Reactivity of *o*-Diphenylphosphinobenzaldehyde toward $[Pt(C_2H_4)(PPh_3)_2]$. *X*-Ray Structure of $[Pt(OCC_6H_4PPh_2\text{-}o)H(PPh_3)]\cdot C_6H_6$ *

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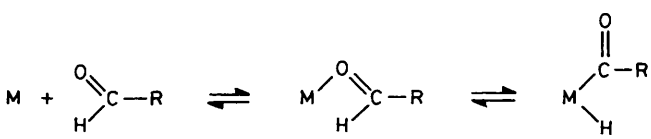
The compound *o*-diphenylphosphinobenzaldehyde reacts with $[Pt(C_2H_4)(PPh_3)_2]$ under mild conditions to give the acyl hydride $[Pt(OCC_6H_4PPh_2\text{-}o)H(PPh_3)]$. In the presence of butanol a complete decarbonylation of the aldehyde occurs with formation of $[Pt(PPh_3)_3]$. The *X*-ray crystal structure of the acyl complex has been determined. The crystals are orthorhombic, space group $Pn2_1a$, with a = 17.673(9), b = 16.586(8), and c = 12.160(6) Å. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by least squares to final R and R' of 0.049 and 0.046 respectively. The metal atom is surrounded in a distorted square-planar geometry by the acyl ligand, a triphenylphosphine and a hydride ligand.

The oxidative addition of an aldehydic functional group to a metal centre with formation of an acyl hydride derivative is the fundamental step in the mechanism proposed for stoicheiometric or catalytic decarbonylation of aldehydes[1] (Scheme 1). However, except for a very few reactions, it is not possible to isolate stable acyl hydrides as a result of the oxidative addition of simple aldehydes to organometallic species.[2]



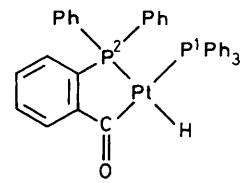
Scheme 1.

Suggs[3] and Rauchfuss[4,5] were able to prepare two acyl hydrides by the chelate-assisted oxidative addition respectively of quinoline-8-carbaldehyde and *o*-diphenylphosphinobenzaldehyde to rhodium(I) and iridium(I) substrates. In these cases the chelating effect on the one hand promotes the attack of the CHO group on the metal centre {$[Ir(PPh_3)_2(CO)Cl]$ does not react with benzaldehyde}, and on the other hand stabilizes the acyl hydride (in both cases the decarbonylation is completed only by pyrolysis). These two *ortho*-functionalized ligands have been found to react (Scheme 2) with platinum(II) substrates with formation respectively of an acyl derivative (**A**)[4] and a unique compound (**B**) (L = PR_3 or AsR_3)[6] in which a weak interaction between the metal atom and the aldehydic hydrogen has been found by n.m.r. studies.

We have now investigated the reactivity of $o\text{-}Ph_2PC_6H_4\text{-}CHO$ towards $[Pt(C_2H_4)(PPh_3)_2]$. The reaction occurs under mild conditions with formation of either $[Pt(OCC_6H_4PPh_2\text{-}o)H(PPh_3)]$ or $[Pt(PPh_3)_3]$, depending on the solvent.

Results and Discussion

The ligand $o\text{-}Ph_2PC_6H_4CHO$ reacts rapidly with $[Pt(C_2H_4)(PPh_3)_2]$ in benzene solution to form orange-yellow crystals of $[Pt(OCC_6H_4PPh_2\text{-}o)H(PPh_3)]$. The complex is air-



(**C**)

sensitive and soluble without decomposition in common organic solvents such as CH_2Cl_2, $CHCl_3$, and CH_3COCH_3.

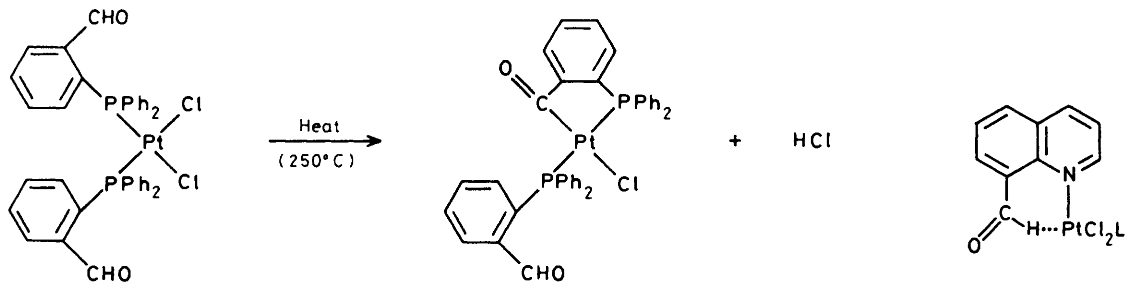
The i.r. spectrum (Nujol mull) shows bands at 2 080s and 1 610vs cm^{-1} attributable respectively to Pt–H and Pt–CO(acyl) stretching vibrations. The room-temperature ^1H n.m.r. spectrum (CD_2Cl_2) shows a doublet of doublets (1 H) at δ = 1.21 with satellites due to coupling to platinum-195 [^1J(H–Pt) = 1 360 Hz]. This pattern indicates coupling to two non-equivalent phosphorus atoms with $^2J(H\text{-}P^1)$ = 30 and $^2J(H\text{-}P^2)$ = 174 Hz, P^1 being *cis* and P^2 *trans* as in (**C**). The $^{31}P\text{-}\{^1H\}$ spectrum is in accord with this result showing two doublets at δ_1 = 24.2 and δ_2 = 51.9 p.p.m. [^2J(P–P) = 6.1 Hz] attributable to two non-equivalent weakly coupled phosphorus atoms. From the satellites the couplings $^1J(P^2\text{-}Pt)$ = 2 054 and $^1J(P^1\text{-}Pt)$ = 1 600 Hz were determined. The undecoupled ^{31}P spectrum shows that the absorption at δ = 51.9 p.p.m. must be attributed to the *trans* phosphorus, *i.e.* from PPh_2.

The molecular structure of the compound consists of $[Pt(OCC_6H_4PPh_2\text{-}o)H(PPh_3)]$ molecules and benzene molecules interspersed in the lattice. The Figure shows a perspective view, and selected bond distances and angles are given in Table 1. The co-ordination around the platinum atom is distorted square planar, with the acyl ligand occupying two *cis* co-ordination sites with the phosphorus and the acyl carbon. A triphenylphosphine ligand is *trans* to the acyl carbon and a hydride ligand, whose presence has been inferred by structural considerations as well as spectroscopic data, completes the co-ordination *trans* to the phosphorus of the acyl ligand. The distortion of the square-planar geometry seems mainly due to the short bite of the bidentate ligand [P(2)–Pt–C 82.5(6)°]; however the crowding of the bulky triphenylphosphine group with respect to the small hydride ligand also plays a role. The benzoyl fragment is not planar, the torsion angle C(16)–C(26)–C–O being 37.6°; moreover the angle between the CO vector and the least-squares plane passing through P(1),P(2), and C is 21.1°.

The Pt–P bond distances of 2.317(6) and 2.290(6) Å appear

* (*o*-Diphenylphosphinobenzoyl-*CP*)hydrido(triphenylphosphine)-platinum–benzene (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



(A) (B)

Scheme 2.

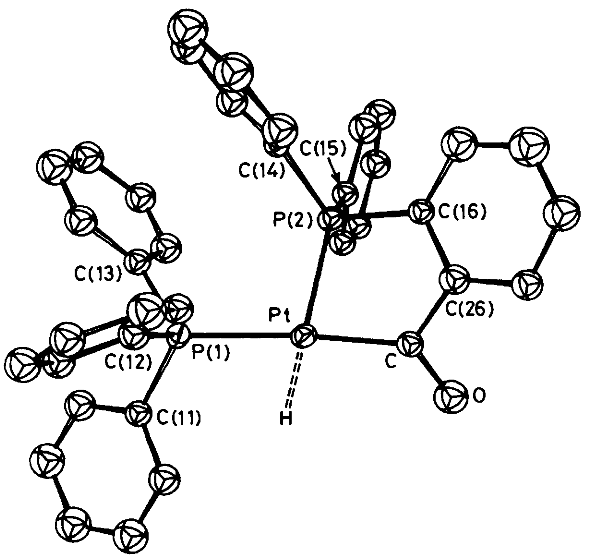


Figure. Perspective view of [Pt(OCC$_6$H$_4$PPh$_2$-*o*)H(PPh$_3$)]. ORTEP drawing with 30% probability ellipsoids

normal, falling in the accepted range of values.[7] The small difference between them could be significant, and is probably due to the larger *trans* influence of the acyl group with respect to the hydride ligand. Concerning the bond distances involving the acyl carbon, the somewhat short Pt–C distance [1.99(2) Å] with respect to the sum of covalent radii (2.07 Å) resembles the values found in other acyl-platinum and -palladium complexes, where some d_π–p_π metal–carbon back bonding has been suggested.[7] The C–O bond distance of 1.28(3) Å, somewhat larger than the value found for the free ligand, 1.19(5),[5] is however comparable with the value of 1.23(2) Å reported for [Pt(SnCl$_3$)(COPh)(PEt$_3$)$_2$].[7]

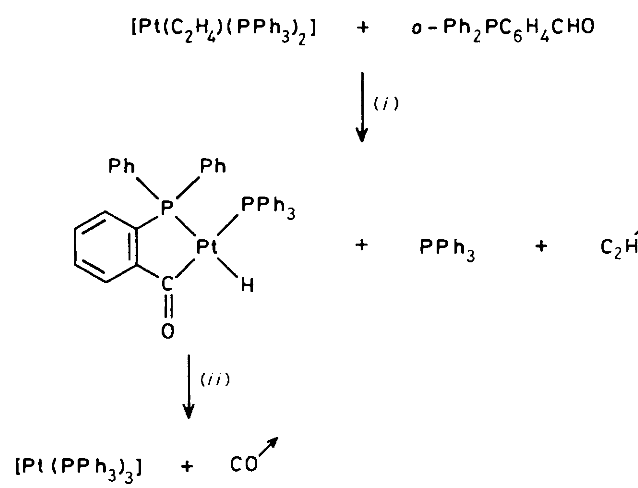
When the reaction of *o*-Ph$_2$PC$_6$H$_4$CHO with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] is carried out in benzene–alcohol solution (ethanol or butanol) a yellow solution is obtained from which, after evaporation of the solvent, the complex [Pt(PPh$_3$)$_3$] can be isolated (identified by comparison with a sample prepared as previously described[8]).

Another experiment has shown that the planar acyl hydride in CH$_2$Cl$_2$ solution decomposes after addition of ethanol to form an orange solution from which we were unable to isolate any identifiable compound. When the latter experiment is carried out in the presence of 1 mol equivalent of triphenylphosphine the reaction with ethanol again results in the formation of [Pt(PPh$_3$)$_3$]. Since [Pt(PPh$_3$)$_3$] can be formed

* Passage of N$_2$ through a solution of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] has been reported to result in the formation of orthometallated species.[9]

Table 1. Selected bond distances (Å) and angles (°) for [Pt(COC$_6$H$_4$PPh$_2$-*o*)H(PPh$_3$)]

Pt–P(1)	2.317(6)	C(16)–C(26)	1.40(3)
Pt–P(2)	2.290(6)	C(26)–C(36)	1.40(3)
Pt–C	1.99(2)	C(26)–C	1.50(3)
P(1)–C(11)	1.82(1)	C(36)–C(46)	1.45(3)
P(1)–C(12)	1.84(1)	C(46)–C(56)	1.34(4)
P(1)–C(13)	1.83(1)	C(56)–C(66)	1.34(4)
P(2)–C(14)	1.84(2)	C(66)–C(16)	1.42(3)
P(2)–C(15)	1.81(1)	C–O	1.28(3)
P(2)–C(16)	1.85(2)		
P(1)–Pt–P(2)	102.9(2)	C(15)–P(2)–C(16)	104.8(8)
P(1)–Pt–C	171.2(6)	P(2)–C(16)–C(26)	112.5(14)
P(2)–Pt–C	82.5(6)	P(2)–C(16)–C(66)	124.9(16)
Pt–P(1)–C(11)	115.9(5)	C(26)–C(16)–C(66)	122.5(20)
Pt–P(1)–C(12)	110.9(5)	C(16)–C(26)–C	117.6(17)
Pt–P(1)–C(13)	116.3(5)	C(36)–C(26)–C	123.1(18)
C(11)–P(1)–C(12)	101.6(7)	C(16)–C(26)–C(36)	119.2(18)
C(11)–P(1)–C(13)	105.3(7)	C(26)–C(36)–C(46)	114.5(19)
C(12)–P(1)–C(13)	105.5(6)	C(36)–C(46)–C(56)	125.1(21)
Pt–P(2)–C(14)	122.4(5)	C(46)–C(56)–C(66)	120.4(24)
Pt–P(2)–C(15)	116.0(5)	C(56)–C(66)–C(16)	118.0(22)
Pt–P(2)–C(16)	101.1(6)	Pt–C–O	128.9(15)
C(14)–P(2)–C(15)	106.4(6)	Pt–C–C(26)	119.5(15)
C(14)–P(2)–C(16)	103.8(8)	C(26)–C–O	111.5(17)



Scheme 3. (*i*) Benzene, N$_2$; (*ii*) benzene–ethanol, N$_2$

from [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] only by addition of PPh$_3$,* the above results conclusively show that, in the presence of an alcohol, one triphenylphosphine ligand is derived from the acyl compound. Thus the overall process of oxidative addition of the aldehyde

Table 2. Positional parameters ($\times 10^4$)

Atom	x	y	z
Pt	−978(1)	0	−1 490(1)
P(1)	−1 347(3)	−725(3)	48(5)
P(2)	127(3)	−618(3)	−1 993(5)
O	−1 036(8)	1 297(9)	−3 167(11)
C	−821(11)	587(13)	−2 898(17)
C(11)	−1 881(8)	−166(9)	1 079(9)
C(21)	−2 433(8)	388(9)	760(9)
C(31)	−2 878(8)	769(9)	1 552(9)
C(41)	−2 771(8)	596(9)	2 664(9)
C(51)	−2 219(8)	42(9)	2 984(9)
C(61)	−1 774(8)	−339(9)	2 191(9)
C(12)	−2 023(7)	−1 524(8)	−326(10)
C(22)	−2 041(7)	−1 773(8)	−1 422(10)
C(32)	−2 568(7)	−2 348(8)	−1 760(10)
C(42)	−3 076(7)	−2 674(8)	−1 004(10)
C(52)	−3 057(7)	−2 426(8)	92(10)
C(62)	−2 531(7)	−1 850(8)	431(10)
C(13)	−592(8)	−1 234(7)	811(12)
C(23)	41(8)	−769(7)	1 075(12)
C(33)	643(8)	−1 114(7)	1 647(12)
C(43)	613(8)	−1 923(7)	1 957(12)
C(53)	−19(8)	−2 388(7)	1 694(12)
C(63)	−622(8)	−2 043(7)	1 120(12)
C(14)	262(8)	−1 715(9)	−1 893(11)
C(24)	732(8)	−2 063(9)	−1 102(11)
C(34)	785(8)	−2 900(9)	−1 021(11)
C(44)	368(8)	−3 389(9)	−1 731(11)
C(54)	−102(8)	−3 041(9)	−2 521(11)
C(64)	−155(8)	−2 204(9)	−2 602(11)
C(15)	989(8)	−160(7)	−1 483(10)
C(25)	1 693(8)	−467(7)	−1 790(10)
C(35)	2 354(8)	−76(7)	−1 460(10)
C(45)	2 311(8)	622(7)	−823(10)
C(55)	1 607(8)	929(7)	−515(10)
C(65)	946(8)	538(7)	−846(10)
C(16)	138(11)	−422(11)	−3 488(18)
C(26)	−353(10)	206(13)	−3 790(15)
C(36)	−425(12)	410(13)	−4 906(18)
C(46)	49(11)	−56(23)	−5 641(18)
C(56)	546(15)	−624(16)	−5 323(22)
C(66)	619(14)	−814(15)	−4 256(21)
C(17)*	−2 429(14)	−2 731(11)	−6 201(14)
C(27)*	−1 856(14)	−3 282(11)	−6 436(14)
C(37)*	−1 116(14)	−3 128(11)	−6 097(14)
C(47)*	−949(14)	−2 422(11)	−5 522(14)
C(57)*	−1 523(14)	−1 870(11)	−5 287(14)
C(67)*	−2 263(14)	−2 025(11)	−5 626(14)

* Atom belonging to the solvent molecule.

and reductive elimination of the acyl group can be summarized in Scheme 3.* It is difficult to propose a mechanism for the step (*ii*) without the identification of some intermediates. Monitoring of the reaction by i.r. spectroscopy did not show any evidence for the formation of metal–carbonyl species when the band due to the CO(acyl) disappeared.

The iridium–acyl hydride prepared by an analogous reaction[5] does not react with alcohol, being recovered practically unchanged from methylene chloride–ethanol solution. Probably this inertness is due to the higher saturation of the octahedral geometry compared with the planar one.

Experimental

Proton and ^{31}P n.m.r. spectra were measured at 300 and 121.4 MHz, respectively on a Varian VXR 300 spectrometer. Chemical shifts are quoted with respect to $SiMe_4$ (^{1}H) or phosphoric acid (^{31}P).

Preparation of the Compounds.—The reactions were carried out under a current of dry nitrogen. *o*-Diphenylphosphinobenzaldehyde was prepared as previously described.[10]

[Pt(OCC$_6$H$_4$PPh$_2$-*o*)H(PPh$_3$)]·C$_6$H$_6$. A solution of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (1 mmol) in benzene (10 cm^3) was added, at room temperature, to a solution of *o*-Ph$_2$PC$_6$H$_4$CHO (1 mmol) in benzene (10 cm^3). After *ca.* 1 h, hexane (10 cm^3) was added and, after evaporation of the solvent, orange-yellow crystals precipitated. They were filtered off, washed with benzene–hexane (1:1), and dried in a current of nitrogen. Yield 80% (Found: C, 62.90; H, 4.35; P, 8.05. Calc. for $C_{43}H_{35}OP_2Pt$: C, 62.60; H, 4.30; P, 7.50%).

[Pt(PPh$_3$)$_3$]. The reaction was carried out as described above, but using butanol instead of hexane. After evaporation of the solvent, yellow crystals of [Pt(PPh$_3$)$_3$] precipitated. Yield 53% (Found: C, 65.90; H, 4.75; P, 9.80. Calc. for $C_{54}H_{45}P_3Pt$: C, 66.05; H, 4.60; P, 9.45%).

* The fundamental role of the 'chelate trapping' is demonstrated by the complete inertness of PhCHO toward [Pt(C$_2$H$_4$)(PPh$_3$)$_2$].

Crystallography.—*Crystal data.* $C_{43}H_{35}OP_2Pt$, *M* 824.79, orthorhombic, space group $Pn2_1a$, $a = 17.673(9)$, $b = 16.586(8)$, $c = 12.160(6)$ Å, $U = 3\,564.4$ Å^3, $Z = 4$, $D_c = 1.536$ g cm^{-3}, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 40.9 cm^{-1}, $F(000) = 1\,636$.

Data collection and processing. A prismatic crystal of dimensions 0.07 × 0.08 × 0.40 mm was selected and mounted on a Philips PW 1100 diffractometer. The cell parameters were determined by least-squares refinement of the setting angles of 21 carefully centred reflections. Data collection was carried out using the ω—2θ scan technique within $2\theta \leqslant 50°$. The scan width was calculated according to the formula $A + B\tan\theta$, with $A = 0.7°$ and $B = 0.34$; the scan speed was 0.07° s^{-1}. Stationary background measurements were taken before and after each scan for a time equal to half the scan time. The intensities of three standard reflections measured every 2 h showed no systematic trend. The intensities were assigned standard deviations $\sigma(I)$ calculated by using a value of 0.03 for the instability factor *p*.[11] Of the total 3 537 measured reflections, 1 912 having $I \geqslant 3\sigma(I)$ were considered observed. Intensity data were corrected for Lorentz-polarization effects and an empirical correction for absorption effects was made by using the program DIFABS.[12]

Solution and refinement. All the calculations were carried out on a SEL 32/77 computer, installed in our Institute, by using SHELX 76[13] and ORTEP[14] programs. Atomic scattering factors for neutral atoms were taken from ref. 15 for non-hydrogen atoms and from ref. 16 for hydrogen atoms. All non-hydrogen scattering factors were corrected for both the real and the imaginary components of anomalous dispersion.[17] The refinement was based on F_o, the quantity minimized by least squares being $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + gF_o^2]$, with $g = 0.0$. The structure was solved by the heavy-atom method, a Patterson map showing the platinum atom position. Successive Fourier maps revealed all the non-hydrogen atoms. Full-matrix least-squares refinements were carried out allowing anisotropic thermal motion for the platinum and phosphorus atoms and isotropic for the others. The phenyl rings, with the exception of the benzoyl one, were treated as rigid groups, the carbon atoms being assigned individual thermal parameters. The hydrogen atoms were introduced in calculated positions, but were not refined. Owing to the polar space group $Pn2_1a$, the direction of the polar axis was determined. Refinements of the x,y,z structure and of the inverted one $\bar{x},\bar{y},\bar{z}$ gave R and R' values of 0.060 and 0.058 and 0.056 and 0.053, respectively, indicating the latter to be correct. In order to detect the hydride ligand, several Fourier difference maps with a gradual lowering of the $(\sin \theta)/\lambda$ cut-off were constructed. However, none of the residual peaks detected corresponded to a chemically reasonable site for the hydride ligand. Final refinement converged at R and R' 0.049 and 0.046 respectively. Final positional parameters are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Acknowledgements

Thanks are due to Mr. F. Cecconi, Mr. G. Scapacci, and Mr. S. Vasacci for technical assistance.

References

1 L. H. Pignolet, 'Homogeneous Catalysis with Metal Phosphine Complexes,' Plenum, New York, London, 1983, p. 343.
2 D. L. Thorn, *J. Am. Chem. Soc.*, 1980, **102**, 7109; C. Bianchini, A. Meli, M. Peruzzini, A. Vacca, and F. Zanobini, *Organometallics*, 1987, **6**, 2453.
3 J. W. Suggs, *J. Am. Chem. Soc.*, 1978, **100**, 640.
4 T. B. Rauchfuss, *J. Am. Chem. Soc.*, 1979, **101**, 1045.
5 E. F. Laudvatter and T. B. Rauchfuss, *Organometallics*, 1980, **1**, 506.
6 A. Albinati, C. G. Anklin, F. Ganazzoli, H. Rüegg, and P. S. Pregosin, *Inorg. Chem.*, 1987, **26**, 503.
7 A. Albinati, U. Von Gunten, P. S. Pregosin, and H. J. Rüegg, *J. Organomet. Chem.*, 1985, **295**, 239 and refs. therein.
8 U. Belluco, 'Organometallic and Coordination Chemistry of Platinum,' Academic Press, London, New York, 1974, p. 7.
9 F. Glocking, T. McBride, and R. J. Pollock, *J. Chem. Soc., Chem. Commun.*, 1973, 650.
10 J. E. Hoots, T. B. Rauchfuss, and D. A. Wrobleski, *Inorg. Synth.*, 1983, **21**, 175.
11 P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1976, **6**, 197.
12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
13 G. M. Sheldrick, SHELX System of Computing Programs, University of Cambridge, Cambridge, 1976.
14 C. K. Johnson, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.
15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 99.
16 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
17 Ref. 15, p. 149.

Received 28*th October* 1987; *Paper* 7/1919