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CRYSTAL AND MOLECULAR STRUCTURE, AND ^{31}P N.M.R. CHARACTERISTICS OF DI-μ-CHLORODI(PROPIONYL)BIS(DIMETHYLPHENYLPHOSPHINE)-DIPLATINUM(II). TRANS-INFLUENCE OF LIGANDS IN BINUCLEAR COMPLEXES

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Summary

The ^{31}P n.m.r. spectra of the *cis* and *trans* isomers of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ reveal $^1J(Pt\text{-}P)$ coupling constants of *ca* 5400 Hz. The crystal structure of the *trans* isomer has been determined by *X*-ray diffraction methods. The Pt-P and Pt-C bond lengths are 2.209(1) and 1.972(5) Å. The μ-Pt-Cl distances, 2.498(1) Å *trans* to COEt and 2.393(1) Å *trans* to PMe_2Ph, suggest that, relative to phosphine, σ-carbon donor ligands exert a greater *trans*-influence in binuclear complexes than they do in mononuclear platinum(II) derivatives.

Introduction

Unusually large $^1J(Pt\text{-}P)$ coupling constants in halogen-bridged binuclear complexes of platinum(II) have recently been reported by several authors [1-3]. In view of the proposed correlation between Pt-P coupling constants and bond lengths [4] we have undertaken an investigation of the ^{31}P n.m.r. spectrum and solid state structure of trans-$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$, for which $^{1}J(Pt\text{-}P)$ is exceptionally large, even in relation to other halogen-bridged platinum(II) complexes. The results of this work are also pertinent to any consideration of the cis- and trans-influence of ligands in such systems. Up till now the extensive discussion of these topics in platinum chemistry has focussed on mononuclear species [5-7]; the extent to which this discussion is directly applicable to binuclear complexes merits consideration.

Results and Discussion

The title compound was prepared smoothly and in high yield from the reaction between cis-$[PtCl_2(CO)(PMe_2Ph)]$ and Et_2Hg [8]. The colourless crystals are stable to air and moisture, and dissolve readily in most organic solvents. The ^{31}P n.m.r. spectra of the solutions reveal the presence of cis and trans isomers. The ratio of the concentrations of the two isomers is dependent on the solvent, changing from 1:3 in $CDCl_3$ and CD_2Cl_2 to 1:7 in C_7D_8. Since the major isomer is favoured by the less polar solvent, we tentatively assign it a trans configuration [1]. Recrystallisation from methylene chloride/ether produces crystals of the trans complex.

There now appears to be considerable evidence that complexes of the type $[Pt_2L_2(\mu\text{-}X)_2Y_2]$ (L = tertiary phosphine, X = halogen, and Y = halogen, alkyl, aryl, acyl, or aroyl) exist in solution as mixtures of cis and trans isomers [1,2,8b,9]. In general, trans isomers predominate for the tetrahalide complexes whereas cis isomers are more common when Y = alkyl or aryl. Thus, in the case of the methyl complex $[Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2]$ only the cis isomer was observed [10]. Interconversion between the two

TABLE 1

^{31}P N.M.R. CHEMICAL SHIFTS (P.P.M) AND COUPLING CONSTANTS (HZ) FOR $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ AT -40°C

SOLVENT	cis-Isomer				trans-Isomer			
	δP^a	$^1J(Pt\text{-}P)$	$^3J(Pt\text{-}P)$	$^4J(Pt\text{-}P)$	δP^a	$^1J(Pt\text{-}P)$	$^3J(Pt\text{-}P)$	$^4J(P\text{-}P)$
CD_2Cl_2	-12.2	5445	±11	<±1	-11.7	5316	-5.6	±2.9
$CDCl_3$	-11.6	5424			-11.5	5310		
C_7D_8	-11.2	5538			-11.6	5403		

[a] Positive is downfield from external H_3PO_4.

isomers occurs readily in solution for most, and possibly for all, of these bridged complexes. Thus, the ratios of cis to trans isomers adjust rapidly in different solvents, and usually only one isomer is obtained on crystallisation. The intermolecular scrambling of mixed compounds of this type is also rapid [3,11]. Moreover, broadening of some of the room-temperature n.m.r. signals of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$, and also of related compounds [9], suggests that the isomerisation processes are still rapid on the n.m.r. time scale.

^{31}P N.M.R. Spectra

Chemical shifts and coupling constants for cis- and trans-$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ are presented in Table 1. Additionally, the $^2J(Pt\text{-}Pt)$ coupling constant at -70°C in CD_2Cl_2 was identified for the more abundant trans-isomer at ±152Hz. The most remarkable features of the spectra are the $^1J(Pt\text{-}P)$ coupling constants which are ca 5400 Hz in both the cis and trans isomers. The values show some solvent dependence, but in the same solvent the cis compound displays a coupling 115 - 135 Hz greater than the trans form.

The $^1J(Pt\text{-}P)$ couplings found here are at the upper end of the range typical of halogen-bridged binuclear species containing tertiary organophosphines (ca 3900 - 5500 Hz) [2-3], and are nearly double those found in mononuclear cis-dichloroplatinum(II)-phosphine complexes [e.g. 2754 - 3720 Hz for $^1J(Pt\text{-}PEt_3)$ in cis-$[PtCl_2(PEt_3)L]$ complexes, L = Cl, phosphine, phosphite, and various carbon-donor ligands [12]]. The values do not depend on the halogen bridges only, since those for tetrahalides are considerably lower than the corresponding coupling constants for their dichlorobis(organo)-counterparts. For example, for trans-$[Pt_2Cl_4(PMe_2Ph)_2]$ $^1J(Pt\text{-}P)$ is 3931 Hz [3]. It has been suggested that the high trans-influence of terminal organic groups could cause bridge weakening and thus affect the values of ^1J(Pt-P) [2]. Alternatively, these variations may reflect the differing cis-influence of terminal organo and chloro ligands. This view is consistent with the near equality of the ^1J(Pt-P) coupling constants for cis and trans isomers in Table 1. Moreover, it has been observed that in mononuclear complexes changes in the nature of one of the ligands cis to phosphine may lead to variations in ^1J(Pt-P) of ca 1000 Hz [12].

Crystal and Molecular Structure of trans-$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$

The crystals are built from discrete binuclear molecules separated by normal van der Waals contacts. Selected bond lengths and angles are presented in Table 2 and a view of the molecule is shown in the Figure.

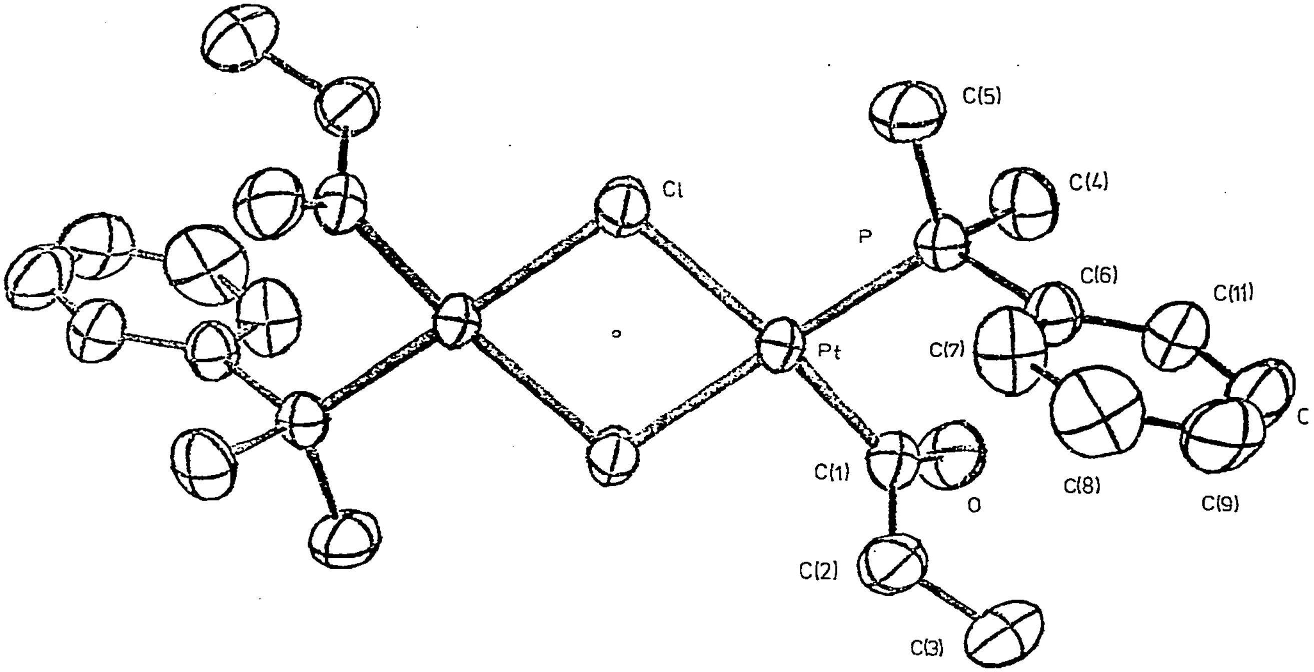

Figure A view of the molecular structure showing the atomic numbering scheme. Hydrogen atoms are omitted and the thermal ellipsoids display 50% probability. The small circle represents a crystallographic centre of symmetry.

TABLE 2

SELECTED INTERATOMIC DISTANCES AND ANGLES

Bond Lengths (Å)

Pt-Cl	2.498(1)	C(1)-C(2)	1.526(7)
Pt-Cl'	2.393(1)	C(2)-C(3)	1.501(10)
Pt-P	2.209(1)	C(6)-C(7)	1.389(8)
Pt-C(1)	1.972(5)	C(6)-C(11)	1.375(8)
P-C(4)	1.799(6)	C(7)-C(8)	1.398(10)
P-C(5)	1.800(6)	C(8)-C(9)	1.351(12)
P-C(6)	1.818(5)	C(9)-C(10)	1.379(11)
O-C(1)	1.208(7)	C(10)-C(11)	1.383(8)

Bond angles (°)

Cl-Pt-Cl'	83.7(1)	Pt-C(1)-O	123.2(4)
Cl-Pt-P	97.4(1)	Pt-C(1)-C(2)	115.3(4)
Cl-Pt-C(1)	174.9(1)	O-C(1)-C(2)	121.3(5)
Cl'-Pt-P	178.8(1)	C(1)-C(2)-C(3)	113.8(5)
Cl'-Pt-C(1)	91.2(1)	P-C(6)-C(7)	116.7(4)
P-Pt-C(1)	87.6(1)	P-C(6)-C(11)	123.1(4)
Pt-Cl-Pt'	96.3(1)	C(7)-C(6)-C(11)	120.2(5)
Pt-P-C(4)	113.6(2)	C(6)-C(7)-C(8)	118.0(6)
Pt-P-C(5)	113.9(3)	C(7)-C(8)-C(9)	122.7(7)
Pt-P-C(6)	112.3(2)	C(8)-C(9)-C(10)	118.1(6)
C(4)-P-C(5)	104.3(3)	C(9)-C(10)-C(11)	121.4(7)
C(4)-P-C(6)	106.9(3)	C(10)-C(11)-C(6)	119.6(6)
C(5)-P-C(6)	105.0(3)		

Each molecule is constrained to exact $\underline{C}_i$ symmetry. This implies that the Pt_2Cl_2 bridging unit is exactly planar. Each metal atom has a slightly distorted square-planar co-ordination, with the two planes sharing a common edge so that the two platinum and six ligand-donor atoms all lie within 0.013Å of their common plane. Bond lengths and angles within the PMe_2Ph ligand are unexceptional. The conformation adopted by this ligand is such that methyl carbon C(5) lies close to the metal co-ordination plane, and the phenyl ring plane passes near C(4), as shown by respective Cl-Pt-P-C(5) and C(4)-P-C(6)-C(11) torsion angles of -9.6(3) and 5.2(5)°. Bond lengths and valency angles within the propionyl ligand are also normal. The P-Pt-C(1)-O and Pt-C(1)-C(2)-C(3) torsion angles are 72.7(4) and 161.1(5)°. This conformation leads to a somewhat short intramolecular Pt...H contact, involving a hydrogen atom attached to C(2), of 2.8 Å.

The metal-ligand bond lengths display two points of interest. First, despite the large ^1J(Pt-P) coupling constant, the Pt-P distance [2.209(1)Å] is only slightly shorter than the run of comparable Pt-P(trans to Cl) bond lengths [2.21 - 2.28Å] in mononuclear complexes containing alkyl- or aryl- substituted tertiary phosphines [12,13]. Indeed, it is equal, to within experimental error, to the shortest such value: 2.215(4)Å in the anion $[PtCl_3(PEt_3)]^-$. However, this anion displays a $^1J(Pt-PEt_3)$ coupling constant of 3704Hz [14], some 30% smaller than that for trans-$[Pt_2(\mu-Cl)_2(COEt)_2(PMe_2Ph)_2]$. These results suggest that the proposed correlation between Pt-P coupling constants and bond lengths [4] breaks down if the complexes compared differ too greatly. Second, the Pt-(μ-Cl) distances [2.393(2) and 2.498(1)Å] differ substantially and are consistent with σ-propionyl exerting a much greater trans-influence than phosphine on the bridge bonds. This result is surprising, since

TABLE 3

BOND LENGTHS (Å) in trans-[$Pt_2X_2(\mu\text{-}Cl)_2Y_2$] COMPLEXES

COMPLEX	X	Y	Pt-X	Pt-Y	Pt-Cl (trans to X)	Pt-Cl (trans to Y)	Ref.
$[Pt_2Cl_6]^{2-}$	Cl	Cl	2.265	2.279	2.318	2.330	15
	Cl	Cl	2.280	2.268	2.337	2.327	
$Pt_2Cl_4\{CH_2C(OMe)_2\}_2$	σ-C	Cl	2.09(3)	2.264(8)	-	2.324(7)	16
$Pt_2Cl_4(C_5H_8)_2$	π-C=C	Cl	2.20(2)	2.264(6)	2.349(5)	2.320(5)	17
$Pt_2Cl_4(C_7H_{12})_2$	π-C=C	Cl	2.12(2)	2.257(6)	2.362(6)	2.328(6)	17
$Pt_2Cl_4(C_7H_{12})_2$	π-C=C	Cl	2.07-2.25(2)	2.273(5)	2.382(5)	2.342(5)	18
$Pt_2Cl_4(PPr^n_3)_2$	PPr^n_3	Cl	2.230(9)	2.279(9)	2.425(8)	2.315(8)	19
$Pt_2Cl_4(AsMe_3)_2$	$AsMe_3$	Cl	2.308(2)	2.268(6)	2.394(6)	2.312(5)	20
$Pt_2Cl_2(C_{11}H_{15}O)_2$	σ-C	π-C=C	2.07	2.11-2.23	2.51	2.34	21
$Pt_2Cl_2(C_{12}H_9N_2)_2$	σ-C	N	1.94(2)	1.98(2)	2.460(5)	2.326(6)	22
$Pt_2Cl_2(Bu^t_2PCH_2CMe_2CH_2)_2$	σ-C	Bu^t_2P-	2.06	2.200	2.460	2.402	23
$Pt_2Cl_2(COEt)_2(PMe_2Ph)_2$	σ-C	PMe_2Ph	1.972(5)	2.209(1)	2.498(1)	2.393(1)	Present work

Pt-Cl distances in mononuclear complexes, 2.36 - 2.39Å *trans* to tertiary phosphine and 2.40 - 2.42Å *trans* to σ-carbon donors [6], suggest that the *trans*-influence of phosphines is only slightly less than that of σ-carbon donor ligands.

The generality of these conclusions is confirmed by a survey of bond lengths in *trans*-$[Pt_2X_2(\mu\text{-}Cl)_2Y_2]$ molecules (Table 3) [15-23]. In these molecules each bridging chlorine atom participates in two Pt-Cl bonds which are *trans* to different terminal ligands. The data in Table 3 do not indicate any significant relationship between the lengths of the two Pt-(μ-Cl) bonds formed by a given chlorine atom. Instead, each Pt-(μ-Cl) distance appears to reflect the influence of the *trans*-terminal ligand, according to the series $Cl < \pi\text{-}C{=}C < AsMe_3 \leq PR_3 < \sigma\text{-}C$. Apart from the previously noted disparity between the relative magnitude of the *trans*-influence of PR_3 and σ-C, this series is identical with that derived from mononuclear complexes [5-7]. The terminal platinum-ligand bonds in Table 3, including those to tertiary phosphine, are *on average ca* 0.03Å shorter than corresponding bonds *trans* to chlorine in mononuclear complexes, while the Pt-(μ-Cl) bonds are typically *ca* 0.03Å longer than Pt-Cl bonds in mononuclear complexes *trans* to similar ligands. These features seem compatible with current views of *trans*-influence [5-7].

Experimental

The experimental and computational procedures used in the analysis were all of standard type and have already been described in detail [24].

Crystal Data $C_{22}H_{32}Cl_2O_2P_2Pt_2$, M.W. = 851.5. Triclinic, space group $P\bar{1}$, a = 7.839(1), b = 8.531(1), c = 11.892(1)Å, α = 73.88(1), β = 73.19(1), γ = 65.05(1)°, U = 679.06Å^3, Z = 1, D_c = 2.082 g cm^{-3}, $F(000)$ = 400. Molecular symmetry $\bar{1}$-C_i. Mo-K_α radiation, λ = 0.71069Å, μ(Mo-K_α) = 107.2 cm^{-1}.

TABLE 4

(a) FRACTIONAL COORDINATES (x10^4)

Atom	*x*	*y*	*z*
Pt	544.5(2)	-1607.2(2)	1349.2(1)
Cl	1561(2)	800(2)	-1(1)
P	2468(2)	-2397(2)	2613(1)
O	-1465(7)	-3321(6)	3303(4)
C(1)	-431(7)	-3446(6)	2330(4)
C(2)	73(10)	-4998(8)	1735(6)
C(3)	-103(14)	-6608(9)	2598(8)
C(4)	1231(10)	-1829(8)	4060(5)
C(5)	4232(10)	-1395(9)	2131(7)
C(6)	3846(7)	-4749(6)	2852(5)
C(7)	4995(10)	-5464(9)	1847(6)
C(8)	6027(10)	-7277(10)	1999(8)
C(9)	5946(11)	-8345(8)	3074(8)
C(10)	4777(11)	-7604(8)	4055(7)
C(11)	3738(9)	-5815(7)	3953(5)

Measurements The unit cell dimensions and the integrated intensities of all independent reflexions with $\theta(\text{Mo-}K_\alpha) \leq 30°$ were measured on an Enraf-Nonius CAD-4F diffractometer. The analysis was carried out with 3194 structure amplitudes which had been corrected for Lorentz, polarisation, and absorption effects. Transmission factors (on F^2) were 0.17 - 0.60.

(b) ANISOTROPIC TEMPERATURE FACTORS

	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	35.0(1)	36.2(1)	32.0(1)	-10.5(1)	-4.0(1)	-2.1(1)
Cl	55.0(6)	57.6(7)	46.4(6)	-29.8(6)	-18.8(5)	10.4(5)
P	42.4(6)	39.9(5)	39.5(6)	-10.7(5)	-9.7(5)	-4.8(5)
O	76(3)	78(3)	46(2)	-41(2)	8(2)	-10(2)
C(1)	44(2)	47(2)	40(2)	-17(2)	-8(2)	1(2)
C(2)	81(4)	58(3)	52(3)	-34(3)	-8(3)	-9(2)
C(3)	135(7)	60(4)	95(6)	-49(4)	-35(5)	2(4)
C(4)	75(4)	63(3)	45(3)	-13(3)	-9(3)	-22(2)
C(5)	67(4)	66(4)	91(5)	-35(3)	-32(3)	4(3)
C(6)	45(2)	38(2)	45(2)	-6(2)	-13(2)	-5(2)
C(7)	67(4)	66(4)	55(3)	0(3)	-8(3)	-15(3)
C(8)	69(4)	72(4)	96(6)	11(3)	-9(4)	-44(4)
C(9)	71(4)	42(3)	107(6)	-3(3)	-30(4)	-15(3)
C(10)	84(4)	46(3)	89(5)	-23(3)	-30(4)	11(3)
C(11)	65(3)	49(3)	54(3)	-18(2)	-9(3)	-2(2)

[a] The form used was $\exp(-2\pi^2 \times 10^{-3} \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*)$.

Structure Analysis. The positions of all atoms, including hydrogen, were determined by Patterson and difference Fourier methods. Full-matrix least squares adjustment of 136 scale, positional, and thermal parameters (Table 4) converged with R = 0.026 and R_w = 0.033. Hydrogen atoms were included in these calculations but their parameters were not refined. A final difference synthesis displayed regions of $\pm 1.6 e\mathring{A}^{-3}$ close to the platinum atom; elsewhere function values were within $\pm 0.8 e\mathring{A}^{-3}$. Mean values of $\underline{w}\Delta^2 (w = \sigma^{-2}(F_o), q=0.04)$ [24] showed no significant variation with $|F_o|$ or $\sin\theta/\lambda$. Atomic scattering factors and anomalous dispersion corrections for Pt, Cl, and P atoms were taken from ref. 25. Tables of observed and calculated structure factors are available from the authors on request.

^{31}P N.M.R. Spectra were recorded on a Varian HX-100 in the F.T. mode.

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