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Preliminary communication

TRIOSMIUM-INDUCED DEHYDROGENATION OF TRIETHYLAMINE. THE CRYSTAL STRUCTURE OF $HOs_3(CO)_{10}(^-CHCH{=}^+NEt_2)$

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Summary

The reaction of $Os_3(CO)_{10}(NCCH_3)_2$ and triethylamine provides $H_2Os_3(CO)_{10}$ and $HOs_3(CO)_{10}(CHCHNEt_2)$ in equimolar amounts. The structure of the latter compound has been shown to involve an iminium ion center anchored to the Os_3 framework by a bridging (substituted) methylene moiety.

Dehydrogenation is a characteristic reaction of hydrocarbon moieties interacting with the Os_3 cluster framework, but the nature of the dehydrogenated product is still frequently unpredictable [1—3]. We have found that the lightly stabilized species $Os_3(CO)_{10}(NCCH_3)_2$ [4] stoichiometrically dehydrogenates triethylamine under mild conditions. The resulting compound has been characterized spectroscopically and crystallographically as an Os_3 cluster involving a formally 1,3-dipolar $^-CHCH{=}^+NEt_2$ iminium ion ligand.

Brief (<30 min) treatment of $Os_3(CO)_{10}(NCCH_3)_2$ in refluxing benzene with excess triethylamine provided a clear, yellow-brown solution, from which the solvent was removed under vacuum. Thin layer chromatography of the residue (silica/petroleum ether) provided two major products, purple $H_2Os_2(CO)_{10}$ (30%) and orange $HOs_3(CO)_{10}(CHCHNEt_2)$ (36%). The formula of the latter compound was established by its mass spectrum (^{192}Os) m/e 955(M^+), and by its ^1H NMR spectrum ($CDCl_3$, 30°C): τ 2.90(d, $1H_a$, $CHCH_aNEt_2$), 5.20(dd, $1H_b$, CH_bCHNEt_2), 6.4—6.8 (m,$4H_c$), 8.70(t,$3H_d$), 8.71(t,$3H_e$), 26.75(d,$1H_f$), J_{ab} 13.9 Hz, J_{bf} 2.5 Hz, $J_{cd} = J_{ce} = 7.2$ Hz. The IR ($\nu(CO)$) spectrum shows bands at 2093w, 2048vs, 2039s, 2011s, 1995s, 1987m, 1979m, 1966s cm^{-1} (C_6H_{12}). This spectrum differs significantly from that characteristic of the σ,π-alkenyl compounds $HOs_3(CO)_{10}(CH{=}CHR)$ [5,6] which have a formula related to the present $HOs_3(CO)_{10}(CHCHNEt_2)$ by simple substitution of R for NEt_2.

The molecular stereochemistry of $HOs_3(CO)_{10}(CHCHNEt_2)$ has been determined unambiguously by means of a full three-dimensional single-crystal X-ray diffraction study. Diffraction data were collected with a Syntex $P2_1$ diffractometer as described previously [7] and the structure was solved by a combination of Patterson, Fourier and full-matrix least-squares refinement techniques using an in-house Syntex XTL structure determination system. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a 7.676(2) Å, b 18.392(5) Å, c 16.026(4) Å, β 97.57(2)°, $Z = 4$, V 2243(1) Å^3. All non-hydrogen atoms were accurately located; the bridging hydride ligand H(br) and the hydrogen atom attached to C(1) were also located and their parameters refined. All other hydrogen atoms were input with idealized geometry, the ethyl groups each being assumed to have the usual staggered conformation. The final discrepancy indices were R_F 5.03% and R_{wF} 4.59% for 1434 crystallographically independent reflections with $3.5° < 2\theta < 35.0°$ (Mo-K_α radiation). The overall geometry of the molecule is shown in Fig. 1.

The bond distances Os(1)—Os(3) 2.870(2) Å and Os(2)—Os(3) 2.866(2) Å are normal (cf. Os—Os(aver) 2.877(3) Å in $Os_3(CO)_{12}$ [8], whereas the di-bridged Os(1)—Os(2) bond is reduced to 2.785(2) Å in length. We note that, whereas a single unsupported μ_2-hydrido ligand normally causes a lengthening of its bridged metal—metal vector, this effect is counterbalanced by the (M—M) bond shortening influence of bridging ligands containing a single carbon atom as the bridging moiety [9a]; reduction of the M—M bond lengths in M(μ-H)-

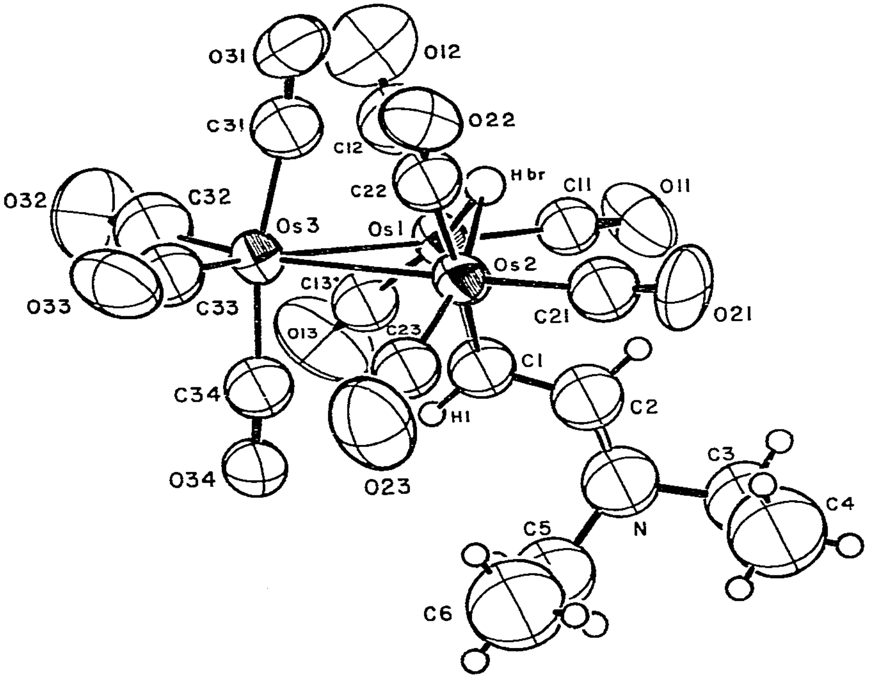

Fig.1. Molecular geometry of $HOs_3(CO)_{10}(CHCH{=}NEt_2)$ [ORTEP-II diagram; 50% probability contours for all nonhydrogen atoms.]

(μ-C)M systems has previously been observed in $HRu_3(CO)_{10}(C{=}NMe_2)$ [9] and $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ [10]. The osmium—hydride distances are Os(1)—H(br) 1.76(15) Å and Os(2)—H(br) 1.82(17) Å, with Os(1)—H(br)—Os(2) 102(8)°. The Os(1)—H(br)—Os(2) system makes and angle of 110.7° with triosmium plane.

The dipolar $^-CHCH{=}^+NEt_2$ ligand takes up a symmetrical bridging position, with Os(1)—C(1) 2.15(3) Å, Os(2)—C(1) 2.16(3) Å and ∠Os(1)—C(1)—Os(2) 80.6(9)°. The Os(1)—C(1)—Os(2) plane makes an angle of 105.9° with the triosmium plane and 143.4° with the Os(1)—H(br)—Os(2) plane. Bond lengths within the $^-CHCH{=}^+NEt_2$ ligand are as follows: C(1)—C(2) 1.42(3) Å, C(2)—N 1.28(3) Å, N—C(3) 1.65(3) Å and N—C(5) 1.57(3) Å. The nitrogen atom has a planar geometry, with ∠ C(2)—N—C(3) 119(2)°, ∠ C(2)—N—C(5) 128(3)°, and ∠ C(3)—N—C(5) 113(2)°.

The μ_2-(substituted)-methylene, 1,3-dipolar ligands found for $HOs_3(CO)_{10}$-$(^-CHCH_2{}^+PMe_2Ph)$ [10] and for $HOs_3(CO)_{10}(^-CHCH{=}^+NEt_2)$ are both formal three-electron donors and form closely similar structures. Carty and coworkers [11] have characterized compounds with related 1,3-dipolar iminium ion ligands generated by amine attack on the σ,π-bridging acetylide in $Fe_2(CO)_6$-$(C{=}CPh)PPh_2$. The present work is the report of such a group prepared by a dehydrogenation reaction. However, M_3-induced dehydrogenation of tertiary methyl amines ($Me_2NCH_2SnMe_3$, M = Ru [9b]; Me_3N, Me_2NCH_2Ph, M = Os [2]) has resulted in compounds ($HM_3(CO)_{10}{}^-C{=}^+NRR'$) with 1,2-dipolar ligands.

The dehydrogenation of triethylamine is probably initiated by oxidative addition of an α-C—H bond of the coordinated amine, by analogy with the proposals for dehydrogenation of NMe_3 [2] and PEt_3 [12]. However, in the present case the α-addition is followed by β-elimination, leading to $H_2Os_3(CO)_{10}$ and $CH_2{=}CHNEt_2$; the olefin then reacts with $Os_3(CO)_{10}$-$(NCCH_3)_2$ to form the title compound. The apparent involvement of the free enamine suggests a straightforward, higher-yield route to $HOs_3(CO)_{10}$-$(CHCH{=}NEt_2)$ and related derivatives. This possibility, together with the propensity of the iminium ion site in the molecule to undergo addition reactions are being investigated.

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