Iridium Nitrosyl Complexes: Insertion of NO into a Methinic C–H Bond promoted by Nitriles. *X*-Ray Crystal Structure of $[Ir\{(2\text{-}C_5H_4N)\text{–}CH{=}N\text{–}N{=}C(NOH)\text{–}(2\text{-}C_5H_4N)\}\text{-}\{Me(EtO)C{=}NH\}(PPh_3)_2][PF_6]_2$

Mauro Ghedini,[a] Anna Maria Manotti Lanfredi,[b] Francesco Neve,[a] and Antonio Tiripicchio[b]

[a] *Dipartimento di Chimica, Università della Calabria, I 87030 Arcavacata (CS), Italy*
[b] *Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del CNR,*
Via M. D'Azeglio 85, I 43100 Parma, Italy

A C–N bond is formed by insertion of co-ordinated NO into a C–H bond of the –HC=N–N=CH– moiety of 2-pyridinecarbaldehyde azine (paa) in $[Ir(NO)(paa)(PPh_3)_2]^{2+}$, promoted by nitriles, as shown by an *X*-ray structure of the complex $[Ir\{(2\text{-}C_5H_4N)\text{–}CH{=}N\text{–}N{=}C(NOH)\text{–}(2\text{-}C_5H_4N)\}\{Me(EtO)C{=}NH\}(PPh_3)_2][PF_6]_2$.

The activation of co-ordinated NO with subsequent formation of C–N bonds is an important topic in transition metal chemistry and currently the subject of much research.[1] We report here one of the few examples of insertion of co-ordinated NO into a C–H bond promoted by RCN (R = Me, Ph). In a previous paper we described the reactivity of the cationic iridium(III) nitrosyl complex $[Ir(NO)(MeCN)_3\text{-}(PPh_3)_2][PF_6]_2$ with the ligand 2-pyridinecarbaldehyde azine (paa) at room temperature with tetrahydrofuran (THF) as solvent.[2] Under these experimental conditions the product of the reaction was the pentaco-ordinate iridium(I) cationic complex $[Ir(NO)(paa)(PPh_3)_2][PF_6]_2$, (**1**), where the NO group, bonded as NO^+, and the chelated paa ligand lie on the equatorial plane of a trigonal bipyramid (tbp), while the two PPh_3 ligands occupy the apical positions. We now describe the reactivity of (**1**).

The pale yellow complex (**1**), when treated with acetonitrile (neat, 12 h) or benzonitrile (in a 1:30 v/v solution of dichloromethane, 24 h), gave rise to deep violet solutions from which, on addition of diethyl ether, violet microcrystalline solids, (**2**) and (**3**), were precipitated in 95 and 80% yield, respectively. Elemental analyses confirmed the formation of these nitrile addition products, while their i.r. data,† showing a ν(NO) decrease of *ca.* 450 cm^{-1}, suggested dramatic structural changes in the NO group.

Many attempts were made to grow crystals suitable for *X*-ray analysis. The best results were obtained for (**2**) using CH_2Cl_2–EtOH (1:2) as solvent mixture, which required nonetheless a very long crystallization time (two months). The few violet crystals thus formed were examined by i.r. spectroscopy and showed ν(NO) at 1350 cm^{-1}, no band fingerprints of ν(C≡N) present, and two new absorptions, tentatively attributable to ν(NH) and ν(C=N), at 3330 and 1630 cm^{-1} respectively. In the $^{31}P\{^1H\}$ n.m.r. spectrum a single resonance occurred at −6.96 p.p.m. The general appearance of both i.r. and ^{31}P n.m.r. spectra of this new

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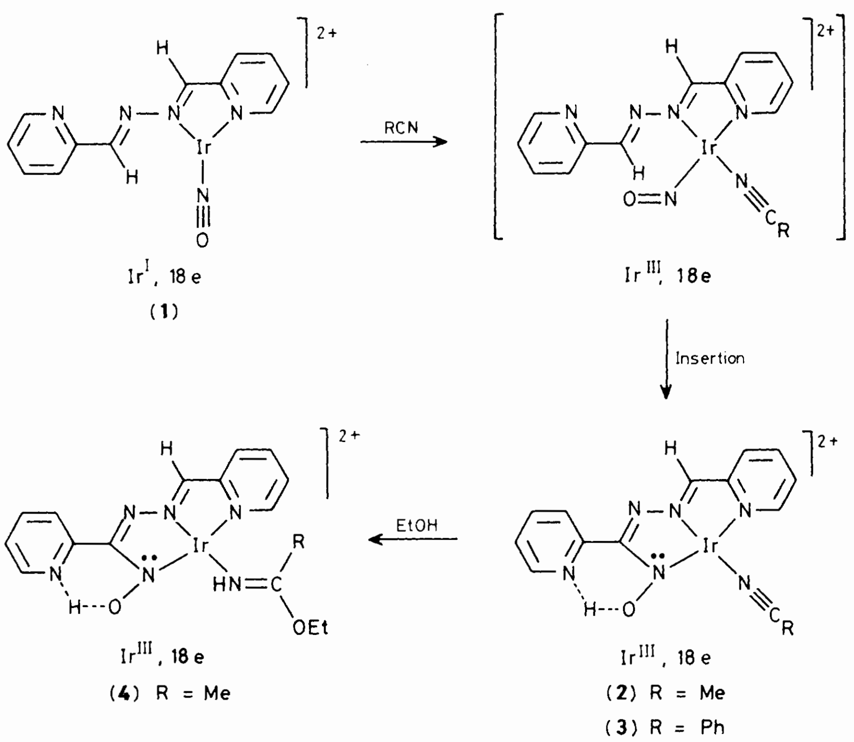
† The new complexes (**2**) and (**3**) were characterized by elemental analysis, conductivity measurements, and i.r. and $^{31}P\{^1H\}$ n.m.r. spectroscopy. Conductivity $\Lambda_M(MeNO_2, 10^{-3}\ \text{M})\ \Omega^{-1}\ cm^2\ mol^{-1}$; i.r. ν(KBr) cm^{-1}; $^{31}P\{^1H\}$ n.m.r. (p.p.m. relative to 85% H_3PO_4) δ (CD_2Cl_2): (**2**) $\Lambda_M = 172.70$, ν(CN) 2325 and 2300, ν(NO) 1354, δ (P) −7.34; (**3**) $\Lambda_M = 172.80$, ν(CN) 2270, ν(NO) 1355, δ (P) −7.10.



Scheme 1. PPh_3 groups attached to Ir are omitted for clarity. All complexes contain $[PF_6^-]$ anions.

product, (**4**), and of its parent (**2**), as well as the microanalytical data, indicate very close structural features.

The structure of (**4**) has been elucidated by an *X*-ray diffraction analysis.‡ It consists of cationic complexes, $[Ir\{(2\text{-}C_5H_4N)\text{–}CH\text{=}N\text{–}N\text{=}C(NOH)\text{–}(2\text{-}C_5H_4N)\}\{Me(EtO)C\text{=}NH\}(PPh_3)_2]^{2+}$, depicted in Figure 1, and of $[PF_6^-]$ anions. The iridium atom is octahedrally co-ordinated by two P atoms from PPh_3 ligands in *trans* positions and by four nitrogen atoms, one from the ethylacetoimidate ligand and the other three from an unexpected ligand obtained by the insertion of a nitrosyl group into a methinic C–H bond of the starting paa ligand. The $Ir(NO)C\text{=}N\text{–}N\text{=}C\text{–}C_5H_4N$ moiety is planar [the maximum deviation from the mean plane passing through them is 0.15(3) Å for the C(5) atom] and forms an angle of 22.3(6)° with the unco-ordinated pyridyl ring. It is noteworthy that the distance between the O(1) atom from the NOH group and the N(5) atom from the unco-ordinated pyridyl group is rather short [O(1)–N(5) 2.56(2) Å] which is consistent with a strong

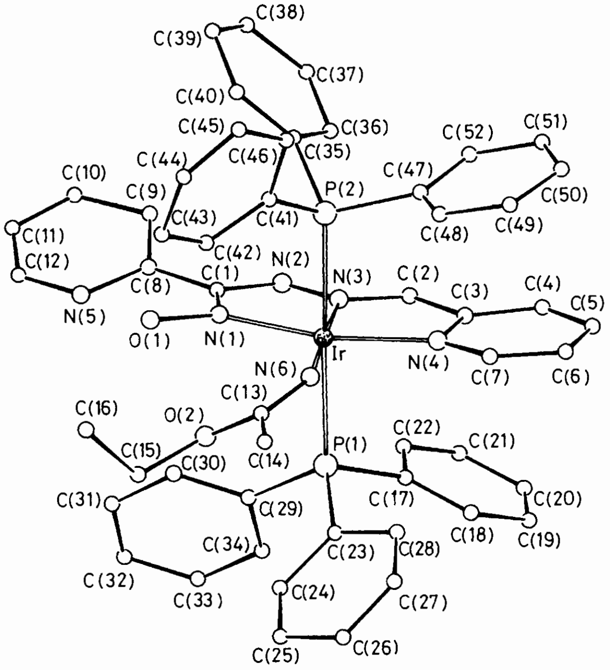


Figure 1. View of the structure of the cationic complex of (**4**) with the atomic numbering scheme. Selected bond distances (Å) and angles (°): Ir–N(1) 2.00(2), Ir–N(3) 1.92(2), Ir–N(4) 2.04(1), Ir–N(6) 2.05(2), Ir–P(1) 2.43(1), Ir–P(2) 2.40(1), C(1)–N(1) 1.37(3), N(1)–O(1) 1.38(2), N(6)–C(13) 1.23(2); N(3)–Ir–N(4) 82.3(7), N(3)–Ir–N(1) 77.5(8), N(1)–Ir–N(6) 104.4(8), N(6)–Ir–N(4) 95.8(7), P(1)–Ir–P(2) 176.4(3), C(1)–N(1)–O(1) 117(2), Ir–N(1)–C(1) 111(1), Ir–N(1)–O(1) 132(1), Ir–N(6)–C(13) 134(2), O(2)–C(13)–N(6) 116(2), N(6)–C(13)–C(14) 127(2), O(2)–C(13)–C(14) 117(2).

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‡ *Crystal data* for (**4**): $C_{52}H_{49}F_{12}IrN_6O_2P_4$, $M = 1334.09$, monoclinic, space group *Cc*, $a = 12.405(6)$, $b = 43.836(12)$, $c = 11.126(7)$ Å, $\beta = 112.1(2)°$, $U = 5606(9)$ Å^3, $Z = 4$, $D_c = 1.58$ g cm^{-3}, $F(000) = 2656$, $\mu(\text{Mo-}K_\alpha) = 25.7$ cm^{-1}. The intensities of 4649 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3—24°) using the θ–2θ scan technique and niobium-filtered Mo-K_α radiation. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares on the basis of 3394 observed reflections [$I \geqslant 2\sigma(I)$] with anisotropic thermal parameters for the non hydrogen atoms except those of the phenyl rings. All hydrogen atoms were placed at their geometrically calculated positions excepting that of the NOH group, whose position was determined from a ΔF map (see text), and introduced in the final structure factor calculations. Final R and R_w values were 0.057 and 0.073. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

intramolecular hydrogen bond. Taking account of the unique peak found between these two atoms in the final ΔF map, this might suggest that the hydrogen atom is symmetrically disposed between them [H(1)–O(1) 1.34, H(1)–N(5) 1.34 Å, O(1)–H(1)–N(5) 145°].

The bonding of the NO group to the Ir atom should be represented as $Ir \leftarrow \ddot{N}(R)OH$ with this ligand behaving as a formal two-electron negatively charged donor. Co-ordinating $\leftarrow \ddot{N}(R)OH$ ($R = C_6H_{11}$) and $\leftarrow \ddot{N}(H)OH$ groups have already been reported in the literature.[3] The *X*-ray crystal structure determination on complex (**4**), in agreement with the i.r. evidence, shows the presence of ethylacetoimidate Me(EtO)C=NH N-co-ordinated to the iridium(III) centre. From the literature it is known that such species can be formed by reaction between alcohol and co-ordinated nitrile,[4] so in the present case it seems reasonable to assume that compound (**4**) results from a slow reaction occurring during the recrystallization of (**2**) between solvent EtOH and the co-ordinated MeCN contained in (**2**).

The structure determination of complex (**4**), together with analytical and spectroscopic data, allows us to conclude that the nitrile complexes (**2**) and (**3**) differ from (**4**) only with respect to the nature of the monodentate neutral ligand. Consequently it can be affirmed that (**2**) and (**3**) are derived from (**1**) through the insertion of NO into the neighbouring C–H bond of the paa ligand. This occurs (see Scheme 1) presumably upon co-ordination of the nitrile to complex (**1**), *via* the internal redox processes $Ir^{I} \rightarrow Ir^{III}$ and $NO^{+} \rightarrow NO^{-}$, which provide the driving force for the attack of nitrogen at the methinic carbon.

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