

Polyhedron 18 (1999) 1207-1210



Synthesis and characterisation of $[OC-6-33][OsCl_2(CO)_2L_2]$ (L=phosphine). Crystal structure of $[OC-6-33][OsCl_2(CO)_2(PEt_3)_2]$

Howard C.S. Clark, Karl S. Coleman, John Fawcett, John H. Holloway, Eric G. Hope*, Jane Redding, David R. Russell

Department of Chemistry, University of Leicester, Leicester, LE1 7RH, UK

Received 21 September 1998; accepted 16 November 1998

Abstract

A series of $[OC-6-33][OsCl_2(CO)_2L_2]$ (L=phosphine) complexes have been prepared by cleavage of $[OsCl(\mu-Cl)(CO)_3]_2$ with a variety of phosphines for a comparison of spectroscopic data with those for the related $[OC-6-13][OsF_2(CO)_2L_2]$ (L=phosphine). The X-ray structural characterisation of $[OC-6-33][OsCl_2(CO)_2(PEt_3)_2]$ represents the first structural characterisation for this class of complex. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Osmium(II) complexes; Carbonyl; Phosphine; Crystal structure

1. Introduction

We have recently described the preparation of a range of $[OC-6-13][OsF_2(CO)_2L_2]$ (L=phosphine) complexes [1] and were surprised to find that, even though the first example of one of the structurally related chloride complexes, [OC-6-33][OsCl₂(CO)₂(PPh₃)₂], was first reported in 1966 [2,3], there was little ³¹P NMR data with which to compare those for our fluoride complexes, and that there had been no single crystal X-ray structural characterisations. Although a wide variety of synthetic routes to examples of the osmium dichloride complexes, particularly when $L=PPh_3$, have been described in the literature [4], there is no single, general route to prepare these derivatives. Since our route [1] to the fluoride complexes, namely cleavage of the fluoride-bridged, tetrameric $[OsF_2(CO)_3]_4$, represents a widely applicable synthetic procedure and since a clean, high-yield route to a similar, chloridebridged, starting material, $\{[OsCl(\mu-Cl)(CO)_3]_2\}$, had recently been reported [5], we have re-investigated the cleavage of this dimer with a range of phosphine ligands. Early applications of this synthetic route include the preparation of $[OC-6-33][OsCl_2(CO)_2(PPh_3)_2]$ [2,6] and $[OC-6-33][OsCl_2(CO)_2(P\{C_6H_{11}\}_3)_2]$ [2]. Here, we report the synthesis and characterisation of a series of established and novel [OC-6-33][OsCl₂(CO)₂L₂] complexes, including the structural characterisation of $[OC-6-33][OsCl_2(CO)_2(PEt_3)_2]$, and compare results from this study with those from the related study of the difluoride complexes.

2. Experimental

¹H and ³¹P NMR spectroscopic studies were carried out on a Bruker ARX 250 spectrometer at 250.13 and 101.26 MHz or a Bruker DRX 400 spectrometer at 400.13 and 161.98 MHz, respectively. All chemical shifts are quoted in ppm using the high-frequency positive convention; ¹H NMR spectra were referenced internally to tetramethylsilane and ³¹P NMR spectra were referenced externally to 85% H₃PO₄. IR spectra were recorded on a Digilab FTS40 Fourier transform spectrometer for Nujol mulls held between KBr plates at 4 cm⁻¹ resolution. Elemental analyses were performed by Butterworth Laboratories and fast atom bombardment (FAB) mass spectra

Dichloromethane was dried by heating to reflux over CaH_2 and was stored over molecular sieves in a closed ampoule. The phosphines (Aldrich, Fluorochem) were used without purification and, where appropriate, were handled under nitrogen. The $[OsCl(\mu-Cl)(CO)_3]_2$ was prepared by the literature route [5].

In a typical experiment, $[OsCl(\mu-Cl)(CO)_3]_2$ (100 mg,

^{*}Corresponding author. Fax: +44-116-2523789.

0.145 mmol) and the ligand (0.658 mmol) in dichloromethane (40 cm³) were heated to reflux for 4 h under nitrogen. The solution was allowed to cool, filtered, and the solvent was removed by rotary evaporation to give the products as cream solids in 75–80% yields.

Product identification was achieved using IR and NMR spectroscopic studies (Table 1) and FAB mass spectrometry. [OC-6-33][OsCl₂(CO)₂L₂]: L=PEt₃, m/z 526 (M^{+}) , 491 $([M-Cl]^{+})$; L=P(C₆H₁₁)₃, m/z 878 (M^{+}) , 843 ($[M-Cl]^+$); L=PPh₃, m/z 807 ($[M-Cl]^+$), 779 $([M-Cl-CO]^+); L=PMePh_2, m/z 718 (M^+), 683 ([M-$ Cl]⁺), 655 ([M-Cl-CO]⁺); L=PEtPh₂, m/z 746 (M⁺), 711 $([M-Cl]^+)$, 683 $([M-Cl-CO]^+)$. Satisfactory elemental analyses were obtained for representative products: $[OsCl_2(CO)_2{P(C_6H_{11})_3}_2]$ (Found: C, 51.86; H, 7.44; P, 7.02. C₃₈H₆₆Cl₂O₂OsP₂ requires C, 52.04; H, 7.58; P, 7.06); [OsCl₂(CO)₂(PMePh₂)₂] (Found: C, 46.79; H, 3.52; P, 8.28. C₂₈H₂₆Cl₂O₂OsP₂ requires C, 46.87; H, 3.65; P, 8.63); [OsCl₂(CO)₂(PEtPh₂)₂] (Found: C, 48.32; H, 4.03; P, 7.23. C₃₀H₃₀Cl₂O₂OsP₂ requires C, 48.33; H, 4.06; P, 8.31).

2.1. Crystal structure determination of $[OC-6-33][OsCl_2(CO)_2(PEt_3)_2]$

Crystals were grown by slow evaporation from a solution of the complex in dichloromethane.

2.2. Crystal data

C₁₄H₃₀Cl₂O₂OsP₂, *M*=553.42, monoclinic, *a*= 8.286(1), *b*=20.210(3), *c*=12.717(1) Å, *β*=107.5(1)°, *U*=2031.0(4) Å³ (by least-squares refinement on diffractometer angles from 39 centred reflections, 5.03 to 12.53°), *T*=190(2) K, space group P2₁/c, graphite-monochromated Mo-Kα radiation, λ =0.71073 Å, *Z*=4, *D_c*=1.810 g cm⁻³, *F*(000)=1080, dimensions 0.60×0.21×0.17 mm, μ (Mo-Kα)=6.700 mm⁻¹, semiempirical absorption cor-

Table 1

Spectroscopic data for cis-,cis-,trans-[OsX2(CO)2L2] (X=F, Cl; L=phosphine)

rection based on ψ scans, maximum and minimum transmission factors of 0.464 and 0.1043, respectively, Siemens P4 diffractometer, ω scans, data collection range 5.16 $< 2\theta < 54.00^\circ$, $-1 \le h \le 10$, $-1 \le k \le 25$, $-16 \le l \le 15$, no crystal decay was detected from periodically measured check reflections; 5050 reflections were measured, and 3964 were unique ($R_{int} = 0.0347$). The data were corrected for Lorentz and polarisation effects.

2.3. Structure solution and refinement

Structure solution by Patterson methods and structure refinement of F^2 employed SHELXTL/PC version 5.0 [7]. Hydrogen atoms were included in calculated positions (C–H=0.96 Å) with isotropic displacement parameters set to 1.2 $U_{eq}(C)$ for methylene H atoms and 1.5 $U_{eq}(C)$ for methylene H atoms were refined with anisotropic displacement parameters. Final, R_1 =0.0278, wR_2 =0.0678 (0.033 and 0.070, respectively, for all data) for 190 variables. The final residual Fourier map showed peaks of +1.174 and -1.294 eÅ⁻³ at <1 Å from the osmium atom.

3. Results and discussion

As shown previously in the cleavage of the fluoride bridges in $[OsF_2(CO)_3]_4$ with phosphines [1], cleavage of the chloride bridges in $[OsCl_2(CO)_3]_2$ represents a clean and widely applicable route to a range of osmium–phosphine–carbonyl–halide complexes. Although this methodology had been utilised in the earliest preparations of complexes of this type, the straightforward new synthetic route to the chloride-bridged starting material has allowed a comprehensive series of these complexes to be prepared (Table 1). The *cis-,cis-,trans-*geometry for these complexes is, and has previously been, implied from the IR spectroscopic data and our results are in acceptable agreement with that in the literature. This geometry is now

	$\nu(\mathrm{CO})^{\mathrm{a}}/\mathrm{cm}^{-1}$		$\delta(\mathrm{P})^{\mathrm{b}}/\mathrm{ppm}$			
L	F^{c}	Cl	Br	F^{c}	Cl	Br
PEt ₃	2034, 1963	2029, 1953	_	11.1	-9.3	_
$P(C_6H_{11})_3$	2005, 1925	2008, 1931	_	15.5	-2.2^{d}	_
PPh ₃	2017, 1937	2041, 1970	2035, 1970 ^e	1.0	-9.9	-16.5 ^{d,f}
PEtPh,	2031, 1950	2043, 1962	2046, 1977 ^g	4.4	-6.0^{d}	_
PMePh ₂	2026, 1941	2043, 1971	2045, 1970 ^{f,h}	-1.8	-14.6^{d}	-23.6 ^{d,f}

^aRecorded as Nujol mulls unless otherwise stated; $\pm 2 \text{ cm}^{-1}$.

^bSpectra recorded in CD₂Cl₂ unless otherwise stated.

^cData taken from ref. [1].

^dCDCl₃ solution.

^eKBr pellets, data taken from ref. [3].

^fData taken from ref. [8].

^gCHCl₃ solution, data taken from ref. [9].

^hCH₂Cl₂ solution.

confirmed by a single crystal X-ray crystallographic study (vide infra). When L=PPh₃, PMePh₂ and PEtPh₂, the data confirm our earlier contention [1] that ν (CO) is lower for fluoride than chloride≈bromide, which may be accounted for by π -electron donation by the fluoride ligand [10]. However, this trend is not repeated for the better σ -donor ligands PEt₃ and P(C₆H₁₁)₃. Indeed, when L=PEt₃, ν (CO) for fluoride $\geq \nu$ (CO) for chloride, indicating that, here, the electron-withdrawing effects of the fluoride ligands are only partially offset by Os-F π bonding, which must arise from the different σ -donor/ π -acceptor properties of the axial phosphine ligands. Further work is necessary in this area to fully understand the nature of the metal-halide interaction in these low-valent metal complexes.

The ³¹P{¹H} NMR data (Table 1) again confirm our earlier suggestion [1] that $\delta(P)$ F>Cl>Br is part of a general trend in line with the nephelauxetic effect. However, here again, the effect is more pronounced for the alkyl than the aryl phosphines, mirroring the variations in ν (CO), and suggesting differences in the metal–ligand interactions between the two groups of complexes.

Slow evaporation from a dichloromethane solution of $[OC-6-33][OsCl_2(CO)_2(PEt_3)_2]$ produces colourless crystals that were studied by X-ray crystallography. The molecular structure of $[OC-6-33][OsCl_2(CO)_2(PEt_3)_2]$ is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. All other crystallographic data may be obtained from the Cambridge Crystallographic Data Centre, where the CIF file has been deposited (deposition number 103014). The complex is pseudo-octahedral with the two phosphine ligands *trans* to each other and the two chloride ligands trans to the carbonyl groups, as indicated by IR spectroscopy. The Os-P bond lengths are similar and entirely reasonable. However, the Os-Cl and the Os-C bond lengths, which are consistent, appear unusually long and short, respectively, in comparison with other Os(II)-Cl or Os(II)-CO bond lengths [11]. Indeed, the osmium-chlorine bond lengths are closer to the Os-Cl_{bridging} bond lengths in [OsCl₂(CO)₃]₂ than to the Os-Cl_{terminal} bond length [5]. However, the unusually short C-O bond lengths and unusually high carbonyl stretching frequencies for this dimer suggest that it contains a distorted charge distribution. The carbonyl and chloride ligands and the osmium atom are essentially co-planar, with the largest inter-ligand angle occurring between the two carbonyl ligands. The ethyl substituents on the mutually trans phosphine ligands adopt a staggered conformation in contrast to the eclipsed conformation in [OC-6-13][MF₂(CO)₂L₂] [M=Ru, L=PEtPh₂; M=Os, L= $P(C_6H_{11})_3$ [1]. Although the P(1)-Os(1)-P(2) axis bends slightly (178°) towards the chloride ligands, there are no H...Cl interactions that are significantly shorter than the sum of the van der Waals radii of H and Cl $[r_{vdw}$ (H)= 1.20, r_{vdw} (Cl)=1.75 Å] [12]. Hence, intra- and intermolecular interactions, which appear to be important in the



Fig. 1. Molecular structure of $[OC-6-33][OsCl_2(CO)_2(PEt_3)_2]$, showing the atom labelling scheme with 30% probability ellipsoids. H atoms are shown as spheres of arbitrary radii.

related diffuoride complexes $[OC-6-13][MF_2(CO)_2L_2]$ [M=Ru, L=PPh₃, PEtPh₂; M=Os, L=PPh₃, P(C₆H₁₁)₃] [1,13], do not appear to influence the packing or ligand arrangement for $[OC-6-33][OsCl_2(CO)_2(PEt_3)_2]$ in the solid state.

Table 2								
Selected	bond	distances	(Å)	and	angles	(°)	for	[OC-6-
33][OsCl	$(CO)_{2}(I)$	$PEt_3)_2$]						

Os(1)–C(2)	1.867(4)	Os(1)–C(1)	1.869(5)
Os(1) - P(2)	2.4048(11)	Os(1)-P(1)	2.4054(11)
Os(1)-Cl(2)	2.444(1)	Os(1)-Cl(1)	2.4452(11)
C(1)–O(1)	1.132(5)	C(2)–O(2)	1.134(5)
P(1) - C(5)	1.818(4)	P(2) - C(9)	1.820(5)
P(1) - C(3)	1.826(5)	P(2)-C(11)	1.823(4)
P(1)-C(7)	1.826(4)	P(2)–C(13)	1.831(4)
C(1)-Os(1)-C(2)	93.5(2)	C(1)-Os(1)-Cl(1)	178.10(14)
Cl(1)-Os(1)-Cl(2)	88.61(4)	Cl(2)-Os(1)-C(2)	176.96(14)
C(1)–Os(1)–Cl(2)	89.50(14)	C(2)-Os(1)-Cl(1)	88.36(14)
P(1) - Os(1) - P(2)	178.05(3)	P(1) - Os(1) - Cl(1)	89.22(4)
O(1)-C(1)-Os(1)	179.3(4)	O(2)-C(2)-Os(1)	178.1(4)
C(5)-P(1)-C(3)	105.7(2)	C(5)-P(1)-C(7)	105.9(2)
C(7)-P(1)-C(3)	100.5(2)	C(3) - P(1) - Os(1)	114.3(2)
C(5)-P(1)-Os(1)	114.7(2)	C(7)-P(1)-Os(1)	114.3(2)

4. Conclusions

Cleavage of halide bridges in $[OsX_2(CO)_3]_n$ complexes with donor ligands offers a high yield route to $[OsX_2(CO)_2L_2$ species. Spectroscopic data [$\nu(CO)$ and $\delta(P)$] do not vary in a systematic way with X and L. Structural characterisation when X=Cl and L=PEt₃ confirms the *cis-,cis-,trans*-ligand arrangement suggested by the spectroscopic studies.

Supplementary data

Available from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, on request, quoting the deposition number 103014.

Acknowledgements

We would like to thank the EPSRC (H.C.S.C. and K.S.C.) and the Royal Society (E.G.H.) for financial support.

References

- K.S. Coleman, J. Fawcett, J.H. Holloway, E.G. Hope, D.R. Russell, J. Chem. Soc. Dalton Trans. (1997) 3557.
- [2] V. Frey, W. Hieber, Z. Naturforsch Teil. B. 21 (1966) 704.
- [3] J.P. Collman, W.R. Roper, J. Am. Chem. Soc. 88 (1966) 3504.
- [4] N.C. Thomas, Coord. Chem. Rev. 93 (1989) 225.
- [5] W.A. Herrmann, E. Herdtweck, A. Schäfer, Chem. Ber. 121 (1998) 1907.
- [6] L.A.W. Hales, R.J. Irving, J. Chem. Soc. A (1969) 1932.
- [7] G.M. Sheldrick, SHELXTL/PC vers. 5.0, Madison, WI: Siemens Analytical Instruments, 1996.
- [8] Y.-S. Chen, S.-L. Wang, R.A. Jacobson, R.J. Angelici, Inorg. Chem. 25 (1986) 1118.
- [9] J. Chatt, D.P. Mellville, R.L. Richards, J. Chem. Soc. A (1971) 1169.
- [10] K.G. Caulton, O. Eisenstein, J.T. Poulton, M.P. Sigalas, W.E. Streib, Inorg. Chem. 33 (1994) 1476.
- [11] F.H. Allen, L. Brammer, O. Kennard, A.G. Orpen, R. Taylor, D.G. Watson, J. Chem. Soc. Dalton Trans. (1989) S1.
- [12] A. Bondi, J. Phys. Chem. 68 (1964) 441.
- [13] S.A. Brewer, K.S. Coleman, J. Fawcett, J.H. Holloway, E.G. Hope, D.R. Russell, P.G. Watson, J. Chem. Soc. Dalton Trans. (1995) 1073.