J. CHEM. SOC., CHEM. COMMUN., 1986

High-valent Oxo Complexes of Osmium as Selective Oxidants for Cyclohexene Oxidation. Complexation of the Bisamide Tetradentate Ligand bpb to Osmium and the X-Ray Structure of *trans*-[Os^{III}(bpb)(PPh₃)Cl] [bpbH₂ = N,N'-Bis(2'-pyridine-carboxamide)-1,2-benzene]

Chi-Ming Che,^a Wing-King Cheng,^a and Thomas C. W. Mak^b

^a Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

^b Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

The reaction of N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene (bpbH₂) with K₂[OsO₂(OH)₄] yielded *trans*-[Os^{VI}(bpbH₂)O₂]²⁺ which in turn gave *trans*-[Os^{III}(bpb)(PPh₃)Cl] upon treatment with PPh₃; the Os^{III} complex has been characterized by X-ray crystallography and found to catalyse the epoxidation of cyclohexene in the presence of iodosobenzene.

The design of suitable chelating ligands for inorganic oxidizing agents has received much attention.¹ Examples on the use of highly oxidizing porphyrin complexes in oxidation chemistry have been reported.² We have recently been interested in the co-ordination chemistry of the ligand N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene (bpbH₂) that is known to co-ordinate to the central metal in either neutral or deprotonated amide form.³ The doubly deprotonated amide form of bpbH₂ is expected to be reasonably resistant to oxidation and hence useful in forming stable highly oxidizing metal complexes. Here the oxidation chemistry of osmium complexes containing this ligand is described; the Os^{III}(bpb)(PPh₃)Cl species, as characterized by X-ray crystallography, has been found to catalyse the epoxidation of cyclohexene in the presence of iodosobenzene (PhIO).

The synthesis of Os(bpb) complexes is outlined in Scheme $1.^{\dagger}$ As expected for a d² trans-Os^{VI} dioxo complex, (1) is

diamagnetic and exhibits an intense i.r. band at 850 cm⁻¹ characteristic of the v_{asym} (Os=O) stretch. Medium intense N-H stretching bands at 3320 cm⁻¹ were also observed, indicating that the ligand in (1) co-ordinates as a neutral tetradentate ligand. Treatment of (1) with base gave the doubly deprotonated form (2). Reduction of (1) or (2) with PPh₃ in acetonitrile resulted in the formation of a deep green solution from which Os^{III}(bpb)(PPh₃)Cl (3) was isolated. The i.r. spectrum of (3) exhibits no absorption in the usual v(N-H) stretch region in accord with its formulation. Complex (3) has been characterized by X-ray crystallography.

Crystal data: $C_{36}H_{27}N_4ClPO_2Os$, (3), M = 804.26, monoclinic, space group Cc, a = 9.448(2), b = 21.037(9), c = 15.579(6) Å, $\beta = 96.06(2)^\circ$, U = 3079(1) Å³, Z = 4, D_m (flotation in CCl₄-BrCH₂CH₂Br) = 1.748, $D_c = 1.735$ g cm⁻³, F(000) = 1579.6, $\mu(Mo-K_{\alpha}) = 43.24$ cm⁻¹. Crystal dimensions: $0.20 \times 0.16 \times 0.06$ mm. Intensities ($2\theta_{max.} = 48^\circ$; $h, k, \pm l$; ω —2 θ scan at 2.02—8.37° min⁻¹; 2326 unique data) were measured at 22 °C on a Nicolet R3m diffractometer,⁴ and empirical absorption corrections ($\mu r = 0.28$, transmission factors 0.396—0.586)⁵ were applied. The structure was solved

 $[\]dagger$ Satisfactory elemental analysis results have been obtained for (1) and (3).



Scheme 1. Reagents and conditions: i, MeOH-HCl (2 M); ii, Et₃N in MeOH; iii, PPh₃ in MeCN, ca. 50—60 °C, 15 min.

by the heavy atom method. The three phenyl rings were handled as rigid groups,⁶ and the remaining non-hydrogen atoms were varied anisotropically in refinement. Hydrogen atoms were generated geometrically and included in structure factor calculations with fixed isotropic thermal parameters. All computations were performed with the SHELXTL programs,⁷ and analytic expressions of neutral-atom scattering factors were employed.⁸ Convergence for 2233 (*n*) observed data ($|F_o| > 3\sigma|F_o|$) and 278 variables (*p*) was reached at $R_F \equiv \Sigma\Delta/\Sigma|F_o| = 0.037$, $R_G \equiv [\Sigma w \Delta^2/\Delta w |F_o|^2]^{\frac{1}{2}} = 0.042$, and $S \equiv [\Sigma w \Delta^2/(n-p)]^{\frac{1}{2}} = 1.073$, where $\Delta \equiv ||F_o| - |F_c||$ and $w = [\sigma^2(|F_o|) + 0.0008|F_o|^2]^{-1}$. Residual extrema in the final difference map lie between +0.97 and -0.70 a Å⁻³.‡

To our knowledge the structure constitutes the first reported example of an Os^{III} complex bearing the N, N'-coordinated bisamide ligand bpb (Figure 1). The two Os-N(amide) bonds are significantly shorter than those involving the pyridyl N atoms and comparable to the Os^{IV}–N(amide) bonds of 1.980(3) and 1.960(4) Å in [Os^{IV}(η⁴-CHBA-Et)(py)₂], [H₄CHBA-Et = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane].¹ The Os-P, Os-Cl, and Os-N(pyridyl) bond distances are in the usual range and the structural parameters of the co-ordinated bpb ligand agree with those reported for Cu(bpb)(H₂O).³ The Os atom is displaced slightly out of the mean plane of the four N atoms towards the P atom as a consequence of steric repulsion between the phenvl rings and the bpb ligand.

The formation of (3) and Ph₃P=O by PPh₃ reduction of (1) indicates that the intermediate Os^{IV} species is unstable and presumably reactive towards PPh₃. Similar studies on Os^{VI}-(η^4 -CHBA-Et)O₂, however, yielded Os^{IV} complexes as the reation products.¹ The E_f° value of the [Os^{IV}(bpb)(PPh₃)-Cl]+/Os^{III}(bpb)(PPh₃)Cl couple is 0.09 V vs. the cp₂Fe⁺/cp₂Fe⁰ couple, (cp = cyclopentadienyl) which is substantially



Figure 1. A perspective view of (3) with thermal ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Os–Cl, 2.410(4); Os–P, 2.356(3); Os–N(1), 2.11(1); Os–N(4), 2.11(1); Os–N(2), 1.99(1); Os–N(3), 1.96(1); N(2)–C(6), 1.35(2); N(3)–C(13), 1.36(2); N(2)–C(7), 1.41(2); N(3)–C(12), 1.48(2); O(1)–C(6), 1.22(2); O(2)–C(13), 1.24(2); P–C(24), 1.841(9); P–C(30), 1.833(9); P–C(36), 1.837(10); Cl–Os–P, 173.8(1); Cl–Os–N(1), 85.0(3); Cl–Os–N(4), 83.2(3); Cl–Os–N(2), 89.7(3); Cl–Os–N(3), 89.0(3); N(1)–Os–N(2), 80.0(4); N(3)–Os–N(4), 79.4(5); N(1)–Os–N(4), 116.8(4); N(2)–Os–N(3), 82.7(5); Os–N(2)–C(6), 121(1); Os–N(2)–C(7), 114(1); C(6)–N(2)–C(7), 125(1); Os–N(3)–C(13), 121(1); Os–N(3)–C(12), 115(1); C(12)–N(3)–C(13), 122(1); Os–P–C(24), 113.7(3); Os–P–C(30), 118.7(3); Os–P–C(36), 113.6(3).



Figure 2. Cyclic voltammogram of (3) in MeCN. Supporting electrolyte, 0.1 M tetrabutylammonium perchlorate; working electrode, pyrolytic graphite; scan rate, 100 mV s⁻¹.

higher than that for the Os(η^4 -CHBA-Et) complexes (-0.39 to -0.70 V) (Figure 2).

The potential usefulness of Os(bpb) complexes as selective oxidants for organic substrate oxidation has been examined. As with other *trans*-Ru^{VI} and Os^{VI} dioxo complexes,⁹ (1) performed stoicheiometric oxidation of cyclohexene without attack on the C=C double bond, yielding cyclohexenol together with a trace amount of α , β -unsaturated cyclohexenone. In contrast to this, (3) was found to catalyse the epoxidation of cyclohexene in the presence of PhIO. The catalytic reaction was carried out in the dark at 25 °C with (3) (1.4 mg), cyclohexene (1 ml), and PhIO (200 mg) in CH₂Cl₂ (3 ml). After 6.5 h a 3.6% yield of cyclohexene oxide (based on PhI produced; product identified by g.c.-mass spectra) was obtained, which represents a turnover of 18 based on (3).

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The observed selectivity of the (3)-PhIO system in the epoxidation reacton of cyclohexene is in some ways similar to the oxidation chemistry found for high-valent oxo metalloporphyrin complexes. We note that addition of PhIO to a CH_2Cl_2 solution of (3) yielded a red species which is highly reactive towards alkene. The exact nature of this species is as yet unknown, and the possibility that it might be a high-valent osmium(v) oxo complex provides an incentive for further investigation.

Received, 23rd September 1985; Com. 1382

References

1 See for example, F. C. Anson, J. A. Christie, T. J. Collins, R. J. Coots, T. T. Furutani, S. L. Gipson, J. T. Keech, T. E. Krafft, B. D. Santarsiero, and G. H. Spies, J. Am. Chem. Soc., 1984, 106, 4460; J. A. Christie, T. J. Collins, T. E. Krafft, B. D. Santarsiero, and G. H. Spies, J. Chem. Soc., Chem. Commun., 1984, 198.

- 2 See for example, J. T. Groves, W. J. Kruper, Jr., and R. C. Haushalter, J. Am. Chem. Soc., 1980, 102, 6377; J. P. Collman, T. Kodadek, S. A. Raybuck, J. I. Brauman, and L. M. Papazian, ibid., 1985, 107, 4343; J. P. Collman, J. I. Brauman, B. Meunier, S. A. Raybuck, and T. Kodadek, Proc. Natl. Acad. Sci. USA, 1984, 81, 3245.
- 3 R. L. Chapman, F. S. Stephens, and R. S. Vagg, Inorg. Chim. Acta, 1980, 43, 29.
- 4 R. A. Sparks, 'Crystallographic Computing Techniques,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1976, p. 452.
- 5 G. Kopfmann and R. Huber, Acta Crystallogr., Sect. A., 1968, 24, 348; A. C. T. North, D. C. Phillips, and F. S. Mathews, ibid., p. 351.
- 6 R. J. Doedens, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1969, p. 198. G. M. Sheldrick, 'Computational Crystallography,' ed. D. Sayre,
- 7 Oxford University Press, New York, 1982, p. 506.
- 'International Tables for X-Ray Crystallography,' Kynoch Press, 8 Birmingham, 1974, vol. 4, pp. 99, 149.
- 9 C. M. Che, unpublished results.