(14)	0.6372(20)	5(1)
O(23)	0.099(02)	0.2727(10)	0.9025(16)	7(1)	C(23)	0.110(03)	0.2407(12)	0.8276(17)	4(1)
O(31)	0.389(03)	0.0882(12)	1.007(15)	8(1)	C(31)	0.305(03)	0.0696(12)	0.9271(19)	4(1)
O(32)	–0.121(02)	–0.0266(10)	0.6309(14)	5.9(9)	C(32)	–0.020(03)	–0.0035(13)	0.6951(19)	4(1)
O(33)	–0.111(02)	0.0613(10)	0.9197(14)	5.5(9)	C(33)	–0.012(03)	0.0500(13)	0.8803(17)	4(1)
O(34)	0.254(02)	–0.1448(10)	0.8670(16)	7(1)	C(34)	0.210(03)	–0.0778(14)	0.8425(19)	5(1)
N	0.375(02)	0.1813(09)	0.7415(15)	4.1(9)	H	0.151(16)	0.137(07)	0.604(11)	1(1)
C(1)	0.500(03)	0.1932(14)	0.8474(18)	5(1)					

Table III. Intramolecular Distances for 1[a]

atom	atom	distance	atom	atom	distance
Os(1)	Os(2)	2.778(1)	Os(3)	C(32)	1.93(3)
Os(1)	Os(3)	2.869(1)	Os(3)	C(33)	1.87(3)
Os(1)	N	2.12(2)	Os(3)	C(34)	1.89(3)
Os(1)	C(11)	1.94(2)	N	C(1)	1.59(3)
Os(1)	C(12)	1.84(2)	N	C(3)	1.50(2)
Os(1)	C(13)	1.90(3)	C(1)	C(2A)	1.60(5)
Os(2)	Os(3)	2.853(1)	C(1)	C(2B)	1.45(5)
Os(2)	N	2.11(2)	C(2A)	C(3)	1.35(6)
Os(2)	C(21)	1.88(2)	C(2B)	C(3)	1.71(5)
Os(2)	C(22)	1.90(2)	H	Os(2)	1.8(1)
Os(2)	C(23)	1.83(2)	H	Os(1)	1.9(1)
Os(3)	C(31)	1.94(2)	O	C(av)	1.15(2)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table IV. Intramolecular Bond Angles for 1[a]

atom	atom	atom	angle	atom	atom	atom	angle
Os(2)	Os(1)	Os(3)	60.68(3)	N	Os(2)	C(22)	92.1(8)
Os(2)	Os(1)	N	48.9(5)	N	Os(2)	C(23)	100(1)
Os(3)	Os(1)	N	87.0(5)	N	Os(2)	H	78(4)
N	Os(1)	C(11)	167.7(8)	Os(1)	Os(3)	Os(2)	58.07(3)
N	Os(1)	C(12)	99.7(8)	Os(1)	N	Os(2)	82.1(6)
N	Os(1)	C(13)	94.3(9)	C(1)	C(2A)	C(3)	90(3)
Os(1)	Os(2)	Os(3)	61.25(3)	C(1)	C(2B)	C(3)	82(2)
Os(1)	Os(2)	N	49.0(4)	Os	C	O(av)	177(2)
Os(3)	Os(2)	N	87.4(4)	Os(2)	H	Os(1)	97(7)
N	Os(2)	C(21)	166.2(8)				

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Reagent-grade solvents were stored over 4-Å molecular sieves. Technical-grade octane was purchased from Phillips Co. and was purified by treatment with sulfuric acid and distillation from sodium/benzophenone prior to use. Azetidine ($H\overline{NCH_2CH_2C}H_2$) was purchased from Aldrich Chemical Co. and was used without further purification. $Os_3(CO)_{10}(NCMe)_2$ was prepared by the published procedure.[7] Chromatographic separations were performed in air on TLC plates (0.25-mm silica gel 60 F_{254}). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^{1}H NMR spectra were taken on a Brüker AM-300 or a Brüker AM-500 spectrometer. Mass spectra were recorded on a VG Model 70SQ mass spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with Azetidine. A 100-mg amount (0.107 mmol) of $Os_3(CO)_{10}(NCMe)_2$ was dissolved in 80 mL of CH_2Cl_2, and a 20-μL amount of azetidine was added via syringe. The solution was then heated to reflux for 6 h. After cooling, the solvent was removed in vacuo, and the residue was separated by TLC. Elution with a CH_2Cl_2/hexane (1/9) solvent mixture yielded 32.5 mg of $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2C}H_2)(\mu\text{-}H)$ (1) (34%) as a yellow band. IR (in hexane) for 1: ν (CO, cm^{-1}) 2103

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(6) Adams, R. D.; Chen, G. *Organometallics* **1992**, *11*, 3510.
(7) Aime, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1807.

Table V. Positional Parameters and B(eq) Values (Å^2) for $Os_3(CO)_{10}(\mu\text{-}NCHCH_2CH_3)(\mu\text{-}H)$ (2)

atom	*x*	*y*	*z*	*B*(eq)	atom	*x*	4y	*z*	*B*(eq)
Os(1A)	0.61583(04)	0.20517(02)	0.70988(06)	3.52(3)	N(1A)	0.5863(07)	0.1282(04)	0.5956(10)	3.7(5)
Os(1B)	0.33281(04)	0.48757(02)	0.17346(06)	3.71(3)	N(1B)	0.2152(08)	0.5406(04)	0.0741(12)	4.2(6)
Os(1C)	0.01266(04)	0.13337(02)	0.07221(07)	4.01(3)	N(1C)	0.1293(08)	0.1722(06)	0.1712(13)	4.0(6)
Os(1D)	0.0082(10)	0.1196(06)	–0.1038(17)	4.5(8)	C(1A)	0.5403(11)	0.0864(07)	0.6108(15)	5.7(9)
Os(2A)	0.67538(04)	0.14654(02)	0.45552(06)	3.49(3)	C(1B)	0.1434(11)	0.5718(07)	0.1123(18)	6(1)
Os(2B)	0.26982(04)	0.52424(02)	–0.12085(06)	4.21(3)	C(1C)	0.1443(10)	0.2138(07)	0.2643(16)	4.9(8)
Os(2C)	0.20483(04)	0.10345(03)	0.06606(07)	4.26(3)	C(2A)	0.4792(11)	0.0860(07)	0.7256(19)	7(1)
Os(2D)	0.1218(10)	0.1305(09)	0.1728(17)	4.2(8)	C(2B)	0.1205(14)	0.5777(09)	0.266(02)	9(1)
Os(3A)	0.54848(04)	0.25243(02)	0.42464(06)	3.33(3)	C(2C)	0.0725(12)	0.2539(08)	0.3304(19)	8(1)
Os(3B)	0.27269(04)	0.40451(02)	–0.04899(06)	4.08(3)	C(3A)	0.484(02)	0.0341(09)	0.790(03)	15(2)
Os(3C)	0.08659(04)	0.15196(03)	–0.19106(07)	4.30(3)	C(3B)	0.0639(16)	0.6323(11)	0.298(02)	12(2)
Os(3D)	0.1982(09)	0.1455(07)	–0.0894(17)	4.8(8)	C(3C)	0.0699(17)	0.3175(09)	0.292(02)	11(2)
O(11A)	0.7040(08)	0.1446(05)	0.9998(12)	7.2(7)	C(11A)	0.6721(10)	0.1665(06)	0.8924(16)	4.6(8)
O(11B)	0.4080(08)	0.5818(04)	0.3915(12)	6.8(6)	C(11B)	0.3785(09)	0.5497(06)	0.3089(15)	4.4(8)
O(11C)	–0.0276(09)	0.1052(05)	0.3779(13)	7.8(7)	C(11C)	–0.0128(11)	0.1157(06)	0.2633(18)	5.3(9)
O(12A)	0.4213(07)	0.2513(05)	0.7846(11)	6.0(6)	C(12A)	0.4959(11)	0.2326(06)	0.7623(14)	4.5(8)
O(12B)	0.2366(07)	0.4333(05)	0.3951(12)	6.6(7)	C(12B)	0.2752(10)	0.4527(06)	0.3142(16)	4.4(8)
O(12C)	–0.1256(08)	0.2441(05)	0.0069(13)	7.3(7)	C(12C)	–0.0752(11)	0.2022(07)	0.0347(17)	5.1(9)
O(13A)	0.6910(08)	0.3176(05)	0.8241(11)	6.6(6)	C(13A)	0.6625(10)	0.2769(07)	0.7802(14)	4.8(8)
O(13B)	0.5165(07)	0.4045(05)	0.2435(12)	5.8(6)	C(13B)	0.4491(10)	0.4345(06)	0.2179(14)	3.9(7)
O(13C)	–0.1254(09)	0.0573(06)	–0.0992(15)	9.2(9)	C(13C)	–0.0744(12)	0.0854(07)	–0.036(02)	7(1)
O(21A)	0.8185(08)	0.0367(05)	0.5259(14)	8.4(8)	C(21A)	0.7658(11)	0.0775(07)	0.5037(16)	5.0(8)
O(21B)	0.2812(09)	0.6550(05)	–0.1540(13)	7.9(7)	C(21B)	0.2783(11)	0.6068(07)	–0.1415(14)	5.1(8)
O(21C)	0.3051(09)	0.0484(06)	0.3583(15)	9.2(8)	C(21C)	0.2648(11)	0.0695(07)	0.2479(20)	6(1)
O(22A)	0.5663(08)	0.1016(05)	0.1693(12)	6.7(7)	C(22A)	0.6117(09)	0.1171(06)	0.2777(16)	4.0(7)
O(22B)	0.0874(09)	0.5198(07)	–0.3356(15)	10(1)	C(22B)	0.1562(12)	0.5230(07)	–0.2558(19)	6(1)
O(22C)	0.3639(08)	0.1668(05)	0.0129(13)	7.4(7)	C(22C)	0.3060(10)	0.1431(06)	0.0312(17)	5.2(8)
O(23A)	0.8022(07)	0.2041(05)	0.2907(12)	6.4(6)	C(23A)	0.7549(10)	0.1820(06)	0.3512(15)	4.6(8)
O(23B)	0.3871(08)	0.4864(05)	–0.3673(12)	6.6(7)	C(23B)	0.3424(11)	0.5001(06)	–0.2726(16)	4.6(8)
O(23C)	0.2640(09)	–0.0044(06)	–0.1224(15)	9.0(8)	C(23C)	0.2453(11)	0.0374(08)	–0.057(02)	7(1)
O(31A)	0.3937(08)	0.1726(05)	0.3906(12)	7.0(7)	C(31A)	0.4519(10)	0.2014(06)	0.4052(14)	4.0(7)
O(31B)	0.0784(08)	0.4441(05)	0.0384(14)	8.1(8)	C(31B)	0.1491(11)	0.4306(07)	0.0043(17)	5.1(8)
O(31C)	0.1247(08)	0.2731(05)	–0.0542(12)	6.8(7)	C(31C)	0.1139(11)	0.2269(07)	–0.1005(16)	5.3(9)
O(32A)	0.5318(08)	0.2683(05)	0.0904(11)	65.(6)	C(32A)	0.5379(09)	0.2618(06)	0.2133(17)	4.2(7)
O(32B)	0.1967(10)	0.3465(06)	–0.3450(14)	10(1)	C(32B)	0.2281(12)	0.3699(08)	–0.2389(20)	7(1)
O(32C)	0.2279(10)	0.1498(07)	–0.4043(15)	11(1)	C(32C)	0.1775(13)	0.1511(08)	–0.3181(20)	7(1)
O(33A)	0.7223(07)	0.3171(05)	0.4813(11)	6.1(6)	C(33A)	0.6579(10)	0.2940(06)	0.4610(13)	3.9(7)
O(33B)	0.4754(07)	0.3874(04)	–0.1201(11)	6.0(6)	C(33B)	0.4004(11)	0.3935(05)	–0.0937(14)	3.9(7)
O(33C)	0.0501(10)	0.0246(06)	–0.2803(16)	9.7(9)	C(33C)	0.0605(12)	0.0716(08)	–0.2507(17)	6(1)
O(34A)	0.4125(08)	0.3569(05)	0.5178(12)	6.6(6)	C(34A)	0.4639(10)	0.3195(06)	0.4839(15)	4.6(8)
O(34B)	0.3077(07)	0.2987(05)	0.1544(13)	6.6(6)	C(34B)	0.2940(10)	0.3372(07)	0.0780(16)	4.8(8)
O(34C)	–0.0933(09)	0.2107(06)	–0.3806(15)	8.9(8)	C(34C)	–0.0283(12)	0.1872(08)	–0.3128(18)	6(1)

Table VI. Intramolecular Distances for 2[a]

atom	atom	distance	atom	atom	distance
Os(1A)	Os(2A)	2.8117(9)	Os(2C)	Os(3C)	2.847(1)
Os(1A)	Os(3A)	2.832(1)	Os(2C)	N(1C)	2.07(1)
Os(1A)	N(1A)	2.07(1)	Os(2C)	C(21C)	1.89(2)
Os(1A)	C(11A)	1.93(2)	Os(2C)	C(22C)	1.92(2)
Os(1A)	C(12A)	1.90(2)	Os(2C)	C(23C)	1.92(2)
Os(1A)	C(13A)	1.92(1)	Os(3A)	C(31A)	1.95(1)
Os(1B)	Os(2B)	2.815(1)	Os(3A)	C(32A)	1.92(2)
Os(1B)	Os(3B)	2.840(1)	Os(3A)	C(33A)	1.96(1)
Os(1B)	N(1B)	2.06(1)	Os(3A)	C(34A)	1.94(2)
Os(1B)	C(11B)	1.96(2)	Os(3B)	C(31B)	1.95(2)
Os(1B)	C(12B)	1.90(2)	Os(3B)	C(32B)	1.93(2)
Os(1B)	C(13B)	1.94(2)	Os(3B)	C(33B)	1.95(2)
Os(1C)	Os(2C)	2.802(1)	Os(3B)	C(34B)	1.93(2)
Os(1C)	Os(3C)	2.850(1)	Os(3C)	C(31C)	1.94(2)
Os(1C)	N(1C)	2.10(1)	Os(3C)	C(32C)	1.89(2)
Os(1C)	C(11C)	1.91(2)	Os(3C)	C(33C)	1.97(2)
Os(1C)	C(12C)	1.89(2)	Os(3C)	C(34C)	1.95(2)
Os(1C)	C(13C)	1.93(2)	N(1A)	C(1A)	1.27(2)
Os(2A)	Os(3A)	2.829(1)	N(1B)	C(1B)	1.27(2)
Os(2A)	N(1A)	2.06(1)	N(1C)	C(1C)	1.27(2)
Os(2A)	C(21A)	1.93(2)	C(1A)	C(2A)	1.48(2)
Os(2A)	C(22A)	1.88(2)	C(1B)	C(2B)	1.49(2)
Os(2A)	C(23A)	1.90(2)	C(1C)	C(2C)	1.47(2)
Os(2B)	Os(3B)	2.849(1)	C(2A)	C(3A)	1.34(2)
Os(2B)	N(1B)	2.05(1)	C(2B)	C(3B)	1.44(3)
Os(2B)	C(21B)	1.94(2)	C(2C)	C(3C)	1.50(2)
Os(2B)	C(22B)	1.91(2)	O	C(av)	1.13(1)
Os(2B)	C(23B)	1.88(2)			

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

(w), 2062 (vs), 2050 (m), 2019 (s), 2007 (m), 1997 (vw), 1986 (s), 1976 (w). ^{1}H NMR (ppm, in $CDCl_3$ at 25 °C) for 1: 4.43 (2H, t, $^3J_{H\text{-}H}$ = 6.9 Hz), 3.99 (2H, t, $^3J_{H\text{-}H}$ = 6.9 Hz), 2.53 (2H, q, $^3J_{H\text{-}H}$ = 6.9 Hz), −14.00 (1H, s). Anal. Calcd (found) for 1: C, 17.18 (17.19); H, 0.77 (0.67); N, 1.54 (1.50).

Pyrolysis of 1 at 125 °C. A 37.5-mg amount of 1 was dissolved in 40 mL of octane and heated to reflux for 20 h. After cooling, the solvent was removed *in vacuo*. The residue was dissolved in a minimal amount of CH_2Cl_2 and separated by TLC. Elution with a CH_2Cl_2/hexane (1/9) solvent mixture yielded the following bands in order: 10.0 mg (27%) of $Os_3(CO)_{10}(\mu\text{-}NCHCH_2CH_3)(\mu\text{-}H)$ (2) as a yellow band, 6.7 mg of unreacted 1, 5.5 mg of $Os_3(CO)_9(\mu_3\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)$ (3) (15% yield) as a UV–visible band, and 1.4 mg of $Os_5(CO)_{14}(\mu\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)_3$ (4) (3% yield) as a yellow band. In ^{1}H NMR spectra of reaction mixtures, small amounts of the known compound $Os_4(CO)_{12}(\mu\text{-}H)_4$ were also observed.[8] The yield of this compound was not determined. For 2: IR (ν(CO), cm^{-1}, in hexane): 2105 (w), 2067 (vs), 2055 (s), 2021 (vs), 2010 (s), 2003 (vw), 1996 (vs), 1981 (w). ^{1}H NMR (ppm, in C_6D_6, 25 °C): 6.45 (1H, dd, ^3J = 5.3 Hz, ^3J = 4.4 Hz, CH), 2.04 (1H, ddq, ^2J = 15.3 Hz, ^3J = 7.7 Hz, ^3J = 4.4 Hz, C*H*H), 1.90 (1H, ddq, ^2J = 15.3 Hz, ^3J = 7.7 Hz, ^3J = 5.3 Hz, CH*H*), 0.52 (3H, t, ^3J = 7.7 Hz, CH_3), −15.23 (1H, s, OsH). Anal. Calcd (found): C, 17.18 (17.50); H, 0.77 (0.74); N, 1.54 (1.62). For 3: IR (ν(CO), cm^{-1}, in hexane): 2096 (w), 2069 (s), 2043 (vs), 2017 (vs), 2006 (w), 1998 (m), 1984 (vw), 1972 (w). ^{1}H NMR (ppm, in CD_2Cl_2, −43 °C): 4.82 (1H, ddd, ^2J = 9.9 Hz, ^3J = 5.3 Hz, ^3J = 3.1 Hz, NCH), 4.16 (1H, ddd, ^2J = 9.9 Hz, ^3J = 4.6 Hz, ^3J = 3.1 Hz, NCH), 3.84 (1H, ddd, ^2J = 16.0 Hz, ^3J = 5.3 Hz, ^3J = 3.1 Hz, CCH), 3.48 (1H, ddd, ^2J = 16.0 Hz, ^3J = 3.1 Hz, CCH), −17.98 (1H, s, OsH); MS (EI, ^{192}Os): *m/z* 883 (M$^+$). Anal. Calcd (found) C, 16.41

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[8] Kaesz, H. D.; Knox, S. A. R.; Koepke, J. W.; Sâillant, R. B. *J. Chem. Soc., Chem. Commun.* 1971, 477.

Table VII. Intramolecular Bond Angles for 2[a]

atom	atom	atom	angle	atom	atom	atom	angle
Os(2A)	Os(1A)	Os(3A)	60.18(2)	N(1B)	Os(2B)	C(22B)	99.0(6)
Os(2A)	Os(1A)	N(1A)	46.8(3)	N(1B)	Os(2B)	C(23B)	167.4(5)
Os(3A)	Os(1A)	N(1A)	81.3(3)	Os(1C)	Os(2C)	Os(3C)	60.60(3)
N(1A)	Os(1A)	C(11A)	94.6(5)	Os(1C)	Os(2C)	N(1C)	48.2(3)
N(1A)	Os(1A)	C(12A)	99.0(5)	Os(3C)	Os(2C)	N(1C)	81.9(3)
N(1A)	Os(1A)	C(13A)	166.1(5)	N(1C)	Os(2C)	C(21C)	93.2(6)
Os(2B)	Os(1B)	Os(3B)	60.49(3)	N(1C)	Os(2C)	C(22C)	98.7(6)
Os(2B)	Os(1B)	N(1B)	46.7(3)	N(1C)	Os(2C)	C(23C)	166.0(6)
Os(3B)	Os(1B)	N(1B)	83.1(3)	Os(1A)	Os(3A)	Os(2A)	59.56(3)
N(1B)	Os(1B)	C(11B)	94.9(5)	Os(1B)	Os(3B)	Os(2B)	59.32(3)
N(1B)	Os(1B)	C(12B)	97.5(5)	Os(1C)	Os(3C)	Os(2C)	58.93(2)
N(1B)	Os(1B)	C(13B)	166.2(5)	Os(1A)	N(1A)	Os(2A)	85.8(4)
Os(2C)	Os(1C)	Os(3C)	60.47(3)	Os(1A)	N(1A)	C(1A)	137.4(9)
Os(2C)	Os(1C)	N(1C)	47.4(3)	Os(2A)	N(1A)	C(1A)	136.6(9)
Os(3C)	Os(1C)	N(1C)	81.4(3)	Os(1B)	N(1B)	Os(2B)	86.3(4)
N(1C)	Os(1C)	C(11C)	90.8(5)	Os(1B)	N(1B)	C(1B)	138(1)
N(1C)	Os(1C)	C(12C)	99.3(6)	Os(2B)	N(1B)	C(1B)	135(1)
N(1C)	Os(1C)	C(13C)	167.6(6)	Os(1C)	N(1C)	Os(2C)	84.4(5)
Os(1A)	Os(2A)	Os(3A)	60.26(2)	Os(1C)	N(1C)	C(1C)	136(1)
Os(1A)	Os(2A)	N(1A)	47.3(3)	Os(2C)	N(1C)	C(1C)	139(1)
Os(3A)	Os(2A)	N(1A)	81.6(3)	N(1A)	C(1A)	C(2A)	124(1)
N(1A)	Os(2A)	C(21A)	95.0(5)	N(1B)	C(1B)	C(2B)	125(1)
N(1A)	Os(2A)	C(22A)	97.6(4)	N(1C)	C(1C)	C(2C)	126(1)
N(1A)	Os(2A)	C(23A)	165.7(5)	C(1A)	C(2A)	C(3A)	115(2)
Os(1B)	Os(2B)	Os(3B)	60.19(3)	C(1B)	C(2B)	C(3B)	115(2)
Os(1B)	Os(2B)	N(1B)	47.0(3)	C(1C)	C(2C)	C(3C)	114(1)
Os(3B)	Os(2B)	N(1B)	83.1(3)	Os	C(av)	O	177(1)
N(1B)	Os(2B)	C(21B)	92.1(5)				

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table VIII. Positional Parameters and *B*(eq) Values (Å²) for $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\overline{\text{NCH}_2\text{CH}_2\text{C}})(\mu\text{-H})$ (3)

atom	*x*	*y*	*z*	*B*(eq)	atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.36086(07)	0.24999(07)	0.50216(09)	2.29(3)	N(1A)	0.3135	0.3621	0.3193	2.3
Os(2)	0.01862(07)	0.27744(07)	0.27415(09)	2.28(3)	C(1B)	0.1597	0.3749	0.2230	2.6
Os(3)	0.25972(08)	0.20456(07)	0.14331(09)	2.50(3)	C(2)	0.184(02)	0.4729(17)	0.148(02)	3.2(9)
O(11)	0.3638(19)	0.0326(16)	0.637(03)	7(1)	C(3)	0.360(02)	0.4557(18)	0.261(02)	3.4(9)
O(12)	0.4048(17)	0.3964(14)	0.8483(18)	4.9(7)	C(11)	0.363(02)	0.115(02)	0.590(03)	3.6(4)
O(13)	0.7058(15)	0.2114(16)	0.5312(20)	5.5(8)	C(12)	0.391(02)	0.3402(18)	0.721(03)	3.0(4)
O(21)	−0.1822(18)	0.4308(16)	0.456(02)	6.3(9)	C(13)	0.577(02)	0.2295(17)	0.528(02)	3.0(4)
O(22)	−0.2379(16)	0.2897(15)	−0.0809(19)	5.6(8)	C(21)	−0.107(02)	0.3754(19)	0.390(03)	3.4(4)
O(23)	−0.0677(18)	0.0561(15)	0.325(02)	5.9(9)	C(22)	−0.142(02)	0.2814(18)	0.056(03)	3.5(4)
O(31)	0.5789(17)	0.1608(20)	0.091(02)	8(1)	C(23)	−0.039(02)	0.1377(20)	0.311(03)	3.5(4)
O(32)	0.0674(19)	0.2258(18)	−0.239(02)	7(1)	C(31)	0.460(02)	0.1779(19)	0.110(03)	3.7(4)
O(33)	0.220(02)	−0.0343(14)	0.139(03)	7(1)	C(32)	0.142(02)	0.2133(20)	−0.096(03)	4.1(4)
N(1)	0.1597(18)	0.3749(13)	0.223(02)	2.6(7)	C(33)	0.233(02)	0.057(02)	0.138(03)	4.4(5)
C(1)	0.3135(15)	0.3621(13)	0.3193(20)	2.3(7)					

Table IX. Intramolecular Distances for 3[a]

atom	atom	distance	atom	atom	distance
Os(1)	Os(2)	3.022(1)	N(1)	C(1)	1.34(2)
Os(1)	Os(3)	2.764(1)	N(1)	C(2)	1.53(2)
Os(1)	C(1)	2.11(2)	C(1)	C(3)	1.49(2)
Os(2)	Os(3)	2.759(1)	C(2)	C(3)	1.54(3)
Os(2)	N(1)	2.07(2)	H	Os(1)	1.69
Os(3)	N(1)	2.26(2)	H	Os(2)	1.98
Os(3)	C(1)	2.23(2)			

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table X. Intramolecular Bond Angles for 3

atom	atom	atom	angle	atom	atom	atom	angle
Os(2)	Os(1)	Os(3)	56.75(3)	Os(2)	N(1)	C(2)	152(1)
Os(2)	Os(1)	C(1)	66.2(3)	Os(3)	N(1)	C(1)	72(1)
Os(3)	Os(1)	C(1)	52.5(4)	Os(3)	N(1)	C(2)	119(1)
Os(1)	Os(2)	Os(3)	56.91(3)	C(1)	N(1)	C(2)	92(1)
Os(1)	Os(2)	N(1)	66.4(4)	Os(1)	C(1)	Os(3)	79.0(6)
Os(3)	Os(2)	N(1)	53.5(4)	Os(1)	C(1)	N(1)	112(1)
Os(1)	Os(3)	Os(2)	66.34(3)	Os(1)	C(1)	C(3)	150(1)
Os(1)	Os(3)	N(1)	69.7(4)	Os(3)	C(1)	N(1)	73.7(9)
Os(1)	Os(3)	C(1)	48.5(4)	Os(3)	C(1)	C(3)	121(1)
Os(2)	Os(3)	N(1)	47.5(4)	N(1)	C(1)	C(3)	96(1)
Os(2)	Os(3)	C(1)	70.3(3)	N(1)	C(2)	C(3)	87(1)
Os(2)	N(1)	Os(3)	79.0(6)	C(1)	C(3)	C(2)	86(1)
Os(2)	N(1)	C(1)	115(1)	Os(1)	H	Os(2)	110.58

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

(17.27); H, 0.57 (0.55); N, 1.59 (1.49). For 4: IR (ν(CO), cm^{-1}, in hexane): 2104 (w), 2073 (vs), 2051 (s), 2043 (s), 2026 (w), 2017 (m), 2007 (w), 2001 (m). ^{1}H NMR (ppm, in CDCl$_3$, 25 °C): 4.38 (2H, t, J = 3.0 Hz), 3.16 (2H, t, J = 3.0 Hz), −16.96 (1H, t, J = 0.7 Hz), −20.07 (2H, d, J = 0.7 Hz). MS (EI): m/z 1401 (M$^+$) for the formula $\text{Os}_5(\text{CO})_{14}(\text{NC}_3\text{H}_4)\text{H}_3$.

Crystallographic Analyses. Orange crystals of 1 suitable for X-ray diffraction analyses were grown from solution in MeCN solvent by slow evaporation of solvent at 25 °C. Yellow crystals of 2 were grown from pure MeOH solvent by slow evaporation of solvent at 0 °C. Pale yellow crystals of 3 were grown from a MeOH/CH$_2$Cl$_2$ solvent mixture by slow evaporation of solvent at 0 °C. Orange crystals of 4 were grown from solution in a hexane/CH$_2$Cl$_2$ solvent mixture by cooling to −15 °C. All crystals used in data collection were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromatized Mo Kα radiation. The unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by

Table XI. Positional Parameters and B(eq) Values (Å^2) for $Os_5(CO)_{14}(\mu\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)_3$ (4)

atom	*x*	*y*	*z*	*B*(eq)	atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.21465(10)	0.15528(06)	0.28256(10)	2.24(4)	N	–0.0403(19)	0.2456(12)	–0.0585(20)	2.6(4)
Os(2)	–0.06347(10)	0.27829(07)	0.14674(11)	2.69(5)	C(1)	0.070(02)	0.2208(15)	–0.095(02)	2.6(5)
Os(3)	0.18749(10)	0.36576(06)	0.28083(10)	2.24(4)	C(2)	–0.145(03)	0.2405(18)	–0.217(03)	4.1(6)
Os(4)	0.27050(10)	0.20815(07)	0.05229(10)	2.36(4)	C(3)	–0.021(03)	0.2112(17)	–0.262(03)	3.8(5)
Os(5)	0.45951(10)	0.23529(07)	0.36709(10)	2.65(5)	C(11)	0.226(02)	0.1789(16)	0.484(03)	2.5(5)
O(11)	0.2319(19)	0.1923(13)	0.6024(19)	5(1)	C(12)	0.364(03)	0.0370(19)	0.311(03)	3.6(5)
O(12)	0.4469(17)	–0.0393(11)	0.3278(18)	4(1)	C(13)	0.082(03)	0.0681(19)	0.205(03)	4.0(6)
O(13)	0.0148(19)	0.0063(12)	0.175(02)	6(1)	C(21)	–0.064(03)	0.3068(18)	0.338(03)	4.1(6)
O(21)	–0.0710(19)	0.3265(15)	0.454(02)	6(1)	C(22)	–0.186(03)	0.1871(19)	0.066(03)	4.4(6)
O(22)	–0.272(02)	0.1355(14)	0.018(03)	7(1)	C(23)	–0.220(03)	0.3845(20)	0.078(03)	4.0(6)
O(23)	–0.317(02)	0.4476(13)	0.037(02)	7(1)	C(31)	0.180(03)	0.4109(18)	0.472(03)	3.9(6)
O(31)	0.1776(20)	0.4391(13)	0.592(02)	5(1)	C(32)	0.300(03)	0.459(02)	0.319(03)	4.9(6)
O(32)	0.369(02)	0.5168(13)	0.335(02)	7(1)	C(33)	0.030(03)	0.4694(19)	0.195(03)	4.0(6)
O(33)	–0.0539(18)	0.5382(11)	0.145(02)	5(1)	C(41)	0.332(03)	0.2794(18)	–0.035(03)	3.4(5)
O(41)	0.373(02)	0.3227(14)	–0.087(02)	6(1)	C(42)	0.329(02)	0.0829(18)	–0.066(03)	3.1(5)
O(42)	0.355(02)	0.0118(12)	–0.1379(19)	6(1)	C(51)	0.480(03)	0.2871(18)	0.576(03)	3.7(5)
O(51)	0.4985(18)	0.3134(14)	0.6941(18)	5(1)	C(52)	0.621(03)	0.1239(19)	0.425(03)	3.7(5)
O(52)	0.7143(20)	0.0595(13)	0.4594(19)	6(1)	C(53)	0.570(03)	0.315(02)	0.359(03)	5.1(6)
O(53)	0.633(02)	0.3655(17)	0.347(03)	8(1)					

Table XII. Intramolecular Distances for 4[a]

atom	atom	distance	atom	atom	distance
Os(1)	Os(2)	2.915(2)	Os(4)	Os(5)	2.933(2)
Os(1)	Os(3)	2.823(2)	Os(4)	C(1)	2.03(2)
Os(1)	Os(4)	2.943(2)	N	C(1)	1.32(3)
Os(1)	Os(5)	2.847(2)	N	C(2)	1.51(3)
Os(2)	Os(3)	2.900(2)	C(1)	C(3)	1.55(3)
Os(2)	N	2.11(2)	C(2)	C(3)	1.51(4)
Os(3)	Os(4)	2.971(2)	O	C(av)	1.15(3)
Os(3)	Os(5)	2.860(2)			

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

using the TEXSAN structure solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[9a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[9b] Full matrix least-squares refinements minimized the function:

$$\sum_{hkl} w(|F_o| - |F_c|)^2$$

where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compound 1 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was determined uniquely from the systematic absences observed during the collection of data. The structures was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. The coordinates of the metal atoms were obtained by direct methods (MITHRIL). The positions of all remaining non-hydrogen atoms and of the hydride ligand were obtained from difference Fourier syntheses. The methylene group labeled C(2) was found to be disordered between two positions. Refinement converged by using carbon atoms at 50% occupancy at both sites. All of the non-hydrogen atoms except for C(2) were refined with anisotropic thermal parameters. The hydride ligand and the carbon atom of the disordered methylene group C(2) were refined with isotropic parameters. The positions of the hydrogen atoms on the methylene groups were calculated by assuming idealized geometry and C–H = 0.95 Å. The scattering contributions of all these hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compounds 2–4 each crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solutions and refinements of each of the structures. All three structures were solved by a combination of direct methods and difference Fourier syntheses. The coordinates of the metal atoms were obtained by direct methods (MITHRIL), and all non-hydrogen atoms were subsequently obtained from difference Fourier syntheses.

Compound 2 contained three independent molecules in the asymmetric crystal unit. All nonhydrogen atoms were refined with anisotropic thermal parameters. After all non-hydrogen atoms were located and refined, three significant residual peaks (≈3 e$^-$/Å^3) were observed in a difference Fourier map in the proximity of the metal atoms of one of the three clusters. The peaks lay approximately 3 Å apart and formed a triangle whose plane was inclined 31° from the original three metal atoms. These peaks were assumed to represent a minor disorder component of this one cluster. They were assigned as metal atoms Os(1D), Os(2D), and Os(3D), and occupancy refinement converged to 4%. This model was included in the final refinement. Due to the small amount of disorder, ligands on this component could not be located and were ignored. The hydride ligand and the hydrogen atom bonded to C_1 were located in difference Fourier syntheses for all three independent molecules. Each hydride ligand was refined on its positional parameters only. For compound 3 it was not possible to distinguish the nitrogen atom from the carbon atom for the two atoms of the heterocycle that were coordinated. A disorder was suspected and an occupancy refinement converged with a 50% contribution of carbon and nitrogen at each site. All atoms heavier than carbon were refined with anisotropic thermal parameters. The hydride ligand was located in a difference Fourier synthesis, but it could not be refined to a convergence. It was included as a fixed contribution in the final stages of the analysis. The positions of the other hydrogen atoms were calculated by assuming idealized geometries for both structures. The scattering contributions of all hydrogen atoms were added to the structure factor calculations, but their positions were not defined.

For compound 4 all atoms heavier than nitrogen were refined with anisotropic thermal parameters. The relative positions of the nitrogen and carbon atoms in the coordinated heterocycle were unambiguously established by refining the coordinated atoms as N and C in one configuration and then interchanging these assignments and refining again. When those atoms bonded to Os(2) and Os(4) were refined as nitrogen and carbon, respectively, the temperature factors converged to 2.60 and 2.60 Å^2, but when the assignments were interchanged, the temperature factors converged to 0.89 and 4.67 Å^2. The former values are by far the most reasonable, and this configuration was assumed to be correct. The positions of the hydrogen atoms on the carbon atoms were calculated by using an idealized geometry, and the positions of the hydride ligands were located and calculated by energy minimization using the program HYDEX with the metal–hydrogen bond distances fixed at 1.85 Å.[10] The positions of the hydrogen atoms were not refined.

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(9) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

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

Table XIII. Intramolecular Bond Angles for 4[a]

atom	atom	atom	angle	atom	atom	atom	angle
Os(2)	Os(1)	Os(3)	60.68(6)	Os(1)	Os(4)	Os(5)	57.96(5)
Os(2)	Os(1)	Os(4)	83.72(6)	Os(1)	Os(4)	C(1)	94.7(7)
Os(2)	Os(1)	Os(5)	120.42(5)	Os(3)	Os(4)	Os(5)	57.94(6)
Os(3)	Os(1)	Os(4)	61.98(5)	Os(3)	Os(4)	C(1)	91.6(7)
Os(3)	Os(1)	Os(5)	60.58(5)	Os(5)	Os(4)	C(1)	146.3(7)
Os(4)	Os(1)	Os(5)	60.85(5)	C(1)	Os(4)	C(41)	97(1)
Os(1)	Os(2)	Os(3)	58.08(5)	C(1)	Os(4)	C(42)	92(1)
Os(1)	Os(2)	N	90.9(5)	Os(1)	Os(5)	Os(3)	59.30(5)
Os(3)	Os(2)	N	88.4(5)	Os(1)	Os(5)	Os(4)	61.19(5)
N	Os(2)	C(21)	174(1)	Os(3)	Os(5)	Os(4)	61.69(6)
N	Os(2)	C(22)	88(1)	Os(2)	N	C(1)	133(1)
N	Os(2)	C(23)	90(1)	Os(2)	N	C(2)	133(2)
Os(1)	Os(3)	Os(2)	61.24(6)	C(1)	N	C(2)	93(2)
Os(1)	Os(3)	Os(4)	60.99(5)	Os(4)	C(1)	N	124(2)
Os(1)	Os(3)	Os(5)	60.12(5)	Os(4)	C(1)	C(3)	142(2)
Os(2)	Os(3)	Os(4)	83.50(6)	N	C(1)	C(3)	94(2)
Os(2)	Os(3)	Os(5)	120.51(6)	N	C(2)	C(3)	88(2)
Os(4)	Os(3)	Os(5)	60.37(5)	C(1)	C(3)	C(2)	85(2)
Os(1)	Os(4)	Os(3)	57.03(5)				

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

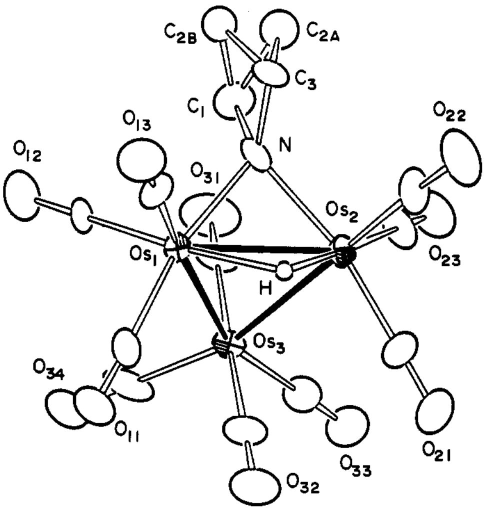


Figure 1. ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2CH_2})(\mu\text{-}H)$ (1) showing 50% probability thermal ellipsoids.

Results

Compound 1 was obtained in 34% yield from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with azetidine $[HN(CH_2)_3]$ in CH_2Cl_2 solvent at reflux for 6 h. This compound was characterized by IR, and ^1H NMR, and a single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of 1 is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected bond distances and angles are listed in Tables III and IV, respectively. Compound 1 was found to contain an azetidine ring system bridging two of the osmium atoms of a triangular cluster through its nitrogen atom. The hydrogen atom was shifted to the cluster to become a hydride ligand that bridges the same osmium–osmium bond as the nitrogen atom, $\delta = -14.00$ ppm, but lies on the other side of the Os_3 plane. The azetidine ring is slightly puckered, and the methylene group at the 3-position was disordered between two sites. The dihedral angle equals 24.5°. Because of the disorder, the positions of the carbon atoms were not accurately determined and the C–C bond lengths span a wide range (1.35(6)–1.71(5) Å) and have large errors. It is felt that the deviations from normal values are of no chemical significance. The metal–nitrogen distances are normal.

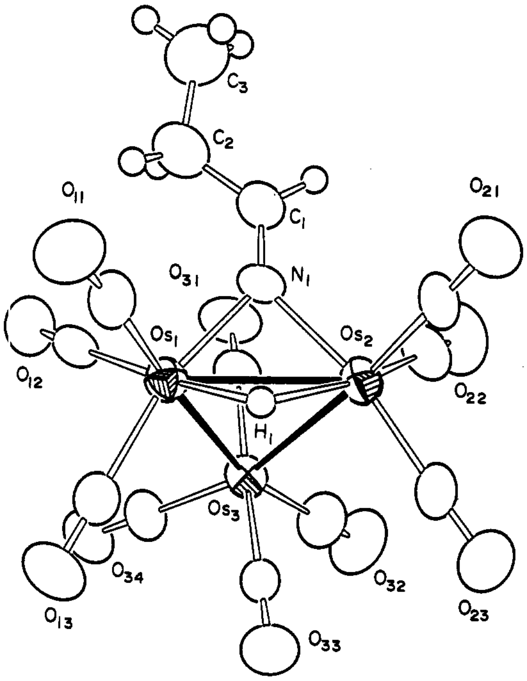


Figure 2. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}N{=}C(H)Et](\mu\text{-}H)$ (2) showing 50% probability thermal ellipsoids.

When heated to 125 °C for 20 h, compound 1 was transformed into three new compounds: $Os_3(CO)_{10}[\mu\text{-}N{=}C(H)Et](\mu\text{-}H)$ (2) in 27% yield, $Os_3(CO)_9[\mu_3\text{-}NCCH_2CH_2](\mu\text{-}H)$ (3) in 15% yield, and a small amount of a pentaosmium complex, $Os_5(CO)_{14}(\mu\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)_3$ (4), in 2% yield. All three products were characterized crystallographically.

In the crystal of compound 2 there are three independent molecules in the asymmetric unit. All three molecules are structurally similar, and an ORTEP drawing of the one of these is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected bond distances and intramolecular angles are listed in Tables VI and VII. The molecule consists of a triangular cluster of three osmium atoms with ten linear carbonyl ligands, but the most interesting ligand is a bridging ethyliminyl ligand. The nitrogen atom bridges the Os(1)–Os(2) bond symmetrically. There is a double bond between the atoms C(1) and N, 1.27(2) Å, and an ethyl group and one hydrogen atom are bonded to C(1). The latter exhibits a deshielded shift, $\delta = 6.45$ ppm. A hydride ligand (located and refined crystallographically, $\delta = -15.23$ ppm) bridges the Os(1)–

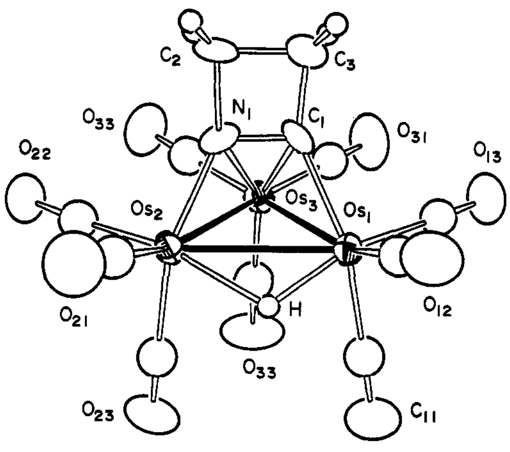


Figure 3. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)$ (**3**) showing 50% probability thermal ellipsoids.

Os(2) bond on the side of the Os_3 plane opposite to the nitrogen atom. The previously reported triosmium complexes $Os_3(CO)_{10}(\mu\text{-}N{=}CHCF_3)(\mu\text{-}H)$[11] and $Os_3(CO)_9(PMe_2Ph)(\mu\text{-}N{=}CHCF_3)(\mu\text{-}H)$[12] also have N-bridging iminyl ligands.

An ORTEP drawing of compound **3** is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected bond distances and angles are listed in Tables IX and X, respectively. This complex also consists of a triosmium cluster with three metal–metal bonds. The most interesting ligand is the four-membered heterocyclic ring $\overline{NCH_2CH_2C}$ that bridges the face of the triosmium cluster in the μ_3-‖ coordination mode. The C=N bridging bonding is similar to that in the triruthenium complex $Ru_3(CO)_9[\mu_3\text{-}\eta^2\text{-}\overline{N{=}CCH_2CH_2CH_2}](\mu\text{-}H)$ (**5**).[13] This ligand is the smallest ring system containing nitrogen observed in this type of coordination mode, but the length of the coordinated C–N bond, 1.34(2) Å, is essentially identical to that observed for the complexes **5**, 1.34(1) Å, and $Ru_3(CO)_3[\mu_3\text{-}\eta^2\text{-}MeC{=}NEt)(\mu\text{-}H)$, 1.343(8) Å.[14] This four-membered ring is planar (mean deviation from plane < 0.001 Å). The compound contains one hydride ligand (located crystallographically, but not refined, $\delta = -15.23$ ppm) that bridges the long Os(1)–Os(2) bond, 3.022(2) Å.

An ORTEP drawing of compound **4** is shown in Figure 4. Final atomic positional parameters are listed in Table XI. Selected bond distances and angles are listed in Tables XII and XIII, respectively. This cluster of **4** contains five metal atoms arranged in the form of a capped butterfly tetrahedron. It also contains a four-membered heterocyclic ring $\overline{NCH_2CH_2C}$ similar to that in **3**, but has adopted a completely different coordination mode. In **4** the ligand bridges the wing tips of the butterfly portion of the cluster with the nitrogen atom σ-bonded to the metal Os(2), Os(2)–N = 2.11(2) Å, and the carbon C(1) σ-bonded to Os(4), Os(4)–C(1) = 2.03(2) Å. The divalent carbon C(1) could be viewed as a carbene center; the C(1)–N distance of 1.32(3) Å is typical of amine-substituted carbene ligands.[15] Day et al. have reported the preparation and structural characterization of the complex $Ru_4(CO)_{11}[C{=}N(Me)CH_2CH_2CH_2](\mu\text{-}H)_4$ which contains a aminocarbene ligand formed by the dehydrogenation of a methylene group in the reaction of $Ru_3(CO)_{12}$ with *N*-methylpyrrolidine, but in this complex the nitrogen atom was not coordinated.[13] Compound **4** contains three hydride ligands. Two are equivalent by NMR, −20.07 ppm (2H, d, *J* = 0.7 Hz), and are weakly coupled to the third hydride, −16.96 ppm (1H, t, *J* = 0.7 Hz). These ligands were not located in the structural analysis. Their positions were determined instead by use of the program HYDEX.[16]

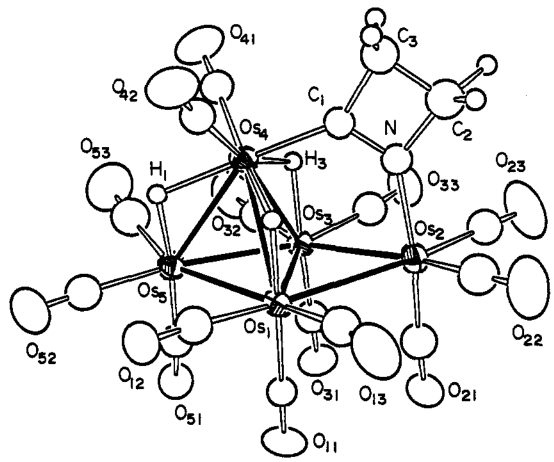
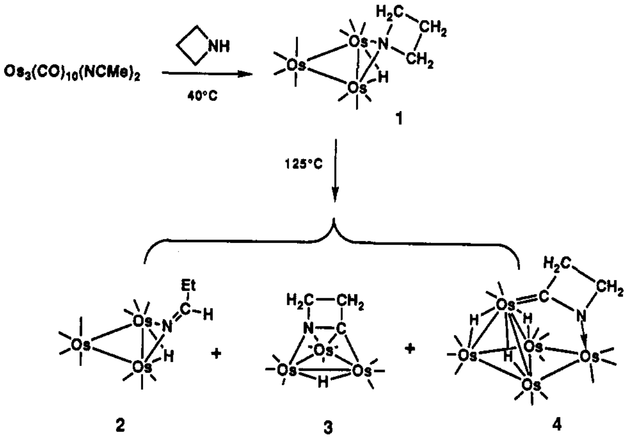


Figure 4. ORTEP diagram of $Os_5(CO)_{14}(\mu\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)_3$ (**4**) showing 50% probability thermal ellipsoids.

Scheme I



Discussion

A summary of the reactions in this study is shown in Scheme I. $Os_3(CO)_{10}(NCMe)_2$ reacted with azetidine under mild conditions to yield the complex **1** in which the hydrogen atom on the nitrogen atom was transferred to the cluster to become a bridging hydride ligand, and the nitrogen atom became a bridge across two of the metal atoms in the triangular cluster. Rosenberg et al. obtained a similar product, $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2CH_2CH_2})(\mu\text{-}H)$

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[11] (a) Dawoodi, Z.; Mays, M. J.; Orpen, A. G. *J. Organomet. Chem.* **1981**, *219*, 251. (b) Laing, M.; Sommerville, P. J.; Wheatley, P. J.; Mays, M. J.; Dawoodi, Z. *Acta Crystallogr.* **1981**, *B37*, 2230.

[12] (a) Adams, R. D.; Katahira, D. A.; Yang, L.-Y. *J. Organomet. Chem.* **1981**, *219*, 241. (b) Adams, R. D.; Katahira, D. A.; Yang, L.-Y. *J. Organomet. Chem.* **1981**, *219*, 85.

[13] Day, M. W.; Hajela, S. Kabir, S. E.; Irving, M.; McPhillips, T.; Wolf, E.; Hardcastle, K. I.; Rosenberg, E.; Milone, L.; Gobetto, R.; Osella, D. *Organometallics* **1991**, *10*, 2743.

[14] Aime, S.; Gobetto, R.; Padovan, F.; Botta, M.; Rosenberg, E.; Gellert, R. W. *Organometallics* **1987**, *6*, 2074.

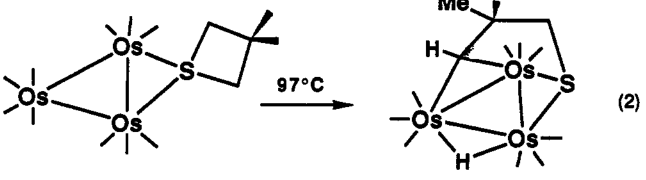
[15] Schubert, U. In *Transition Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissel, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: West Germany, 1983.

[16] Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

(6), from the reaction of pyrrolidine with $Os_3(CO)_{10}(NCMe)_2$.[17]

When heated to 125 °C for a period of 20 h, compound 1 was transformed into three new compounds 2–4. The ligand in complex 2 was clearly formed by a ring-opening process involving a cleavage of one of the carbon–nitrogen bonds in the azetidine ligand and a shift of one of the hydrogen atoms of the methylene group that was not involved in the C–N cleavage to the methylene group that was involved in the C–N cleavage. This shift resulted in the formation of the C–N double bond and the ethyl group. Efforts to obtain evidence for metal-mediated C–H activation processes were performed by labeling the hydride site in 1 with ^2H prior to transformation to 2, but these results were inconclusive due to lack of specificity and evidence for rapid H/D exchange processes that were apparently unrelated to the H-shift leading to 2.[18] The low yield of 2 combined with CH activation steps in competing reactions (e.g., formation of 3) and cluster fragmentation processes may have contributed to this.

The thermal ring opening of this four-membered nitrogen containing a heterocyclic ligand compares favorably with a related ring-opening transformation the four-membered sulfur-containing heterocyclic ligand $SCH_2CMe_2CH_2$ in the complex $Os_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2)$ (7) (eq 2).[5a,g] Compound 7 undergoes ring opening by a



(2)

7 8

C–S bond cleavage at 125 °C, but in that transformation a CH activation occurred at the methylene group where the C–S bond was cleaved and the hydrogen atom was shifted to the cluster to become a hydride ligand in the complex $Os_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH)(\mu\text{-}H)$ (8).

The formation of 3 occurred by the cleavage of both C–H bonds at one of the nitrogen-bonded methylene groups and resulted in the formation of the triply bridging four-membered heterocycle NCH_2CH_2C. It has been shown that compound 6 undergoes a similar transformation into the compound $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}N{=}CCH_2CH_2CH_2](\mu\text{-}H)$ having a triply bridging five-membered heterocycle via the isolable intermediate $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}N{=}CCH_2CH_2CH_2](\mu\text{-}H)$ that contains an edge bridging heterocycle.[17] However, there was no report for the existence of a competing ring-opening transformation in the pyrolysis of 6.

The isolation of compound 4 shows that the four-membered heterocycle NCH_2CH_2C can also adopt an alternative bridging mode in which the carbon and nitrogen atoms are coordinated principally through σ-bonding. The increased metal nuclearity of 4 demonstrates that cluster fragmentation reactions are also occurring under these conditions although the low yield indicates that these are not the dominant processes.

The formation of 2 at 125 °C demonstrates that bridging coordination can promote the opening of the four-membered nitrogen-containing heterocycle $NCH_2CH_2CH_2$ by carbon–nitrogen bond cleavage, a key step in the hydrodenitrogenation process. Metal-promoted ring-opening transformations of azetidines could also provide new ways for developing the organic chemistry of these molecules.[19] For example, Alper et al. have recently reported the catalytic carbonylation of azetidines by $Co_2(CO)_8$ to yield pyrrolidinones by insertion of a CO molecule into one of the C–N bonds.[20]

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for all four of the structural analyses (14 pages). Ordering information is given on any current masthead page.

OM9300134

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[17] Rosenberg, E.; Kabir, S. E.; Hardcastle, K. I.; Day, M.; Wolf, E. *Organometallics* **1990**, *9*, 2214.

[18] Adams, R. D.; Chen, G. Unpublished results.

[19] Moore, J. A.; Ayers, R. S. In *Small Ring Heterocycles*, Part 2; Hassner, A., Ed.; Interscience: New York, 1983; pp 1–217.

[20] Roberto, D.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 7539.