Inorganica Chimica Acta, 31 (1978) 171–175

Crystal and Molecular Structure of *cis*-Chloro-*p*-tolyl-bis(triethylphosphine)-platinum(II) and of *cis*-Chloro-perfluorophenyl-bis(triethylphosphine)platinum(II)

N. BRESCIANI-PAHOR, M. PLAZZOTTA and L. RANDACCIO*
Istituto di Chimica, Università di Trieste, 34127 Trieste, Italy
G. BRUNO, V. RICEVUTO and R. ROMEO
Istituto di Chimica Generale, Università di Messina, 98100 Messina, Italy
U. BELLUCO
Istituto di Chimica, Facoltà di Ingegneria, Università di Padova, 35100 Padova, Italy
Received March 21, 1978

The crystal structure of the title compounds has been determined from X-ray data and refined to R = *0.048 for both compounds. Crystals of (I) are orthorhombic, space group* Pna2_1 *with cell dimensions* a = *19.91(1),* b = *14.98(1),* c = *7.82(1) Å. Crystals of (II) are monoclinic, space group* P2_1/n *with* a = *11.07(1),* b = *21.64(1),* c = *10.05(1)* Å, *β* = *91.24(3)°. The co-ordination of Pt(II) is nearly square planar in both complexes. The Pt–Cl bond lengths of 2.392(8) (I) and 2.387(7)* Å *(II) are equal within experimental errors, whereas the two chemically non-equivalent Pt–P bond lengths are significantly different in both (I) and (II). Their values are 2.320(9)* Å *(*trans *to $C_6H_4CH_3$) and 2.247(6)* Å *(*trans *to Cl) for (I) and 2.326(7)* Å *(*trans *to C_6F_5) and 2.226(7)* Å *(*trans *to Cl) for (II). No significant difference is found in Pt–C bond lengths (2.05(3) in (I) and 2.08(2)* Å *in (II)), which however appear significantly longer than the values reported for Pt–C bond lengths having partial double bond character.*

Introduction

Since Appleton *et al.* [1] reviewed in 1973 the experimental and theoretical aspects of *trans*-influence in square planar Pt(II) complexes, numerous structural studies on this subject have been reported and empirical correlations have been attempted [2, 3].

For monomeric chloro-platinum(II) complexes, containing carbon donor ligands *trans* to Cl, it has been demonstrated that there is a correlation between the extent of Pt–C multiple bonding and the Pt–Cl bond length [4]. Thus the electron withdrawing through π-back donation from Pt to carbon, in the Cl–Pt–C unit, leads to a shortening of the Pt–C bond. Consequently the flow of electron density towards carbon increases the positive charge on the metal, which in turn increases the electrostatic interaction between metal and Cl^-, provoking also a shortening of the Pt–Cl bond. Such a model takes into account the bond length values found, *e.g.*, in the OC–Pt–Cl unit (Pt–C, 1.85(1) and Pt–Cl, 2.277(3) Å) of *cis*-$PtCl_2(CO)PPh_3$ [5] and in the Me_3SiCH_2–Pt–Cl unit (Pt–C, 2.08(1) and Pt–Cl, 2.415(5) Å) of *trans*-$PtCl(CH_2SiMe_3)(PPhMe_2)_2$ [6]. Similar effects should operate in the P–Pt–Cl unit, when electron withdrawing substituents are bonded to phosphorus [3]. In fact in *cis*-$PtCl_2(PEt_3)PF_3$, the geometry of F_3P–Pt–Cl (Pt–P, 2.141(3) and Pt–Cl, 2.305(3) Å) and Et_3P–Pt–Cl (Pt–P, 2.272(3) and Pt–Cl, 2.357(3) Å) units supports this model.

These results prompted us to investigate if such a mechanism may be valid also for the P–Pt–X unit, when a phosphine is *trans* to X groups with different π-acceptor properties, such aryl and perfluoroaryl ligands.

We report the crystal and molecular structure of *cis*-chloro-*p*-tolyl-bis(triethylphosphine)platinum(II), (I) and of *cis*-chloro-perfluorophenyl-bis(triethylphosphine)platinum(II), (II).

Experimental

Crystal Data

a) (I); $PtClP_2C_{19}H_{37}$, *M* = 557.7. Orthorhombic, *a* = 19.91(1), *b* = 14.98(1), *c* = 7.82(1) Å, *U* = 2332 Å^3, D_m (by flotation) = 1.58 g cm^{-3}, *Z* = 4, D_c = 1.59 g cm^{-3}; Mo*K*α, λ = 0.7107 Å, μ(Mo*K*α) = 66 cm^{-1}. Space group *Pna*2_1 (from structure determination); b) (II), $PtClP_2C_{18}F_5H_{30}$, *M* = 633.9, monoclinic, *a* = 11.07(1), *b* = 21.64(1), *c* = 10.05(1) Å, *β* = 91.24(3)°, *U* = 2406, D_m (by flotation) = 1.80 g

---

*Address all correspondence to this author.

TABLE I. Atomic Parameters of Non-hydrogen Atoms ($\times 10^4$) for Compound (I) with Estimated Standard Deviations in Parentheses. Anisotropic temperature factors are in the Form: exp $-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})$.

	X	Y	Z	B
Pt	1647(0)	1556(1)	0(7)	*
Cl	1350(5)	36(5)	−567(14)	*
P(1)	1997(3)	2980(4)	172(19)	*
P(2)	568(4)	1696(5)	1086(16)	*
C(1)	2560(16)	1202(21)	−1002(57)	*
C(2)	2683(17)	1190(20)	−2813(57)	*
C(3)	3341(14)	955(18)	−3522(66)	*
C(4)	3861(16)	729(19)	−2349(67)	*
C(5)	3724(15)	701(22)	−502(64)	*
C(6)	3067(12)	944(16)	344(31)	*
C(7)	4568(17)	472(23)	−2917(62)	*
C(8)	2807(14)	3228(17)	−891(47)	*
C(9)	3001(16)	4261(22)	−750(58)	*
C(10)	2096(15)	3424(23)	2355(35)	*
C(11)	2623(19)	2933(26)	3310(74)	*
C(12)	1394(17)	3760(21)	−983(45)	*
C(13)	1394(24)	3562(28)	−2963(71)	*
C(14)	505(16)	918(25)	2994(57)	*
C(15)	986(17)	1183(24)	4418(22)	*
C(16)	−100(13)	1273(15)	−378(31)	*
C(17)	−272(22)	1857(33)	−1856(70)	*
C(18)	231(15)	2784(21)	1970(52)	*
C(19)	−493(20)	2693(21)	2785(60)	*

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Pt	19(0)	−0(0)	3(5)	25(0)	−22(5)	194(2)
Cl	38(2)	−9(5)	4(13)	27(3)	−31(14)	302(38)
P(1)	20(2)	−7(4)	−9(19)	27(2)	34(22)	203(18)
P(2)	20(2)	−6(4)	13(12)	23(3)	3(16)	253(21)
C(1)	28(9)	−12(19)	−66(51)	34(13)	27(67)	254(80)
C(2)	36(10)	−9(19)	14(54)	27(11)	36(62)	219(95)
C(3)	11(5)	−7(17)	5(59)	37(12)	−30(69)	417(22)
C(4)	22(9)	−12(17)	15(60)	23(11)	−72(69)	465(24)
C(5)	23(8)	−5(20)	19(58)	50(15)	15(77)	240(74)
C(6)	26(6)	7(14)	−42(26)	38(10)	65(36)	0(56)
C(7)	29(10)	−3(22)	98(54)	40(17)	−89(76)	392(4)
C(8)	23(7)	−21(15)	17(41)	34(13)	0(50)	2031(64)
C(9)	29(9)	−40(18)	79(51)	49(14)	−36(64)	315(17)
C(10)	33(8)	−13(23)	11(32)	64(15)	−3(58)	4(42)
C(11)	33(10)	5(25)	−52(67)	55(19)	48(91)	367(30)
C(12)	48(10)	35(20)	34(46)	53(14)	47(55)	64(53)
C(13)	49(14)	−1(31)	−55(71)	65(22)	76(90)	321(13)
C(14)	29(9)	−13(23)	−38(54)	59(18)	61(74)	261(93)
C(15)	33(10)	10(23)	10(24)	57(17)	2(29)	12(40)
C(16)	25(7)	−10(14)	−9(31)	35(10)	9(36)	55(75)
C(17)	43(14)	−32(33)	−3(77)	105(30)	118(5)	285(13)
C(18)	24(8)	26(18)	92(43)	56(15)	−44(64)	279(83)
C(19)	45(12)	−18(23)	37(64)	38(15)	77(62)	281(96)

cm^{-3}, $Z = 4$, $D_c = 1.81$ g cm^{-3}; $\mu(\text{Mo}K\alpha) = 64$ cm^{-1}. Space group $P2_1/n$. Cell parameters were determined from Weissenberg and precession photographs and refined with an on-line automatic Siemens diffractometer.

Intensity Measurements

Three-dimensional intensity data were collected on a Siemens diffractometer by the θ–2θ scan technique with Mo$K\alpha$ radiation for a maximum 2θ angle of 50° for both compounds. Crystals of mean

TABLE II. Atomic Parameters of Non-hydrogen Atoms ($\times10^4$) for Compound (II) with Estimated Standard Deviations in Parentheses. Anisotropic temperature factors are in the form: $\exp -(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})$

	X	*Y*	*Z*	*B*
Pt	2582(1)	3183(0)	3092(1)	*
P(1)	2289(7)	3884(3)	1496(7)	*
P(2)	2607(6)	2292(3)	1798(8)	*
Cl	2875(7)	2498(3)	4933(7)	*
F(1)	4762(15)	3913(8)	4535(17)	7.9(4)
F(2)	4884(18)	4710(9)	6514(20)	9.7(5)
F(3)	2813(19)	5154(10)	7608(20)	10.1(5)
F(4)	606(19)	4714(10)	6681(21)	10.4(6)
F(5)	514(15)	3910(8)	4685(17)	7.8(4)
C(7)	2386(29)	2316(15)	−100(33)	8.3(9)
C(8)	2556(29)	1666(14)	−784(34)	8.0(8)
C(1)	2615(23)	3876(11)	4524(26)	5.1(6)
C(2)	3696(24)	4105(13)	5063(27)	5.6(6)
C(3)	3755(23)	4524(13)	6095(26)	5.5(6)
C(4)	2737(28)	4726(14)	6575(31)	7.4(8)
C(5)	1675(27)	4508(15)	6154(30)	7.1(7)
C(6)	1626(25)	4089(13)	5087(28)	6.1(7)
C(9)	4048(28)	1833(15)	2201(31)	7.7(7)
C(10)	5200(36)	2287(19)	1889(42)	10.7(11)
C(11)	1466(29)	1687(15)	2375(33)	8.1(8)
C(12)	161(33)	1980(18)	2419(38)	9.8(10)
C(13)	2230(24)	4678(11)	2115(26)	5.6(6)
C(14)	2002(29)	5182(15)	997(32)	7.8(8)
C(15)	878(26)	3775(13)	500(29)	6.4(7)
C(16)	−257(28)	3808(15)	1372(33)	7.5(8)
C(17)	3470(31)	3890(16)	217(35)	8.3(9)
C(18)	4722(33)	4064(18)	861(37)	9.4(10)

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Pt	89(1)	5(1)	−13(1)	22(−0)	−5(2)	117(1)
P(1)	139(8)	−2(6)	−27(15)	29(2)	0(6)	128(10)
P(2)	116(7)	11(7)	5(15)	31(2)	−19(9)	196(10)
Cl	146(8)	17(7)	−39(14)	24(2)	15(7)	113(9)

cylindrical radii r of 0.04 and 0.06 mm for (I) and (II) respectively were used. A total of 1064 for (I) and 1284 for (II) independent reflections, having $I_o > 3\ \sigma(I_o)$, were corrected for Lorentz-polarization factors and used in the subsequent calculations. No correction for absorption was applied ($\mu \cdot r$, 0.20–0.30 for (I) and 0.35–0.50 for (II)).

Structure Determination and Refinement

Both structures were solved by conventional Patterson and Fourier methods. The final anisotropic refinement for all non-hydrogen atoms of (I) and for only Pt, P and Cl atoms of (II) reduced R to 0.048 for both compounds. The used weighting schemes were: $w = 1/(A + |F_o| + B|F_o|^2)$ where $A = 29$, $B = 0.003$ for (I) and $A = 43$, $B = 0.002$ for (II) were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $\sin\theta/\lambda$. No attempt to locate hydrogen atoms was made. Final atomic parameters are listed in Tables I and II together with their e.s.d's. The numbering schemes of the atoms are shown in Figures 1 and 2. Bond lengths and angles are listed in Tables III and IV. A list of observed and calculated structure factors is available from the Editor. Atomic scattering factors were those of ref. 7.

Calculations

All calculations were carried out on a CDC 6200 computer with programs described in ref. 8.

Results and Discussion

Both platinum compounds are four-co-ordinate square planar complexes with slight deviations of the co-ordination atoms from their mean plane. The Pt–Cl bond lengths (2.392(8) (I) and 2.387(7) Å, (II)) are equal in the two complexes within experimental

TABLE III. Bond Lengths and Angles for Compound (I) with Estimated Standard Deviations in Parentheses.

a) Bond Lengths (Å)			
Pt–Cl	2.392(8)	C(2)–C(3)	1.47(5)
Pt–P(1)	2.247(6)	C(3)–C(4)	1.42(6)
Pt–P(2)	2.320(9)	C(4)–C(5)	1.47(7)
Pt–C(1)	2.05(3)	C(4)–C(7)	1.53(5)
P(1)–C(8)	1.85(3)	C(5)–C(6)	1.51(4)
P(1)–C(10)	1.84(3)	C(8)–C(9)	1.60(4)
P(1)–C(12)	1.90(3)	C(10)–C(11)	1.48(5)
P(2)–C(14)	1.90(4)	C(12)–C(13)	1.58(7)
P(2)–C(16)	1.87(3)	C(14)–C(15)	1.52(5)
P(2)–C(18)	1.89(3)	C(16)–C(17)	1.49(6)
C(1)–C(2)	1.44(6)	C(18)–C(19)	1.58(5)
C(1)–C(6)	1.51(5)		
b) Bond Angles (°)			
Pt–P(1)–C(8)	115.7(9)	P(2)–C(14)–C(15)	112(2)
Pt–P(1)–C(10)	116(1)	P(2)–C(16)–C(17)	116(2)
Pt–P(1)–C(12)	111(1)	P(2)–C(18)–C(19)	113(2)
Pt–P(2)–C(14)	107(1)	C(1)–C(2)–C(3)	122(3)
Pt–P(2)–C(16)	114(1)	C(1)–C(6)–C(5)	110(3)
Pt–P(2)–C(18)	123(1)	C(2)–C(1)–C(6)	125(3)
Pt–C(1)–C(2)	122(2)	C(2)–C(3)–C(4)	118(4)
Pt–C(1)–C(6)	113(2)	C(3)–C(4)–C(5)	120(3)
Cl–Pt–P(1)	172.0(5)	C(3)–C(4)–C(7)	123(4)
Cl–Pt–P(2)	85.7(3)	C(4)–C(5)–C(6)	126(3)
Cl–Pt–C(1)	84.4(9)	C(5)–C(4)–C(7)	117(3)
P(1)–Pt–P(2)	100.4(3)	C(8)–P(1)–C(10)	104(1)
P(1)–Pt–C(1)	89.6(9)	C(8)–P(1)–C(12)	102(1)
P(1)–C(8)–C(9)	112(2)	C(10)–P(1)–C(12)	107(1)
P(1)–C(10)–C(11)	111(3)	C(14)–P(2)–C(16)	103(1)
P(1)–C(12)–C(13)	110(2)	C(14)–P(2)–C(18)	103(2)
P(2)–Pt–C(1)	170(1)	C(16)–P(2)–C(18)	105(1)

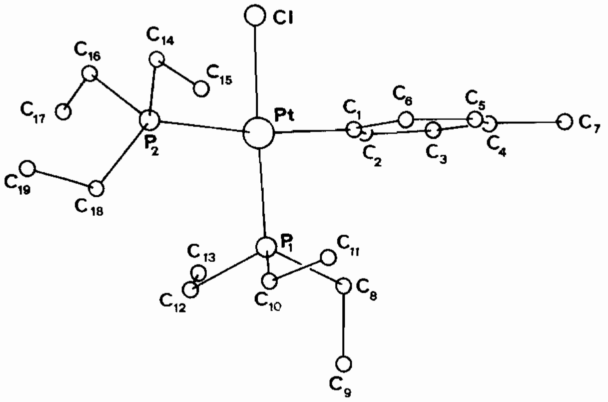

Figure 1. Numbering scheme for the atoms of compound (I).

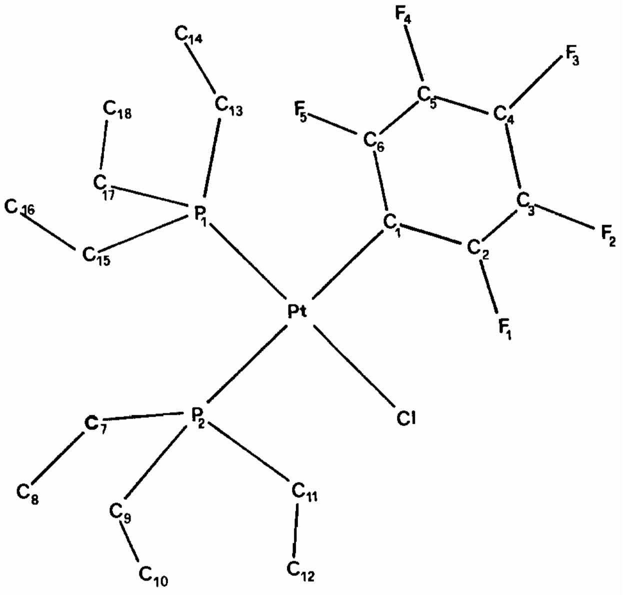

Figure 2. Numbering scheme for the atoms of compound (II).

errors. On the contrary the two chemically not equivalent Pt–P bond lengths in both compounds are significantly different, their values being 2.320(9) and 2.247(6) Å for (I) and 2.326(7) and 2.226(7) Å for (II) respectively. The largest values refer to P *trans* to the *p*-tolyl in (I) and perfluorophenyl in (II) respectively. Finally no significant difference is found in the Pt–C bond lengths (2.05(3) in (I) and 2.08(2) Å in (II)), which appear significantly larger than that of 1.85(1) Å found in *cis*-$PtCl_2(CO)(PPh_3)$ [5]. The

TABLE IV. Bond Lengths and Angles for Compound(II) with Estimated Standard Deviations in Parentheses.

a) Bond Lengths (Å)			
Pt–Cl	2.387(7)	C(15)–C(16)	1.55(4)
Pt–P(1)	2.226(7)	C(17)–C(18)	1.56(5)
Pt–P(2)	2.326(7)	C(1)–C(2)	1.39(4)
Pt–C(1)	2.08(2)	C(2)–C(3)	1.38(4)
P(1)–C(13)	1.83(2)	C(3)–C(4)	1.31(4)
P(1)–C(15)	1.85(3)	C(4)–C(5)	1.33(4)
P(1)–C(17)	1.85(4)	C(5)–C(6)	1.40(4)
P(2)–C(7)	1.92(3)	C(6)–C(1)	1.33(4)
P(2)–C(9)	1.92(3)	C(2)–F(1)	1.37(3)
P(2)–C(11)	1.92(3)	C(3)–F(2)	1.37(3)
C(9)–C(10)	1.64(5)	C(4)–F(3)	1.39(4)
C(11)–C(12)	1.58(5)	C(5)–F(4)	1.38(4)
C(7)–C(8)	1.58(4)	C(6)–F(5)	1.34(3)
C(13)–C(14)	1.58(4)		
b) Bond Angles (°)			
C(1)–Pt–Cl	84.9(7)		
P(2)–Pt–Cl	85.2(2)		
P(2)–Pt–P(1)	99.5(3)		
C(1)–Pt–P(1)	90.4(7)		
Pt–P(1)–C(15)	114.2(9)		
Pt–P(1)–C(13)	113.6(9)		
Pt–P(1)–C(17)	114(1)		
C(17)–P(1)–C(13)	105(1)		
C(15)–P(1)–C(13)	106(1)		
C(17)–P(1)–C(15)	103(1)		
Pt–P(2)–C(7)	122(1)		
Pt–P(2)–C(11)	112(1)		
Pt–P(2)–C(9)	109(1)		
C(7)–P(2)–C(9)	108(1)		
C(11)–P(2)–C(9)	98(1)		
C(11)–P(2)–C(7)	104(1)		
Pt–C(1)–C(2)	122(2)		
Pt–C(1)–C(6)	123(2)		
C(2)–C(1)–C(6)	115(2)		
C(1)–C(2)–C(3)	124(2)		
F(1)–C(2)–C(1)	119(2)		
F(1)–C(2)–C(3)	118(3)		
C(2)–C(3)–C(4)	118(3)		
F(2)–C(3)–C(4)	125(2)		
F(2)–C(3)–C(2)	117(2)		
C(3)–C(4)–C(5)	122(3)		
F(3)–C(4)–C(5)	121(3)		
F(3)–C(4)–C(3)	117(2)		
C(4)–C(5)–C(6)	119(3)		
F(4)–C(5)–C(4)	121(3)		
F(4)–C(5)–C(6)	119(2)		
C(5)–C(6)–C(1)	122(3)		
F(5)–C(6)–C(5)	116(2)		
F(5)–C(6)–C(1)	122(2)		
C(8)–C(7)–P(2)	113(2)		
C(10)–C(9)–P(2)	107(2)		
C(12)–C(11)–P(2)	110(2)		
C(16)–C(15)–P(1)	112(2)		
C(14)–C(13)–P(1)	114(2)		
C(18)–C(17)–P(1)	110(2)		

co-ordination bond angles are nearly equal in (I) and (II) within the experimental errors. The P–Pt–P bond angle is rather wider (100.4(3)° in (I) and 99.5(3)° in (II)) than the other three bond angles, probably because of steric repulsions between the two *cis* phosphines. The geometry of the P–Pt–Cl unit in both compounds nearly follows the correlation between Pt–P and Pt–Cl distances for mutually *trans* Pt–PR_3 and Pt–Cl bonds in complexes of type *cis*-$PtCl_2L(PR_3)$ found by Hitchcock *et al.* [3]. The values reported for such compounds, however, fall into the range 2.22–2.28 Å. Thus it is beyond doubt that Pt–P bond length values of (I) and (II) are indicative of a strong *trans*-influence exerted by the *p*-tolyl and perfluorophenyl ligands. These values of 2.320(9) (I) and 2.326(7) (II) Å are comparable with that of 2.310(7) Å reported for *cis*-$Pt(CH(CF_3)_2)(PPh_3)_2F$ [9], although shorter than that of 2.362(5) Å reported in *cis*-$Cl(CF_2COCF_2Cl)(PPh_3)_2Pt$ [10]. Since the Pt–C bond lengths in the above compounds (2.07(2) and 2.06(2) Å) and (II) do not differ from those found in (I) and in other Pt–alkyl compounds, we think that Pt–C bond length in perfluoro derivatives having *trans* P atom has no π-bonding contribution detectable by X-ray measurements. This is also consistent with the values found in (I) and (II) for Pt–P bond lengths which do not differ when the *trans* ligand is either an aryl or a perfluoroaryl group. Further investigation and more accurate measurements, however, of Pt–C bond lengths must be performed for a definitive assessment.

Acknowledgements

The authors thank C.N.R. (Rome) for financial support.

References

1. T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev., 10,* 335 (1973).
2. A. N. Caldwell, Lj. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc. Dalton,* 2265 (1977).
3. P. B. Hitchcock, B. Jacobson and A. Pidcock, *J. Chem. Soc. Dalton,* 2043 (1977.
4. Lj. Manojlović-Muir and K. W. Muir, *Inorg. Chim. Acta, 10,* 47 (1974).
5. Lj. Manojlović-Muir and R. Walken, *J. Organometal. Chem., 66,* C21 (1974).
6. B. Jovanović, Lj. Manojlović-Muir and K. W. Muir, *J. Chem. Soc. Dalton,* 195 (1974).
7. F. H. Moore, *Acta Cryst., 16,* 1169 (1963).
8. V. Albano, A. Domenicano and A. Vaciago, *Gazzetta, 96,* 922 (1966); A. Immirzi, *Ric. Sci., 10,* 846 (1967).
9. J. Howard and P. Woodward, *J. Chem. Soc. Dalton,* 1840 (1973).
10. D. R. Russel and P. A. Tucher, *J. Chem. Soc. Dalton,* 2222 (1975).