

Structure and Mechanism of Formation of $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2\{\text{C}(\text{=CH}_2)\text{-NC}_6\text{H}_{11}\text{-C}(\text{=N}^+\text{HC}_6\text{H}_{11})\}]\text{BPh}_4^-$. A New Type of Intramolecular Oxidative Addition to Isocyanide Co-ordinated to Iron

Giuseppe Cardaci,^{a*} Gianfranco Bellachioma,^a and PierFrancesco Zanazzi^b

^a Dipartimento di Chimica, University of Perugia, Via Elce di Sotto, 8, 06100 Perugia, Italy

^b Dipartimento di Scienze della Terra, Sez. Cristallografia, University of Perugia, Piazza Università, 06100 Perugia, Italy

The structure of the title complex (**1b**) was resolved by X-ray diffraction methods and is supported by i.r. and ¹H n.m.r. spectral evidence; its formation proceeds *via* insertion of isocyanide into an iron–methyl bond, intramolecular oxidative addition to another co-ordinated isocyanide ligand, and finally iminium–enammonium rearrangement.

The insertion of isocyanide into a metal–alkyl bond to give η^1 -iminoalkyl derivatives has been studied extensively;¹ according to theoretical predictions² it proceeds *via* a dihapto-iminoalkyl intermediate, which in a few cases has been isolated and characterized.³ In some cases polyinsertion of isocyanide ligands has also been observed, in particular with Ni, Pd, and Fe derivatives.⁴ The nitrogen of the η^1 -iminoalkyl derivatives also reacts with electrophiles to give carbene structures.^{3,5} In this communication we describe a new type of intramolecular reaction, which gives ferraheterocyclic butane derivatives.

The reaction of $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2(\text{Me})\text{I}]$ (**2**) and $\text{C}_6\text{H}_{11}\text{NC}$ in benzene gave the complex $[\text{Fe}(\text{CO})(\text{PMe}_3)_2(\text{COMe})(\text{CNC}_6\text{H}_{11})\text{I}]$ (**3**), (ν_{CO} 1940, ν_{COMe} 1585, and ν_{CN} 2160 cm^{-1}). Complex (**3**) reacted further with $\text{C}_6\text{H}_{11}\text{NC}$ to give the ionic precipitate $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2\{\text{C}(\text{=CH}_2)\text{-NC}_6\text{H}_{11}\text{-C}(\text{=NHC}_6\text{H}_{11})\}]^+\text{I}^-$ (**1a**),[†] which was transformed into the tetraphenylborate salt (**1b**).[†] Good crystals of (**1b**) were obtained by adding LiI in MeOH in order to control the formation rate.

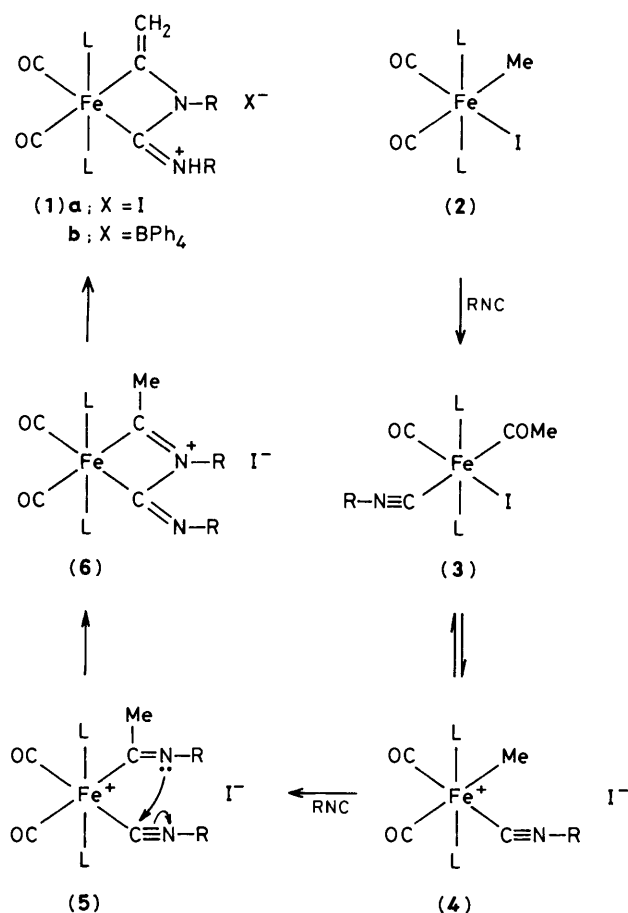
Analysis was carried out by X-ray diffraction methods.[‡] Complex (**1b**) crystallized in the monoclinic system with $a = 20.175(4)$, $b = 14.833(3)$, $c = 16.052(2)$ Å, $\beta = 106.97(2)^\circ$, $D_c = 1.179$ g cm^{-3} , $Z = 4$, space group $P2_1/a$. Intensity data were measured with a Philips PW 1100 single-crystal diffractometer, using Mo- K_α radiation, $\mu = 4.02$ cm^{-1} . The structure was resolved by direct methods and refined by full-matrix least squares with SHELX-76.⁶ The refinement converged at R 0.077 and R_w 0.083 for 231 parameters and 2172 observed reflections. Anisotropic thermal parameters were refined for Fe, P, O, and N atoms and for the carbon atoms linked to iron.

The molecular structure of the cation $[\text{Fe}(\text{CO})_2(\text{PMe}_3)_2\{\text{C}(\text{=CH}_2)\text{-NC}_6\text{H}_{11}\text{-C}(\text{=NHC}_6\text{H}_{11})\}]^+$ is shown in Figure 1 and selected bond lengths and angles are given in the caption.

Complex (**1b**) has an octahedral arrangement with two *cis* carbonyl ligands and two *trans* phosphine ligands. The organic moiety occupies the remaining two *cis* co-ordination sites; it bonds to iron by two σ -carbon bonds, forming a cyclic structure of four atoms with the iron. The atoms N(2)–C(17)–

[†] Elemental analyses of complexes (**1a**) and (**1b**) are in agreement with the formulae proposed.

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Scheme 1. L = PMe₃; R = C₆H₁₁.

N(1)–C(9)–C(10) lie in the same plane (maximum atomic deviation from the least squares plane is 0.04 Å); there is extensive conjugation along this series of atoms as indicated by the bond lengths and angles. The structure of complex (1b) is supported by the ¹H n.m.r. spectrum which shows two multiplets of equal intensity at τ 4.86 and 5.10 assigned to the olefinic CH₂ group; the multiplet structure of these bands is due to the coupling of one hydrogen atom with the other and with the two P atoms through iron.⁷ There is no spectroscopic or X-ray evidence to indicate the position of the hydrogen atom co-ordinated to the nitrogen atom N(2). The planar structure of the organic moiety probably supports a bond with the N(2) atom to give an iminium structure. It is known⁸ that the hydrogen atom in this structure is often not observable in n.m.r. spectra. In the i.r. spectrum a band at 3152 cm⁻¹ (KBr pellet) is observed which can be assigned to the N–H stretching. A possible mechanism for the formation of the complex (1a) is shown in Scheme 1.

Scheme 1 shows initial CO insertion assisted by C₆H₁₁NC to give (3), which is in equilibrium with the ionic complex (4), as observed for similar complexes with other Lewis bases.⁹ Isocyanide insertion gives (5). In complex (5) the positive charge on the iron makes the carbon atom of the terminal isocyanide ligand positive and induces nucleophilic attack by the iminic nitrogen to give complex (6), which has an iminium structure. The nucleophilic attack of NHR¹R² on the carbon atom of a terminal isocyanide ligand in Pt complexes has recently been described.¹⁰ The iminium structure rearranges to the enammonium structure of complex (1a). The equilibrium between iminium and enammonium derivatives has been observed in many organic compounds.^{11,12} However, whereas

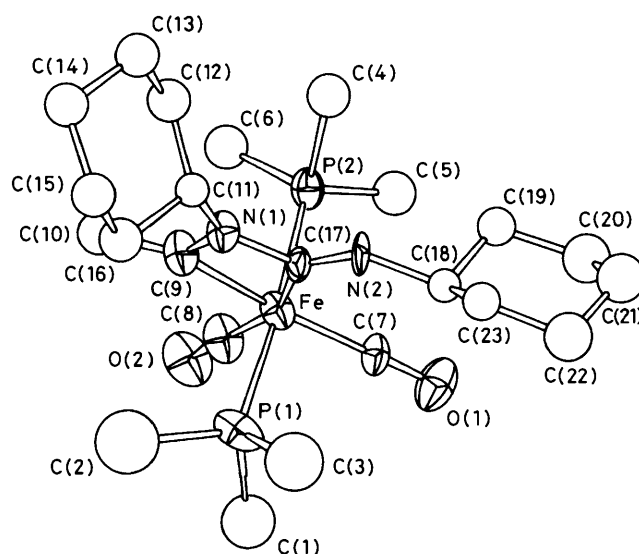


Figure 1. View of the [Fe(CO)₂(PMe₃)₂(C(=CH₂)-NC₆H₁₁-C(=NHC₆H₁₁))]⁺ cation. Relevant bond lengths (Å) and angles (°) are: Fe–C(9) 1.982(12), Fe–C(17) 1.970(12), C(9)–C(10) 1.364(17), C(9)–N(1) 1.426(14), N(1)–C(17) 1.374(13), N(2)–C(17) 1.337(13), N(1)–C(11) 1.476(13), C(9)–N(1)–C(17) 101(1), N(1)–C(9)–Fe 95(1), N(1)–C(17)–Fe 98(1), C(10)–C(9)–N(1) 125(1), C(9)–N(1)–C(11) 131(1), C(17)–N(1)–C(11) 128(1), C(17)–N(2)–C(18) 124(1), C(10)–C(9)–Fe 140(1).

in organic compounds^{11,12} the equilibrium is shifted towards the iminium structure,¹³ in complex (1a) the enammonium structure is stabilized.

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