Arenediazonium Ion Insertion into an Iron–Phosphine Bond; Synthesis and Crystal Structure of $[Fe(NO)_2\{PPh_2CH_2CH_2P(Ph)_2NN(C_6H_4F\text{-}p)\}][PF_6]\cdot OC_4H_8$

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The reaction of $[Fe(NO)_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with $[N_2C_6H_4F\text{-}p][PF_6]$ gave $[Fe(NO)_2\{PPh_2CH_2CH_2P(Ph)_2NN(C_6H_4F\text{-}p)\}][PF_6]$ X-ray studies on which revealed the formation of a novel chelating ligand bound to iron through phosphine and η^2-N=N functionalities and resulting from insertion of an arenediazo group into an iron–phosphorus bond.

While arenediazonium ions are well known as precursors to aryldiazenido complexes of transition metals[1] they may also act as mild one-electron oxidants[2] or undergo electrophilic addition to co-ordinated hydrocarbons providing routes to C–aryl and C–N_2(aryl) bonds.[3] We now show that the reaction between $[Fe(NO)_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and diazonium salts leads to the unprecedented insertion of an arenediazonium ion into an iron–phosphorus bond.

Treatment of $[Fe(NO)_2(dppe)]$ **1** (290 mg, 0.564 mmol) with $[N_2C_6H_4F\text{-}p][PF_6]$ (303 mg, 1.130 mmol) in CH_2Cl_2 at −78 °C (acetone–dry ice bath) gave, after 1.5 h, a deep red solution from which dark red microcrystals of $[Fe(NO)_2\{PPh_2CH_2CH_2P(Ph)_2NN(C_6H_4R\text{-}p)\}][PF_6]$ **2** (R = F) were isolated after filtration, addition of *n*-hexane, partial removal of the solvent *in vacuo* to induce precipitation, and recrystallisation of the precipitate from tetrahydrofuran (thf)–*n*-hexane (yield 355 mg, 74%). The IR spectrum of compound **2** (R = F) shows two nitrosyl bands at 1804 and 1756 cm^{-1}, *ca.* 90 cm^{-1} higher in energy than those of **1** (1716, 1668 cm^{-1}). Although the shift in ν(NO) is compatible with metal-based one-electron oxidation of **1** to $\mathbf{1}^+$, as anticipated on the basis of cyclic voltammetry (one reversible oxidation wave at 0.53 V), the elemental analysis (C, H and N) of **2** (R = F) was consistent only with a product containing the elements of both reactants in a 1 : 1 ratio. Moreover, the ^1H NMR spectrum showed **2** (R = F) to be diamagnetic, with sharp resonances due to the Ph and CH_2 groups of the dppe ligand, the C_6H_4 group of the arenediazo fragment, and the thf solvent of crystallisation (see below). The ^{31}P NMR spectrum (in $CDCl_3$, at 21 °C) clearly showed the presence of two inequivalent phosphorus atoms [two doublets at δ 39.04 and 40.26, $J(^{31}P^{31}P)$ 14 Hz] {as well as the septet [$J(^{31}P^{19}F)$ 713 Hz] at δ 56.34 due to the $[PF_6]^-$ anion} but in the absence of further useful spectroscopic information, a single-crystal structure analysis* was carried out on **2** (R = F) as its thf solvate using crystals grown from thf–*n*-hexane.

The molecular structure of the cation of **2** (R = F) is shown in Fig. 1. The complex is the result of insertion of the terminal diazonium nitrogen into one of the Fe–P bonds of **1** and η^2 co-ordination of the resultant N=N double bond to the iron atom. Formally the positive charge resides on the quaternary phosphorus, P(2). The iron atom is therefore in oxidation state −II and displays the expected approximately tetrahedral co-ordination (assuming that the η^2-N=N moiety occupies one site) with near-linear nitrosyl ligands. The C–N=N–P fragment shows a *trans* doubly bent geometry [P(2)–N(1)–N(2)–C(27) torsion angle −142.3(8)°] distorted from planarity so as to move C(27) and P(2) away from Fe. The dimensions of the η^2-co-ordinated R_3P^+–N=N–aryl unit (see caption to Fig. 1) may be compared with the same fragment in $[(Ph_3P)N{=}NC_6H_4\text{-}NEt_2\text{-}p][BF_4]$ which has bond lengths P–N 1.648(5), N–N 1.308(6), N–C 1.356(7) Å, and torsion angle C–N–N–P −175.7°.[5] The lengthening of the N=N distance (by *ca.* 0.1 Å) on co-ordination is striking and consistent with Dewar–Chatt–Duncanson interaction of the N=N π system with the iron atom. The FeP_2C_2N six-membered ring in **2** (R=F) adopts a chair conformation which allows the η^2-N=N fragment to lie near the plane containing the Fe–P(1) bond [P(1)–Fe–N(1)–N(2) torsion angle 178.0°] presumably to allow optimum π back-bonding.

At low temperatures analogues of compound **2** (R = F) are formed with $[N_2C_6H_4R\text{-}p][PF_6]$ (R = NO_2 or OMe). However, at room temperature, the reaction of **1** with arenediazonium ions gives **2** (R = F, NO_2 or OMe) mixed with a second species **3** (R = F, NO_2 or OMe) which shows two nitrosyl bands, also at high energy [*e.g.* for **3** (R = F, NO_2 or OMe) ν(NO) 1804 and 1756, 1799 and 1752, and 1810 and 1764 cm^{-1} respectively] indicating the formation of another cationic dinitrosyl complex of iron. As yet it has proved impossible to characterise this species. However, the relative amounts formed of **2** and **3** depend not only on the reaction temperature but also on the *para* substituent of the arenediazonium ion; that the second species is formed more readily at higher temperatures and by using the *para*-nitro derivative $[N_2C_6H_4NO_2\text{-}p][PF_6]$

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* Crystal data. $C_{36}H_{36}F_7FeN_4O_3P_3$, M = 854.4, monoclinic, space group $P2_1/n$ (no. 14), a = 13.623(6), b = 22.809(9), c = 14.465(7) Å, β = 117.33(2)°, U = 3993(3) $Å^3$, Z = 4, D_c = 1.42 g cm^{-3}, λ = 0.710 73 Å, μ = 5.7 cm^{-1}, $F(000)$ = 1752, T = 295 K, crystal dimensions 0.3 × 0.45 × 0.7 mm, final difference map features in range 0.37 to −0.26 e$Å^{-3}$. Data were collected on a Nicolet P3m diffractometer for a unique portion of reciprocal space for $4 < 2\theta < 51°$. The structure was solved by heavy-atom methods and refined by full-matrix least squares (SHELXL 93,[4] 534 variables) against all 7390 unique F^2 data corrected for absorption (transmission coefficients 0.77–0.90), to $R1$ = 0.071 and $wR2$ = 0.128 for the 4005 observed [$I > 2\sigma(I)$] data. The solvent and anion molecules are disordered. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

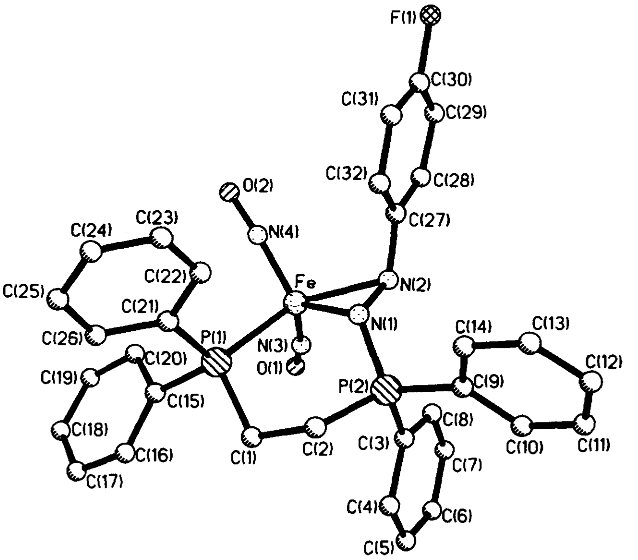

Fig. 1 Molecular geometry of the cation of **2** (R = F). Important bond lengths (Å) and angles (°): Fe–N(4) 1.665(5), Fe–N(3) 1.681(5), Fe–N(1) 2.004(4), Fe–N(2) 2.032(4), Fe–P(1) 2.301(2), P(2)–N(1) 1.656(4), O(1)–N(3) 1.162(5), O(2)–N(4) 1.164(5), N(1)–N(2) 1.403(5), C(27)–N(2) 1.437(6); N(4)–Fe–N(3) 116.4(2), N(4)–Fe–N(1) 118.7(2), N(3)–Fe–N(1) 121.4(2), N(4)–Fe–N(2) 105.5(2), N(3)–Fe–N(2) 106.1(2), N(1)–Fe–N(2) 40.70(14), N(4)–Fe–P(1) 100.2(2), N(3)–Fe–P(1) 98.6(2), N(1)–Fe–P(1) 90.17(11), N(2)–Fe–P(1) 130.84(11), N(2)–N(1)–P(2) 117.7(3), N(2)–N(1)–Fe 70.7(2), P(2)–N(1)–Fe 117.0(2), N(1)–N(2)–C(27) 110.9(3), N(1)–N(2)–Fe 68.6(2), C(27)–N(2)–Fe 112.2(3), O(1)–N(3)–Fe 168.1(5), O(2)–N(4)–Fe 171.1(5)

suggests **3** is most likely formed with loss of dinitrogen from the arenediazo moiety.

Acknowledgements

We thank the SERC for a Studentship (to F. L. A.).

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Received 28*th January* 1994; *Communication* 4/00537F