Reactivity of the Iridium Nitrosyl Complex $[Ir(NO)(paa)(PPh_3)_2][PF_6]_2$ (paa = 2-Pyridinecarbaldehyde Azine) with Nucleophiles: Insertion of NO into a Methinic C–H Bond; Crystal Structure of $[Ir\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(2\text{-}C_5H_4N)\}\{Me(EtO)C{=}NH\}(PPh_3)_2][PF_6]_2$*

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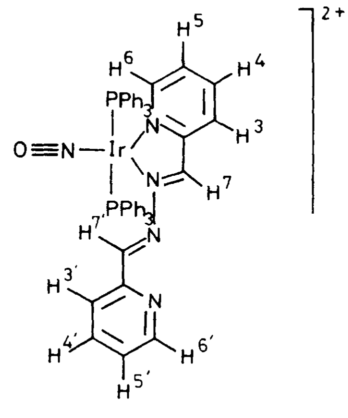
The nitrosyl complex $[Ir(NO)(paa)(PPh_3)_2][PF_6]_2$ (paa = 2-pyridinecarbaldehyde azine) reacts either with RCN (R = Me, Ph, or Ph_2CH) or X^- (X = Cl or SCN) at room temperature, to give cyclometallated compounds containing the $\underbrace{\mathrm{Ir{-}\overset{\|}{N}{-}N{=}\overset{|}{C}{-}N}}\mathrm{(OH)}$ moiety. These complexes were characterised by elemental analysis, conductivity measurements, i.r. and n.m.r. spectroscopy. The metallated ring can be envisaged as resulting from intramolecular insertion of the NO group, activated by the iridium co-ordination of RCN or X^-, into the methinic C–H bond of the unco-ordinated paa fragment. Addition of ethanol to the compound containing MeCN or PhCN gives imidate complexes. The structure of the acetoimidate complex $[Ir\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(2\text{-}C_5H_4N)\}\{Me(EtO)C{=}NH\}(PPh_3)_2][PF_6]_2$ has been determined by *X*-ray diffraction. Crystals are monoclinic, space group *Cc*, with unit-cell dimensions a = 12.405(6), b = 43.836(12), c = 11.126(7) Å, β = 112.1(2)°, and Z = 4. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by block-matrix least squares to final R and R' values of 0.057 and 0.073 for 3 394 observed reflections. In the cation four N atoms, one from the neutral ethylacetoimidate ligand and the other three from the monoanionic ligand resulting by intramolecular insertion of NO into a methinic C–H bond of the starting paa ligand, are arranged in the equatorial positions of the iridium co-ordination octahedron whose apices are occupied by P atoms from PPh_3 molecules. The new $\mathrm{{=}\overset{|}{C}{-}\overset{|}{\underline{N}}OH}$ fragment displays a C–N bond length of 1.37(3) Å and the OH group is involved in a strong intramolecular hydrogen bond with the unco-ordinated pyridyl nitrogen atom.

The synthesis from NO of nitrogen-containing organic molecules is among the purposes of many recent investigations on the chemistry of transition-metal nitrosyl complexes. In these studies, of relevance is the carbon–nitrogen bond formation through NO migration from the metal to the organic moiety, a critical step in the whole process.

The reactivity of the ligand NO is strongly affected by its co-ordination mode. Thus, it can behave either as an electrophile, when linear NO^+, or as a nucleophile when bent NO^-.[1] Briefly, some examples recently reported in the literature concerning significant progress in this chemistry are: (*i*) nucleophilic attack on benzyl bromide by a co-ordinated NO group of $[Ru(NO)_2(PPh_3)_2]$;[2] (*ii*) migratory insertion of NO into cobalt– or ruthenium–carbon bonds;[3] (*iii*) insertion of NO^+ into a cobalt cluster–carbon bond;[4] (*iv*) insertion of NO^+ into a carbon–hydrogen bond of the Me group contained in $[Cr(\eta^5\text{-}C_5H_5)(NO)_2Me]$.[5]

We describe here a further example of C–N bond formation. This reaction arises from a nucleophile-promoted migratory insertion of co-ordinated NO into a methinic C–H bond. The starting complex is a derivative of 2-pyridinecarbaldehyde azine (paa), $[Ir(NO)(paa)(PPh_3)_2][PF_6]_2$ (**1**), whose synthesis and characterisation have been previously reported.[6] In this cation the co-ordination of Ir, as deduced by spectroscopic investigations, is trigonal bipyramidal with two equivalent PPh_3 molecules in apical positions and the NO group, ν(NO) 1 800 cm^{-1}, linearly bound to the iridium centre, in the plane of the paa ligand which forms a five-membered chelate ring. The nucleophilic reagents reacting with (**1**) are nitriles and the anions Cl^- or SCN^-. A preliminary account of this work has been given.[7]



(**1**)

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* (1-Ethoxyethanimine-*N*)(α-hydroxyamino-2-pyridinecarbaldehyde azinato)bis(triphenylphosphine)iridium(III) bis(hexafluorophosphate).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Proton n.m.r. assignments (δ)*

Compound	Chemical shifts	Coupling constants
(**2**)	H^{6}, 8.24; H^{5}, 6.89 H^{4}, 7.20; H^{3}, 6.65	$J(H^{6}H^{5}) = 5.0$; $J(H^{5}H^{4}) = J(H^{4}H^{3}) = 7.8$
	$H^{6'}$, 8.33; $H^{5'}$, n.o. $H^{4'}$, 7.77; $H^{3'}$, 7.25	$J(H^{6'}H^{5'}) = 5.0$, $J(H^{6'}H^{4'}) = 1.7$, $J(H^{6'}H^{3'}) = 1.0$, $J(H^{5'}H^{4'}) = 7.8$, $J(H^{5'}H^{3'}) = 1.0$, $J(H^{4'}H^{3'}) = 8.0$
	H^{7}, 7.05	$^{4}J(PH) = 3.1$
	MeCN, 2.26	
(**3**)	H^{6}, 8.47; H^{5}, 7.03 H^{4}, 7.21; H^{3}, 6.59	$J(H^{6}H^{5}) = 5.0$, $J(H^{6}H^{4}) = 1.3$, $J(H^{5}H^{3}) = 1.5$, $J(H^{5}H^{4}) = J(H^{4}H^{3}) = 8.0$
	$H^{6'}$, 8.36; $H^{5'}$, n.o. $H^{4'}$, 7.80; $H^{3'}$, n.o.	$J(H^{6'}H^{5'}) = 5.0$; $J(H^{6'}H^{4'}) = 1.7$, $J(H^{6'}H^{3'}) = 0.9$, $J(H^{5'}H^{4'}) = J(H^{4'}H^{3'}) = 8.0$
	H^{7}, 6.99	
	MeCN, 2.20	
(**4**)	H^{6}, 8.32; H^{5}, 6.96 H^{4}, 7.22; H^{3}, 6.68	$J(H^{6}H^{5}) = 5.0$—6.0, $J(H^{5}H^{4}) = 7.8$, $J(H^{5}H^{3}) = 1.3$, $J(H^{4}H^{3}) = 8.0$
	$H^{6'}$, 8.33; $H^{5'}$, n.o. $H^{4'}$, 7.79; $H^{3'}$, 7.29	$J(H^{6'}H^{5'}) = 4.9$, $J(H^{6'}H^{4'}) = 1.6$, $J(H^{6'}H^{3'}) = 0.9$, $J(H^{5'}H^{4'}) = 7.9$, $J(H^{4'}H^{3'}) = 8.0$
	H^{7}, 7.09	$^{4}J(PH) = 3.2$
	PhCN, 7.75 (1 H), 7.01 (2 H)	
(**5**)	H^{6}, 8.25; H^{5}, 6.95 H^{4}, n.o.; H^{3}, 6.58	$J(H^{6}H^{5}) = 5.6$, $J(H^{4}H^{3}) = 7.9$
	$H^{6'}$, 8.35; $H^{5'}$, n.o. $H^{4'}$, 7.80; $H^{3'}$, n.o.	$J(H^{6'}H^{5'}) = 5.0$, $J(H^{6'}H^{4'}) = 1.7$, $J(H^{6'}H^{3'}) = 0.9$, $J(H^{5'}H^{4'}) = J(H^{4'}H^{3'}) = 7.9$
	H^{7}, 6.95	
	$Ph_2C\mathit{H}CN$, 5.84	
	Ph_2CHCN, 7.08 (4 H)	
(**6**)	H^{6}, 7.52; H^{5}, 6.31 H^{4}, 7.20; H^{3}, 6.86	$J(H^{6}H^{5}) = 5.8$, $J(H^{5}H^{4}) = 7.4$, $J(H^{5}H^{3}) = 1.2$, $J(H^{4}H^{3}) = 8.0$
	$H^{6'}$, 8.37; $H^{5'}$, n.o. $H^{4'}$, 7.71; $H^{3'}$, 7.00	$J(H^{6'}H^{5'}) = 5.0$, $J(H^{6'}H^{4'}) = 1.7$, $J(H^{6'}H^{3'}) = 0.9$, $J(H^{5'}H^{4'}) = 7.3$, $J(H^{4'}H^{3'}) = 8.0$
	H^{7}, 6.81	$^{4}J(PH) = 2.6$
(**7**)	H^{6}, 7.02; H^{5}, 6.31 H^{4}, 7.26; H^{3}, 6.93	$J(H^{6}H^{5}) = 5.8$, $J(H^{5}H^{4}) = 7.5$, $J(H^{5}H^{3}) = 1.2$, $J(H^{4}H^{3}) = 8.0$
	$H^{6'}$, 8.32; $H^{5'}$, n.o. $H^{4'}$, 7.72; $H^{3'}$, 7.07	$J(H^{6'}H^{5'}) = 5.0$, $J(H^{6'}H^{4'}) = 1.7$, $J(H^{5'}H^{4'}) = J(H^{4'}H^{3'}) = 7.9$
	H^{7}, 6.95	$^{4}J(PH) = 2.7$
(**8**)	H^{6}, 8.67; H^{5}, 6.92 H^{4}, 7.19; H^{3}, 6.67	$J(H^{6}H^{5}) = 5.5$, $J(H^{5}H^{4}) = 7.9$, $J(H^{4}H^{3}) = 7.9$
	$H^{6'}$, 8.32; $H^{5'}$, n.o. $H^{4'}$, 7.77; $H^{3'}$, 7.26	$J(H^{6'}H^{5'}) = 5.0$, $J(H^{6'}H^{4'}) = 1.7$, $J(H^{6'}H^{3'}) = 0.8$, $J(H^{5'}H^{4'}) = J(H^{4'}H^{3'}) = 8.0$
	H^{7}, 7.10	$^{4}J(PH) = 3.2$
	$\mathit{Me}(CH_3CH_2O)CNH$, 2.35 $Me(C\mathit{H}_3CH_2O)CNH$, 1.20 $Me(CH_3C\mathit{H}_2O)CNH$, 3.65	$^{2}J(HH) = 7.1$
(**9**)	H^{6}, 9.31; H^{5}, 6.81 H^{4}, 7.10; H^{3}, 6.37	$J(H^{6}H^{5}) = 5.0$, $J(H^{5}H^{4}) = 7.5$, $J(H^{4}H^{3}) = 7.9$
	$H^{6'}$, 8.32; $H^{5'}$, n.o. $H^{4'}$, 7.73; $H^{3'}$, n.o.	$J(H^{6'}H^{5'}) = 5.4$, $J(H^{6'}H^{4'}) = 1.5$, $J(H^{5'}H^{4'}) = 7.8$, $J(H^{4'}H^{3'}) = 7.9$
	H^{7}, 7.00	$^{4}J(PH) = 2.5$
	$\mathit{Ph}(CH_3CH_2O)CNH$, 6.89 $Ph(C\mathit{H}_3CH_2O)CNH$, 1.20 $Ph(CH_3C\mathit{H}_2O)CNH$, 3.66	$^{2}J(HH) = 7.5$

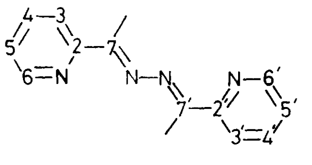
* The values (relative to $SiMe_4$) were obtained in CD_2Cl_2 solution. J values in Hz. The free-ligand values are given in ref. 6 (Table 1). n.o. = Not observed because superimposed on PPh_3 protons.

Table 2. Proton n.m.r. co-ordination shifts ($\Delta\delta$)*

Compound	H^6	H^5	H^4	H^3	$H^{6'}$	$H^{5'}$	$H^{4'}$	$H^{3'}$	H^7
(2)	−0.49	−0.48	−0.60	−1.48	−0.40	n.c.	−0.03	−0.88	−1.65
(3)	−0.26	−0.34	−0.59	−1.54	−0.37	n.c.	0.00	n.c.	−1.71
(4)	−0.41	−0.41	−0.58	−1.45	−0.40	n.c.	−0.01	−0.84	−1.61
(5)	−0.48	−0.48	n.c.	−1.55	−0.38	n.c.	0.00	n.c.	−1.76
(6)	−1.21	−1.06	−0.60	−1.27	−0.36	n.c.	−0.09	−1.13	−1.89
(7)	−1.71	−1.06	−0.54	−1.20	−0.41	n.c.	−0.08	−1.06	−1.75
(8)	−0.06	−0.45	−0.61	−1.46	−0.41	n.c.	−0.03	−0.87	−1.60
(9)	+0.58	−0.56	−0.70	−1.76	−0.41	n.c.	−0.07	n.c.	−1.70

* $\Delta\delta = \delta(\text{complex}) - \delta(\text{free})$, positive values being downfield shifts. n.c. = Not calculated because the relative signal was not assigned.

Table 3. Carbon-13 n.m.r. data (δ) for the free paa ligand and its nitrile complexes (**2**) and (**4**)[a]

	162.1($C^{7,7'}$)		150.0($C^{6,6'}$)		122.5($C^{5,5'}$)		136.6($C^{4,4'}$)		125.1($C^{3,3'}$)		152.9($C^{2,2'}$)	
(2)	164.57[b]	160.86[b]	154.93	145.83[b]	144.62	140.67	139.20	136.70[c]	127.36	126.31	126.26	123.44
(4)	164.58[b]	160.80[b]	155.18	145.84[b]	144.64	140.84	139.30	137.02[c]	127.43	126.65	126.26	123.60

[a] The values (p.p.m. relative to $SiMe_4$) were obtained in CD_2Cl_2 solution at 20 °C. For the PPh_3 and RCN signals see Experimental section. [b] Quaternary carbon. [c] This signal shows a triplet structure due to ^{31}P coupling [$^3J(PC)$ = 4—6 Hz].

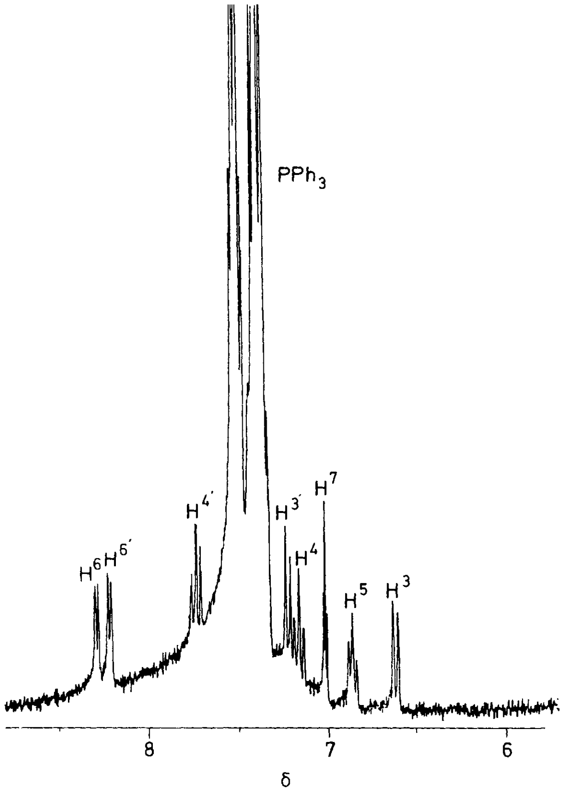


Figure 1. Proton n.m.r. spectrum (300 MHz) at 20 °C of complex (**2**) in the aromatic region

Results and Discussion

Reactions with Acetonitrile.—Complex (**1**) was prepared by reaction between the six-co-ordinated nitrosyl complex [$Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2$ and paa at room temperature with tetrahydrofuran (thf) as solvent.[6] The pale yellow compound (**1**) when dissolved in acetonitrile gives rise to a purple solution from which, after 12 h, a violet microcrystalline solid, compound (**2**), can be separated by addition of diethyl ether (95% yield).

The product (**2**) was characterised by elemental analysis, which accounts for a stoicheiometry [$Ir(NO)(MeCN)(paa)(PPh_3)_2][PF_6]_2$, conductivity measurements (is a 1:2 electrolyte in nitromethane[8]), and spectroscopic methods (data in Experimental section and Tables 1—3).

Interestingly the i.r. spectrum (KBr) shows two weak absorptions, at 2 325 and 2 300 cm^{-1}, attributable to a C≡N stretch, and a very low-frequency NO stretch at 1 354 cm^{-1}. The presence of two bands in the ν(CN) region at high frequency with respect to free acetonitrile is diagnostic of its end-on co-ordination,[9] while the NO stretching frequency is in agreement either with a nitrosoalkane ligand M–N(=O)–R[3a] or with a metal-bonded nitroxide group $M\text{–}\bar{N}(R)\text{–}O^{\bullet}$.[10]

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum displays a single resonance (δ −7.34 p.p.m.) indicating the equivalence of two mutually *trans* phosphines co-ordinated to an iridium(III) centre.[11,12] The ^1H n.m.r. spectrum of complex (**2**) is reported in Figure 1. The assignments of the paa ligand signals, performed as previously described,[6] and their shifts upon co-ordination are reported in Tables 1 and 2 respectively. Noteworthy, as far as the two N=CH protons present in free paa are concerned, is that only one of them is detectable. Such a proton, observed as a triplet in the spectral region free from PPh_3 protonic resonances, appears strongly shielded (Δδ 1.65) and coupled with the phosphorus nuclei with $^4J(PH)$ = 3.1 Hz; it is assigned to the N=CH moiety having the nitrogen atom co-ordinated to the metal.[6] The spectral multiplicity of this signal has been confirmed by comparison with the ^1H n.m.r. spectrum of the homologous arsino complex, (**3**) (see Experimental section and Tables 1 and 2), synthesised *ad hoc* for this experiment. Finally, the MeCN ligand displays the methyl signal slightly downfield with respect to its unco-ordinated situation.

The analysis of the ^{13}C-{^{1}H} n.m.r. spectrum (Figure 2) shows that the signals can be divided into three different sets, due to the PPh_3, the MeCN, and the paa respectively. The twelve distinct resonances forming the latter set (Table 3), compared with the spectral pattern of unco-ordinated paa, display some interesting features, namely: (*i*) in the low-field end of the spectrum (δ 165.0—145.0 p.p.m.), together with two expected signals at δ 164.57 and 160.86 p.p.m. tentatively assigned to C^2 and $C^{2'}$ respectively (δ 152.9 p.p.m. for free paa), a further resonance attributable to a quaternary carbon atom is present at δ 145.83 p.p.m., and (*ii*) the C^7 resonance, a triplet at δ 136.70 p.p.m. with $^{3}J(CP)$ = 4—6 Hz, is shifted significantly to highfield ($\Delta\delta \approx -35$).

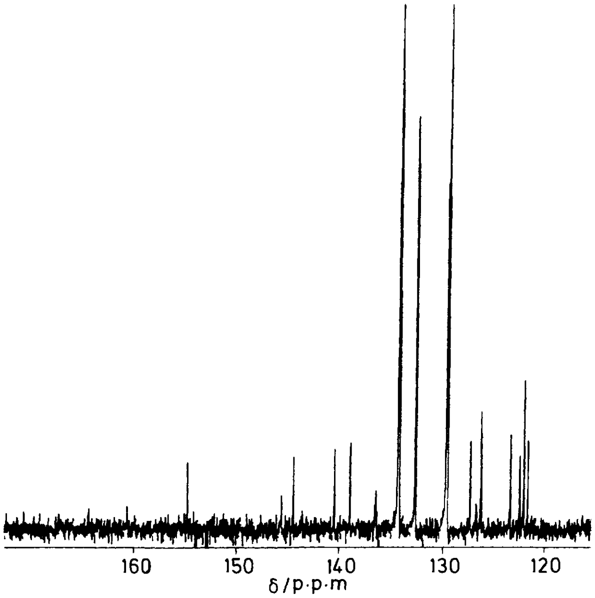


Figure 2. Low-field end of the ^{13}C-{^{1}H} n.m.r. spectrum (75 MHz) of complex (2) in CD_2Cl_2 solution

The ^{1}H and ^{13}C-{^{1}H} n.m.r. data permit the assignments of the third quaternary carbon atom present in the skeleton of the complexed paa ligand. The ^{1}H spectrum shows no structural changes in both the pyridyl rings and in the co-ordinated $-N=C^7-H$ moiety, hence in complex (**2**), where the second N=CH proton is not seen, the remaining $N=C^{7'}$ carbon atom is quaternary.

The structure of the complex cation, of stoicheiometry $[Ir(NO)(MeCN)(paa)(PPh_3)_2]^{2+}$, will be discussed later.

Reactions with Other Nitriles.—Benzonitrile or diphenylacetonitrile reacted with complex (**1**) in dichloromethane, but over a longer period than with MeCN (24 h and 7 d respectively), giving rise to violet compounds (**4**) and (**5**) (*ca.* 80% yields) similar to complex (**2**). The new products, identified by elemental analysis, conductivity measurements, i.r., ^{1}H, ^{31}P-{^{1}H}, and, for (**4**) only, ^{13}C-{^{1}H} n.m.r. spectroscopy (Experimental section and Tables 1—3) differ from (**2**) only in the nitrile ligand.

Reactions with X^- (X = Cl *or* SCN).—The iridium nitrosyl complex (**1**), dissolved in CH_2Cl_2, and the LiX salt (X = Cl or SCN) in ethanolic solution (1:5 molecular ratio; reaction time 12 h) react affording violet products (**6**) and (**7**) (Experimental section and Tables 1 and 2). Both microanalytical data and the behaviour in nitromethane solutions (1:1 electrolytes[8]) are in agreement with the stoicheiometry $[Ir(NO)X(paa)(PPh_3)_2][PF_6]$, X = Cl (**6**) or SCN (**7**).

Their i.r. spectra (KBr) display a NO stretch at 1 350 cm^{-1}, moreover the spectrum of (**7**) shows a strong absorption at 2 105 cm^{-1} assigned to the SCN group, probably S-bonded.[13] The ^{31}P-{^{1}H} n.m.r. spectra consist of single resonances at

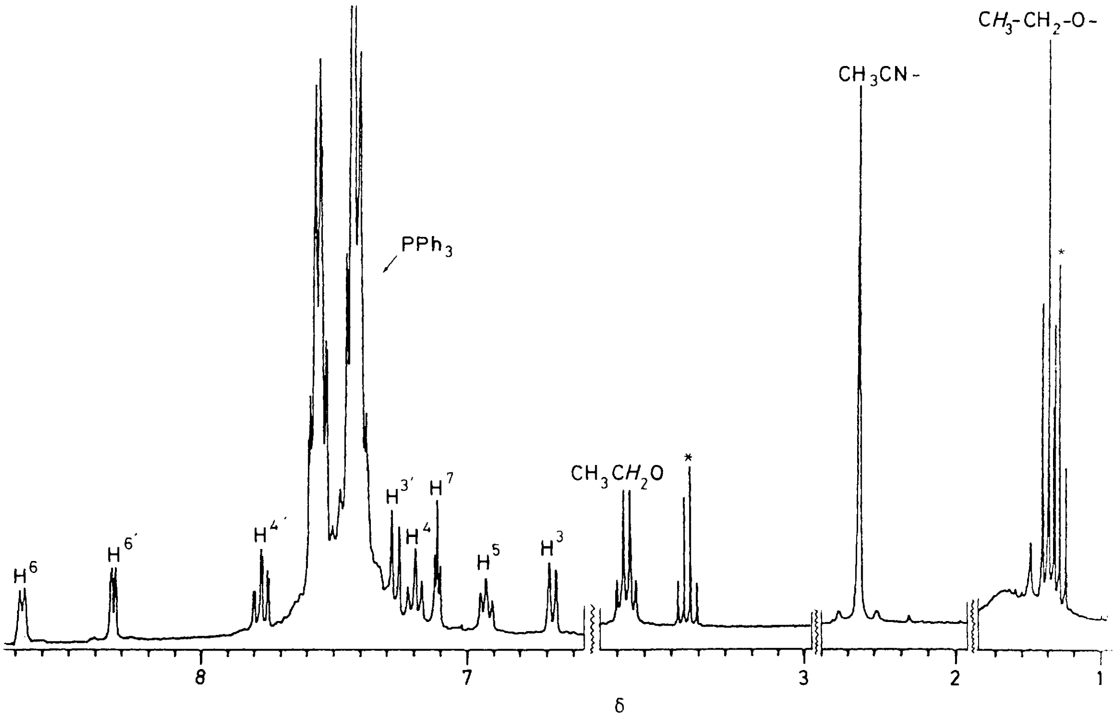


Figure 3. Proton n.m.r. spectrum (300 MHz) at 20 °C of the imidate complex (**8**). Peaks with an asterisk represent free ethanol

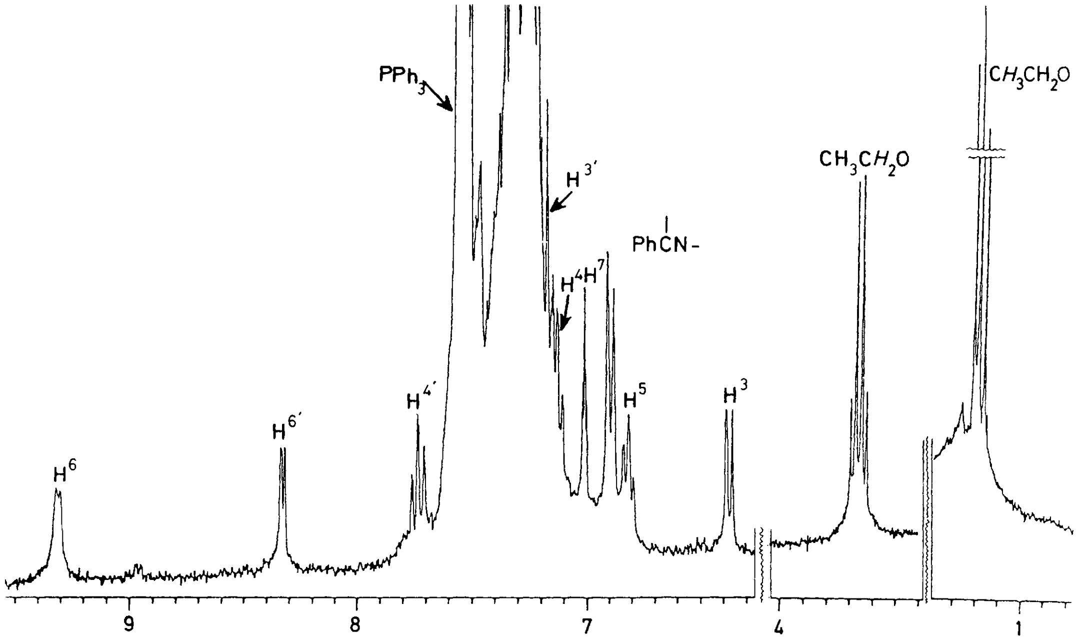


Figure 4. Proton n.m.r. spectrum (300 MHz) at 20 °C of the imidate complex (9)

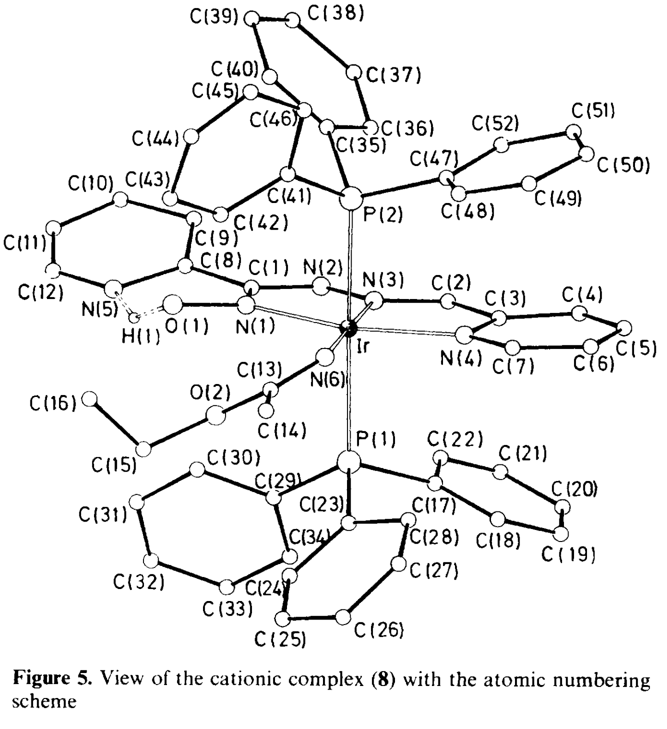


Figure 5. View of the cationic complex (8) with the atomic numbering scheme

δ −12.15 and −9.16 respectively [two equivalent PPh$_3$ co-ordinated to an iridium(III) centre] while the ^{1}H n.m.r. spectra exhibit patterns very similar to those of (2)—(5), the only difference being enhanced upfield shifts of the H^5, H^6, and H^7 signals (Table 2).

The physical properties above reported as a whole indicate that (6) and (7) are isostructural with complexes (2)—(5) with the NO group in a similar bonding situation.

Reaction of Complexes (**2**) *and* (**4**) *with Ethanol.*—The reactivity of the nitrile complex (**2**) was first observed during the many attempts carried out to grow crystals of such a compound from solvent mixtures containing ethanol.

As reported in the literature, transition-metal-co-ordinated nitriles M–N≡CR react with alcohols R′OH giving rise to M–NH=C(OR′)R complexes.[9,14] In the same way, complexes (**2**) and (**4**) dissolved in a CH$_2$Cl$_2$–EtOH solution (1:2, v/v) over a long time (about 2 months) at room temperature afford the corresponding imidate derivatives (**8**) and (**9**). These complexes have been characterised by spectroscopic methods. The addition of EtOH to the co-ordinated nitrile has been confirmed by both i.r. (Experimental section) and ^{1}H n.m.r. data (Tables 1 and 2), while their very similar structural features to the parents (**2**) and (**4**) are evident in the general appearance of the i.r. [ν(NO) in KBr: (**8**), 1 350s; (**9**), 1 358s cm^{-1}], ^{31}P-{^{1}H} [in CH$_2$Cl$_2$: (**8**), δ −6.96; (**9**), −8.29], and ^{1}H n.m.r. spectra (Figures 3 and 4).

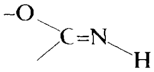
X-*Ray Crystal Structure of Complex* (**8**).—The crystal structure of complex (**8**) consists of discrete cations [Ir{(2-C$_5$H$_4$N)CH=N–N=C(NOH)(2-C$_5$H$_4$N)}{Me(EtO)C=NH}(PPh$_3$)$_2$]$^{2+}$ and PF$_6^-$ counter anions. Relevant bond distances and angles in the cation are given in Table 4. A view of the cationic complex is shown in Figure 5 together with the atomic numbering system. The slightly distorted octahedral co-ordination around the iridium centre involves two mutually *trans* P atoms from PPh$_3$ ligands and, in equatorial positions, four N atoms, one from the neutral ethylacetoimidate ligand, N(6), and the other three, N(1), N(3), and N(4), from the monoanionic ligand arising from the insertion of a nitrosyl group into a methinic C–H bond of the starting paa ligand, with the formation of a new C–N bond whose length is 1.37(3) Å. The tridentate moiety of this ligand, including the two fused penta-atomic chelating rings and the co-ordinated pyridyl group, is nearly planar [maximum deviation from the mean plane passing also through the Ir and O(1) atoms is 0.15(3) Å for C(5)] with the unco-ordinated pyridyl group tilted by 22.3(6)°. The C–N [C(1)–N(1) 1.37(3), C(1)–N(2) 1.34(3), C(2)–N(3) 1.33(3), and C(3)–N(4) 1.41(2) Å] and N–N [N(2)–N(3) 1.32(3) Å] bond lengths, even if their standard

Table 4. Selected bond distances (Å) and angles (°) in complex (**8**)

Ir–P(1)	2.430(8)	Ir–P(2)	2.403(7)
Ir–N(1)	2.00(2)	Ir–N(4)	2.04(1)
Ir–N(3)	1.92(2)	Ir–N(6)	2.05(2)
N(1)–O(1)	1.38(2)	N(2)–N(3)	1.32(3)
N(1)–C(1)	1.37(3)	N(3)–C(2)	1.33(3)
C(1)–N(2)	1.34(3)	C(2)–C(3)	1.45(3)
C(1)–C(8)	1.49(3)	N(4)–C(3)	1.41(2)
N(6)–C(13)	1.23(2)	O(2)–C(15)	1.49(3)
O(2)–C(13)	1.33(2)	C(15)–C(16)	1.38(6)
C(13)–C(14)	1.53(3)		
O(1)–H(1)	1.34		
N(1)–Ir–N(3)	77.5(8)	P(1)–Ir–N(3)	90.9(6)
N(1)–Ir–N(4)	159.4(8)	P(1)–Ir–N(1)	96.2(6)
N(1)–Ir–N(6)	104.4(8)	P(1)–Ir–P(2)	176.4(3)
N(3)–Ir–N(4)	82.3(7)	P(2)–Ir–N(6)	87.0(7)
N(3)–Ir–N(6)	177.8(8)	P(2)–Ir–N(4)	90.0(6)
N(4)–Ir–N(6)	95.8(7)	P(2)–Ir–N(3)	92.1(7)
P(1)–Ir–N(6)	90.0(7)	P(2)–Ir–N(1)	86.5(6)
P(1)–Ir–N(4)	87.5(5)	C(7)–N(4)–Ir	135(2)
Ir–N(6)–C(13)	134(2)	O(2)–C(13)–C(14)	117(2)
N(6)–C(13)–O(2)	116(2)	C(13)–O(2)–C(15)	123(2)
N(6)–C(13)–C(14)	127(2)	C(16)–C(15)–O(2)	117(3)
C(1)–N(1)–O(1)	117(2)	C(2)–N(3)–Ir	117(1)
O(1)–N(1)–Ir	132(1)	N(3)–C(2)–C(3)	115(2)
C(1)–N(1)–Ir	111(1)	C(2)–C(3)–N(4)	115(2)
N(1)–C(1)–N(2)	120(2)	C(2)–C(3)–C(4)	122(2)
N(1)–C(1)–C(8)	124(2)	N(4)–C(3)–C(4)	123(2)
N(2)–C(1)–C(8)	116(2)	C(3)–N(4)–C(7)	114(2)
C(1)–N(2)–N(3)	109(2)	C(3)–N(4)–Ir	111(1)
N(2)–N(3)–Ir	122(1)	N(1)–O(1)–H(1)	98
N(2)–N(3)–C(2)	120(2)		

deviations are rather high, indicate an extensive conjugation in this moiety. With regard to the Ir–N bond distances in this ligand, it should be noted that the Ir–N(3) bond, sharing the two chelating penta-atomic rings, is significantly shorter [1.92(2) Å] than the Ir–N(4) [2.04(1) Å] and Ir–N(1) [2.00(2) Å] ones. This distance is the shortest found up to now for Ir–N bonds involved in a five-membered Ir–N=C–C=N moiety, while Ir–N(4) is as expected for Ir–N(sp^2) co-ordination.[12–15] For the Ir–N(1) bond no comparison can be made as, to the best of our knowledge, the present case is the first characterised example of a metal complex containing the Ir–$\bar{N}$(OH)–C fragment.

The N–O bond distance [1.38(2) Å] agrees well with those found in similar moieties in [Cr(η^5-C_5H_5)$(NO)_2${N(CH_2)-OH}]$^+$ [1.392(7) Å][5] and [$RuCl_2${PhN=NC(NOH)Ph}$_2$] [1.369(11) and 1.372(9) Å][16] in which the NOH groups, from the formaldoxime or the phenylazo-oxime ligands respectively, are N-co-ordinated to the metal and are also involved in an intermolecular (with the counter anion) or intramolecular (within the complex) hydrogen bond. In the present case the distance between O(1), from the NOH group, and N(5), from the unco-ordinated pyridyl group, is rather short [O(1) ··· N(5) 2.56(2) Å] and indicative of the presence of a strong intramolecular hydrogen bond. Moreover, the unique peak found between these two atoms in the final ΔF map might suggest that the hydrogen atom is symmetrically disposed between them [O(1)–H(1) 1.34, N(5)–H(1) 1.34 Å, O(1)–H(1)–N(5) 145°]. Thus, the bonding mode displayed by this monoanionic tridentate bis(chelate) ligand can be described as the result of an α-di-imine chelate moiety fused with a new chelate ring whose closure is achieved through the bond between the Ir atom and the negatively charged N(1) atom. Other examples of a nitrogen atom behaving as a formal two-electron negatively charged donor have been reported for the complexes [$OsCl_2$(NHOH)(NO)$(PPh_3)_2$][17] and [Zr(η^5-C_5H_5)$_2$Cl(C_6H_{11}NCHNC_6H_{11})].[18]

The fourth equatorial position in the iridium co-ordination sphere is occupied by the neutral ethylacetoimidate ligand, probably the first structurally characterised example of a N-co-ordinated acyclic imidate ether. However, the Ir–N(6) bond [2.05(2) Å] can be compared with that found in the metallacycle [Ir(CH_2OCMe=NH)$(PMe_3)_4$][PF_6][BF_4] [2.080(12) Å].[19] Moreover, the structural parameters of the imidate skeleton are in agreement with the expected ones except for the C(15)–C(16) distance [1.38(6) Å], which involves a rather disordered ethyl group. On the other hand the imidate ligand seems to adopt an apparently sterically congested position between the apical PPh_3 ligands, with a number of atom–atom contacts approaching, or less than, the sum of the van der Waals radii [O(2)–C(23) 3.12(3), O(2)–C(24) 3.20(4), N(6)–C(23) 3.18(4), N(6)–C(28) 3.21(4), N(6)–C(42) 3.12(2), C(13)–C(23) 3.20(4), and C(13)–C(42) 3.21(4) Å]. The torsion angle Ir–N(6)–C(13)–O(2) of 1.7° suggests the  *Z* configuration for the imidate ether. Steric effects are probably responsible for this unusual configuration in this case.[20]

The iridium octahedral co-ordination sphere is completed by two *trans* PPh_3 ligands with Ir–P bonds [Ir–P(1) 2.430(8) and Ir–P(2) 2.403(7) Å] which compare well with those observed in similar six-co-ordinated cationic iridium(III) complexes.[12,21]

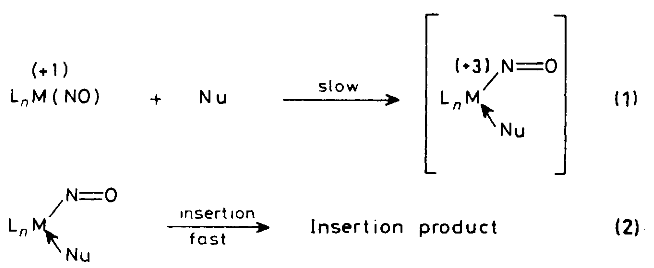
Of the two independent PF_6^- anions, the one involving P(4) shows larger thermal parameters than that involving P(3), probably because the latter is involved in shorter contacts (some of them probably hydrogen bonds) with the cations.

Conclusions

The new complexes (**2**) and (**4**)—(**7**) have been synthesised in good yield from reactions of the five-co-ordinated species (**1**) with MeCN, PhCN, Ph_2CHCN, Cl^-, and SCN^-. Alternatively, (**2**) and (**4**) can be prepared in a one-step reaction from [Ir(NO)$(MeCN)_3(PPh_3)_2$][PF_6]$_2$ and paa (1:1 mol ratio) in neat nitrile solutions (Experimental section). The co-ordinated nitrile molecule of (**2**) and (**4**) at room temperature slowly reacts with EtOH; the same reaction with (**5**) (wherein the nitrile is Ph_2CHCN) gave in 2 months no product other than the starting complex, therefore under such conditions (**5**) appears to be inert toward EtOH.

Compounds (**2**)—(**9**) display very similar spectroscopic data [*e.g.* ν(NO) ≈ 1 350—1 360 cm^{-1} and δ(P) ~ −6 to −12 p.p.m.], therefore their molecular structure, except for a unidentate ligand that in turn is MeCN, PhCN, Ph_2CHCN, Cl^-, SCN^-, MeC(OEt)NH, or PhC(OEt)NH, seems to be basically the same. Thus the main feature of these complexes is that the nitrogen atom of the IrNO group, by insertion into the methinic C–H bond of the paa fragment not involved in co-ordination to the metal, forms a new cyclometallated ring Ir–N–N=C–N(OH).

Such an insertion, which is promoted by a wide range of nucleophiles either neutral, such as nitriles, or anionic, such as Cl^- and SCN^-, can be summarised as in the Scheme. The formation of complexes (**2**)—(**7**) is proposed to proceed in two steps: (1) co-ordination of the nucleophile to complex (**1**) with contemporary internal redox $Ir^I \longrightarrow Ir^{III}$ and $NO^+ \longrightarrow NO^-$ and (2) attack of the nitrogen on the methinic carbon; the former seems to be rate determining in view of the fact that only the final insertion products were obtained from the reaction mixtures.



Scheme. Proposed steps in the formation of complexes (**2**)—(**7**); Nu = nucleophile

Experimental

All the reactions were carried out in an oxygen-free nitrogen atmosphere. Solvents were dried and deaerated prior to use. The ^1H, $^{13}C-\{^1H\}$ (75.5 MHz, CD_2Cl_2, standard $SiMe_4$), and $^{31}P-\{^1H\}$ (121.5 MHz, CH_2Cl_2, external standard 85% H_3PO_4) n.m.r. spectra were recorded on a Bruker WH 300 spectrometer, i.r. spectra for KBr pellets on a Perkin-Elmer 1330 spectrophotometer. Conductivity measurements were performed using an LKB 5300 B Conductolyser conductivity bridge. The melting points are uncorrected. Elemental analyses were carried out by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Italy.

Preparation of Compounds.—The ligand 2-pyridinecarbaldehyde azine (paa) was prepared by a standard procedure.[22] The complexes $[Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2$[23] and $[Ir(NO)(paa)(PPh_3)_2][PF_6]_2$[6] were prepared by published procedures; $[Ir(NO)(MeCN)_3(AsPh_3)_2][PF_6]_2$ was prepared in a similar way to the triphenylphosphine derivative starting from $[IrI_2(NO)(AsPh_3)_2]$.[24]

Reaction of $[Ir(NO)(paa)(PPh_3)_2][PF_6]_2$ (**1**) *with* MeCN: $[Ir\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(2\text{-}C_5H_4N)\}(MeCN)(PPh_3)_2][PF_6]_2$ (**2**). A yellow solution of complex (**1**) (0.10 g, 0.08 mmol) in MeCN (5 cm^3) was left overnight after which time a clear violet solution had developed. The volume of solvent was reduced (2 cm^3) and diethyl ether was added giving in quantitative yield a microcrystalline violet precipitate of (**2**), m.p. 243—244 °C (Found: C, 45.9; H, 3.3; N, 6.3. $C_{50}H_{43}F_{12}IrN_6OP_4$ requires C, 46.6; H, 3.3; N, 6.5%). Molar conductivity, $\Lambda = 177.35\ \Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} mol dm^{-3}) in nitromethane. I.r. (KBr disc): 2 325w and 2 300w (CN), 1 354s cm^{-1} (NO). N.m.r.: $^{31}P-\{^1H\}$, δ_P −7.34 p.p.m.; $^{13}C-\{^1H\}$, δ_C 134.51 [12 C, t, J(PC) = 5.0, $C^{2,6}$ (PPh_3)], 132.86 [6 C, s, C^4 (PPh_3)], 129.73 [12 C, t, J(PC) = 5.0, $C^{3,5}$ (PPh_3)], 126.78 [1 C, s, CN (MeCN)], 122.14 [6 C, t, J(PC) = 28.5 Hz, C^1 (PPh_3)], and 4.00 p.p.m. [1 C, s, Me (MeCN)].

Reaction of $[Ir(NO)(paa)(AsPh_3)_2][PF_6]_2$ *with* MeCN: $[Ir\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(2\text{-}C_5H_4N)\}(MeCN)(AsPh_3)_2][PF_6]_2$ (**3**). $[Ir(NO)(MeCN)_3(AsPh_3)_2][PF_6]_2$ (0.08 g, 0.064 mmol) and paa (0.014 g, 0.064 mmol) were mixed in acetonitrile (4 cm^3). The resulting green solution turned violet in *ca.* 10 min. After 3 h the solution was taken to dryness under reduced pressure, the violet residual solid was triturated with diethyl ether, filtered off, and vacuum dried, m.p. 155—156 °C. Yield 0.08 g (94%) (Found: C, 43.3; H, 3.1; N, 6.5. $C_{50}H_{43}As_2F_{12}IrN_6OP_2$ requires C, 43.6; H, 3.1; N, 6.1%). Λ = 166.90 $\Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} mol dm^{-3}) in nitromethane. I.r. (KBr disc): 2 320w and 2 300w (CN), 1 350s cm^{-1} (NO).

Reaction of complex (**1**) *with* PhCN: $[Ir\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(2\text{-}C_5H_4N)\}(PhCN)(PPh_3)_2][PF_6]_2$ (**4**). Benzonitrile (0.1 cm^3) was added to a solution of complex (**1**) (0.06 g, 0.047 mmol) in CH_2Cl_2 (3 cm^3) and the reaction mixture was left for 24 h, producing a violet solution. The solvent was removed under vacuum and the solid residue crystallised from CH_2Cl_2–cyclohexane as violet plates, m.p. 225—226 °C, yield 0.05 g (80%) (Found: C, 49.7; H, 3.4; N, 6.0. $C_{55}H_{45}F_{12}IrN_6OP_4$ requires C, 49.4; H, 3.4; N, 6.3%). Λ = 172.80 $\Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} mol dm^{-3}) in nitromethane. I.r. (KBr disc): 2 270w (CN) and 1 355s cm^{-1} (NO). N.m.r.: $^{31}P-\{^1H\}$, δ_P −7.10 p.p.m.; $^{13}C-\{^1H\}$, δ_C 136.44 [1 C, s, C^4 (PhCN)], 134.49 [12 C, t, J(PC) = 5.0, $C^{2,6}$ (PPh_3)], 134.22 [2 C, s, $C^{2,6}$ (PhCN)], 132.88 [6 C, s, C^4 (PPh_3)], 129.88 [12 C, t, J(PC) = 5.0, $C^{3,5}$ (PPh_3)], 129.61 [2 C, s, $C^{3,5}$ (PhCN)], 126.78 [1 C, s, CN (PhCN)], 122.18 [6 C, t, J(PC) = 28.8 Hz, C^1 (PPh_3)], and 108.45 p.p.m. [1 C, s, C^1 (PhCN)].

Complexes (**2**) and (**4**) were also prepared by reaction of $[Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2$ and paa (mol ratio 1:1) in acetonitrile or benzonitrile respectively.

Reaction of complex (**1**) *with* Ph_2CHCN: $[Ir\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(2\text{-}C_5H_4N)\}(Ph_2CHCN)(PPh_3)_2][PF_6]_2$ (**5**). Diphenylacetonitrile (0.195 g, 1 mmol) was added to a solution of complex (**1**) (0.042 g, 0.034 mmol) in CH_2Cl_2 (8 cm^3) and the reaction mixture stirred for 7 d. The undissolved excess of the nitrile was removed by filtration and the volume of the filtrate reduced under vacuum. Addition of diethyl ether to the violet solution gave a microcrystalline precipitate of (**5**), m.p. 220 °C, yield 0.038 g (78%) (Found: C, 49.1; H, 3.1; N, 5.2. $C_{62}H_{51}F_{12}IrN_6OP_4{\cdot}CH_2Cl_2$ requires C, 49.6; H, 3.5; N, 5.5%). Λ = 156.35 $\Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} mol dm^{-3}) in nitromethane. I.r. (KBr disc): 2 290w (CN) and 1 348s cm^{-1} (NO). $^{31}P-\{^1H\}$ N.m.r.: δ_P −6.25 p.p.m.

Reaction of complex (**1**) *with* LiCl: $[IrCl\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(2\text{-}C_5H_4N)\}(PPh_3)_2][PF_6]$ (**6**). A solution of LiCl (0.017 g, 0.4 mmol) in EtOH (10 cm^3) was added to a solution of complex (**1**) (0.100 g, 0.078 mmol) in CH_2Cl_2 (5 cm^3). The solution immediately turned blue-violet and a microcrystalline violet solid was formed overnight, m.p. 265—267 °C, yield 0.082 g (93%) (Found: C, 50.2; H, 3.4; N, 5.8. $C_{48}H_{40}ClF_6IrN_5OP_3$ requires C, 50.7; H, 3.5; N, 6.2%). Λ = 77.10 $\Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} mol dm^{-3}) in nitromethane. I.r. (KBr disc): 1 350s cm^{-1} (NO). $^{31}P-\{^1H\}$ N.m.r.: δ_P −12.15 p.p.m.

Reaction of complex (**1**) *with* LiSCN: $[Ir(SCN)\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(2\text{-}C_5H_4N)\}(PPh_3)_2][PF_6]$ (**7**). To a stirred solution of complex (**1**) (0.05 g, 0.039 mmol) in CH_2Cl_2 (4 cm^3) was added a solution of LiSCN (0.013 g, 0.2 mmol) in EtOH (12 cm^3). The resulting yellow solution immediately turned blue-violet and a microcrystalline violet precipitate was formed overnight, m.p. 267 °C, yield 0.031 g (67%) (Found: C, 50.7; H, 3.5; N, 7.2. $C_{49}H_{40}F_6IrN_6OP_3S$ requires C, 50.8; H, 3.5; N, 7.2%). Λ = 77.00 $\Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} mol dm^{-3}) in nitromethane. I.r. (KBr disc): 2 105s (CN) and 1 350s cm^{-1} (NO). $^{31}P-\{^1H\}$ N.m.r.: δ_P −9.16 p.p.m.

Reaction of complex (**2**) *with* EtOH: $[Ir\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(2\text{-}C_5H_4N)\}\{Me(EtO)C{=}NH\}(PPh_3)_2][PF_6]_2$ (**8**). When a CH_2Cl_2–EtOH (1:2) solution of the nitrile complex (**2**) was stirred for 40 d a violet solid which was recrystallised from CH_2Cl_2–EtOH (1:2) was obtained. After 20 d violet microcrystals of (**8**) were obtained. I.r. (KBr disc): 3 330w (NH), 1 638m (CN), and 1 350s cm^{-1} (NO). $^{31}P-\{^1H\}$ N.m.r.: δ_P −6.96 p.p.m.

Reaction of complex (**4**) *with* EtOH: $[Ir\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(2\text{-}C_5H_4N)\}\{Ph(EtO)C{=}NH\}(PPh_3)_2][PF_6]_2$ (**9**). When the nitrile complex (**4**) was recrystallised from CH_2Cl_2–EtOH (1:2) after about 30 d needle-like violet crystals of (**4**) were formed. From the mother-liquor, after another 30 d, flat violet crystals of (**9**) separated. I.r. (KBr disc): 3 370w (NH), 1 600m (CN), and 1 358s cm^{-1} (NO). $^{31}P-\{^1H\}$ N.m.r.: δ_P −8.29 p.p.m.

Crystal Structure Determination of Complex (**8**).—*Crystal data.* $C_{52}H_{49}F_{12}IrN_6O_2P_4$, M = 1 334.09, monoclinic, space group

Table 5. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for the non-hydrogen atoms

Atom	X/a	Y/b	Z/c
Ir	0	1 278(1)	2 500
P(1)	−1 443(5)	1 087(1)	3 303(6)
P(2)	1 396(4)	1 499(1)	1 734(5)
P(3)	4 359(5)	2 406(1)	8 996(7)
P(4)	−4 738(13)	681(3)	−3 622(13)
O(1)	−1 184(13)	1 034(3)	−303(14)
O(2)	−2 574(12)	1 457(3)	439(16)
N(1)	−426(14)	999(4)	969(18)
N(2)	886(15)	676(4)	2 521(19)
N(3)	975(14)	929(4)	3 200(17)
N(4)	881(13)	1 446(3)	4 312(14)
N(5)	−980(20)	469(4)	−757(22)
N(6)	−992(13)	1 660(5)	1 804(18)
C(1)	143(20)	725(5)	1 300(21)
C(2)	1 683(19)	940(5)	4 444(22)
C(3)	1 678(18)	1 229(4)	5 084(21)
C(4)	2 458(23)	1 288(6)	6 355(23)
C(5)	2 394(21)	1 591(7)	6 842(22)
C(6)	1 617(19)	1 793(5)	6 123(19)
C(7)	921(18)	1 709(6)	4 893(25)
C(8)	29(19)	472(4)	365(21)
C(9)	920(24)	254(5)	532(31)
C(10)	634(35)	43(5)	−525(36)
C(11)	−441(43)	44(7)	−1 659(36)
C(12)	−1 114(30)	263(6)	−1 630(29)
C(13)	−1 977(19)	1 705(4)	994(25)
C(14)	−2 616(21)	2 010(5)	660(31)
C(15)	−3 713(26)	1 469(7)	−677(37)
C(16)	−3 678(35)	1 525(9)	−1 883(38)
C(17)	−742(17)	971(5)	4 974(21)
C(18)	−735(20)	1 141(6)	6 034(23)
C(19)	−165(27)	1 031(5)	7 303(31)
C(20)	412(25)	783(7)	7 464(31)
C(21)	462(19)	600(5)	6 450(24)
C(22)	−82(21)	708(5)	5 262(24)
C(23)	−2 508(20)	1 366(5)	3 254(25)
C(24)	−3 700(25)	1 319(6)	2 536(29)
C(25)	−4 552(27)	1 546(7)	2 361(34)
C(26)	−4 206(31)	1 811(8)	3 094(37)
C(27)	−3 057(26)	1 880(7)	3 712(30)
C(28)	−2 189(19)	1 664(5)	3 907(23)
C(29)	−2 293(17)	765(4)	2 532(20)
C(30)	−2 637(25)	712(6)	1 185(29)
C(31)	−3 363(20)	460(5)	605(25)
C(32)	−3 739(22)	255(6)	1 295(27)
C(33)	−3 392(21)	310(6)	2 649(25)
C(34)	−2 654(22)	561(6)	3 258(26)
C(35)	2 323(17)	1 229(4)	1 308(22)
C(36)	2 958(20)	1 020(5)	2 266(24)
C(37)	3 718(22)	805(6)	1 999(27)
C(38)	3 744(26)	820(7)	713(31)
C(39)	3 147(24)	1 018(6)	−169(28)
C(40)	2 385(22)	1 227(5)	136(27)
C(41)	840(16)	1 731(4)	318(20)
C(42)	−303(19)	1 687(5)	−615(23)
C(43)	−755(23)	1 870(6)	−1 741(29)
C(44)	−40(23)	2 084(6)	−1 904(26)
C(45)	1 055(24)	2 123(6)	−1 118(28)
C(46)	1 544(21)	1 961(6)	31(25)
C(47)	2 309(20)	1 761(5)	2 965(24)
C(48)	1 913(20)	2 063(6)	2 913(24)
C(49)	2 543(27)	2 255(7)	3 860(33)
C(50)	3 553(32)	2 171(8)	4 781(37)
C(51)	3 983(30)	1 902(8)	4 764(36)
C(52)	3 357(21)	1 678(6)	3 881(25)
F(1)	3 179(14)	2 332(4)	7 854(17)
F(2)	5 027(18)	2 238(4)	8 250(20)
F(3)	5 532(17)	2 493(4)	10 115(19)
F(4)	3 675(21)	2 541(5)	9 795(24)
F(5)	4 341(20)	2 086(5)	9 630(23)
F(6)	4 303(19)	2 725(5)	8 463(24)
F(7)	−5 328(28)	824(6)	−2 648(37)
F(8)	−5 992(40)	528(12)	−4 424(49)
F(9)	−4 226(38)	544(9)	−4 607(43)
F(10)	−3 530(39)	811(10)	−2 719(41)
F(11)	−4 471(29)	391(7)	−2 848(32)
F(12)	−5 286(34)	936(9)	−4 363(41)

Cc, a = 12.405(6), b = 43.836(12), c = 11.126(7) Å, β = 112.1(2)° U = 5 606(9) Å^3 (by least-squares refinement of the θ values of 27 accurately measured reflections), Z = 4, λ = 0.7107 Å, D_c = 1.58 g cm^{-3}, F(000) = 2 656, μ(Mo-K_α) = 25.66 cm^{-1}. A flattened crystal of approximate dimensions 0.06 × 0.40 × 0.65 mm was used for the structure analysis. A correction for absorption[25] was applied (maximum and minimum transmission factors 1.2472 and 0.7547 respectively) using the program ABSORB.[26]

Data collection and processing. Siemens AED diffractometer, θ—2θ scan mode, using niobium-filtered Mo-K_α radiation; all the reflections with θ in the range 3—24° were measured. Of 4 649 independent reflections, 3 394, having $I > 2\sigma(I)$, were considered observed and used in the analysis.

Structure solution and refinement. Patterson and Fourier methods, block-matrix least squares with anisotropic thermal parameters in the last cycles for the non-hydrogen atoms except those of the phenyl rings. All hydrogen atoms were placed at their geometrically calculated positions except that of the NOH group, whose position was determined from a ΔF map, and introduced in the final structure-factor calculation. Final R and R' values were 0.057 and 0.073. The SHELX system of computer programs was used.[27] Atomic scattering factors, corrected for anomalous dispersion of Ir and P atoms, were taken from ref. 28. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 5.

Additional data available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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