Preparation of the Five-co-ordinate Complexes $[PdX_2(PMe_2Ph)_3]$ (X = Cl, Br, or I) and the Crystal and Molecular Structure of Dichlorotris-[dimethylphenylphosphine]palladium

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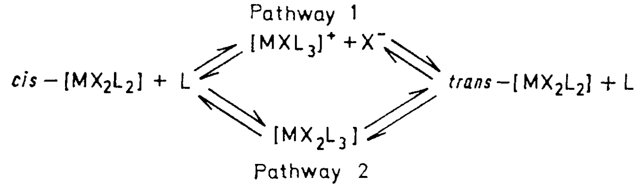
The preparation of tris(dimethylphenylphosphine)dihalogenopalladium(II) complexes and the crystal structure of dichlorotris(dimethylphenylphosphine)palladium(II) are reported. The co-ordination of the palladium ion is distorted square pyramidal with one palladium–chloride bond of 2.96 Å.

The possibility of the five-co-ordinate complex being a tight ion-pair, $[PdX(PMe_2Ph)_3][X]$, is discussed in terms of the u.v.–visible spectra of $[PdX_2(PMe_2Ph)_3]$ and $[PdX(PMe_2Ph)_3][PF_6]$.

Two mechanisms have been suggested for the catalyzed isomerization of square planar complexes, namely a consecutive displacement mechanism [1] (pathway 1) and pseudo-rotation of a five-co-ordinate intermediate [2] (pathway 2):



M = Pt or Pd; X = halide; L = phosphine, arsine, or stibine

Circumstantial evidence for the likelihood of a five-co-ordinate intermediate would be found if such a compound were synthesized and fully characterized. Unlike the chemistry of Ir^I and Rh^I, where numerous compounds having five unidentate ligands in the co-ordination shell are known, the Pd^{II} and Pt^{II} low-spin d^8 compounds exhibiting high co-ordination numbers usually involve polydentate ligands.[3]

Two series of complexes have however been reported which are of considerable importance to those studying the isomerization mechanism. These are $[MX_2L_3]$ complexes, L = 2-phenylisophosphindoline, M = Pt or Pd, and X = halide; [4] and L = dimethylphenylphosphine, for M = Pt, and X = Br, I, or SCN.[5]

Crystal-structure analyses of these compounds are, therefore, important. Unfortunately suitable crystals could not be obtained for the platinum complexes; however, the palladium analogues $[PdX_2(PMe_2Ph)_3]$ (X = Cl, Br, or I) also exist and suitable crystals can be grown.

This study reports the successful synthesis of these palladium complexes and the structure determination of the complex $[PdCl_2(PMe_2Ph)_3]$.

EXPERIMENTAL

Preparation of Tris(dimethylphenylphosphine)dihalogenopalladium(II) (*Halogeno = Chloro, Bromo, or Iodo*).—*trans*-$[PdX_2(PMe_2Ph)_2]$ (X = Cl, Br, or I) was dissolved in the minimum amount of dichloromethane and 1 equivalent of PMe_2Ph was added. The volume was reduced under vacuum to a few ml and diethyl ether was added. The volume was reduced again until the product precipitated out. The precipitate was filtered off and washed with diethyl ether (For X = Cl, Found: C, 47.1; H, 5.65; Cl, 12.4. Calc. for $[PdCl_2(PMe_2Ph)_3]$: C, 48.7; H, 5.6; Cl, 12.0%. For X = Br, Found: C, 42.4; H, 4.95, Br, 24.25. Calc. for $[PdBr_2(PMe_2Ph)_3]$: C, 42.35; H, 4.9; Br, 23.5%. For X = I, Found: C, 37.35; H, 4.35; I, 33.1. Calc. for $[PdI_2(PMe_2Ph)_3]$: C, 37.2; H, 4.3; I, 32.75%).

These compounds can also be prepared in the same manner as that reported for $[PtX_2(PMe_2Ph)_3]$.[5]

Preparation of trans-*Dichlorobis(dimethylphenylphosphine)-palladium*(II).—$K_2[PdCl_4]$ (8 g) was dissolved in water (20 ml) and PMe_2Ph (6.8 ml) in ethanol (80 ml) was added dropwise to the stirred solution. Stirring was continued for 1 h. The brown-yellow precipitate was filtered off, and recrystallized from dichloromethane–ethanol. The yellow crystals were then washed with diethyl ether. *trans*-$[PdBr_2(PMe_2Ph)_2]$ and *trans*-$[PdI_2(PMe_2Ph)_2]$ were prepared according to the reported method [6] except that *trans*-$[PdCl_2(PMe_2Ph)_2]$ was first dissolved in the minimum of dichloromethane before acetone was added, and complexes were recrystallized from dichloromethane–ethanol.

Preparation of Chlorotris(dimethylphenylphosphine)palladium(II) *Hexafluorophosphate*.–*trans*-$[PdCl_2(PMe_2Ph)_2]$ was suspended in acetone and 1 equivalent of PMe_2Ph and excess of $[NH_4][PF_6]$ (dissolved in acetone) were added. A white precipitate ($[NH_4]Cl$) was filtered off and the volume of the filtrate decreased under vacuum. Ethanol was added and the solution cooled. An oil formed initially but on heating and cooling a few times a precipitate formed, which was recrystallized from acetone–ethanol (Found: C, 41.4; H, 4.8; Cl, 5.1. Calc. for $[PdCl(PMe_2Ph)_3][PF_6]$: C, 41.1; H, 4.7; Cl, 5.0%).

Preparation of Tris(dimethylphenylphosphine)halogenopalladium(II) *Hexafluorophosphate* (*Halogeno = Bromo or Iodo*).—A solution of lithium bromide (0.055 g, 1 mol equiv.) in acetone (10 ml) was added to $[PdCl(PMe_2Ph)_3][PF_6]$ (0.4 g) dissolved in acetone (10 ml). The volume was reduced and ethanol was added. The volume was decreased further and the solution cooled. The yellow precipitate was filtered off and washed with water and ethanol (Found: C, 39.5; H, 4.75; Br, 11.2. Calc. for $[PdBr(PMe_2Ph)_3][PF_6]$: C, 38.65; H, 4.45; Br, 10.7%).

$[PdI(PMe_2Ph)_3][PF_6]$ was prepared in the same manner,

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TABLE 1

Fractional atomic co-ordinates and anisotropic thermal parameters (× 10^4)

	x	y	z		x	y	z
Pd	0.250 0	0.132 8(1)	0.250 0	H(11b)	0.001(6)	−0.013(12)	0.105(9)
Cl(1)	0.337 2(2)	0.311 9(3)	0.162 9(2)	H(11c)	0.044(6)	0.099(10)	0.042(9)
Cl(2)	0.336 2(2)	0.150 9(2)	0.527 1(2)	H(12a)	0.120(6)	−0.118(11)	0.020(9)
Cl(3)	0.219 9(2)	0.438 1(3)	−0.261 9(3)	H(12b)	0.205(7)	−0.244(13)	0.127(10)
Cl(4)	0.162 8(2)	0.153 7(3)	−0.199 2(3)	H(12c)	0.105(7)	−0.245(12)	0.086(10)
C(S)	0.248 8(6)	0.268 0(10)	−0.197 5(8)	H(14)	0.212(6)	−0.028(10)	0.499(9)
P(1)	0.140 6(1)	−0.025 0(2)	0.218 7(2)	H(15)	0.193(6)	−0.236(11)	0.660(9)
P(2)	0.164 1(2)	0.317 6(3)	0.305 0(2)	H(16)	0.461(6)	−0.334(10)	0.642(9)
P(3)	0.355 4(1)	−0.040 8(2)	0.241 8(2)	H(17)	−0.047(6)	−0.320(10)	0.422(9)
C(11)	0.045 2(5)	0.054 3(8)	0.135 4(8)	H(18)	0.018(6)	−0.235(10)	0.257(9)
C(12)	0.153 5(5)	−0.171 5(9)	0.106 8(8)	H(21a)	0.261(6)	0.432(11)	0.451(9)
C(13)	0.113 1(5)	−0.118 1(7)	0.361 5(7)	H(21b)	0.197(6)	0.547(11)	0.415(9)
C(14)	0.163 6(5)	−0.112 4(8)	0.482 9(8)	H(21c)	0.267(6)	0.507(10)	0.294(9)
C(15)	0.142 7(6)	−0.188 5(10)	0.591 6(8)	H(22a)	0.082(6)	0.353(10)	0.463(9)
C(16)	0.070 6(7)	−0.270 6(10)	0.572 9(10)	H(22b)	0.148(6)	0.224(11)	0.501(9)
C(17)	0.016 3(6)	−0.273 6(10)	0.454 7(11)	H(22c)	0.068(6)	0.198(11)	0.403(9)
C(18)	0.037 2(6)	−0.198 7(9)	0.347 7(8)	H(24)	−0.008(6)	0.443(11)	0.281(9)
C(21)	0.104 0(5)	0.269 7(8)	0.434 3(8)	H(25)	−0.105(6)	0.494(11)	0.099(9)
C(22)	0.229 1(5)	0.471 6(8)	0.374 5(7)	H(26)	−0.076(6)	0.603(10)	−0.102(9)
C(23)	0.088 6(5)	0.402 8(7)	0.174 6(7)	H(27)	0.053(6)	0.531(11)	−0.155(10)
C(24)	0.012 2(5)	0.456 1(9)	0.195 1(8)	H(28)	0.179(6)	0.417(11)	0.073(10)
C(25)	−0.042 3(6)	0.525 6(11)	0.098 0(10)	H(31a)	0.457(6)	0.124(11)	0.358(10)
C(26)	−0.019 6(7)	0.536 9(9)	−0.026 0(10)	H(31b)	0.508(7)	−0.029(12)	0.306(9)
C(27)	0.054 3(6)	0.482 1(12)	−0.050 1(9)	H(31c)	0.481(6)	0.105(10)	0.199(10)
C(28)	0.109 7(5)	0.412 3(10)	0.048 8(8)	H(32a)	0.372(6)	−0.160(11)	0.450(9)
C(31)	0.359 0(5)	−0.184 5(8)	0.361 7(8)	H(32b)	0.402(7)	−0.243(13)	0.353(10)
C(32)	0.458 9(5)	0.042 5(9)	0.286 6(8)	H(32c)	0.308(7)	−0.244(12)	0.326(10)
C(33)	0.359 8(5)	−0.126 0(9)	0.082 2(7)	H(34)	0.365(6)	−0.346(11)	0.155(9)
C(34)	0.362 0(6)	−0.275 7(9)	0.070 6(9)	H(35)	0.352(6)	−0.452(11)	−0.053(9)
C(35)	0.362 0(6)	−0.335 6(10)	−0.053 9(10)	H(36)	0.343(6)	−0.317(10)	−0.249(9)
C(36)	0.359 1(6)	−0.248 1(13)	−0.162 5(11)	H(37)	0.349(6)	−0.050(11)	−0.247(9)
C(37)	0.357 8(6)	−0.097 7(12)	−0.149 4(9)	H(38)	0.357(6)	0.087(10)	0.016(9)
C(38)	0.357 5(5)	−0.039 1(9)	−0.025 6(9)	H(Sa)	0.284(6)	0.249(10)	−0.089(9)
H(11a)	0.020(6)	0.138(11)	0.212(10)	H(Sb)	0.283(5)	0.215(10)	−0.258(9)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	260(3)	269(3)	388(3)	−8(4)	19(2)	−3(4)
Cl(1)	375(17)	330(14)	415(13)	−46(12)	91(11)	40(11)
Cl(2)	383(13)	426(12)	414(11)	−23(11)	17(9)	−57(10)
Cl(3)	966(29)	727(17)	684(16)	−146(15)	149(19)	−80(16)
Cl(4)	818(21)	807(20)	874(19)	−241(17)	179(16)	−86(17)
C(S)	701(72)	699(67)	454(55)	−3(60)	110(54)	−140(46)
P(1)	296(15)	327(13)	349(12)	−93(10)	35(9)	−50(10)
P(2)	249(16)	280(14)	316(12)	49(12)	−14(10)	−11(11)
P(3)	270(15)	261(12)	398(12)	35(9)	57(9)	23(10)
C(11)	311(53)	415(51)	509(51)	−88(42)	−125(37)	−49(44)
C(12)	481(62)	502(59)	618(56)	−138(44)	225(44)	−293(44)
C(13)	341(53)	228(43)	376(46)	−109(37)	126(37)	−31(36)
C(14)	495(58)	359(52)	408(50)	−46(43)	101(42)	35(41)
C(15)	631(72)	539(60)	520(58)	30(52)	111(49)	66(47)
C(16)	810(85)	386(58)	719(71)	9(57)	390(64)	79(49)
C(17)	443(67)	501(61)	850(77)	−96(49)	203(57)	−40(56)
C(18)	529(68)	422(53)	614(58)	−174(48)	259(49)	−59(46)
C(21)	334(55)	396(50)	499(49)	57(41)	95(40)	−36(40)
C(22)	357(57)	343(49)	502(51)	−20(40)	−67(40)	−122(40)
C(23)	376(61)	235(45)	361(47)	−11(38)	−27(38)	−12(34)
C(24)	208(56)	496(54)	576(57)	109(46)	0(42)	−23(45)
C(25)	485(73)	483(66)	676(72)	22(53)	−10(54)	89(55)
C(26)	679(92)	372(65)	567(67)	−17(54)	−189(53)	55(50)
C(27)	293(70)	705(75)	549(70)	244(60)	−16(51)	177(58)
C(28)	380(63)	678(65)	426(53)	82(49)	−17(44)	93(46)
C(31)	486(58)	352(51)	549(52)	165(41)	22(42)	38(40)
C(32)	210(50)	533(56)	584(53)	111(43)	82(38)	3(45)
C(33)	269(52)	462(54)	454(49)	118(44)	20(37)	−93(46)
C(34)	479(66)	456(61)	634(64)	50(47)	65(46)	−41(49)
C(35)	585(71)	469(63)	747(70)	45(50)	108(53)	−73(56)
C(36)	435(69)	842(84)	749(75)	44(58)	38(53)	−415(68)
C(37)	537(71)	920(88)	483(59)	247(57)	126(46)	22(55)
C(38)	314(57)	524(58)	547(59)	54(43)	50(41)	59(49)

except that NaI was used (Found: C, 36.85; H, 4.25; I, 14.3. Calc. for $[PdI(PMe_2Ph)_3][PF_6]$: C, 36.35; H, 4.2; I, 16.0%).

U.v.–Visible Spectra.—Table 4 lists the u.v.–visible peaks for $[MX_2L_2]$, $[MX_2L_3]$, and $[MXL_3][PF_6]$ (M = Pt or Pd, L = PMe_2Ph, and X = Cl, Br, or I).

Crystals.—Large deep orange crystals were grown from a $[PdCl_2(PMe_2Ph)_3]$ solution in mixed ether–dichloromethane at 0 °C.

Crystal Data.—$C_{24}H_{33}Cl_2P_3Pd{\cdot}CH_2Cl_2$, $M = 676.7$, Monoclinic, $a = 16.01(2)$, $b = 9.28(1)$, $c = 10.27(1)$ Å, $\beta = 99.5(1)°$, $D_m = 1.50(2)$ g cm^{-3} (by flotation), $Z = 2$, $D_c =$

1.492 g cm^{-3}, $F(000) = 688$. Space group Pn ($h0l$, $h + l = 2n$), Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ (Mo-K_α) = 11.3 cm^{-1}. A small crystal, cut to roughly cubical shape, with edge lengths of *ca.* 0.2 mm, was used for cell-parameter determination and for the collection of intensity data. A Philips PW 1 100 four-circle diffractometer, equipped with a graphite monochromator, was used and the cell parameters obtained from a least-squares refinement of the 2θ values of 25 high-angle reflections. The ω—2θ scan mode was used during data collection with a scan rate of 0.04° s^{-1} in θ and a constant scan width of 1.2° θ. The background on each side of a reflection was counted for half the total scanning time. A unique set of reflections in the range $3 < \theta < 22°$ was measured. Three reference reflections were measured at regular intervals and both their optimum positions and intensities stayed constant during data collection. Of the 1 672 independent reflections, 132 were regarded as unobserved with $I < 2\sigma(I)$. Lorentz and polarization corrections were applied but no corrections were made for absorption.

Structure Solution and Refinement.—The systematic absences observed fulfil the requirements of space groups $P2/n$ and Pn. The choice of the non-centrosymmetric space group Pn was indicated by the expected geometry of the molecule and confirmed by the successful structure analysis. The structure was solved by the application of the heavy-atom method. The y co-ordinate of the Pd atom was obtained from the Harker vector and the x and z co-ordinates (which are arbitrary) were both chosen to be 1/4. The position of the Cl and P atoms bonded to the Pd atom were derived from the Pd–Cl and Pd–P vectors. Since the Cl and P atoms could not be distinguished using peak heights from the Patterson map, all five were included as Cl atoms in a Fourier map phased by their contributions. As two pairs of these lighter atoms are related by a pseudo-twofold rotation axis at 1/4, y, 1/4 (the Pd atom being placed at 1/4, 0.13, 1/4) the contribution of the remaining atom did not reduce the induced pseudo-symmetry far enough to allow selection of the correct positions of the remaining atoms. Omission of one atom from each pair in the calculation of structure factors had the required effect, however, and all the Cl and P atoms could then be placed and identified. The positions of the carbon atoms were found in a subsequent Fourier synthesis.

Refinement was by full-matrix least-squares methods minimizing the quantity $\Sigma w(|F_o| - |F_c|)^2$. The R index was reduced to 0.055 on isotropic refinement and to 0.034 on on anisotropic refinement. All the hydrogen positions were found from a difference electron-density synthesis at this stage. The isotropic temperature factors for the hydrogen atoms were kept constant at $U = 0.05$ and the positional parameters were refined together with all other atomic parameters. An individual weight, $w = 1/\sigma^2$ for each reflection, was used for the last cycles. The R indices quoted are $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R' = [\Sigma w(\Delta F)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$, with unobserved reflections excluded. The final values were R 0.025 and R' 0.024. Scattering factors were taken from ref. 7 except for hydrogen, which was taken from ref. 8. All

TABLE 2

Bond lengths (Å) with estimated standard deviations in parentheses

Pd–P(1)	2.265(3)	P(2)–C(22)	1.841(8)
Pd–P(2)	2.326(3)	P(2)–C(23)	1.829(7)
Pd–P(3)	2.344(3)	C(23)–C(24)	1.367(12)
Pd–Cl(1)	2.434(3)	C(24)–C(25)	1.373(12)
Pd–Cl(2)	2.956(3)	C(36)–C(37)	1.403(16)
C(S)–Cl(3)	1.745(10)	C(37)–C(38)	1.383(13)
C(S)–Cl(4)	1.736(10)	C(25)–C(26)	1.385(15)
P(1)–C(11)	1.782(8)	C(26)–C(27)	1.347(16)
P(1)–C(12)	1.814(9)	C(27)–C(28)	1.393(12)
P(1)–C(13)	1.818(8)	C(28)–C(23)	1.392(12)
C(13)–C(14)	1.370(10)	P(3)–C(31)	1.810(8)
C(14)–C(15)	1.407(12)	P(3)–C(32)	1.818(8)
C(15)–C(16)	1.370(14)	P(3)–C(33)	1.832(8)
C(16)–C(17)	1.372(14)	C(33)–C(34)	1.396(12)
C(17)–C(18)	1.387(14)	C(34)–C(35)	1.394(14)
C(18)–C(13)	1.415(11)	C(35)–C(36)	1.374(15)
P(2)–C(21)	1.819(9)	C(38)–C(33)	1.365(12)

TABLE 3

Bond angles (°) with estimated standard deviations in parentheses

Around Pd

	P(2)	P(3)	Cl(1)	Cl(2)
P(1)	92.2(2)	95.4(2)	150.0(2)	113.6(2)
P(2)		166.8(2)	89.1(2)	85.7(2)
P(3)			89.8(2)	81.3(2)
Cl(1)				96.4(2)

Around P(1)

	C(11)	C(12)	C(13)
Pd	112.4(3)	114.2(3)	118.5(3)
C(11)		100.6(4)	106.4(4)
C(12)			102.8(4)

Around P(2)

	C(21)	C(22)	C(23)
Pd	113.7(3)	110.4(3)	119.1(3)
C(21)		103.8(4)	106.0(4)
C(22)			102.2(4)

Around P(3)

	C(31)	C(32)	C(33)
Pd	115.1(3)	109.3(3)	117.6(3)
C(31)		102.5(4)	106.8(4)
C(32)			104.0(4)

P(1)–C(13)–C(14)	122.1(6)	C(25)–C(26)–C(27)	120.7(9)
P(1)–C(13)–C(18)	119.3(5)	C(26)–C(27)–C(28)	121.0(9)
C(18)–C(13)–C(14)	118.7(7)	C(27)–C(28)–C(23)	118.9(8)
C(13)–C(14)–C(15)	121.4(7)	P(3)–C(33)–C(34)	120.8(6)
C(14)–C(15)–C(16)	118.2(8)	P(3)–C(33)–C(38)	118.1(7)
C(13)–C(16)–C(17)	122.1(9)	C(38)–C(33)–C(34)	121.1(8)
C(16)–C(17)–C(18)	119.4(9)	C(33)–C(34)–C(35)	118.6(8)
C(17)–C(18)–C(13)	120.1(7)	C(34)–C(35)–C(36)	120.2(9)
P(2)–C(23)–C(24)	122.9(6)	C(35)–C(36)–C(37)	120.6(9)
P(2)–C(23)–C(28)	118.3(6)	C(36)–C(37)–C(38)	118.8(9)
C(28)–C(23)–C(24)	118.8(7)	C(37)–C(38)–C(33)	120.7(8)
C(23)–C(24)–C(25)	122.3(8)	Cl(3)–C(S)–Cl(4)	112.9(5)
C(24)–C(25)–C(26)	118.3(9)		

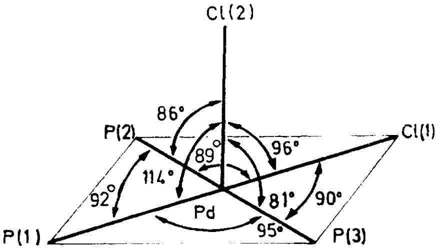

FIGURE 1 A diagram of the structure showing the numbering system and a few angles of interest

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calculations were done with the '*X*-Ray system' of programs.[9] Stereoscopic drawings were obtained by the thermal ellipsoid plotting program ORTEP.[10] Atomic co-ordinates and temperature factors are listed in Table 1, and bond lengths and angles in Tables 2 and 3. The atom numbering of the Cl and P atoms is shown in Figure 1, the carbon atoms being numbered according to the phosphine group to which they are bonded and the hydrogen atoms are numbered according to the carbon atoms to which they are bonded. Observed and calculated structure factors are listed in supplementary Publication No. SUP 21939 (23 pp., microfiche).*

The molecular structure of the complex is illustrated by the stereopair in Figure 2 whilst the contents of the unit cell and the crystal packing are shown in Figure 3.

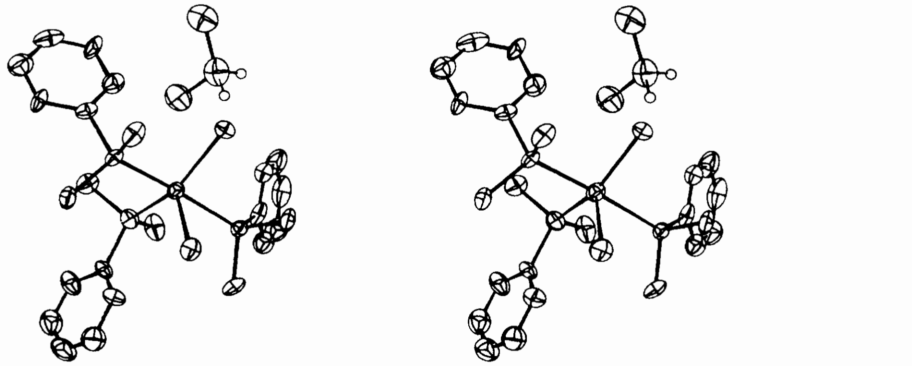

FIGURE 2 Stereoscopic drawing of the complex showing the thermal ellipsoids at the 50% probability level

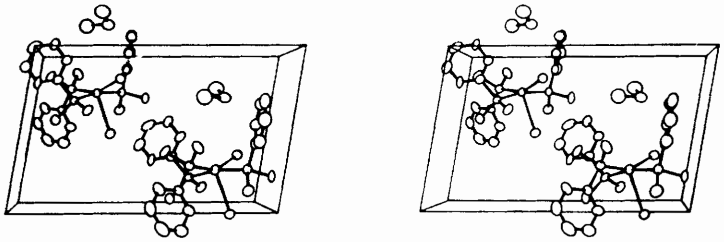

FIGURE 3 Stereoscopic view down the *b* axis of the contents of the unit cell. The *a* axis is horizontal and the *c* axis vertical

TABLE 4

U.v.–visible bands for $[MX_2L_2]$, $[MX_2L_3]$, and $[MXL_3]^+ [PF_6]^-$ (M = Pt or Pd, X = Cl, Br, or I, L = PMe_2Ph) in nm [a, b]

M	X	$[MX_2L_2]$ [c]	Colour	$[MX_2L_3]$ [c]	Colour	$[MXL_3][PF_6]$ [c]	Colour
Pt	Cl	*cis* 265 (sh), 272 (sh), 320 (sh)	White	350	Yellow	Characterless spectrum	White
		trans 252, 264	Yellow				
Pt	Br	*cis* 265 (sh), 272 (sh), 300 (sh)	White	375 (1 440)	Yellow	Characterless spectrum	White
		trans 280	Pale yellow				
Pt	I	*cis* 360	Pale yellow	445 (3 014)	Pale orange	320 (sh)	Yellow
		trans 292, 310 (sh), 330	Yellow				
Pd	Cl	*trans* 242 (sh), 320	Yellow	410 (sh) [d] (1 020)	Orange	323 [d] (25 950)	Yellow
Pd	Br	*trans* 262, 347	Pale orange	444 [d] (1 190) 320 (sh),[d] (11 400)	Red	292 [d] (18 370)	Yellow
Pd	I	*trans* 240 (sh), 263, 283 (sh), 343, 400	Orange	500 [d] (2 360), 397 [d] (4 160)	Dark red	395 [d] (3 838), 306 [d] (21 730)	Orange

[a] Wavelength in nm with extinction coefficients (ε/l mol^{-1} cm^{-1}) in parentheses: sh = shoulder. [b] 20% CH_2Cl_2/80% pentane solution unless stated otherwise. [c] L = PMe_2Ph. [d] CH_2Cl_2 solution. For $[PdX_2L_3]$ a drop of L was added in order to push the equilibrium $[PdX_2L_2] + L \rightleftharpoons [PdX_2L_3]$ over to the right-hand side.

DISCUSSION

The most striking feature in the structural data is the difference in the two Pd–Cl bond lengths [Pd–Cl(1) 2.43 and Pd–Cl(2) 2.96 Å]. The long Pd–Cl(2) bond length raises the question of whether this is a four- or five-co-ordinate complex, since the sum of the ionic radii of Pd and Cl is 2.45 Å. From the very different u.v.–visible spectra listed in Table 4 it is evident that $[MX_2(PMe_2Ph)_3]$ is not the same as the cationic complex $[MX(PMe_2Ph)_3]$-$[PF_6]$, and this changes the question to whether the $[MX_2L_3]$ complexes are five-co-ordinate or a tight ion-pair.

Traditionally ion-pairs have been defined as outer-sphere complexes.[11] The counter ion of the ion-pair only has an effect on the metal-to-ligand (M $\longrightarrow$ L) or

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

ligand-to-metal (L $\longrightarrow$ M) charge-transfer bands and only to the extent that these bands are shifted slightly to longer wavelengths.[11] From Table 4 it can be seen that in going from $[MXL_3]^+$ to $[MX_2L_3]$, there is no shift in the u.v. spectra, but new bands appear in the visible region. The extinction coefficients of these bands vary between 1 000 and 4 000, which is very high for *d–d* transitions. Venanzi *et al.*,[12,13] however, found similar bands for d^6-, d^7-, and d^8-five-co-ordinate metal complexes but nevertheless assigned these bands to *d–d* transitions. Furthermore, in accordance with the spectrochemical series these $[MX_2L_3]$ low-energy bands move to higher energy in the order I < Br < Cl and Pd < Pt.[13] This drastic difference in u.v.–visible spectra between $[MXL_3]^+$ and $[MX_2L_3]$ and the similarity of the $[MX_2L_3]$ spectra with those reported by Venanzi is most probably not caused by ion pairing in the traditional sense but rather by five-co-ordination.

One should however keep in mind that ion-pairs of four-co-ordinate complexes are rather novel. These ion-pairs will most probably not obey the outer-sphere complex definition since the d^8 systems are co-ordinatively unsaturated, and therefore the possibility exists that the counter ion can enter the co-ordination sphere.

It is noteworthy that the colours of the solid $[MX_2L_3]$ complexes are the same as the colours of their solution, (this colour being considerably different from that of the equivalent $[MXL_3]^+$) which suggests roughly the same stereochemical arrangement in the solid and solution.

The geometry of the $[PdCl_2(PMe_2Ph)_3]$ co-ordination polyhedron is intermediate between a square pyramid (SP) and a trigonal bipyramid (TBP). The mean deviation of the bond angles is 9.5° from a square pyramid with the Pd in the base plane, and 9.7° from a trigonal bipyramid with trigonal symmetry.

Gillespie[14] has very successfully explained the geometry of five-co-ordinate d^7-, d^8-, and d^9-complexes by treating the interactions between the ligand electrons and non-bonding *d* electrons by means of the valence shell electron-pair repulsion theory (VSEPR).

Most d^7-, d^8-, and d^9-five-co-ordinate complexes studied crystallographically so far have a square-pyramidal structure with a long axial bond in accordance with the prolate ellipsoidal *d*-shell postulation of Gillespie. For the trigonal bipyramidal structure of $[PdCl_2(PMe_2Ph)_3]$ Gillespie predicts that the two Pd–Cl bonds should both be in the equatorial plane and should be equivalent in length. The very different bond lengths of 2.434 (3) and 2.956 (3) Å for Pd–Cl(1) and Pd–Cl(2) found in this complex therefore suggest that its structure should be viewed as a distorted square-pyramidal arrangement with a long axial bond [Pd–Cl(2)], and the distortion is due to the steric requirements of the bulky phosphine groups.[15]

A similar lengthening of the apical bond in a distorted square pyramidal co-ordination was observed in the crystal structure of dibromotris(2-phenylisophosphindoline)palladium(II)[4] where the apical and equatorial Pd–Br bond lengths had values of 2.93 and 2.52 Å.

The distortion from square-pyramidal geometry in the $[PdCl_2(PMe_2Ph)_3]$ complex is illustrated by the deviations from planarity of the atoms in the basal plane. The magnitude of the distortion is reflected in the values of the angles in Figure 1. P(1) and Cl(1) are displaced away from, and P(2) and P(3) displaced towards, Cl(2). The deviations of atoms Pd, Cl(1), P(1), (P2), and P(3) from their mean plane are 0.140, −0.462, −0.467, 0.405, and 0.384 Å respectively.

The bond lengths of 2.326(3) and 2.344(3) Å observed for Pd–P(2) and Pd–P(3) are similar to the values 2.326 (7), 2.333(8), and 2.333(7) Å observed for the comparable Pd–P distances in the dimer *trans*-$[\{PdI_2(PMe_2Ph)_2\}_2]$.[16,17] P(1) is *trans* to Cl(1), and whether the *trans*-effect can account for the shortening of the Pd–P(1) distance to a value of 2.265(3) Å is still to be proved. The magnitude of this shortening (0.07 Å) is of the same order as that observed in dibromotris(2-phenylisophosphindoline)palladium(II).[4]

The values observed for the other bond lengths and angles are typical for this type of complex.[18]

The molecule of dichloromethane present as solvent of crystallization is not bonded to the palladium atom since the shortest Pd–Cl(3) distance is 4.598(5) Å.

Conclusion.—One of the mechanisms of the rearrangement of five-co-ordinate systems is considered to be the Berry pseudo-rotation mechanism,[19] which is basically an equilibrium between the SP and TBP geometries. The fact that the $[PdCl_2(PMe_2Ph)_3]$ geometry is intermediate between SP and TBP makes this complex a very likely candidate for pseudo-rotation and therefore increases the possibility for it to be a five-co-ordinate intermediate in the pseudo-rotation mechanism of square-planar complexes.

[6/114 *Received*, 19*th January*, 1976]

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