Preparation and Properties of Rh^I and Ir^I Ethylene Complexes Containing the Chiral *P,N*-Chelate Ligand (4*S*)-2-[2-(Diphenylphosphanyl)phenyl]-4-isopropyl-1,3-oxazoline

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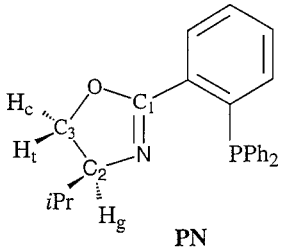
The synthesis and characterization of the chiral complexes [MCl(η^2-C_2H_4)(PN)] [M = Rh (**1**), Ir (**2**)] and [IrCl(η^2-C_2H_4)$_2$(PN)] (**3**) {PN = (4*S*)-2-[2-(diphenylphosphanyl)-phenyl]-4-isopropyl-1,3-oxazoline}, including the X-ray crystal structure of **2**, are reported. The solution behavior has been studied by NMR spectroscopy. For the rhodium complex **1** it is shown that a rotation of the olefin about the Rh-midpoint of the ethylene axis must be operating in solution at ambient temperature. The iridium analogue **2** is, however, stereochemically rigid and interconverts in solution, in the presence of ethylene, with the bis-ethylene derivative **3**.

Introduction

Many important enantioselective catalytic reactions employ transition metal complexes with chiral ligands as catalysts.[1] In this context, chiral chelate phosphino−oxazoline ligands have recently proven to be useful in the control of the enantioselectivity of various metal-catalyzed asymmetric reactions.[2] The pronounced difference in electronic as well as steric properties between the two chelating atoms (hard N and soft P) has been shown to be the key to these reactions. Most of the published work in this field focuses on the catalytic aspects of the reactions and, in some instances, the involved metallic species have not been fully characterized. For example, although mixtures of chiral phosphino−oxazoline ligands and different diolefin rhodium(I) complexes have been successfully applied as catalysts in the hydrosilylation of ketones, the potentially active complexes formed have not been characterized.[2a−2c] Analogously, asymmetric allylic alkylations have been carried out using catalysts prepared in situ from [Ir(μ-Cl)(cod)]$_2$ and phosphino−oxazoline ligands.[2d] However, the crystal structure of a cationic iridium complex [Ir(cod)(PN)]$^+$ {PN = (4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4-isopropyl-1,3-oxazoline, Figure 1} − an efficient catalyst for the enantioselective hydrogenation of prochiral imines − has been determined by X-ray diffraction.[2e] In the present paper, we report the preparation, characterization, and NMR spectroscopic properties of the new rhodium(I) and iridium(I) ethylene complexes [RhCl(η^2-C_2H_4)(PN)] (**1**) and [IrCl(η^2-C_2H_4)$_n$(PN)] [*n* = 1 (**2**), 2 (**3**)] containing the chelating enantiopure ligand PN. In the rhodium complex **1** the ethylene is fluxional. Three motions can be envisaged for coordinated ethylene: i) rotation about the metal−alkene bond, ii) rotation about the carbon−carbon bond, and iii) alkene dissociation.[3] The spectroscopic data indicated that, whereas the olefin rotation takes place at an intermediate rate at room temperature, the intermolecular exchange of ethylene is very slow.



PN

Figure 1. (4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4-isopropyl-1,3-oxazoline (PN)

Results and Discussion

The reaction of the dimers [M(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ (M = Rh,[4] Ir[5]) with PN, in a 1:2 molar ratio, led to an orange precipitate which was analyzed as [MCl(η^2-C_2H_4)(PN)] [M = Rh (**1**), Ir (**2**)]. However, when the mononuclear tetrakis(ethylene)iridium(I) complex [IrCl(η^2-C_2H_4)$_4$][5] was reacted in diethyl ether with PN (1:1 molar ratio, 20 °C), a

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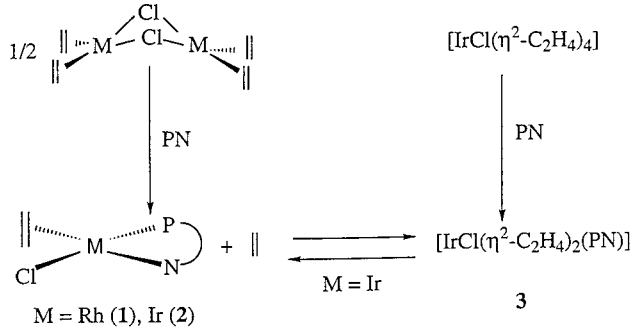
mixture of the mono- (**2**) and the bis(ethylene) complex [IrCl(η^2-C_2H_4)$_2$(PN)] (**3**) was obtained instead (Scheme 1). Complexes **1** and **2** decomposed slowly as solids, even under an atmosphere of ethylene, over a period of a few days and did so more rapidly in solution (several hours). In solution, at temperatures higher than −10 °C, the pentacoordinate adduct **3** is also unstable to the loss of ethylene.



Scheme 1

Only one set of signals was observed in the NMR spectra of compounds **1** and **2**, indicating that, in both cases, one single geometrical isomer exists in solution. The $^{13}C\{^1H\}$ NMR spectrum of the rhodium complex **1**, measured in $CDCl_3$ at −40 °C, showed two doublets at δ = 58.81 and 53.48 for the ethylene carbons, with $^1J_{RhC}$ coupling constants of 14.7 and 11.5 Hz, respectively.[6] Because no $^{13}C-^{31}P$ coupling was observed, we assume that the olefin and the phosphorus atom of the phosphino−oxazoline ligand occupy positions mutually *cis*. NOE measurements at −80 °C in CD_2Cl_2 showed interactions between the ethylene protons at ca. δ = 3.32 and some of the phenyls protons of the phosphino−oxazoline ligand. However, no NOE enhancement of the ethylene protons was observed when the CH_3 protons of the isopropyl oxazoline group were irradiated. These NOE data support the above-mentioned *cis* disposition. In the case of the iridium complex **2**, two sharp singlets at δ = 44.90 and 38.11 were observed, at ambient temperature, for the C_2H_4 carbons. Furthermore, the ^{13}C and ^1H NMR spectra of complex **1** showed a temperature dependence for the signals of the ethylene ligand, clearly indicating fluxionality: in the ^{13}C NMR spectrum, at room temperature, only one broad signal centered at ca. δ = 55.9 (line-width at half-height of 150 Hz) appeared for the C_2H_4 carbons, while the other peaks remained sharp. Upon heating to 45 °C (the rate of ethylene loss precluded measurements at higher temperatures) this signal becomes sharper indicating the equivalence of the two carbons.

The ^1H NMR spectra provided additional information about the behavior of the molecules in solution. Thus, at room temperature, the four ethylene protons of the rhodium complex **1** gave rise, in deuterated chloroform, to a broad resonance centered at ca. δ = 3.0 (line-width at half-height of 150 Hz), which progressively sharpened upon heating (line-width at half-height of 75 Hz at 45 °C). Unfortunately, a sharp time-averaged spectrum was not obtained. On cooling to −40 °C, the broad signal resolved into three broad humps centered at ca. δ = 3.32, 2.25 and 2.08, with respective integrals of 2, 1, and 1 protons. On the other hand, at room temperature, the signal of added ethylene,[7] at ca. δ = 5.4, showed only a slight broadening (line-width at half-height of 24 Hz), indicating that the exchange equilibrium between **1** and free ethylene is slow. An estimate of the barrier for the fluxional process in **1** gives a value of about 54 kJ·mol^{-1}, obtained as the resonances begin to broaden above the limiting low-temperature spectrum.[8] This value is similar to those found for other 16-electron square-planar rhodium(I) or platinum(II) ethylene derivatives such as [Rh(acac)(η^2-C_2H_4)$_2$] (51.3 kJ·mol^{-1})[9] or [Pt(acac)X(η^2-C_2H_4)] [X = Cl (52.3 kJ·mol^{-1}),[10] Br (53.1 kJ·mol^{-1}),[11] in which the fluxional mechanism has been proposed to be the rotation of the olefin about the metal-centroid of the olefin axis. The encountered value for the activation energy definitively ruled out the possibility of intermolecular exchange of the ethene molecule as the main fluxional process because the rhodium−ethylene bond dissociation energy has been measured as ca. 130 kJ·mol^{-1}.[12] On the other hand, a rotation about the carbon−carbon double bond axis would disrupt the coordination bond and the expected energy requirements would be therefore greater than the 54 kJ·mol^{-1} observed.[13] Consequently, to account for the equilibration of the protons and the carbons of the olefin in the rhodium complex, an intramolecular restricted rotation about the rhodium−alkene bond must be operating. The unequivocal detection of this mode of rotation (through the ^{13}C NMR measurements) was facilitated by the chirality of the PN ligand. It should be noted that in symmetrical, nonrigid, square-planar ethylene complexes it is not possible to distinguish between the two intramolecular motions because it is invisible to conventional spectroscopic probes, whereas experiments using complexes with chiral centers allow the distinction between rotation about the metal−alkene or the carbon−carbon axes.

For the iridium complex [IrCl(η^2-C_2H_4)(PN)] (**2**), ^1H NMR measurements revealed that the fluxional movement of the ethylene ligand was slowed down since its proton resonances appeared invariantly as three broad peaks at δ = 2.80, 2.02 and 1.67 (2,1,1 protons, respectively) from ambient temperature to 45 °C. At room temperature, its ^{31}P NMR spectrum consisted of a narrow singlet at δ = 9.42. Ethylene rotation barriers are usually higher in Ir^I compounds than in their Rh^I analogues. Thus, for example, the reported ethylene rotation barrier for [(η^5-C_5H_5)Rh(η^2-C_2H_4)$_2$][14] is 65.6 kcal mol^{-1}, while it is 80.7 kJ·mol^{-1} for the analogous iridium complex;[15] as in our case, no rotation has been observed for related penta- or tetracoordinated complexes of Ir^I.[16] Although it is not clear how the metal and alkene characteristics may affect the relative importance of the σ and the π back-donation,[17] the more basic iridium atom will most probably give rise to a stronger metal−ligand π-interaction. The stronger back-donation to the empty π* orbitals of the ethylene will additionally weaken the C=C bond, and this may be a plausible explanation for the higher barrier for the rotation of the olefin observed in the iridium complexes.

As stated above, the bis(ethylene)iridium complex **3** loses ethylene above −10 °C to form complex **2**. The ^{31}P NMR spectrum of CD_2Cl_2 solutions of **3**, at ambient temperature, displayed a broad signal centered at δ = 8.9 (linewidth at half-height of 73 Hz). This signal sharpened progressively as the temperature increased and became sharp at 45 °C. Below −20 °C, the singlet splits into two broad signals of approximately the same intensity centered at δ = 9.4 and 0.4. The relative intensity of these signals changes with temperature, the amount of the resonance at higher field increasing as the temperature decreases. Thus, at −40 °C the ratio (signal at ca. δ = 9.4 to signal at ca. δ = 0.4) was 2:8 and at −90 °C, 1:9. When ethylene was bubbled through the mixture at −40 °C (2 min) the resonance centered at ca. δ = 9.4 disappeared, whereas the signal at ca. δ = 0.4 remained. Removal of the ethylene atmosphere, by passing a stream of argon, regenerated the signal at δ = 9.4. A reversible equilibrium [Equation (1)] between species **2** (δ = 9.43, −40 °C) and **3** (δ = 0.35, −40 °C) can explain all these observations. As expected, bubbling ethylene or lowering the temperature displaces equilibrium 1 to the right and vice versa.

$$\underset{\mathbf{2}}{[IrCl(\eta^2\text{-}C_2H_4)(PN)]} + C_2H_4 \rightleftharpoons \underset{\mathbf{3}}{[IrCl(\eta^2\text{-}C_2H_4)_2(PN)]} \quad (1)$$

Recently, Milstein et al.[16b] reported that in the related $[IrCl(\eta^2\text{-}C_2H_4)_2L_2]/[IrCl(\eta^2\text{-}C_2H_4)L_2]$ (L = PEt_3) system, the bis(ethylene) adduct is more stable than the mono(ethylene) one. As the authors stated, the strong electron-donating character of the PEt_3 ligands could stabilize the pentacoordinated species. In good agreement with this proposal is the fact that, in the analogous PPh_3 system, the bis(ethylene) adduct is unstable to the loss of ethylene at temperatures higher than −50 °C.[18] Therefore, our results are in agreement with the expected intermediate electron-donating properties of the PN ligand.

We have carried out a crystal X-ray diffraction study of complex **2** in order to establish unambiguously the proposed structure. A molecular representation of the molecule is shown in Figure 2. Selected bond lengths and angles are given in Table 1.

The principal structural feature of **2** is the square-planar geometry about the iridium atom with the coordinated ethylene molecule nearly perpendicular to the best PN−Ir−Cl plane and *cis* to the phosphorus atom of the phosphino−oxazoline, as indicated by the spectroscopic data. As is usually observed in square-planar olefin complexes, the structure shows some deviation from ideal symmetry[19] [max. dev. 0.125(1) Å out of coordination plane for Cl atom]. The ethylene C−C bond is inclined at 84.7(3)° to the coordination plane and its center is 0.044(6) Å out of this plane. The C=C bond length is 1.392(8) Å, quite similar to the bond length found in the closely related square-planar Ir^I−ethylene complex *trans*-$[IrCl(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ [1.376(10) Å][19] and compares well with the range of other reported Ir^I−ethylene complexes [1.35−1.47 Å, mean value 1.411(3) Å].[20] The PN ligand and the iridium atom form a six-membered chelate ring, puckered towards a screw-boat conformation[21] [Q = 0.604(3), F = 19.0(5)°, q = 61.8(5)°], with all three carbon atoms situated above the plane of the complex.

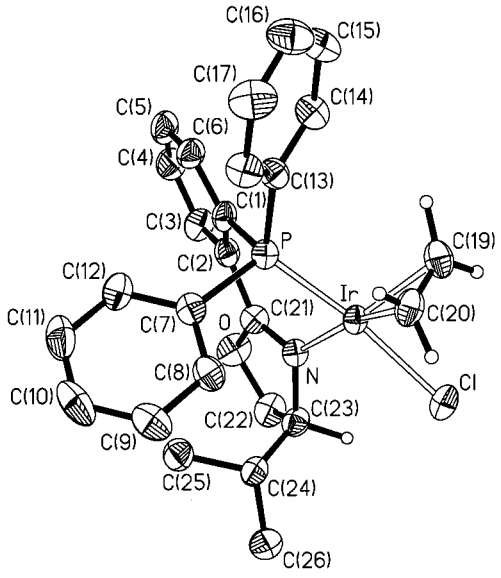


Figure 2. A molecular representation of complex **2** showing the atomic labelling scheme used; hydrogens are shown for the ethylene ligand and the asymmetric carbon of the oxazoline ligand

Table 1. Selected bond lengths (Å) and angles (°) for complex **2**

Bond lengths (Å)		Bond angles (°)	
Ir−N	2.084(4)	N−Ir−P	86.70(12)
Ir−P	2.1741(14)	N−Ir−Cl	90.20(13)
Ir−Cl	2.4170(13)	N−Ir−G[a]	176.3(2)
Ir−C(19)	2.123(6)	P−Ir−Cl	172.90(5)
Ir−C(20)	2.137(5)	P−Ir−G[a]	95.73(17)
Ir−G[a]	2.013(6)	Cl−Ir−G[a]	87.69(17)
C(19)−C(20)	1.392(8)	C(19)−Ir−C(20)	38.2(2)

[a] G represents the midpoint of the olefinic C(19)−C(20) bond.

Experimental Section

General Comments: The compounds described herein were handled with exclusion of air by using standard Schlenk techniques. All solvents were dried by known procedures and distilled under argon prior to use. NMR spectra were recorded on a Varian UNITY, a Varian Gemini 2000, or a Bruker ARX 300 MHz spectrometers. Chemical shifts (δ values) are given relative to TMS (^1H and ^{13}C) or to 85% H_3PO_4 aqueous solution (^{31}P). Coupling constants (J) are given in Hertz. For proton and carbon labelling, see Figure 1. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Nicolet 550 spectrometer. The C, H and N analyses were performed on a Perkin−Elmer 2400 CHNS/O analyzer. The precursors $[Ir(\mu\text{-}Cl)(\eta^2\text{-}C_8H_{14})_2]_2$,[22] $[M(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ (M = Rh, Ir)[4,5] and $[IrCl(\eta^2\text{-}C_2H_4)_4]$[5] and the ligand (4*S*)-2-[2-(di-

phenylphosphanyl)phenyl]-4-isopropyl-1,3-oxazoline (PN)[23] were prepared according to published procedures.

Synthesis of [RhCl(η²-C_2H_4)(PN)] (1): A solution of PN (237 mg, 0.634 mmol) in dichloromethane (2 mL) was added to a suspension of [Rh(μ-Cl)(η²-C_2H_4)$_2$]$_2$ (124 mg, 0.319 mmol) in diethyl ether (10 mL) at ambient temperature under argon. After 1 h, the resulting solution was concentrated to ca. 5 mL and a solid precipitated. The solvent was removed with a syringe and the solid residue washed with cold Et_2O and dried in vacuo to give **1** as an orange powder. Yield 285 mg (83%). Solid **1** must be stored under ethylene at 4 °C. $C_{26}H_{28}ClNOPRh$ (539.57): calcd. C 57.87, H 5.23, N 2.59; found C 57.85, H 5.37, N 2.44. ^{1}H NMR ($CDCl_3$, room temp.): δ = 8.00−6.98 (m, 14 H, Ph's of PN), 5.46 (ddd, *J* = 2.7, 5.5, 8.7, 1 H, H_g of PN), 4.26 (m, 2 H, H_c and H_t of PN), 2.45 (dsept, *J* = 2.7, 7.0, 1 H, C*H*Me$_2$ of PN), 3.01 (br. s, 4 H, C_2H_4), 0.79 (d, *J* = 7.0, 3 H, Me of PN), 0.05 (d, *J* = 7.0, 3 H, Me of PN). ^{13}C NMR ($CDCl_3$, −40 °C): δ = 161.79 (d, J_{PC} = 7.8, C_1 of PN), 135.2−126.9 (m, Ph's of PN), 70.43 (s, C_2/C_3 of PN), 67.79 (s, C_3/C_2 of PN), 58.81 (d, $^1J_{RhC}$ = 14.71, C_2H_4), 53.48 (d, $^1J_{RhC}$ = 11.54, C_2H_4), 30.83 (s, *C*HMe$_2$ of PN), 18.86 (s, Me of PN), 12.83 (s, Me of PN). ^{31}P NMR ($CDCl_3$, room temp.): δ = 52.5 (d, $^1J_{RhP}$ = 177). IR: ν(CN) 1616 cm^{-1}; ν(CO) 1242 cm^{-1}.

Synthesis of [IrCl(η²-C_2H_4)(PN)] (2): Under argon, a red suspension of the bis(ethylene)iridium(I) dimer [Ir(μ-Cl)(η²-C_2H_4)$_2$]$_2$ [5b] (75 mg, 0.132 mmol) in diethyl ether (15 mL) was cooled to −20 °C and PN was added (98 mg, 0.262 mmol). A deep red solution was immediately formed and after a short time a red powder precipitated. After stirring the solution for one hour, solid **2** was filtered off, washed with diethyl ether and dried in vacuo. Yield 116 mg (70%). Complex **2** must be stored under ethylene at 4 °C. $C_{26}H_{28}ClIrNOP$ (629.11): calcd. C 49.64, H 4.48, N 2.23; found C 50.24, H 4.74, N 2.02. ^{1}H NMR ($CDCl_3$, room temp.): δ = 8.07−7.01 (m, 14 H, Ph's of PN), 5.72 (m, *J* = 2.7, 1 H, H_g of PN), 4.32 (m, 2 H, H_c and H_t of PN), 2.49 (dsept, *J* = 2.7, 7.0, 1 H, C*H*CMe$_2$ of PN), 2.80 (br. s, 2 H, C_2H_4), 2.02 (br. s, 1 H, C_2H_4), 1.67 (br. s, 1 H, C_2H_4), 0.81 (d, *J* = 7.0, 3 H, Me of PN), 0.16 (d, *J* = 7.0, 3 H, Me of PN). ^{13}C NMR ($CDCl_3$, room temp.): δ = 162.10 (d, J_{PC} = 5.96, C_1 of PN), 137.0−127.0 (m, Ph′s of PN), 70.58 (s, C_2/C_3 of PN), 68.35 (s, C_3/C_2 of PN), 44. 90 (s, C_2H_4), 38.11 (s, C_2H_4), 31.09 (s, *C*HMe$_2$ of PN), 18.66 (s, Me of PN), 13.32 (s, Me of PN). ^{31}P NMR ($CDCl_3$, room temp.): δ = 9.42 (s). IR (Nujol): ν(CN) 1616 cm^{-1}; ν(CO) 1245 cm^{-1}.

Preparation of a Mixture of [IrCl(η²-C_2H_4)(PN)] (2) and [IrCl(η²-C_2H_4)$_2$(PN)] (3): Ethylene was bubbled through a pale orange suspension of [Ir(μ-Cl)(η²-C_8H_{14})$_2$]$_2$ (100 mg, 0.112 mmol) in diethyl ether (5 mL) at −20 °C. After stirring for 15 min, PN (83 mg, 0.222 mmol) was added to the resulting colorless solution containing the tetrakis(ethylene)iridium(I) [IrCl(η²-C_2H_4)$_4$]. After 20 min stirring, an orange solid precipitated which was filtered off under an argon atmosphere and dried in vacuo. The solid obtained was characterized as a mixture of **2** and **3**.

3: ^{1}H NMR (CD_2Cl_2, −90 °C): δ = 8.40−6.90 (m, 14 H, Ph's of PN), 5.56 (m, 1 H, H_g of PN), 4.55 (m, 2 H, H_c and H_t of PN), 2.72 (br. s, 1 H, C_2H_4), 2.63 (br. s, 1 H, C_2H_4), 2.44 (m, 2 H, C*H*CMe$_2$ of PN and 1 H of C_2H_4), 2.22 (br. s, 1 H, C_2H_4), 2.04 (br. s, 2 H, C_2H_4), 1.74 (br. s, 2 H, C_2H_4), 0.90 (br. s, 3 H, Me of PN), 0.83 (br. s, 3 H, Me of PN). ^{31}P NMR (CD_2Cl_2, −90 °C): δ = 0.40 (s).

Crystallographic Data Collection and Refinement of the Structure: Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a solution of **2** in dichloromethane under an ethylene atmosphere; a red irregular block (0.36 × 0.38 × 0.42 mm) was glued to the end of a glass fiber and mounted on a four-circle diffractometer (Siemens P4) working with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and operating at 173 K. A summary of crystal data, intensity collection procedure, and refinement parameters for the structural analysis is reported in Table 2. Precise lattice parameters were determined by a least-squares fit from 64 centered reflections in the region 25 ≤ 2θ ≤ 38°. Three standard reflections were monitored every 97 measured reflections to check crystal and instrument stability throughout data collection; no significant variations of the intensities were observed. All data were corrected for Lorentz and polarization effects, and a semiempirical (ψ-scan method) absorption correction was also applied.[24] The structure was solved by Patterson and conventional Fourier techniques, and refined by full-matrix least-squares methods on F^2 (SHELXL-97)[25] with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms of the methyl groups were included in calculated positions (C−H = 0.98 Å), and the remaining hydrogens were located in difference Fourier maps; all were included in the refinement riding on their respective carbon atom with four different common isotropic thermal parameters for the distinct types of H atoms. The absolute structure was estimated by the refinement of the Flack parameter, *x* = −0.006(7).[26] Atomic scattering factors, corrected for anomalous dispersion for heavy atoms, were taken from ref.[27] Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167640. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44−1223/336−033; Email: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data and data collection and refinement for complex **2**

Formula	$C_{26}H_{28}ClIrNOP$
Mol. wt.	629.11
Space group	orthorhombic, $P2_12_12_1$ (no. 19)
a, Å	10.7695(9)
b, Å	12.9389(11)
c, Å	17.5393(15)
V, Å^3	2444.0(3)
Z	4
D_{calcd}, g cm^{-3}	1.710
m, mm^{-1}	5.66
No. of data collected	6042 (4 ≤ 2θ ≤ 54°)
No. of unique data	5304 (R_{int} = 0.0234)
Min, max transm fact	0.056, 0.081
No. data/params/restraints	5304/286/0
*R*1 (*F*) [$F^2 \geq 4\sigma(F^2)$][a]	0.0262
wR (all data)[b]	0.0622
S[c]	1.027

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for 5036 observed reflections. [b] $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0330P)^2 + 3.98P]$, where $P = [\max(F_o^2, 0) + 2F_c^2)]/3$. [c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* the number of parameters.

Acknowledgments

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