

Synthesis and structural characterisation of osmium carbonyl clusters containing azo ligands

Fung-Sze Kong, Wing-Tak Wong *

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

Received 4 May 1999

Abstract

Treatment of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ (**1**) with 1-(2-thiazolylazo)-2-naphthol resulted in two new clusters $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\{\text{NC}_3\text{HS-N=N-C}_{10}\text{H}_6(\text{OH})\}]$ (**2**) and $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^3\text{-NC}_3\text{H}_2\text{S(N=N)C}_{10}\text{H}_6(\text{O}))]$ (**3**) in 30 and 45% yields, respectively. Cluster **2** contains an azo ligand moiety in the usual orthometallated mode. In cluster **3**, the O–H bond is cleaved in the azo ligand and acts as a five-electron donor in the triosmium framework. Treatment of **1** with 4-nitro-4'-aminoazobenzene yields only $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-NHC}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{NO}_2)]$ (**4**) (35%) where the nitrogen atom symmetrically bridges the Os–Os bond. In another class of azo ligands, 2-[4-(diethylamino)phenylazo]benzoic acid reacts with **1** to give two complexes $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{O}_2\text{CC}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{NEt}_2)]$ (**5**) (50%) and $[\text{Os}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-}\eta^2\text{-OC(O)C}_6\text{H}_4\text{N=NHC}_6\text{H}_4\text{NEt}_2)]$ (**6**) (17%). In cluster **5**, the ligand is bonded to the metal core through a carboxylate which takes up an axial position; while in cluster **6**, the two nonbonded Os atoms are symmetrically bridged by a chloride and by oxygen atom in the azo ligand. Treatment of **1** with 2-[4-(diethylamino)phenylazo]benzoic acid in refluxing THF produced **5** as the sole product. All the complexes **2–6** have been fully characterized in solution by conventional spectroscopic methods and in the solid state by single-crystal X-ray diffraction analysis. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Osmium; Carbonyl; Clusters; Azo ligands

1. Introduction

The investigation of the activation of multiple-bonded organic substrates in the ligand sphere of clusters have so far been focused on C–C– and C–N-bonded systems [1]. While in C–O- and N–N-bonded systems, the former of these (acyl, formyl, alkoxy and alkoxy carbene) are well established in organometallic cluster chemistry, the latter (azo and hydrazides) have not been used in great detail as ligands or substrates in cluster-centered reactions. These azo and hydrazides have potential for basic cluster reactions as well as for organic reactions in the ligand sphere, due to their electron-rich nature and their relatively weak N–N bonds. The chemistry of carbonyl clusters in iron triads containing azo ligands has been well studied [2–8]. It has been shown that $\text{Fe}_3(\text{CO})_{12}$

reacts with azoalkanes, R_2N_2 ($\text{R} = \text{Et}, \text{Pr}$) to give $[\text{Fe}_3(\text{CO})_9(\mu_2\text{-}\eta^3\text{-N}_2\text{R}_2)]$ [9]. Subsequent thermolysis leads to N–N bond cleavage and the formation of nitrene-bridged clusters $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-NR})_2]$. Previously, we reported the reactions of 2-phenylazopyridine (2-PAP) with the activated triosmium cluster $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$, which yielded $[\text{Os}_3(\text{CO})_{10}(\mu_2\text{-}\eta^3\text{-NC}_5\text{H}_4\text{N=N-C}_6\text{H}_5)]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-}\eta^2\text{-NC}_5\text{H}_3\text{-N=N(O)-C}_6\text{H}_5)]$ [10]. Also, the reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (Br-PADAP) gave $[\text{Os}_3(\text{CO})_{10}\{\mu\text{-N(H)(C}_5\text{H}_3\text{NBr})\}\{\mu\text{-N(C}_{10}\text{H}_{13}\text{NO})\}]$ [11], containing two types of amido moieties in which N–N cleavage of the azo ligand was observed. Herein we describe the preparation of new osmium carbonyl clusters generated from the reaction of the $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with 1-(2-thiazolylazo)-2-naphthol, 4-nitro-4'-aminoazobenzene and 2-[4-(diethylamino)phenylazo]benzoic acid, in which N=N bonds remain intact in these reactions.

* Corresponding author. Fax: +852-25472933.

E-mail address: wtwong@hkucc.hku.hk (W.-T. Wong)

2. Results and discussion

2.1. Synthesis and crystal structures of $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\{\text{NC}_3\text{HS}\text{-N=N}\text{-C}_{10}\text{H}_6(\text{OH})\}]$ (**2**) and $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^3\text{-NC}_3\text{H}_2\text{S}(\text{N=N})\text{C}_{10}\text{H}_6(\text{O}))]$ (**3**)

Treatment of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ (**1**) with a slight excess of 1-(2-thiazolylazo)-2-naphthol in dichloromethane at room temperature gives purple products $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\{\text{NC}_3\text{HS}\text{-N=N}\text{-C}_{10}\text{H}_6(\text{OH})\}]$ (**2**) and $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^3\text{-NC}_3\text{H}_2\text{S}(\text{N=N})\text{C}_{10}\text{H}_6(\text{O}))]$ (**3**) in 30 and 45% yield, respectively (see Scheme 1). An IR spectrum reveals the presence of terminal carbonyl ligands. Moreover, the IR spectra in KBr showed intense signals at 1425 cm^{-1} (for **2**) and 1385 cm^{-1} (for **3**), which suggested that the azo moieties remain uncoordinated in clusters **2** and **3** when compared with the $\nu(\text{N=N})$ of the free ligand (1430 cm^{-1}). The $^1\text{H-NMR}$ spectra of **2** and **3** in CD_2Cl_2 confirm the presence of the organic ligands and metal hydrides (see Table 1). In **2**, the very low-field signal at 14.31 ppm is due to the hydroxy group. This is comparable to the signal of the

hydroxy proton in salicylic acid where intra-molecular hydrogen bonding is present. The positive FAB mass spectra of **2** and **3** exhibit an envelope centered at $m/z = 1108$ and 1080 , each showing a stepwise loss of carbonyls. To establish the molecular structures of **2** and **3**, an X-ray analysis has been carried out on the purple crystals obtained from slow evaporation of CH_2Cl_2 -*n*-hexane at room temperature.

The molecular structure of **2** is illustrated in Fig. 1 and some relevant bond parameters are collected in Table 2. The IR spectrum of **2** in the carbonyl stretching region is very similar to those of other *ortho*-metalated pyridine-metal cluster derivatives [12]. The molecular structure consists of a triosmium metal core $[\text{Os}(1)\text{-Os}(2), 2.8940(7); \text{Os}(2)\text{-Os}(3), 2.9346(6); \text{Os}(1)\text{-Os}(3), 2.8802(7)\text{ \AA}]$ with the longest $\text{Os}(2)\text{-Os}(3)$ edge doubly bridged by a hydride and an azo ligand. The $\text{N}(2)\text{-N}(3)$ length [$1.29(1)\text{ \AA}$] is almost identical to those of other clusters containing azo ligands [10–12]. The bond distances $\text{Os}(2)\text{-C}(5)$ [$1.97(1)\text{ \AA}$] and $\text{Os}(3)\text{-C}(10)$ [$1.91(1)\text{ \AA}$] are consistent with the stronger *trans* influence exerted by a $\sigma\text{-C}$ donor than the N donor. The

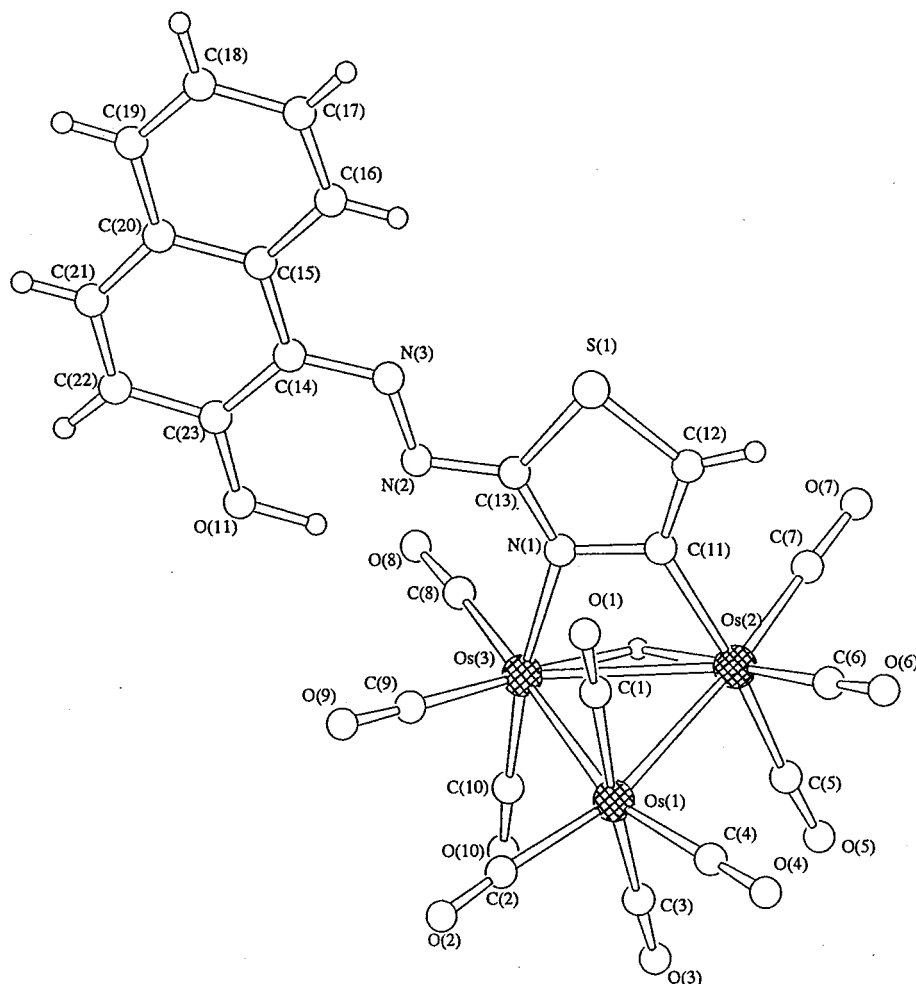
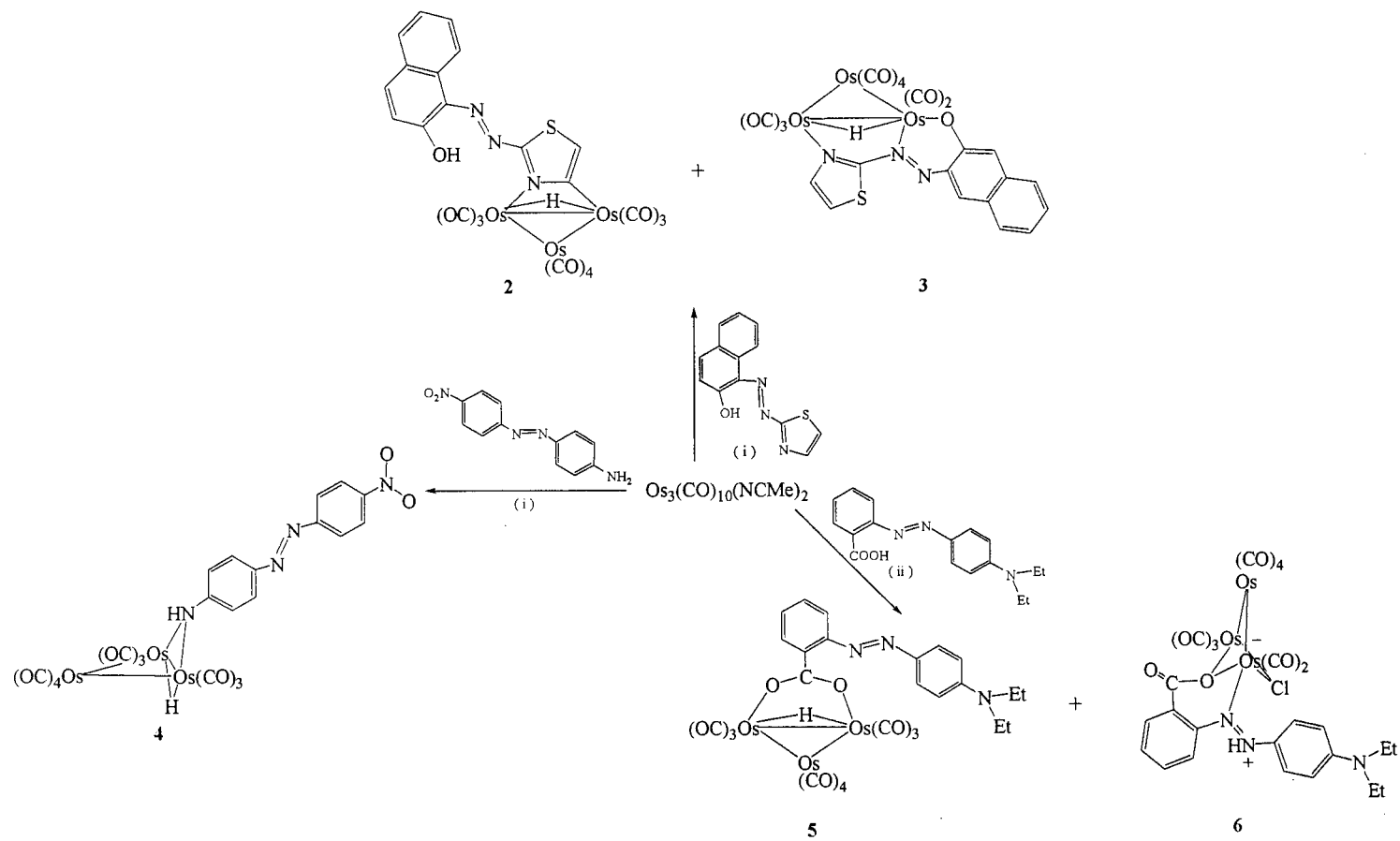


Fig. 1. A perspective drawing of the molecular structure of **2**.



Scheme 1. (i) Stir in CH_2Cl_2 at room temperature; (ii) reflux in CHCl_3 .

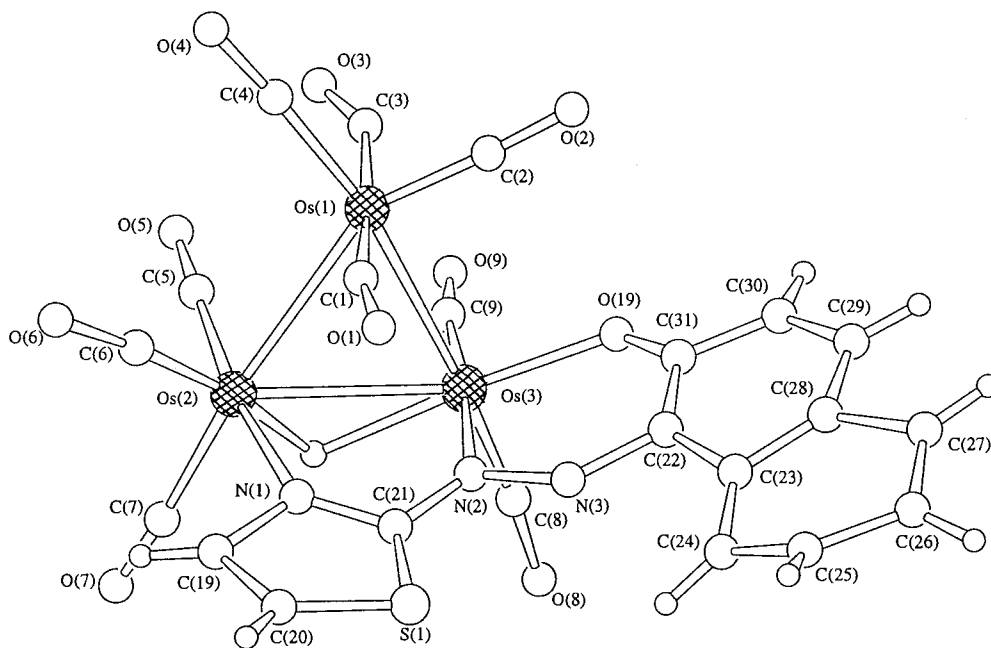


Fig. 2. A perspective drawing of the molecular structure of **3**.

torsion angle as defined by C(13)–N(2)–N(3)–C(14) is $178(1)^\circ$, indicating that *trans* conformation of the ligand remains almost intact upon coordinating to the cluster framework.

The molecular structure of **3** revealed a closed triangular metal framework (Fig. 2). The thiazolyl nitrogen and the azo nitrogen atom are coordinated to the metal framework. Instead of a C–H bond cleavage in the thiazolyl ring of **2**, O–H bond cleavage is observed in **3** to give O(19)–Os(3) bond [2.06(3) Å] (Table 3). The bonding mode of the azo ligand in **3** behaves in the same manner as that found in the triosmium cluster $[(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu\text{-}\eta^3\text{-Et}_2\text{NC}_6\text{H}_3(\text{O})(\text{N}=\text{N})\text{C}_5\text{NH}_3\text{Br}\}]$ [13]. Of the ligand domain, the ligand moiety adopts a $\mu\text{-}\eta^3$ bonding mode core and behaves as a five-electron donor, by virtue of the involvement of the two π -electrons of the N=N bond. The N(2)–N(3) bond distance [1.42(6) Å] is significantly longer than that in **2** [1.29(1) Å] and is comparable to a N–N single bond. The examples documented in which the 2-phenylazopyridine ligand moiety behaves as a six-electron donor are the dinuclear complex $[\text{Fe}_2(\text{CO})_2(4\text{-CH}_3\text{-2PAP})_3]$ [14] [1.41(1) and 1.44(1) Å] and the trinuclear complex $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^3\text{-NC}_5\text{H}_4\text{-N}=\text{N}\text{-Ph})]$ [10] [1.42(4) Å] in which the N=N bond distances are close to that observed in **3**. Within the molecule, [N(1), Os(2), Os(3), N(2) and C(21)] and [N(3), N(2), Os(3), O(19), C(31) and C(22)] form five- and six-membered rings, respectively. The planar azo ligand and the osmium triangle is almost perpendicular to each other [dihedral angle, 101.16°]. The characteristic 48 cluster-valence-electron (CVE) count is observed with the naphtholic oxygen atom [O(19)] acting as an one-electron donor.

2.2. Synthesis and crystal structures of $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-NHC}_6\text{H}_4\text{-N}=\text{N}\text{-C}_6\text{H}_4\text{NO}_2)]$ (**4**)

Treatment of **1** and 4-nitro-4'-aminoazobenzene reflux in CHCl_3 gives a yellow product $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-NHC}_6\text{H}_4\text{-N}=\text{N}\text{-C}_6\text{H}_4\text{NO}_2)]$ (**4**) in 35% yield (Scheme 1). An IR spectrum reveals the presence of terminal carbonyl ligands. The $\nu(\text{N}=\text{N})$ of the free ligand appears at 1412 cm^{-1} , thus this frequency is appreciably lowered in complex **4** (1435 cm^{-1}), which remains intact without any cleavage. The $^1\text{H-NMR}$ spectra of **4** in CD_2Cl_2 confirm the presence of the organic ligands and metal hydrides, where a broad resonance is assigned to the proton of the μ_2 -amido ligand at δ 8.28. The positive FAB mass spectrum of **4** exhibits an envelope centered at $m/z = 1093$, showing stepwise losses of carbonyls. To establish the molecular structures of **4**, an X-ray analysis has been carried out on a red crystal obtained by slow evaporation of CH_2Cl_2 –*n*-hexane at room temperature.

The molecular structure of **4** is depicted in Fig. 3 while the selected bond parameters are given in Table 4. The structure of **4** comprises a triangle of osmium atoms with ten terminal carbonyl groups. The organic ligand is attached to the cluster via a nitrogen atom, which bridges Os(2) and Os(3) acting as a three-electron donor. The approximately tetrahedral geometry of both N(1) and C(13) indicates that the ligand is saturated. It has a C(13)–N(1) distance of 1.44(2) Å and is consistent with a single C–N bond. The NH hydrogen atom was not located. The $^1\text{H-NMR}$ spectra show a broad resonance that is assigned to the proton of the μ_2 -amido ligand at δ 5.75, which is similar to that in $[\text{Os}_3(\mu\text{-H})(\mu\text{-}$

$\text{NHCH}_2\text{CF}_3(\text{CO})_{10}$] [15] (δ 7.65) $[\text{Os}_3(\text{exo-}\mu_2\text{-N(H)Ph-}(\mu_2\text{-I})(\text{CO})_{10})$] [16] (δ 3.88), and $[\text{Os}_3(\text{endo-}\mu_2\text{-N(H)Ph}(\mu_2\text{-I})(\text{CO})_{10})$] [16] (δ 4.73). The bridged Os(2)–Os(3) distance [2.800(1) Å] is shorter than those non-bridged [2.8519(9) and 2.8519(1) Å] by approximately the same amount as those found in the related clusters of the type $[\text{Os}_3(\mu\text{-H})(\mu\text{-X})(\text{CO})_{10}]$, where X is an N donor ligand. Examples include $[\text{Os}_3(\mu\text{-H})(\mu\text{-NHCH}_2\text{CF}_3)(\text{CO})_{10}]$ [15], $[\text{Os}_3(\mu\text{-H})(\mu\text{-N=CHCF}_3)(\text{CO})_{10}]$ [17], and $[\text{Os}_3(\mu\text{-H})(\mu\text{-NHSO}_2(\text{C}_6\text{H}_4\text{Me-}p)(\text{CO})_{10})$] [18].

2.3. Synthesis and crystal structures of $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{O}_2\text{CC}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{NEt}_2)]$ (**5**) and $[\text{Os}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-}\eta^2\text{-OC(O)C}_6\text{H}_4\text{N=NHC}_6\text{H}_4\text{NEt}_2)]$ (**6**)

Treatment of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with a stoichiometric amount of 2-[4-(diethylamino)phenylazo]benzoic acid in refluxing CHCl_3 gives a reddish–brown mixture from which good yields of $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{O}_2\text{CC}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{NEt}_2)]$ (**5**) (50%) and $[\text{Os}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-}\eta^2\text{-OC(O)C}_6\text{H}_4\text{N=NHC}_6\text{H}_4\text{NEt}_2)]$ (**6**) (17%) can be isolated. Both complexes were fully characterized by spectroscopic methods (Table 1). The IR spectra of both clusters in the carbonyl region show signals due to terminal carbonyl ligands only. Moreover, the IR spectra in KBr displayed intense signals at 1477 cm^{-1} (for **5**) and 1456 cm^{-1} (for **6**) and suggested that the azo moieties remain uncoordinated when compared with the $\nu(\text{N=N})$ of the free ligand (1448 cm^{-1}). The spectrum of **5** is similar to those of carboxylato compounds

such as $[\text{Os}_3\text{H}(\text{HCO}_2)(\text{CO})_2]$ [19], $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\text{C}_2\text{O}_4)]$ [20] and $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)]$ [21]. The $^1\text{H-NMR}$ spectrum shows signals from the azo-ligand in **5** and **6** and the presence of the metal hydride in **5** only.

Single crystals of **5** and **6** were obtained from CHCl_3 –cyclohexane and CH_2Cl_2 –petroleum ether mixtures, respectively. The structures of the compounds were revealed by X-ray crystallographic studies. The molecular structure of **5** (Fig. 4), together with important bond parameters (Table 5) is presented. The structure of **5** is similar to that of $[\text{HOs}_3(\text{HCO}_2)(\text{CO})_{10}]$ [19] and the bridged Os(1)–Os(2) edge [2.9168(5) Å] is significantly longer than those unbridged [Os(2)–Os(3), 2.8793(5) and Os(1)–Os(3), 2.8770(6) Å]. The carboxylate ligand takes up an essentially axial position and the five-membered Os–O–C–O–Os plane is almost perpendicular to the triosmium triangle in **5** [dihedral angle: 99.56°]. In **5**, the bridging carboxylate has a mean O–C–O angle and C–O bond distance that lie in the normal range of delocalized carboxylate ligands. In terms of electron count, **5** has 48 CVEs for which the $\{\text{O}_2\text{CC}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{NEt}_2\}$ moiety is considered to be a three-electron donor.

A perspective drawing of **6** is depicted in Fig. 5 and its selected bond parameters are given in Table 6. The molecule possesses two Os–Os bonds of lengths Os(1)–Os(2), 2.850(1) and Os(1)–Os(3), 2.8199(7) Å, which is comparable to the average Os–Os bond length of 2.8771(3) Å in $[\text{Os}_3(\text{CO})_{12}]$ [22]. The doubly bridged Os–Os distance is 3.23(1) Å and is regarded as non-

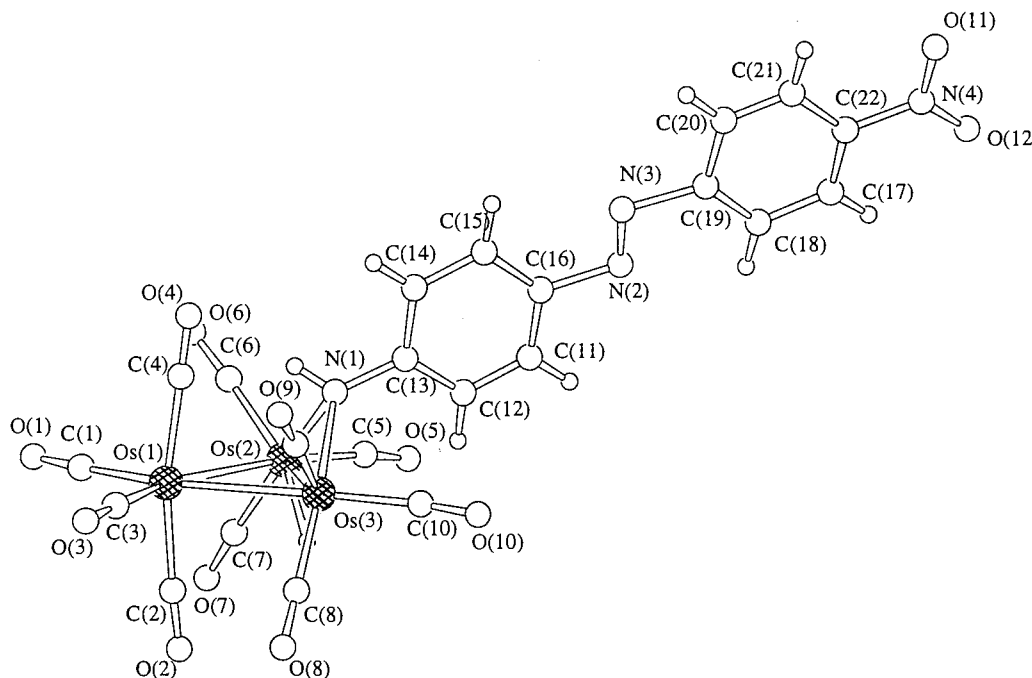


Fig. 3. A perspective drawing of the molecular structure of **4**.

Table 1
Spectroscopic data for compounds 2–6

| Compound | IR $\nu(\text{CO})$ (cm^{-1}) ^a | ¹ H-NMR $\delta(J)$ (Hz) ^b | MS (m/z) ^c |
|----------|---|---|---------------------------|
| 2 | 2103w, 2064vs, 2053s, 2022s, 2010s, 1993sh, 1972(sh) [N=N (KBr) 1425] | 14.31 (1H, s, OH), 8.48 (1H, d, $J = 8.3$, aryl H), 7.95 (1H, d, $J = 9.3$, aryl H), 7.60 (1H, d, $J = 8.3$, aryl H), 7.56 (1H, m, aryl H), 7.45 (1H, m, aryl H), 7.07 (1H, d, $J = 9.3$, aryl H), 6.59 (1H, s, aryl H), –14.9 (1H, s, Os–H) | 1104 (1104) |
| 3 | 2120w, 2089s, 2070w, 2047vs, 2016vs, 1985s, 1949w, 1923w [N=N (KBr) 1385] | 8.25 (1H, d, $J = 8.2$, aryl H), 8.14 (1H, d, $J = 8.2$, aryl H), 7.86 (1H, d, $J = 9.3$, aryl H), 7.61 (1H, d, $J = 4.2$, aryl H), 7.49 (1H, m, aryl H), 7.32(1H, m, aryl H), 7.10 (1H, d, $J = 4.2$, aryl H), 6.73 (1H, d, $J = 9.3$, aryl H), –20.29 (1H, s, Os–H) | 1077 (1077) |
| 4 | 2107w, 2068s, 2053s, 2022vs, 2005s, 1993s [N=N (KBr) 1435] | 8.28 (2H, d, $J = 8.8$, aryl H), 7.94 (2H, d, $J = 8.8$, aryl H), 7.82 (2H, d, $J = 8.7$, aryl H), 6.92 (2H, d, $J = 8.7$, aryl H), 5.75 (1H, br, NH) | 1093 (1093) |
| 5 | 2113w, 2074vs, 2062s, 2024vs, 1981w [C=O (KBr) 1570, N=N (KBr) 1477] | 7.72 (2H, d, $J = 9.0$, aryl H), 7.38 (3H, m, aryl H), 7.13 (1H, m, aryl H), 7.1, CH ₂ , 1.12 (6H, t, $J = 6.64$ (2H, d, $J = 9.0$, aryl H), 3.33 (4H, q, $J = 7.1$, CH ₃), –10.28 (1H, s, Os–H) | 1148 (1148) |
| 6 | 2103w, 2068s, 2013vs, 1974w, 1935w [C=O (KBr) 1668, N=N (KBr) 1456] | 8.20 (1H, br, NH), 7.90 (1H, d, $J = 8.0$, aryl H), 7.71 (1H, dd, $J = 2.2, 3.4$, aryl H), 7.61 (1H, t, $J = 7.5$, aryl H), 7.53 (1H, dd, $J = 2.2, 3.4$, aryl H), 7.46 (1H, t, $J = 7.5$, aryl H), 7.29 (1H, d, $J = 8.0$, aryl H), 6.80 (2H, d, $J = 9.0$, aryl H), 3.55 (4H, q, $J = 7.1$, CH ₂), 1.30 (6H, t, $J = 7.1$, CH ₃) | 1154 (1154) |

^a In CH₂Cl₂.

^b In CD₂Cl₂.

^c Simulated values given in parentheses.

bonding. The chloride ligand symmetrically bridges the nonbonded Os atoms with Os(2)–Cl(1) and Os(3)–Cl(1) bond lengths of 2.463(3) and 2.500(3) Å, respectively, which is comparable to the average Os–Cl bond length [2.466(7) Å] in [Os₃(μ₂-Cl)₂(CO)₁₀] [23]. The Os–Cl–Os bond angle is 81.15(8)°, which also compares well to the average Os–Cl–Os bond angle of 82.4(5)° in [Os₃(μ₂-Cl)₂(CO)₁₀] [23]. The azo ligand bridges the nonbonded Os(2)–Os(3) edge via the carboxylato oxygen and the azo nitrogen atoms via a σ bond. The Os(3)–N(1) [2.208(9) Å] is slightly longer than the value measured

in [(μ-H)Os₃(CO)₉{μ-η³-Et₂NC₆H₃(O)(N=N)C₅NH₃-Br}] [13] [2.10(3) Å] and cluster **3** [2.12(5) Å]. The bond distance of C(10)–O(10) [1.31(1) Å] is longer than that of C(10)–C(11) [1.20(1) Å]. The N–N distance is 1.29(1) Å and indicates a significant amount of double-bond character. The torsion angle defined for C(16)–N(1)–N(2)–C(17) is 173°, indicating that there is a considerable twist about the N–N bond and the original *trans* conformation of the ligand moiety is retained.

Selected bond lengths (Å) and angles (°) for complex **3**

Table 2
Selected bond lengths (Å) and angles (°) for complex **2**

| Bond lengths (Å) | | | |
|-------------------|-----------|-------------------|-----------|
| Os(1)–Os(2) | 2.8940(7) | Os(1)–Os(3) | 2.8802(7) |
| Os(2)–Os(3) | 2.9346(6) | Os(2)–C(11) | 2.11(1) |
| Os(3)–N(1) | 2.123(9) | Os(2)–C(5) | 1.97(1) |
| Os(3)–C(10) | 1.91(1) | N(1)–C(11) | 1.39(1) |
| O(11)–H | 1.09 | N(2)–N(3) | 1.29(1) |
| Bond angles (°) | | | |
| Os(1)–Os(2)–Os(3) | 59.22(2) | Os(2)–Os(1)–Os(3) | 61.09(2) |
| Os(1)–Os(3)–Os(2) | 59.69(2) | Os(2)–C(11)–N(1) | 113.4(7) |
| Os(3)–N(1)–C(11) | 109.5(7) | Os(2)–Os(3)–N(1) | 69.3(2) |
| Os(3)–Os(2)–C(11) | 67.8(3) | N(2)–N(3)–C(14) | 117(1) |
| N(3)–N(2)–C(13) | 112.4(9) | | |

| Bond lengths (Å) | | | |
|-------------------|----------|-------------------|----------|
| Os(1)–Os(2) | 2.927(4) | Os(1)–Os(3) | 2.925(4) |
| Os(2)–Os(3) | 2.959(5) | Os(2)–N(1) | 2.20(3) |
| Os(3)–N(2) | 2.12(5) | Os(3)–O(19) | 2.06(3) |
| O(19)–C(31) | 1.21(4) | N(3)–C(22) | 1.37(5) |
| N(2)–N(3) | 1.42(6) | N(1)–C(21) | 1.31(6) |
| N(2)–C(21) | 1.32(6) | C(22)–C(31) | 1.48(5) |
| Bond angles (°) | | | |
| Os(1)–Os(2)–Os(3) | 59.7(1) | Os(2)–Os(1)–Os(3) | 60.7(1) |
| Os(1)–Os(3)–Os(2) | 59.7(1) | Os(2)–Os(3)–N(2) | 81(1) |
| Os(3)–Os(2)–N(1) | 79.7(9) | Os(2)–N(1)–C(21) | 127(2) |
| Os(3)–N(2)–C(21) | 127(3) | N(1)–C(21)–N(2) | 119(4) |
| Os(3)–O(19)–C(31) | 129(2) | O(19)–C(31)–C(22) | 131(3) |
| C(31)–C(22)–N(3) | 117(3) | C(22)–N(3)–N(2) | 133(3) |
| N(3)–N(2)–Os(3) | 119(2) | N(2)–Os(3)–O(19) | 89(1) |

Table 4
Selected bond lengths (Å) and angles (°) for complex **4**

| Bond lengths (Å) | | | |
|-------------------|----------|-------------------|-----------|
| Os(1)–Os(2) | 2.859(1) | Os(1)–Os(3) | 2.8519(9) |
| Os(2)–Os(3) | 2.800(1) | Os(2)–N(1) | 2.16(1) |
| Os(3)–N(1) | 2.16(1) | N(1)–C(13) | 1.44(2) |
| N(2)–N(3) | 1.17(2) | N(1)–H | 0.87 |
| Bond angles (°) | | | |
| Os(1)–Os(2)–Os(3) | 60.51(2) | Os(2)–Os(3)–Os(1) | 60.76(2) |
| Os(2)–Os(1)–Os(3) | 58.73(2) | Os(2)–N(1)–Os(3) | 80.8(4) |
| N(1)–Os(2)–Os(3) | 49.6(3) | N(1)–Os(3)–Os(2) | 49.5(3) |

Table 5
Selected bond lengths (Å) and angles (°) for complex **5**

| Bond lengths (Å) | | | |
|-------------------|-----------|-------------------|-----------|
| Os(1)–Os(2) | 2.9168(5) | Os(1)–Os(3) | 2.8770(6) |
| Os(2)–Os(3) | 2.8793(5) | Os(1)–C(12) | 2.119(7) |
| Os(2)–O(11) | 2.143(7) | C(11)–O(11) | 1.26(1) |
| C(11)–O(12) | 1.27(1) | C(11)–C(12) | 1.49(1) |
| N(1)–N(2) | 1.25(1) | | |
| Bond angles (°) | | | |
| Os(1)–Os(2)–Os(3) | 59.52(1) | Os(1)–Os(3)–Os(2) | 60.89(1) |
| Os(2)–Os(1)–Os(3) | 59.59(1) | Os(1)–Os(2)–O(11) | 81.1(2) |
| Os(2)–Os(1)–O(12) | 80.6(2) | Os(2)–O(11)–C(11) | 125.9(6) |
| Os(1)–O(12)–C(11) | 127.5(6) | O(11)–C(11)–O(12) | 124.4(9) |
| C(18)–N(2)–N(1) | 113.8(9) | C(17)–N(1)–N(2) | 113.3(9) |

To explain this bonding situation around the azo moiety, we suggested that a dipolar ion formulation of **6** with the protonation at the uncoordinated N atom of the azo group.

The origin of the chloride atom in **6** is suspected to come from the chlorinated solvent CHCl_3 . If we perform the reaction of **1** with ethyl red in refluxing THF, this yields complex **5** as the sole product and no complex **6** is formed.

2.4. Electronic absorption spectra

The UV–vis absorption spectral data for complex **6** in solvents of different polarity ranging between 300 and 820 nm and data from the corresponding azo ligand are summarized in Table 7. The absorption band of **6** at ca. 516 nm with an extinction coefficient of $7217 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ is assigned to the $d\pi(\text{Os}) \rightarrow \pi^*(\text{azo})$ metal-to-ligand charge-transfer (MLCT) transition. The study of complex **6** in a variety of organic solvents by UV–vis spectroscopy showed that it exhibits some degree of negative solvatochromism (hypsochromic shift). That is, the MLCT absorption blue shifts in progressively more polar solvent media ($\mu_g > \mu_e$, where μ_g and μ_e are the dipole moments in the ground state and the excited state, respectively). In the ground state, complex **6** has its metal–ligand bonds substantially polarized,

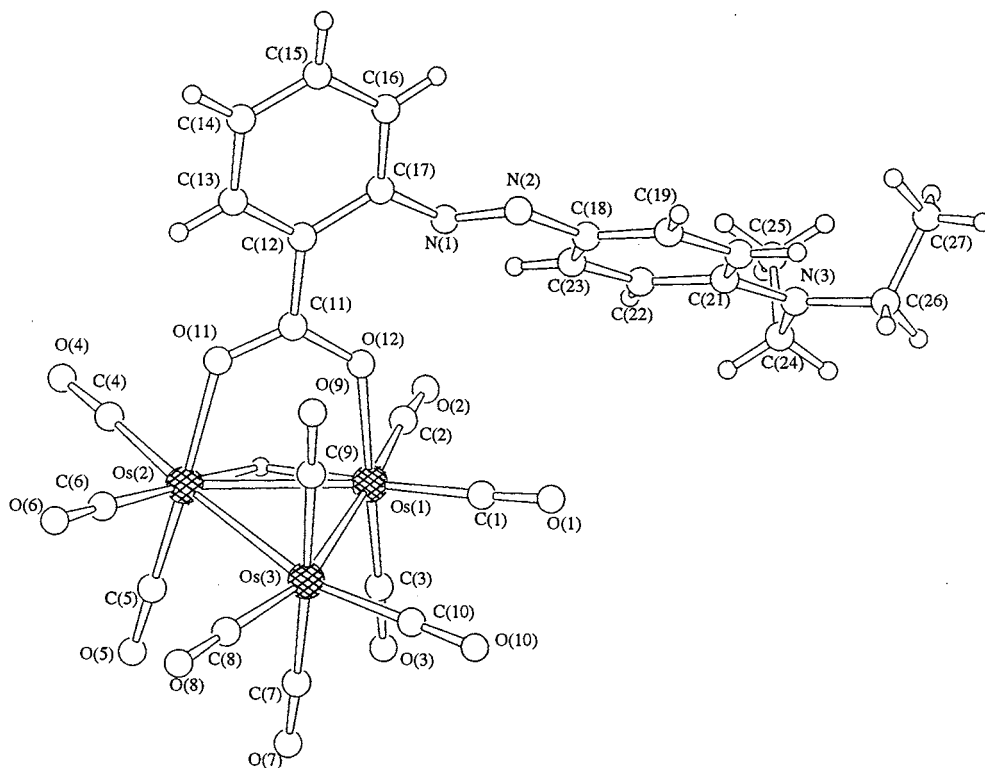
which is probably due to a dominating σ -donation from the coordinating azo ligand. On MLCT excitation, the electric dipole moment associated with the excited state of the solute molecule may be reduced, reversed or realigned by electron transfer from the metal-based orbital into the unoccupied π^* orbital of the organic ligand. This leads to a less polar excited state. Subsequently, a polar medium can be considered to stabilize the ground-state species to a greater extent than the excited-state molecule. Complex **6** can be described as a charge-separated zwitterionic compound. Infrared spectroscopy offers an ideal method for confirming this charge separation. The solution IR spectra of this species show unusually low carbonyl stretching frequencies for neutral clusters.

2.5. Conclusions

We have observed previously that the reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with ligands possessing $-\text{N}=\text{N}-$ functionality yields a series of osmium carbonyl clusters having the following structures: (1) the azo moieties remain uncoordinated [10] and (2) $-\text{N}=\text{N}-$ cleavage of the azo ligand forming two types of amido moieties [11]. In clusters **2–6**, the $-\text{N}=\text{N}-$ bond remain intact. Cluster **6** is a charge-separated zwitterionic compound exhibiting some degree of negative solvatochromism. The coordination ability of the azo group is rather low. In the presence of other donor ligands, the interaction of azo moiety with metal cluster core is significantly reduced. In cluster **2**, an orthometallation occurs instead of azo coordination. In cluster **3**, oxidation addition involving the OH group is observed. In the presence of an amine substituent, no azo coordination is observed in cluster **4**. Carboxylate is also clearly a better ligand comparable to azo group, as observed in cluster **5** and **6**.

Table 6
Selected bond lengths (Å) and angles (°) for complex **6**

| Bond lengths (Å) | | | |
|-------------------|----------|-------------------|-----------|
| Os(1)–Os(2) | 2.850(1) | Os(1)–Os(3) | 2.8199(7) |
| Os(2)–Cl(1) | 2.463(3) | Os(3)–Cl(1) | 2.500(3) |
| Os(2)–O(10) | 2.119(7) | Os(3)–O(10) | 2.152(7) |
| Os(3)–N(1) | 2.208(9) | C(10)–O(10) | 1.31(1) |
| C(10)–O(11) | 1.20(1) | N(1)–N(2) | 1.29(1) |
| N(2)–H | 0.75 | Os(2)···Os(3) | 3.230(1) |
| Bond angles (°) | | | |
| Os(2)–Os(1)–Os(3) | 69.40(2) | Os(1)–Os(2)–Cl(1) | 86.56(7) |
| Os(1)–Os(3)–Cl(2) | 86.52(7) | Os(1)–Os(2)–O(10) | 81.0(2) |
| Os(1)–Os(3)–O(10) | 81.2(2) | Os(2)–Cl(1)–Os(3) | 81.15(8) |
| Os(2)–O(10)–Os(3) | 98.2(3) | O(10)–Os(2)–Cl(1) | 76.4(2) |
| O(10)–Os(3)–Cl(1) | 75.0(2) | O(10)–Os(3)–N(1) | 79.6(3) |
| C(10)–O(10)–Os(3) | 129.5(7) | C(16)–N(1)–Os(3) | 107.9(7) |

Fig. 4. A perspective drawing of the molecular structure of **5**.

3. Experimental

3.1. General procedures

All reactions and manipulations were carried out under an inert atmosphere using standard Schlenk techniques. All chemicals and solvents were obtained commercially and used as received. Infrared spectra were recorded on a Bio-Rad FTS-7 IR spectrometer, using 0.5 mm calcium fluoride solution cells. Proton NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer using CD_2Cl_2 and referenced to SiMe_4 (δ 0). Mass spectra were recorded on a Finnigan MAT 95 instrument by fast atom bombardment techniques, using *m*-nitrobenzyl alcohol as the matrix solvents. Electronic absorption spectra were obtained from a

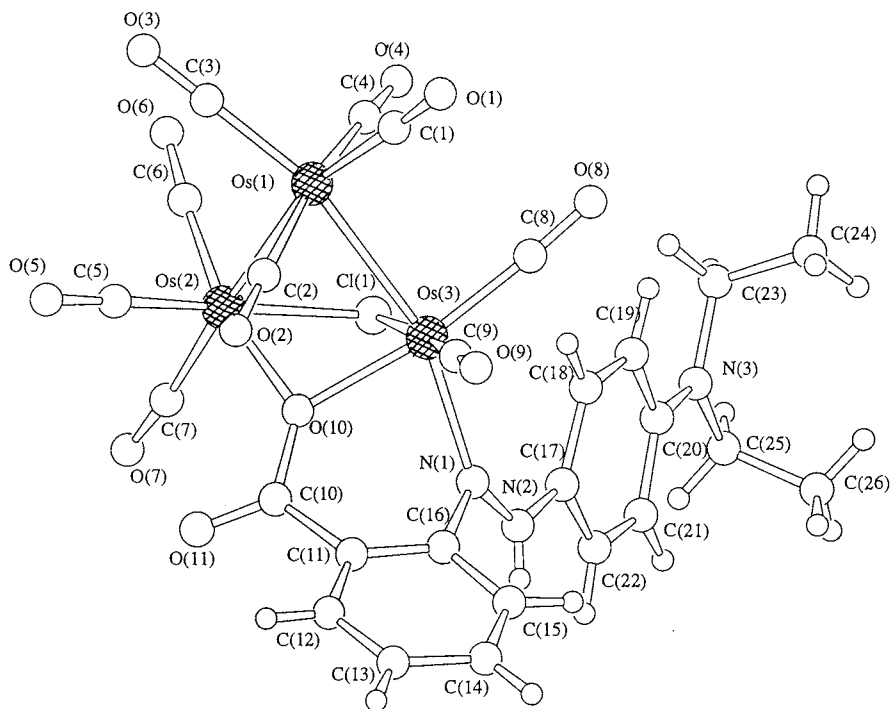
microprocessor-controlled HP 8450A diode array spectrophotometer using quartz cells of 1 cm path length. Routine purification of products was carried out in air by thin-layer chromatography (TLC) on plates coated with Merck Kieselgel 60 GF₂₅₄.

3.2. Reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with 1-(2-thiazolylazo)-2-naphthol

The compounds $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ (**1**) (932 mg, 1.0 mmol) and 1-(2-thiazolylazo)-2-naphthol (281 mg, 1.1 mmol) were dissolved in CH_2Cl_2 (60 cm^3). The colour of the solution changed from yellow to dark brown. After stirring for 6 h at room temperature, the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 and chromatographed by preparative TLC on silica gel. Elution with CH_2Cl_2 -*n*-hexane

Table 7
Electronic absorption spectral data for the complex **6** and the corresponding free ligand

| Compounds | λ_{max} (nm) ϵ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) | | | | |
|-----------|---|---------------------------------------|--------------------------|--------------------------|--------------------------|
| | Hexane | CH_2Cl_2 | MeOH | CHCl_3 | Me_2CO |
| Ethyl red | | 292 (1467) 324 (637) 498 (4381) | | | |
| 6 | 458 (4367) 538 (2590) | 466 (6640) 516 (7217) | 452 (2859) 514 (3267) | 460 (2350) 514 (2388) | 458 (7305) 508 (8681) |

Fig. 5. A perspective drawing of the molecular structure of **6**.Table 8
Summary of crystal data and data collection parameters for compounds **2–6**

| | 2 | 3 | 4 | 5 | 6 |
|---|---|---|--|--|--|
| Empirical formula | C ₂₃ H ₈ N ₃ O ₁₁ Os ₃ S | C ₂₂ H ₈ N ₃ O ₁₀ Os ₃ S | C ₂₂ H ₁₀ N ₄ O ₁₂ Os ₃ | C ₂₇ H ₁₉ N ₃ O ₁₂ Os ₃ | C ₂₆ ClH ₁₉ N ₃ O ₁₁ Os ₃ |
| Molecular weight | 1104.99 | 1076.98 | 1092.94 | 1148.06 | 1155.50 |
| Colour, habit | Purple, block | Purple, block | Red, block | Yellow, block | Red, plate |
| Crystal size (mm) | 0.13 × 0.18 × 0.25 | 0.14 × 0.16 × 0.24 | 0.29 × 0.31 × 0.38 | 0.21 × 0.26 × 0.31 | 0.26 × 0.28 × 0.34 |
| Crystal system | <i>P</i> $\bar{1}$ (no. 2) | <i>P</i> $\bar{1}$ (no. 2) | <i>P</i> $\bar{1}$ (no. 2) | <i>P</i> $\bar{1}$ (no. 2) | <i>P</i> $\bar{1}$ (no. 2) |
| Space group | Triclinic | Triclinic | Triclinic | Triclinic | Triclinic |
| <i>a</i> (Å) | 7.909(1) | 25.226(8) | 11.329(4) | 9.461(1) | 13.009(3) |
| <i>b</i> (Å) | 8.553(1) | 7.644(2) | 13.050(3) | 12.316(1) | 13.315(3) |
| <i>c</i> (Å) | 21.891(1) | 15.478(6) | 10.026(2) | 14.403(1) | 9.500(2) |
| α (°) | 97.43(2) | 91.86(3) | 103.76(2) | 71.27(2) | 97.64(2) |
| β (°) | 97.21(2) | 121.06(2) | 101.48(2) | 86.60(2) | 102.67(2) |
| γ (°) | 109.73(2) | 93.80(2) | 97.74(2) | 88.34(2) | 71.53(2) |
| <i>U</i> (Å ³) | 1359.3(4) | 2543(1) | 1384.9(7) | 1586.5(3) | 1519.3(7) |
| <i>Z</i> | 2 | 4 | 2 | 2 | 2 |
| <i>D</i> _{calc.} (g cm ⁻³) | 2.700 | 2.813 | 2.621 | 2.403 | 2.526 |
| <i>F</i> (000) | 998 | 1940 | 988 | 1052 | 1058 |
| μ (Mo–K α) (cm ⁻¹) | 141.19 | 150.86 | 137.88 | 120.41 | 126.57 |
| No. of reflections collected | 12546 | 6835 | 3839 | 13260 | 4182 |
| No. of unique reflections | 4437 | 6653 | 3621 | 5389 | 3971 |
| No. of observed reflections [<i>I</i> > 1.5 σ (<i>I</i>)] | 3678 | 2909 | 2569 | 4470 | 3150 |
| <i>R</i> ^a | 0.044 | 0.041 | 0.039 | 0.044 | 0.030 |
| <i>R</i> ^b | 0.050 | 0.033 | 0.036 | 0.053 | 0.029 |
| <i>g</i> in weighting scheme ^c | 0.019 | 0.003 | 0.009 | 0.023 | 0.012 |
| Goodness-of-fit (S) | 1.22 | 1.27 | 1.28 | 1.19 | 1.09 |
| Maximum Δ / σ | 0.01 | 0.08 | 0.01 | 0.03 | 0.02 |
| No. of parameters | 370 | 354 | 370 | 406 | 397 |
| Maximum, minimum density in ΔF map close to Os (e Å ⁻³) | 0.96, -1.42 | 1.16, -0.94 | 1.02, -0.92 | 1.02, -2.27 | 0.36, -0.46 |

(1:1 v/v) resolved three bands. The first yellow band was $[\text{Os}_3(\text{CO})_{12}]$ (14.1 mg, 0.016 mmol, 5%) followed by one purple and one brown band with R_f 0.8 and 0.65, respectively. These were isolated and characterized as $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{NC}_3\text{HS-N=N-C}_{10}\text{H}_6(\text{OH}))]$ (**2**) (331.2 mg, 0.30 mmol, 30%) and $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^3\text{-NC}_3\text{H}_2\text{S(N=N)C}_{10}\text{H}_6(\text{O}))]$ (**3**) (484.7 mg, 0.45 mmol, 45%), respectively. (Found: C, 25.01; H, 0.72; N, 3.82. Anal. Calc. for $\text{C}_{23}\text{H}_8\text{N}_3\text{O}_{11}\text{Os}_3\text{S}$ (**2**): C, 25.00; H, 0.72; N, 3.80. Found: C, 24.52; H, 0.75; N, 3.87. Anal. Calc. for $\text{C}_{22}\text{H}_8\text{N}_3\text{O}_{10}\text{Os}_3\text{S}$ (**3**): C, 24.51; H, 0.74; N, 3.90%).

3.3. Reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with 4-nitro-4'-aminoazobenzene

A solution of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ (932 mg, 1.0 mmol) was dissolved in a solution of CH_2Cl_2 and 4-nitro-4'-aminoazobenzene (266 mg, 1.1 mmol) was added. The dark brown solution was stirred for 12 h. After removal of the solvent in vacuo, the residue was chromatographed on TLC using CH_2Cl_2 -*n*-hexane (1:1 v/v) as eluent. The first fraction was a yellow band of $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-NHC}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{NO}_2)]$ (**4**) (326 mg, 0.3 mmol, 35%). (Found: C, 24.21; H, 0.81; N, 5.10. Anal. Calc. for $\text{C}_{22}\text{H}_{10}\text{N}_4\text{O}_{12}\text{Os}_3$ (**4**): C, 24.18; H, 0.82; N, 5.13%).

3.4. Reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with 2-[4-diethylamino]phenylazo]benzoic acid

A solution of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ (932 mg, 1.0 mmol) and 2-[4-diethylamino]phenylazo]benzoic acid (327 mg, 1.1 mmol) was refluxed in CHCl_3 (50 ml) for 12 h. The solvent of the dark red solution was removed in vacuo. The residue was redissolved in CH_2Cl_2 and subject to TLC to give two bands. The first fraction was an orange-yellow band $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{O}_2\text{CC}_6\text{H}_4\text{N=N-C}_6\text{H}_4\text{NEt}_2)]$ (**5**) (466 mg, 0.41 mmol, 50%) and the second red band $[\text{Os}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-}\eta^2\text{-OC(O)C}_6\text{H}_4\text{N=NHC}_6\text{H}_4\text{NEt}_2)]$ (**6**) (158 mg, 0.14 mmol, 17%). (Found: C, 28.24; H, 1.67; N, 3.65. Anal. Calc. for $\text{C}_{27}\text{H}_{19}\text{N}_3\text{O}_{12}\text{Os}_3$ (**5**): C, 28.22; H, 1.65; N, 3.66. Found: C, 27.02; H, 1.75; N, 3.61. Anal. Calc. for $\text{C}_{26}\text{ClH}_{19}\text{N}_3\text{O}_{11}\text{Os}_3$ (**6**): C, 26.98; H, 1.73; N, 3.63%).

3.5. X-ray data collection and structural determination of complexes **2–6**

All pertinent crystallographic data and other experimental details are summarized in Table 8. Intensity data were collected at ambient temperature on either a Rigaku AFC7R diffractometer (complexes **3**, **4** and **6**) or a MAR research image plate scanner (complexes **2** and **5**) equipped with graphite-crystal monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) using $\omega - 2\theta$ and ω

scan types, respectively. Diffracted intensities were corrected for Lorentz and polarization effects. An approximate absorption correction by inter-image scaling was also applied. Scattering factors were taken from Ref. [24a] and anomalous dispersion effects [24b] were included in F_c . The structures were solved by direct methods (SIR92 [25] for **2**; SHELX-86 [26] for **3**, **4** and **6**) or heavy-atom Patterson methods (PATTY [27] for **5**) and expanded by Fourier-difference techniques (DIRDIF94) [28]. The solutions were refined by full-matrix least-squares analysis on F . Hydrogen atoms were generated in their ideal positions except N(H) which were located from a difference Fourier synthesis, and included in the structure factor calculations but not refined. Calculations were performed on a Silicon-Graphics computer, using the program package TEXSAN [29].

The crystal structures are deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 119655–CCDC119659.

Acknowledgements

We gratefully acknowledge the financial support from the Hong Kong Research Grants Council and the University of Hong Kong. F.-S.K. acknowledges the receipt of a postgraduate studentship, administered by the University of Hong Kong.

References

- [1] H. Vahrenkamp, in: H. Werner, G. Erker (Eds.), *Organometallics in Organic Synthesis*, Springer-Verlag, Heidelberg, 1989, p. 235.
- [2] B. Hansert, M. Tasi, A. Tiripicchio, M. Tiripicchio Camellini, H. Vahrenkamp, *Organometallics* 10 (1991) 4070.
- [3] H. Bantel, B. Hansert, A.K. Powell, M. Tasi, H. Vahrenkamp, *Angew. Chem. Int. Ed. Engl.* 28 (1989) 1509.
- [4] J.A. Smieja, J.E. Gozum, W.L. Gladfelter, *Organometallics* 6 (1987) 1311.
- [5] M. Tasi, A.K. Powell, H. Vahrenkamp, *Chem. Ber.* 124 (1991) 1549.
- [6] B. Hansert, H. Vahrenkamp, *Chem. Ber.* 126 (1993) 2017.
- [7] B. Hansert, H. Vahrenkamp, *Chem. Ber.* 126 (1993) 2023.
- [8] B. Hansert, A.K. Powell, H. Vahrenkamp, *Chem. Ber.* 124 (1991) 2697.
- [9] E.J. Wucherer, M. Tasi, B. Hansert, A.K. Powell, M.T. Garland, J.F. Halet, J.Y. Saillard, H. Vahrenkamp, *Inorg. Chem.* 28 (1989) 3564.
- [10] Y.K. Au, K.K. Cheung, W.T. Wong, *Inorg. Chim. Acta* 238 (1995) 193.
- [11] W.T. Wong, T.S. Wong, *J. Organomet. Chem.* 542 (1997) 29.
- [12] K. Burgess, B.F.G. Johnson, J. Lewis, *J. Organomet. Chem.* 233 (1982) C55.
- [13] T.S. Wong, unpublished results.
- [14] M.N. Ackermann, J.W. Naylor, E.J. Smith, G.A. Mines, N.S. Amin, M.L. Kerns, C. Woods, *Organometallics* 11 (1992) 1919.

- [15] Z. Dawoodi, M.J. Mays, K. Henrick, *J. Chem. Soc. Dalton Trans.* (1984) 433.
- [16] D.L. Ramage, G.L. Geoffroy, A.L. Rheingold, B.S. Haggerty, *Organometallics* 11 (1992) 1242.
- [17] Z. Dawoodi, M.J. Mays, A.G. Orpen, *J. Organomet. Chem.* 219 (1981) 251.
- [18] M.R. Churchill, F.J. Hollander, J.R. Shapely, J.B. Keister, *Inorg. Chem.* 19 (1980) 1271.
- [19] J.R. Shapley, G.M. St. George, M.R. Churchill, F.J. Hollander, *Inorg. Chem.* 21 (1982) 3295.
- [20] B.F.G. Johnson, J. Lewis, P.R. Raithby, V.P. Saharan, W.T. Wong, *J. Chem. Soc. Chem. Commun.* (1991) 365.
- [21] S.M. Lee, K.K. Cheung, W.T. Wong, *J. Organomet. Chem.* 506 (1996) 77.
- [22] M.R. Churchill, B.G. DeBoer, *Inorg. Chem.* 16 (1977) 878.
- [23] F.W.B. Einstein, T. Jones, K.G. Tyers, *Acta Crystallogr. B* 38 (1982) 1272.
- [24] (a) D.T. Cromer, J.T. Waber, *International Tables for X-ray Crystallography*, vol. 4, Kynoch, Birmingham, 1974, Table 22B and 2.3.1.
- [25] SIR 92, A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, G. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Cryst.* 27 (1994) 435.
- [26] G.M. Sheldrick, SHELXS-86, Program for crystal structure solution, *Acta Crystallogr. Sect. A* 46 (1990) 467.
- [27] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.
- [28] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Isrel, J.M.M. Smits, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
- [29] TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.