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ARYLDIAZENIDO, ARYLDIAZENE AND ARYLHYDRAZIDO COMPLEXES. ADDITION AND SUBSTITUTION REACTIONS OF HYDROGEN CHLORIDE WITH THE *ortho*-METALATED ARYLHYDRAZIDO COMPLEX $[Ir(NHNHC_6H_3NO_2)(CO)(PPh_3)_2]BF_4$

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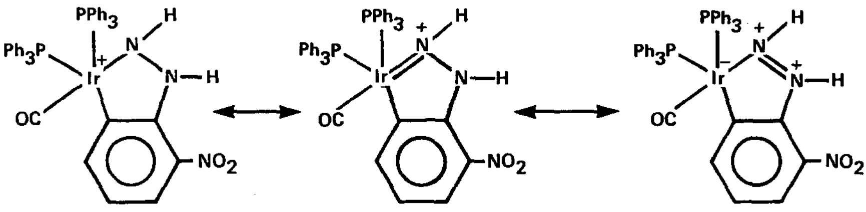
Summary

Reaction of the *ortho*-metalated arylhydrazido complex $[Ir(NHNHC_6H_3NO_2)$-$(CO)(PPh_3)_2]BF_4$ with hydrogen chloride occurs without rupture of the Ir–*ortho*-carbon bond. The products are dependent on the experimental conditions. In organic solvents a 1/1 HCl adduct is produced, in which addition of HCl across the Ir–N multiple bond has occurred to give the *ortho*-metalated arylhydrazine complex $[IrCl(NH_2NHC_6H_3NO_2)(CO)(PPh_3)_2]BF_4$. In liquid hydrogen chloride reaction also occurs at the metalated aromatic ring, involving chloride substitution at the 3-position and conversion of the 2-nitro group to 2-nitroso. The structure of this complex has been determined by X-ray crystallography.

Introduction

The crystal structure and spectroscopic properties of the iridium complex $[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$ (**1**) reported earlier [1] indicate extensive



1a　　1b　　1c

delocalization within the metallocycle formed by *ortho*-metalation of the 2-nitrophenylhydrazido(1 –) ligand. The electronic structure of the cation is inter-

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mediate between valence representations **1a–1c**. Whilst 1a and 1b formally involve iridium(III), the oxidation state in 1c is iridium(I) and, here, the ligand may be described as an N(2)-protonated aryldiazene. Notably, on deprotonation it is this N(2)-proton which is removed [1,2]. In view of the presence of the iridium–*ortho*-carbon bond, together with the suggestion of unsaturation in the Ir–N(1) bond, indicated by **1b**, we were interested in examining the reaction of **1** with hydrogen chloride to determine the site of addition and to observe whether or not cleavage of the Ir–C bond would occur.

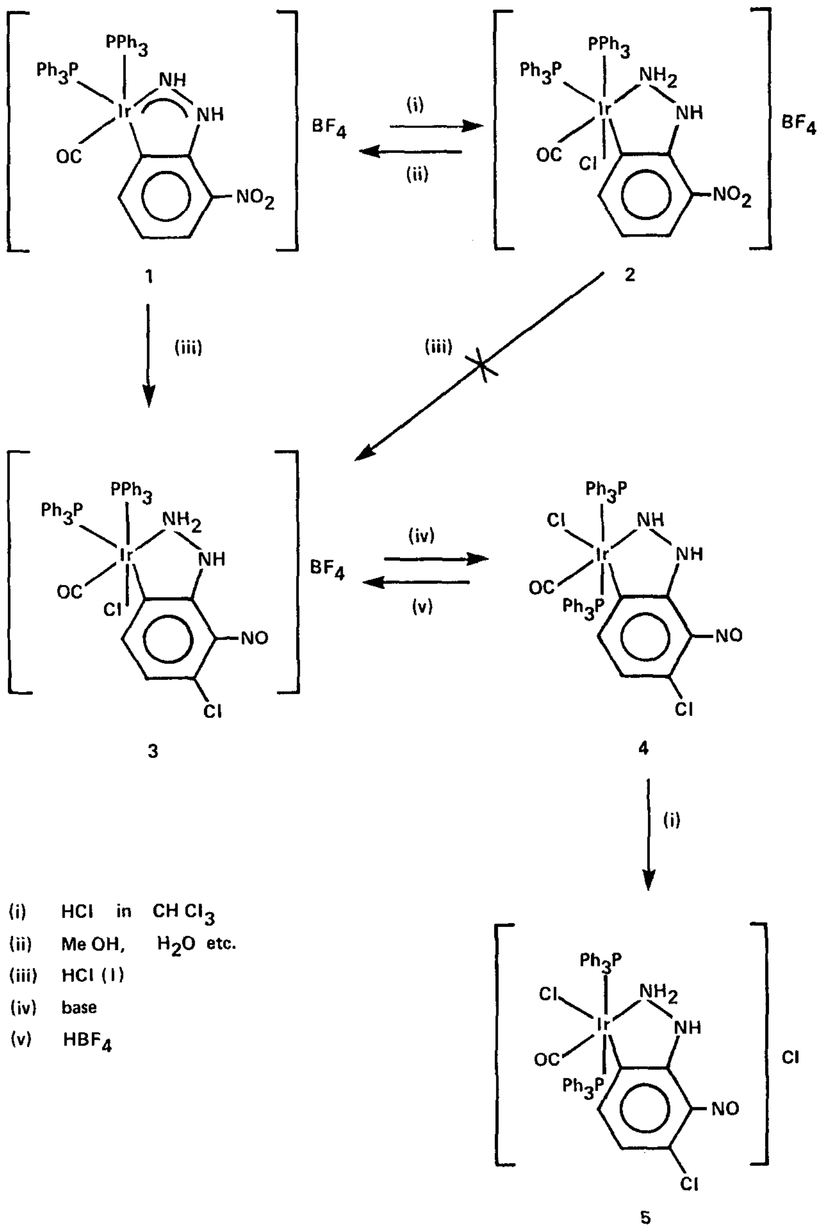
Results and discussion

When a red $CHCl_3$ solution of **1** is treated with an amount of HCl (added either as a solution in $CHCl_3$, or as a gas) sufficient to give a permanent brownish-yellow color, a light-sensitive, yellow solid is obtained after precipitation with ether. This is a 1/1 HCl adduct, identified as the *ortho*-metalated arylhydrazine complex **2** (see Scheme 1), as follows. The mass spectrum obtained by fast atom bombardment exhibited the parent peak expected for the cation in **2** at m/e 932 and showed the correct isotopic distribution pattern for the expected contribution from Ir, C, H and, particularly, Cl isotopes. In the IR spectrum, ν(NH) occurred at 3330w, 3240w and 3140w cm^{-1}, the increased complexity and positions compared with complex **1** indicating an arylhydrazine. The ν(CO) mode occurred at 2065vs cm^{-1} (increased from 2000 cm^{-1} in **1**) consistent with an Ir^{III} oxidation state and chloride coordination; ν(IrCl) occurred weakly at 290 cm^{-1}. Absorptions due to the NO_2 group and BF_4^- were also still present. Unfortunately, the ^1H NMR was not especially useful for identifying the NH resonances, which were weak, broad and of variable position, probably due to traces of H^+. These generally occurred near 9.2, 8.2 and 6.5 ppm, each integrated for one proton, and all disappeared on addition of D_2O. The first resonance was somewhat sharper than the others (which consistently appeared to be poorly resolved doublets of ca. 10 Hz separation), and more constant in position. Attempts to identify the position of the added hydrogen atom uniquely, by the use of DCl and ^{15}N isotopic substitution, or to exchange all NH atoms with D_2O and then record the deuterium spectrum, were generally inconclusive, again indicative of a moderate rate of exchange of hydrogens between the NH positions and with traces of H^+. We tentatively assign the 9.2 ppm resonance to N(2)H and the others to the two magnetically inequivalent N(1)H atoms in the chiral cation. As in complex **1** [2], the 400 MHz spectrum reveals well-separated resonances due to the 2-, 3- and 4-positions of the phenyl groups, whilst further separated from these are the resonances due to the 3-, 4- and 5-positions of the *ortho*-metalated ring. The latter H(3) and H(4) resonances are each shifted upfield by about 0.5 ppm by comparison with **1**. This easily allows the observation of traces of **1**, when present, such as occurs when H_2O or D_2O are added due to the equilibrium $\mathbf{1} + HCl \rightleftarrows \mathbf{2}$. This is further confirmation of the retention of the iridium–*ortho*carbon bond in **2**. Complex **1** can be quantitatively regenerated by treating **2** with a base such as K_2CO_3.

The stereochemistry ascribed to **2** has not been unambiguously determined, and that shown is based upon the coordination of Cl^- to the apparent vacant sixth position in the idealized square-based pyramidal geometry of **1**. The pair of doublets (J 8 Hz) in the ^{31}P NMR, confirms that the triphenylphosphines are in a *cis* arrangement. The mean position of these resonances lies some 25 ppm upfield of the room temperature resonance for **1**.

Liquid hydrogen chloride at −110°C reacts with **1** to produce a yellow solution of unknown composition. Removal of the excess hydrogen chloride under vacuum leaves the maroon solid **3** which may be deprotonated by base to give dark red-brown **4** (Scheme 1). Subsequent reprotonation with hydrogen chloride gives maroon **5**, but this complex is not simply the chloride salt of **3**, since the ^{31}P NMR

Scheme 1



spectra demonstrate clearly that, while the phosphines are *cis* in **3**, they are *trans* in the deprotonated complex **4** and remain so, on addition of HCl, to give **5**. Other than this, all available evidence points to the cations in **3** and **5** being identical. Both give identical parent ions in the mass spectrum (obtained by fast atom bombardment) with the correct intensity distribution of isotopic contributions expected for a cation of formulation $[C_{43}H_{35}Cl_2IrN_3O_2P_2]^+$ ($m/e = 950$ for ^{193}Ir).

In order to identify as exactly as possible the constitution of **3** or **5**, an X-ray structure determination was carried out. We were unsuccessful in crystallizing **3**, and only relatively poor quality crystals of **5** could be obtained. This, together with disorder of CH_2Cl_2 of solvation, limited the precision of the analysis of **5** but the interesting feature, namely the non-hydrogen atom arrangement, is clearly revealed (Fig. 1). The iridium metallocycle has been preserved. The 2-NO_2 group has been converted to a nitroso group (or possibly an oxime, NOH) and chlorine substitution has occurred at the 3-position. The stereochemical arrangement of the triphenylphosphine, chloro and carbonyl groups, with respect to the *ortho*-metalated ring, is similar to that observed previously in X-ray structures of related *ortho*-metalated aryldiazene complexes [1,3–5], so that Cl is *trans* to the Ir–C(6) bond and CO *trans* to the Ir–N(1) bond. Unfortunately, the low precision does not justify a detailed analysis of the bond lengths and angles (Table 1) although, for the most part, they appear to compare well with those of similar bonds in the related structures mentioned. The location of the three non-aromatic hydrogen atoms expected on the basis of the mass spectrum is open to some doubt. A reasonable formulation is that

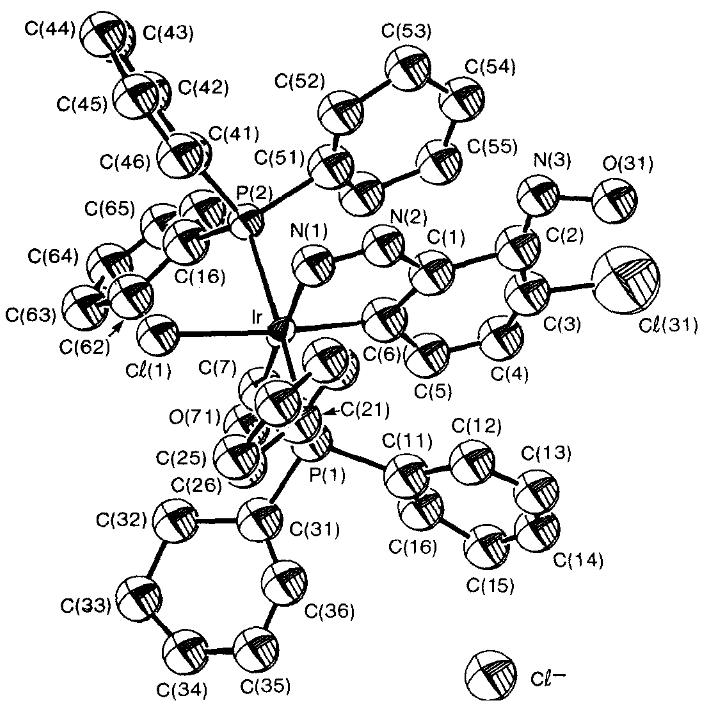


Fig. 1. A perspective view of an ion pair in $[Ir(N_2H_3C_6H_2(NO)Cl)Cl(CO)(PPh_3)_2]Cl$, with atom numbering.

TABLE 1

SELECTED BOND DISTANCES AND ANGLES FOR [Ir($N_2H_3C_6H_2$(NO)Cl)Cl(CO)(PPh_3)$_2$]Cl (Errors are quoted in parentheses and refer to the least significant figure)

Distances (Å)

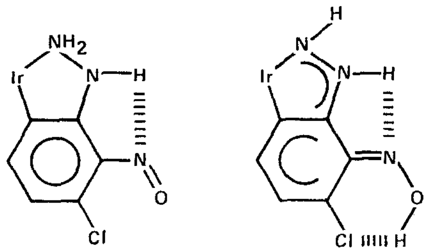
Ir–Cl(1)	2.47(2)	P(1)–C(11)	1.83(8)
Ir–P(1)	2.43(2)	P(1)–C(21)	1.84(8)
Ir–P(2)	2.42(2)	P(1)–C(31)	1.75(8)
Ir–N(1)	2.00(6)	P(2)–C(41)	1.86(8)
Ir–C(6)	2.01(7)	P(2)–C(51)	1.88(8)
Ir–C(7)	1.88(7)	P(2)–C(61)	1.81(8)
N(1)–N(2)	1.31(8)		
N(2)–C(1)	1.45(9)	av. C–C(phenyl) 1.40(9) [a]	
C(2)–N(3)	1.21(9)		
N(3)–O(31)	1.40(7)		
C(3)–Cl(31)	1.88(8)		
C(7)–O(71)	1.05(8)		

Angles (°)

Cl(1)–Ir–P(1)	86.1(7)	Ir–P(1)–C(11)	118(3)
Cl(1)–Ir–P(2)	90.7(7)	Ir–P(1)–C(21)	110(3)
Cl(1)–Ir–N(1)	87(2)	Ir–P(1)–C(31)	114(3)
Cl(1)–Ir–C(6)	170(2)	C(11)–P(1)–C(21)	103(4)
Cl(1)–Ir–C(7)	100(2)	C(11)–P(1)–C(21)	100(4)
P(1)–Ir–P(2)	176.3(7)	C(21)–P(1)–C(31)	111(4)
P(1)–Ir–N(1)	92(2)		
P(1)–Ir–C(6)	94(2)	Ir–P(2)–C(41)	117(3)
P(1)–Ir–C(7)	92(3)	Ir–P(2)–C(51)	112(3)
P(2)–Ir–N(1)	86(2)	Ir–P(2)–C(61)	113(3)
P(2)–Ir–C(6)	89(2)	C(41)–P(2)–C(51)	103(3)
P(2)–Ir–C(7)	91(3)	C(41)–P(2)–C(61)	102(3)
N(1)–Ir–C(6)	84(3)	C(51)–P(2)–C(61)	110(4)
N(1)–Ir–C(7)	172(3)		
C(6)–Ir–C(7)	89(3)	av. C–C–C(phenyl) 120(9) [a]	
Ir–C(6)–C(1)	113(5)		
Ir–C(7)–O(71)	176(6)		
Ir–N(1)–N(2)	110(4)		
N(1)–N(2)–C(1)	126(6)		
N(2)–C(1)–C(6)	107(6)		
Ir–C(6)–C(5)	131(5)		
N(2)–C(1)–C(2)	129(6)		
C(2)–N(3)–O(31)	104(6)		

[a] Typical errors in individual bond distances and angles were 0.10 Å and 7°, respectively.

5 is an arylhydrazine complex with a nitroso group in the 2-position **5a**, oriented so as to allow effective N–H···N hydrogen bonding with N(2)–H. It is possible, however, that the 2-position may be an oxime **5b**, oriented to allow O–H···Cl hydrogen bonding, but the consequent loss of aromaticity makes this a less likely formulation.

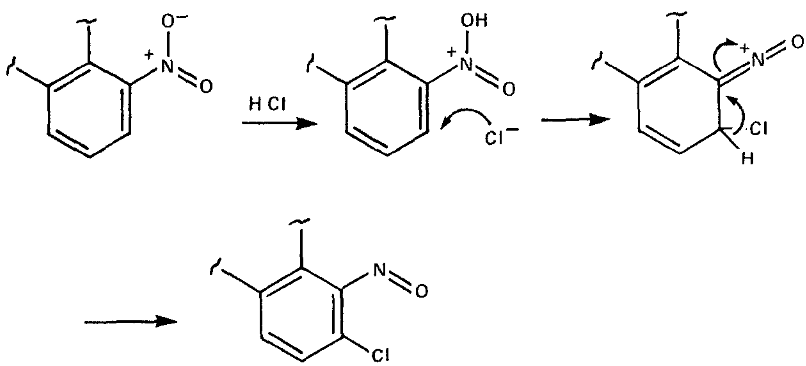


5a 5b

Infrared and NMR spectroscopy have failed to resolve this problem unambiguously. Allowing for $\nu(BF_4)$, the IR of **3** and **5** are virtually identical. Weak bands at 3360 and 3245 cm^{-1} seem best assigned to ν(NH), rather than ν(OH), by comparison with **1** and **2**. We have been quite unable to locate any resonance assignable to NH or OH in the ^1H NMR for **3** or **5** despite numerous attempts using a variety of solvents, pH, temperatures, instruments and drying techniques. However, the neutral complex **4** did give a resonance at 13.1 ppm and a clearly visible IR band at 3355 cm^{-1}, assignable to NH.

A possible mechanism for the transformation on the arene ring in the presence of molecular hydrogen chloride is shown in Scheme 2. An influence of the metallocycle is indicated by the fact that neither nitrobenzene nor *o*-nitrophenylhydrazine undergo this transformation in liquid HCl.

Scheme 2



Experimental

All reactions were carried out in Schlenk apparatus under nitrogen. Solvents were dried by normal procedures and distilled under nitrogen. Infrared spectra were recorded using a Perkin–Elmer Model 599B or a Nicolet 7199 FTIR instrument, as KBr discs, or as evaporated films on KBr plates. The IR spectrum of a single crystal of **5** was obtained by diffuse reflectance FTIR. NMR spectra were obtained using Varian XL-100 FT or Bruker WM400 instruments. Chemical shifts are listed in ppm relative to $SiMe_4$ (^1H and ^{13}C) and H_3PO_4 (^{31}P) with positive values in the direction of increasing frequency. Mass spectra were measured on samples dispersed in sulfolane using a MS-9 mass spectrometer, by the technique of xenon fast atom bombardment, courtesy of the University of Alberta. $[Ir(NHNHC_6H_3\text{-2-}NO_2)(CO)(PPh_3)_2][BF_4]$ (**1**), was synthesized from $IrCl(CO)(PPh_3)_2$, as described previously [2].

$[Ir(NH_2NHC_6H_3\text{-2-}NO_2)Cl(CO)(PPh_3)_2][BF_4]$ (2)

Complex **1** (20 mg) was dissolved in $CHCl_3$ (2 ml) in a foil-wrapped Schlenk tube and a freshly-made solution of HCl in $CHCl_3$ was added dropwise, with stirring, until the color was permanently yellow-brown. Alternatively, HCl gas could be slowly bubbled through the solution directly. The pale yellow air- and light-sensitive product was precipitated by addition of diethyl ether, washed twice with ether and vacuum dried. Yield 90%. IR: 3330w, 3240w, 3140w (ν(NH)), 2065vs (ν(CO)), 1512m ($\nu_{as}(NO_2)$), 1340m, 1300s ($\nu_s(NO_2)$), 1054s ($\nu(BF_4)$), 519m ($\nu(BF_4)$), 292w (ν(IrCl)). Anal. Found: C, 49.53; H, 3.65; N, 4.10. $C_{43}H_{36}BClF_4IrN_3O_3P_2$ calcd: C, 50.44; H, 3.54; N, 4.10%. Chlorine analysis was variable and indicated partial substitution of Cl^- for BF_4^-. Mass spectrum: m/e 932 (^{193}Ir), with appropriate intensity distribution of isotopic peaks from m/e 928–936 ($[Ir(NH_2NHC_6H_3\text{-2-}NO_2)Cl(CO)(PPh_3)_2]^+$). NMR ($CDCl_3$): ^1H, 400 MHz; ca. 9.2 br, ca. 8.8–8.2 br (occurs as a broad doublet in $^{15}N(1)$-substituted complex, $^1J(^{15}NH)$ 82 Hz), ca. 6.2 [NH]; 7.66 d (J 8 Hz) [3-aryl]; 7.49 d (J 8 Hz) [5-aryl]; 7.44 cplx, 7.28 cplx, 7.20 cplx [phenyl]; 6.54 d of d (J 8 Hz) [4-aryl]. ^{31}P (40.5 MHz, $(CD_3)_2CO$) −9.60 d (J 8 Hz), −13.10 d (J 8 Hz).

$[Ir\{N_2H_3C_6H_2(NO)Cl\}Cl(CO)(PPh_3)_2][BF_4]$ (3)

Compound **2** (75 mg) was cooled to liquid nitrogen temperature in a Schlenk tube under nitrogen and hydrogen chloride (ca. 1.5 ml, dried through $CaCl_2$, then conc. H_2SO_4 and, finally, in a −78°C trap) was condensed onto it, the liquid nitrogen was then removed and the mixture stirred at ca. −110°C for a few minutes, to give a yellow solution. Pumping off HCl produced a deep maroon solid which was washed three times with water to remove hydrogen chloride, then reprecipitated from acetone/hexane. Yield 95%. Anal. Found: C, 49.82; H, 3.36; N, 4.01; Cl, 7.52; P, 6.46. $C_{43}H_{35}BCl_2F_4IrN_3O_2P_2$ calcd: C, 49.66; H, 3.37; N, 4.04; Cl, 6.82; P, 5.97%. Mass spectrum: m/e 950 (^{193}Ir), $[Ir\{N_2H_3C_6H_2(NO)Cl\}Cl(CO)(PPh_3)_2]^+$ with appropriate intensity distribution of isotopic peaks from m/e 948–955. ^{31}P NMR (40.5 MHz, $CDCl_3$): −9.2d (J 11 Hz), −12.05d (J 11 Hz).

$[Ir\{N_2H_2C_6H_2(NO)Cl\}Cl(CO)(PPh_3)_2]$ (4)

Compound **3** in methanol was stirred with excess $NaHCO_3$ in methanol for 30 min. The color changed from deep purple to red-orange. The solution was filtered and evaporated under vacuum to leave a red-brown solid which was washed three times with water and pumped to dryness. Yield 95%. IR: ν(NH) 3355, ν(CO) 2020 cm^{-1}, $\nu(BF_4)$ absent. Anal. Found: C, 52.36; H, 3.57; N, 4.13; Cl, 7.78. $C_{43}H_{34}Cl_2IrN_4O_2P_2$ calcd: C, 53.64; H, 3.53; N, 4.36; Cl, 7.37%. NMR ($CDCl_3$): ^1H, 13.1 br (NH); ^{31}P, −4.7s. Mass spectrum: m/e 950 (^{193}Ir), $[Ir\{N_2H_3C_6H_2(NO)Cl\}Cl(CO)(PPh_3)_2]^+$, identical with that of **3**.

$[Ir\{N_2H_3C_6H_2(NO)Cl\}Cl(CO)(PPh_3)_2]Cl$ (5)

Compound **4** in $CHCl_3$ was reprotonated by addition of a solution of HCl in $CHCl_3$. The solution became deeply purple and solvent was stripped to leave a deep

TABLE 2

FINAL POSITIONAL PARAMETERS FOR $[Ir(N_2H_3C_6H_2(NO)Cl)Cl(CO)(PPh_3)_2]Cl$ (Errors are quoted in parentheses and refer to the least significant figure)

Atom	x	y	z	B_{iso} [a]
Ir	0.2358(2)	0.0615(3)	0.0503(2)	2.5(2)
Cl(1)	0.115(1)	0.027(2)	−0.033(1)	4.7(6)
Cl(31)	0.587(2)	0.163(3)	0.211(1)	12.7(10)
Cl	0.289(1)	0.468(2)	0.346(1)	7.1(7)
P(1)	0.206(1)	0.256(2)	0.032(1)	4.6(7)
P(2)	0.261(1)	−0.135(2)	0.061(1)	3.4(7)
O(31)	0.600(3)	0.147(4)	0.090(2)	6.(0)
O(71)	0.173(3)	0.064(4)	0.158(2)	6.(0)
N(1)	0.289(3)	0.057(5)	−0.017(2)	6.(0)
N(2)	0.363(3)	0.074(5)	0.007(3)	6.(0)
N(3)	0.530(3)	0.091(5)	0.069(3)	6.(0)
C(1)	0.402(4)	0.097(6)	0.072(3)	6.(0)
C(2)	0.495(4)	0.115(6)	0.106(3)	6.(0)
C(3)	0.487(4)	0.137(6)	0.159(3)	6.(0)
C(4)	0.449(4)	0.136(6)	0.202(3)	6.(0)
C(5)	0.369(4)	0.119(6)	0.171(3)	6.(0)
C(6)	0.342(4)	0.089(6)	0.106(3)	6.(0)
C(7)	0.198(4)	0.062(7)	0.121(3)	6.(0)
C(11)	0.278(4)	0.355(6)	0.075(3)	6.(0)
C(12)	0.337(4)	0.412(7)	0.053(3)	6.(0)
C(13)	0.388(4)	0.464(6)	0.098(3)	6.(0)
C(14)	0.381(4)	0.474(6)	0.158(3)	6.(0)
C(15)	0.332(4)	0.430(7)	0.187(3)	6.(0)
C(16)	0.285(4)	0.358(6)	0.138(3)	6.(0)
C(21)	0.196(4)	0.290(6)	−0.050(3)	6.(0)
C(22)	0.251(4)	0.279(6)	−0.081(3)	6.(0)
C(23)	0.234(4)	0.315(6)	−0.142(3)	6.(0)
C(24)	0.167(4)	0.356(6)	−0.171(3)	6.(0)
C(25)	0.107(4)	0.364(6)	−0.143(3)	6.(0)
C(26)	0.119(4)	0.333(7)	−0.085(3)	6.(0)
C(31)	0.126(4)	0.300(6)	0.054(3)	6.(0)
C(32)	0.051(4)	0.225(6)	0.053(3)	6.(0)
C(33)	−0.008(4)	0.280(6)	0.067(3)	6.(0)
C(34)	−0.009(4)	0.388(6)	0.076(3)	6.(0)
C(35)	0.053(4)	0.461(6)	0.073(3)	6.(0)
C(36)	0.114(4)	0.402(6)	0.062(3)	6.(0)
C(41)	0.234(4)	−0.218(6)	−0.011(3)	6.(0)
C(42)	0.230(4)	−0.339(7)	−0.007(3)	6.(0)
C(43)	0.220(4)	−0.399(6)	−0.060(3)	6.(0)
C(44)	0.206(4)	−0.360(6)	−0.123(3)	6.(0)
C(45)	0.202(4)	−0.244(6)	−0.121(3)	6.(0)
C(46)	0.219(4)	−0.170(6)	−0.069(3)	6.(0)
C(51)	0.367(4)	−0.164(6)	0.095(3)	6.(0)
C(52)	0.400(4)	−0.192(6)	0.052(3)	6.(0)
C(53)	0.485(4)	−0.212(6)	0.077(3)	6.(0)
C(54)	0.521(4)	−0.175(6)	0.141(3)	6.(0)
C(55)	0.476(4)	−0.148(6)	0.184(3)	6.(0)
C(56)	0.390(4)	−0.147(6)	0.151(3)	6.(0)
C(61)	0.207(4)	−0.203(6)	0.108(3)	6.(0)
C(62)	0.132(4)	−0.174(7)	0.100(3)	6.(0)

TABLE 2 (continued)

Atom	x	y	z	B_{iso} [a]
C(63)	0.088(4)	−0.229(6)	0.137(3)	6.(0)
C(64)	0.134(4)	−0.305(6)	0.186(3)	6.(0)
C(65)	0.203(4)	−0.321(5)	0.193(3)	6.(0)
C(66)	0.241(4)	−0.273(6)	0.155(3)	6.(0)

The Ir atom was refined anisotropically resulting in U_{ij} values of:

U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
0.034(2)	0.018(2)	0.043(2)	0.002(3)	−0.006(2)	0.001(3)

Anisotropic temperature factors are of the form:
$\exp[-2\pi^2(U_{11}h^2a^{\star 2}+U_{22}k^2b^{\star 2}+U_{33}l^2c^{\star 2}+2U_{12}hka^\star b^\star+2U_{13}hla^\star c^\star+2U_{23}klb^\star c^\star)]$

[a] $B_{iso} = 8\pi^2U$.

maroon solid. IR: ν(NH) 3360, 3240, ν(CO) 2068 cm^{-1}. ^{31}P NMR ($CDCl_3$) −7.7s. Anal. Found: C, 51.06, H, 3.67, N, 4.05, Cl, 9.00. $C_{43}H_{35}Cl_3IrN_3O_2P_2$ calcd: C, 51.68; H, 3.51; N, 4.21; Cl, 10.65%. Mass spectrum: m/e 950 (^{193}Ir), $[Ir\{N_2H_3C_6H_2(NO)Cl\}Cl(CO)(PPh_3)_2]^+$, identical with that of **3**.

X-Ray structure determination on $[Ir\{N_2H_3C_6H_2(NO)Cl\}Cl(CO)(PPh_3)_2]Cl$ (5)

Needle-shaped crystals of **5** were grown by slow diffusion of cyclohexane or petroleum ether into a solution of **5** in CH_2Cl_2. These crystals exhibited a mass spectrum identical with that of the bulk material and (allowing for solvent of crystallization) a virtually identical FTIR spectrum, confirming that no change in composition of the complex had occurred during crystallization.

Crystals were small, of poor quality and adequate only for collection of data over a limited sphere of reciprocal space. Weissenberg and precession photographs defined the space group uniquely as $P2_1/c$. Accurate cell dimensions were obtained, for a crystal of dimensions 0.20 × 0.02 × 0.08 mm, mounted in a Lindemann glass capillary, by least-squares analysis of accurately centered reflections from various regions of reciprocal space (10° < 2θ < 17°). A Picker FACS-1 computer-controlled diffractometer equipped with a graphite monochromator and a scintillation counter with pulse-height discrimination, was used with Mo-K_α radiation (λ 0.71069 Å). Data were collected at 293 K using a symmetrical θ–2θ scan (at 1° min^{-1}) of (1.6 + 0.692 tan θ)°. The take-off angle was 3°. Stationary crystal-stationary counter background counts of 20% scan time were taken each side of the scan. Two standard reflections were measured every 70 data points. Data were scaled according to the variation in the standards but there was no evidence of crystal decomposition.

Intensities were measured for 1111 independent reflections ($2\theta \le 25.0°$) of which 709 were classed observed [$I \ge 2.3\sigma(I)$]. Lorentz, polarization and absorption corrections have been applied.

The structure was solved, with difficulty, by Patterson and Fourier methods. It was not possible to refine atomic positions until most of the non-hydrogen atoms had been located. Aromatic H-atoms were included at calculated positions. An electron density difference map showed residual peaks due to disordered CH_2Cl_2 which were fitted by inclusion of four carbon and four chlorine atoms. Block-diagonal least-squares refinement, with anisotropic temperature factors for Ir, variable isotropic temperature factors for Cl and P atoms, and fixed isotopic temperature factors for O, N and C atoms gave final agreement factors of $R = 0.070$ and $R_w = 0.082$ for 205 variables. The largest shift/error ratio during the final cycle was 0.16. Unit weights were applied. Atomic scattering factors including anomalous dispersion were taken from ref. 6. Final positional parameters and temperature factors are contained in Table 2. Crystal data: $C_{43}H_{35}Cl_3IrN_3O_2P_2$, solv. F.W. 986.30 (excl. solv.). Monoclinic, $P2_1/c$, a 18.051(9) Å, b 12.130(12) Å, c 22.318(7) Å, β 106.36(3)°, U 4689 Å^3, $Z = 4$, $d_c = 1.40$ (excl. solv.), $\mu = 32.9$ (incl. solv.).

A listing of observed and calculated structure factors may be obtained from the authors.

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