257. Transition Metal Complexes with Bidentate Ligands Spanning *trans*-Positions

Part XIII[1])

Preparation, Properties and Crystal and Molecular Structures of Chlorocarbonyl-2,11-bis(diphenylphosphinophenyl)benzo[*c*]phenanthreneiridium (I) and Trichlorocarbonyl-2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthreneiridium(III)

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Summary

The complex $[IrCl_3(CO)(\mathbf{1})]$(**4**,**1** = 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene) has been prepared by $CuCl_2$-oxidation of $[IrCl(CO)(\mathbf{1})]$(**2a**). It is shown that the chlorine oxidation of **2a** gives a mixture of products whose composition depends on the reaction conditions. The X-ray crystal structures of **2a** and **4** have been determined. The small conformational differences observed for the *trans*-spanning ligand **1** in the two complexes are likely to be caused by the difference in Ir-P bond lengths in square planar **2a** and octahedral **4** (2.310(4) and 2.411(3) Å, respectively).

Introduction. – In an earlier publication [2] it was reported that the ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**) forms complexes of the type *trans*-$[MX(CO)(\mathbf{1})]$ (**2**; M = Ir, Rh; X = Cl, Br, I, SCN) and that the addition of Cl_2 to *trans*-$[IrCl(CO)(\mathbf{1})]$(**2a**) gives a complex mixture of products. In the same publication the formation of some Ir(III) six-coordinate species containing ligand **1** was also reported, *e.g.*, $[IrHCl_2(CO)(\mathbf{1})]$ (**3**), prepared by oxidatively adding HCl to **2a**, and it was concluded that: '*... the presence of ligand* **1** *does not prevent the formation of six-coordinate species and that compounds of this type are best obtained if at least one of the ligands is hydrogen*'. It was, therefore, of interest to establish whether $[IrCl_3(CO)(\mathbf{1})]$ (**4**) could be prepared and, if this proved to be the case, to get a better understanding of the complex reaction between

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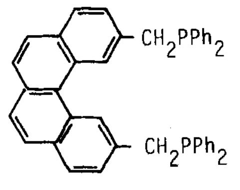
[1]) Part XII: see [1].



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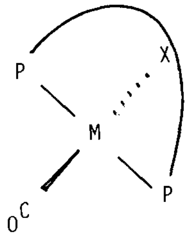

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chlorine and **2a**. This contrasts the Cl_2-oxidation of the corresponding complexes with monodentate phosphines, $[IrCl(CO)(PR_3)_2]$, which produces smoothly the corresponding Ir(III)-species [3].

Formation of $[IrCl_3(CO)(1)]$ (4). – This complex is easily obtained in high yields by reacting **2a** with $CuCl_2$ as described by *Cash & Harris* [4] for the preparation of $[IrCl_2(NCO)(CO)(PPh_3)_2]$ from *trans*-$[Ir(NCO)(CO)(PPh_3)_2]$:

$$[IrCl(CO)(\mathbf{1})] + 2\,CuCl_2 \rightarrow [IrCl_3(CO)(\mathbf{1})] + 2\,CuCl.$$

While this reaction runs smoothly at room temperature, most of the product decomposes in the reaction medium already at 40–50°.

The complex *trans*-$[Ir(CO)(CH_3CN)(\mathbf{1})][BF_4]$ can also be used as a starting material for the preparation of **4** by the above method.

The smooth oxidation of **2a** to **4** by $CuCl_2$ is in marked contrast with the action of other oxidants on **2a**. Thus, *i.* the addition of a solution of $[PPh_4]_2[IrCl_6]$, in CH_3CN containing $[PPh_4]Cl$, to a CH_3CN-solution of **2a** led to rapid decomposition of complex **2a** and *ii.* as mentioned earlier [2] the reaction of Cl_2 with **2a** gives a mixture of products. As it was found that this mixture contained **4**, the Cl_2-oxidation of **2a** was reexamined as follows: the stoichiometric amount of chlorine, in CCl_4, was added to a solution of **2a** in CH_2Cl_2 which had been cooled down to liquid N_2 temperature[2]). The mixture was then allowed to warm up and examined by ^{31}P-NMR spectroscopy. The results are summarized in *Table 1*. As can be seen, initially two products, corresponding to

Table 1. *The Time-Dependence of the Product-Distribution in the Reaction of* trans-*[IrCl(CO)(1)] and* Cl_2

Temp. [°K]	Time [h]	^{31}P-Resonances observed [ppm][a]) A	B	C	Other low-intensity resonances observed [ppm]
230	0.1	12.5 (4)	–	–3.7 (10)	
240	1.0	12.5 (3.8)	–	–3.7 (10)	–23.5
260	1.8	12.5 (2.5)	6.5 (1.5)	–3.7 (10)	
280	2.2	12.5 (1.8)	6.5 (2.2)	–3.7 (10)	
298	4.0	12.5 (1.3)	6.5 (2.7)	–3.7 (10)	8.9 –22.7, –24.0
298	340	–	6.5 (4)	–3.7 (10)	0.8, –2.1, –22.7, –24.0

[a]) The approximate values of the relative intensities of the signals are given in brackets and are expressed relative to that of the signal at –3.7 ppm which is given the arbitrary value of 10.

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[2]) To remove traces of HCl the CH_2Cl_2 was filtered immediately before using it through a column of anhydrous aluminum oxide.

the resonances A and C, are formed. While resonance C could be assigned to **4**, the species giving rise to resonance A is still unidentified. It is, however, significant that A gradually disappears with the concomitant formation of [$IrHCl_2(CO)$(**1**)] (**3**, resonance B at 6.5 ppm). Mention should also be made that in addition to these resonances one also observes low-intensity signals, some of which gradually disappear with time while others appear.

Further studies of the Cl_2-oxidation of **2a** have established that the product distribution is strongly dependent on the reaction conditions. Thus, the addition of a CCl_4-solution of Cl_2 to a $CHCl_3$-solution of **2a** at room temperature resulted in the formation of four major products as indicated by their ^{31}P-NMR resonances occurring at 3.61, 1.93, –5.31 (compound **4**) and –24.00 ppm with relative intensities of 3:10:1:1; *i.e.*, under these conditions **4** is only a minor component of the mixture. On the other hand when Cl_2 was kept in contact with solid **2a**, at room temperature, for two days, the resulting solid gave a ^{31}P-NMR spectrum showing resonances at 21.59, –5.31 (**4**) and –24.01 ppm with relative intensities 1:10:2.

The differing product mixtures obtained by varying the reaction conditions suggested that this variable behaviour arose from the availability of multiple kinetic pathways of similar activation energies. As these pathways are likely to be related to the molecular structure of **2a** and **4** the molecular structures of these two complexes were determined by X-ray diffraction.

The Molecular Structures of *trans*-[IrCl(CO)(1)] (2a) and *trans*-[IrCl$_3$(CO)(1)] (4). – Relevant bond lengths and angles are reported in *Table 2. Fig. 1* and *2* show the molecular structures of the two complexes.

The coordination about the metal atom is distorted square-planar in **2a** and distorted octahedral in **4**. In both compounds the two P-atoms are *trans* to each other.

The angles subtended at the metal centres deviate significantly from the values of 90° and 180° defining the regular conformation. Also the Ir-C-O angle, especially in **4**, is far from 180°.

These distortions from the basic geometries appear to result either from the rigidity of ligand **1** (P-Ir-P angles), or from the minimization of its interactions with the other ligands [Cl(1)-Ir-Cl(2) and Cl(1)-Ir-C angles in **4**].

The orientation of the coordination plane containing the P-atoms and the carbonyl group, with respect to the skeleton of ligand **1**, differs in **2a** and **4** by a rotation of *ca.* 90° around the P(1)... P(2) direction.

The overall structure of **2a** closely resembles that of its Rh-analog [RhCl(CO)(**1**)] [5] (see *Tables 3* and *4*). In this context it should be noted that **2a**, when recrystallized from CH_3CN, gives single crystals which are isomorphous with those of [RhCl(CO)(**1**)] [5].

The Ir-Cl bond length in **2a** [2.355(4) Å] differs only slightly from the average value 2.366(3) Å of those found in **4** (for a comparison with Ir-Cl bond lengths found for some square-planar Ir(I)- and octahedral Ir(III)-complexes see *Table 3*).

The Ir-CO lengths [1.85(2) Å in **2a**, 1.90(1) Å in **3**] fall within the range (1.81-2.08 Å) quoted for distances of second- and third-row transition-metal carbonyls [6] (see *Table 3*).

The mutually *trans*-Ir-P bonds in **2a** [average length 2.310(4) Å] are noticeably shorter than in **4** [average length 2.411(3) Å]. These values fall at the extremes of the range (2.30–2.40 Å) found for Ir-P bond lengths in a number of Ir(I)- and Ir(III)-complexes [7].

Table 2. *A Selection of Interatomic Distances* (Å) *and Angles* (°) *in* **2a** *and* **4**. Standard deviations are given in parentheses[a]).

	2a	**4**		**2a**	**4**
Ir-Cl(1)	–	2.357(3)	X-Ir-P(1)	87.3(2)	91.4(1)
Ir-Cl(2)	–	2.366(3)	X-Ir-P(2)	87.4(2)	91.3(1)
Ir-X	2.355(4)	2.371(3)	X-Ir-C	168.9(7)	172.6(4)
Ir-P(1)	2.310(4)	2.403(3)	P(1)-Ir-P(2)	173.9(2)	170.7(1)
Ir-P(2)	2.310(4)	2.419(3)	P(1)-Ir-C	91.8(5)	89.8(4)
Ir-C	1.846(17)	1.895(13)	P(2)-Ir-C	94.0(5)	88.7(4)
C-0	1.109(21)	1.032(16)	Ir-C-0	178.0(14)	171.5(11)
P(1)-C(19)	1.849(15)	1.854(11)	Ir-P(1)-C(19)	113.8(5)	112.0(4)
P(1)-C(21)	1.820(14)	1.816(8)	Ir-P(1)-C(21)	111.6(4)	115.3(3)
P(1)-C(27)	1.821(9)	1.824(9)	Ir-P(1)-C(27)	116.3(4)	119.7(3)
P(2)-C(20)	1.856(19)	1.862(12)	C(19)-P(1)-C(21)	103.9(7)	101.8(5)
P(2)-C(33)	1.831(13)	1.828(7)	C(19)-P(1)-C(27)	102.8(6)	102.8(4)
P(2)-C(39)	1.829(13)	1.816(8)	C(21)-P(1)-C(27)	107.3(6)	103.2(4)
Cl(1)-Ir-Cl(2)	–	168.9(1)	Ir-P(2)-C(20)	116.1(5)	113.0(4)
Cl(1)-Ir-X	–	83.6(1)	Ir-P(2)-C(33)	118.0(4)	119.1(3)
Cl(1)-Ir-P(1)	–	83.6(1)	Ir-P(2)-C(39)	109.9(4)	112.2(3)
Cl(1)-Ir-P(2)	–	87.8(1)	C(20)-P(2)-C(33)	101.0(7)	103.1(5)
Cl(1)-Ir-C	–	103.7(4)	C(20)-P(2)-C(39)	103.9(7)	103.1(5)
Cl(2)-Ir-X	–	85.3(1)	C(33)-P(2)-C(39)	106.6(5)	104.7(4)
Cl(2)-Ir-P(1)	–	96.5(1)	P(1)-C(19)-C(2)	112.1(11)	114.1(8)
Cl(2)-Ir-P(2)	–	92.6(1)	P(2)-C(20)-C(11)	117.0(11)	116.6(8)
Cl(2)-Ir-C'	–	87.4(4)			

[a]) X is for Cl in **2a** and Cl(3) in **4**.

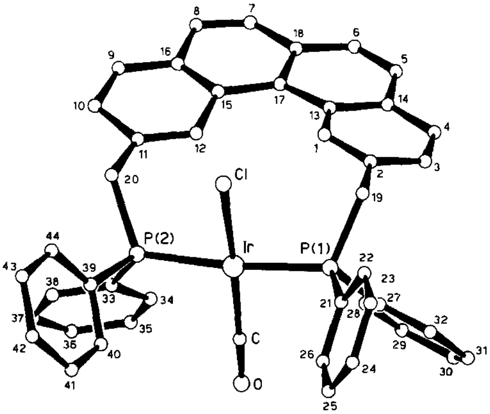

Fig. 1. *A computer-generated drawing of the molecule [IrCl(CO)(*1*)]*

Ir-P distances found for some square-planar Ir(I)- and octahedral Ir(III)-complexes are reported in *Table 3*, together with Ir-Cl and Ir-CO distances.

The difference in the Ir-P bond lengths of *ca.* 0.1 Å on passing from the four-coordinate Ir(I)-complex **2a** to the six-coordinate Ir(III)-complex **4**, is the largest between

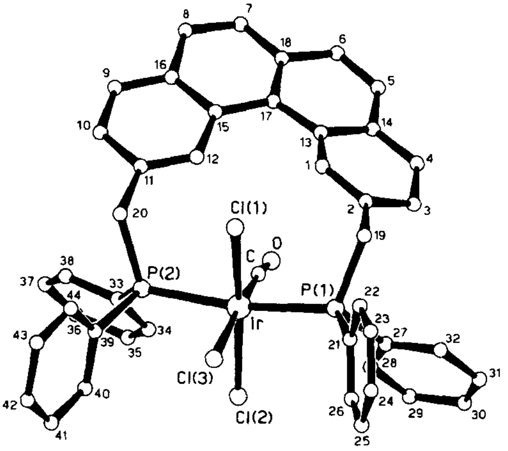

Fig. 2. *A computer-generated drawing of the molecule* $[IrCl_3(CO)(\mathbf{1})]$

Table 3. *Selected Ir–P, Ir–Cl and Ir–CO Bond Distances in Some Ir-Phosphine Complexes*

	Ir–P[a])	Ir–Cl[b])	Ir–CO[b])	Ref.
Ir(I) Square-Planar Complexes				
$[Ir(PPh_3)4]^+$	2.319(4)			[8]
$[IrCl(CO)\{(t\text{-Bu})_2P(CH_2)_{10}P(t\text{-Bu})_2\}]$	2.362(3)	2.405(3)	1.912(9)	[9]
$[IrCl(CO)(P(o\text{-Tol})_3)_2]$	2.338(5)	2.43(1)[c])	1.67(4)[c])	[10]
$[Ir(C_6F_5)(CO)(PPh_3)_2]$	2.316(4)			[11]
$[IrCl(CO)\{(t\text{-Bu})_2PC{\equiv}C(CH_2)_5C{\equiv}CP(t\text{-Bu})_2\}]$	2.335(2)	2.366(2)	1.808(7)	[12]
$[IrCl(CO)(\mathbf{1})]$	2.310(4)	2.355(4)	1.846(17)	Present work
$[RhCl(CO)(\mathbf{1})]$[d])	2.315(3)	2.377(2)	1.798(8)	[5]
Ir(III) Octahedral Complexes				
$[IrCl(C_3Ph_3)(CO)(PMe_3)_2]^+$	2.365(5)			[13]
$[IrCl(CN)(NCS)(CO)(PPh_3)_2]$	2.418(3)	2.37(1)	1.84(4)[c])	[14]
$[IrCl(4\text{-fluorophenyldiimide-}2C,N')(CO)(PPh_3)_2]^+$	2.386(8)			[15]
$[IrCl_2(4\text{-methoxyphenyldiimide-}2C,N')(PPh_3)_2]$	2.370(2)			[16]
$[IrCl_2(CHF_2)(CO)(PPh_3)_2]$	2.421(8)	2.375(8)	1.85	[17]
$[IrH_3(PPh_3)_3]$ (*mer*-isomer)	2.286(3)			[18]
$[IrHBr(Ph)(CO)(PEt_3)_2]$	2.333(5)			[19]
$[IrCl_3(CO)(\mathbf{1})]$	2.411(3)	2.371(3)	1.895(13)	Present work

[a]) Only the average length of mutually trans Ir-P bonds are quoted.

[b]) Only the length of Ir-Cl and Ir-CO bonds *trans* to each other are quoted.

[c]) Because of the crystallographically imposed symmetry chlorine and carbonyl ligands were treated as randomly disordered: bond distances are therefore not of high precision.

[d]) Also the Rh-P, Rh-Cl and Rh-CO bond lengths found in the Rh-analog of **2a** are reported for comparison purposes.

the two structures and is perhaps responsible for other small differences. In fact the longer Ir-P bonds increase the strain imposed by the rigid *trans*-spanning ligand **1** in complex **4** which is relieved by closing up the P-Ir-P angle to 170.7(1)°.

The conformation of the twelve-membered ring, formed by ligand **1** and the Ir-atom is almost the same in the two complexes. It is characterized by the two methylene-P bonds, C(19)–P(1) and C(20)–P(2), oriented in the same direction with respect to the tetranuclear part of the ligand. Some dihedral angles describing this conformation are given in *Table 4*.

Table 4. *Some Dihedral Angles Characterizing the Conformation of Ligand* **1** *in the Complexes* **2a**, **4** *and [RhCl(CO)(***1***)]*

	2a	**4**	[RhCl(CO)(**1**)]
C(1)–C(2)–C(19)–P(1)	79(2)°	93(1)°	80.9(9)°
C(2)–C(19)–P(1)–M	–71(1)°	–65(1)°	–69.2(7)°
C(12)–C(11)–C(20)–P(2)	–51(2)°	–59(1)°	–43.7(10)°
C(11)–C(20)–P(2)–M	65(1)°	74(1)°	66.5(7)°
C(19)–P(1) ... P(2)–C(20)	1(1)°	–16(1)°	–7.5(4)°

Geometry and dimensions of **1** are similar to those found in other complexes [5]. The out-of-plane distortion of the overcrowded tetranuclear system confers chirality on the complexes. Complex **2a** is present in the centrosymmetric crystals as a racemate. For complex **4** with space group $P2_12_12_1$ only one of the two enantiomers is present.

The shortest contact distances between Cl- and H-atoms in idealized positions are 2.65 and 2.85 Å in **2a** [Cl ... HC(1), C(19)] and between 2.51 and 2.59 Å in **4** [Cl(1) ... HC(1), C(12), C(19), C(20) and Cl(2) ... HC(22), C(30)]. These values are less than the sum of the *van der Waals* radii [20].

The CH_2Cl_2-molecule in the crystals of **4** has regular geometry [C–Cl = 1.73(2) Å, Cl–C–Cl = 108.4(10)°] and its heavy atoms are at distances greater than 4 Å from other heavy atoms.

Comparison of these two molecular structures shows that the formation of a square pyramidal addition complex between **2a** and Cl_2 should not require a particularly high activation energy. However, the subsequent steps, *i.e.*, those leading to the formation of the octahedral product **4**, could well involve high activation energy as a lengthening of the Ir-P bonds requires significant distortions of the chelate ring. This high energy barries could then be competitive with other pathways, *e.g.* radical reactions, leading to the formation of several products.

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Experimental Part

Physical measurements were carried out as described elsewhere [21]. Ligand **1** and complex **2a** were prepared as described by *Reed & Venanzi* [2].

*[IrCl₃(CO)(***1***)]* (**4**). A mixture of **2a** (200 mg, 0.23 mmol) and $CuCl_2 \cdot 2H_20$ (90 mg, 0.53 mmol) was suspended in 80 ml acetone/CH_2Cl_2 (3:1) and the mixture stirred for 2 h. The solvents were evaporated *i.v.* and the residue extracted twice with MeOH (5 ml) to remove unreacted $CuCl_2$. The residual solid was extracted with CH_2Cl_2 (50 ml), the solution filtered through *Celite* and evaporated *i.v.* to a small volume (*ca.* 4 ml). MeOH (10 ml) was then added to precipitate the product. This was obtained in 87% yields as the CH_2Cl_2 monosolvate after filtering off the

mother liquor, washing the residue twice with MeOH and drying *i.v.* Decomp. pt. > 270°. Found: C, 53.20; H, 3.48; P, 6.02; Cl, 17.08%. Calc. for $C_{46}H_{36}Cl_5IrOP_2$: C, 53.32; H, 3.50; P, 5.98; Cl, 17.11%.

Yellow crystals of [IrCl(CO)(**1**)] (**2a**) and of [$IrCl_3$(CO)(**1**)] (**4**) were obtained by recrystallization from $CHCl_3$- and CH_2Cl_2-solutions, respectively. A molecule of CH_2Cl_2 per molecule of complex **4** was found during the X-ray analysis.

Crystals of **2a** are triclinic, space group $P\bar{1}$; those of 4 are orthorhombic, space group $P2_12_12_1$.

Unit cell dimensions were determined from the angular positions of 15 reflections measured with a *Syntex P*2$_1$ automated diffractometer. In *Table 5* a summary of crystal data is reported.

Table 5. *Crystal Data for* **2a** *and* **4**

Compound	[IrCl(CO)(**1**)]	[$IrCl_3$(CO)(**1**) · CH_2Cl_2]
Formula	$C_{45}H_{34}ClIrOP_2$	$C_{46}H_{36}Cl_5IrOP_2$
Formula wt.	880.4	1036.2
Cell constants	a = 9.978(3) Å α = 101.76(2)°	a = 13.168(10) Å
	b = 12.017(3) β = 93.11(3)	b = 10.116(9)
	c = 15.889(6) γ = 104.13(2)	c = 30.861(15)
	V = 1798(1) Å^3	V = 4111(5) Å^3
Space group	$P\bar{1}$	$P2_12_12_1$
Density calcd.	1.626 gcm^{-3}	1.674 gcm^{-3}
Experimental[a])	1.63(1) gcm^{-3}	1.63(1) gcm^{-3}
Crystal dimension	0.04 × 0.13 × 0.25 mm	0.32 × 0.38 × 0.62 mm
Radiation	Graphite monochromatized Mo$K\alpha$ (λ = 0.71069 Å)	
μ(Mo$K\alpha$)	39.0 cm^{-1}	36.8 cm^{-1}

[a]) Measured by flotation in ZnI_2-solution.

Intensity data were collected by the ω-scan technique on a computer controlled automatic diffractometer *Syntex P*2$_1$. The data were processed as previously described [22]. The ignorance factor, p, was assigned values of 0.010 and 0.014 (for **2a** and **4**) according to the variance of the standard reflections [23].

The values of I and $\sigma(I)$ were corrected for *Lorentz*, polarization and shape anisotropy effects. For the latter correction the procedure described in [24] [25] was followed. For **2a** and **4**, 2511 and 4960 reflections respectively with $F_0^2 > 3\sigma(F_0^2)$ were considered observed and used in subsequent calculations.

Both structures were solved by *Patterson* and *Fourier* methods and refined by least-squares methods. The isotropic refinements converged at $R = 0.079$ (**2a**) and $R = 0.060$ (**4**). In the subsequent least-squares cycles the contributions of the H-atoms, geometrically positioned[3]), were included while the heavier atoms and the C-atoms not belonging to the phenyl rings or to the benzo[*c*]phenanthrene systems, were allowed to vibrate anisotropically. Phenyl rings were refined as rigid groups (D_{6h}-symmetry, C–C = 1.392 Å). The H-atoms were then repositioned and included in the final structure factor calculation: $R = 0.058$ and 0.047 ($R_w = 0.030$ and 0.048) for **2a** and **4**, respectively.

The refinements were carried out with a two-block (**2a**) and three-block (**4**) approximation of the normal equation matrix, the function minimized being $\Sigma w(|F_0| - |F_c|)^2$ with $w = 4F_0^2/\sigma^2(F_0^2)$.

Atomic scattering factors and anomalous dispersion terms were taken from the *International Tables for X-Ray Crystallography* [26].

The calculations were performed, using local programmes, on the UNIVAV 1100/20 computer of the University of Rome [27] and on the *HP 21 MX* minicomputer of the CNR Research Area [28]. The programmes used are described in [29].

The positional parameters for the non-H-atoms are given in *Tables 6* and *7*.

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[3]) C–H = 1.0 Å, C–C–H = 120° (sp^2), H–C–H = 109.0° (sp^3), dihedral angle 90°; each H-atom was assigned an isotropic thermal parameter equal to that of the C-atom to which it is attached.

Table 6. *Final Positional Parameters* ($\times 10^4$) *for the Non-H-Atoms of* **2**. Standard deviations are given in parentheses.

	x	y	z	
Non-Group Atoms				
Ir	121(1)	1398(1)	2318(1)	
Cl	−1623(4)	1336(4)	3261(3)	
P(1)	557(5)	−208(4)	2759(3)	
P(2)	−391(5)	3061(4)	2019(3)	
C	1222(16)	1236(13)	1427(12)	
O	1861(14)	1152(11)	880(8)	
C(1)	1683(17)	1956(14)	4655(10)	
C(2)	1659(17)	781(14)	4489(10)	
C(3)	2797(19)	456(14)	4831(11)	
C(4)	3898(19)	1260(17)	5349(12)	
C(5)	5015(18)	3309(16)	6103(11)	
C(6)	5064(19)	4394(17)	6265(11)	
C(7)	4242(18)	6127(16)	6063(11)	
C(8)	3459(20)	6638(15)	5725(12)	
C(9)	1598(18)	6523(15)	4634(12)	
C(10)	592(18)	5977(15)	3940(11)	
C(11)	393(16)	4708(14)	3657(10)	
C(12)	1192(16)	4136(13)	4065(10)	
C(13)	2852(17)	2862(14)	5138(10)	
C(14)	3895(18)	2436(15)	5525(11)	
C(15)	2161(16)	4738(13)	4800(10)	
C(16)	2387(18)	5944(15)	5032(11)	
C(17)	2997(16)	4146(14)	5250(10)	
C(18)	4144(20)	4917(17)	5904(12)	
C(19)	443(16)	−148(13)	3924(9)	
C(20)	−773(17)	4103(13)	2952(11)	
Rigid Group Atoms (derived parameters)				
C(21)	−723(10)	−1567(8)	2228(8)	Ph(1)
C(22)	−1604(12)	−2286(11)	2664(6)	
C(23)	−2565(11)	−3303(9)	2201(7)	
C(24)	−2645(10)	−3600(8)	1303(8)	
C(25)	−1764(12)	−2881(11)	867(6)	
C(26)	−803(11)	−1864(9)	1329(7)	
C(27)	2269(8)	−450(10)	2612(6)	Ph(2)
C(28)	3379(12)	526(7)	2646(6)	
C(29)	4708(10)	382(9)	2547(6)	
C(30)	4927(8)	−738(10)	2413(6)	
C(31)	3818(12)	−1714(7)	2378(6)	
C(32)	2489(10)	−1570(9)	2478(6)	
C(33)	927(11)	4058(11)	1571(7)	Ph(3)
C(34)	2316(12)	4040(8)	1672(6)	
C(35)	3318(9)	4820(13)	1348(8)	
C(36)	2931(11)	5617(11)	923(7)	
C(37)	1542(12)	5634(8)	822(6)	
C(38)	540(9)	4855(13)	1146(8)	
C(39)	−1973(10)	2641(9)	1263(7)	Ph(4)
C(40)	−1967(9)	1848(9)	492(7)	
C(41)	−3170(12)	1391(8)	−86(6)	
C(42)	−4377(10)	1728(9)	107(7)	
C(43)	−4383(9)	2521(9)	878(7)	
C(44)	−3180(12)	2977(8)	1456(6)	

Table 7. *Final Positional Parameters* (× 10^4) *for the Non-H-Atoms of* **3**. Standard deviations are given in parentheses.

	x	y	z	
Non-Group Atoms				
Ir	1407(0)	1809(0)	889(0)	
Cl(1)	2731(2)	3331(3)	1012(1)	
Cl(2)	–46(2)	599(3)	675(1)	
Cl(3)	796(3)	3467(3)	413(1)	
P(1)	639(2)	2886(3)	1501(1)	
P(2)	2439(2)	856(3)	321(1)	
C	1751(9)	353(13)	1247(4)	
O	1830(6)	–490(9)	1432(3)	
C(1)	2998(9)	1669(13)	1971(4)	
C(2)	2106(9)	2133(11)	2133(3)	
C(3)	1677(9)	1588(14)	2514(4)	
C(4)	2284(12)	631(15)	2738(5)	
C(5)	3767(11)	–777(15)	2810(4)	
C(6)	4639(12)	–1228(15)	2663(5)	
C(7)	5855(10)	–1606(14)	2089(4)	
C(8)	6184(11)	–1529(15)	1667(5)	
C(9)	5822(10)	–880(12)	917(4)	
C(10)	5243(10)	–260(13)	616(4)	
C(11)	4390(8)	488(11)	741(3)	
C(12)	4109(9)	565(12)	1173(4)	
C(13)	3531(9)	564(11)	2147(3)	
C(14)	3168(10)	136(13)	2569(4)	
C(15)	4664(9)	–91(11)	1506(4)	
C(16)	5558(10)	–840(13)	1361(4)	
C(17)	4395(9)	–99(12)	1958(4)	
C(18)	5002(11)	–941(14)	2229(4)	
C(19)	1589(9)	3327(12)	1921(3)	
C(20)	3815(9)	1238(12)	382(3)	
Cl(4)	5476(6)	1108(7)	4045(2)	solvent molecule
Cl(5)	6497(5)	1345(8)	3249(2)	
C(45)	6544(4)	1754(17)	3793(6)	
Rigid Group Atoms (derived parameters)				
C(21)	61(6)	4479(7)	1387(3)	Ph(1)
C(22)	547(5)	5666(10)	1481(2)	
C(23)	76(7)	6862(7)	1384(3)	
C(24)	–881(6)	6869(7)	1192(3)	
C(25)	–1367(5)	5681(10)	1099(3)	
C(26)	–896(7)	4486(7)	1196(3)	
C(27)	–336(6)	2029(8)	1813(3)	Ph(2)
C(28)	–611(6)	729(9)	1723(2)	
C(29)	–1396(6)	133(7)	1953(3)	
C(30)	–1906(6)	837(8)	2274(3)	
C(31)	–1632(6)	2137(9)	2364(2)	
C(32)	–847(6)	2733(7)	2134(3)	

Table 7. *Final Positional Parameters* ($\times 10^4$) *for the Non-H-Atoms of* **3**. Standard deviations are given in parentheses.

	x	y	z	
C(33)	2428(7)	−935(6)	243(3)	Ph(3)
C(34)	1682(5)	−1735(9)	425(2)	
C(35)	1693(6)	−3092(8)	352(3)	
C(36)	2451(7)	−3650(6)	96(3)	
C(37)	3197(5)	−2850(9)	−86(2)	
C(38)	3186(6)	−1493(8)	−13(3)	
C(39)	2135(7)	1535(9)	−208(2)	Ph(4)
C(40)	1292(6)	1050(8)	−428(3)	
C(41)	1016(6)	1593(8)	−826(3)	
C(42)	1583(7)	2622(9)	−1002(2)	
C(43)	2426(6)	3107(8)	−781(3)	
C(44)	2702(6)	2564(8)	−384(3)	

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