and J.M.V. the CIRIT (Generalitat de Catalunya) for fellowships.

Supplementary Material Available: Tables of crystal data and refinement details, bond distances and angles, positional and thermal parameters, and torsion angles and packing diagrams for 5 (15 pages). Ordering information is given on any current masthead page.

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Ring Opening of Strained-Ring Heterocycles Containing Nitrogen by an Osmium Cluster Complex

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Summary: The osmium cluster complex $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2CH_2})(\mu\text{-}H)$ (**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 $\overline{NCH_2CH_2CH_2}$ ring bridging two of the metal atoms via the nitrogen atom. When heated to 125 °C, **1** was transformed to the new complex $Os_3(CO)_{10}[\mu\text{-}N{=}C(H)Et](\mu\text{-}H)$ (**2**; 27% yield) by an opening of the four-membered ring and a hydrogen shift. 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, $R = 0.024$.

The ring opening of nitrogen-containing heterocycles is an integral step in the process of hydrodenitrogenation.[1] The mechanism by which this step occurs is poorly understood, and a considerable amount of research has been devoted to modeling the heterogeneous reaction by using homogeneous catalysts.[2,3] Although it has considerable ring strain, the four-membered ring of azetidine, HNC_3H_6, is opened thermally only at temperatures in excess of 400 °C.[4] Recently, we have shown that the four-membered sulfur-containing heterocycles thietanes exhibit an enhanced tendency to ring-open when the sulfur atom is coordinated to certain metal cluster complexes in a bridging position.[5] We have now prepared the cluster complex $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2CH_2})(\mu\text{-}H)$ (**1**), which contains a four-membered heterocycle that bridges two of the metal atoms through its nitrogen atom, and have found that this heterocycle opens when the complex is heated to only 125 °C.

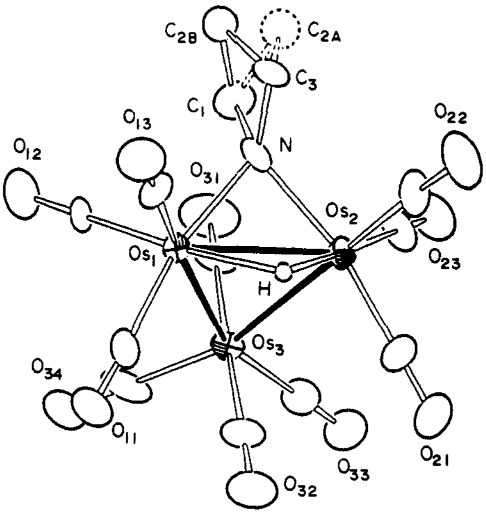

Figure 1. ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}NC_3H_6)(\mu\text{-}H)$ (1). Selected interatomic distances (Å) and angles (deg): Os(1)–N = 2.12 (2), Os(2)–N = 2.11 (2), N–C(1) = 1.59 (3), N–C(3) = 1.50 (2); C(1)–N–C(3) = 85 (2).

Complex **1** was prepared in 34% yield from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with azetidine in CH_2Cl_2 solvent at reflux for 6 h.[6] It was characterized by a single-crystal X-ray diffraction analysis and was found to contain an azetidine ring system bridging two of the osmium atoms of a triangular cluster through its nitrogen atom (see Figure 1).[7,8] The azetidine ring is slightly puckered, the dihedral angle equals 24.5°, and the methylene group at the 3-position is disordered between two sites. As a result, the C–C bond lengths span a wide range (1.35 (6)–1.71 (5) Å) with large errors, but it is felt that the deviations from

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(6) A solution consisting of 100 mg of $Os_3(CO)_{10}(NCMe)_2$ (0.107 mmol) and 20 μL of azetidine in 80 mL of CH_2Cl_2 was heated to reflux for 6 h. The product was separated by TLC on silica gel using a CH_2Cl_2/hexane (1/9) solvent mixture to yield 32.5 mg of yellow $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2CH_2})(\mu\text{-}H)$ (1; 34%). IR (ν(CO), cm^{-1}; in hexane): 2103 (w), 2062 (vs), 2050 (m), 2019 (s), 2007 (m), 1997 (vw), 1986 (s), 1976 (w). ^1H NMR (ppm; in $CDCl_3$ at 25 °C): 4.43 (2 H, t, $^3J = 6.9$ Hz), 3.99 (2 H, t, $^3J_{H-H} = 6.9$ Hz), 2.53 (2 H, q, $^3J_{H-H} = 6.9$ Hz), −14.00 (1 H, s). Anal. Calcd (found): C, 17.18 (17.19); H, 0.77 (0.67); N, 1.54 (1.50).

(7) 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, $R = 0.039$.

(8) Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The structure solution and refinement was made by using the TEXSAN structure-solving program library (v5.0) of the Molecular Structure Corp., The Woodlands, TX. An absorption correction was applied to the data.

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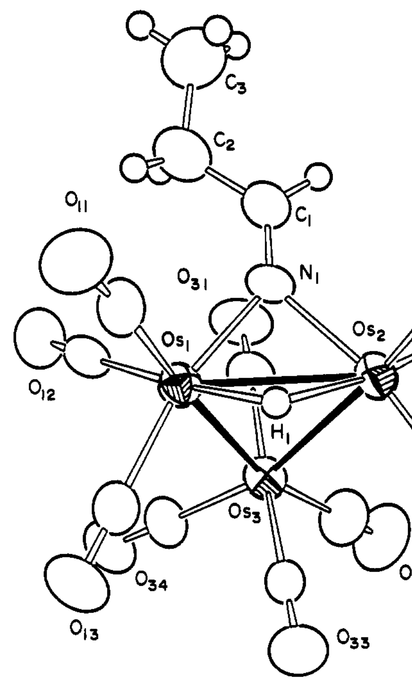
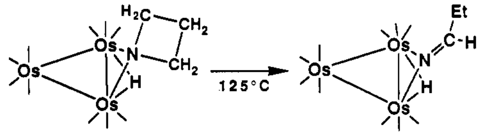


Figure 2. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}N{=}C(H)Et](\mu\text{-}H)$ (**2**). Selected interatomic distances (Å) and angles (deg): Os(1)–N = 2.08 (1), Os(2)–N = 2.06 (1), N–C(1) = 1.27 (2), N–C(3) = 1.50 (2); N–C(1)–C(2) = 125 (1). These values are an average over the three independent molecules.[11]

normal values are of no chemical significance. The metal–nitrogen distances are normal.[9] One hydride ligand bridges the same osmium–osmium bond as the nitrogen atom (δ −14.00 ppm) but lies on the other side of the Os_3 triangle.

When heated to 125 °C for 20 h, compound **1** was transformed to the new compound $Os_3(CO)_{10}[\mu\text{-}N{=}C(H)Et](\mu\text{-}H)$ (**2**) in 27% yield.[10] Compound **2** was characterized crystallographically, and an ORTEP drawing of its molecular structure is shown in Figure 2.[8,11] The molecule consists of a triangular cluster of 3 osmium atoms with 10 linear carbonyl ligands and a bridging ethyliminyl ligand. The nitrogen atom bridges the Os(1)–Os(2) bond symmetrically, and C(1) and N are joined by a double bond (1.27 (2) Å). There is an ethyl group and one hydrogen atom bonded to C(1). The latter exhibits a low-field shift value (δ 6.45 ppm). Iminyl ligands related to this one have been observed previously.[12] This ligand was clearly formed by a ring-opening transformation of the azetidine ring of **1** (eq 1). The C–N bond cleavage was accompanied



(1)

by the removal of a hydrogen atom from the methylene group that was not cleaved from the nitrogen atom and the addition of a hydrogen atom to the methylene group that was cleaved from the nitrogen atom. Preliminary attempts to test for possible involvement of the hydride ligand in this process were made by thermally transforming the labeled complex $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2C}H_2)(\mu\text{-}D)$.[13] Although there appears to be no significant deuterium incorporation into the methyl group of the **2** that was formed, the observation of substantial amounts of hydrogen at the hydride site both in the product and in the **1** recovered from the reaction suggests the existence of hydrogen-exchange processes that are more rapid than the ring-opening transformation and thus render the test inconclusive.

The opening of the four-membered heterocycle in **1** contrasts with the thermal transformation of the five-membered N-bridging pyrrolidine ligand in the complex $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2CH_2C}H_2)(\mu\text{-}H)$, where only C–H activation at a methylene group α to the nitrogen atom was observed.[14] The formation of a multiple bond between carbon and nitrogen distinguishes the opening of this heterocycle from the opening of thietanes where metallacycles are formed.[5]

Metal-promoted ring-opening transformations of azetidines could provide new routes for developing the organic chemistry of these molecules.[15] For example, Alper et al. have recently reported the catalytic carbonylation of azetidines by $Co_2(CO)_8$ to yield pyrrolidinones.[16]

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Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for both of the structural analyses (23 pages). Ordering information is given on any current masthead page.

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(10) A solution of 37.5 mg of **1** in 40 mL of octane was heated to reflux for 20 h. Workup by TLC on silica gel yielded 10.0 mg (27% yield) of yellow product **2** and 6.7 mg of unreacted **1**. 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); ^1H NMR (ppm; in $CDCl_3$ at 25 °C) 6.45 (1 H, dd, $^3J_{H-H}$ = 5.3, 4.4 Hz, CH), 2.04 (1 H, ddq, $^2J_{H-H}$ = 15.3 Hz, $^3J_{H-H}$ = 7.7, 4.4 Hz, C*H*H), 1.90 (1 H, ddq, $^2J_{H-H}$ = 15.3 Hz, $^3J_{H-H}$ = 7.7, 5.3 Hz, CH*H*), 0.52 (3 H, t, $^3J_{H-H}$ = 7.7 Hz, CH_3), −15.23 (1 H, s, OsH). Anal. Calcd (found): C, 17.18 (17.50); H, 0.77 (0.74); N, 1.54 (1.62). Two minor products, A and B, were also isolated from this reaction and are currently being further characterized. Their spectra are as follows. A: IR (in hexane; cm^{-1}) 2096 (w), 2069 (s), 2043 (vs), 2017 (s), 2006 (w), 1998 (m), 1984 (vw), 1927 (w); ^1H NMR (ppm; in CD_2Cl_2 at −43 °C) 4.82 (1 H, ddd, J = 9.9, 5.3, 3.1 Hz), 4.16 (1 H, ddd, J = 9.9, 4.6, 3.1 Hz), 3.84 (1 H, ddd, J = 16.0, 5.3, 3.1 Hz), 3.48 (1 H, ddd, J = 16.0, 4.6, 3.1 Hz), −17.98 (1 H, s). B: IR (in hexane; cm^{-1}) 2104 (w), 2073 (vs), 2051 (s), 2043 (s), 2026 (w), 2017 (m), 2007 (w), 2001 (m); ^1H NMR (ppm; in $CDCl_3$) 4.38 (t, 2 H, J = 3.0 Hz), 3.16 (t, 2 H, J = 3.0 Hz), −16.96 (t, 1 H, J = 0.7 Hz), −20.07 (d, 2 H, J = 0.7 Hz).

(11) Crystal data for **2**: space group $P\bar{1}$, a = 14.626 (3) Å, b = 22.961 (6) Å, c = 9.089 (2) Å, α = 92.73 (2)°, β = 99.03 (2)°, γ = 81.52 (2)°, Z = 6, 4862 reflections, R = 0.024. The crystal of **2** contains three symmetry-independent molecules in the asymmetric crystal unit. All three molecules are structurally similar.

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(13) $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2C}H_2)(\mu\text{-}D)$ (1-d_1; containing >95% ^2H by ^1H NMR analysis) was prepared by heating a solution of **1** in MeOD/NaOMe to 40–43 °C for 10 h.

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