Aryldiazenato-complexes: Synthesis and Structure of Complexes derived from the Oxidative Addition of Diazonium Ions to *trans*-Carbonylchlorobis(triphenylphosphine)iridium(I)

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Vaska's complexes $[IrX(CO)(PPh_3)_2]$ (X = Cl or Br) react with aryldiazonium tetrafluoroborates to form cationic iridium(III) aryldiazenato-complexes of the type $[\{Ir(X)(N_2Ar)(CO)(PPh_3)_2\}_n][BF_4]_n$, and in the presence of lithium chloride to form the neutral six-co-ordinate complexes $[IrXCl(N_2Ar)(CO)(PPh_3)_2]$. The presence of the ' doubly-bent ' aryldiazenato-group (as required by the Ir^{III} oxidation state in an 18 valence-electron complex) has been confirmed by a single crystal *X*-ray structure determination for $[IrCl_2(o\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2]$. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a cell of dimensions: $a = 12.202(7)$, $b = 15.441(8)$, $c = 12.762(6)$ Å, $\alpha = 96.41(3)$, $\beta = 89.01(3)$, $\gamma = 105.09(3)$°. The structure was solved by Patterson and Fourier methods and refined by least-squares procedure (1 616 reflections) to *R* 0.089. Selected dimensions in the aryldiazenato-ligand are Ir–N(1) 2.05(4), N(1)–N(2) 1.19(4), N(2)–C(11) 1.47(5) Å; Ir–N(1)–N(2) 115(3), N(1)–N(2)–C(7) 115(3)°. The aryldiazenato-ligand appears to exert a strong *trans*-influence, since the chloride *trans* to it has Ir–Cl(2) 2.48(1) Å, *vs.* Ir–Cl(1) 2.37(1) Å for the *cis*-chloride.

VASKA's complex, *trans*-$[IrCl(CO)(PPh_3)_2]$, is the most thoroughly studied of the square-planar d^8 (16-electron) iridium(I) complexes, and is outstanding in the scope and variety of its oxidative-addition reactions.[1-4] One interpretation of certain of its reactions attributes Lewis-base properties to the d^8 iridium(I), so that a number of electrophiles such as BF_3 (ref. 5) or NO^+ (ref. 6) may act as ' ligands ' by ' Lewis-acid addition '.[7] We have studied the reactions of the weakly electrophilic aryldiazonium tetrafluoroborates with Vaska's complex. The reactions are quite solvent-dependent, and we have already described the results of reactions in solutions containing ethanol or propan-2-ol which are complicated owing to participation of these alcohols in the reactions.[8,9] The products are dependent not only upon the presence, but also upon the concentrations of these alcohols in solution.

However, in ' non-participating ' solvents at lowered temperatures diazonium ions react straightforwardly to yield aryldiazenato-complexes of stoicheiometry $[\{IrCl(N_2Ar)(CO)(PPh_3)_2\}_n][BF_4]_n$. Furthermore, co-ordination of an additional chloride ligand occurs in the presence of LiCl to yield molecular six-co-ordinate complexes $[IrCl_2(N_2Ar)(CO)(PPh_3)_2]$. An *X*-ray structure determination on one example of the latter has been undertaken to establish the stereochemistry of the complex and particularly the geometry of the aryldiazenato-ligand.

Molecular Complexes of the Type $[IrCl_2(N_2Ar)(CO)(PPh_3)_2]$.—These were prepared by adding an acetone solution of the diazonium ion containing lithium chloride

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[1] L. Vaska and J. W. Diluzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679.

[2] J. P. Collman, *Accounts Chem. Res.*, 1968, **1**, 135.

[3] L. Vaska, *Accounts Chem. Res.*, 1968, **1**, 335.

[4] J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.

[5] R. N. Scott, D. F. Shriver, and L. Vaska, *J. Amer. Chem. Soc.*, 1968, **90**, 1079.

[6] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2345; D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1968, **90**, 4486.

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[8] A. B. Gilchrist and D. Sutton, *Canad. J. Chem.*, 1974, **52**, 3387.

[9] F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1972, **94**, 645; F. W. B. Einstein and D. Sutton, *J.C.S. Dalton*, 1973, 434.

to a suspension of $[IrCl(CO)(PPh_3)_2]$ in acetone at or below room temperature. The yellow Vaska's complex soon dissolved to give an orange solution from which the orange or orange-yellow product generally precipitated quickly, or upon cooling. The complexes have also been obtained by the addition of acetone or ethanol solutions of diazonium salts containing LiCl to benzene solutions of Vaska's complex, but these methods are not recommended as the product is contaminated with $LiBF_4$ and the use of ethanol is liable to give rise to side reactions, such as orthometallation of the aryldiazenato-ligand.[9] Complexes have been obtained for a variety of substituents in *ortho-*, *meta-*, and *para-*positions. The products appear to be most readily obtained when electron-withdrawing substituents are present, but this is not a necessary requirement as the *p*-methoxy-compound has also been obtained. Properties are dependent somewhat upon the substituent but in general these are air-stable crystalline solids, and have been kept satisfactorily for some months at −14 °C, though they tend to be rather less stable at room temperature, and are somewhat light-sensitive. They are soluble in benzene, chloroform, and dichloromethane, slightly soluble in acetone, and insoluble in methanol, ethanol, acetonitrile, diethyl ether, and water. Solutions at room temperature are stable for only a few hours, but rapid recrystallization may be accomplished from benzene–acetone (which frequently yields acetone solvates on the basis of analysis and i.r. spectroscopy) or dichloromethane–ethanol without appreciable decomposition. The compounds obtained are listed in Table 1. Similar compounds have been reported briefly.[10,11] $[IrCl_2(N_2Ph)(CO)(PMe_2Ph)_2]$ was synthesized[10] by treating $[IrCl(CO)(PMe_2Ph)_2]$, PhN_2BF_4, and LiCl in aqueous methanol. We have confirmed this synthesis, but have found this solvent to be quite unsuitable for the triphenylphosphine complexes since there was a high recovery of Vaska's complex and a low yield of a product, which was probably a mixture of the desired complex and nitrogen-free impurities, judging from analytical data and i.r. spectra.

TABLE 1

Analytical and spectroscopic data for aryldiazenato-complexes

Complex	Colour	M.p.(t/°C) [a]	Analysis (%) [b] C	H	N	ν(CO)/ cm^{-1}	δ(CH)/ cm^{-1}	ν(NN)/ cm^{-1}	ν(Ir–Cl)/ cm^{-1}
$[IrCl_2(N_2Ph)(CO)(PPh_3)_2]\cdot Me_2CO$	Orange	126	56.7 (56.41)	4.25 (4.23)	2.7 (2.86)	2 058	*c*	1 470 (1 464) [d]	309, 260
$[IrCl_2(p\text{-}N_2C_6H_4F)(CO)(PPh_3)_2]\cdot Me_2CO$	Yellow-orange	148	55.4 (55.43)	4.05 (4.04)	2.75 (2.81)	2 055	840	1 470	
$[IrCl_2(p\text{-}N_2C_6H_4Br)(CO)(PPh_3)_2]$	Orange	138	5.06 (51.64)	3.55 (3.45)	2.5 (2.80)	2 050	830	1 465	
$[IrCl_2(p\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2]\cdot Me_2CO$	Purple	176	54.3 (53.96)	3.75 (3.94)	4.2 (4.10)	2 069	834	1 467	305, 267
$[IrCl_2(p\text{-}N_2C_6H_4OMe)(CO)(PPh_3)_2]$	Yellow		54.15 (55.50)	3.95 (3.93)	2.25 (2.93)	2 050	835	1 455	
$[IrCl_2(o\text{-}N_2C_6H_4F)(CO)(PPh_3)_2]$	Orange		54.85 (55.01)	3.75 (3.66)	2.6 (2.99)	2 060	*c*	1 465sh	
$[IrCl_2(o\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2]\cdot 2Me_2CO$	Orange	161	53.35 (54.40)	3.9 (4.29)	3.5 (3.88)	2 062	*c*	1 462	320, 263, 247
$[IrCl_2(m\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2]$	Orange		53.3 (53.39)	3.55 (3.55)	4.35 (4.35)	2 055	803, 835	1 455	
$[IrCl_2(N_2C_6H_3F_2\text{-}2,6)(CO)(PPh_3)_2]$	Orange-yellow	130	52.95 (53.97)	3.9 (3.48)	2.45 (2.93)	2 060	790, 710	1 470	
$[\{IrCl(N_2C_6H_5)(CO)(PPh_3)_2\}_n[BF_4]_n$	Yellow	95	53.35 (53.13)	3.85 (3.63)	2.6 (2.88)	2 055	*c*	1 510	270br
$[\{IrCl(p\text{-}N_2C_6H_4F)(CO)(PPh_3)_2\}_n][BF_4]_n$	Yellow	105—110	51.45 (52.16)	3.55 (3.46)	2.75 (2.83)	2 044	850	1 474sh	
$[\{IrCl(p\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2\}_n][BF_4]_n$ [e]	Pink	85—90	50.9 (50.78)	3.7 (3.37)	3.95 (4.13)	2 068	835	1 473 (1 462) [d]	280br
$[\{IrCl(o\text{-}N_2C_6H_4F)(CO)(PPh_3)_2\}_n][BF_4]_n$	Yellow	110—115	52.3 (52.16)	3.65 (3.46)	2.7 (2.83)	2 058		1 478sh	
$[\{IrCl(o\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2\}_n][BF_4]_n$	Brown-orange	90—92	50.5 (50.78)	3.8 (3.37)	3.6 (4.13)	2 064		1 471	
$[\{IrCl(o\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2\}_n][PF_6]_n\cdot Me_2CO$	Brown-orange	90—92	48.45 (48.75)	3.85 (3.56)	3.5 (3.71)	2 062		1 470	
$[\{IrCl(N_2C_6H_3\cdot 2,6\text{-}F_2)(CO)(PPh_3)_2\}_n][BF_4]_n$	Yellow	110—115	51.0 (51.23)	3.6 (3.30)	2.3 (2.78)	2 058	795	1 470	

[a] Decomp. [b] Calc. value in parentheses. [c] Band obscured by phenylphosphine absorption. [d] Frequency when iridium-bonded nitrogen is ^{15}N. [e] Found: Cl, 3.6, calc.: Cl, 3.87.

A single-crystal *X*-ray structure analysis on $[IrCl_2(o\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2]$ has confirmed the discrete molecular nature of the complex and revealed the general stereochemistry shown in the Figure, in which the phosphine groups remain *trans*, but the chlorine atoms are mutually *cis*. The main purpose of the structure determination was to identify the geometry of the co-ordinated aryldiazenato-group. A brief, but over-simplified, resumé of current ideas on the bonding and geometry of this ligand [12] is that where the group is formally ArN_2^+ it approximates to the 'singly-bent' structure (1a) [although in bonding to a very poor π-donor a totally linear structure (1b) could possibly arise], whereas if it occurs

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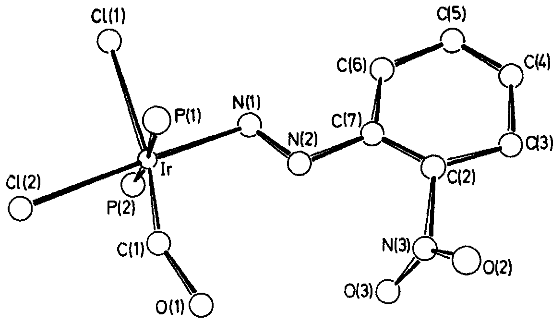
[10] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), **1969**, 1128.

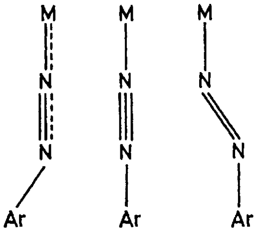
[11] B. L. Haymore and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 3052.

[12] D. Sutton, *Chem. Soc. Rev.*, 1975, **4**, 443.



Perspective view of a molecule of $[IrCl_2(o\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2]$ (phosphine phenyl groups omitted for clarity)

formally as ArN_2^-, then it adopts the ' doubly-bent ' structure (1c).



(1a) (1b) (1c)

In this compound, as can be seen in the Figure, the aryldiazenato-ligand is unambiguously ' doubly-bent ', and the oxidation state of iridium is (III), so that the reaction may be written as an oxidative-addition of ArN_2^+ and Cl^- to Vaska's complex [equation (1)]. It may be noted

$$[Ir^{I}Cl(CO)(PPh_3)_2] + ArN_2BF_4 + LiCl \longrightarrow [Ir^{III}Cl_2(N_2Ar)(CO)(PPh_3)_2] + LiBF_4 \quad (1)$$

that this formulation prescribes an 18-electron configuration for iridium, whereas the $Ir^{I}(N_2Ar^+)$ formulation would result in a less satisfactory 20-electron configuration. The values of ν(CO) which occur in the region of 2 060 cm^{-1} are also consistent with the presence of Ir^{III}.

TABLE 2

Selected distances and angles for $[IrCl_2(o\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2]\cdot 2Me_2CO$, with estimated standard deviations in the least significant figures in parentheses

(*a*) Bond distances (Å)

Ir–Cl(1)	2.37(1)	C(3)–C(4)	1.40(7)
Ir–Cl(2)	2.48(1)	C(4)–C(5)	1.31(7)
Ir–P(1)	2.37(1)	C(5)–C(6)	1.41(8)
Ir–P(2)	2.37(1)	C(6)–C(7)	1.35(6)
Ir–C(1)	1.56(10)	C(2)–N(3)	1.60(6)
Ir–N(1)	2.05(4)	N(3)–O(2)	1.22(6)
C(1)–O(1)	1.36(10)	N(3)–O(3)	1.18(6)
N(1)–N(2)	1.19(4)		
N(2)–C(7)	1.47(5)	Mean P–C(Ph)	1.82(2)
C(7)–C(2)	1.33(6)	Mean C–C(PPh_3)	1.39(2)
C(2)–C(3)	1.41(7)		

(*b*) Bond angles (°)

Cl(1)–Ir–Cl(2)	94.3(4)	Ir–N(1)–N(2)	115(3)
Cl(1)–Ir–P(1)	87.4(4)	N(1)–N(2)–C(7)	115(3)
Cl(1)–Ir–P(2)	87.4(4)	N(2)–C(7)–C(2)	120(4)
Cl(1)–Ir–C(1)	169(3)	N(2)–C(7)–C(6)	124(4)
Cl(1)–Ir–N(1)	86.8(9)	C(2)–C(7)–C(6)	115(4)
Cl(2)–Ir–P(1)	91.3(4)	C(7)–C(2)–C(3)	129(4)
Cl(2)–Ir–P(2)	88.1(4)	C(7)–C(2)–N(3)	117(4)
Cl(2)–Ir–C(1)	75(3)	C(3)–C(2)–N(3)	114(4)
Cl(2)–Ir–N(1)	174.4(9)	C(2)–N(3)–O(2)	113(4)
P(1)–Ir–P(2)	174.6(4)	C(2)–N(3)–O(3)	117(4)
P(1)–Ir–C(1)	91(3)	O(2)–N(3)–O(3)	129(5)
P(1)–Ir–N(1)	94.3(9)	C(2)–C(3)–C(4)	110(4)
P(2)–Ir–C(1)	94(3)	C(3)–C(4)–C(5)	126(5)
P(2)–Ir–N(1)	86.4(9)	C(4)–C(5)–C(6)	118(5)
C(1)–Ir–N(1)	104(3)	C(5)–C(6)–C(7)	122(4)
Ir–C(1)–O(1)	154(7)		

TABLE 3

Comparison of selected bond distances (Å) and angles (°) for doubly-bent aryldiazenato-complexes from *X*-ray structure determinations

Complex	M–N	M–Cl(*trans*)	M–Cl(*cis*)	N–N	N–C(Ph)	M–N–N	N–N–C
$[IrCl_2(o\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2]$ [a]	2.05(4)	2.48(1)	2.37(1)	1.19(4)	1.47(5)	115(3)	115(3)
$[RhCl(N_2Ph)(PhP\{(CH_2)_3PPh_2\}_2)]^+$ [b]	1.961(7)		2.403(2)	1.172(9)	1.445(11)	125.1(6)	118.9(8)
$[PtCl(p\text{-}N_2C_6H_4F)(PEt_3)_2]$ [c]	1.975(28)	2.413(6)		1.17(3)	1.49(3)	118(2)	118(2)

[a] This work. [b] Ref. 13. [c] Ref. 14.

Unfortunately a combination of relatively poor quality, small crystals and their decomposition during data collection has resulted in a data set of undesirably low quality. Consequently, although the general stereochemical questions have been settled, as a result of the large errors only limited information can be derived from the bond lengths and angles (Table 2). In particular, rather unrepresentative dimensions were obtained for the carbonyl group, which probably shows no significant deviation from linearity, nor possesses such short Ir–C, or long C–O bond lengths. The aryldiazenato-group does however, appear to be reasonably well behaved. This is only the third complex containing a doubly-bent aryldiazenato-ligand whose crystallographic structure has been reported, and is indeed the first for a six-coordinate metal. Previously, doubly-bent aryldiazenato-ligands in square pyramidal $[RhCl(N_2Ph)(PhP\{(CH_2)_3PPh_2\}_2)]^+$ (ref. 13) and in square planar $[PtCl(p\text{-}N_2C_6H_4F)(PEt_3)_2]$ (ref. 14) have been described, and some comparison of the dimensions in all three complexes can be made (Table 3). The doubly-bent ArN_2^- ligand appears to have a large *trans*-lengthening influence on the *trans*-chloride ligand, reflected in an Ir–Cl(2) distance of 2.48(1) Å *vs.* Ir–Cl(1) 2.37 (1) Å for the *cis*-chloride ligand, the latter value being in the range expected on the basis of literature values [15] for the single-bond radii of Ir^{III} and Cl. A rather long Pt–Cl bond *trans* to the ArN_2^- ligand [2.413(6) Å] was observed in the platinum complex, and of course the site *trans* to the ArN_2^- ligand in

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[13] A. P. Gaughan and J. A. Ibers, *Inorg. Chem.*, **1975**, **14**, 352.

[14] S. Krogsrud and J. A. Ibers, *Inorg. Chem.*, **1975**, **14**, 2298.

[15] M. R. Churchill, *Perspectives in Structural Chem.*, 1970, **3**, 91; see Appendix 1, p. 157.

the rhodium complex is unoccupied, and co-ordination of an additional Cl^- ligand is reported to be difficult.[16] The metal–N_2Ar dimensions in each complex appear to be remarkably similar and as expected. The N–N bonds in the platinum and rhodium compounds are possibly slightly shorter than the values for double bonds and the value reported here is not significantly different. In each case the geometry about the N–N bond is *trans*, and the dihedral angle between the planes defined by the *o*-nitrophenyl ring and by N(1), N(2), C(7) is 6° which may be compared with corresponding angles of 12° in the platinum complex and *ca.* 10° in the rhodium complex. The plane of the nitro-group makes an angle of 50° with the plane of the phenyl group (*cf.* only 14° in *p*-nitrobenzoic acid) which can be ascribed to the steric interference of O(3) with the nitrogen N(2) of the azo-group, the observed contact being 2.82 Å.

The pattern of aromatic CH out-of-plane deformation frequencies in the region of 800 cm^{-1} in the i.r. spectra of aryldiazenato-complexes is frequently helpful in distinguishing the *N*-bonded ligand from the orthometallated (*N, C*-bonded) ligand which we have previously found to arise under certain situations in diazonium ion co-ordination chemistry. The pattern of these i.r. absorption bands in the six-co-ordinate aryldiazenato-complexes and its similarity with that of the diazonium salt itself clearly suggests the presence of the simple (not orthometallated) ligand in all these compounds, as expected from the *X*-ray structure results. This is most readily seen for the *para*-substituted ligands where a single band at *ca.* 835 cm^{-1} is present, typical of the 1,4-substituted aromatic nucleus, whereas the expected 1,2,4-substituted pattern of two bands at *ca.* 830 and 880 cm^{-1} is typically seen when these ligands are orthometallated.[17]

These aryldiazenato-complexes may be converted into the corresponding aryldiazene complexes by protonation with HBF_4, and the reaction reversed with Et_3N [equation (2)].

$$[IrCl_2(p\text{-}N_2C_6H_4F)(CO)(PPh_3)_2] \underset{Et_3N}{\overset{H[BF_4]}{\rightleftharpoons}} [IrCl_2(p\text{-}HNNC_6H_4F)(CO)(PPh_3)_2][BF_4] \quad (2)$$

Although the doubly-bent aryldiazenato ligand possesses a lone pair on both nitrogen atoms, there is crystallographic [18,19] and n.m.r.[19-21] precedence for N(1) being the site of protonation, as suggested by this atom's formal negative charge in the principal valence-bond structure for the ArN_2^- ligand. We presume that this is also the protonated nitrogen atom in these compounds. In $[IrCl_2(p\text{-}HNNC_6H_4F)(CO)(PPh_3)_2][BF_4]$ for example, the i.r. spectrum shows, in addition to typical $\nu(BF_4^-)$ absorptions, a medium intensity band near 3 100 cm^{-1} which is removed on treatment with base, and is assigned to ν(NH). Significantly, ν(CO) is at 2 090 cm^{-1} *vs.* 2 055 cm^{-1} for the diazenato-complex. We were unable to record the ^1H n.m.r. spectrum for lack of a suitable solvent. Attempts to dissolve the diazene complex in methanol, ethanol, or acetonitrile in each case resulted in reconversion into the diazenato-complex, whereas acetone and chloroform both induced more general decomposition, and the formation of some free diazonium ion [ν(NN) 2 280 cm^{-1} in i.r.]. In fact the diazene complex could only be recovered unchanged from liquids in which it is insoluble (*e.g.* diethyl ether, benzene, water).

Cationic Complexes $[\{IrCl(N_2Ar)(CO)(PPh_3)_2\}_n][BF_4]_n$.—Attempts to obtain reproducible samples of these complexes by reactions at room temperature were quite unsuccessful, and it now seems clear that unless conditions are carefully controlled the products are contaminated with impurities which include σ-aryl compounds, thereby frequently generating low nitrogen analyses. By carrying out reactions of various diazonium salts with $[IrCl(CO)(PPh_3)_2]$ quickly at −25 °C a range of analytically pure and reproducible samples have been obtained (Table 1). The phenyldiazenato-complex has previously been referred to briefly, without preparative details.[11]

Some time ago, Ibers and co-workers [6] synthesized $[IrCl(NO)(CO)(PPh_3)_2][BF_4]$ from NO^+ and $[IrCl(CO)(PPh_3)_2]$ and showed it to contain the square-pyramidal cation, incorporating an apical bent (NO^-) ligand. By analogy therefore, it is possible to assume that in these syntheses ArN_2^+ reacts similarly to yield structurally analogous aryldiazenato-complexes. However, we have no structural evidence on which to base an assumption that the cation is truly five-co-ordinate (still less square-pyramidal), and for this reason we prefer to formulate these cationic complexes as $[\{IrCl(CO)(N_2Ar)(PPh_3)_2\}_n][BF_4]_n$, implying for example, were $n = 2$, that the cation could be a chlorine-bridged dimer. This is not entirely without good reason. The i.r. spectra of the molecular six-co-ordinate complexes clearly show bands attributable to ν(IrCl) in the range expected {*cf.* $[IrCl_2(N_2C_6H_5)(CO)(PMe_2Ph)_2]$ (ref. 10) where ν(IrCl) occurs at 311 and 248 cm^{-1}}. The high-frequency band is assigned to ν(IrCl) for the chlorine *trans* to CO and the low value of ν(IrCl) for the chlorine *trans* to ArN_2^- further reflects the *trans*-influence of the aryldiazenato-ligand. However, although ν(IrCl) for $[IrCl(NO)(CO)(PPh_3)_2]^+$ occurs at 335 cm^{-1}, for the cationic complexes we find only broad bands at 280 cm^{-1} for $[\{IrCl(p\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2\}_n][BF_4]_n$ and 270 cm^{-1} for $[\{IrCl(N_2C_6H_5)(CO)(PPh_3)_2\}_n][BF_4]_n$, which must be assigned to iridium–chlorine stretches since they do not occur for the corresponding bromide complex. This is quite consistent with the presence of bridging chloride ligands but would be difficult to confirm except by *X*-ray analysis, since dissociation to monomeric solvated species would probably occur for such a species in solution, obviating conductivity and molecular weight determinations. In any case we feel that solutions are too unstable for the necessary experimental accuracy required.

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[19] B. L. Haymore and J. A. Ibers, *J. Amer. Chem. Soc.*, 1975, **97**, 5369.

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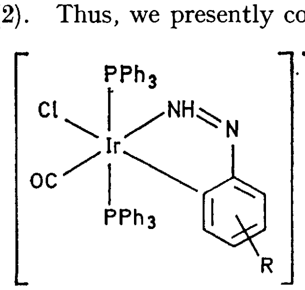
These complexes are soluble in acetone, dichloromethane, and chloroform but insoluble in benzene, hexane, and diethyl ether. They are not very stable to decomposition at room temperature, but have been kept for some months at −14 °C without appreciable decomposition. This stability is greatest with the fluoro- (especially 2,6-difluoro-) and nitrophenyl-derivatives. The ease of synthesis and yield also relates to the substituent, being greatest for the aforementioned, and negligible for *p*-NEt_2, *p*-OMe, and 2,6-dimethyl. This is an expected trend if the diazonium salt is behaving as an electrophile in the reaction. The phenyl- and fluorophenyl-diazenato-complexes appear to decompose rapidly at room temperature in solution or even on contact with liquids in which they do not dissolve. The nitro-substituted compounds are considerably more stable and may be handled in solution for some hours, or recrystallized from acetone. An interesting example of the instability of these cationic complexes was observed when we attempted to synthesize them by metathesis of the six-co-ordinate $[IrCl_2(N_2Ar)(CO)(PPh_3)_2]$ complexes with $AgBF_4$ in 1 : 1 molar ratio in benzene solution according to reaction (3). In all cases AgCl was formed quantitatively, but in no case were we able successfully to isolate the cationic complex; instead virtually quantitative decomposition had occurred to give the diazonium salt and Vaska's complex.

$$[IrCl_2(N_2Ar)(CO)(PPh_3)_2] + AgBF_4 \nrightarrow AgCl + [\{IrCl(N_2Ar)(CO)(PPh_3)_2\}_n][BF_4]_n \quad (3)$$

Similar results occurred for a wide range of substituents, including *p*-F, *p*-Br, *p*-OMe, *o*-F, and *m*-NO_2. In the case of $[\{IrCl(p\text{-}N_2C_6H_4F)(CO)(PPh_3)_2\}_n][BF_4]_n$ a separate experiment showed that this pure, solid complex, when stirred with benzene under nitrogen decomposed to the diazonium salt and Vaska's complex within 3 min at room temperature. Our experience with these compounds indicates that, depending on the circumstances, decomposition may also involve extrusion of dinitrogen. However, in no case do we have evidence for the formation of the cationic orthometallated aryldiazene isomers (2) of these cationic complexes (described elsewhere [9,17]) except when the solvent includes ethanol or propan-2-ol; these solvents are known to be participants in the synthesis of (2). Thus, we presently conclude that the formation of the isomeric orthometallated aryldiazene species is not, in general, a simply accessible decomposition route for these cationic complexes, and that they do not rearrange to the orthometallated species by a simple mechanism such as proton transfer. This matter will be dealt with more fully in a subsequent paper.[17]



(2)

We have not yet been able to establish the structures of these cationic complexes crystallographically owing to the low stability of the crystallizing solutions, and the poor quality of crystals so far obtained, but the i.r. spectra show some important differences from those of the corresponding orthometallated compounds, which support the presence of the simple (not orthometallated) aryldiazenato-ligand. In general, with some familiarity with these compounds, it is possible to distinguish simple aryldiazenato-ligands from orthometallated aryldiazenato- or aryldiazene ligands. Absorption due to ν(NH) which is so clearly seen at *ca.* 3 150 cm^{-1} in the orthometallated aryldiazene complexes is absent here, and the pattern of the out-of-plane aromatic CH bending is quite different, but similar to that already discussed for the six-co-ordinate complexes. The ready dissociation to give the free diazonium ion is also quite inconsistent with orthometallation. Thus it seems quite certain that these cationic complexes are aryldiazenato-complexes of the type described, but a more exact indication of their stereochemistry and structure will have to await future developments.

EXPERIMENTAL

All solvents were dried by usual methods and distilled under dry nitrogen. All reactions and manipulations were carried out under dry argon or nitrogen. The initial iridium complexes were prepared by published procedures, and $[IrX(CO)(PPh_3)_2]$ prepared by metathesis of a suitable salt of X^- with $[IrCl(CO)(PPh_3)_2]$. Aryldiazonium salts were recrystallized from acetone–diethyl ether.

I.r. spectra were recorded by use of Perkin-Elmer 457 and Beckman IR 12 instruments, using samples pressed in KBr discs. Far-i.r. spectra were recorded as Nujol mulls between Polythene discs. M.p.s were recorded on a Fisher–Johns apparatus.

$[IrCl_2(N_2Ar)(CO)(PPh_3)_2]$.—In a typical preparation of $[IrCl_2(N_2Ph)(CO)(PPh_3)_2]$, a solution of benzenediazonium tetrafluoroborate (0.019 g, 0.1 mmol) in cold acetone (3 ml) containing excess of LiCl was added to a suspension of $[IrCl(CO)(PPh_3)_2]$ (0.078 g, 0.1 mmol) in acetone (2 ml). The complex immediately dissolved to give an orange solution, which on continued stirring precipitated the orange product. This was washed with cold acetone and hexane and recrystallized from cold benzene–acetone as the acetone solvate (68%). When recrystallized from benzene–hexane this complex gave the benzene adduct (Found: C, 58.5; H, 4.6; N, 2.8. Calc. for $C_{49}H_{41}Cl_2IrN_2OP_2$: C, 58.9; H, 4.2; N, 2.8%). In certain cases, such as the *o*-NO_2, *p*-NO_2, and *o,o*-diF derivatives syntheses were best carried out at −25 °C, and sometimes the LiCl was added after the ***in situ*** formation of $[\{IrCl(N_2Ar)(CO)(PPh_3)_2\}_n][BF_4]_n$ at this temperature, in order to obtain uncontaminated precipitates. In addition to the compounds listed in Table 1, $[IrBr_2(p\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2]$ and $[IrCl_2(o\text{-}N_2C_6H_4NO_2)(CO)(PPh_2Me)_2]$ were synthesized similarly.

$[IrCl_2(p\text{-}HNNC_6H_4F)(CO)(PPh_3)_2][BF_4]$.— $[IrCl_2(p\text{-}N_2C_6H_4F)(CO)(PPh_3)_2]$ (0.235 g, 0.25 mmol) was suspended with stirring in diethyl ether (10 ml) under argon, and 48% aqueous HBF_4 (0.1 ml) added. After stirring for 1 h, the resultant pale yellow precipitate was washed with diethyl ether containing a small amount of ethanol and dried *in vacuo* (0.205 g, 80%) (Found: C, 50.8; H, 3.4; N, 2.8. Calc. for $C_{43}H_{35}BCl_2F_5IrN_2OP_2$: C, 50.5; H, 3.1; N, 2.7%). A stirred suspension of this product (0.020 g) in diethyl ether on treatment with Et_3N (0.02 ml) reverted to a suspension of the original diazenato-complex, identified by i.r. spectroscopy and elemental analysis.

$[\{IrCl(N_2Ar)(CO)(PPh_3)_2\}_n][BF_4]_n$.—Acetone (2 ml) at −25 °C was added to a well-ground mixture of $[IrCl(CO)(PPh_3)_2]$ (0.192 g, 0.25 mmol) and $[p\text{-}FC_6H_4N_2][BF_4]$ (0.052 g, 0.25 mmol) also at −25 °C under N_2. The orange solution was stirred until all the Vaska's complex had dissolved (5 min) and hexane (1.5 ml) was added. Further stirring at −25 °C precipitated the pale yellow product (0.187 g, 77%) which was filtered off, washed with cold hexane (15 ml), dried *in vacuo*, and stored under nitrogen at −14 °C. The 2,6-difluorophenyldiazenato-complex was best prepared at −40 °C.

Decomposition of $[\{IrCl(p\text{-}N_2C_6H_4F)(CO)(PPh_3)_2\}_n][BF_4]_n$ *in Benzene*.—The complex (40 mg) was stirred with benzene (10 ml) at room temperature for 3 min under N_2. The white insoluble solid which formed was washed with benzene, dried *in vacuo*, and shown to be $p\text{-}FC_6H_4N_2BF_4$ (75%) by i.r. spectroscopy. The yellow benzene filtrate was freeze-dried to a yellow solid (31 mg), and shown (i.r.) to be slightly impure $[IrCl(CO)(PPh_3)_2]$.

Reaction of $[\{IrCl(o\text{-}N_2C_6H_4F)(CO)(PPh_3)_2\}_n][BF_4]_n$ *with* LiCl.—The solid complex (26 mg) under argon at −25 °C was treated with 0.05-M LiCl (2 ml) in acetone at −25 °C and stirred. Dissolution occurred immediately, followed by precipitation of the orange $[IrCl_2(o\text{-}N_2C_6H_4F)(CO)(PPh_3)_2]$ which was washed quickly with cold acetone (some product dissolved) and dried *in vacuo*.

Reaction of $[IrCl_2(p\text{-}N_2C_6H_4F)(CO)(PPh_3)_2]$ *with* $Ag[BF_4]$.—The complex (0.03 mmol) was dissolved in benzene (5 ml) at room temperature under argon. The reaction vessel was protected from light by aluminium foil. $AgBF_4$ (0.03 mmol) was added to the yellow solution and stirred for 15 min. The resulting suspension was centrifuged to give a white solid and a yellow solution. The benzene solution was freeze-dried to give a yellow solid identified as $[IrCl(CO)(PPh_3)_2]$. The white solid was stirred with acetone resulting in a white insoluble solid (AgCl, 75—100%) and a solution from which $p\text{-}FC_6H_4N_2BF_4$ was precipitated with diethyl ether and identified by i.r.

X-*Ray Structure Analysis of* $[IrCl_2(o\text{-}N_2C_6H_4NO_2)(CO)(PPh_3)_2]\cdot 2Me_2CO$.—Preliminary oscillation and Weissenberg photographs showed the crystals to be triclinic. Accurate cell dimensions were obtained by least-squares analysis of 12 accurately centered reflections in the range 2θ 25—35°, using a Picker FACS 1 automatic diffractometer and Mo-K_α radiation (λ 0.709 26 Å). Crystals decomposed in the *X*-ray beam, one crystal of dimensions *ca.* 0.3 × 0.3 × 0.3 mm being used for the cell dimensions, and four similar sized ones for the data collection, by use of Nb-filtered Mo-K_α radiation and a scintillation counter with pulse-height discrimination. A θ—2θ scan was used, of basewidth 1.5° (with allowance for dispersion) at a scan rate of 2° min^{-1} in 2θ, and take-off angle of 3.5°. Background counts of 20 s were taken at either side of the reflection. Two standard reflections were measured at frequent intervals to monitor the decomposition and to scale the data for the four separate crystals. A total of 1 877 unique reflection intensities in the range $2\theta \leqslant 35°$ were measured, of which 1 616 were considered observed, having $I > 2.3\sigma(I)$ {where $\sigma^2(I)$ = [Scan count + $(t_s/t_b)^2$ background count + $(0.03I)^2$] and t_s, t_b are the scan and background times} and were classed as observed. Intensities were corrected for Lorentz and polarization effects, but not for absorption.

TABLE 4

Final atomic parameters: atomic fractional co-ordinates, with estimated standard deviations in parentheses, ×10⁵ for iridium, ×10⁴ for phosphorus and chlorine, and ×10³ for the carbon, nitrogen, and oxygen

	x	*y*	*z*	10³-*U*/Å²
Ir	34 560(16)	16 987(14)	25 556(17)	*
P(1)	4 045(11)	3 208(8)	2 131(10)	36(4)
P(2)	2 780(10)	154(8)	2 823(9)	23(4)
Cl(1)	2 866(11)	1 270(8)	775(10)	57(4)
Cl(2)	1 592(9)	1 908(7)	3 161(9)	37(4)
N(1)	495(3)	141(2)	212(2)	19(10)
N(2)	573(3)	173(2)	271(2)	19(10)
N(3)	763(4)	258(3)	401(3)	70(14)
O(1)	427(3)	230(2)	466(3)	83(12)
O(2)	825(4)	334(3)	417(4)	144(17)
O(3)	702(3)	215(3)	460(3)	112(14)
O(4)	31(5)	552(3)	182(4)	162(20)
O(5)	224(6)	363(5)	680(6)	244(35)
C(1)	363(7)	203(5)	376(8)	164(31)
C(2)	778(4)	208(3)	286(3)	31(13)
C(3)	892(4)	210(3)	262(4)	52(15)
C(4)	897(5)	167(3)	160(4)	69(17)
C(5)	810(5)	122(3)	100(4)	68(17)
C(6)	701(4)	125(3)	136(4)	53(15)
C(7)	684(3)	163(2)	233(3)	8(12)
C(8)	404(3)	414(3)	307(3)	24(13)
C(9)	342(3)	399(3)	402(3)	33(14)
C(10)	337(4)	477(3)	474(3)	41(14)
C(11)	394(4)	562(3)	452(4)	49(15)
C(12)	456(4)	575(3)	359(4)	72(18)
C(13)	461(4)	501(3)	288(3)	43(15)
C(14)	549(4)	339(3)	162(3)	34(14)
C(15)	564(4)	297(3)	64(4)	53(16)
C(16)	674(5)	310(3)	31(4)	72(17)
C(17)	765(4)	365(3)	86(4)	64(17)
C(18)	748(4)	403(3)	184(4)	58(16)
C(19)	637(4)	397(3)	228(4)	63(16)
C(20)	324(4)	351(3)	102(4)	40(14)
C(21)	377(5)	393(4)	24(5)	104(21)
C(22)	299(6)	416(4)	−41(5)	119(24)
C(23)	182(5)	406(4)	−21(5)	92(20)
C(24)	143(4)	363(3)	62(4)	68(17)
C(25)	211(4)	338(3)	131(4)	50(15)
C(26)	245(3)	2(2)	412(3)	17(12)
C(27)	324(4)	19(3)	495(4)	60(16)
C(28)	311(5)	10(3)	599(4)	76(18)
C(29)	200(5)	−19(3)	629(4)	75(18)
C(30)	113(4)	−44(3)	558(5)	73(18)
C(31)	137(4)	−34(3)	449(4)	56(16)
C(32)	154(4)	−52(3)	207(3)	34(14)
C(33)	131(4)	−143(3)	195(4)	53(15)
C(34)	31(4)	−196(3)	140(4)	59(16)
C(35)	−46(4)	−154(3)	103(4)	54(15)
C(36)	−29(4)	−63(4)	115(4)	64(16)
C(37)	71(4)	−10(3)	171(3)	40(14)
C(38)	380(3)	−56(3)	255(3)	17(12)
C(39)	394(4)	−121(3)	311(3)	44(14)
C(40)	462(4)	−174(3)	278(4)	54(16)
C(41)	514(4)	−158(3)	183(4)	37(14)
C(42)	505(4)	−106(4)	117(4)	74(18)
C(43)	431(3)	−49(3)	152(3)	30(13)
C(44)	174(10)	299(9)	648(9)	227(51)
C(45)	71(8)	296(5)	587(7)	179(34)
C(46)	188(7)	217(7)	646(7)	191(37)
C(47)	10(7)	550(5)	250(6)	133(27)
C(48)	210(6)	622(5)	243(5)	142(26)
C(49)	73(5)	489(4)	325(5)	115(22)

* Anisotropic thermal parameters, U_{ij} for the expression $\exp[-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2a^*b^*hkU_{12} + 2b^*c^*klU_{23} + 2a^*c^*hlU_{13}]$ for iridium are $(\text{Å}^2 \times 10^4)$: U_{11} 49(15), U_{22} 354(17), U_{33} 280(19), U_{12} 75(15), U_{23} −43(15), U_{13} −118(15).

Crystal Data.—$C_{43}H_{34}Cl_2IrN_3O_3P_2\cdot2(CH_3)_2CO$, Triclinic, $M = 1\,082.0$, $a = 12.202(7)$, $b = 15.441(8)$, $c = 12.762(6)$ Å, $\alpha = 96.41(3)$, $\beta = 89.01(3)$, $\gamma = 105.09(3)°$, $U = 2\,306.7$ Å^3, $D_m = 1.55(1)$, $Z = 2$, $D_c = 1.558$ g cm^{-3}. Space group $P\bar{1}$. μ(Mo-K_α) = 33.1 cm^{-1}.

The space group was assumed to be the centrosymmetric $P\bar{1}$ and the choice was confirmed by the structure refinement. The iridium, chlorine, and phosphorus atomic positions were determined from the unsharpened Patterson function and the remaining non-hydrogen atoms of the molecule together with those of two molecules of solvent of crystallization (acetone) were found in subsequent electron-density difference maps. Refinement of the positional and isotropic temperature factors for all atoms by the method of full-matrix least squares (minimizing the function $\Sigma w(|F_o| - |F_c|)^2$) gave R 0.128. An electron-density difference synthesis indicated anisotropic thermal motion of iridium, and inclusion of anisotropic coefficients for this atom in refinement reduced R to 0.100.

At this stage a number of aromatic hydrogen atom positions appeared in an electron-density difference map, so positions were calculated for all hydrogen atoms, and these were included as fixed contributions in structure-factor calculations. Further refinement reduced R to 0.089. A final difference map indicated peaks in the vicinity of phosphorus and chlorine atoms as the major contributions. Attempts to refine anisotropic thermal parameters for these atoms gave unreasonable results and refinement was terminated at this point. Final positional and thermal parameters are listed in Table 4. Atomic scattering and anomalous dispersion factors used were taken from ref. 22, and hydrogen-atom scattering factors from ref. 23. In the latter stages of refinement weights w based on counting statistics were used ($w = 1/\sigma(F^2)$). Final observed and calculated structure factors are listed in Supplementary Publication No. 21906 (16 pp., 1 microfiche).* Programs used are listed in ref. 24.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

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