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CRYSTAL AND MOLECULAR STRUCTURE OF $[IrP\{(OC_6H_3Me)_2(OC_6H_4Me)\}Cl(\gamma\text{-PICOLINE})_2]$ FORMED BY THE *ortho*-CYCLOMETALLATION OF TWO *ortho*-TOLYL GROUPS ON A SINGLE TRI-*ortho*-TOLYLPHOSPHITE LIGAND

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Summary

The title molecule crystallizes in the monoclinic space group $P2_1/c$ with *a* 9.12(2), *b* 17.36(2), *c* 20.65(2) Å and β 90.5(1)°. The structure was solved by Patterson and Fourier methods and refined by least-squares, using 2583 reflections, to *R* 0.04. The structure consists of independent monomeric units. The iridium atom is in a distorted octahedral environment with one phosphorus, two *ortho* carbon atoms of two *o*-tolyl groups, one chloride ion and two nitrogens from two γ-picoline ligands occupying the octahedral positions. Metal—ligand bond lengths observed are Ir—Cl 2.44, Ir—P 2.14, Ir—C 2.04 and 2.05, and Ir—N 2.17 and 2.17 Å. Bond angles related to the chelate rings are discussed as are other relevant parameters in the structure.

Experimental

The interaction of three molar equivalents of tri-*o*-tolylphosphite with the dimer $[CODIrCl]_2$ has produced a yellow powder containing a compound approximating to the stoichiometry $[Ir_2Cl_2\{P(O\text{-}o\text{-tolyl})_3\}_3]$ [1]. Treatment of this complex with carbon monoxide gave the dimeric carbonyl $[IrCl(CO)\{P(O\text{-}o\text{-tolyl})_3\}]_2$ which underwent typical bridge-splitting reaction with pyridine and γ-picoline to give the monomeric compound $[IrCl(CO)\{P(O\text{-}o\text{-tolyl})_3\}L]$ (L = γ-pic and py). Both carbonyls were white in colour and contained single ν(CO) absorptions in their IR spectra at 2075 and 2045 cm^{-1} respectively which seemed to preclude their formulation as square-planar iridium(I) complexes. Other reactions of the yellow powder with a series of neutral donor ligands produced stable white monomeric compounds of general formula $[IrCl\{P(O\text{-}o\text{-tolyl})_3\}L_2]$ in 30—60% yields. The colour of these latter products provided further evidence for an iridium(III) oxidation state in these complexes suggesting that the single tri-*o*-tolylphosphite ligand was bonding as a tridentate dimetallated group. Although numerous examples exist [2] in which a single aromatic group on a tertiary phosphine or phosphite ligand undergoes intramolecular substitution via oxidative addition of a transition metal ion to a β-carbon—hydrogen bond only one example is known where bis-chelation occurs with two aromatic groups on the same phosphine. Thus to date [Pt{($CH_2C_6H_4$)P-t-Bu($C_6H_4CH_2$)} {P-t-Bu(*o*-tolyl)$_2$}], formed by heating [PtMe{($CH_2C_6H_4$)P-t-Bu(*o*-tolyl)} {P-t-Bu(*o*-tolyl)$_2$}], represents the only example of this type of linkage [3]. Metal methyls do, however, constitute much better leaving groups [4] for internal metal—carbon bond formation than hydrides or chlorides and this may account for the previous absence of dimetallated species from interaction of phosphines or phosphites with metal—halide precursors. It was hence desirable to structurally characterise one of these white iridium complexes to confirm the mode of bonding of the tri-*o*-tolylphosphite to the iridium. To that end the structure of [$\overline{\text{Ir}\{\text{P(OC}}_6\text{H}_3\text{Me)}_2$-($OC_6H_4Me$)}Cl($\gamma$-pic)$_2$] has been determined by X-ray diffraction.

Crystal data

$IrClPO_3N_2C_{33}H_{33} \cdot H_2O$; Mol. wt. 782.29; monoclinic, space group $P2_1/c$, a 9.12(2), b 17.36(2), c 20.65(2) Å, β 90.5(1)°; D_m 1.57, D_c 1.59 g cm^{-3}; U 3268.6 Å^3; Z 4; μ(Mo-K_α) 45.0 cm^{-1}; λ(Mo-K_α) 0.7107 Å. A white needle-shaped crystal of dimensions 0.10 × 0.12 × 0.22 mm was used to obtain intensity data between 3 and 20° θ on the Philips PW 1100 four-circle single crystal diffractometer at the NPRL, CSIR. 3177 reflections were scanned in the $\omega - 2\theta$ mode for 30 s with graphite-monochromated Mo-K_α radiation and background readings were recorded for the same time. 2583 reflections were considered observed on the basis of $I > 2\sigma(I)$. Standard reflections (1 $\bar{3}$ 1), (4 2 2) and (14 0 3) were remeasured every hour and their intensities had decreased by 2.8, 0.3 and 3.7% respectively after 56 h. Background and Lp corrections were applied, as well as absorption corrections by means of numerical integration. Transmission factors varied between 0.54 and 0.57. No extinction or decomposition corrections were made.

Determination of the structure

Positions for all the non-hydrogen atoms were found by means of Patterson and Fourier methods. An IBM 360/65 computer was used for least-squares refinement of positional and isotropic (C) and anisotropic (Ir, Cl, P, O, N) thermal parameters and the residual value ($R = (\Sigma \| F_o| - |F_c\|)/\Sigma |F_o|$) was reduced to 0.040. A weighting scheme was applied to reflections having large F and/or small θ-values. Scattering factors, corrected for anomalous dispersion, were those of Cromer and Mann [5]. All calculations were done by the X-ray system of crystallographic programs [6] and figures were drawn by the ORTEP program of Johnson [7]. Observed and calculated structure factors are available. The Table of structure factors can be obtained from the authors.

Results and discussion

Positional and thermal parameters are given in Table 1, while Tables 2 and 3 contain bond lengths and angles. Table 4 lists particulars of planes through various parts of the molecule and Table 5 gives some non-bonded distances. Fig. 1 explains the atomic numbering scheme. Coordination around the Ir atom is slightly distorted from octahedral, with two picoline groups and a Cl atom taking up three *facial* positions. The three remaining coordination sites are filled by the tridentate chelating tritolylphosphite ligand, viz. by P and the *ortho* carbon atoms of two of the tolyl groups. The two internal metal—carbon bonds are *cis* to each other and *trans* to the two γ-picoline ligands. Though numerous examples are known in which triphenylphosphite and its derivatives form bidentate monometallated complexes and the structure of one, namely chlorobis[2-(diphenoxyphosphinooxy)phenyl](triphenylphosphite)iridium(III) (I) has been elucidated [8], this represents the first example reported in which a single phosphite ligand is bonded via two aryl—carbon metal bonds. The formation of two five-membered chelate rings involves very little additional steric strain and in fact angles associated with these rings are very close to those found for the monometallated phosphites in I. For example the P—Ir—C angles of 79 and 80° compare well with the mean 79.6° found in I as do Ir—P—O angles of 110° (107° for I). Similarly P—O—C angles are 112 and 113° (116° in I). As a comparison the Ir—P—O(13) angle is 125° and P—O(13)—C(131) is 128° in the non-chelated group. The chelate rings do not deviate much from planarity with root-mean-square deviations of the atoms from the planes of 0.06 and 0.09 Å. The remaining part of each phenyl ring is tilted slightly from these planes by 1.8 and 5.5°. It appears that chelate ring closure pulls the phosphorus approximately 10° towards the metal—carbon bond (cf. C(112)—Ir—P(1) 80°) and 0.30 Å out of the plane defined by Ir, O(12), C(121) and C(122). In forming a *facial* bis-chelated product, the phosphorus is also pulled 11° towards the other metal—carbon bond (cf. C(122)—Ir—P1 79°), 0.21 Å out of the plane defined by Ir, O(11), C(111) and C(112). These two planes are approximately perpendicular (89°), with the effect that the formation of the second ring causes very little extra intramolecular strain on the first ring. The Ir—P(1) bond is tilted towards C(112) and C(122) in the plane C(112)—C(122)—Ir, 14° away from the normal. With tris-chelation, however, metallation of the third arene group via an *ortho*-phenyl carbon atom would require significant and excessive distortion of the third chelate ring. The position of a new metal—carbon bond is limited geometrically to one of the two positions *trans* to an existent one and distortions in opposite directions would be required. Because of this it seems unlikely that trimetallation will be effected in aryl phosphites via *ortho*-aryl carbon—metal bonds. From a model of this complex, however, it is possible to metallate the non-bonded arene group via the *ortho*-methyl group, causing very little extra strain in the metallated rings and forming a fairly strain-free six-membered ring. Attempts in this direction are at present underway.

The Ir—C bond lengths of 2.04 and 2.05 Å are slightly but significantly shorter than those of 2.09 and 2.12 Å found for the two *cis*-bonded C atoms on the two different phosphite ligands in I and may simply represent variation due to the different crystallographic *trans*-effects of the N and P atoms. Similarly

(continued on p. 392)

TABLE 1

ATOMIC COORDINATES [a] WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	y	z	B or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	0,06429(4)	0,31548(3)	0,34270(2)	0,0379(3)	0,0388(3)	0,0347(3)	0,0017(2)	0,0008(2)	−0,0010(2)
Cl(1)	−0,0155(3)	0,4494(2)	0,3357(1)	0,0604(19)	0,0405(17)	0,0587(19)	0,0079(15)	0,0004(15)	−0,0001(15)
P(1)	0,1214(3)	0,1967(2)	0,3329(1)	0,0408(17)	0,0435(19)	0,0401(17)	0,0024(14)	−0,0037(13)	−0,0011(14)
O(11)	−0,0235(8)	0,1468(4)	0,3227(4)	0,0445(47)	0,0414(45)	0,0671(53)	0,0060(38)	−0,0038(39)	−0,0042(40)
O(12)	0,2133(8)	0,1836(5)	0,2685(3)	0,0470(44)	0,0569(49)	0,0480(45)	0,0114(40)	0,0107(35)	−0,0047(42)
O(13)	0,2135(8)	0,1484(4)	0,3838(3)	0,0558(48)	0,0410(45)	0,0495(47)	0,0119(38)	−0,0134(38)	−0,0065(37)
C(111)	−0,1503(11)	0,1928(6)	0,3108(5)	3,13(27)					
C(112)	−0,1359(11)	0,2715(6)	0,3153(5)	3,10(27)					
C(113)	−0,2652(13)	0,3145(7)	0,3051(6)	4,22(31)					
C(114)	−0,3074(14)	0,2755(8)	0,2890(6)	4,75(34)					
C(115)	−0,4006(13)	0,1968(7)	0,2843(6)	4,32(32)					
C(116)	−0,2772(12)	0,1524(6)	0,2953(5)	3,58(29)					
C(117)	−0,2772(14)	0,0663(8)	0,2896(6)	5,12(36)					
C(121)	0,1998(12)	0,2471(7)	0,2251(5)	3,69(30)					
C(122)	0,1309(11)	0,3132(7)	0,2486(5)	3,25(26)					
C(123)	0,1188(14)	0,3716(8)	0,2039(6)	4,82(35)					
C(124)	0,1739(16)	0,3631(9)	0,1387(7)	6,19(42)					
C(125)	0,2375(15)	0,2944(8)	0,1206(7)	5,46(38)					
C(126)	0,2529(13)	0,2353(7)	0,1622(6)	4,18(32)					
C(127)	0,3213(17)	0,1590(9)	0,1429(7)	6,40(43)					

C(131)	0,2797(12)	0,0760(7)	0,3749(5)	3,90(30)					
C(132)	0,2148(15)	0,0200(8)	0,3365(7)	5,70(39)					
C(133)	0,2822(17)	−0,0538(9)	0,3313(7)	6,59(43)					
C(134)	0,4110(17)	−0,0668(9)	0,3661(7)	6,64(44)					
C(135)	0,4733(15)	−0,0098(9)	0,4042(7)	5,83(41)					
C(136)	0,4081(13)	0,0637(7)	0,4093(6)	4,30(31)					
C(137)	0,4762(16)	0,1271(8)	0,4501(7)	5,90(40)					
C(21)	0,4750(13)	0,3586(7)	0,4512(6)	4,09(31)					
C(22)	0,3440(12)	0,3287(7)	0,4265(5)	3,97(30)					
N(23)	0,2740(9)	0,3605(5)	0,3753(4)	3,33(22)					
C(24)	0,3346(13)	0,4227(7)	0,3480(6)	4,07(31)					
C(25)	0,4655(14)	0,4561(7)	0,3713(6)	4,76(34)					
C(26)	0,5341(13)	0,4238(7)	0,4239(6)	4,04(31)					
C(27)	0,6744(15)	0,4593(8)	0,4518(7)	5,72(39)					
C(31)	−0,0128(13)	0,3810(7)	0,5469(6)	4,33(32)					
C(32)	0,0273(12)	0,3777(7)	0,4827(5)	3,60(29)					
N(33)	−0,0050(9)	0,3186(5)	0,4432(4)	3,43(22)					
C(34)	−0,0847(13)	0,2602(7)	0,4676(6)	4,52(33)					
C(35)	−0,1312(15)	0,2591(8)	0,5332(7)	5,50(38)					
C(36)	−0,0927(13)	0,3226(8)	0,5724(6)	4,56(32)					
C(37)	−0,1430(18)	0,3231(10)	0,6440(8)	7,26(47)					
O(2)	−0,1221(10)	0,0436(4)	0,4770(4)	0,0897(63)	0,0205(42)	0,0948(65)	0,0119(41)	−0,0416(52)	−0,0142(42)

[a] The anisotropic temperature factors are of the form

$$T = \exp[-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*}l^2U_{33} + 2a^{*}b^{*}hkU_{12} + 2a^{*}c^{*}hlU_{13} + 2b^{*}c^{*}klU_{23})]$$

TABLE 2

BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Ir—P(1)	2.14(1)	Ir—Cl(1)	2.44(1)
Ir—N(23)	2.17(1)	Ir—N(33)	2.17(1)
Ir—C(112)	2.05(1)	Ir—C(122)	2.04(1)
P(1)—O(11)	1.59(1)	P(1)—O(12)	1.59(1)
O(11)—C(111)	1.42(1)	O(12)—C(121)	1.43(1)
C(111)—C(112)	1.38(2)	C(121)—C(122)	1.40(2)
C(112)—C(113)	1.41(2)	C(122)—C(123)	1.38(2)
C(113)—C(114)	1.42(2)	C(123)—C(124)	1.45(2)
C(114)—C(115)	1.37(2)	C(124)—C(125)	1.38(2)
C(115)—C(116)	1.38(2)	C(125)—C(126)	1.35(2)
C(111)—C(116)	1.39(2)	C(121)—C(126)	1.40(2)
C(116)—C(117)	1.50(2)	C(126)—C(127)	1.52(2)
C(21)—C(22)	1.40(2)	C(31)—C(32)	1.38(2)
C(22)—N(23)	1.35(1)	C(32)—N(33)	1.34(1)
N(23)—C(24)	1.34(1)	N(33)—C(34)	1.35(2)
C(24)—C(25)	1.41(2)	C(34)—C(35)	1.42(2)
C(25)—C(26)	1.37(2)	C(35)—C(36)	1.41(2)
C(21)—C(26)	1.38(2)	C(31)—C(36)	1.36(2)
C(26)—C(27)	1.53(2)	C(36)—C(37)	1.55(2)
P(1)—O(13)	1.58(1)	C(134)—C(135)	1.38(2)
O(13)—C(131)	1.41(1)	C(135)—C(136)	1.41(2)
C(131)—C(132)	1.38(2)	C(131)—C(136)	1.38(2)
C(132)—C(133)	1.43(2)	C(136)—C(137)	1.52(2)
C(133)—C(134)	1.39(2)		

the Ir—P(1) bond length of 2.14 Å, substantially smaller due to π-acidity effects than average Ir—P values of 2.37—2.40 Å for phosphines [9], is of the same order of magnitude as that found in I for the phosphorus *trans* to chlorine. The slight significant shortening of this bond length compared with that in I is probably related to the shorter Ir—C parameters and the Ir—P(1) bond length thus represents an equilibrium position imposed by the constraints of the two chelate rings.

As found in I the phenyl rings of the tri-*o*-tolylphosphite ligand are distorted from six-fold symmetry. The average endocyclic angle at the O-substituted C atom is 126° compared to the average value of 116° for the *ortho*-position. The remaining angles average 121°. This phenomenon is more pronounced for the two metallated tolyl rings than the remainder. The distortion is explained [8] in terms of a charge-transfer from the O-substituted C atom to the neighbouring O and *ortho*-ring C atoms. Likewise, the picoline rings exhibit perturbations caused by replacement of CH by N [10]. The average ring angle subtended at N is 118°, whereas the neighbouring angles at the *ortho*-ring positions average 123°. The average of the remainder equals 119°.

The Ir—Cl(1) distance of 2.44 Å agrees satisfactorily with the value of 2.416 Å in I for Cl *trans* to P. The P(1)—Ir—Cl(1) angle of 171° is virtually identical with its counterpart in I although certain questions are raised in this respect. Internal strain in the tridentate tri-*o*-tolyl phosphite ligand causes the "bite" angles to be smaller than and equal to 90°. Relaxation among the remaining ligands would then have produced angles larger than 90° around Ir. Instead it is observed that the Cl(1) atom and two picoline groups are clustered together and their angles around Ir are also smaller than 90°. Intramolecular interaction between Cl(1)

TABLE 3

BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

O(11)—P(1)—O(13)	103.5(4)	O(12)—P(1)—O(13)	101.5(4)
P(1)—Ir—Cl(1)	170.6(2)	O(11)—P(1)—O(12)	104.7(4)
P(1)—Ir—C(112)	80.3(3)	P(1)—Ir—C(122)	79.4(3)
P(1)—Ir—N(23)	99.3(3)	P(1)—Ir—N(33)	100.8(3)
Cl(1)—Ir—C(112)	94.3(3)	Cl(1)—Ir—C(122)	93.1(3)
Cl(1)—Ir—N(23)	86.3(3)	Cl(1)—Ir—N(33)	86.8(3)
C(112)—Ir—N(33)	90.4(4)	C(122)—Ir—N(23)	91.9(4)
C(112)—Ir—N(23)	177.8(4)	C(122)—Ir—N(33)	179(2)
C(112)—Ir—C(122)	90.1(4)	N(23)—Ir—N(33)	87.6(3)
Ir—P(1)—O(11)	109.6(3)	Ir—P(1)—O(12)	110.3(3)
P(1)—O(11)—C(111)	112.8(7)	P(1)—O(12)—C(121)	111.8(7)
O(11)—C(111)—C(112)	118.0(9)	O(12)—C(121)—C(122)	116.9(9)
C(111)—C(112)—Ir	118.2(8)	C(121)—C(122)—Ir	119.1(8)
O(11)—C(111)—C(116)	115.4(9)	O(12)—C(121)—C(126)	116(1)
C(111)—C(116)—C(117)	121(1)	C(121)—C(126)—C(127)	121(1)
C(117)—C(116)—C(115)	123(1)	C(127)—C(126)—C(125)	122(1)
Ir—C(112)—C(113)	125.8(8)	Ir—C(122)—C(123)	127.0(9)
C(116)—C(111)—C(112)	127(1)	C(126)—C(121)—C(122)	127(1)
C(111)—C(112)—C(113)	116(1)	C(121)—C(122)—C(123)	114(1)
C(112)—C(113)—C(114)	119(1)	C(122)—C(123)—C(124)	122(1)
C(113)—C(114)—C(115)	121(1)	C(123)—C(124)—C(125)	119(1)
C(114)—C(115)—C(116)	122(1)	C(124)—C(125)—C(126)	122(1)
C(115)—C(116)—C(111)	116(1)	C(125)—C(126)—C(121)	116(1)
Ir—N(23)—C(22)	120.4(7)	Ir—N(33)—C(32)	122.3(7)
Ir—N(23)—C(24)	121.7(7)	Ir—N(33)—C(34)	120.1(7)
C(27)—C(26)—C(25)	121(1)	C(37)—C(36)—C(35)	119(1)
C(27)—C(26)—C(21)	120(1)	C(37)—C(36)—C(31)	122(1)
C(26)—C(21)—C(22)	120(1)	C(36)—C(31)—C(32)	119(1)
C(21)—C(22)—N(23)	122(1)	C(31)—C(32)—N(33)	124(1)
C(22)—N(23)—C(24)	117.8(9)	C(32)—N(33)—C(34)	117.6(9)
N(23)—C(24)—C(25)	123(1)	N(33)—C(34)—C(35)	122(1)
C(24)—C(25)—C(26)	119(1)	C(34)—C(35)—C(36)	117(1)
C(25)—C(26)—C(21)	119(1)	C(35)—C(36)—C(31)	120(1)
Ir—P(1)—O(13)	125.3(3)	C(136)—C(131)—C(132)	123(1)
P(1)—O(13)—C(131)	127.8(7)	C(131)—C(132)—C(133)	119(1)
O(13)—C(131)—C(132)	121(1)	C(132)—C(133)—C(134)	118(1)
O(13)—C(131)—C(136)	116(1)	C(133)—C(134)—C(135)	121(1)
C(131)—C(136)—C(137)	121(1)	C(134)—C(135)—C(136)	121(1)
C(137)—C(136)—C(135)	122(1)	C(135)—C(136)—C(131)	117(1)

TABLE 4

PLANES THROUGH VARIOUS PARTS OF THE MOLECULE

Plane [a]	σ [b]	x [c]	Δ [d]	C(12)	C(13)	C(2)	C(3)	CH(11)	CH(12)
C(11)	0.008	2.0	C(117), 0.02	86.6	25.7	46.8	84.5	1.8	82.7
C(12)	0.007	1.3	C(127), 0.03		68.8	85.1	48.5	86.1	5.5
C(13)	0.002	0.1	C(137), 0.02			54.5	84.5	25.8	73.2
C(2)	0.009	2.0	C(27), 0.05				56.5	48.6	85.1
C(3)	0.005	0.8	C(37), 0.01					82.8	44.4
CH(11)	0.063	202.6							82.0
CH(12)	0.093	416.4		R(2)					
R(1)	0.012	4.4	P(1), 0.21	88.8					
R(2)	0.012	4.2	P(1), 0.30						

[a] Names are abbreviated in the following manner: C(11) is the plane through the phenyl ring C(111) to C(116); similarly C(12) represents C(121) to C(126); C(13) represents C(131) to C(136); C(2) represents C(21) to C(26); C(3) represents C(31) to C(36). CH(11) and CH(12) represent the chelating rings through Ir, P(1), O(11), C(111) and C(112) and Ir, P(1), O(12), C(121) and C(122) respectively, while R(1) and R(2) are defined by Ir, O(11), C(111), C(112) and Ir, O(12), C(121) and C(122) respectively. [b] σ is the standard deviation (in Å) of the atoms from the plane they define. [c] x is the statistical quantity x^2 of each distribution. [d] Δ is the deviation of the atom named, from the plane (Å).

TABLE 5

SELECTED INTRAMOLECULAR DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Cl(1)—H(113)	2.69(1)	Cl(1)—H(32)	2.84(1)
Cl(1)—H(123)	2.64(1)	C(137)—H(22)	3.13(1)
Cl(1)—H(24)	2.80(1)		

and closely approaching H atoms (Cl—H 2.63 Å) has been invoked before [11] to explain unusual angles. The hypothetical positions of H(113), H(123), H(24) and H(32), calculated at 1.0 Å from their respective C atoms, give Cl(1)—H distances that vary between 2.64 and 2.84 Å (see Table 5). It appears, therefore, that the Cl(1) atom maintains equilibrium at a position approximately equidistant from these four H atoms.

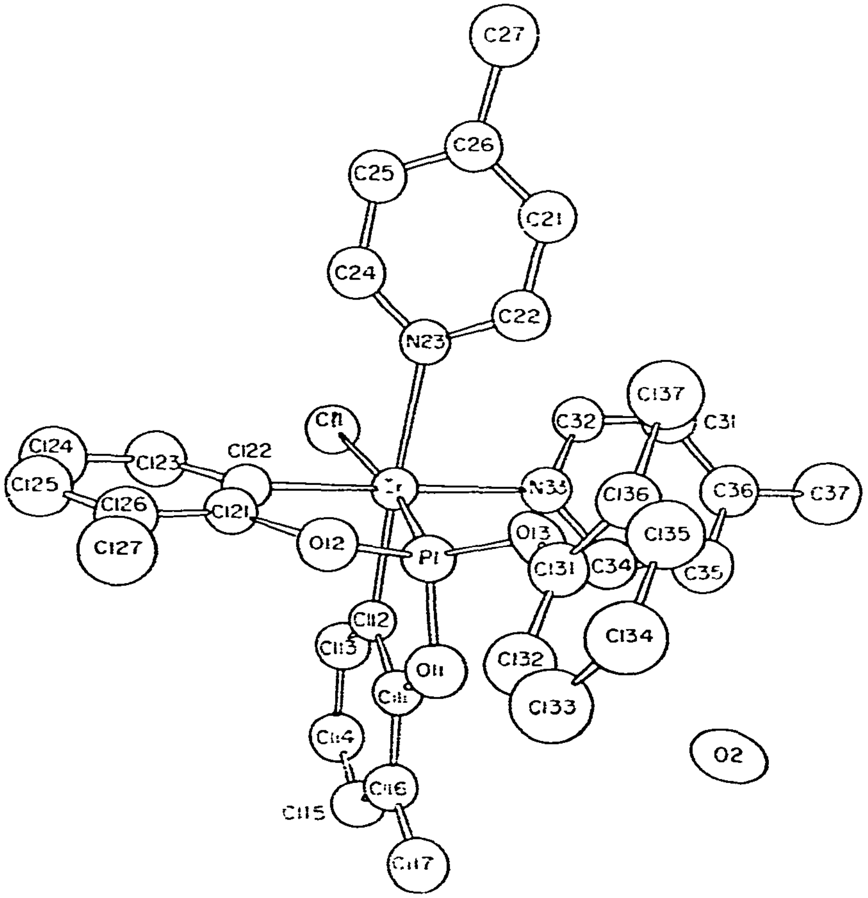

Fig. 1. Atom-numbering scheme.

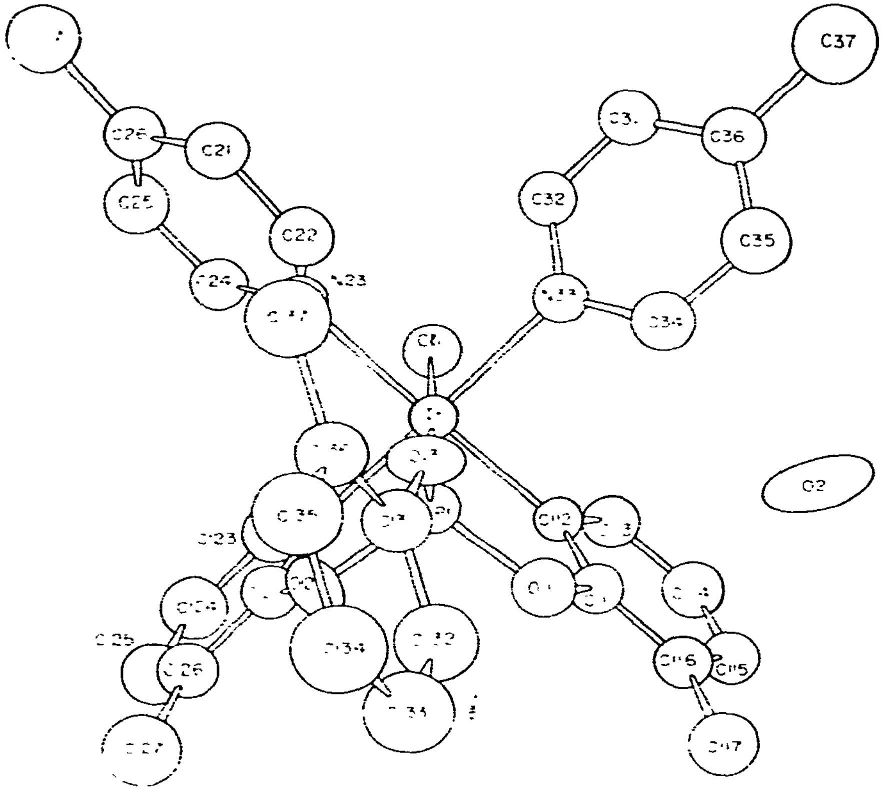

Fig. 2. Projection onto the plane defined by P(1), O(11) and O(12).

It remains to comment on the relative twists of the two picoline and the unmetallated tolyl ring. Steric interaction between the methyl C(137) of the tolyl ring and the O—P(1)—O moiety of the metallated rings requires a rotation so that C(137) is pointed away from this moiety. The O(13), C(137) and its H atoms are barriers to free rotation of the picoline rings, whose atoms H(22), H(24), H(32) and H(34) are liable to steric interaction with them. The final conformation is seen in Fig. 2.

References

1 M.J. Nolte, E. Singleton and E. van der Stok, J. Organometal. Chem., 105 (1976) C13.
2 J. Dehand and M. Pfeffer, Coord. Chem. Rev., 18 (1976) 327.
3 A.J. Cheney, W.S. McDonald, K. O'Flynn, B.L. Shaw and B.L. Turtle, Chem. Commun., (1973) 128.
4 M.I. Bruce, Angew. Chem. Int. Ed. Engl., 16 (1977) 73.
5 D.T. Cromer and J.B. Mann, Acta Crystallogr., A 24 (1968) 321.
6 J.M. Stewart, G.J. Kruger, H. Ammon, C.H. Dickinson and S.R. Hall, Comput. Sci. Tech. Rep. TR-192, Univ. of Maryland, 1972.
7 C.K. Johnson, ORTEP, Oak Ridge National Laboratory Report ORNL-3794, 1965.
8 J.M. Guss and R. Mason, J. Chem. Soc. Dalton, (1972) 2193.
9 G. Perego, G. Del Piero, M. Cesari, M.G. Clerici and E. Perrotti, J. Organometal. Chem., 54 (1973) C51.
10 C.A. Coulson and H. Looyenga, J. Chem. Soc. (1965) 6592.
11 B. Cetinkaya, M.F. Lappert, G.M. McLaughlin and K. Turner, J. Chem. Soc. Dalton, (1974) 1591.