DALTON

Dimetallic gold(I) and platinum(II) complexes containing a trioxoosmium(VIII) moiety. Crystal structures of $[\mathrm{Au(PPh_3)(NOsO_3)}]$ and *cis*-$[\mathrm{Pt(PMe_3)_2(NOsO_3)_2}]$

Wa-Hung Leung,*,[a] **Joyce L. C. Chim**[a] **and Wing-Tak Wong**†,[b]

[a] *Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*

[b] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*

Reaction of $[\mathrm{NBu^n{}_4}][\mathrm{OsO_3N}]$ with $[\mathrm{Au(PPh_3)(CF_3SO_3)}]$ and *cis*-$[\mathrm{Pt(PMe_3)_2(CF_3SO_3)_2}]$ afforded the dimetallic complexes $[\mathrm{Au(PPh_3)(NOsO_3)}]$ and *cis*-$[\mathrm{Pt(PMe_3)_2(NOsO_3)_2}]$, respectively, which have been characterised by X-ray crystallography.

Complexes containing the trioxoosmium(VIII) moiety, notably $[\mathrm{OsO_4}]$ and $[\mathrm{OsO_3(NR)}]$, have attracted much attention due to their applications to organic synthesis, specifically in the enantioselective dihydroxylation[1] and aminohydroxylation[2] of alkenes. In an attempt to develop novel oxoosmium reagents for organic transformations, we set out to study dimetallic osmium complexes containing electrophilic metals. Herein we describe the syntheses and crystal structures of the first dimetallic $\mathrm{Au^I}$–$\mathrm{Os^{VIII}}$ and $\mathrm{Pt^{II}}$–$\mathrm{Os^{VIII}}$ complexes containing the trioxoosmium(VIII) moiety.

Our approach to the synthesis of high-valent dimetallic complexes of the type $[\mathrm{OsO_3(NML}_n)]$, which are isolobal with the known imidotrioxoosmium complex $[\mathrm{OsO_3(NR)}]$, involves the reaction of the $[\mathrm{OsO_3N}]^-$ anion with the cationic metal complexes $[\mathrm{ML}_n]^+$. Accordingly, the interaction of $[\mathrm{NBu^n{}_4}][\mathrm{OsO_3N}]$ (ref. 3) with one equivalent of $[\mathrm{Au(PPh_3)(CF_3SO_3)}]$ (ref. 4) led to the isolation of the dimetallic $\mathrm{Au^I}$–$\mathrm{Os^{VIII}}$ complex $[\mathrm{Au(PPh_3)(NOsO_3)}]$ **1**‡ in good yield. The structure of complex **1** (Fig. 1)§ consists of a tetrahedral Os and a linear Au centre, which are bridged *via* the linear Os–N–Au linkage [Au–N–Os 168(1)°]. The mean Os–O (1.71 Å) and Os–N distance [1.69(2) Å] for **1** are similar to those for the alkylimido analogue $[\mathrm{OsO_3(NC_{10}H_{15})}]$ [$\mathrm{C_{10}H_{15}}$ = 1-adamantyl; Os–O 1.715(4), Os–N 1.697(4) Å].[8] The Au–N distance [2.02(2) Å] is comparable to those for nitridogold(I) clusters (*e.g.* $[\{\mathrm{Au(PPh_3)}\}_5(\mu_5\text{-N})]^{2+}$, Au–N *ca.* 2.06 Å).[9] These structural data are consistent with the formulation of $[\mathrm{(Ph_3P)Au{-}N{\equiv}OsO_3}]$ for **1**. The dimetallic $\mathrm{Pt^{II}}$–$\mathrm{Os^{VIII}}$ complex *cis*-$[\mathrm{Pt(PMe_3)_2(NOsO_3)_2}]$ **2**¶ was synthesised similarly by treatment of *cis*-$[\mathrm{Pt(PMe_3)_2(CF_3SO_3)_2}]$ (ref. 10) with two equivalents of $[\mathrm{NBu^n{}_4}][\mathrm{OsO_3N}]$. The geometry around Pt in **2** is square planar with two *cis* tetrahedral $[\mathrm{OsO_3N}]$ units (Fig. 2).§

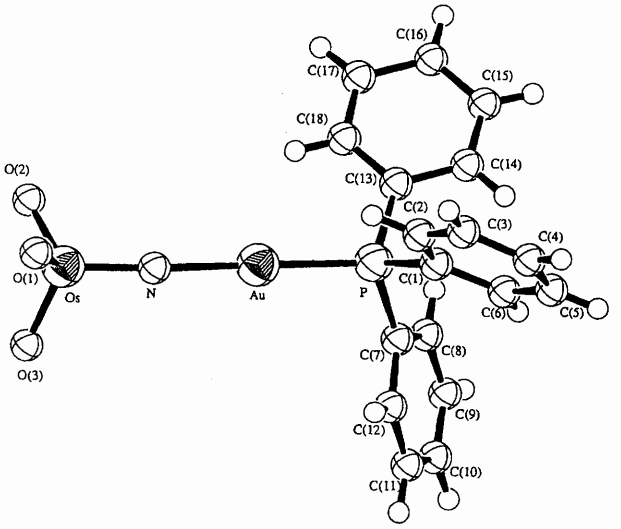


Fig. 1 Perspective view of $[\mathrm{Au(PPh_3)(NOsO_3)}]$ **1**. Selected bond lengths (Å) and angles (°): Os–O(1) 1.67(2), Os–O(2) 1.72(2), Os–O(3) 1.74(2), Os–N 1.69(2), Au–N 2.02(2), Au–P 2.250(5); Au–N–Os 168(1), P–Au–N 179.1(5), O(1)–Os–O(2) 109(1), O(1)–Os–O(3) 105.7(9), O(1)–Os–N 111.8(8), O(2)–Os–O(3) 105.7(9), O(2)–Os–N 109.7(8), O(3)–Os–N 109.8(8)

---

† To whom inquiries about the crystallography should be addressed.

‡ Complex **1** was obtained as a pale yellow solid by the reaction of $[\mathrm{NBu^n{}_4}][\mathrm{OsO_3N}]$ (200 mg, 0.405 mmol) with $[\mathrm{Au(PPh_3)(CF_3SO_3)}]$ (250 mg, 0.411 mmol) in $\mathrm{CH_2Cl_2}$ (20 cm^3) at room temperature for 2 h (yield 215 mg, 75%). X-Ray-quality crystals were obtained by recrystallisation from $\mathrm{CH_2Cl_2}$–hexane at room temperature. NMR: ^{1}H(CDCl$_3$), δ 7.55–7.88 (m, PPh$_3$); ^{31}P-{^{1}H} (CDCl$_3$, H$_3$PO$_4$ as reference), δ 28.24 (s). IR (Nujol): 910, 894 [ν(Os=O)], 1102 and 1088 [ν(Os≡NAu)] cm^{-1}. UV/VIS [CH$_2$Cl$_2$, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 269 (2740) and 326 (2290) (Found: C, 31.5; H, 2.5; N, 2.0. Calc. for $\mathrm{C_{18}H_{15}AuNO_3OsP}$: C, 30.4; H, 2.1; N, 2.0%).

§ Crystal data. **1**, $\mathrm{C_{18}H_{15}AuNO_3OsP}$, M = 711.46, monoclinic, space group $P2_1/n$ (no. 14), T = 296 K, a = 10.207(2), b = 12.286(4), c = 15.211(3) Å, β = 101.58(2)°, U = 1868.7(8) Å^3, crystal size 0.22 × 0.23 × 0.33 mm, Z = 4, D_c = 2.529 g cm^{-3}, $F(000)$ = 1296, graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å, μ = 147.59 cm^{-1}. Of 3661 reflections, 3457 were unique with R_{int} = 0.036; absorption correction was based on the ψ-scan method.[5] The structure was solved by direct methods (SIR 92)[6] and refined by full-matrix least squares on F_o to R = 0.054 and R' = 0.055 where $R' = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma[w(F_o)^2]\}^{\frac{1}{2}}$ with $w = 4F_o{}^2/[\sigma^2(F_o) + 0.005F_o{}^2]$. **2**, $\mathrm{C_6H_{22}N_2O_6Os_2P_2Pt}$, M = 855.69, orthorhombic, space group *Pnma* (no. 62), T = 303 K, a = 16.162(2), b = 9.334(2), c = 11.264(2) Å, U = 1699.3(5) Å^3, crystal size 0.40 × 0.14 × 0.11 mm, Z = 4, D_c = 3.344 g cm^{-3}, $F(000)$ = 1520, graphite-monochromated Mo-Kα radiation, λ = 0.710 69 Å, μ = 232.95 cm^{-1}, 1562 reflections observed; absorption correction based on the ψ scan method.[5] The structure was solved by direct methods (SIR 88)[7] and refined by full-matrix least squares on F_o to R = 0.047 and R' = 0.074 {R' as for **1**, $w = 4F_o{}^2/[\sigma^2(F_o) + 0.004F_o{}^2]$}. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/155.

¶ Complex **2** was obtained as a bright yellow solid by the reaction of $[\mathrm{NBu^n{}_4}][\mathrm{OsO_3N}]$ (220 mg, 0.445 mmol) with *cis*-$[\mathrm{Pt(PMe_3)_2(CF_3SO_3)_2}]$ (145 mg, 0.223 mmol) in $\mathrm{CH_2Cl_2}$ (20 cm^3) at room temperature for 12 h (yield 123 mg, 65%). X-Ray-quality crystals were obtained by recrystallisation from *N*,*N*-dimethylformamide (dmf)–Et$_2$O at room temperature. NMR: ^{1}H [(CD$_3$)$_2$SO], δ 1.84 (t, 18 H, PMe$_3$); ^{31}P-{^{1}H} [(CD$_3$)$_2$SO], δ −24.3 (t). IR (Nujol): 894 [ν(Os=O)], 1088, 1072 cm^{-1}[ν(Os≡NPt)]. UV/VIS [dmf, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 329 (4880) and 378 (sh) (846) (Found: C, 8.7; H, 2.1; N, 3.3. Calc. for **$\mathrm{C_6H_{22}N_2O_6Os_2P_2Pt}$: C. 8.5: H. 2.1: N. 3.3%)**.

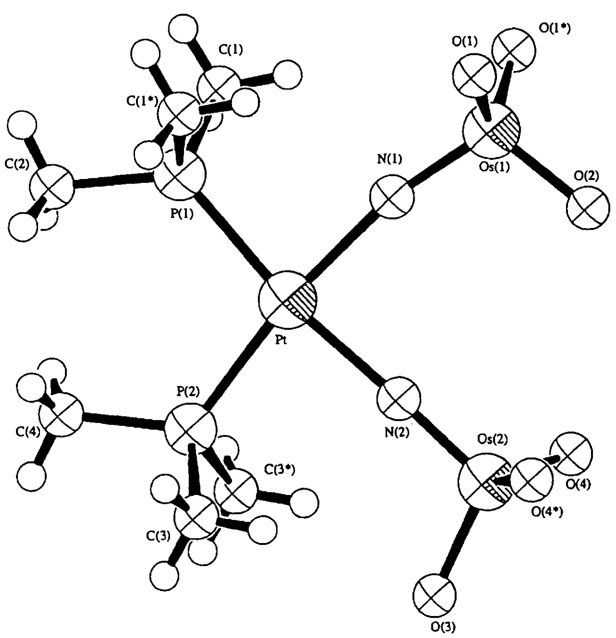
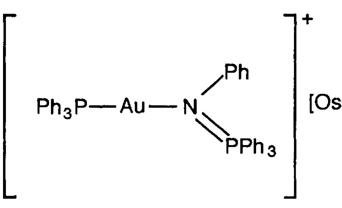


Fig. 2 Perspective view of *cis*-[Pt(PMe$_3$)$_2$(NOsO$_3$)$_2$] **2**. Selected bond lengths (Å) and angles (°): Os(1)–O(1) 1.78(4), Os(1)–O(1*) 1.78(4), Os(1)–O(2) 1.71(7), Os(1)–N(1) 1.68(4), Pt–N(1) 2.03(4), Pt–P(1) 2.26(1), Pt–P(2) 2.27(1); Pt–N(1)–Os(1) 169(2), P(1)–Pt–N(1) 86(1), O(1)–Os(1)–O(1*) 116(2), O(1)–Os(1)–O(2) 107(1), O(1)–Os(1)–N(1) 107(1), O(1*)–Os(1)–O(2) 107(1), O(1*)–Os(1)–N(1) 107(1), O(2)–Os(1)–N(1) 107(2)

The mean Os–O, Os–N and Pt–N distances and Pt–N–Os angles are 1.76, 1.68(4) and 2.03(4) Å and 169(2)°, respectively. The Os≡N and Pt–N bond lengths for complex **2** are also consistent with the formulation of Pt–N≡Os.

The Os=O stretching frequencies for **1** (910 and 894 cm^{-1}) and **2** (894 cm^{-1}) are higher than for [OsO$_3$N]$^-$ (890 and 858 cm^{-1})[3] but lower than for [OsO$_3$(NBu^t)] (925 and 912 cm^{-1}),[3] demonstrating that the Au and Pt substituents of the nitride slightly strengthened the Os=O bonds in complexes **1** and **2** but not as much as an alkyl substituent. The ν(Os≡N) bands for **1** (1102 and 1088 cm^{-1}) and **2** (1088 and 1072 cm^{-1}) are higher than that for [OsO$_3$N]$^-$ (1023 cm^{-1})[3] suggesting that the Os≡N bonds are strengthened upon co-ordination to the Au(PPh$_3$) and Pt(PMe$_3$)$_2$ moieties. The optical spectrum for complex **1** exhibits ligand-to-metal charge-transfer bands at 269 and 326 nm, which are blue-shifted relative to [OsO$_3$N]$^-$.

Complex **1** is stable in the solid state over periods of days but is somewhat light-sensitive in solution. It reacts with 4-*tert*-butylpyridine (L) to give the five-co-ordinate Os^{VIII} complex [OsO$_3${NAu(PPh$_3$)}(L)] **3**, which displays a lower ν(Os–O) band (868 cm^{-1}) than does complex **1**. It seems likely that complex **3** is isostructural with the reported [{OsO$_3$[NMe$_2$(CH$_2$)$_4$-Me]}$_2$(μ-dabco] (dabco = 1,4-diazabicyclo[2.2.2]octane) [ν(Os=O) 875 and 850 cm^{-1}][11] which has a trigonal-bipyramidal geometry around osmium and the three oxo groups in the equatorial plane. Reaction of complex **1** with tertiary phosphines led to the isolation of dark insoluble solids, presumably osmium oxides. Unlike [OsO$_3$(NR)], which undergoes cycloaddition with alkenes,[12] no reaction between complex **1** and alkenes such as styrene was observed even in the presence of pyridine. In an attempt to prepare the first 'imido(nitrido)osmium' complex *via* oxo–imido exchange, the reaction between complex **1** and PhN=PPh$_3$ was studied. However, this yielded only an air-stable pale grey complex [Au(PPh$_3$){N(=PPh$_3$)Ph}][OsO$_3$N] **4**.* Apparently the phosphinimine substitutes for the weakly co-ordinating OsO$_3$N moiety of **1** instead of reacting with the Os=O groups. The study of the reactivities of the dimetallic oxoosmium complexes is underway.



4

Acknowledgements

We thank the Hong Kong University of Science and Technology, the University of Hong Kong and the Hong Kong Research Grants Council for support.

---

* Complex **4** was obtained as a pale grey solid by the reaction of complex **1** (100 mg, 0.141 mmol) with 1 equivalent of PhN=PPh$_3$ (50 mg, 0.142 mmol) in CH$_2$Cl$_2$ (20 cm^3) at room temperature for 12 h and recrystallised from CH$_2$Cl$_2$–hexane (yield 110 mg, 79%). NMR: ^{1}H (CDCl$_3$), δ 7–8 (m, 35 H, phenyl H); ^{31}P-{^{1}H} [(CD$_3$)$_2$SO], δ 29.2 (s) and 32.0 (s). IR (Nujol): 888 [ν(Os=O)], 1104 [ν(Os≡N)] and 1250 cm^{-1} [ν(N=PPh$_3$)]. UV/VIS (CH$_2$Cl$_2$, λ_{max}/nm): 318 (sh) and 365 (sh). The solid-state structure of complex **4** has been confirmed by a diffraction study[13] (Found: C, 46.6; H, 3.4; N, 2.6. Calc. for C$_{42}$H$_{35}$AuN$_2$O$_3$OsP$_2$: C, 47.4; H, 3.3; N, 2.6%).

References

1 H. C. Holb, M. S. VanNieuwenhze and K. B. Sharpless, *Chem. Rev.*, 1994, **94**, 2483.
2 G. Li, H.-T. Chang and K. B. Sharpless, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 451 and refs. therein.
3 A. F. Clifford, C. S. Kobayashi, J. Wuller and T. Moeller, *Inorg. Synth.*, 1960, **6**, 204.
4 P. B. Braustein, H. Lehner, D. Matt, K. Burgess and M. J. Ohlmeyer, *Inorg. Synth.*, 1990, **27**, 218.
5 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
6 G. Cascarano, L. Favia and C. Giacovazzo, *J. Appl. Crystallogr.*, 1992, **25**, 310.
7 M. C. Burla, M. Camalli, G. Cascarano, C. Giacorazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Crystallogr.*, 1989, **22**, 389.
8 W. A. Nugent, R. L. Harlow and R. J. McKinney, *J. Am. Chem. Soc.*, 1979, **10**, 7265.
9 A. Grohmann, J. Riede and H. Schmidbaur, *Nature*, 1990, **345**, 140.
10 P. J. Stang, D. H. Cao, S. Saito and A. M. Arif, *J. Am. Chem. Soc.*, 1995, **117**, 6273.
11 W. P. Griffith, N. T. McManus, A. C. Skapski and A. D. White, *Inorg. Chim. Acta*, 1985, **105**, L11.
12 K. B. Sharpless, D. W. Patrick, L. K. Truesdale and S. A. Biller, *J. Am. Chem. Soc.*, 1975, **97**, 2305.
13 W.-H. Leung, J. L. C. Chim and W.-T. Wong, unpublished work.

Received 8*th May* 1996; *Communication* 6/03210I