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Activation of 1,3,5-trimethyl-1,3,5-triazacyclohexane by $Os_3(CO)_{12}$ to form amidino $[(MeN)_2CH]$ cluster complexes

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Abstract

Reaction of 1,3,5-trimethyl-1,3,5-triazacyclohexane $[(MeNCH_2)_3]$ with $Os_3(CO)_{12}$ in refluxing toluene results in C–H and C–N bond activation of the $(MeNCH_2)_3$ ligand to afford three amidino cluster complexes $(\mu\text{-}H)Os_3(CO)_{10}[\mu,\eta^2\text{-}CH(NMe)_2]$ (**1**), $(\mu\text{-}H)Os_3(CO)_9[\mu_3,\eta^2\text{-}CH(NMe)_2]$ (**2**), and $Os_2(CO)_6[\mu,\eta^2\text{-}CH(NMe)_2]_2$ (**3**). The controlled experiments show that thermolysis of **1** yields **2**, and heating **2** in the presence of $(MeNCH_2)_3$ ligand produces **3**. The molecular structures of **1** and **3** have been determined by an X-ray diffraction study.
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1. Introduction

The six-membered 1,3,5-trimethyl-1,3,5-triazacyclo-hexane molecule $[(MeNCH_2)_3]$ is an attractive ligand for η^1- to η^3-metal complexation [1–11]. For example, $M(CO)_6$ (M = Cr, Mo, W) reacts with $(MeNCH_2)_3$ to produce $M(CO)_3$ $[\eta^3\text{-}(MeNCH_2)_3]$, which are good starting compounds for the preparation of a variety of organometallic derivatives [12–14]. Recently, we described that treatments of $M_3(CO)_{12}$ (M = Fe, Ru) or $Os_3(CO)_{11}(NCMe)$ with $(MeNCH_2)_3$ afforded the ani-onic hydrido clusters $[(\mu\text{-}H)M_3(CO)_{11}^-][MeN(MeN\text{-}CH_2)_2CH^+]$ via an unusual hydride-transfer process from the triazacyclohexane molecule [15]. In contrast, $Os_3(CO)_{12}$ reacted with $(MeNCH_2)_3$ quite differently to yield amidino $[CH(NMe)_2]$ cluster complexes. Presented in this paper are complete characterizations of the reac-tion products and information concerning their generation.

2. Results and discussion

Reaction of $Os_3(CO)_{12}$ and $(MeNCH_2)_3$ in refluxing toluene leads to C–H and C–N bond activation of the triazacyclohexane ligand to afford the amidino complexes $(\mu\text{-}H)Os_3(CO)_{10}[\mu,\eta^2\text{-}CH(NMe)_2]$ (**1**), $(\mu\text{-}H)Os_3(CO)_9[\mu_3,\eta^2\text{-}CH(NMe)_2]$ (**2**), and $Os_2(CO)_6[\mu,\eta^2\text{-}CH(NMe)_2]_2$ (**3**) (Scheme 1). The relative yields of **1**, **2**, and **3** are dependent on the reaction conditions. Such that, compound **2** is dominant (61% yield) in refluxing toluene (110 °C) for 4 h, while compound **3** becomes the major product (56% yield) when the reaction time is extended to 20 h. On the other hand, no reaction oc-curs between $Os_3(CO)_{12}$ and $(MeNCH_2)_3$ below 80 °C, while the reaction of the acetonitrile-substituted labile cluster $Os_3(CO)_{10}(NCMe)_2$ and $(MeNCH_2)_3$ occurs at 60–70 °C for 2.5 h to afford compound **1** (3 mg, 30%)

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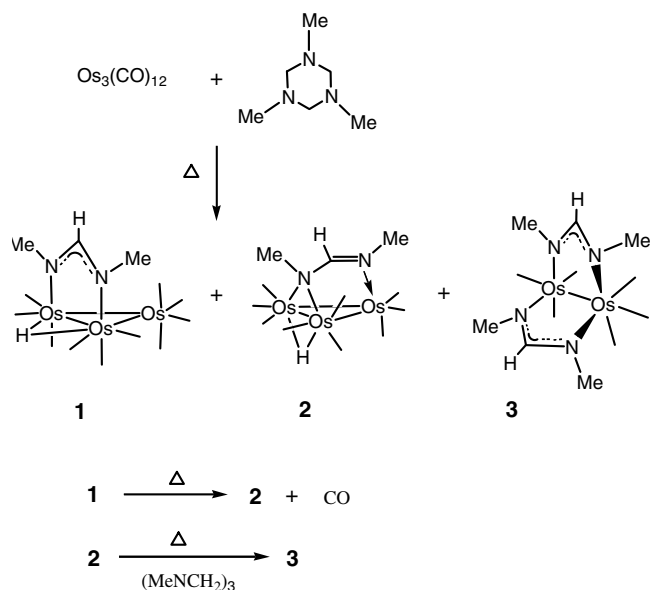
Scheme 1.

predominantly. Furthermore, heating **2** in toluene gives no reactions, but it readily degrades to form **3** in the presence of (MeNCH$_2$)$_3$ ligand.

It is apparent that the triazacyclohexane molecule loses a (CH$_2$)$_2$NMe fragment upon reaction with the osmium cluster to form the amidino species, but the details remain unknown due to lack of mechanical information. Nevertheless, it is clear that compound **1** is formed initially, which can undergo a thermal decarbonylation, together with migration of the amidino ligand from an edge-bridging form (a 3e$^-$ donor) into a face-capping form (a 5e$^-$ donor), to give **2**. The subsequent transformation from **2** to **3** occurs only in the presence of (MeNCH$_2$)$_3$, suggesting that the cluster degradation from Os$_3$ to Os$_2$ is induced by triazacyclohexane attack at **2**. Lewis and coworkers [16] have previously reported a few analogues of **1** and **2** by treating Os$_3$ (CO)$_{10}$(NCMe)$_2$ with amidines (HN=CR–NHR′), whereas the formation of compound **3** shown here is unprecedented.

Compounds **1**–**3** form air-stable, yellow crystalline solids, while **1** is slightly thermal sensitive (undergoing a decarbonylation to yield **2**) and should be stored in the freezer. The characterization and crystal structure of **2** has been previously described [15]. The FAB mass spectra of **1** and **3** display their molecular ion peaks and fragments resulting from successive loss of CO ligands. The isotopic distribution of the envelope surrounding the molecular ion matches that calculated for each compound. The ^{1}H NMR spectrum of **1** shows a 1H singlet at 7.41 ppm, a 6H singlet at 3.25 ppm, and a 1H singlet at −12.65 ppm, corresponding to the N$_2$C–H, N–CH$_3$, and μ-H proton resonances, respectively. The ^{1}H NMR spectrum of **3** displays a 1H singlet

at 8.17 ppm and a 6H singlet at 3.49 ppm. In addition, the ^{13}C{^{1}H} NMR spectrum of **3** appears quite simply to present two signals at 182.7 and 176.5 ppm in an approximate 2:1 ratio for the CO carbons, a signal at 173.5 ppm for the N$_2$C–H carbon, and a signal at 52.7 ppm for the CH$_3$ carbons, suggesting a symmetric configuration in the NMR time-scale.

Upon crystallization of crude **1** (containing a small amount of **3**) from *n*-hexane at −20 °C, a single crystal chosen for the X-ray diffraction study was found to consist of **1** and **3**, which were mutually separated by normal van der Waals' distances. The ORTEP drawing for **1** is shown in Fig. 1. The selected bond distances and bond angles are collected in Table 1. Compound **1** is based upon a triangular array of osmium atoms in which the three Os–Os distances are slightly but significantly different [Os3–Os4 2.9152(5), Os4–Os5 2.9077(5), and Os3–Os5 2.8841(5) Å]. The Os3 and Os4 atoms are each linked with three carbonyl ligands, while the Os5 atom is linked with four. All carbonyl ligands are terminal and approximately linear. However, the Os–CO bond lengths associated with the Os3 and Os4 atoms (av. 1.91 Å) are slightly shorter than those with the Os5 atom (av. 1.95 Å), consistent with the stronger net donor capability of the amidino and hydride ligands compared with CO. The bridging hydride ligand was not located, however, the distribution of the carbonyl groups indicates that it lies in the Os$_3$ plane and bridges the Os3–Os4 edge. The amidino ligand, acting as a three-electron donor, bridges the Os3–Os4 edge through the N5 and N6 atoms in two axial sites. The Os3, N5, C23, C24, N6, C25, and Os4 atoms are planar, and this plane makes a dihedral angel of 96.4° with the Os$_3$ triangle. The N5–Os3 and N6–Os4 lengths are about the
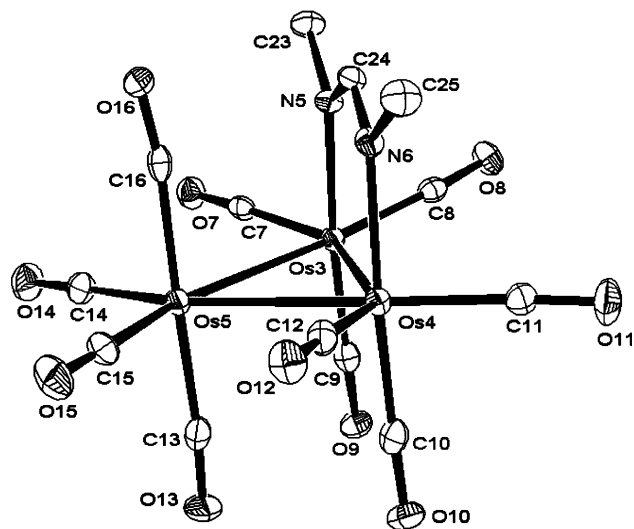

Fig. 1. Molecular structure of **1**. The hydrogen atoms have been artificially omitted for clarity.

Table 1
Selected bond lengths and bond angles for **1**

Bond distances (Å)

Os3–N5	2.133(7)	Os3–C7	1.911(1)
Os3–C8	1.919(1)	Os3–C9	1.901(1)
Os4–N6	2.134(7)	Os4–C10	1.893(1)
Os4–C11	1.929(1)	Os4–C12	1.890(1)
Os5–C13	1.967(1)	Os5–C14	1.926(1)
Os5–C15	1.930(1)	Os5–C16	1.956(1)
Os3–Os4	2.9152(5)	Os4–Os5	2.9077(5)
Os3–Os5	2.8841(5)		

Bond angles (°)

Os5–Os3–Os4	60.18(1)	Os5–Os4–Os3	59.37(1)
Os3–Os5–Os4	60.44(1)	Os3–Os4–C10	94.9(3)
Os3–Os4–C11	116.1(3)	Os3–Os4–C12	145.4(3)
Os4–Os3–C7	146.1(3)	Os4–Os3–C8	115.1(3)
Os4–Os3–C9	94.1(3)	Os5–Os4–N6	90.9(2)
Os5–Os3–N5	90.0(2)	C24–N5–C23	116.6(8)
C24–N6–C25	116.4(8)	N5–C24–N6	126.4(8)
C24–N6–Os4	124.2(6)	C25–N6–Os4	118.7(7)
C23–N5–Os3	119.3(6)	C24–N5–Os3	124.0(6)

Table 2
Selected bond lengths and bond angles for **3**

Bond distances (Å)

Os1–C1	1.924(1)	Os1–C2	1.896(1)
Os1–C3	1.905(1)	Os1–N1	2.130(8)
Os1–N3	2.121(7)	Os2–C4	1.884(1)
Os2–C5	1.978(1)	Os2–C6	1.924(1)
Os2–N2	2.132(8)	Os2–N4	2.132(8)
N1–C17	1.45(1)	N1–C18	1.30(1)
N2–C18	1.33(1)	N2–C19	1.47(1)
N3–C20	1.46(1)	N3–C21	1.32(1)
N4–C21	1.33(1)	N4–C22	1.46(1)
Os1–Os2	2.7821(5)		

Bond angles (°)

N3–Os1–N1	82.9(3)	N3–Os1–Os2	84.2(2)
N1–Os1–Os2	81.7(2)	C1–Os1–Os2	173.7(3)
N4–Os2–N2	85.1(3)	N2–Os2–Os1	82.1(2)
N4–Os2–Os1	81.0(2)	C5–Os2–Os1	170.0(3)
C17–N1–Os1	120.4(6)	C18–N1–Os1	121.9(6)
C19–N2–Os2	121.3(6)	C18–N2–Os2	119.7(6)
C18–N1–C17	117.5(8)	C18–N2–C19	118.1(8)
C21–N3–C20	116.9(8)	C21–N4–C22	117.3(9)

same, being 2.133 ± 0.008 Å, and the N5–C24 and N6–C24 distances are equal [1.32(1) Å], indicating delocalization of one pair π electrons over the N–C–N unit.

The ORTEP drawing for **3** is shown in Fig. 2. The selected bond distances and bond angles are collected in Table 2. This compound consists of an $Os_2(CO)_6$ group and two amidino bridges. Each osmium atom is associated with three terminal carbonyl groups with the Os–C–O bond angles ranging from 174.0(10)° to 178.6(9)°. The Os1–Os2 distance of 2.7821(5) Å is 0.13 Å shorter than the Os3–Os4 distance in **1**. The atoms bonded to Os1 and Os2 form two distorted octahedrons, which are
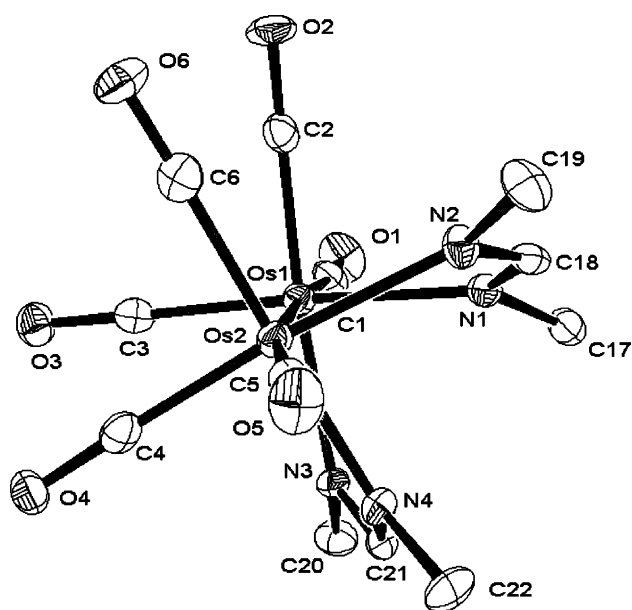

Fig. 2. Molecular structure of **3**. The hydrogen atoms have been artificially omitted for clarity.

staggered to reduce steric interactions. The torsional angles are C2–Os1–Os2–C6 23.8°, C3–Os1–Os2–C4 25.1°, N1–Os1–Os2–N2 21.7°, and N3–Os1–Os2–N4 19.1°. The two axial carbonyl ligands are not collinear with the Os1–Os2 vector, showing the bond angles of Os1–Os2–C5 170.0(3)° and Os2–Os1–C1 173.7(3)°. The bond lengths C18–N1 1.30(1), C18–N2 1.33(1), C21–N3 1.32(1), and C21–N4 1.33(1) Å are essentially equal, indicating a delocalized π bond over each N–C–N unit. However, the C19–N2–C18–N1–C17 link and C22–N4–C21–N3–C20 link are not planar, where the C19–N2 and C17–N1 bonds are bent away from the N2–C18–N1 plane by 9.0° and 15.9°, respectively, and the C22–N4 and C20–N3 bonds are bent away from the N4–C21–N3 plane by 2.7° and 5.7°, respectively. The amidino ligands are each counted as a three-electron donor, and the cluster valence electron count is 34. This electron count requires only one metal–metal bound to provide an 18-electron configuration on each osmium atom, in agreement with the structural observations.

3. Experimental

3.1. General Methods

All manipulations were carried out under an atmosphere of dinitrogen with standard Schlenk techniques. $Os_3(CO)_{12}$ [17] and $Os_3(CO)_{10}(NCMe)_2$ [18] were prepared by literature methods. 1,3,5-trimethyl-1,3,5-triazacyclohexane [(MeNCH$_2$)$_3$] (from TCI) was dried over 3 Å molecular sieves before use. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer

chromatographic (TLC) plates were prepared from silica gel (Merck). Infrared spectra were recorded with a 0.1 mm path CaF_2 solution cell on a Hitachi I-2001 IR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer at 500 and 125.7 MHz, respectively. Fast-atom-bombardment (FAB) mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

3.2. Reaction of $(MeNCH_2)_3$ and $Os_3(CO)_{12}$

$Os_3(CO)_{12}$ (20 mg, 0.02 mmol), $(MeNCH_2)_3$ (10 μl, 0.07 mmol), and toluene (5 ml) were introduced into a Schlenk flask, and the mixture was heated to reflux for 4 h under dinitrogen. The solution was cooled to room temperature, and the solvent removed under vacuum. The residue was separated by TLC with an *n*-hexane/dichloromethane (4:1, v/v) eluant. Isolation of the material forming the first yellow band afforded $(\mu\text{-H})Os_3 (CO)_{10}[\mu,\eta^2\text{-CH(NMe)}_2]$ (**1**; 2 mg, 7%). Isolation of the material forming the second yellow band afforded $Os_2 (CO)_6[\mu,\eta^2\text{-CH(NMe)}_2]_2$ (**3**; 3 mg, 14%). Isolation of the material forming the third, major yellow-orange band afforded the known $(\mu\text{-H})Os_3(CO)_9[\mu_3,\eta^2\text{-CH(NMe)}_2]$ (**2**; 12 mg, 61%).

1: MS (FAB): *m/z* 928 (M[+],[192]Os). IR (*n*-hexane, ν_{CO}): 2104m, 2052vs, 2016s, 1996vs, 1970sh, 1952w cm^{−1}. ^{1}H NMR (CDCl₃, 25 °C): 7.41 (s, 1H, CH), 3.25 (s, 6H, Me), −12.65 (s, μ-H) ppm.

3: MS (FAB): *m/z* 694 (M[+], [192]Os). IR (*n*-hexane, ν_{CO}): 2080m, 2032s, 1988vs, 1974m, 1960s cm^{−1}. ^{1}H NMR (CDCl₃, 25 °C): 8.17 (s, 1H, CH), 3.49 (s, 6H, Me). ^{13}C{^{1}H} NMR (CDCl₃, 25 °C): 182.7, 176.5 (*C*O), 173.5 (*C*H), 52.7(*C*H₃). Anal. Found: C, 20.81; H, 2.29; N, 7.97. $C_{12}H_{14}N_4O_6Os_2$ Anal. Calc.: C, 20.87; H, 2.04; N, 8.11%.

3.3. Extended thermal reaction of $(MeNCH_2)_3$ and $Os_3(CO)_{12}$

A solution of $Os_3(CO)_{12}$ (30 mg, 0.03 mmol) and $(MeNCH_2)_3$ (23 μl, 0.15 mmol) in toluene (6 ml) was heated to reflux for 20 h under dinitrogen. The reaction was worked up in a fashion identical with that above. Compound **2** (2 mg, 6%) and compound **3** (17 mg, 56% based on Os atom) were isolated, while compound **1** was not found.

3.4. Reaction of $(MeNCH_2)_3$ and $Os_3(CO)_{10}(NCMe)_2$

A solution of $Os_3(CO)_{10}(NCMe)_2$ (10 mg, 0.01 mmol) and $(MeNCH_2)_3$ (8 μ l, 0.05 mmol) in benzene (5 ml) was heated at 60–70 °C for 2.5 h. The solvent was

removed and the residue separated by TLC (silica gel) with an *n*-hexane/dichloromethane (4:1, v/v) eluant. Compound **1** (3 mg, 30%) was obtained from the first yellow band, while compounds **2** and **3** were not produced.

3.5. Transformation of **1** into **2**

A solution of compound **1** (3 mg) in *n*-heptane (3 ml) was refluxed under dinitrogen for 3 h, at which point the IR spectrum no absorptions due to the starting cluster. Compound **2** (2.2 mg, 76%) was obtained after purification by TLC. Compound **3** was not found.

3.6. Thermal conversion of **2** to **3** in the presence of Me_3tach

Compound **2** (5 mg, 0.0056 mmol) and $(MeNCH_2)_3$ (3 μl, 0.017 mmol), and toluene (2 ml) were introduced into a Schlenk flask, and the mixture was heated to reflux for 20 h under dinitrogen, at which point the IR spectrum showed no absorptions due to the starting cluster. Compound **3** (3.7 mg, 64%) was obtained after TLC separation.

3.7. Thermal reaction of **2** without the presence of $(MeNCH_2)_3$

Compound **2** (5 mg) in toluene (2 ml) was heated to reflux for 20 h. No evidence for the formation of **3** was indicated.

3.8. Structure determination for **1** + **3**

Compounds **1** and **3** were co-crystallized from *n*-hexane at −20 °C. A suitable single crystal with

Table 3
Crystallographic data and refinement details for **1** + **3**

Formula	$C_{25}H_{18}N_6O_{16}Os_5$
T (K)	150 (1)
Crystal system	Monoclinic
Space group	P_1/n
Unit cell dimensions	
a (Å)	15.3646 (1)
b (Å)	14.9538 (1)
c (Å)	16.6059 (1)
β (°)	109.9732 (3)
V (Å³)	3585.9 (4)
Z	4
D_{calc} (g cm⁻³)	2.981
$F(000)$	2872
μ (mm⁻¹)	17.729
θ Range (°)	1.56–27.50
R_1	0.0374
wR_2	0.0913
Goodness-of-fit on F^2	1.152

approximate dimensions of $0.08 \times 0.05 \times 0.05$ mm^3 was mounted in a thin-walled glass capillary and aligned on the Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 150 K. All data were corrected for the effects of absorption. The structures were solved by the direct method and refined by full-matrix least-square on F^2. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package [19]. A summary of relevant crystallographic data is provided in Table 3.

Acknowledgements

Appendix A. Supplementary material

Crystallographic data for the structural analysis of **1 + 3** have been deposited with Cambridge Crystallographic Data Centre, CCDC No. 243910. Copy of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.a-c.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.09.005.

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