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Trans-INFLUENCE AND ELECTRONEGATIVITY. CRYSTAL AND MOLECULAR STRUCTURE OF cis-DI-IODOBIS(TRIMETHYLPHOSPHINE) PLATINUM(II)*

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SUMMARY

The crystal and molecular structure of cis-[$PtI_2(PMe_3)_2$] has been determined. Crystals are monoclinic, space group $P2_1/n$, a = 12.893(9), b = 11.776(7), c = 9.330(4)Å, β = 96.77(6)°, Z = 4. Intensities were measured by diffractometer and the structure solved by the heavy atom method and refined to R = 0.057. The crystal comprises discrete molecules with bond lengths Pt-P 2.244(4) and 2.271(4) Å, and Pt-I 2.665(2) and 2.672(2) Å. The platinum and donor atoms are nearly coplanar, but steric repulsion, particularly between the PMe_3 ligands [∠ P-Pt-P 95.0(1)°], causes deviations from square-planar co-ordination. Bond lengths in this and related complexes are used to determine a trans influence order (C> P>Cl, Br, I) which is consistent with orders based on n.m.r. coupling constants, and which is not determined by the electronegativity of the donor atom.

INTRODUCTION

The trans influence of a ligand L, as measured by the length of Pt-Cl bonds trans to L, has been shown to correlate with the electronegativity of the donor atom of L when this is H, C, O, Si, P and Cl [1]. However, less direct measurements of trans influence such as ν(M-X) [2] or ^1J(Pt-P) [3] are available for a wider range of ligands L, and these indicate that the trans influence of heavier donor atoms (Ge-Br, Sn-I etc.) is significantly lower than for light atoms of similar electronegativity. Since the electronegativities of C(2.5), Cl(3.0), and I(2.5) [4] do not correlate with values of ^1J(Pt-P) for Pt-PR_3 bonds trans to these

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elements (C, 1790 [5]; Cl, 3480; I, 3306 Hz [6]), and bond lengths are known for PR_3 *trans* to C [7] and Cl [8, 9], an *X*-ray crystal structure determination for *cis*-$[PtI_2(PMe_3)_2]$ has been undertaken to determine the Pt–P bond length *trans* to I.

EXPERIMENTAL

Crystals of *cis*-$[PtI_2(PMe_3)_2]$ were obtained from dichloromethane–diethyl ether [10].

Crystal Data

$C_6H_{18}I_2P_2Pt$, M = 601.07, Monoclinic, a = 12.893(9), b = 11.776(7), c = 9.330(4) Å, β = 96.77(6)°, U = 1415.4 Å^3, Z = 4, D_m = 2.74 (by flotation), D_c = 2.84 g cm^{-3}, $F(000)$ = 1072, Mo-$K\alpha$ radiation, $\mu(\text{Mo}\bar{K\alpha})$ = 55.5 cm^{-1}, space group $P2_1/n$ from systematic absences 0k0 for k odd and h 0 ℓ for $h + \ell$ odd.

Crystallographic Measurements

The crystal was bounded by faces of the form {110} , {1$\bar{1}$0}, and {001} with distances between parallel faces of 0.09, 0.09 and 0.875 mm. It was accurately centred on a Y290 Hilger and Watts four circle diffractometer (graphite crystal monochromator) and unit cell parameters were determined by least squares treatment of the accurate setting angles of 12 strong reflections [λ (Mo-$K\alpha_1$) = 0.70926 Å]. Data was collected by an $\omega/2\theta$ scan in 80 steps of 0.5sec to 2θmaximum 60°; backgrounds at either side of each peak were counted for 20 sec. The intensities of three standard reflections, remeasured after every 100 reflections, varied by only ± 2%, so corrections for crystal decay were unnecessary. Lorentz and polarization corrections were applied and the data corrected for absorption with the program ABSCOR [11]. Symmetry equivalent reflections were averaged to give 2667 independent reflections with $I > 3\sigma(I)$.

Structure Determination

The positions of all the non-hydrogen atoms were obtained by the usual Patterson and Fourier methods. Scattering factor curves were taken from ref 12. The anomalous dispersion for iodine, phosphorus, and platinum were taken from ref. 13. The atoms were refined by full-matrix least squares with anisotropic Debye-Waller factors to R 0.057 and R_ω 0.077. The final weighting scheme was determined from $\omega = 1/\{1 + [(F_o-40.0)/39.4]^2\}$ which gave approximately constant averages of $\omega(|F_o|-|F_c|)^2$ vs. $|F_o|$. The final maximum change to error was 0.104 and the final difference Fourier map was everywhere less than 0.54 e$Å^{-3}$; hydrogen atoms were not located. Structure solution and refinement were carried out using the X-RAY program system [14].

RESULTS AND DISCUSSION

Final atomic co-ordinates are given in Table 1, anisotropic thermal parameters are given in Table 2, and a diagram of the molecular structure with the numbering scheme for the atoms is given in Figure 1.

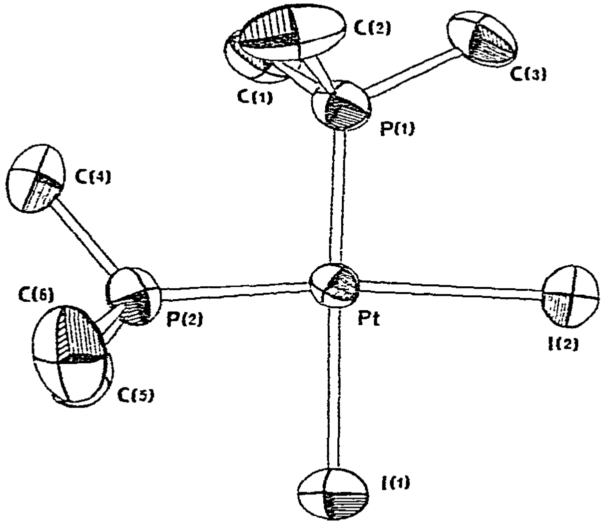

Fig. 1. A view of the molecular structure; thermal ellipsoids enclose 50% of probability.

The crystals are composed of discrete units separated by normal van der Waals contacts. Bond lengths, angles, and selected intramolecular non-bonded distances are given in Table 3. The platinum, iodine, and phosphorus atoms deviate only slightly from coplanarity (Table 4), but the bond angles at platinum show substantial differences from square-planar geometry. That there is strong steric repulsion between the phosphine ligands is revealed by the large angles P(1)-Pt-P(2) 95.0(1)°, Pt-P(2)-C(4) 122.3(6)° (mean angle Pt-P-C 116.1°), and

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH STANDARD DEVIATIONS

Atom	x	y	z
Pt	8707.7(4)	1563.2(4)	1563.3(5)
I(1)	10020(1)	3022(1)	532(1)
I(2)	9662(1)	2052(1)	4193(1)
P(1)	7630(3)	333(3)	2485(4)
P(2)	8099(3)	1197(3)	-777(4)
C(1)	6248(14)	535(19)	1972(22)
C(2)	7954(17)	-1131(17)	2109(25)
C(3)	7654(19)	221(22)	4442(23)
C(4)	6920(18)	293(21)	-1297(20)
C(5)	7754(17)	2454(19)	-1898(23)
C(6)	9074(17)	482(23)	-1700(22)

TABLE 2

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) OF THE FORM $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)]$ WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	352(3)	317(2)	315(2)	16(2)	65(2)	-1(2)
I(1)	581(6)	763(8)	626(7)	-173(6)	112(5)	96(6)
I(2)	680(7)	755(8)	472(6)	-148(6)	-50(5)	-5(5)
P(1)	484(20)	483(20)	446(18)	-37(16)	92(15)	36(16)
P(2)	538(20)	463(19)	384(17)	67(17)	57(15)	-29(15)
C(1)	448(90)	758(141)	787(128)	-12(90)	145(86)	15(109)
C(2)	692(94)	488(88)	891(200)	33(8)	221(109)	135(112)
C(3)	825(131)	1057(178)	608(95)	-336(13)	179(88)	248(108)
C(4)	859(130)	890(14)	519(102)	-198(107)	-146(90)	-130(96)
C(5)	841(138)	640(112)	684(123)	-5(105)	-188(105)	206(98)
C(6)	729(118)	1163(186)	572(113)	425(123)	64(91)	-218(120)

TABLE 3

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH STANDARD DEVIATIONS

Bond Lengths		Bond angles	
Pt-I(1)	2.665(2)	I(1)-Pt-I(2)	87.17(6)
Pt-I(2)	2.672(2)	P(1)-Pt-P(2)	95.0(1)
Pt-P(1)	2.244(4)	I(1)-Pt-P(2)	86.4(1)
Pt-P(2)	2.271(4)	I(2)-Pt-P(1)	91.4(1)
		I(1)-Pt-P(1)	178.5(1)
P(1)-C(1)	1.80(2)	I(2)-Pt-P(2)	172.5(1)
P(1)-C(2)	1.82(2)		
P(1)-C(3)	1.83(2)	Pt-P(1)-C(1)	116.5(7)
P(2)-C(4)	1.87(2)	Pt-P(1)-C(2)	111.9(7)
P(2)-C(5)	1.84(2)	Pt-P(1)-C(3)	119.4(8)
P(2)-C(6)	1.81(2)	Pt-P(2)-C(4)	122.3(6)
		Pt-P(2)-C(5)	115.2(7)
Intramolecular non-bonded distances		Pt-P(2)-C(6)	111.5(6)
		C(1)-P(1)-C(2)	108.3(9)
I(1)...I(2)	3.680(3)	C(1)-P(1)-C(3)	100.1(10)
C(3)...I(2)	3.39(2)	C(2)-P(1)-C(3)	98.5(11)
C(5)...I(1)	3.54(2)	C(4)-P(2)-C(5)	100.2(10)
C(6)...I(1)	3.76(2)	C(4)-P(2)-C(6)	101.4(10)
C(1)...C(4)	3.27(3)	C(5)-P(2)-C(6)	103.8(11)

TABLE 4

DEVIATION OF ATOMS FROM LEAST-SQUARES PLANE[a] FOR P(1), P(2), I(1), and I(2)

Atom	Deviation(Å)	Atom	Deviation
Pt	-0.044	C(1)	-1.395
P(1)	-0.034	C(2)	1.587
P(2)	0.035	C(3)	-0.232
I(1)	-0.032	C(4)	-0.080
I(2)	0.031	C(5)	-1.201
		C(6)	1.591

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[a] Defined by $0.6646\,x - 0.7166\,y - 0.2116\,z = 5.9684$

C(1)-P(1)-C(2) 108.3(9) (mean angle C-P-C 102.0°); a molecular model (Corey-Pauling-Kolthum) shows qualitatively similar distortions and indicates that a hydrogen atom on C(4) is sited between the methyl groups of C(1) and C(2). The C...I distances (Table 2) and the model imply that there are several H...I distances shorter than the normal van der Waals contacts, and the steric pressure between the ligands appears to be the cause of the significant difference (*ca.* 0.027 Å) in the Pt-P lengths. Since the hydrogen atoms were not located in the structure determination, a detailed analysis of the steric interactions is not possible, but it is evident that the steric interactions are stronger in *cis* than in *trans*-[$PtI_2(PMe_3)_2$] [15], where phosphine-phosphine interactions are absent and the shortest C...I distance [3.49(2) Å] is longer than the C(3)...I(2) distance [3.39(2) Å] in the *cis* complex.

The mean Pt-P distance in *cis*-[$PtI_2(PMe_3)_2$] [2.257(4) Å] is identical to that in *cis*-[$PtCl_2(PEt_3)_2$] [2.258(2) Å] [9] and does not differ significantly from that in *cis*-[$PtCl_2(PMe_3)_2$] [2.247(7) Å] [8] or in *cis*-[$PtBr_2(CNPh)(PEt_3)$] [2.257(16)] [16]. In these complexes the phosphine ligands are subject to the *cis* and the *trans* influence of halide ligands, but the Pt-P lengths in *trans*-[$PtBr_2(PEt_3)_2$] [2.314(8) Å] [17] and *trans*-[$PtI_2(PMe_3)_2$][2.315(4) Å] [15] indicate that the halide ligands do not differ significantly in their *cis* influence. It appears therefore that differences in the *trans* influence of Cl, Br, and I are insufficient to cause observable changes in the lengths of *trans* Pt-P bonds. For these ligands the *trans* influence on Pt-P bonds does not appear to increase with decreasing electronegativity, and this suggests that the correlation between *trans* influence and electronegativity [1] may be satisfactory only for lighter donor atoms. Since steric pressure on the phosphine ligands of the *cis* complexes must increase in the sequence Cl>Br>I, steric effects would tend to enhance rather than offset a trend in electronic *trans* influence Cl<Br<I.

The Pt-P lengths in *trans*-[$PtI_2(PMe_3)_2$] [2.315(4)] [15] and in *trans*-[$PtBr_2(PEt_3)_2$] [2.315(4)], [17] which have P *trans* to P, are greater than when P is *trans* to Cl, Br, or I. In *cis*-[$PtPh(GePh_2OH)(PEt_3)_2$] the Pt-P lengths are 2.317(5) Å (*trans* to C) and 2.328(5) Å (*trans* to Ge) [7]. The results combine to give a *trans* influence order Ge> C> P> Cl, Br, I, which is consistent with that derived from coupling constants ^1J(Pt-P) [2, 18]. However, the fact that the Pt-P lengths differ by ca. 0.027Å in cis-$[PtI_2(PMe_3)_2]$, even when the ligands trans to P are identical shows that small differences in Pt–P lengths in cis complexes, such as that found in cis-$[PtPh(GePh_2OH)(PEt_3)_2]$, may not give a reliable indication of relative trans influence.

The trans influence order C> P>I is also evident from the Pt–I lengths in trans-$[Pt(CH_3)I(PPh_3)_2]SO_2$ [2.707(1) Å] [19], cis-$[PtI_2(PMe_3)_2]$ [mean 2.669(2) Å], and trans-$[PtI_2(PMe_3)_2]$ [2.599(2) Å] [15]. Platinum-iodine and Pt–Cl distances show greater sensitivity to trans influence than Pt–P bonds [9].

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