Synthesis, Crystal Structure and some Reactions of *trans*-$[Ir(CO)Cl_2(PEt_3)_2(PCl_2)]$ †

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Reaction between *trans*-$[Ir(CO)Cl(PEt_3)_2]$ (1) and PCl_3 gives *trans*-$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ (2), which has been characterised by partial elemental analysis, *X*-ray crystal-structure analysis, and mass and n.m.r. spectra. Reaction with HCl leads to slow cleavage of the Ir–P′ bond at room temperature, but HCl–BCl_3 (1 : 1) protonates the $P'Cl_2$ group. A BH_3 adduct is formed with B_2H_6 at low temperature, but with an excess of B_2H_6 at room temperature a mixture of adducts is produced containing both Ir–H and P′–H bonds. An equimolar adduct is formed by (2) with BCl_3 but not with BF_3. Reaction with O_2, S_8, or Se_8 gives *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(Y)\}]$ (Y = O, S, or Se): the reaction with O_2 is very slow, but *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(O)\}]$ (3) is also formed from (2) and N_2O_4. The crystal structure of (3) was also determined and has been shown to form adducts with both BCl_3 and $AlCl_3$. Complex (2) reacts with H_2Se to give first *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'HCl(Se)\}]$, then *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'H(Se)(Se'H)\}]$, and finally *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'H_2(Se)\}]$, the last of which was isolated. Reaction with H_2S is much slower, and gives only *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'HCl(S)\}]$. With water, the phosphinate complex *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'H(O)(OH)\}]$ is formed, which crystallizes with $H_3O^+Cl^-$. The Ir–P′ bond is broken by methanol. There is no reaction with either $[\{RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)\}_2]$ or $[PtCl_2(cod)]$ (cod = cyclo-octa-1,5-diene).

We have recently described a series of complexes of iridium containing Ir–PF_2 groups.[1,2] We have also observed [3] an unexpected series of reactions between PCl_3 and *trans*-$[PtCl(PEt_3)_2H]$. In the light of these studies, we have investigated the reaction between PCl_3 and *trans*-$[Ir(CO)Cl(PEt_3)_2]$ (1), and have explored the reactions of the product with protonic acids, Group 6 elements, and some boron and transition-metal acceptors. The reaction of the product with Cl_2 is described elsewhere.[4]

Results

N.m.r. spectroscopic details are given in Table 1.

Reaction between PCl_3 *and* (1).—PCl_3 and (1) react together in dichloromethane at or above 240 K to give a single P-containing product which has been identified by C and H analysis, mass and n.m.r. spectra, and by its crystal structure as *trans*-$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ (2). The crystal structure shows that P′ is *trans* to Cl; structural details are discussed later. The $^{31}P\text{-}\{^1H\}$ spectrum shows a resonance at very high frequency ($\delta = 304$ p.p.m.), associated [1,2,5] with MPX_2 groups, and is assigned to P′; the resonances due to P′ and to the PEt_3 nuclei show the expected triplet and doublet patterns, and in the ^{13}C spectrum the CO resonance shows no coupling larger than 10 Hz. The mass spectrum contains a peak due to the molecular ion; brief details are given in the Experimental section. Compound (2) was found to be stable for extended periods at room temperature either as a solid or in solvents such as CH_2Cl_2, in the absence of air or moisture.

Reaction between (2) *and* HCl.—The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of a solution in CH_2Cl_2 of equimolar amounts of (2) and HCl did not change as the temperature of the solution was raised from 190 to 250 K. At higher temperatures, singlet resonances due to PCl_3 and to *trans*-$[Ir(CO)Cl_2H(PEt_3)_2]$ appeared and increased slowly in intensity relative to the resonances of (2); after some hours at room temperature, all (2) had been consumed. No evidence was observed to suggest the formation of even small concentrations of a complex protonated at P′; the triplet resonance due to P′ remained sharp throughout the temperature range studied.

Reaction between (2) *and* BCl_3.—The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of an equimolar mixture of (2) and BCl_3 in CH_2Cl_2 at 190 K was different from that of (2). The doublet due to PEt_3 was at somewhat higher frequency; the peak due to P′ was shifted from 304 to 127.8 p.p.m., and was a 1 : 1 : 1 : 1 quartet. The $^{11}B\text{-}\{^1H\}$ spectrum showed a single broad resonance in which a doublet splitting of 137 Hz could be resolved. We conclude that the adduct *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(BCl_3)\}]$ was formed.

Reaction between (2) *and an Equimolar Mixture of* HCl *and* BCl_3.—The $^{31}P\text{-}\{^1H\}$ and $^{11}B\text{-}\{^1H\}$ n.m.r. spectra of a solution containing equimolar amounts of (2), HCl, and BCl_3 showed that at low temperature the $P'Cl_2$ group was protonated, giving *trans*-$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2H)]^+[BCl_4]^-$. At 190 K the $^{31}P\text{-}\{^1H\}$ spectrum showed a doublet in the PEt_3 region and a broad singlet at 42.8 p.p.m. in place of the triplet due to P′ at 304 p.p.m. in (2). The large shift to low frequency implies an increase in the co-ordination number at P′. With proton coupling retained, the resonance at 42.8 p.p.m. split into a wide doublet [$^1J(P'H) = 569$ Hz], showing that one H was bound to P′. The $^{11}B\text{-}\{^1H\}$ spectrum at 190 K showed the sharp singlet ($w_{\frac{1}{2}} \sim 2$ Hz) at 7.4 p.p.m., typical [6,7] of $[BCl_4]^-$. The ^1H spectrum showed a wide doublet of broad peaks due to the P′H proton. The P′*H* resonances remained broad as the temperature of the solution was allowed to rise to 300 K, although the coupling did not change significantly; the $^{11}B\text{-}\{^1H\}$ resonance broadened ($w_{\frac{1}{2}} \sim 60$ Hz) and shifted to 10.5 p.p.m. at 300 K. The $^{31}P\text{-}\{^1H\}$ spectrum degraded slowly if the solution was kept at 300 K.

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† Carbonyldichloro(dichlorophosphido)bis(triethylphosphine)-iridium(III).

Supplementary data available (No. SUP 56019, 12 pp.): anisotropic and isotropic thermal parameters, full bond distances and angles, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. N.m.r. parameters [a] for *trans*-$[\mathrm{Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)}]$ (2) and its derivatives

Compound	δ(P′)/ p.p.m.	δ(P)/ p.p.m.	δ(P′H)/ p.p.m.	^1J(P′H)/ Hz	^2J(PP′)/ Hz	^2J(PP)/ Hz	^3J(PH)/ Hz	*T*/K	Other
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)}]$ [b]	304.0	−9.2	—	—	34.0	—	—	300	δ(^{13}C), 162.7
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2(P'Cl_2H)}][\mathrm{BCl_4}]$ [c]	42.8	−5.8	8.78	569	*ca.* 10	—	n.r.	300	δ(^{11}B), 7.4 (at 190 K)
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(O)\}}]$ [c]	6.45	−8.1	—	—	17.1	—	—	300	—
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(S)\}}]$ [d]	44.2	−10.7	—	—	13.7	—	—	300	—
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(Se)\}}]$ [d]	19.2	−11.6	—	—	12.4	—	—	300	δ(^{77}Se), 581.3; ^1J(P′Se) = 775
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(BH_3)\}}]$ [c]	190.1	−9.0	—	—	4.55	—	—	270	δ(B), −19.1; δ(BH), 2.0; ^1J(BH) = 100
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(BCl_3)\}}]$ [c]	127.8	−6.6	—	—	6.1	—	—	190	δ(B), 7.0; ^1J(P′B) = 137
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'HCl(S)\}}]$ [b]	19.4	−11.2 −15.4	8.0	489	13.7	327	4 9	300	—
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'HCl(Se)\}}]$ [b]	−9.1	−9.1 −16.1	7.0	482	13	318.7	9.8 n.r.	220	δ(Se), 245; ^1J(P′Se) = 687
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'H(Se)(Se'H)\}}]$ [c]	−60.1	−11.1 −14.1	7.4	437	14	329	11.6 n.r.	220	δ(Se), 32.2; ^1J(P′Se) = 596 δ(Se′), 324; ^1J(P′Se′) = 317.1
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'H_2(Se)\}}]$ [b]	−105.1	−14.2	4.2	405	14	—	6.4	220	δ(Se), −168; ^1J(P′Se) = 534
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'H(O)(OH)\}}]$ [b]	39.2	−9.0	8.1	503	15	—	2.6	300	—
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(OBCl_3)\}}]$ [c]	38.2	−7.7	—	—	16.5	—	—	300	δ(B), 7.6; ^2J(P′B) = 10.5
$[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(OAlCl_3)\}}]$ [c]	39.9	−7.2	—	—	16.6	—	—	300	—
$[\mathrm{Ir(CO)ClH(PEt_3)_2\{P'H_2(BHCl_2)\}}]$ [c]	−116.4	−10.0	3.4	325.4	15.1	—	5.6	300	δ(B), −2.95; δ(BH), 4.03; δ(IrH), −8.66 ^1J(P′B) = 87, ^1J(BH) = 142, ^2J(PH) = 13.2, ^2J(P′IrH) = 131.2, ^2J(P′BH) = 24
$[\mathrm{Ir(CO)ClH(PEt_3)_2\{P'H_2(BCl_3)\}}]$ [c]	−102.4	−11.1	3.8	333.2	19.1	—	5.7	300	δ(B), 4.3; δ(IrH), −8.76 ^1J(P′B) = 126, ^2J(P′H) = 138.0, ^2J(PH) = 13.1

[a] Shifts are given as positive to high frequency of 85% H_3PO_4 (for P), $SeMe_2$ (for Se), $BF_3{\cdot}OEt_2$ (for B), and $SiMe_4$ (for H, C); n.r. = not resolved. [b] In toluene. [c] In dichloromethane. [d] In chloroform.

Reaction with BF_3.—The ^{31}P-{^{1}H} n.m.r. spectrum of a solution in CH_2Cl_2 containing equimolar amounts of (2) and BF_3 was the same as that of (2) at temperatures between 190 and 300 K, and after prolonged standing at 300 K. We conclude that no adduct is formed between (2) and BF_3.

Reaction with B_2H_6.—At 200 K, (2) and B_2H_6 in 2 : 1 molar ratio reacted in CH_2Cl_2 to give what we formulate as the adduct $[\mathrm{Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(BH_3)\}}]$. The ^{31}P-{^{1}H} n.m.r. spectrum (at 200 K) showed a broad singlet at 189.0 p.p.m., assigned to P′, and a sharp doublet due to PEt_3 at −9.0 p.p.m. The ^{11}B-{^{1}H} spectrum showed a broad peak ($w_{\frac{1}{2}} \sim 100$ Hz) in which no splitting could be resolved; when proton coupling was retained, a quartet pattern [^1J(BH) = 100 Hz] was observed. In the proton spectrum, a broad featureless hump at 1.85 p.p.m. was enhanced by irradiating ^{11}B, and so we assign it to the BH protons. There were no peaks assignable to P′H protons, and the only IrH resonance observed was due to a small amount of $[\mathrm{Ir(CO)Cl_2H(PEt_3)_2}]$. The adduct persisted in solution to 270 K without decomposition, but at room temperature it decomposed.

Reaction between equimolar amounts of (2) and B_2H_6 was less simple. At 190 K the initial product was the same as that formed in the 2 : 1 reaction. However, as the solution was allowed to warm up, the spectrum became complicated. At room temperature there were two products, identified by their n.m.r. spectra. One we formulate as *trans*-$[\mathrm{Ir(CO)ClH(PEt_3)_2\{P'H_2(BCl_3)\}}]$. The P′ resonance was shifted to −102.4 p.p.m., and appeared as a broad 1 : 1 : 1 : 1 quartet ($w_{\frac{1}{2}} \sim 100$ Hz), each component of which split into a wide 1 : 2 : 1 triplet [^1J(P′H) ~ 350 Hz] when proton coupling was restored. The ^{1}H spectrum contained P′H [δ = 3.8 p.p.m., ^1J(P′H) = 333.2 Hz] and IrH [δ = −8.76 p.p.m., ^2J(P′H) = 138.0, ^2J(PH) = 13.1 Hz] resonances, in a ratio (from integration) of 2 : 1. The large value of ^2J(P′H), and the value of δ(IrH), show that H is *trans* to P′ and not to Cl or CO. The ^{11}B-{^{1}H} spectrum gave a doublet [δ = 4.3 p.p.m., ^1J(P′B) = 126 Hz] that was unaffected by retention of proton coupling.

The other product we formulate as $[\mathrm{Ir(CO)ClH(PEt_3)_2\{P'H_2(BHCl_2)\}}]$. The ^{31}P-{^{1}H} resonance due to P′ was at −116.4 p.p.m., and showed a broad 1 : 1 : 1 : 1 quartet structure, each component of which split into a wide 1 : 2 : 1 triplet [^1J(P′H) ~ 350 Hz] when proton coupling was restored. In the ^{1}H spectrum, the P′H resonance (δ = 3.4 p.p.m.) showed a wide doublet coupling [^1J(P′H) = 325.4 Hz], and the IrH resonance (δ = −8.66 p.p.m.), whose integrated intensity was half that of the P′H resonance, was a wide doublet [^2J(P′IrH) = 131.2 Hz] of triplets [^2J(PH) = 13.2 Hz]. A broad doublet [^2J(P′H) = 24 Hz] centred at 4.03 p.p.m. in the ^{1}H spectrum was enhanced by irradiating ^{11}B, and so was assigned to the BH proton. The ^{11}B-{^{1}H} resonance (δ = −2.95 p.p.m.) showed ^1J(P′B) of 87 Hz, and split into a doublet [^1J(BH) = 142 Hz] when proton coupling was restored. Here too the magnitude of ^2J(P′IrH) and the chemical shift of this proton indicate that H is *trans* to P′.

Reaction between (2) *and* $[\mathrm{PtCl_2(cod)}]$ *or* $[\{\mathrm{RuCl_2}(\eta^6\text{-}\mathrm{MeC_6H_4CHMe_2}\text{-}p)\}_2]$.—The ^{31}P-{^{1}H} spectrum of a solution in CH_2Cl_2 containing (2) and $[\{\mathrm{RuCl_2}(\eta^6\text{-}\mathrm{MeC_6H_4CHMe_2}\text{-}p)\}_2]$ in 2 : 1 molar ratio was the same as that of (2) and did not change over several days at room temperature; similarly, there was no apparent reaction between (2) and $[\mathrm{PtCl_2(cod)}]$ (cod = cyclo-octa-1,5-diene) in 2 : 1 molar ratio in CH_2Cl_2 over several days at room temperature.

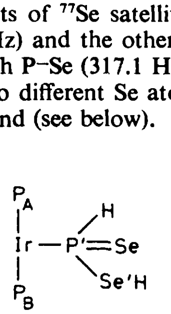
Reaction between (2) *and* O_2, S_8, *or* Se_8.—When (2) was allowed to react with sulphur or red selenium in a mixture of CS_2 and $CHCl_3$ at room temperature for 15 h, solids were obtained which were shown by C and H analysis and n.m.r. spectroscopy to be *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(Y)\}]$ (Y = S or Se). Solutions were stable in toluene at 300 K. The P′ resonance was shifted in each case from *ca.* 304 p.p.m. in (2) to *ca.* 20—40 p.p.m. in the product; for Y = Se the triplet due to P′ showed ^{77}Se satellites [$^1J(P'Se) = 775$ Hz, in the range associated with P=Se] and the ^{77}Se-$\{^1H\}$ resonance was a triplet.

The ^{31}P-$\{^1H\}$ spectrum of (2) in CH_2Cl_2 in the presence of O_2 disappeared over several days at room temperature, and peaks due to a new product grew in its place. The new product was the same as that formed from the reaction of (2) and N_2O_4, and its characterisation as *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(O)\}]$ is described below.

Synthesis of trans-$[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(O)\}]$ *from* (2) *and* N_2O_4.—Reaction between N_2O_4 and (2) in CH_2Cl_2 at room temperature was rapid and gave a product identified by C, H, and Cl analysis, mass and n.m.r. spectra, and by *X*-ray crystallography to be *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(O)\}]$ (3). The mass spectrum contained a peak due to the molecular ion. In the ^{31}P-$\{^1H\}$ spectrum, the triplet due to P′ was shifted from 304 p.p.m. [in (2)] to 6.45 p.p.m. The crystal structure confirmed the formulation, and showed that P′ was *trans* to Cl; details of the structure are given later. The volatile product of the reaction was identified spectroscopically as N_2O.

Reaction between (2) *and* H_2Se.—Reaction between (2) and H_2Se in a 2 : 1 molar ratio in toluene at room temperature gave three products in succession. The first, A, formed after 15 min, was identified by its ^{31}P-$\{^1H\}$ and ^1H n.m.r. spectra as $[Ir(CO)Cl_2(PEt_3)_2\{P'HCl(Se)\}]$. The spectra were recorded at 220 K to avoid further reaction. The resonance due to P′ was broad, and barely showed a triplet structure; it appeared at −9.1 p.p.m., and had ^{77}Se satellites [$^1J(P'Se) = 687$ Hz]. When proton coupling was restored, this resonance showed a wide doublet coupling [$^1J(P'H) = 482$ Hz], confirming the presence of the P′–H bond. The resonance due to the PEt_3 phosphorus nuclei was complicated, since P′ is chiral and the two PEt_3 groups are no longer equivalent, but at 360 MHz it could be analysed as approximating to an ABX spin system. The resonance of the P′ proton confirmed this analysis; it showed a wide doublet splitting due to $^1J(P'H)$, each line of which was further split into a narrow *doublet* due to coupling with one but not both of the PEt_3 nuclei [$^3J(PH) = 9.8$ Hz]. The ^{77}Se resonance appeared as a simple doublet due to P′–Se coupling under the conditions of resolution employed.

After the solution had been allowed to stand for 2 h at room temperature, peaks due to two new species, B and C, appeared and those due to A became weaker; after 12 h at room temperature, much red selenium was present in the tube, and the sole P-containing product was C. This was identified by partial elemental analysis and by its n.m.r. spectra as $[Ir(CO)Cl_2(PEt_3)_2\{P'H_2(Se)\}]$. In the ^{31}P-$\{^1H\}$ spectrum the resonance due to P′ appeared as a broad peak with incipient triplet form at −105.1 p.p.m.; Se satellites were well defined [$^1J(P'Se) = 534$ Hz]. When proton coupling was retained, the resonance split into a wide triplet [$^1J(P'H) = 405$ Hz]. The PEt_3 resonance appeared as a narrow doublet [$^2J(PP') = 14$ Hz], confirming that the groups were equivalent. The resonance of protons bound to P′ showed the expected pattern of a wide doublet of triplets [$^3J(PH) = 6.4$ Hz]. The intermediate species B could only be identified by its n.m.r. spectra, from which we deduce it to be *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'H(Se)(Se'H)\}]$. In the ^{31}P-$\{^1H\}$ spectrum, the resonance due to P′, at −60.1 p.p.m., was broad with a poorly defined triplet form which split into a wide doublet [$^1J(P'H) = 437$ Hz] when proton coupling was retained, showing that one proton was bound to P′. The most surprising feature of the resonance was the presence of *two* sets of ^{77}Se satellites, one with $^1J(P'Se)$ typical of P=Se (596 Hz) and the other with $^1J(P'Se')$ in the range associated[7,8] with P–Se (317.1 Hz). Hence P′ is bound to Ir, to H, and to two different Se atoms, one by a double and one by a single bond (see below).



In such a system, P′ is chiral and so the two PEt_3 nuclei should not be equivalent; in keeping with this, the PEt_3 resonance appeared as the AB part of an ABX pattern. In the ^1H spectrum, the P′H nucleus gave rise to a wide doublet of narrow doublets, confirming the inequivalence of the PEt_3 nuclei. In the ^{77}Se-$\{^1H\}$ spectrum, we observed the P′=Se nucleus as a doublet at 32.2 p.p.m.; the resonance due to Se′ we assign to a weak doublet at 324 p.p.m., but very long accumulation times were necessary to observe this resonance and the assignment must be regarded as tentative. We have no direct evidence for the presence of the proton bound to Se′; we did not observe its resonance, which may have been hidden under the PEt_3 proton resonances. However, its presence must be postulated if Se and Se′ are to remain distinct.

Reaction between (2) *and* H_2S.—Reaction between (2) and H_2S in 1 : 2 molar ratio in toluene was slow at room temperature; after 12 h at 323 K, the ^{31}P-$\{^1H\}$ spectrum showed that (2) had been completely converted into a single product, which was isolated as a white solid and identified by partial elemental analysis and by n.m.r. spectroscopy as $[Ir(CO)Cl_2(PEt_3)_2\{P'HCl(S)\}]$. The spectra were very similar to those of product A, described in the previous section. The resonance due to P′, at 19.4 p.p.m., was a broad triplet; the PEt_3 resonance was analysed as the AB part of an ABX pattern, confirming the chirality of P′; the resonance due to the proton bound to P′ was a wide doublet [$^1J(P'H) = 489$ Hz] each component of which showed coupling to two *different* P nuclei, confirming the inequivalence of the PEt_3 groups. We have no direct evidence for the presence of Cl bound to P′, but the chemical shift of P′ is closer to that of P′ in product A above, with only one Se nucleus bound to P′, than to product B with two different Se nuclei bound to it.

Reaction between (2) *and Water*.—Reaction between (2) and an excess of water in toluene at room temperature for 4 h gave a single product which was isolated as a white crystalline solid. We formulate it as $[Ir(CO)Cl_2(PEt_3)_2\{P'H(O)(OH)\}][H_3O]Cl$, partly on the basis of C and H analysis and partly from the ^{31}P-$\{^1H\}$ and ^1H n.m.r. spectra. In the ^{31}P-$\{^1H\}$ spectrum, the resonance due to P′ was at 39.2 p.p.m., implying oxidation to P^V. It appeared as a triplet [$^2J(PP') = 15$ Hz], and showed a wide doublet coupling [$^1J(P'H) = 503$ Hz] when proton coupling was retained. The PEt_3 resonance was a simple doublet, implying equivalence of the two P nuclei, and the resonance of the proton bound to P′ appeared as a wide doublet of narrow triplets [$^3J(PH) = 2.6$ Hz]. Hence P′ is not chiral. Moreover, there was no strong peak in the i.r. spec-

Table 2. Selected bond lengths (Å) and angles (°) in complexes (2) and (3). Values marked with an asterisk involve disordered atoms with partial site occupancies

	(2a)	(2b)	(3a)	(3b)
Ir–P	2.389(6)	2.411(6)	2.418(5)	2.425(6)
	2.399(6)	2.391(7)	2.422(5)	2.401(5)
Ir–P′	2.324(7)	2.293(10)	2.290(5)	2.286(6)
Ir–Cl(P)	2.431(6)	2.455(6)	2.412(6)	2.431(6)
Ir–Cl(C)	2.372(5)	2.402(8)	2.368(5)	2.321(12) *
				2.360(19) *
Ir–C	1.812(19)	2.069(21)	1.817(18)	1.92(6) *
				1.52(5) *
P′–Cl	2.089(10)	1.927(15) *	2.051(8)	2.030(10)
	2.134(9)	1.955(15) *	2.061(8)	2.020(9)
		1.844(21) *		
C–O	1.128(23)	0.73(3)	1.089(24)	1.05(7) *
				1.45(6) *
P′–O			1.503(14)	1.551(18)
P–Ir–P	175.75(20)	173.26(20)	174.71(18)	172.19(19)
P–Ir–P′	83.93(21)	90.4(3)	87.99(18)	89.80(21)
	100.19(22)	95.7(3)	97.29(19)	96.73(21)
P–Ir–Cl(P)	87.44(21)	86.89(21)	86.04(19)	86.66(19)
	88.32(20)	87.64(22)	88.67(18)	87.57(19)
P–Ir–Cl(C)	88.74(19)	91.91(25)	89.53(17)	92.6(3) *
				86.3(5) *
	90.89(20)	91.91(25)	90.54(18)	88.4(5) *
				92.4(3) *
P–Ir–C	89.1(6)	86.7(6)	89.1(6)	82.6(18)
				91.1(18)
	91.6(6)	92.7(6)	91.0(6)	84.2(18)
				102.6(18)
P′–Ir–Cl(P)	167.24(22)	169.7(3)	172.19(19)	170.41(21)
P′–Ir–Cl(C)	81.05(21)	82.8(3)	84.74(18)	83.2(3) *
				100.5(5) *
P′–Ir–C	95.3(6)	97.1(6)	93.7(6)	93.4(18)
				81.6(18)
Cl(P)–Ir–Cl(C)	88.67(20)	87.35(24)	88.18(18)	87.7(3) *
				88.7(5) *
Cl(P)–Ir–C	95.0(6)	92.7(6)	93.4(6)	95.5(18)
				89.9(18)
Cl(C)–Ir–C	176.3(6)	178.5(6)	178.3(6)	175.2(18)
				168.9(18)
Ir–P′–Cl	106.6(3)	114.0(6) *	112.6(3)	112.1(3)
	110.1(3)	116.3(6) *	111.2(3)	112.7(3)
		115.0(7) *		
Cl–P′–Cl	97.9(4)	105.4(7) *	98.5(3)	99.8(4)
		118.7(8) *		
		83.4(8) *		
Ir–P′–O			118.4(6)	117.4(7)
Cl–P′–O			105.7(6)	110.3(7)
			108.5(6)	102.7(7)
Ir–C–O	176.1(17)	171.5(26)	175.6(17)	168(5) *
				155(4) *

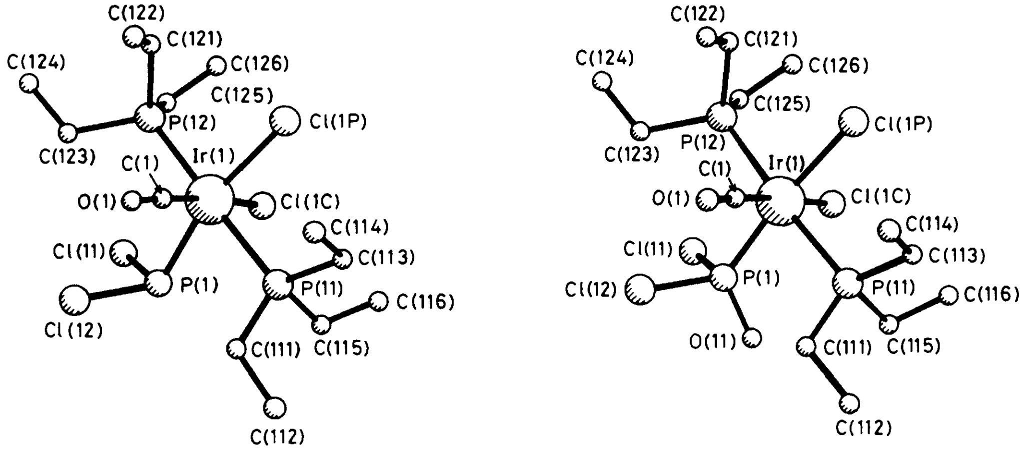
trum that we could assign to P′=O. We conclude that the product was a phosphinate complex of iridium(III), in which the OH proton forms a symmetrical hydrogen bond between two oxygen atoms bound to P′. This is a common structural feature of such complexes, and is fully consistent with the n.m.r. spectra and the analytical results.

Reaction between (2) *and Methanol.*—The ^{31}P-{^{1}H} spectrum of a solution in toluene of (2) and methanol in 1 : 2 molar ratio showed that all (2) had been consumed after 15 min and two P-containing products had been formed. These were identified spectroscopically[6] as $PH(O)(OMe)_2$ and $[Ir(CO)Cl_2H(PEt_3)_2]$.

Reaction of (3) *with* BCl_3.—The ^{31}P-{^{1}H} spectrum of an equimolar solution in CH_2Cl_2 of (3) and BCl_3 was significantly different from that of (3). The peak due to P′ was shifted by some 30 p.p.m. to higher frequency, and was distinctly broad. The ^{11}B-{^{1}H} spectrum showed a doublet at 7.6 p.p.m. [$^{2}J(P'B) = 10.5$ Hz]. We conclude that an equimolar adduct had been formed, presumably $[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(OBCl_3)\}]$.

Reaction of (3) *with* $AlCl_3$.—The ^{31}P-{^{1}H} spectrum of an equimolar solution in CH_2Cl_2 of (3) and $AlCl_3$ was different from that of (3). In particular, the resonance due to P′ was shifted by *ca.* 30 p.p.m. to higher frequency. We conclude that the equimolar adduct $[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(OAlCl_3)\}]$ was formed.

Crystal Structures.—The structures of *trans*-$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ (2) and *trans*-$[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(O)\}]$ (3)



(2) (3)

Figure. Perspective drawings of the ordered molecules in complexes (2) and (3)

are essentially isomorphous, and contain two molecules per asymmetric unit. The first molecule [(2a) and (3a)] lies near $\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{4}$, and symmetry-related positions in the unit cell, giving an approximately face-centred array of iridium atoms. It is well ordered in both structures. The other molecule [(2b) and (3b)] also gives an approximately face-centred array of iridium atoms near $\frac{3}{4}$, $\frac{1}{2}$, $\frac{1}{2}$ and symmetry-related positions. It has significant disorder, described in the Experimental section. A list of selected bond lengths and angles is given in Table 2. Chemically equivalent distances and angles are grouped together. The two molecules do not differ significantly in either compound; allowing for the disorder, the main differences are minor changes in the conformation of the ethyl groups. Perspective views of the ordered molecules in the two structures are given in the Figure.

Discussion of the structures. The chemical identities of (2) and (3) are established beyond doubt by the crystallographic results. However, the close structural similarity between the two compounds is surprising. It extends to the intermolecular relationships between units in the lattice, an aspect that will not be discussed further here; but at the molecular level it is unexpected to find analogous complexes containing $P'Cl_2$ and $P'Cl_2(O)$ ligands to be so similar. The Ir–P′ bond is slightly shorter in (3) than in (2), as are the P′–Cl bonds; the change in P′–Cl bond length from (2) to (3) is in keeping with the shortening from gaseous PCl_3 [d(PCl) = 2.039 Å][9] to $PCl_3(O)$ [d(PCl) = 1.993 Å].[10] However, in general it appears that the structural effect of the oxygen atom bound to P′ in (3) is very like that of the lone pair at P′ in (2). This similarity extends to other structural features. The Ir–P bonds in both (2) and (3) are substantially longer than the Ir–P′ bonds, a difference partly associated with the different *trans* ligand (P′ is *trans* to Cl and P is *trans* to P); however, the Ir–P bonds in (2) and (3) are the same length. The Ir–Cl distance *trans* to P′ is greater in both (2) and (3) than the Ir–Cl distance *trans* to CO, the difference being a little greater in (2) than in (3). These observations imply that the *trans* influences of $P'Cl_2$ and of $P'Cl_2(O)$ are similar, and greater than that of CO. We have no data for complexes containing singly co-ordinated $P'F_2$ bound to Ir; in complexes of the type[2] $[Ir(CO)Cl_2(PEt_3)_2\{P'F_2(Q)\}]$, where Q is O or a transition-metal group, the Ir–P′ and Ir–Cl distances are very similar to those found in the species described in this paper. The Cl–P′–Cl angles in (2) and (3) are smaller than those in PCl_3 or $PCl_3(O)$, and much smaller than the F–P′–F angles in the $P'F_2$ complexes mentioned above.

The P′–O bond, 1.50 Å in the ordered molecules, is significantly longer than in $PCl_3(O)$ (1.45 Å),[10] but much shorter than a typical P–O single bond (1.60 Å). This suggests that there is significant negative charge on the oxygen atom. There is something of a contrast between (3) and $[Ir(CO)Cl_2(PEt_3)_2\{P'F_2(O)\}]$, in which the length of the P′–O bond,[2] 1.446 Å, is much closer to that in $PF_3(O)$, 1.436 Å.[10]

There is a striking difference between the two P–Ir–P′ angles, especially in (2), where the $P'Cl_2$ group is bent towards the PEt_3 group further from the chlorine atoms. This distortion is necessitated by the large chlorine atoms and is not seen in the analogous $P'F_2$ compounds,[2] where P–Ir–P′ is near 90°. Another difference, also probably related to the size of the chlorine atoms, is the magnitude of the OC–Ir–P′–Cl torsion angles. In the $P'F_2$ species the OC–Ir–P′–F torsion angles are both *ca.* $\pm 120°$. In (2) and (3) the $P'Cl_2$ groups are twisted through 100°, so that one torsion angle is *ca.* 16°.

Experimental

Volatile compounds were handled in conventional vacuum systems fitted with greased glass or with greaseless Sovirel taps, and involatile and air-sensitive materials using a Schlenk line under dry nitrogen. Iridium starting materials were prepared as described elsewhere.[11] The n.m.r. spectra were recorded using JEOL FX60-Q (^{31}P), Bruker WP200 (^{1}H, ^{31}P, ^{77}Se, and ^{11}B), and Bruker WH360 (^{1}H, ^{13}C, ^{31}P, ^{77}Se, and ^{11}B) spectrometers. Infrared spectra were recorded using Perkin-Elmer 457 (4 000—250 cm^{-1}) or 577 (4 000—250 cm^{-1}) spectrometers, and C and H microanalyses by means of a Perkin-Elmer 240 elemental analyser. The mass spectrum was recorded by courtesy of Kratos Ltd. using a Kratos-80RF spectrometer with fast-atom bombardment.

Analytical data are given in Table 3 and i.r. spectral data in Table 4.

Reactions between iridium complexes and volatile materials were allowed to take place in n.m.r. tubes using standard procedures. The metal complex (*ca.* 0.1 mmol) was weighed into an n.m.r. tube, the appropriate solvent (*ca.* 0.5 cm^3) distilled in, and the volatile reagent allowed to condense in the tube, which was then sealed and studied at the chosen temperature.

Isolation of $[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ (2) *and its Derivatives.*—The sealed n.m.r. tube in which the complex had been made was opened under N_2 and the solvent removed on a Schlenk line. The solids were then dried under vacuum.

Table 3. Analytical data for complexes isolated

	Found (calc.)	
Complex	C(%)	H(%)
$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$	24.6 (24.8)	4.7 (4.8)
$[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(O)\}]$ *	24.4 (24.2)	4.9 (4.7)
$[Ir(CO)Cl_2(PEt_3)_2\{P'HCl(S)\}]$	24.8 (25.0)	5.0 (5.1)
$[Ir(CO)Cl_2(PEt_3)_2\{P'H_2(Se)\}]$	24.4 (24.4)	4.8 (5.0)
$[Ir(CO)Cl_2(PEt_3)_2\{P'H(O)(OH)\}]$-$[H_3O]Cl$	24.7 (24.1)	5.4 (5.4)

* Cl(%) = 22.2 (22.0).

Table 4. Infrared data (cm^{-1}) for the complexes isolated

$[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$	2 045vs, 1 235w, 1 225m, 1 090m, 1 030s, 935s, 925s, 900s, 770m, 740s, 710m, 670w, 615m, 575s, 515w, 495m, 480w, 478m, 411w, 375w, 320m, 305w, 280w (sh), 270m
$[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(O)\}]$	2 065vs, 1 260m, 1 215s, 1 040s, 775m, 750m, 720m, 565s, 530m (sh), 525s, 505m (sh), 500s, 475s, 420w, 390w, 330w, 295w, 285vw (sh)
$[Ir(CO)Cl_2(PEt_3)_2\{P'HCl(S)\}]$	2 390w, 2 050vs, 1 260m, 1 240m, 1 030s, 925m, 885m, 758s, 740s, 730s, 710m, 645s, 565m, 510w, 460s, 430 (sh), 390w, 350w, 320w, 305vw
$[Ir(CO)Cl_2(PEt_3)_2\{P'H_2(Se)\}]$	2 340w, 2 320w, 2 290w, 2 055vs, 1 260m, 1 105m, 1 070s, 885s, 765s, 740s, 710w, 550m
$[Ir(CO)Cl_2(PEt_3)_2\{P'H(O)(OH)\}]$-$[H_3O]Cl$	3 160br w, 2 720w, 2 680w, 2 280w, 2 050vs, 1 300w, 1 260m, 1 165w, 1 150w, 1 097m, 1 054w, 1 032s, 988w, 935s, 925s, 900s, 850br (sh), 770s, 740s, 720m, 710s, 670w, 620w, 565s, 512m, 442m, 428m, 380m, 320m, 300w, 280w (sh), 265m

Complexes $[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ (2) and $[Ir(CO)Cl_2(PEt_3)_2\{P'Cl_2(O)\}]$ (3) were crystallised by redissolving the solids obtained above in dichloromethane and adding n-pentane.

The reaction of H_2Se with (2) produced a yellow solution and an orange oil. The yellow solution was drawn off and the solvent removed under vacuum, yielding a yellow solid.

Mass Spectrum of $[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ (2).—The mass spectrum of (2) contained a molecular ion peak at *m/e* 629 $\{[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ requires 629$\}$. Other prominent peaks were observed at *m/e* 593 (629 − Cl), 558 (629 − 2Cl), 529 (629 − PCl_2 + H), 492 (629 − PCl_3), and 465 (629 − PCl_4 − CO).

Crystal Data.—Both (2) and (3) were crystallised from dichloromethane as colourless prisms. Chunks (*ca.* 0.2 mm^3 in volume) were cut from larger crystals and used for determining cell-dimensions and data collection. Unit-cell parameters were based on 20 automatically centred reflections. All measurements were made using Mo-K_α radiation (λ = 0.710 69 Å).

Table 5. Fractional co-ordinates for complex (2) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ir(1)	0.730 46(7)	0.755 94(3)	0.228 31(3)
P(11)	0.900 0(6)	0.659 8(3)	0.230 48(24)
C(111)	0.861 5(21)	0.588 0(10)	0.277 2(7)
C(112)	0.965(3)	0.527 0(14)	0.286 5(10)
C(113)	1.074 4(21)	0.687 2(11)	0.246 2(7)
C(114)	1.088(3)	0.718 2(15)	0.304 4(10)
C(115)	0.923(3)	0.606 8(13)	0 170 5(9)
C(116)	0.021(3)	0.632 0(17)	0.135 3(12)
P(12)	0.573 8(6)	0.859 0(3)	0.225 4(3)
C(121)	0.633(3)	0.942 7(12)	0.256 5(8)
C(122)	0.677(3)	0.943 4(13)	0.309 0(10)
C(123)	0.417 8(23)	0.841 0(11)	0.263 5(8)
C(124)	0.316(3)	0.905 4(14)	0.265 8(10)
C(125)	0.517 9(25)	0.883 8(12)	0.164 0(9)
C(126)	0.615(3)	0.929 2(14)	0.135 1(10)
Cl(1P)	0.916 4(6)	0.846 1(3)	0.223 7(3)
Cl(1C)	0.733 3(6)	0.749 1(3)	0.136 80(19)
P(1)	0.577 7(6)	0.657 8(3)	0.217 2(3)
Cl(11)	0.408 9(7)	0.692 3(4)	0.173 3(3)
Cl(12)	0.473 9(7)	0.643 5(3)	0.289 1(3)
C(1)	0.718 9(20)	0.757 1(10)	0.298 2(7)
O(1)	0.716 2(14)	0.754 4(7)	0.341 7(5)
Ir(2)	0.830 42(8)	0.511 92(4)	0.496 06(3)
P(21)	0.967 0(6)	0.402 5(3)	0.479 47(25)
C(211)	1.155(3)	0.409 5(16)	0.493 0(11)
C(212)	1.198(4)	0.422 7(17)	0.543 0(13)
C(213)	0.957(3)	0.369 8(13)	0.415 2(9)
C(214)	0.829(3)	0.335 7(14)	0.394 8(9)
C(215)	0.916(3)	0.326 1(13)	0.519 3(9)
C(216)	0.990(3)	0.248 1(18)	0.514 6(10)
P(22)	0.679 6(7)	0.611 5(4)	0.519 3(3)
C(221)	0.565(3)	0.577 8(17)	0.566 9(12)
C(222)	0.466(5)	0.633 0(24)	0.584 5(17)
C(223)	0.762(3)	0.699 4(13)	0.545 8(10)
C(224)	0.822(3)	0.690 0(14)	0.596 5(10)
C(225)	0.590(4)	0.660 2(20)	0.465 1(14)
C(226)	0.486(4)	0.612 6(22)	0.442 0(15)
Cl(2P)	0.629 7(6)	0.429 6(3)	0.502 88(25)
Cl(2C)	0.775 3(9)	0.525 5(4)	0.406 1(3)
C(2)	0.874 8(22)	0.502 6(11)	0.574 0(8)
O(2)	0.896 7(19)	0.494 5(10)	0.600 4(7)
P(2)	1.000 2(9)	0.595 6(6)	0.476 0(4)
Cl(21)	1.124 1(10)	0.616 6(6)	0.532 3(4)
Cl(22)	1.117 9(11)	0.570 0(7)	0.417 4(4)
Cl(23)	0.946 0(19)	0.672 9(10)	0.433 8(7)

Complex (2). $C_{13}H_{30}Cl_4IrOP_3$, M = 629.3, orthorhombic, a = 9.720(3), b = 17.975(9), c = 25.881(8) Å, U = 4 522 Å^3, space group $P2_12_12_1$ (no. 19), Z = 8, D_c = 1.85 g cm^{-3}, $F(000)$ = 2 448, μ(Mo-K_α) = 69.25 cm^{-1}.

Complex (3). $C_{13}H_{30}Cl_4IrO_2P_3$, M = 645.3, orthorhombic, a = 9.784(2), b = 17.918(2), c = 25.980(6) Å, U = 4 555 Å^3, space group $P2_12_12_1$ (no. 19), Z = 8, D_c = 1.88 g cm^{-3}, $F(000)$ = 2 512, μ(Mo-K_α) = 68.8 cm^{-1}.

Data Collection and Processing.—CAD4 diffractometer, $\omega/2\theta$ mode with scan width 1.0 + 0.35tanθ, scan time up to 1 min, graphite-monochromatised radiation. Data were collected for the $+h,k,l$ octant to θ = 22° (2) and 25° (3), giving 3 135 independent data for (2) and 4 479 for (3). 2 460 (3 342) Reflections with $I > 3\sigma(I)$ were used for structure determination and refinement. A significant fall in intensity was noted for (2), and an approximately linear correction was applied, the maximum normalised correction being ±20% over the 40 h of data collection.

Table 6. Fractional co-ordinates for complex (3) with estimated standard deviations in parentheses

Atom	x	y	z
Ir(1)	0.719 76(6)	0.758 19(3)	0.227 44(3)
P(11)	0.892 2(5)	0.661 59(25)	0.229 20(22)
C(111)	0.858 4(18)	0.592 0(9)	0.278 2(7)
C(112)	0.967 0(21)	0.531 1(11)	0.282 7(8)
C(113)	1.063 1(20)	0.694 4(11)	0.242 0(8)
C(114)	1.082 3(21)	0.722 5(11)	0.298 6(8)
C(115)	0.911 5(19)	0.607 7(10)	0.168 3(7)
C(116)	1.016(3)	0.640 6(16)	0.131 7(12)
P(12)	0.564 1(5)	0.863 3(3)	0.225 66(25)
C(121)	0.635 3(22)	0.948 2(11)	0.255 0(8)
C(122)	0.671(3)	0.946 5(14)	0.311 3(10)
C(123)	0.407 0(24)	0.844 7(12)	0.263 6(9)
C(124)	0.302 8(24)	0.908 9(13)	0.265 2(9)
C(125)	0.510 2(23)	0.890 6(12)	0.162 8(8)
C(126)	0.614 3(25)	0.936 4(13)	0.132 7(9)
Cl(1P)	0.900 2(5)	0.849 7(3)	0.223 04(25)
Cl(1C)	0.721 5(5)	0.754 1(3)	0.136 35(19)
P(1)	0.558 8(5)	0.666 0(3)	0.220 88(24)
Cl(11)	0.398 8(5)	0.695 4(4)	0.174 07(24)
Cl(12)	0.452 1(6)	0.653 7(3)	0.288 77(24)
O(11)	0.603 5(13)	0.590 1(7)	0.202 9(5)
C(1)	0.713 6(18)	0.760 0(10)	0 297 3(7)
O(1)	0.715 1(15)	0.757 3(9)	0.339 2(6)
Ir(2)	0.830 68(7)	0.516 15(4)	0.494 58(3)
P(21)	0.969 3(6)	0.406 2(3)	0.479 30(23)
C(211)	1.154(3)	0.410 7(13)	0.490 0(10)
C(212)	1.197(4)	0.416 3(17)	0.545 7(13)
C(213)	0.968 1(21)	0.374 2(11)	0.414 0(8)
C(214)	0.823(3)	0.337 4(14)	0.395 4(9)
C(215)	0.908(3)	0.328 8(14)	0.517 2(10)
C(216)	0.989(3)	0.256 6(19)	0.511 1(11)
P(22)	0.678 8(5)	0.615 4(2)	0.518 85(21)
C(221)	0.584(3)	0.660 7(16)	0.463 7(11)
C(222)	0.476(3)	0.608 9(18)	0.445 6(13)
C(223)	0.754 7(24)	0.700 1(13)	0.549 4(9)
C(224)	0.820(3)	0.686 6(14)	0.598 3(10)
C(225)	0.557(3)	0.578 8(18)	0.566 7(13)
C(226)	0.461(4)	0.632 7(19)	0.592 6(14)
Cl(2P)	0.638 2(5)	0.431 4(3)	0.503 54(24)
Cl(2C)	0.773 5(12)	0.527 2(6)	0.408 2(5)
Cl(3C)	0.879 2(18)	0.498 1(10)	0.582 7(8)
P(2)	0.994 2(6)	0.602 1(4)	0.473 7(3)
Cl(21)	1.136 8(7)	0.613 2(4)	0.530 0(3)
Cl(22)	1.114 9(7)	0.568 3(4)	0 415 1(3)
O(21)	0 944 8(16)	0 680 0(9)	0 455 4(7)
C(2)	0 879(6)	0 516(3)	0 566 4(22)
O(2)	0 921(4)	0 507 8(24)	0 603 2(15)
C(3)	0 815(5)	0 514(3)	0 436 4(19)
O(3)	0 746(4)	0.527 7(19)	0.388 0(14)

Structure Determinations.—The structure of (2) was solved by normal heavy-atom Patterson techniques. There are two independent molecules in the asymmetric unit, one of which is partially disordered, about the Ir–P′ bond [Ir(2)–P(2)]. Two sites identified as Cl were given fixed site occupancies of 0.8 [Cl(21) and Cl(22)], and one [Cl(23)] a site occupancy of 0.4. There may also be disorder between the carbonyl group [C(2)–O(2)] and its *trans*-chloride [Cl(2C)] but this was not sufficiently clear for refinement. All Ir, Cl, and P atoms, except Cl(23), were refined anisotropically and other non-hydrogen atoms were refined isotropically. Hydrogen atoms were not found in difference electron-density maps, but were included in calculated positions (C–H = 1.0 Å) with fixed thermal parameters, $U = 0.07$ Å^2. Complex atomic scattering factors were used, and defined the enantiomorph of the structure particularly clearly: $R = 0.25$ in the enantiomorph originally tried, $R = 0.08$ without any refinement when the enantiomorph was changed, and the entire data set refined in one cycle from $R = 0.065$ to $R = 0.05$. The partially refined structure was corrected for absorption using the DIFABS procedure (maximum correction ±20% based on I).[12]

In the final stages of refinement, a weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.002F^2$ was used. At convergence, with 263 adjustable parameters, $R = 0.039$, $R' = 0.052$, and a difference electron-density synthesis showed no peaks or troughs >0.8 e Å^{-3}.

The parameters for (2) were used as a starting point for the structure of the isomorphous (3). In this structure, there is no evidence of rotational disorder at the Ir(2)–P(2) bond, but it is clear that Cl(2C) and the carbonyl group C(2)–O(2) are disordered to the extent of approximately 50%, and they were refined (isotropically) in that way. Otherwise, the structure was refined as above, the crystal chosen having the same enantiomorph. The weighting scheme was of the form $w^{-1} = \sigma^2(F) + 0.0007F^2$. At convergence, with 272 adjustable parameters, $R = 0.044$, $R' = 0.055$. A difference electron-density synthesis showed no peaks or troughs >1.2 e Å^{-3}.

Fractional co-ordinates are given in Table 5 for (2) and in Table 6 for (3). Structure solution and refinement were carried out using the SHELX program.[13]

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