Transformation of diaminocarane on a triosmium cluster. Absolute configuration of a cluster with a bridging imidyl ligand

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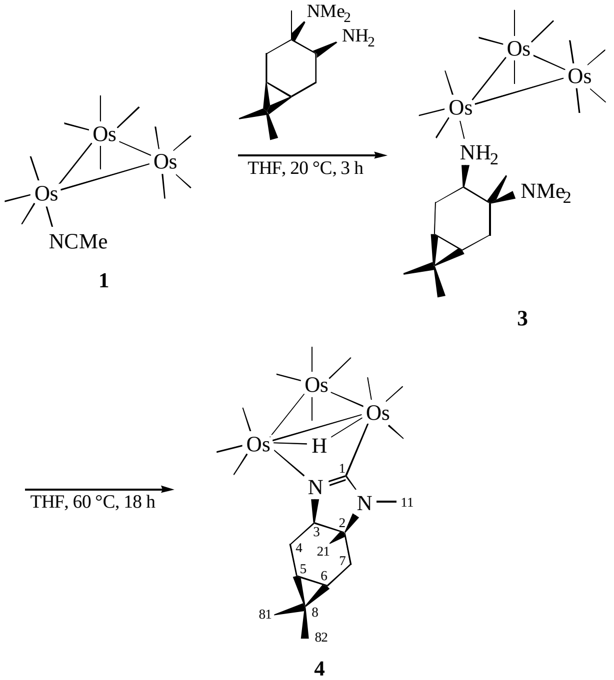
The C–H activation of an NMe_2 group in diaminocarane coordinated to an Os_3 cluster results in the formation of (R,S)-$\{Os_3(CO)_{10}(\mu\text{-H})\{\mu,\eta^2(N,C)$-(4*R*,6*R*,8*S*,10*S*)-1,7,7,10-tetramethyl-1,3-diazatricyclo[3.5.0.0]dec-1-en-2-yl$\}\}$ diastereomers.

The coordination of bulky optically active ligands in cluster complexes can be stereoselective.[1] In the case of L-oxyproline esters, the reaction is stereospecific. Here, we report on a reaction of triosmium cluster $Os_3(CO)_{11}(NCMe)$ **1** with the carane derivative (1*S*,3*S*,4*R*,6*R*)-3-(*N*,*N*-dimethylamino)-4-amino-3,7,7-trimethylbicyclo[4.1.0]heptane (diaminocarane **2**).

Reactions of $Os_3(CO)_{12}$ and its derivatives with amines are among the best studied reactions of triosmium cluster complexes.[2] The interaction of $Os_3(CO)_{11}L$ (L = CO, NCMe) with an excess of a primary or secondary amine results in formation of $(\mu\text{-H})Os_3(\mu\text{-O=CNRR}')(CO)_{10}$ clusters.[2] Decarbonylation of the bridging ligand and the formation of $(\mu\text{-H})Os_3(\mu\text{-NRR}')(CO)_{10}$ clusters occur at refluxing the above species in octane.[3] If these clusters have at least one N–H bond, they lose another CO group at 150 °C to form $(\mu\text{-H})_2Os_3(\mu\text{-NR})(CO)_9$.[4] Tertiary amines, having no active N–H hydrogen atoms, react with triosmium clusters under severe conditions. In these reactions, cleavages of C–H, C–N and C–C bonds take place, and clusters with imine, aminocarbene or aminocarbyne ligands are formed in low yields.[5]

The first step of the reaction of $Os_3(CO)_{11}(NCMe)$ with diaminocarane **2** is similar to that of simple amines. According to TLC data, complex **3** was the main product in solution after 3 h. Its IR spectrum in the region of CO stretching† is characteristic of $Os_3(CO)_{11}L$ clusters with terminally coordinated *n*-donor ligands.[6] Like other triosmium clusters with terminally coordinated amines, this complex is unstable in solution in the absence of an excess of the ligand. When **3** is heated at 60 °C in the presence of an excess of diaminocarane, a complex transformation of the ligand results in the formation of cluster **4** with a bridging tricyclic imidyl ligand (Scheme 1).‡



Scheme 1

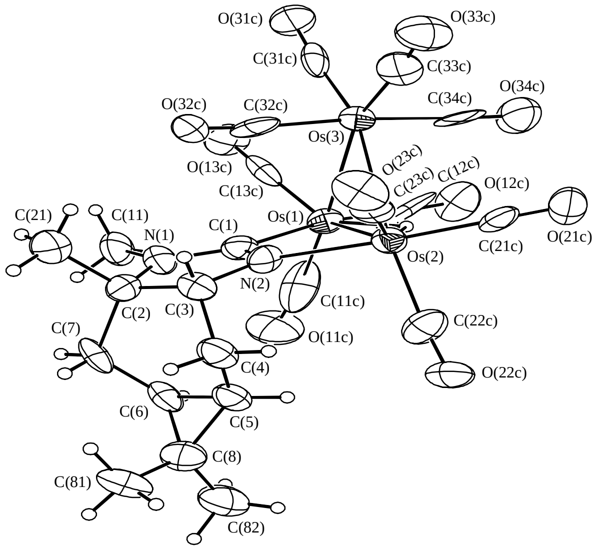


Figure 1 Molecular structure of **4a** (thermal ellipsoids at a 50% probability level). Numbering of atoms does not correspond to the IUPAC nomenclature. Selected bond lengths (Å): Os(1)–Os(2) 2.9397(8), Os(1)–Os(3) 2.8754(9), Os(1)–H(12m) 1.81(5), Os(1)–C(1) 2.10(1), Os(2)–Os(3) 2.8748(9), Os(2)–H(12m) 1.78(5), Os(2)–N(2) 2.08(1), C(1)–N(1) 1.39(2), C(1)–N(2) 1.26(2), N(1)–C(11) 1.45(2), N(1)–C(2) 1.51(2), N(2)–C(3) 1.49(2), C(2)–C(21) 1.53(2), C(2)–C(3) 1.53(2), C(2)–C(7) 1.57(2), C(3)–C(4) 1.53(2), C(4)–C(5) 1.49(2), C(5)–C(6) 1.50(2), C(5)–C(8) 1.49(2), C(6)–C(7) 1.50(2), C(6)–C(8) 1.52(2), C(8)–C(81) 1.50(2), C(8)–C(82) 1.45(2); selected bond angles (°): C(1)–Os(1)–Os(2) 65.7(4), C(1)–Os(1)–Os(3) 86.9(4), N(2)–Os(2)–Os(1) 66.8(3), N(2)–Os(2)–Os(3) 88.7(3), N(1)–C(1)–Os(1) 131(1), N(2)–C(1)–Os(1) 114(1), N(2)–C(1)–N(1) 115(1), C(1)–N(1)–C(11) 128(1), C(1)–N(1)–C(2) 109(1), C(11)–N(1)–C(2) 124(1), C(1)–N(2)–Os(2) 113(1), C(1)–N(2)–C(3) 110(1), C(3)–N(2)–Os(2) 136.7(9), N(1)–C(2)–C(21) 108(1), N(1)–C(2)–C(3) 101(1), N(1)–C(2)–C(7) 110(1), C(21)–C(2)–C(7) 112(1), C(3)–C(2)–C(21) 114(1), C(3)–C(2)–C(7) 112(1), N(2)–C(3)–C(2) 106(1), N(2)–C(3)–C(4) 113(1), C(4)–C(3)–C(2) 112(1), C(5)–C(4)–C(3) 111(1), C(4)–C(5)–C(6) 114(1), C(4)–C(5)–C(8) 124(1), C(8)–C(5)–C(6) 61(1), C(5)–C(6)–C(8) 59(1), C(7)–C(6)–C(5) 113(1), C(7)–C(6)–C(8) 121(1), C(6)–C(7)–C(2) 113(1), C(5)–C(8)–C(6) 60(1), C(81)–C(8)–C(5) 120(1), C(81)–C(8)–C(6) 122(2), C(82)–C(8)–C(5) 116(2), C(82)–C(8)–C(6) 112(2), C(82)–C(8)–C(81) 116(1).

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† IR (hexane, ν_{CO}/cm^{-1}): 2106 (w), 2052 (s), 2034 (s), 2020 (m), 1995 (br. s), 1981 (sh.), 1966 (sh.).

‡ A typical experimental procedure was as follows: 137 mg (1.5×10^{-4} mol) of $Os_3(CO)_{11}(NCMe)$ and 250 mg (1.3×10^{-3} mol) of diaminocarane **2** in 25 ml of THF were stirred at room temperature until all $Os_3(CO)_{11}(NCMe)$ was consumed. Then, the reaction mixture was heated at 60 °C for 18 h and evaporated to dryness; the residue was chromatographed on Silufol using a 4:1 hexane–benzene mixture as the eluent. The first intense yellow band afforded **4** as a mixture of two diastereomers [total yield 28 mg, 18% on an $Os_3(CO)_{11}(NCMe)$ basis].

This transformation is surprising because severe conditions are required for activating tertiary amines on triosmium clusters.[5] Taking into account that the key step of the amine interaction with transition metal carbonyls is the nucleophilic attack of the nitrogen lone pair on a carbonyl carbon atom,[7] it is reasonably to suggest that the formation of cluster **4** proceeds through the nucleophilic attack of a dimethylamino group of terminally coordinated diaminocarane on the carbon atom of a carbonyl group coordinated to neighbouring osmium. As this takes place, the source of the imidyl ring carbon atom is the carbonyl group. However, experiments with $Os_3(CO)_{11}(NCMe)$ enriched with ^{13}CO have shown that the ^{13}C label does not appear in the bridging ligand. Therefore, the source of the imidyl ring carbon atom is one of the methyl groups in NMe_2 rather than CO, and the formation of **4** proceeds through the C–H activation of one of methyls in the dimethylamino group followed by formation of the N=C double bond. Mild conditions of the C–H activation may be caused by steric hindrances arising at coordination of a bulky diaminocarane ligand to a cluster like the reaction of $Os_3(CO)_{10}(NCMe)_2$ with substituted pyridinealdimines, where the C–H activation occurs at ambient temperature.[8]

Because cluster **4** does not contain a symmetry plane, it is formed as a mixture of two diastereomers in the ratio ~4:3 (according to NMR data), which cannot be separated by TLC. Crystallization of the diastereomeric mixture from pentane afforded main diastereomer **4a** as diastereomerically pure crystals. The mother liquor contained mainly the other diastereomer. Its spectra with subtracted signals of **4a** were given as the spectral characteristics of **4b**.[§]

The X-ray analysis of **4a** has been performed, and the absolute configuration of this diastereomer has been determined.[¶] Using the stereochemical nomenclature proposed by us for cluster complexes,[1(*a*)] its absolute configuration can be described as (R)-{$Os_3(CO)_{10}(\mu\text{-}H)${μ,η²(N,C)-(4$R$,6$R$,8$S$,10$S$)-1,7,7,10-tetramethyl-1,3-diazatricyclo[3.5.0.0]dec-1-en-2-yl}}. The adequacy of the absolute configuration determination has been verified by the coincidence of configurations of the C(5), C(6) and C(3) atoms in the cluster and in the free ligand.

The molecular structure of **4a** is shown in Figure 1. The bridging organic ligand is coordinated at the same edge of the Os_3-triangle as the μ-H ligand. The Os_2CN metal-containing ring is nearly planar (the atom deviations from a common plane are no higher than 0.021 Å), the dihedral angle Os_2CN/Os_3 is 77.7(2)°. The angle between the Os_3 and $Os_2(\mu\text{-}H)$ planes is 40(5)°. The bond lengths and valence angles are indicative of some delocalization in the C(1)–N(1)–C(2)–C(3)–N(2) five-membered ring.

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[§] **4a**: ^1H NMR ($CDCl_3$) δ: 3.43 (s, H^3), 2.79 (s, H^{11}), 1.91 (m, $H^7 + H^4_\alpha$), 1.02 (s, H^{21}), 0.97 (s, H^{82}), 0.96 (s, H^{81}), 0.54 (m, $H^4_\beta + H^7_\beta$), 0.18 (m, $H^5 + H^6$), –15.71 (s, μ-H). ^{13}C NMR ($CDCl_3$) δ: 183.82, 183.32, 179.41, 175.88, 175.65, 175.45, 174.55, 173.89 [$Os_3(CO)_{10}$], 160.44 (N=C–), 72.29 (C^3), 63.95 (C^2), 29.2 (C^{11}), 28.29 (C^{82}), 26.27 (C^7), 25.14 (C^{21}), 21.34 (C^4), 17.86 (C^5/C^6), 17.35 (C^8), 16.21 (C^6/C^5), 14.54 (C^{81}). IR (hexane, ν_{CO}/cm^{-1}): 2104 (m), 2062 (s), 2052 (s), 2022 (s), 2010 (s), 2002 (m), 1988 (s), 1975 (w), 1948 (w). MS, *m*/*z*: 1048 (M^+, ^{192}Os) (the atom numbering corresponds to that in Figure 1). $[M]^{16}_{580} = -1186°$ (*c* 0.65, $CHCl_3$).

4b: ^1H NMR ($CDCl_3$) δ: 3.14 (dd, H^3, ^3J 4 and 2 Hz), 2.83 (s, H^{11}), 1.97 (dd, H^7_α, ^2J 16 Hz, ^3J 8 Hz), 1.87 (ddd, H^4_α, ^2J 16 Hz, ^3J 8 and 2 Hz), 0.99 (s, H^{21}), 0.93 (s, H^{82}), 0.89 (s, H^{81}), 0.62 (ddd, H^4_β, ^2J 16 Hz, ^3J 9 and 4 Hz), 0.53 (dd, H^7_β, J 16 and 9 Hz), 0.30 (ddd, H^5, ^3J 9, 9 and 8 Hz), 0.23 (ddd, H^6, ^3J 9, 9 and 8 Hz), –15.83 (s, μ-H). ^{13}C NMR ($CDCl_3$) δ: 183.89, 183.28, 178.58, 176.57, 175.72, 175.59, 175.11, 174.90, 174.64, 173.56 [$Os_3(CO)_{10}$], 160.38 (N=C–), 72.29 (C^3), 64.07 (C^2), 28.92 (C^{11}), 28.45 (C^{21}), 28.15 (C^{82}), 25.69 (C^7), 21.31 (C^4), 18.69 (C^5/C^6), 18.57 (C^8), 17.79 (C^6/C^5), 14.22 (C^{81}). IR (hexane, ν_{CO}/cm^{-1}): 2105 (m), 2060 (s), 2051 (s), 2020 (s), 2012 (s), 1999 (m), 1987 (s), 1973 (w), 1948 (w). MS, *m*/*z*: 1048 (M^+, ^{192}Os).

[¶] *Crystal data for* **4a**: $C_{22}H_{20}N_2O_{10}Os_3$, $M = 1043.00$, $F(000) = 1896$, orthorhombic, $a = 12.647(1)$, $b = 13.370(1)$, $c = 15.848(2)$ Å, $V = 2679.7(4)$ Å³, space group $P2_12_12_1$, $Z = 4$, $d_c = 2.585$ g cm^{-3}, $\mu = 14.245$ mm^{-1}. Data were measured using an Enraf-Nonius CAD4 diffractometer (room temperature, graphite-monochromated MoKα radiation, $\lambda = 0.7107$ Å, $\theta/2\theta$ scan up to $2\theta_{max} = 50°$). To determine the absolute configuration, all reflections were measured together with their Friedel equivalents in the negative-theta ($-2\theta/-\omega$) position. Total 5362 (2681 pairs) of reflections were measured. The structure was solved by direct methods and refined against F^2 in an anisotropic approximation for non-hydrogen atoms using the SHELX-97 program package. The μ-H ligand was located on difference electron density map and refined with fixed $U_{iso} = 0.05$ Å². The rest hydrogen atoms were refined in a ride approximation. The final values are $R_1 = 0.0335$, $wR_2 = 0.0666$ for 3639 $F > 4\sigma(F)$. The absolute configuration was confirmed by a refinement of the Flack parameter, the final value is –0.03(2). Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see ‘Notice to Authors’, *Mendeleev Commun*., Issue 1, 1999. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/55.