

Selective preparation of *cis*- or *trans*-dichlorobis{(*R,R*)-1,2-phenylenebis(methylphenylphosphine-*P*)}osmium(II) from dimethylsulfoxide complex precursors

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Abstract: A synthetic route into *cis*- and *trans*- isomers of [OsCl₂(chiral-at-phosphorus bidentate phosphine)₂] is presented. The choice of the *cis*- or *trans*- isomer of the precursor complex [OsCl₂(DMSO)₄] (DMSO=dimethylsulfoxide) permits selective preparation of either *cis*- or *trans*- isomers of the diphosphine complex. A structural study confirms the retention of both, stereochemistry at the metal and configuration at phosphorus in proceeding from the dimethylsulfoxide complex to form *trans*-[OsCl₂{(*R,R*)-1,2-phenylenebis(methylphenylphosphine)}₂]. © 1997 Elsevier Science Ltd

Complexes of the general formula [RuHX(chiral bidentate phosphine)₂] (X=H, Cl) have been shown to be active catalysts for asymmetric hydrogenation of ketones and carboxylic acids.^{1–5} Selective preparations of *cis*- or *trans*-[OsCl₂(bidentate phosphine)₂] incorporating chiral-at-phosphorus ligands, which are precursors to the analogous osmium complexes, are therefore of interest (in addition to potential enantioselective utility in their own right, studies with the comparatively more inert osmium complexes may afford useful mechanistic information applicable to the more reactive ruthenium system), but established methodologies to synthesize the osmium examples are not completely satisfactory. Some methods require elevated temperatures^{6,7} which may racemize the uncoordinated optically active diphosphine ligand, while others do not provide the flexibility of *cis*- or *trans*- isomers from one synthetic route.^{8,9}

In view of the potential importance of *cis*- and *trans*-[OsCl₂(chiral bidentate phosphine)₂] as precursors to second harmonic generation-active nonlinear optical materials,¹⁰ and as auxiliaries in stoichiometric or catalytic enantioselective applications, we have investigated routes into examples incorporating chiral-at-phosphorus ligands.

Results and discussion

The precursors *cis*- and *trans*-[OsCl₂(DMSO)₄] can be prepared directly from commercially available hexachloroosmic acid.¹¹ We have also found that *trans*-[OsCl₂(DMSO)₄] may be isomerized by heating it at 150°C in DMSO to form the *cis*- complex (Scheme 1). Preparation of the *cis*- or *trans*- isomer of the complex [OsCl₂{(*R,R*)-1,2-phenylenebis(methylphenylphosphine)}₂] involves reacting (*S,S*)-1,2-phenylenebis(methylphenylphosphine) with either *cis*- or *trans*-[OsCl₂(DMSO)₄] in refluxing methanol, avoiding the racemization which ensues at temperatures approaching 80°C (refluxing benzene or ethanol).

The *cis*- and *trans*- isomers are readily distinguished by their ³¹P NMR spectra, which show a pair of triplets at 10.6 and 16.3 ppm for the former and a singlet at 18.1 ppm for the latter.

A crystal of the *trans*- complex was structurally characterized by X-ray diffraction and confirms retention of both stereochemistry at the metal and configuration of the diphosphine ligand (Figure 1). This is the first structural study of an osmium complex incorporating 1,2-

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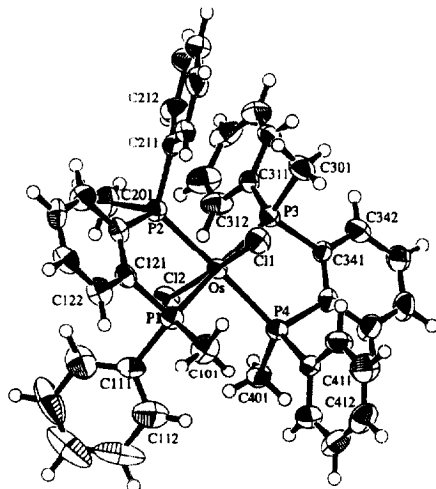
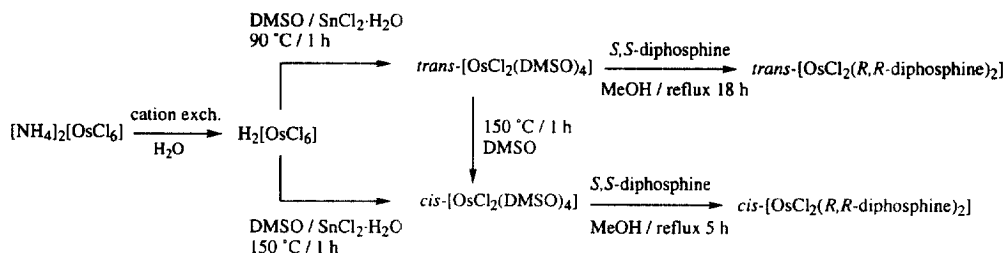


Figure 1. ORTEP drawing of $trans\text{-}[\text{OsCl}_2\{(R,R)\text{-}1,2\text{-phenylenebis(methylphenylphosphine)}\}_2]$. Selected interatomic distances (Å) and angles (deg.) are as follows: Os–Cl(1) 2.445(2), Os–Cl(2) 2.441(2), Os–P(1) 2.328(2), Os–P(2) 2.310(2), Os–P(3) 2.349(2), Os–P(4) 2.337(2), Cl(1)–Os–Cl(2) 171.77(9), Cl(1)–Os–P(1) 82.41(8), Cl(1)–Os–P(2) 87.18(7), Cl(1)–Os–P(3) 88.97(8), Cl(1)–Os–P(4) 96.34(7), Cl(2)–Os–P(1) 90.23(8), Cl(2)–Os–P(2) 88.43(7), Cl(2)–Os–P(3) 98.37(7), Cl(2)–Os–P(4) 88.20(8), P(1)–Os–P(2) 84.25(8), P(1)–Os–P(3) 171.38(7), P(1)–Os–P(4) 97.26(8), P(2)–Os–P(3) 95.37(7), P(2)–Os–P(4) 176.32(8), P(3)–Os–P(4) 83.65(7), Os–P(1)–C(101) 118.4(3), Os–P(1)–C(111) 121.4(3), Os–P(1)–C(121) 108.5(3).

phenylenebis(methylphenylphosphine), although a number of examples of ruthenium complexes with this ligand have been reported previously.^{12–15} Intraligand bond lengths are not unusual, while comparison to the analogous ruthenium complex¹² reveals similar M–P distances [2.304(1), 2.321(1), 2.338(1), 2.354(1) Å, M=Ru versus 2.310(2), 2.328(2), 2.337(2), 2.349(2) Å, M=Os] and a marginal lengthening of M–Cl distances [2.426(1), 2.432(1) Å, M=Ru versus 2.441(2), 2.445(2) Å, M=Os].

Typical barriers to inversion of alkyldiarylphosphines lie in the range 120–130 kJ mol^{−1},¹⁶ for this type of phosphine, the present procedure provides a facile synthesis of both *cis*- and *trans*- isomers of chiral-at-phosphorus bis(diphosphine) osmium complexes which should enable detailed study of their potential as precursors to NLO-active materials or auxiliaries in enantioselective transformations.

Experimental section

Manipulations were performed under a nitrogen atmosphere using Schlenk techniques. The complex $[\text{NH}_4]_2[\text{OsCl}_6]$ and (*S,S*)-1,2-phenylenebis(methylphenylphosphine) were prepared by literature methods.^{17,18} Methanol was dried by distilling over magnesium/iodine; THF was dried by distilling over sodium/benzophenone. “Pet. spirit” refers to a fraction of petroleum ether of boiling range 60–80°C. Cation exchange resin was Dowex 50W-X2, 50–100 mesh. Mass spectra were recorded

using a VG ZAB 2SEQ instrument (30 kV Cs⁺ ions, current 1 mA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix) at the Research School of Chemistry, Australian National University; peaks are reported as *m/z*. Microanalyses were carried out at the Research School of Chemistry, Australian National University.

¹H and ³¹P NMR spectra were recorded using a Varian Gemini-300 FT NMR spectrometer and are referenced to residual CHCl₃ (7.24 ppm) or external 85% H₃PO₄ (0.0 ppm), respectively. Optical rotations were measured at 20°C on a Perkin–Elmer model 241 polarimeter.

trans-[OsCl₂(DMSO)₄]

An aqueous solution of [NH₄]₂[OsCl₅] (500 mg, 1.14 mmol) was passed through a cation exchange column in the protic form, eluting with H₂O, after which the solvent was removed from the eluate using a rotary evaporator. The residue was dissolved in DMSO (4 mL), SnCl₂·2H₂O (400 mg, 1.78 mmol) was added and the resultant solution heated at 90°C for 1 h. The yellow precipitate that formed was collected by filtration and washed with acetone (2×15 mL) and ether (2×15 mL), yielding 300 mg (46%) as a yellow solid. Anal. calcd for C₈H₂₄Cl₂O₄OsS₄: C 16.75, H 4.22%. Found: C 16.43, H 4.10%. ¹H NMR: (δ, 300 MHz, CDCl₃); 3.44 (s, Me).

cis-[OsCl₂(DMSO)₄]

An aqueous solution of [NH₄]₂[OsCl₆] (250 mg, 0.57 mmol) was passed through a cation exchange column in the protic form, eluting with H₂O, after which the solvent was removed from the eluate using a rotary evaporator. The residue was transferred to a Schlenk tube as a solution in methanol and the solvent removed *in vacuo*. The red–black residue was then dissolved in DMSO (1 mL), SnCl₂·2H₂O (200 mg, 0.89 mmol) was added and the mixture was stirred under N₂ for 0.5 h at 120°C, over which time a precipitate formed. The temperature was increased to 150°C and stirring continued for 0.5 h. The mixture was cooled to room temperature and acetone (7 mL) was added. It was then allowed to stand overnight under N₂ whereupon a light gray precipitate formed which was collected and washed with acetone and ether. Recrystallization from CHCl₃/ether afforded 110 mg as white microcrystals (34%). Anal. calcd for C₈H₂₄Cl₂O₄OsS₄: C 16.75, H 4.22%. Found: C 16.67, H 3.87%. ¹H NMR: (δ, 300 MHz, CDCl₃); 2.75 (s, 6H, Me), 3.41 (s, 6H, Me), 3.52 (s, 6H, Me), 3.56 (s, 6H, Me). The complex was also synthesized by stirring *trans*-[OsCl₂(DMSO)₄] (100 mg, 0.17 mmol), prepared as above, in 5 mL of DMSO at 150°C for 1 h. Evaporation of the DMSO *in vacuo* and washing of the resultant white powder with 1: 1 acetone/ether (2×4 mL), and then ether (2×4 mL), yielded 78 mg (78%) of the *cis* product.

(+)₅₈₉-*cis*-[OsCl₂{(R,R)-1,2-Phenylenebis(methylphenylphosphine)}₂]

A mixture of *cis*-[OsCl₂(DMSO)₄] (100 mg, 0.17 mmol) and (*S,S*)-1,2-phenylenebis(methylphenylphosphine) (112 mg, 0.35 mmol) was stirred in refluxing methanol (5 mL) for 5 h. The mixture was allowed to cool to room temperature and the resultant pale yellow precipitate was collected, washed with ether and dried *in vacuo*. 56 mg of powder was collected and a further 20 mg of product was obtained by removing the solvent *in vacuo*, dissolving the residue in CH₂Cl₂ and then precipitating with pet. spirit. Yield 76 mg (48%). [α]_D: +9.0 (*c* 0.22, CH₂Cl₂). MS: 906 ([M]⁺). Anal. calcd for C₄₀H₄₀Cl₂OsP₄: C 53.04, H 4.45%. Found: C 52.84, H 4.36%. ¹H NMR: (δ, 300 MHz, CDCl₃); 1.76 (m, 6H), 2.23 (t, *J*=4 Hz, 6H), 5.99–7.80 (m, 28H, Ph). ³¹P NMR: (δ, 121 MHz, CDCl₃); 10.6 (t, *J*=9 Hz, 2P), 16.3 (t, *J*=9 Hz, 2P).

(-)₅₈₉-*trans*-[OsCl₂{(R,R)-1,2-Phenylenebis(methylphenylphosphine)}₂]

A mixture of *trans*-[OsCl₂(DMSO)₄] (100 mg, 0.17 mmol) and (*S,S*)-1,2-phenylenebis(methylphenylphosphine) (118 mg, 0.36 mmol) was stirred in refluxing methanol (10 mL) for 18 h, and then allowed to cool to room temperature. The yellow microcrystals that formed were collected, washed with pet. spirit and dried *in vacuo* (104 mg, 66%). [α]_D: -397.5 (*c* 0.20, CH₂Cl₂). MS: 906 ([M]⁺). Anal. calcd for C₄₀H₄₀Cl₂OsP₄: C 53.04, H 4.45%. Found: C 52.61, H 4.31%. ¹H NMR: (δ, 300

Table 1. Experimental parameters for the X-ray diffraction study

formula	C ₄₀ H ₄₀ Cl ₂ OsP ₄	Z	4
formula weight	905.76	radiation (λ , Å)	Mo K α ($\lambda = 0.71069$)
crystal system	orthorhombic	T, K	296
space group	P2 ₁ 2 ₁ 2 ₁ (#19)	abs. coeff.(K α), cm ⁻¹	37.20
a, Å	11.642(3)	crystal size, mm ³	0.20 x 0.16 x 0.16
b, Å	12.237(5)	2 θ_{max} , deg	50.1
c, Å	26.463(3)	N	3778
V, Å ³	3770(2)	N ₀	3095
D _{calc} , g cm ⁻³	1.596	R, R _w	0.025, 0.023
F(000)	1800.00		

MHz, CDCl₃); 1.54 (s, 12H, Me), 7.23 to 7.37 (m, 28H, Ph). ³¹P NMR: (δ , 121 MHz, CDCl₃); 18.1 (s). A crystal suitable for X-ray diffraction study was grown from CH₂Cl₂/methanol.

X-Ray structure determination

A unique diffractometer data set was obtained (ω - 2θ scan technique) and yielded *N* independent reflections, *N*_o of these with $I \geq 3.00\sigma(I)$ being considered "observed" and used in full matrix least squares refinement; an empirical psi-type absorption correction was applied. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (*x*, *y*, *z*, *U*_{iso})_H were included constrained at estimated values. Conventional residuals *R* and *R*_w on $|F|$ are given; the weighting function $w = 4F_o^2 / \sigma^2(F_o^2)$ where $\sigma^2(F_o^2) = [S^2(C + 4B) + (pF_o^2)^2] / Lp^2$ (*S*=scan rate, *C*=peak count, *B*=background count, *p*=*p* factor determined experimentally from standard reflections) was employed. Computation used the teXsan package.¹⁹ Specific data collection, solution and refinement parameters are given in Table 1. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Structural Database.

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