Characterisation of Three Isomers of *trans*-$[IrCl_2(EMe_2Ph)_4]ClO_4$ (E = P or As) each containing Adjacent Parallel Phenyl Rings

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The major of three isomers of *trans*-$[IrCl_2(EMe_2Ph)_4]ClO_4$ (E = P or As), identified by their low temperature $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H n.m.r. spectra, corresponds to that found in the crystal (E = P) and each contains adjacent and parallel phenyl rings leading to ^1H n.m.r. (phenyl) resonances as high-field as δ 5.7.

Unexplained features of n.m.r. spectra of several *trans*-octahedral complexes containing four PMe_2Ph ligands in a plane have been described.[1—3] A broad ^1H n.m.r. Me singlet at room temperature has been reported for *trans*-$[IrCl_2(PMe_2Ph)_4]^+$ (**1**)[1] and one PMe_2Ph ligand in the isoelectronic *trans*-$[OsCl_2(PMe_2Ph)_4]$ was thought to be unique, possibly co-ordinated through the phenyl group agostically or by π-complexation.[2] We now show that the Ir complex contains four M–P bonds and that the n.m.r. effects result from the presence of rotamers in exchange, each containing at least two phenyl groups in close parallel alignment.

The complexes *trans*-$[IrCl_2(EMe_2Ph)_4][ClO_4]$, (**1**, E = P) and (**2**, E = As) were prepared as yellow crystals by treating *trans,mer*-$[IrCl_2(H_2O)(EMe_2Ph)_3][ClO_4]$[4] with EMe_2Ph. The single-crystal *X*-ray structure of (**1**) (Figure 1)† shows that two

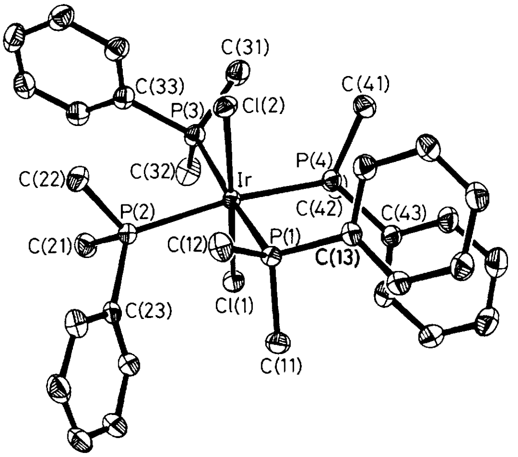

Figure 1. Molecular structure of $[IrCl_2(PMe_2Ph)_4]ClO_4$ (**1**). Selected bond lengths (Å) and angles (°): Ir–Cl(1), 2.359(1); Ir–Cl(2), 2.371(1); Ir–P(1), 2.376(1); Ir–P(2), 2.416(1); Ir–P(3), 2.424(2); Ir–P(4), 2.390(1) (the shorter Ir–P distances are for the phosphines with parallel arene rings); Cl(1)–Ir–P(1), 95.1(1); Cl(1)–Ir–P(2), 84.6(1); Cl(1)–Ir–P(3), 92.5(1); Cl(1)–Ir–P(4), 86.4(1); Cl(2)–Ir–P(1), 87.2; Cl(2)–Ir–P(2), 94.2(1); Cl(2)–Ir–P(3), 85.3(1); Cl(2)–Ir–P(4), 94.8(1) (phosphines alternately up and down); Ir–P–C(methyl), 113.2(2) to 115.9(2), average 114.9; Ir–P–C(phenyl), 118.2(2) to 120.2(2), average 119.2.

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† *Crystal data* for compound (**1**): $C_{32}H_{44}Cl_3IrO_4P_4$, $M = 915.19$, monoclinic, space group $P2_1/c$, $a = 11.185(2)$, $b = 26.301(2)$, $c = 12.551(2)$ Å, $\beta = 90.17(1)°$, $U = 3692$ Å^3, $Z = 4$, $F(000) = 1824$, Mo-K_α radiation (graphite monochromated), $\lambda = 0.71073$ Å, μ(Mo-K_α) = 40.3 cm^{-1}, $D_c = 1.65$ g cm^{-3}, 6487 independent reflections, absorption corrected, 5486 with $F_o > 3\sigma(F_o)$ used. Direct methods (SHELXS-86), $R = 0.035$, $R_w = 0.034$. Non-hydrogen atoms refined anisotropically and hydrogen atoms included in idealised positions, 397 parameters refined. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

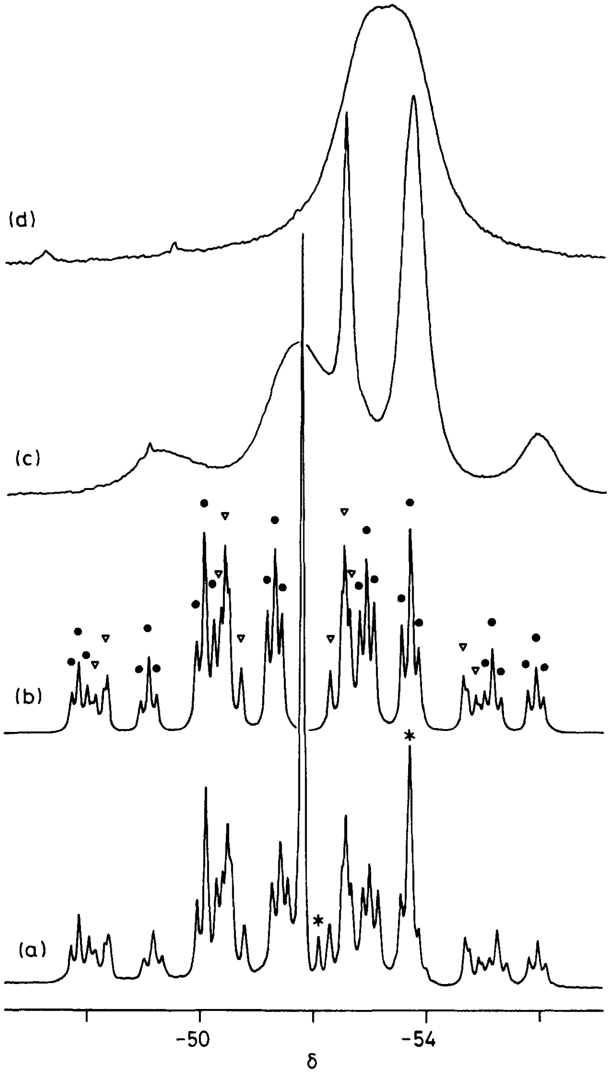
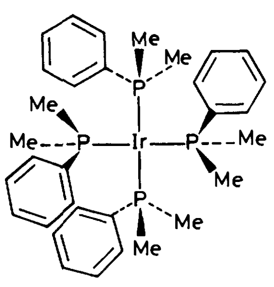
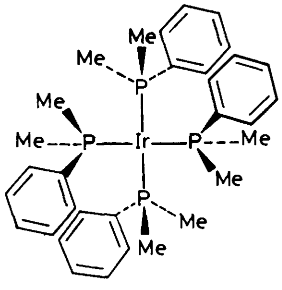


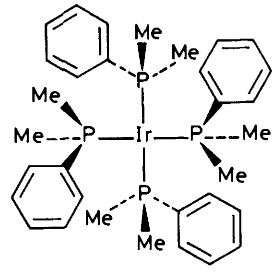
Figure 2. $^{31}P\{^1H\}$ n.m.r. spectra of compound (**1**) (dichloromethane, 161.9 MHz) at −80 °C (a), at −5 °C (c), and at 25 °C (d). Computer simulations of ABCD (●) and AA'BB' (∇) components of the low temperature spectrum are shown in (b). Unassigned resonances (*) are indicated, one of which underlies the central peak of an assigned triplet. Shifts are relative to 80% H_3PO_4.



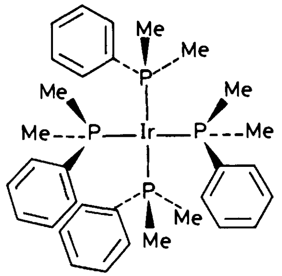
(**A**)



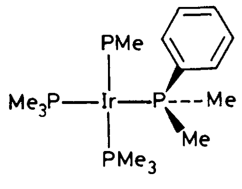
(**B**)



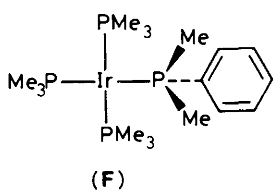
(**C**)



(**D**)



(**E**)



(**F**)

substituents on each phosphorus atom, a Me and a Ph group, lie on one side of the approximate P_4 plane and a Me group on the other. Because of the way the Ph groups occupy available sites, all the PMe_2Ph ligands are different. Two Ph rings are close and parallel (3.83 Å between their centres and 10.6° between rings) while the other two are distant from others. There are four possible rotamers, (**A**) to (**D**), with a Me and a phenyl group of each PMe_2Ph ligand on the same side of the P_4 plane. Rotamer (**A**) is found in the crystal, rotamers (**B**) and (**C**) each have equivalent PMe_2Ph ligands, while rotamer (**D**) has two sets of equivalent *cis*-phosphines. Three interconverting isomers detected by n.m.r. are believed to be (**A**), (**B**), and (**D**).

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ n.m.r. spectra of (**1**) in dichloromethane or chloroform at 20 °C contain very broad coalesced signals. There is no exchange with added PMe_2Ph. Low temperature spectra indicate three isomers in significant abundance, possibly with a very low concentration of a fourth. For example, the $^{31}P\{^1H\}$ spectrum at −80 °C (Figure 2) contains a singlet at δ −51.6, an AA'BB' pattern [δ = −53.15 and −49.46] and an ABCD pattern [δ = −54.37, −53.63, −50.29, and −49.02]. Good simulated spectra were obtained by keeping the *cis* couplings at −23 Hz and the *trans* ones at 363 Hz (or with signs reversed).‡ The predominant ABCD pattern is assigned to rotamer (**A**) found in the crystal. The AA'BB' pattern is only consistent with rotamer (**D**) with equivalent PMe_2Ph arranged mutually *cis* but the singlet (A_4 pattern) could result from either (**B**) or (**C**). Above −80 °C the ABCD and AA'BB' patterns broaden first and the A_4 singlet broadens at higher temperatures. Thus the isomers (**A**) and (**D**) undergo exchange faster than the symmetrical isomer, which is (**B**) or (**C**).

The ^1H and $^{13}C\{^1H\}$ spectra of (**1**) and (**2**) correspond but those of (**2**) without ^{31}P coupling are more easily interpreted. The ^1H n.m.r. spectrum of (**2**) (CD_2Cl_2, 20 °C) contains one Me singlet at 1.60 ($\Delta\nu_{1/2}$ = 60 Hz) and Ph resonances in the range δ 7.24 to 7.50 but at −85 °C sharp signals appear in the

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‡ The separation of this ^{31}P n.m.r. spectrum into three sets of signals was confirmed by a ^{31}P–^{31}P DQF-COSY (phosphorus–phosphorus double quantum field correlation spectroscopy) experiment at −75 °C. Off-diagonal peaks confirm the internal coupling within the AA'BB' and ABCD sets but appropriate peaks were also detected which were consistent with isomer exchange at this temperature.

ranges δ 5.78 to 8.30 (Ph) and δ 0.70 to 1.98 (at least 12 Me singlets), consistent with several isomers present. On raising the temperature to −70 °C signals had broadened considerably except for two sharp Me singlets at δ 1.645 and 1.695 and a single set of Ph resonances at δ 8.04 (d, *ortho*), 7.37 (t, *meta*), 7.32 (t, *meta*), 6.85 (t, *para*), and 6.09 (d, *ortho*), which are assigned to the symmetrical isomer. The close approach of a Me group to a Ph group of a ligand *cis* to it would lead to a low δ value for that Me, which was not observed, and a close parallel alignment of Ph groups would lead to large upfield and downfield shifts for the ring protons depending upon their positions relative to the adjacent ring. This was very clearly observed; note the 2.0 p.p.m. shift between the *ortho*-H doublets for (**2**). Since the Me and Ph groups in the symmetrical isomer do not approach closely but there is a close phenyl alignment, we can be sure this isomer is (**B**) not (**C**). Hence the predominant isomers present, (**A**) (56%), (**B**) (18%), and (**D**) (26%), all have aligned Ph groups and the intuitively attractive isomer (**C**) is present in very low concentrations, if at all (see the weak unassigned peaks in Figure 2).

Restricted rotation is normally associated with bulky phosphines, such as t-butyl substituted ones,[5] and our observations probably depend upon there being four fairly small ligands in a plane. Even *trans*-$[IrCl_2(PMe_3)_3(PMe_2Ph)]ClO_4$ shows two isomers at −75 °C: ABCD (90%) and AB_2C (10%) patterns in the $^{31}P\{^1H\}$ n.m.r. spectrum assigned to rotamers (**E**) (found in the crystal) and (**F**) respectively.

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