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Note

Synthesis and structural characterization of osmium cluster complexes containing 2-phenylazopyridine. Crystal structures of $[Os_3(CO)_{10}(NC_5H_4-N=N-C_6H_5)]$ and $[Os_3(CO)_{10}(\mu-H)(NC_5H_3-N=N(O)-C_6H_5)]$

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Abstract

The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2-phenylazopyridine (2-PAP) affords $[Os_3(CO)_{10}(NC_5H_4-N=N-C_6H_5)]$ (1), $[Os_3(CO)_{10}(\mu-H)(NC_5H_3-N=N(O)-C_6H_5)]$ (2) and a violet product 3, which is an isomer of 1. In 1, the 2-PAP moiety acts as the rarely observed six-electron donor. Cluster 2 contains an 'oxidized' 2-PAP moiety bonding in the usual ortho-metallated mode of pyridine. Both clusters 1 and 2 have been fully characterized in solution by conventional spectroscopic methods and in the solid state by single crystal X-ray diffraction analysis. Crystals of 1 are orthorhombic, space group $P2_12_12_1$, Z=4, with unit cell dimensions a=9.123(1), b=17.217(2), c=16.168(2) Å. Crystals of 2 are triclinic, space group $P\overline{1}$, Z=2, with unit cell dimensions a=9.308(2), b=11.250(2), c=12.934(2) Å, $\alpha=77.23(1)$, $\beta=72.26(1)$, $\gamma=85.21(1)^\circ$.

Keywords: Crystal structures; Osmium complexes; 2-Phenylazopyridine complexes; Carbonyl complexes; Cluster complexes



Fig. 1. 2-Phenylazopyridine.

Molecules containing the azo (-N=N-) functional group such as azoarenes and azoalkanes are prominent in their ability to undergo N–N bond cleavage reactions and in their combination with other organic moieties to form organic products when they are coordinated to cluster frameworks [1–3]. On the other hand, azopyridines (Fig. 1) have only attracted little attention in their chemical reactivities towards metal cluster complexes though their mononuclear and dinuclear coordination chemistry has been well-developed [4– 8]. As part of studies in investigating metal cluster-assisted transformations of heterocyclic molecules [9,10], we report here the synthesis and characterization of two cluster complexes resulting from the labilized triosmium clusters, $[Os_3(CO)_{10}(MeCN)_2]$, and 2-phenylazopyridine (2-PAP). (2-PAP has been known to stabilize complexes of metal in their lower oxidation states [11].)

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ (100 mg, 0.11 mmol) with an equivalent of 2-PAP (20.13 mg) in dichloromethane at room temperature for 1 h under a dinitrogen atmosphere resulted in a colour change from yellow to reddish brown. A





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small amount of blue precipitate in the reaction mixture was observed and remained uncharacterized due to its poor solubility in common organic solvents. Thin layer chromatography of the reaction mixture on silica (eluent: n-hexane/ dichloromethane, 80/20 vol./vol.) afforded yellow [Os₃-(CO)₁₀(NC₅H₄-N=N-C₆H₅)] (1) (45%) ($R_{\rm f}$ =0.55), orange [Os₃(CO)₁₀(μ -H)(NC₅H₃-N=N(O)-C₆H₅] (2) (10%) ($R_{\rm f}$ =0.65) and a violet product 3 (15%) ($R_{\rm f}$ =0.3). Cluster 1 underwent isomerization to give 3 on standing in solution accompanied by a colour change from yellow to dark red. However, the conversion is not reversible (Scheme 1).

The ¹H NMR spectra of 1, 2 and 3 all reveal the presence of the 2-PAP ligand. FAB mass spectra of 1 and 3 both exhibit an envelope of molecular ions with a peak at 1039 while that of 2 has a peak at 1055⁻¹. To establish their molecular structures, crystals of both 1 and 2 suitable for single crystal Xray analysis were obtained from slow evaporation of an n-hexane/dichloromethane solution mixture of 1 and 2, respectively, at -10 °C⁻². The molecular structures of 1 and 2 are shown in Figs. 2 and 3, respectively, together with some relevant bond parameters.

The molecular structure of 1 consists of an open triosmium metal core. The Os(2)–Os(3) (2.919(2) Å) and Os(1)–Os(2) (2.916(2) Å) bonding edges are slightly elongated as compared with the value observed in Os₃(CO)₁₂ (2.877(3) Å) [12]. However, the Os(1)–Os(3) distance

Spectroscopic data for 3: IR (n-hexane) ν (CO) 2105(m), 2062(vs), 2045(w), 2031(vs), 2020(vs), 2004(s), 1990(m), 1975(w), 1934(w) cm⁻¹; ¹H NMR (CD₂Cl₂) δ 7.5 (*m*, 5H), 8.25 (*m*, 4H); FAB mass spectrum *M*⁺ obs. 1039 calc. 1039.

² Crystal data for 1: $C_{21}H_9N_3O_{10}Os_3$, M = 1033.92, orthorhombic, space group $P2_12_12_1$ (No. 19); a = 9.123(1), b = 17.217(2), c = 16.168(2) Å; V = 2539.5(5) Å³; Z = 4, $D_c = 2.704$ g cm⁻³, F(000) = 1856, Mo K α radiation, $\lambda = 0.71073$ Å, μ (Mo K α) = 150.53 cm⁻¹. Brown rectangular block, crystal dimensions: $0.10 \times 0.20 \times 0.35$ mm, 4166 data measured on an Enraf-Nonius CAD4 diffractometer ($2.0 \le 2\theta \le 46.0^\circ$), corrected for absorption by Ψ -scan method, 1753 independent reflections [$I \ge 3\sigma(I)$]. Structure solved by a combination of direct methods (MULTAN) and difference Fourier technique and refined by full-matrix least-squares analysis on F with 164 parameters (Os atoms anisotropic) to R = 0.052 and $R_w = 0.079$. Refinement of the enantiomorph yielded a slightly higher R = 0.054 and $R_w = 0.082$.

Crystal data for 2: $C_{21}H_9N_3O_{11}Os_3$, M = 1049.90, triclinic, space group $P\bar{1}$ (No. 2); a = 9.308(2), b = 11.250(2), c = 12.934(2) Å; $\alpha = 77.23(1)$, $\beta = 72.26(1)$, $\gamma = 85.21(1)^\circ$, V = 1257.8(6) Å³; Z = 2, $D_c = 2.767$ g cm⁻³, F(000) = 944, Mo K α radiation, $\lambda = 0.71073$ Å, μ (Mo K α) = 152.00 cm⁻¹. Orange rectangular block, crystal dimensions: $0.10 \times 0.15 \times 0.15$ mm, 3754 data measured on an Enraf-Nonius CAD4 diffractometer ($2.0 \le 2\theta \le 46.0^\circ$), corrected for absorption by Ψ -scan method, 2704 independent reflections $[I \ge 3\sigma(I)]$. Structure solved by a combination of direct methods (MULTAN) and difference Fourier techniques and refined by full-matrix least-squares analysis on F with 168 parameters (Os atoms anisotropic) to R = 0.041 and $R_w = 0.057$.



Fig. 2. The molecular structure of $[Os_3(CO)_{10}(NC_5H_4-N=N-C_6H_5)]$ (1) showing the atom numbering scheme. Selected bond lengths and angles: Os(1)-Os(2), 2.916(2); Os(2)-Os(3), 2.919(2); $Os(3)\cdots Os(1)$, 3.642(2); Os(1)-N(1), 2.11(4); Os(3)-N(2), 2.10(3); Os(3)-N(3), 2.12(3); Os(1)-N(3), 2.16(3); N(2)-N(3), 1.42(4); N(3)-C(16), 1.43(5); N(2)-C(15), 1.45(6) Å; Os(1)-Os(2)-Os(3), 77.2(1); $Os(1)\cdots Os(3)-Os(2)$, 51.34(5); $Os(2)-Os(1)\cdots Os(3)$, 51.4(1); Os(2)-Os(1)-N(1), 89(1); Os(2)-Os(1)-N(3), 82.6(9); Os(2)-Os(3)-N(2), 97.3(9); Os(2)-Os(3)-N(3), 83.3(9); N(1)-Os(1)-N(3), 80(1); N(2)-Os(3)-N(3), 39(1); Os(3)-N(2)-N(3), 71(2); Os(3)-N(3)-N(2), 70(2)°.

(3.642(2) Å) is so great that it can be regarded as nonbonding. In addition, the N(2)-N(3) bond distance (1.42(4) Å) is significantly elongated as compared with the corresponding value for the isolated N=N bond (1.24 Å) exemplified by trans-azobenzene [13]. Both observations are consistent with the μ - η^3 bonding mode of the 2-PAP ligand moiety which behaves as a six-electron donor by virtue of the involvement of the two π electrons of the N=N bond. Further evidence of the π donation comes from the shifting of ν (N=N) from 1412 cm⁻¹ [11] in the free ligand to 1344 cm^{-1} in 1. Accordingly, the total cluster valence electron of 1 is 50. The only other example in which the 2-PAP ligand moiety behaves as a six-electron donor was found in the complex [Fe₂(CO)₂(4-CH₃-2-PAP)₃] in which the N=N bond distances (1.411(9) and 1.438(10) Å) [11] are close to that observed in cluster 1. The N(1), Os(1), N(3), N(2)and C(15) atoms together form a five-membered ring within the molecule. The torsion angle as defined by C(15)-N(2)-N(3)-C(16) is $127(3)^{\circ}$, indicating that there is a considerable twist about the N-N bond so that the trans conformation of the ligand moiety is significantly distorted. Both the Os(1)-N(3) (2.16(3) Å) and Os(1)-N(1) (2.11(4) Å) distances are slightly longer than the average values in their mononuclear complexes (2.019 Å) [6].

The IR spectrum of 2 in the carbonyl stretching region is very similar to those of other ortho-metallated pyridine-metal

¹ Spectroscopic data for 1: IR (n-hexane) ν (CO) 2095(m), 2064(vs), 2045(s), 2013(s), 1996(vs), 1988(vs), 1972(w), 1964(w) cm⁻¹; ¹H NMR (CD₂Cl₂) δ 7.52 (m, 5H), 8.12 (m, 2H), 8.28 (m, 2H); FAB mass spectrum M^+ obs. 1039 calc. 1039. (based on ¹⁹²Os).

Spectroscopic data for 2: IR (n-hexane) ν (CO) 2103(m), 2062(vs), 2052(s), 2021(s), 2010(s), 2003(m), 1991(m), 1975(w) cm⁻¹, ¹H NMR (CD₂Cl₂) δ – 14.56 (*s*, 1H), 7.52 (*m*, 4H), 8.15 (*m*, 2H), 8.32 (*m*, 2H); FAB mass spectrum *M*⁺ obs. 1055 calc. 1055.



Fig. 3. The molecular structure of $[Os_3(CO)_{10}(\mu-H)(NC_5H_3-N=N(O)-C_6H_5)]$ (2) showing the atom numbering scheme. Selected bond lengths and angles: Os(1)-Os(2), 2.9028(7); Os(1)-Os(3), 2.874(1); Os(2)-Os(3), 2.8667(9); Os(1)-C(11), 2.11(1); Os(2)-N(1), 2.14(2); Os(1)-C(2), 1.92(2); Os(2)-C(4), 1.87(2); O(11)-N(3), 1.25(2); N(1)-C(11), 1.38(1); N(2)-N(3), 1.27(2) Å; Os(1)-Os(2)-Os(3), 59.7(1); Os(2)-Os(1)-Os(3), 59.5(1); Os(1)-Os(3)-Os(2), 60.7(1); Os(1)-C(11)-N(1), 112.5(8); Os(2)-N(1)-C(11), 109.6(8); N(2)-N(3)-C(16), 118(1); O(11)-N(3)-C(16), 118(1); N(3)-N(2)-C(15), $117(1)^\circ$.

cluster derivatives [14]. Surprisingly, the FAB mass spectrum and single crystal X-ray analysis showed that the ligand moiety is actually 2-phenylazoxypyridine (NC₅H₃- $N=N(O)-C_6H_5$). The molecular structure consists of a triosmium metal core with one Os-Os edge doubly bridged by a hydride and the 'oxidized' 2-PAP ligand. The N(3)-O(11) length (1.25(2) Å) is consistent with those found in *cis*azobenzene dioxide (1.268(4) Å) (there is a lack of reliable data on the N-O length in monomeric nitroso compounds in the literature), yet the N(3)-N(2) length (1.27(2) Å) is significantly shorter as compared with other nitroso dimers (1.30-1.32 Å) [15]. The bond distances Os(1)-C(2) (1.92(2) Å) and Os(2)–C(4) (1.87(2) Å) are consistent with the stronger *trans* influence exerted by a σ -C donor than that by an N donor. In contrast to that of 1, the torsion angle as defined by C(15)-N(2)-N(3)-C(16) is $176(1)^{\circ}$, indicating the trans conformation of the ligand remains almost intact upon coordinating to the cluster framework. The atoms N(2), N(3), O(11) and C(6) are almost coplanar with maximun deviation of 0.002 Å from their least-squares plane. The ligand moiety $(NC_5H_3-N=N(O)-C_6H_5)$ has not been reported before, although the azoxybenzene (C₆H₅- $N=N(O)-C_6H_5$) analog is well known [15,16]. We are unable to establish the origin of the 'oxidized' ligand.

Isomerization of cluster 1 to 3 is irreversible. However, the conversion can either be reduced by lowering the temperature or 'frozen' by storing 1 in the solid state. Attempts to obtain a single crystal of 3 were unsuccessful. Nevertheless, ¹H NMR and FAB mass spectra indicated that 3 is an isomer of

1. Attempts to cleave the N=N bond of 1 in refluxing nheptane (98 °C) afforded mainly decomposition products. Photo-activation of 1 under UV radiation only enhanced its isomerization to 3 and produced more decomposition products. This is in contrast to the cleavage of the N=N bond as the major reaction pathway of coordinated azoarenes and azoalkanes on iron carbonyls. As suggested before, the coordination of the additional pyridine nitrogen atom of 2-PAP makes the cleavage of the N=N bond much less facile [11].

Supplementary material

A summary of the crystal data for complex 1 (Table S1) and complex 2 (Table S2) is available from the authors on request.

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