Octahedral and Trigonal-bipyramidal Complexes of Osmium(II) with 1,2-Bis(dicyclohexylphosphino)ethane. Stereochemistry of Addition Reactions to Five-co-ordinate Osmium(II) Derivatives and to Their Ruthenium(II) Analogues

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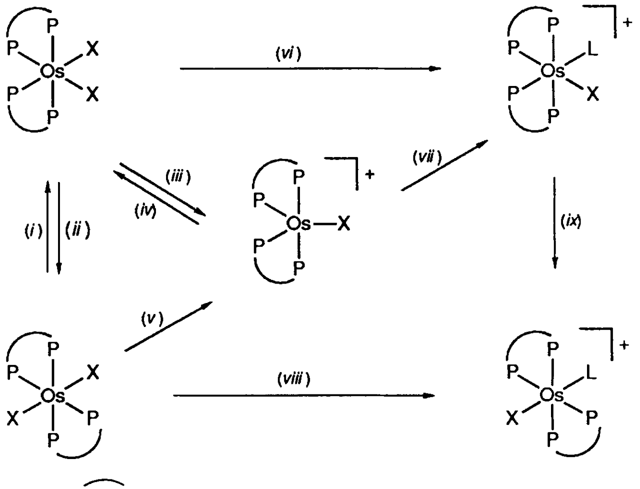
The complexes *cis*- and *trans*-[$OsX_2(dcpe)_2$] [X = Cl or Br; dcpe = 1,2-bis(dicyclohexylphosphino)-ethane] have been prepared, and their physical and chemical properties investigated. The *cis* isomers were found to dissociate quickly in polar solvents to give [$OsX(dcpe)_2$]$^+$, which have been isolated in the solid state as the tetraphenylborate salts. On the basis of ^{31}P n.m.r. and u.v.–visible spectra, the d^6 cations are assigned a trigonal-bipyramidal structure with the halide in an equatorial position. The unsaturated complexes [$OsX(dcpe)_2$]$^+$ readily and stereoselectively add halide or neutral ligands L (CO, MeCN, or PhCN) in dichloromethane solution to form the corresponding *cis* derivatives. The *cis*-[$OsX(L)(dcpe)_2$]$^+$ cations can be thermally converted into the *trans* isomers. The analogous [$RuX(dcpe)_2$]$^+$ species, previously reported to give *trans* addition with X^- and L, were found to form *cis*-[$RuX_2(dcpe)_2$] and *cis*-[$RuX(L)(dcpe)_2$]$^+$ at −60 °C in dichloromethane or acetone solution. Also these species are thermally converted into the thermodynamically stable *trans* isomers. The complexes *cis*-[$RuX_2(dcpe)_2$] were isolated, and the stereochemistry of the various six-co-ordinate complexes of osmium(II) and ruthenium(II) established by ^{31}P n.m.r. and i.r. spectroscopy. The *cis–trans* interconversion of these osmium(II) and ruthenium(II) isomeric pairs in various solvents was also examined.

Six-co-ordination predominates in the chemistry of phosphino complexes of osmium(II), which generally forms *cis*-or *trans*-[OsX_2L_4] derivatives (L = P atom of mono- or bi-dentate phosphine, X = halide).[1,2] However, five-co-ordination becomes favoured when the steric crowding around the metal centre is increased, as in [$OsCl_2(PPh_3)_3$], in which the bulky triphenylphosphine prevents osmium(II) from achieving its usual co-ordination number of six.[3]

Also the chemistry of six-co-ordinate [$OsX_2(L–L)_2$][4–10] appears to be sensitive to the steric properties of the diphosphine (L–L). We have previously reported that the co-ordinatively unsaturated species [$OsX(L–L)_2$]$^+$ can be obtained with the diphosphines $Ph_2P(CH_2)_nPPh_2$ when $n = 3$ but not when n is 1 or 2.[6] Apparently the tendency to dissociate giving five-co-ordinate complexes increases with increasing chelate ring size. A similar behaviour has been observed for the six-co-ordinate ruthenium(II) complexes [$RuX_2(L–L)_2$].[11–13] We have recently obtained unsaturated species [$RuX(L–L)_2$]$^+$ with the ligand 1,2-bis(dicyclohexylphosphino)ethane (dcpe), thus showing that dissociation of [$RuX_2(L–L)_2$] becomes more facile also when the size of the substituents at phosphorus is increased.[14]

Starting from these observations, we have been investigating osmium(II) complexes with the ligand dcpe, and report herein the synthesis of six-co-ordinate *cis*- and *trans*-[$OsX_2(dcpe)_2$], together with those of five-co-ordinate [$OsX(dcpe)_2$]$^+$, which are isolated in the solid state as tetraphenylborate salts. Though theoretical arguments indicate that a square-pyramidal geometry is favoured for the five-co-ordinate complexes formed by d^6 metal ions,[3,15] the [$OsX(dcpe)_2$]$^+$ cations appear to be trigonal-bipyramidal. Other unequivocal examples of low-spin, trigonal-bipyrimidal d^6 complexes have recently been reported.[13,14,16] Moreover, the five-co-ordinate cations [$OsX(dcpe)_2$]$^+$ are of interest because species of this type are thought to be intermediates in isomerization and substitution reactions of [$MX_2(L–L)_2$]$^{n+}$ complexes (M = d^6 metal ion).[17] In this context we have examined the reactions of [$OsX(dcpe)_2$]$^+$ with a variety of ligands (X^-, CO, or RCN), and found that six-co-ordinate *cis* adducts are formed stereoselectively. Also the ruthenium analogues, which have been previously reported to yield six-co-ordinate *trans* adducts,[14] are found to give *cis* addition at low temperature. The isomers *cis*-[$MX_2(dcpe)_2$] and *cis*-[$MX(L)(dcpe)_2$]$^+$ (M = Ru or Os; X = Cl or Br; L = CO or RCN) are converted into the corresponding *trans* isomers with rates dependent on the nature of the metal and solvent. The reactions of osmium complexes are shown in the Scheme.



Scheme. P⌒P = dcpe; X = Cl or Br; L = CO, MeCN, or PhCN. (*i*) In $C_6H_4Cl_2$-*o* at 180 °C; (*ii*) in 2-methoxyethanol at 140 °C; (*iii*) in CH_2Cl_2 or EtOH; (*iv*) LiX in acetone at room temperature (r.t.); (*v*) in CH_2Cl_2 or EtOH (X = Br); (*vi*) L in CH_2Cl_2; (*vii*) L in CH_2Cl_2 at r.t.; (*viii*) L in 2-methoxyethanol at 140 °C; (*ix*) in CH_2Cl_2 at r.t. (L = CO) or in $C_6H_4Cl_2$-*o* at 140 °C (L = MeCN or PhCN)

Results and Discussion

The diamagnetic complexes *trans*-[$OsCl_2(dcpe)_2$] (**1**) and *cis*-[$OsCl_2(dcpe)_2$] (**2**) have been obtained by synthetic procedures

Table 1. ^{31}P N.m.r. data[a]

Complex	δ/p.p.m.	J(P–P′)/Hz	T/K
(1)[b]	−0.9 (s)	—	310
(2)[b]	2.2 (t), 4.7 (t)	7.1	310
(3)[b]	−5.7 (s)	—	310
(4)[b]	−4.8 (t), −2.5 (t)	7.8	310
(5)	25.9 (br), 39.5 (br)[c]	*d*	310
	32.4 (br), 41.2 (br)	*d*	153
(6)	24.6 (br), 39.3 (br)[c]	*d*	310
	31.1 (br), 41.0 (br)	*d*	153
(7)[e]	2.7, 11.0, 11.8, 21.8	18.1, 21.6, 13.4, 1.2, 7.3, 213.4	233
(8)[e]	−3.2, 7.9, 10.5, 15.9	22.1, 17.9, 13.4, 1.7, 210.7, 7.5	233
(9)	17.5 (s)	—	310
(10)	6.0 (s)	—	310
(11)[e]	1.6, 6.9, 8.0, 9.9	9.4, 7.9, 16.4, 1.4, 224.5, 7.4	310
(12)[e]	1.8, 6.2, 6.6, 10.4	12.4, 12.6, 6.2, 2.6, 213.8, 8.0	310
(13)	6.4 (s)	—	310
(14)	7.5 (s)	—	310
(15)[c]	42.6 (t), 52.4 (t)	18.6	213
(16)[c]	36.0 (t), 50.6 (t)	18.4	213
(17)[e]	26.6, 46.8, 52.8, 53.4	24.5, 22.2, 30.1, 239.5, 12.2, 15.4	233
(18)[e]	22.0, 44.9, 48.5, 53.8	23.6, 22.1, 29.4, 215.1, 13.8, 13.8	233
(19)[e]	44.8, 45.8, 46.3, 56.3	246.8, 13.2, 21.4, 27.3, 10.0, 32.9	233
(20)[e]	41.1, 43.2, 43.4, 56.9	19.6, 220.6, 16.4, 20.6, 33.5, 15.3	233

[a] Solvents used, unless otherwise stated: CH_2Cl_2 (310—173 K), CHF_2Cl–CD_2Cl_2 (173—153 K). Multiplicity given in parentheses: s = singlet, t = triplet, br = broad. [b] In benzene solution. [c] In acetone solution. [d] J(P–P′) < 2 Hz. [e] Spectra appear as groups of multiplets; simulations performed assuming positive *trans*-^2J(L–L) and negative *cis*-^2J(L–L) constants; refined parameters reported in the order δ(A), δ(B), δ(C), δ(D); J(AB), J(AC), J(AD), J(BC), J(BD), J(CD) (atom labels in order of increasing positive chemical shift, assignment not attempted). Calculated spectrum for complex (**7**) shown in the Figure.

similar to those reported in the literature. The *trans* derivative (**1**) was prepared in high yield by refluxing $[NH_4]_2[OsCl_6]$ and dcpe in 2-methoxyethanol.[8] Unlike what has been found with other diphosphines,[4] the reaction of dcpe with the triply chlorobridged $[Os_2Cl_3(PEtPh_2)_6]Cl$ in the absence of solvent did not yield the *cis* isomer (**2**), but instead complex (**1**) was obtained quantitatively. Isomer (**2**) was eventually prepared by thermal isomerization of (**1**) in boiling 1,2-dichlorobenzene: under these conditions solutions are formed in which (**1**) and (**2**) are in equilibrium (*ca.* 35 and 65%, respectively). As the insoluble *trans* isomer (**1**) separates upon cooling to room temperature, pure complex (**2**) is recovered from the solution.

Since complex (**1**) is inert towards halide substitution, the *cis* derivative (**2**) was used as starting material for the synthesis of *trans*-$[OsBr_2(dcpe)_2]$ (**3**) and *cis*-$[OsBr_2(dcpe)_2]$ (**4**). Derivative (**3**) was prepared by refluxing (**2**) with an excess of LiBr in 2-methoxyethanol, whereas the *cis* isomer (**4**) was obtained by a stepwise procedure which implies reaction of (**2**) with Br^- to give first five-co-ordinate $[OsBr(dcpe)_2]^+$ and then (**4**). It should be noted that, in contrast to the dichloro derivative (**1**), complex (**4**) can be quantitatively obtained also by thermal isomerization of (**3**) in 1,2-dichlorobenzene at 140 °C. Both *cis* derivatives (**2**) and (**4**) are converted into the sparingly soluble *trans* isomers (**1**) and (**3**) by heating in 2-methoxyethanol. The factors determining the thermodynamically preferred form for $[MX_2(L\text{–}L)_2]$ (M = Ru or Os) have been previously discussed.[4,8]

The geometries of complexes (**1**)—(**4**) can be inferred from ^{31}P-{^{1}H} n.m.r. spectra in benzene solution (Table 1). The *trans* isomers (**1**) and (**3**) show a single resonance at −0.9 and −5.7 p.p.m., respectively. The *cis* isomers exhibit two triplets, centred at 2.2 and 4.7 p.p.m. for (**2**) and −4.8 and −2.5 p.p.m. for (**4**). As the ^{31}P chemical shift of dcpe ($\delta_{\text{free ligand}}$) is 1.3 p.p.m., the ^{31}P co-ordination chemical shifts Δ (defined as $\delta_{\text{complex}}-\delta_{\text{free ligand}}$) for these species are unusually low or negative, in contrast with those generally found for complexes with chelating diphosphines forming five-membered rings.[18] However, it is well known that for isostructural complexes the ^{31}P resonance shifts to high field upon descending in a group.[18,19] In this context it is not surprising that for instance the ^{31}P resonance of complex (**1**) is shifted by about 40 p.p.m. to higher field with respect to its analogue *trans*-$[RuCl_2(dcpe)_2]$ (δ 39.3 p.p.m.), a trend which is similar to that found for *trans*-$[MCl_2(dmpe)_2]$ [dmpe = 1,2-bis(dimethylphosphino)ethane] on going from ruthenium to osmium.[7] The stereochemistries of (**1**) and (**2**) are also supported by the i.r. spectra in the Os–Cl stretching region: (**1**) shows a single band at 278 cm^{-1}, while (**2**) exhibits two bands at 270 and 245 cm^{-1}, which can be assigned to terminal chlorines in mutually *cis* positions (Table 2).

The visible spectra of *trans* isomers (**1**) and (**3**) show, both in the solid state and in benzene solution, a weak absorption in the 400—375 nm region and an intense band at higher frequency (Table 2). Similar spectral patterns have been reported for other six-co-ordinate d^6 complexes *trans*-$[MX_2(L\text{–}L)_2]$ (M = Ru or Os), and the low-energy band has been assigned to the $^1A_{1g} \longrightarrow {}^1E_g$ transition.[8,11,13,20] With respect to the related *trans*-$[RuX_2(dcpe)_2]$, the absorption maxima shift to higher frequency, in agreement with the different positions of the two metals in the spectrochemical series. The *cis* isomers (**2**) and (**4**) are pale yellow and yellow solids, respectively. Both in benzene and in Nujol mulls, their u.v.–visible spectra show no definite bands in the visible region, but only some shoulders blending in the charge-transfer bands which dominate at high energy (Table 2).

Both *cis* isomers (**2**) and (**4**) instantly dissociate in polar solvents such as dichloromethane and methanol according to equilibrium (1). The conducting solutions thus obtained show,

$$cis\text{-}[OsX_2(dcpe)_2] \rightleftharpoons [OsX(dcpe)_2]^+ + X^- \quad (1)$$

together with the absorptions of (**2**) and (**4**), also definite bands at 420—430 and 490—500 nm, which can be assigned to the co-ordinatively unsaturated cations $[\mathrm{OsX(dcpe)_2}]^+$. In co-ordinating solvents such as nitromethane or acetonitrile (solv), equilibrium (1) is shifted to the right with formation of six-co-ordinate colourless adducts of the type *cis*-$[\mathrm{OsX(solv)(dcpe)_2}]^+$. The *trans* isomers show a somewhat different behaviour: while complex (**1**) is insoluble in the usual polar solvents, dibromo species (**3**) dissolves in dichloromethane with slow formation of cationic species (see below).

In agreement with equilibrium (1), the co-ordinatively unsaturated cations $[\mathrm{OsX(dcpe)_2}]^+$ can be precipitated as tetraphenylborate salts by stirring (**2**) or (**4**) in ethanol suspension in the presence of $\mathrm{NaBPh_4}$ at room temperature. The five-co-ordinate bromo derivative is more directly prepared by refluxing (**2**) and an excess of LiBr in ethanol in the presence of $\mathrm{NaBPh_4}$. The *trans* derivative (**1**) does not afford five-co-ordinate species even after prolonged heating in ethanol in the presence of an excess of $\mathrm{NaBPh_4}$, while under the same conditions *trans* dibromo complex (**3**) yields $[\mathrm{OsBr(dcpe)_2}]\mathrm{BPh_4}$ in high yield. The relative ease of halide displacement in *cis* complexes as compared with the *trans* ones appears to be related to the labilizing effect of the phosphorus atom occupying the *trans* position. A similar chemical behaviour has been reported for the isomeric pair $[\mathrm{OsCl_2(dppm)_2}]$ (dppm = $\mathrm{Ph_2PCH_2PPh_2}$).[8] We have also tried to prepare the five-co-ordinate cations by halide abstraction with a silver salt, but treatment of (**1**) and (**3**) with $\mathrm{AgBF_4}$ in acetone results in oxidation to osmium(III) species, probably *trans*-$[\mathrm{OsX_2(dcpe)_2}]\mathrm{BF_4}$, with deposition of metallic silver.

Table 2. I.r. and u.v.–visible spectroscopic data

Complex	I.r.,[a] $\nu_{\mathrm{max.}}/\mathrm{cm}^{-1}$	U.v.–visible,[b] $\lambda_{\mathrm{max.}}$/nm ($\varepsilon_{\mathrm{max.}}/\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ for solution)
(**1**)	278[c]	375 (100), 310 (1 650)
(**2**)	270, 245[c]	370 (sh), 340 (990), 305 (sh)
(**3**)	—	400 (85), 312 (1 650)
(**4**)	—	390 (sh), 350 (1 290), 325 (1 390)
(**5**)	—	620 (sh), 495 (850), 420 (1 980), 315 (sh)[d]
		630 (sh), 490, 420, 325 (sh)[a]
(**6**)	—	630 (sh), 500 (900), 428 (2 100), 325 (sh)[d]
		620 (sh), 500, 430, 325 (sh)[a]
(**7**)	1 953[e]	
(**8**)	1 954[e]	
(**9**)	1 917[e]	
(**10**)	1 913[e]	
(**11**)	2 265[f]	
(**12**)	2 222[f]	
(**13**)	2 215[f]	
(**14**)	2 169[f]	
(**15**)	273, 254[c]	417 (830), 364 (850)
		415, 360[a]
(**16**)	—	430, 370[a]

[a] In Nujol mull. [b] In benzene solution, unless otherwise stated. [c] ν(M–Cl). [d] In acetone solution. [e] ν(CO). [f] ν(CN).

The brown diamagnetic $[\mathrm{OsX(dcpe)_2}]\mathrm{BPh_4}$ [X = Cl, (**5**); or Br, (**6**)] behave as 1:1 electrolytes in dichloromethane or acetone solutions. To rule out a dimeric structure with halide bridges, the nature of (**5**) and (**6**) in acetone solution was confirmed by Hayter's method of conductivity measurements at different concentrations (Table 3).[21] The electronic spectra in acetone or dichloromethane solution of these five-co-ordinate compounds are nearly coincident with those in the solid state, thus suggesting that no structural changes occur upon dissolution in these solvents. Two well developed bands are observed in the visible spectra, with a shoulder at lower frequency. An additional shoulder is present to high energy, which blends into charge-transfer bands (Table 2). These spectral features are strictly related to those of other diamagnetic trigonal-bipyramidal complexes of d^6 metal ions $[\mathrm{MX(L\text{–}L)_2}]^+$ (M = Ru or Os) with the diphosphine ligands spanning axial and equatorial positions, in particular of $[\mathrm{RuCl(dcpe)_2}]^+$ whose solid-state structure has been established by *X*-ray methods.[6,11,13,14] For a regular trigonal-bipyramidal structure the *d* orbital ordering is expected to be d_{xz}, d_{yz} $(e'') < d_{xy}$, $d_{x^2-y^2}$ $(e') < d_{z^2}$ (a_1'), which leads to a ground state with two unpaired electrons in the case of a d^6 low-spin configuration. In the $[\mathrm{MX(L\text{–}L)_2}]^+$ cations the presence of different groups in the equatorial plane probably lowers the symmetry of the co-ordination polyhedron, with consequent removal of e'-orbital degeneracy and spin pairing.

As further evidence for the proposed structure, the room-temperature $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectra of complexes (**5**) and (**6**) in dichloromethane solution show two signals of equal intensity at about 25 and 40 p.p.m. There is no observable coupling between the inequivalent phosphorus atoms of the diphosphine in the temperature range between +80 and −140 °C. When the

Table 3. Analytical and physical data

	Complex	Colour	$\Lambda_M{}^a/\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$	Analysis (%) C	H
(**1**)	*trans*-$[\mathrm{OsCl_2(dcpe)_2}]$	Cream	*b*	56.40 (56.45)	8.80 (8.75)
(**2**)	*cis*-$[\mathrm{OsCl_2(dcpe)_2}]$	Pale yellow	3[c]	56.50 (56.45)	8.75 (8.75)
(**3**)	*trans*-$[\mathrm{OsBr_2(dcpe)_2}]$	Pale orange	*b*	52.15 (52.25)	8.10 (8.10)
(**4**)	*cis*-$[\mathrm{OsBr_2(dcpe)_2}]$	Yellow	8[c]	52.10 (52.25)	8.10 (8.10)
(**5**)	$[\mathrm{OsCl(dcpe)_2}]\mathrm{BPh_4}$	Brown	78[d]	65.40 (65.65)	8.35 (8.40)
(**6**)	$[\mathrm{OsBr(dcpe)_2}]\mathrm{BPh_4}$	Brown	79[d]	63.25 (63.65)	8.15 (8.15)
(**7**)	*cis*-$[\mathrm{OsCl(CO)(dcpe)_2}]\mathrm{BPh_4}$	White	78	64.80 (65.20)	8.30 (8.25)
(**8**)	*cis*-$[\mathrm{OsBr(CO)(dcpe)_2}]\mathrm{BPh_4}$	White	77	63.15 (63.25)	8.05 (8.00)
(**9**)	*trans*-$[\mathrm{OsCl(CO)(dcpe)_2}]\mathrm{BPh_4}$	White	78	65.45 (65.20)	8.30 (8.25)
(**10**)	*trans*-$[\mathrm{OsBr(CO)(dcpe)_2}]\mathrm{BPh_4}$	White	77	63.10 (63.25)	8.15 (8.00)
(**11**)	*cis*-$[\mathrm{OsCl(MeCN)(dcpe)_2}]\mathrm{BPh_4}\cdot\mathrm{Me_2CO}$	White	75	65.30 (65.35)	8.50 (8.45)
(**12**)	*cis*-$[\mathrm{OsCl(PhCN)(dcpe)_2}]\mathrm{BPh_4}$	White	75	66.25 (66.75)	8.10 (8.15)
(**13**)	*trans*-$[\mathrm{OsCl(MeCN)(dcpe)_2}]\mathrm{BPh_4}$	White	75	65.40 (65.45)	8.40 (8.40)
(**14**)	*trans*-$[\mathrm{OsCl(PhCN)(dcpe)_2}]\mathrm{BPh_4}$	Yellow	75	66.10 (66.75)	8.20 (8.15)
(**15**)	*cis*-$[\mathrm{RuCl_2(dcpe)_2}]$	Yellow	*e*	60.95 (61.40)	8.55 (8.50)
(**16**)	*cis*-$[\mathrm{RuBr_2(dcpe)_2}]$	Yellow-orange	33	56.35 (56.45)	8.75 (8.75)

[a] In acetone solution. [b] Insoluble. [c] Equivalent conductivity in $\mathrm{CH_2Cl_2}$ for (**2**) and (**4**) is 6 and 19 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$, respectively. [d] The Onsager coefficient α, determined according to the equation $\Lambda_o = \Lambda_e + \alpha\sqrt{c_e}$ (Λ_o and Λ_e = equivalent conductance at zero and c_e concentration, respectively), is 4.3 and 4.2 $\Omega^{-1}\,\mathrm{dm}^{\frac{7}{2}}\,\mathrm{mol}^{\frac{3}{2}}$ for (**5**) and (**6**), respectively. [e] See text.

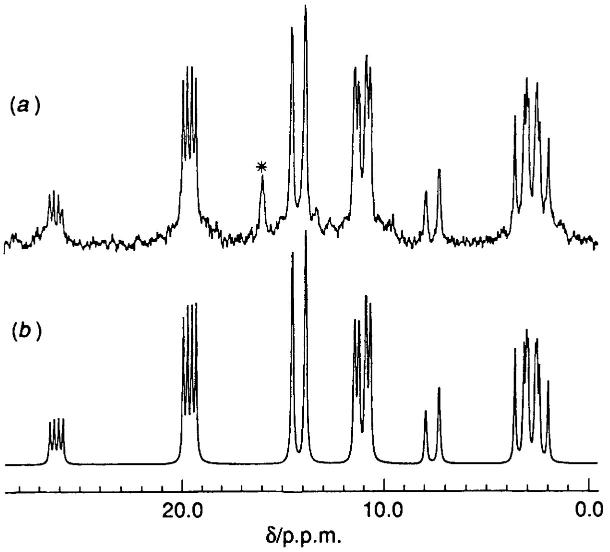


Figure. Experimental (*a*) and simulated ($W_{\frac{1}{2}}$ = 3.0 Hz) (*b*) ^{31}P n.m.r. spectra of *cis*-$[OsCl(CO)(dcpe)_2]BPh_4$ (**7**) at 233 K; * indicates the signal for the *trans* isomer (**9**)

temperature is increased in 1,2-dichloroethane solution the two signals begin to broaden, since the $[OsX(dcpe)_2]^+$ cations probably become stereochemically non-rigid on the n.m.r. time-scale, as previously found for several five-co-ordinate species $[MX(L-L)_2]^+$ (M = d^6 or d^8 metal atom).[14,22] Also when the temperature is lowered below −10 °C the two signals broaden, and remain broad in the range −10 to −100 °C with the one at about 25 p.p.m. shifting downfield. At −120 °C (CD_2Cl_2–CHF_2Cl solution) they eventually sharpen up into two singlets at about 32 and 41 p.p.m. (Table 1). This behaviour suggests that an exchange process occurs at low temperature: we tentatively suggest a dynamic equilibrium involving rapid addition and loss of a solvent molecule to the five-co-ordinate cations (**5**) and (**6**), as previously reported for the analogue $[RuX(dcpe)_2]^+$.[14] It should be noted that solvato derivatives $[OsX(solv)(dcpe)_2]^+$ are instantly formed also at room temperature in more strongly co-ordinating solvents such as acetonitrile. The formation of dimeric, six-co-ordinate species *via* halide bridges can be ruled out, as the ^{31}P n.m.r. spectra of a solution containing equimolecular amounts of (**5**) and (**6**) show the superimposed spectra of the two five-co-ordinate complexes at the same temperature.

Addition of excess of halide ions to dichloromethane or acetone solutions of the five-co-ordinate cations (**5**) and (**6**) results in the stereoselective formation of the six-co-ordinate *cis* species (**2**) and (**4**), which appear to be indefinitely stable at room temperature. The unsaturated complexes (**5**) and (**6**) quickly react with carbon monoxide to give white, six-co-ordinate, *cis*-$[OsX(CO)(dcpe)_2]BPh_4$ [X = Cl, (**7**); or Br, (**8**)]. The same products can be obtained by treating *cis*-$[OsX_2(dcpe)_2]$ with carbon monoxide in the presence of $NaBPh_4$. The monocarbonyl adducts (**7**) and (**8**) are 1:1 electrolytes in acetone, and their geometry was determined by a combination of i.r. and ^{31}P n.m.r. spectroscopy. Their i.r. mull spectra show a strong absorption at *ca.* 1 950 cm^{-1}, assigned to the CO stretching vibration. Like all other $[OsCl(L)(dcpe)_2]^+$ cations reported here, carbonyl species (**7**) exhibits only very weak absorptions in the 250—300 cm^{-1} region, and this hampers the assignment of Os–Cl stretchings. The ^{31}P n.m.r. spectra of freshly prepared dichloromethane solutions of (**7**) and (**8**) show complex spectra (Figure) which can be reproduced by computer simulation assuming an ABCD spin system, and are in accord with those reported for other *cis*-$[MX(Y)(L-L)_2]^{n+}$ complexes.[23] The calculated spectral parameters (Table 1) suggest a structure in which the X and CO groups occupy *cis* positions.

At room temperature in dichloromethane solution, *cis* complexes (**7**) and (**8**) quantitatively isomerize into the thermodynamically more stable *trans* species, as can be conveniently observed by i.r. and ^{31}P n.m.r. spectroscopy. The i.r. band at *ca.* 1 960 cm^{-1} is gradually replaced by new absorption at *ca.* 1 920 cm^{-1}, while in the ^{31}P n.m.r. spectrum a single sharp signal appears and progressively gains in intensity. The isomerization rate is not affected by CO pressure (20 atm, *ca.* 2 × 10^6 Pa; dichloromethane solution), while a very small retardation effect is observed in the presence of a large excess of halide ions in acetone solution. Therefore, it is possible that the *cis–trans* isomerization involves cleavage of the Os–P bond *trans* to CO, with formation of a five-co-ordinate intermediate which contains a unidentate dcpe ligand. A similar mechanism has been proposed for the isomerization of *cis*- $[RuH(CO)(Ph_2PCH_2CH_2PPh_2)_2]^+$.[23d]

The isomers *trans*-$[OsX(CO)(dcpe)_2]BPh_4$ [X = Cl, (**9**); or Br, (**10**)] can be prepared also in a one-pot synthesis by treating *trans*-$[OsX_2(dcpe)_2]$ with CO in boiling 2-methoxyethanol in the presence of $NaBPh_4$. They are white products whose structure is assigned by i.r. and ^{31}P n.m.r. data (Table 1). In contrast to dihalide derivatives (**1**) and (**3**), the *trans*-$[OsX(CO)(dcpe)_2]^+$ adducts appear to be thermodynamically favoured with respect to the *cis* ones. This is probably related to an overall enhancement of metal-to-ligand back bonding when the CO and $P(C_6H_{11})_2$ groups do not compete for the same set of metal π electrons. In agreement with a substantial increase of M–CO back bonding, the i.r. spectra of *trans* isomers (**9**) and (**10**) show ν(CO) absorptions at about 1 920 cm^{-1}, with significant lowering in energy with respect to the *cis* analogues.

Five-co-ordinate (**5**) and (**6**) also react with organic nitriles to give six-co-ordinate *cis*-$[OsX(RCN)(dcpe)_2]BPh_4$. In particular, we have isolated the acetonitrile and benzonitrile adducts, *cis*-$[OsCl(RCN)(dcpe)_2]BPh_4$ [R = Me, (**11**); or Ph, (**12**)]. Both (**11**) and (**12**) are white, and behave as 1:1 electrolytes in acetone. Their i.r. mull spectra show that co-ordination to the $[OsCl(dcpe)_2]^+$ moiety shifts ν(CN) of acetonitrile (2 256 cm^{-1} when free) to the slightly higher value of 2 265 cm^{-1}, while the co-ordination of benzonitrile [ν(CN) 2 231 cm^{-1} when free] results in the decreased value of 2 222 cm^{-1}. A *cis* geometry is inferred for (**11**) and (**12**) from the ^{31}P n.m.r. spectra in dichloromethane solution, which show ABCD patterns similar to those of complexes (**7**) and (**8**). The calculated spectral parameters are reported in Table 1. Addition of RCN to the solutions suppresses nitrile dissociation, which is detected by i.r. and u.v.–visible measurements. Moreover, both complexes readily react with carbon monoxide to give *cis*-$[OsCl(CO)(dcpe)_2]^+$.

The corresponding *trans* isomers can be prepared by reaction of *trans*-dichloro species (**1**) with RCN in a boiling 2-methoxyethanol solution of $NaBPh_4$. Yellow solutions are formed, from which crystals of *trans*-$[OsCl(RCN)(dcpe)_2]BPh_4$ [R = Me, (**13**); or Ph, (**14**)] precipitate upon cooling. Complexes (**13**) and (**14**) were characterized by a combination of microanalytical, i.r. and ^{31}P n.m.r. spectroscopic methods (Tables 1—3). The ^{31}P n.m.r. spectra in dichloromethane solution show sharp singlets, in agreement with a *trans* formulation, and the i.r. mull spectra show absorptions at 2 215 (MeCN) and 2 169 cm^{-1} (PhCN) in the nitrile region. The large decrease in nitrile stretching frequency upon co-ordination suggests strong metal–electron back bonding into nitrile π* orbitals, with weakening of the C≡N bond and strengthening of Os–N bond. That this actually occurs is shown by the fact that, contrary to the *cis* ones, *trans* isomers (**13**) and (**14**) are inert towards nitrile dissociation. Organic nitriles are known to exhibit lowered ν(CN) when co-ordinated to low-valent metals which are capable of substantial back bonding: in particular, this is the case of the metal complexes which strongly bind dinitrogen.[24]

N.m.r. evidence suggests that *cis* derivatives (**11**) and (**12**) do not isomerize at room temperature in dichloromethane solution; however, they are quantitatively converted into *trans* isomers (**13**) and (**14**) in 1,2-dichlorobenzene at 140 °C. During isomerization, the solutions become red-brown, which indicates extensive dissociation and formation of five-co-ordinate intermediates.

Finally, the solution behaviour of *trans* dibromo derivative (**3**) at room temperature requires a brief comment. As shown by conductivity, u.v.–visible, and ^{31}P n.m.r. data, complex (**3**) slowly dissociates in dichloromethane solution to give cation (**6**) in equilibrium with *cis* isomer (**4**) [equation (2)]. This appears

$$\begin{tikzcd} trans\text{-}[OsBr_2(dcpe)_2] \arrow[r] & {[OsBr(dcpe)_2]^+ + Br^-} \arrow[d, shift left] \\ & cis\text{-}[OsBr_2(dcpe)_2] \arrow[u, shift left] \end{tikzcd} \qquad (2)$$

to result from *trans* isomer dissociation and consecutive stereoselective *cis* addition of bromide to the five-co-ordinate intermediate. Reaction (2) represents the classical dissociative path for the *cis–trans* isomerization of octahedral complexes. In agreement with it, complex (**3**) reacts with carbon monoxide or acetonitrile (L) in dichloromethane solution at room temperature to give the *cis* adducts *cis*-$[OsBr(L)(dcpe)_2]^+$.

Addition Reactions to $[RuX(dcpe)_2]^+$.—As pointed out above, the five-co-ordinate $[OsX(dcpe)_2]^+$ cations react with halide and neutral ligands (L = CO or RCN) to form the kinetically favoured, *cis* six-co-ordinate adducts. By contrast, the corresponding $[RuX(dcpe)_2]^+$ are reported to give *trans*, six-co-ordinate isomers under similar conditions. As a parallel behaviour is expected for analogous complexes of ruthenium(II) and osmium(II), we have re-examined the reactions of $[RuX(dcpe)_2]^+$ with X^- and L and found that *cis* adducts are formed at low temperature.

Thus reaction of $[RuX(dcpe)_2]BPh_4$ and LiX at -60 °C in acetone produces yellow solutions whose ^{31}P n.m.r. spectra show A_2B_2 patterns suggesting the formation of *cis*-$[RuX_2(dcpe)_2]$ species (Table 1). When the reactions were performed on a preparative scale at -60 °C, *cis*-$[RuCl_2(dcpe)_2]$ (**15**) and *cis*-$[RuBr_2(dcpe)_2]$ (**16**) were isolated in the solid state, while at room temperature quantitative formation of the *trans* derivatives is observed. The solution chemistry of (**15**) and (**16**) is markedly dependent upon the nature of the solvent. The ^{31}P n.m.r. spectra of freshly prepared benzene solutions of both compounds show the doublet of triplets which is typical of *cis*-$[MX_2(L\text{–}L)_2]$ derivatives. With time the *cis*-dibromo species (**16**) quantitatively isomerizes into the more stable *trans* isomer ($t_{\frac{1}{2}}$ *ca.* 1 h), while the dichloro derivative (**15**) is indefinitely stable in benzene solution at room temperature. When complex (**16**) is dissolved in more polar solvents such as dichloromethane a mixture of five-co-ordinate $[RuBr(dcpe)_2]^+$ and *trans*-$[RuBr_2(dcpe)_2]$ is immediately formed, as detected by ^{31}P n.m.r. spectroscopy. Dissolution of dichloro species (**15**) in the same solvent results in precipitation of insoluble *trans*-$[RuCl_2(dcpe)_2]$ within a few minutes.

Low-temperature ^{31}P n.m.r. measurements show that *cis* adducts are initially formed also in the reaction between $[RuX(dcpe)_2]^+$ and the neutral ligands CO and MeCN. When carbon monoxide is bubbled at -60 °C through dichloromethane solutions of $[RuX(dcpe)_2]BPh_4$, the carbonyl complexes *cis*-$[RuX(CO)(dcpe)_2]^+$ [X = Cl, (**17**); or Br, (**18**)] are immediately formed as indicated by the ^{31}P n.m.r. spectra, which are similar to that shown in the Figure. The spectral parameters, calculated assuming an ABCD spin system, are reported in Table 1. When the sample temperature is raised to room temperature, rapid and quantitative formation of *trans*-$[RuX(CO)(dcpe)_2]^+$ occurs. Similarly, dichloromethane solutions of $[RuX(dcpe)_2]BPh_4$ and MeCN (1:2 molar ratio) prepared and kept at -60 °C in an n.m.r. tube show ABCD ^{31}P n.m.r. patterns (Table 1), which indicate formation of *cis*-$[RuCl(MeCN)(dcpe)_2]^+$ (**19**) and *cis*-$[RuBr(MeCN)(dcpe)_2]^+$ (**20**). Once again, raising the sample temperature results in conversion into the thermodynamically more stable isomers.

Conclusion

These results confirm that the chemistry of diphosphine complexes of osmium(II) parallels that of the corresponding ruthenium(II) derivatives, in which the five-co-ordinate $[MX(L\text{–}L)_2]^+$ become favoured with respect to the six-co-ordiate $[MX_2(L\text{–}L)_2]$ when the steric crowding around the metal centre is increased. With both metals the chelate-ring size and the bulkiness of the diphosphine substituents play a determinant role in the formation of unsaturated species. The preference shown by low-spin, five-co-ordinate d^6 complexes $[MX(L\text{–}L)_2]^+$ (M = Ru or Os) for trigonal-bipyramidal geometry appears also confirmed. Moreover, evidence is presented that the addition reactions to the five-co-ordinate d^6 complexes $[MX(dcpe)_2]^+$ (M = Ru or Os) occur stereoselectively with formation of the corresponding six-co-ordinate *cis* adducts, which are the kinetic products. Depending on the temperature, nature of X and L, and solvent, the species *cis*-$[MX_2(dcpe)_2]$ and *cis*-$[MX(L)(dcpe)_2]^+$ can then isomerize more or less easily into the *trans* analogues.

Experimental

All manipulations were performed under argon with use of standard Schlenk-line techniques. Solvents were purified by standard methods. All chemicals used were of reagent grade or comparable purity. The osmium salt $[NH_4][OsCl_6]$ was purchased from Aldrich. The ligand dcpe was prepared by a literature method,[25] as were the complexes $[RuX(dcpe)_2]BPh_4$ (X = Cl or Br).[14] Yields are based on the metal. Infrared and u.v.–visible spectra were recorded on DS 702 G and Uvidec 505 Jasco spectrophotometers, respectively; ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were recorded on a Bruker WP 80 SY spectrometer. Spectra at temperatures lower than 173 K were run in CD_2Cl_2–CHF_2Cl solutions. Positive ^{31}P chemical shifts are downfield from 85% H_3PO_4 as external standard. N.m.r. spectral simulations were performed on an Aspect 2000 computer using PANIC (Bruker Spectrospin AG). Conductance data were measured on a Metrohm E 518 conductivity bridge. Microanalyses were performed by the Microanalytical Laboratory of our Institute.

Analytical and physical data for the complexes are collected in Table 3, selected spectroscopic data in Tables 1 and 2.

trans-$[OsCl_2(dcpe)_2]$ (**1**).—The ligand dcpe (3.38 g, 8.00 mmol) and $[NH_4]_2[OsCl_6]$ (1.00 g, 2.28 mmol) were suspended in 2-methoxyethanol (50 cm^3), and the slurry was heated to reflux. A red precipitate readily formed, which was slowly replaced by cream microcrystals. After 3 h the slurry was cooled and the solid was filtered off, washed twice with 2-methoxyethanol and ethanol, and dried *in vacuo*. Yield 2.32 g, 92%.

cis-$[OsCl_2(dcpe)_2]$ (**2**).—Complex (**1**) (1.11 g, 1.00 mmol) was suspended in 1,2-dichlorobenzene (40 cm^3) and the slurry was refluxed for 3 h, during which time the solid slowly dissolved giving a yellow-orange solution. On cooling to room temperature, microcrystals of the starting product separated, which were filtered off, washed with hexane, and dried *in vacuo* (0.35 g, 32%). The mother-liquors were evaporated to dryness and the solid residue was dissolved in hot benzene (40 cm^3). After halving the solution volume *in vacuo*, hexane (20 cm^3) was added. The resulting cream precipitate was filtered off, washed with hexane, and dried *in vacuo*. Yield 0.72 g, 65%.

trans-[$OsBr_2(dcpe)_2$] (**3**).—Complex (**2**) (1.11 g, 1.00 mmol) was suspended in a 2-methoxyethanol solution (40 cm^3) containing LiBr (1.74 g, 20.0 mmol), and the slurry was refluxed for 1 h. After cooling the pale orange solid was filtered off, washed with ethanol, and dried *in vacuo*. Yield 0.96 g, 80%.

cis-[$OsBr_2(dcpe)_2$] (**4**).—An acetone solution (10 cm^3) of complex (**6**) (0.72 g, 0.50 mmol) was cooled to 0 °C and treated with LiBr (0.43 g, 5.0 mmol) dissolved in acetone (25 cm^3). The resulting solution turned yellow within 1 min and yellow microcrystals appeared. After 1 h the precipitate was filtered off, washed with cold acetone, and dried *in vacuo*. Yield 0.54 g, 90%.

[$OsCl(dcpe)_2$]BPh_4 (**5**).—Complex (**2**) (1.11 g, 1.00 mmol) was stirred in an ethanol solution (30 cm^3) of $NaBPh_4$ (1.03 g, 3.00 mmol) for 2 h. A brown solid slowly formed, which was filtered off, washed with ethanol, and dried *in vacuo*. Recrystallization from acetone–propan-2-ol. Yield 1.01 g, 73%.

[$OsBr(dcpe)_2$]BPh_4 (**6**).—A slurry of complex (**2**) (1.11 g, 1.00 mmol), LiBr (1.74 g, 20.0 mmol), and $NaBPh_4$ (1.03 g, 3.00 mmol) in ethanol (50 cm^3) was refluxed for 2 h, during which a brown solid formed. After cooling, the precipitate was filtered off, washed with ethanol, and dried *in vacuo*. Recrystallization from acetone–propan-2-ol afforded a pure product. Yield 0.86 g, 60%.

cis-[$OsX(CO)(dcpe)_2$]BPh_4 [X = Cl, (**7**); *or* Br, (**8**)].—Complex (**5**) or (**6**) (0.30 mmol: X = Cl, 0.42; Br, 0.43 g) was dissolved in acetone (10 cm^3), and the resulting brown solution was filtered and cooled to 0 °C. Upon treatment with carbon monoxide the solution became colourless within 2 min, and a white solid began to separate. To complete precipitation, propan-2-ol (10 cm^3) was added and the solution volume was reduced. The precipitate was filtered off, washed with propan-2-ol, and dried *in vacuo*. Yields: (**7**), 70; (**8**), 60%.

trans-[$OsX(CO)(dcpe)_2$]BPh_4 [X = Cl, (**9**); *or* Br, (**10**)].—Complex (**1**) or (**3**) (0.30 mmol: X = Cl, 0.33; Br, 0.36 g) was suspended in a 2-methoxyethanol solution (40 cm^3) of $NaBPh_4$ (1.7 g, 5.0 mmol). During reflux under an atmosphere of carbon monoxide (X = Cl, 1.5; Br, 4 h) the starting product was slowly replaced by white microcrystals. After cooling the solid was filtered off, washed with 2-methoxyethanol and ethanol, and dried *in vacuo*. Recrystallization from dichloromethane–propan-2-ol. Yields: (**9**), 70; (**10**), 75%.

cis-[$OsCl(RCN)(dcpe)_2$]BPh_4 [R = Me, (**11**); *or* Ph, (**12**)].—Treatment of complex (**5**) (0.42 g, 0.30 mmol) with an acetone solution (10 cm^3) of RCN (0.60 mmol: R = Me, 31; Ph, 61 μl) afforded a pale yellow solution. After filtering, propan-2-ol was added, and acetone was pumped off until a white precipitate formed, which was filtered off and washed with ethanol. I.r. and ^1H n.m.r. spectra indicate that complex (**11**) crystallizes as a 1:1 acetone solvate. Yields: (**11**), 91; (**12**), 80%.

trans-[$OsCl(RCN)(dcpe)_2$]BPh_4 [R = Me, (**13**); *or* Ph, (**14**)].—Complex (**1**) (0.33 g, 0.30 mmol) was suspended in a 2-methoxyethanol solution (20 cm^3) containing $NaBPh_4$ (1.03 g, 3.00 mmol) and RCN (0.60 mmol: R = Me, 31; Ph, 61 μl). The slurry was refluxed for 1 h, during which time the solid slowly dissolved yielding a yellow solution. The precipitate which separated upon cooling was filtered off, washed with 2-methoxyethanol, and dried *in vacuo*. Recrystallization from dichloromethane–propan-2-ol. Yields: (**13**), 82; (**14**), 70%.

cis-[$RuX_2(dcpe)_2$] [X = Cl, (**15**); *or* Br, (**16**)].—The complex [$RuX(dcpe)_2$]BPh_4 (0.5 mmol: X = Cl, 0.65; Br, 0.67 g) was dissolved in acetone (10 cm^3) and the solution was cooled to −60 °C. Upon addition of a cold acetone solution (15 cm^3) of LiX (5.0 mmol: X = Cl, 0.21; Br, 0.43 g) the solution turned yellow within 2 min. Yellow crystals separated on standing at −25 °C, which were filtered off and washed with cold acetone. Yields: (**15**), 52; (**16**), 60%.

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