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Five- and Six-coordinate Complexes of Osmium(II) with 1,3-Bis(diphenylphosphino)propane

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Although there is a great number of six-coordinate phosphine derivatives of osmium(II), very few five-coordinate ones have been reported. The complexes with triphenylphosphine $[OsX_2(PPh_3)_3]$, where X= Cl [1] or Br [2], and $[OsHCl(PPh_3)_3]$ [3] and with tricyclohexylphosphine $[OsHX(CO)(PCy_3)_2]$ (X=Cl, Br) [4] have been obtained. With bidentate phosphine ligands, osmium(II) gives rise to the octahedral *cis*- or *trans*-$[OsX_2(diphosphine)_2]$ [5], whereas no five-coordinate species have been isolated so far. In the present paper we report the syntheses of some six- and five-coordinate complexes of osmium(II) containing the diphosphine 1,3-bis(diphenylphosphino)propane, together with some osmium(III) derivatives of the type *trans*-$[OsCl_2(diphosphine)_2]BF_4$.

We find that with the chelating diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ the coordinatively unsaturated species $[OsX(diphosphine)_2]^+$ can be obtained when n=3 (dpp), while when n=1 (dpm) or n=2 (dpe) only the usual *trans*-octahedral complexes are formed. Similar stereochemical effects of diphosphine alkyl-chain length were observed in the case of the analogous d^6 complexes *trans*-$[RuX_2(Ph_2P(CH_2)_nPPh_2)_2]$, which easily dissociate to give the $[RuX(diphosphine)_2]^+$ cations only when three methylene groups are present in the connecting chain between the P atoms [6, 7]. Five-coordinate $[RuX(chelate)_2]^+$ complexes have been obtained also with the hybrid ligand $Ph_2P(CH_2)_2C_5H_4N$ (=1-(2′-pyridyl)-2-(diphenylphosphino)ethane), which forms again a six-membered chelate ring [9].

Experimental

Microanalyses and magnetic measurements (Gouy's method) were performed by Mr. L. Turiaco, Istituto di Chimica Analitica, University of Padua. The reported procedures were used to prepare the ligands. I.r. and visible spectra were recorded on a Perkin Elmer 457 and on an Optica CF4RNI instruments respectively. ^{31}P n.m.r. spectra were recorded on a Bruker WP 60 spectrometer operating at 14.09 kG in the pulse FT mode.

trans-$[OsCl_2(dpp)_2]$

(*a*) The diphosphine dpp (0.64 g, 1.5 mmol) was added to a benzene solution of $[OsCl_2(PPh_3)_3]$ (0.73 g, 0.7 mmol in 50 ml) under nitrogen and the solution stirred at room temperature for 2 hr. The green mixture gradually became yellow and, by adding cyclohexane, pale yellow crystals precipitated which were recrystallized from benzene–cyclohexane (yield 80%).

(*b*) The diphosphine dpp (2.8 g, 6.8 mmol) dissolved in ter-butyl alcohol and $(NH_4)_2OsCl_6$ (1 g, 2.3 mmol) dissolved in water were refluxed together for 48 hr, a dark red solution and a yellowish precipitate being obtained. The cooled mixture was filtered and the solid product dissolved in benzene and chromatographed on alumina. Elution with benzene gave a clear solution, from which the solid compound was obtained on addition of cyclohexane (yield 20%).

$[OsCl(dpp)_2]Y$ ($Y = PF_6$, BPh_4)

(*a*) *trans*-$[OsCl_2(dpp)_2]$ and slight excess of NH_4PF_6 (or $NaBPh_4$) were refluxed in ter-butyl alcohol for 72 hr. The brown precipitate was recrystallised from tetrahydrofuran–ethanol (yield 60%).

(*b*) The diphosphine dpp and $(NH_4)_2OsCl_6$ were reacted as described in the method (*b*) for the preparation of *trans*-$[OsCl_2(dpp)_2]$. The reaction mixture was filtered and NH_4PF_6 (or $NaBPh_4$) were added to the clear red solution. Brown crystals precipitated, which were purified from tetrahydrofuran–ethanol (yield 20%).

$[OsCl(CO)(dpp)_2]PF_6$

A dichloromethane solution of $[OsCl(dpp)_2]PF_6$ was shaken for 2 hr under an atmosphere of carbon monoxide. The resulting pale yellow solution was concentrated and, by addition of ethanol, pale yellow crystals separated. The compound was recrystallised from tetrahydrofuran–iso-propyl alcohol (yield 90%).

$[OsBr(dpp)_2]BPh_4$

trans-$[OsCl_2(dpp)_2]$ (1.09 g, 1 mmol) was refluxed in tetrahydrofuran (50 ml) with LiBr (0.86 g, 10 mmol) and $NaBPh_4$ (3.4 g, 10 mmol) for 72 hr. Tan crystals were gradually formed, which were repeatedly crystallised from dichloromethane–toluene (yield 40%).

trans-$[OsCl_2(diphosph)_2]BF_4 \cdot 0.5\ CH_2Cl_2$ (diphosph=dpp, dpe)

To a suspension of *trans*-$[OsCl_2(diphosph)_2]$ in acetone (1 mmol in 20 ml), $AgBF_4$ was added (0.2 g, 1 mmol). A deep colored solution was immediately formed (violet in the case of dpp, green for dpe) together with metallic Ag. By addition of ethanol, the

TABLE I. Analytical Data and Physical Constants.

Compd	Color	Mp °C	Λ_M[a]	Anal					
				%C		%H		%Cl	
				Calcd	Found	Calcd	Found	Calcd	Found
trans-$[OsCl_2(dpp)_2]$	Yellow	282	0.8[b]	59.72	60.04	4.82	4.78	6.53	7.17
$[OsCl(dpp)_2]PF_6$	Brown	240	80[c]	54.25	54.36	4.38	4.31	2.96	2.86
$[OsCl(dpp)_2]B(C_6H_5)_4$	Brown	260	55	68.23	68.75	5.29	5.07	–	–
$[OsBr(dpp)_2]B(C_6H_5)_4$	Tan	>300	58	66.24	67.00	5.13	5.77	–	–
$[OsCl(CO)(dpp)_2]PF_6$	Yellow	265	83	53.99	53.94	4.28	4.23	2.90	3.16
trans-$[OsCl_2(dpp)_2]BF_4 \cdot \frac{1}{2}CH_2Cl_2$[d]	Violet	223	96	53.86	53.20	4.40	3.92	8.75	8.49
trans-$[OsCl_2(dpe)_2]BF_4 \cdot \frac{1}{2}CH_2Cl_2$[e]	Green	268	93	53.12	52.25	4.33	4.19	–	–

[a] Molar conductance values (S cm^2 mol^{-1}) for 10^{-3} *M* nitromethane solutions at 25 °C, unless otherwise stated. [b] 1,2-Dichloroethane solution. [c] Plot of Λ_e *vs.* $N^{1/2}$, according to the Onsager equation $\Lambda_0 = \Lambda_e + AN^{1/2}$, gives $\Lambda_0 = 85.5$ S cm^2 equiv^{-1} and A = 190 S cm^2 equiv^{-1} $N^{-1/2}$. [d] μ_{eff} at 20 °C = 2.07 B.M. [e] μ_{eff} at 20 °C = 1.98 B.M.

crystalline product precipitated, which was purified from dichloromethane–ethanol (yield 90%).

Results and Discussion

Trans-$[OsCl_2(dpp)_2]$ was made by reaction of $[OsCl_2(PPh_3)_3]$ with the chelate ligand. The *trans*-octahedral structure is inferred from elemental analysis, conductivity (non-electrolyte) and i.r. spectra, which show at 305 cm^{-1} a single band attributable to (Os–Cl) stretching.

The compound slowly dissolves in boiling ter-butyl alcohol giving deep red solutions, from which the diamagnetic five-coordinate complexes $[OsCl(dpp)_2]Y$ ($Y = PF_6$, BPh_4) have been obtained by addition of NH_4PF_6 or $NaBPh_4$.

It must be noted that the usual preparative route for *trans*-$[OsCl_2(diphosphine)_2]$ complexes [5] gives, in the case of dpp, poor yields of the expected product. In fact, when a slight excess of dpp is refluxed with $(NH_4)_2OsCl_6$ in aqueous ter-butyl alcohol, a red solution containing the cation $[OsCl(dpp)_2]^+$ is obtained, together with small amounts of yellow precipitated *trans*-$[OsCl_2(dpp)_2]$. By contrast, no evidence of the formation of five-coordinate species found when $(NH_4)_2OsCl_6$ was reacted with dpe and also when *trans*-$OsCl_2(dpe)_2]$ was refluxed for one week in ter-butyl alcohol.

The different behavior of the *trans*-$[OsCl_2(Ph_2P(CH_2)_nPPh_2)_2]$ (n=2,3) complexes with increasing alkyl-chain length probably arises from steric effects, since the two diphosphines should have rather similar electronic properties. That the diphosphine dpp will have larger steric requirements than dpe has been recently shown by an X-ray investigation on a series of $[PdX_2(Ph_2P(CH_2)_nPPh_2)]$ complexes (n=1,2,3; X=Cl, NCS) [10].

Addition of an excess of LiCl to solutions of $[OsCl(dpp)_2]^+$ produces no detectable changes in the visible spectra, even after prolonged refluxing, while reaction with excess of LiBr slowly yields the corresponding bromo-derivative, $[OsBr(dpp)_2]^+$.

Both $[OsX(dpp)_2]Y$ complexes (X=Cl, Br) behave as uni–univalent electrolytes in nitromethane and, in the case of the chloroderivative, the 1:1 electrolyte nature was confirmed by Hayster's method [11] (see Table I). I.r. spectra of $[OsCl(dpp)_2]^+$ show the (Os–Cl) stretch at 300 cm^{-1}, in the range expected for terminal chlorine ligands.

Visible spectra of the two $[OsX(dpp)_2]^+$ cations (X=Cl, Br) are similar in the solid state (Nujol mull) and in solution (1,2-dichloroethane) (Table II). Two well-developed bands appear around 24 and 19 kK, with a shoulder at lower frequency. The spectra are strictly related to those of the $[RuX(dpp)_2]^+$ cations (Fig. 1), with shifts in the frequencies of the adsorption maxima (Os Ru), in agreement with the different position of the two metals in the spectrochemical series. A third high-frequency absorption which is present in the spectrum of the ruthenium(II) derivative probably falls for $[OsX(dpp)_2]^+$ in the u.v. region and is covered by CT bands.

The proton decoupled ^{31}P n.m.r. spectra of $[OsCl(dpp)_2]BPh_4$ in $CDCl_3$ show two triplets of equal intensities (A_2X_2 spin system, see Table II). The spectral pattern is consistent with a structure near to a trigonal bipyramid, where each diphosphine group spans an equatorial and an axial coordination site. This structure appears to be similar to that reported recently for another five-coordinate d^6 cation, $[RuH(diop)_2]^+$ [12].

$[OsCl(dpp)_2]Y$ readily reacts with uncharged ligands (carbon monoxide, nitriles) and, in the case of carbon monoxide, it was possible to isolate the adduct $[OsCl(CO)(dpp)_2]Y$. I.r. spectra in dichloro-

TABLE II. Electronic (Visible) Spectra and ^{31}P N.m.r. Data.

Compd	Band max, kK (ϵ_M)	^{31}P N.m.r. Data^a
$[OsCl(dpp)_2]BPh_4$	19.5, 23.8^b 16.4(sh), 18.9(760), 24.1(3800)^c	17.4 (t), 24.5 (t) (J_{PP} = 16.5 Hz)
$[OsBr(dpp)_2]BPh_4$	19.0, 23.0^b 16.3(sh), 18.4(690), 23.8(3250)^c	–
$[OsCl(CO)(dpp)_2]BPh_4$	–	40.2 (s)

^{a}$CDCl_3$ solutions at 30 °C; chemical shifts in ppm downfield from 85% aq. H_3PO_4. ^{b}Nujol mull. ^{c}1,2-Dichloroethane solutions at 25 °C.

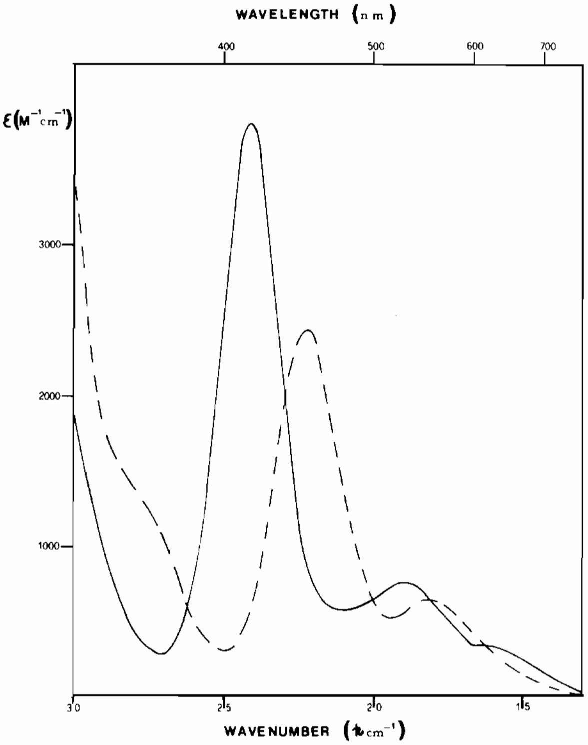

Figure 1. Electronic spectra of $[OsCl(dpp)_2]PF_6$ (——) and of $[RuCl(dpp)_2]PF_6$ (-----) in 1,2-dichloroethane at 25 °C.

methane solution display a single carbonyl absorption at 1945 cm^{-1}, which splits in Nujol mull into two bands of comparable intensities at 1940 and 1920 cm^{-1}, possibly due to solid state effects. The $^{31}P\{^1H\}$ n.m.r. spectra of the tetraphenylboron derivative show a single resonance, which indicates an octahedral structure of the cation, where the chloride and the CO ligands are *trans* to each other.

Starting from *trans*-$OsCl_2(dpe)_2$], we have tried to prepare the corresponding five-coordinate cation by the general method of abstraction of a halide X as X^-, using a silver salt of non-coordinating anions. However, treatment of the *trans*-octahedral complex with $AgBF_4$ in acetone results in the easy oxidation of the osmium(II) with deposit of metallic silver. A similar redox reaction has been observed also with the complex *trans*-$[OsCl_2(dpp)_2]$. From the deeply colored acetone solutions the paramagnetic $[OsCl_2(diphosphine)_2]^+$ cations have been isolated as violet (in the case of dpp) or green (in the case of dpe) crystals of the tetrafluoborate salts. Recrystallization from dichloromethane–iso-propyl alcohol gives the pure solvate $[OsCl_2(diphosphine)_2]BF_4 \cdot \frac{1}{2}CH_2Cl_2$. The *trans*-stereochemistry is inferred from i.r. spectra which show a single (Os–Cl) stretching band at 300 cm^{-1}.

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