Dioxygen Addition to Five-Coordinate Osmium(II) Complexes. X-Ray Crystal Structure of [OsH(η^2-O_2)(dcpe)$_2$]BPh_4 [dcpe = 1,2-Bis(dicyclohexylphosphino)ethane]

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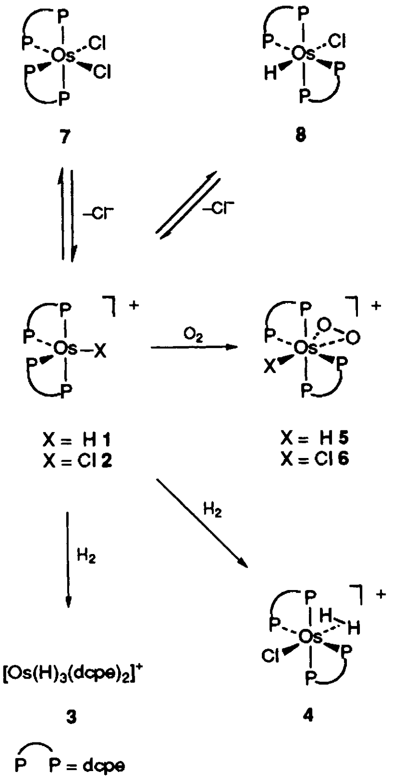
The five-coordinate osmium(II) cations [OsX(dcpe)$_2$]$^+$ [X = H or Cl; dcpe = 1,2-bis(dicyclohexylphosphino)ethane] react with dioxygen in 1 : 1 molar ratio giving the stable peroxo complexes *trans*-[OsX(O_2)(dcpe)$_2$]$^+$.

Most of the peroxo complexes reported in the literature are formed *via* oxidative addition of O_2 onto coordinatively unsaturated species of the later second- and third-row transition metals with d^8 or d^{10} configurations.[1] By contrast, reports of dioxygen addition to five-coordinate d^6 complexes are rare,[2,3] though their number has been increasing lately.[4–6] The coordinating ability of d^6 transition metal complexes toward dioxygen might be of relevance to the homogeneous metal-catalysed oxidations.[7]

For several years we have been studying the highly reactive, five-coordinate complexes [OsX(dcpe)$_2$]BPh_4 (X = H **1**, Cl **2**) containing the bulky diphosphine 1,2-bis(dicyclohexylphosphino)ethane (dcpe).[8] Complexes **1**,**2** form the octahedral adducts [OsX(L)(dcpe)$_2$]$^+$ by addition of neutral donors L such as CO or RCN.[8a] They also react with molecular hydrogen giving the classical trihydride [OsH_3(dcpe)$_2$]$^+$ **3** or the dihydrogen complex [OsCl(H···H)(dcpe)$_2$]$^+$ **4**, respectively, depending on the nature of X (Scheme 1).[8b]

We now find that the coordinatively unsaturated cations **1**,**2** react quantitatively with molecular oxygen at room temperature and pressure in a non-coordinating solvent such as dichloromethane. Complex **1** reacts with dioxygen nearly instantaneously in solution and slowly even in the solid state. The reaction of **2** in solution is complete within 4 h. Addition of propan-2-ol and partial evaporation of the solvent gives diamagnetic products which analyse as [OsX(O_2)(dcpe)$_2$]BPh_4 (X = H **5**, Cl **6**).† Both **5** and **6** behave as 1 : 1 electrolytes in 10^{-3} mol dm^{-3} acetone solution.‡



Scheme 1

The formulation of **5** was confirmed by a crystal structure determination that is, to the best of our knowledge, the first one of a dioxygen complex of osmium.§ The coordination sphere can be described as a highly distorted octahedron with mutually *trans* dioxygen and hydride ligands. The P atoms occupy two different types of sites characterized by significantly different Os–P distances (Fig. 1). The shorter Os–P distances involving P(2) and P(4) appear to be related to the closing of the P(2)–Os–P(4) angle to 136.3(1)° as these P atoms are pushed away from O(1) and O(2) toward the hydride ligand. A similar trend of decreasing M–P bond lengths with decreasing P–M–P angles has been observed also in a number of ruthenium phosphine complexes.[9] The η^2-dioxygen ligand is bound symmetrically to osmium, with Os–O distances identical within standard deviations. The O atoms lie close to the Os–P(2)–P(4) plane, which forms a dihedral angle of 9(1)° with the Os–O(1)–O(2) plane. The O–O distance of 1.45(1) Å, in good agreement with the formulation of **5** as a peroxo complex,[1] is significantly longer than in the structurally characterized ruthenium analogues.[5,6] The C(27)–C(32) cyclohexyl group on P(3) is disordered and exhibits two different chair conformations with occupancy factors of 0.6 and 0.4. The cyclohexyl in the prevailing conformation (Fig. 1) is involved in a short nonbonded contact of 2.92(2) Å between O(1) and C(28).

The solution NMR spectra of **5** indicate a fluxional behaviour. The hydride appears in the room-temperature ^1H NMR spectrum (CD_2Cl_2, 200 MHz) as a quintet at δ −6.83 [*J* (P,H) = 22.5 Hz], which broadens by lowering the tempera-

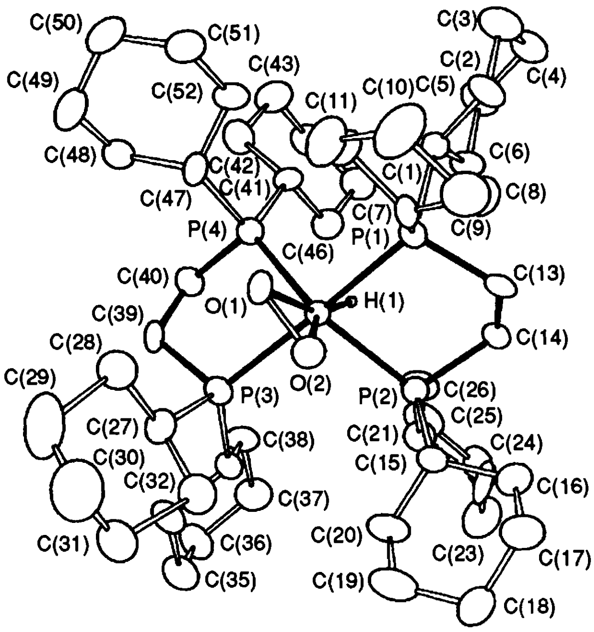


Fig. 1 ORTEP drawing of the cation [OsH(O_2)(dcpe)$_2$]$^+$. Relevant bond distances (Å) and angles (°): Os–P(1) 2.417(3), Os–P(2) 2.373(4), Os–P(3) 2.416(3), Os–P(4) 2.384(4), Os–O(1) 2.045(8), Os–O(2) 2.037(8), Os–H(1) 1.83(9), O(1)–O(2) 1.45(1), P(1)–Os–P(3) 169.2(1), P(2)–Os–P(4) 136.3(1), O(1)–Os–O(2) 41.5(4), Os–O(1)–O(2) 69.0(4), Os–O(2)–O(1) 69.5(4).

ture. At −40 °C the hydride signal is a triplet of triplets [δ −7.00, J(P,H) = 36.8 Hz, J(P′,H) = 6.6 Hz]. The room-temperature ^{31}P NMR spectrum (CD_2Cl_2, 81.0 MHz) shows two broad humps ($w_{1/2} \approx 200$ Hz) centred at *ca.* δ 19 and 30, which move apart by lowering the temperature and are eventually resolved into two slightly broadened triplets at δ 32.8 and 19.5 with a small ^3J(P,P′) of 4.4 Hz (T = −30 °C). The A_2X_2 pattern in the low-limiting spectrum is consistent with the solid-state structure showing two pairs of P atoms having different environments. The ^{31}P NMR spectrum of **6** exhibits a sharp singlet at δ −4.3, in agreement with a *trans*-octahedral geometry with equivalent P atoms. However, also in this case a dynamic behaviour can be observed, as the signal broadens by lowering the temperature. Though at least six groups of distinct signals can be observed at −130 °C (CHF_2Cl–CD_2Cl_2 solution), no resolved spectrum was obtained. The Nujol mull IR spectra of **5** and **6** display new bands at 820 and 810 cm^{-1}, respectively, which we tentatively attribute to the O–O stretching.[1]

Also the six-coordinate complexes *cis*-[$OsCl_2$(dcpe)$_2$] **7** and *trans*-[OsH(Cl)(dcpe)$_2$] **8** react with dioxygen in polar solvents such as ethanol and propan-2-ol, in which they are known to give the five coordinate cations **1**,**2** upon dissolution.[8] The latter reaction was exploited for quantitative gas uptake measurements. Complex **7** was suspended in ethanol under an oxygen atmosphere in a thermostatted glass apparatus equipped with a gas burette. The progress of the reaction was followed volumetrically at constant pressure (1 atm). The reaction was complete in about 8 h, and the total dioxygen uptake confirms that **7** absorbs dioxygen according to a 1 : 1 stoichiometry. Light brown microcrystals of **6** precipitated from the orange solution upon addition of $NaBPh_4$ (55% yield after recrystallization from CH_2Cl_2–propan-2-ol).

The peroxo ligand is not removed by pumping **5**,**6** in the solid state under vacuum at room temperature. Complex **5** is stable in air- or O_2-saturated solutions for several days, while **6** slowly decomposes under the same conditions, and the signals of the diphosphine oxides appear in the ^{31}P NMR spectra. We are investigating the reactivity of **5**,**6** as oxygen-transfer reagents toward a number of substrates.

At difference with the [OsX(dcpe)$_2$]$^+$ cations (X = H or Cl), the solutions of the ruthenium analogues [RuX(dcpe)$_2$]$^+$ (X = Cl, Br or I) react with dioxygen giving paramagnetic species as final products. The nature of these species, which are probably ruthenium(III) complexes, and the mechanism of the reaction are currently under investigation. We are also reexamining the chemistry of the hydrido complexes of ruthenium with dcpe, since the previously reported[10] [RuH(dcpe)$_2$]$^+$ has been proposed to form [RuH(O_2)(dcpe)$_2$]$^+$.[5]

Simultaneous activation of H_2 and O_2 at the same metal centre appears particularly attractive for catalytic applications.[7,11] Only a few coordinatively unsaturated complexes of osmium(II) and ruthenium(II) are known to form both dihydrogen and peroxo complexes.[4,5] This paucity has given support to the idea that the requirements for the coordination of O_2 and H_2 are substantially different.[12] However, the present results support the suggestion that centres which react both with H_2 and with O_2 are less rare than previously thought.[5]

Financial support by the Italian Ministero dell'Università e della Ricerca Scientifica and Consiglio Nazionale delle Ricerche, Rome, is gratefully acknowledged.

Received, 23rd March 1994; Com. 4/01752H

Footnotes

† Yields are 75–85%. Satisfactory elemental (C, H) analyses were obtained.

‡ Conductivity data in 10^{-3} mol dm^{-3} acetone solution: Λ_M = 74 and 78 ohm^{-1} cm^2 mol^{-1} for **5** and **6**, respectively.

§ *Crystal data* for **5**: $C_{76}H_{117}BO_2OsP_4 \cdot 0.4CH_3OH$, M = 1387.69 (excluding CH_3OH), light brown, needle-shaped crystal (0.25 × 0.30 × 0.70 mm) grown from CH_2Cl_2–CH_3OH, space group $P\bar{1}$ (no. 2), a = 13.348(5), b = 14.252(3), c = 21.952(8) Å, α = 84.32(2), β = 87.52(2), γ = 64.34(3)°, U = 3745(2) Å^3, Z = 2, D_c = 1.23 g cm^{-3}, μ(Mo-Kα) = 18.3 cm^{-1}, $F(000)$ = 1460. Of 13 556 reflections collected (Enraf-Nonius CAD 4, Mo-Kα, room temp. $2\theta_{max}$ = 50°), 13169 were independent and corrected for absorption (Ψ-scan), Lorentz and polarization effects. Total decay of 14.6% over data collection, linear correction applied. Structure solution with 5372 independent reflections having $F_o^2 > 3\sigma(F_o^2)$ using conventional Patterson and Fourier methods. Disorder on the C(27)–C(32) cyclohexyl ring solved by splitting C(28) and C(31) into two different positions with occupancy factors of 0.6 and 0.4. Full-matrix least squares (653 variables) with weights $w = 4F_o^2/[\sigma^2(I) + (pF_o^2)^2]$, p = 0.02. All non-H atoms of the complex cation refined anisotropically. A ΔF map showed a CH_3OH molecule (0.4 occupancy) and the hydride H atom, which was refined. Remaining hydrogen atoms included in idealized positions (d_{C-H} = 0.95 Å) except those of the disordered C(27)–C(32) cyclohexyl and MeOH. $R(F_o)$ = 0.054 and $R_w(F_o)$ = 0.058, goodness of fit 1.6, max. positive and negative peaks in ΔF map 1.07 and −0.22 e Å^{-3}. Calculations carried out on a μVAX 2000 computer using the Enraf-Nonius system of programs.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 H. A. Hill and D. G. Tew, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, p. 318; J. S. Valentime, *Chem. Rev.*, 1973, **73**, 235.

2 F. G. Moers, R. W. M. Ten Hoedt and J. P. Langhout, *J. Inorg., Nucl. Chem.*, 1974, **36**, 2279.

3 M. M. Taqui Khan, R. K. Andal and P. T. Manoharan, *J. Chem. Soc., Chem. Commun.*, 1971, 561.

4 M. A. Esteruelas, E. Sola, L. A. Oro, U. Meyer and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1563.

5 M. Jiménez-Tenorio, M. C. Puerta and P. Valerga, *J. Am. Chem. Soc.*, 1993, **115**, 9794.

6 K. Kirchner, K. Mauthner, K. Mereiter and R. Schmid, *J. Chem. Soc., Chem. Commun.*, 1993, 892.

7 R. S. Drago, *Coord. Chem. Rev.*, 1992,. **117**, 185.

8 (*a*) A. Mezzetti, A. Del Zotto and P. Rigo, *J. Chem. Soc., Dalton Trans.*, 1990, 2515; (*b*) A. Mezzetti, A. Del Zotto, P. Rigo and E. Farnetti, *J. Chem. Soc., Dalton Trans.*, 1991, 1525.

9 R. G. Ball and J. Trotter, *Inorg. Chem.*, 1981, **20**, 261.

10 A. Mezzetti, A. Del Zotto, P. Rigo and N. Bresciani Pahor, *J. Chem. Soc., Dalton Trans.*, 1989, 1045.

11 S. N. Gamage and B. R. James, *J. Chem. Soc., Chem. Commun.*, 1989, 1624.

12 P. G. Jessop and R. H. Morris, *Coord. Chem. Rev.*, 1992, **121**, 131.