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Preliminary communication

SYNTHESIS OF COORDINATED CARBON MONOXIDE FROM ISOCYANIDE IRON(II) COMPOUNDS. CRYSTAL STRUCTURE OF [Fe(dppe)(CO)(CN-*p*-tol)(*p*-tolN=C–N-*p*-tol–C=N-*p*-tol)]

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Summary

The compounds [Fe(dppe)(CO)(CNR)(RN=C–NR–C=NR)] (IIa: R = Ph, IIb: R = *p*-tol = 4-methylphenyl) have been prepared by reaction of $[Fe(dppe)(CNR)_4](ClO_4)_2$ with KOH. The structure of IIb has been determined by X-ray diffraction. IIb can be protonated in two steps with $HClO_4$ to give the cationic complex species {Fe(dppe)(CO)(CNPh)[PhN=C–NPh–C(NHPh)]}$[ClO_4]$ and *trans*-{Fe(dppe)(CO)$(CNPh)_2[C(NHPh)_2]$}$[ClO_4]_2$.

Isocyanides bonded to a metal can be attacked by a great variety of reagents such as amines and alcohols [1], organolithium compounds [2] or KOH [3], to give carbene, iminoacyl, and carbamoyl derivatives, respectively. In the last case, a further attack by acid on the compound $\{(PPh_3)_2Pt(CNMe)[C(O)NHMe]\}^+$ in the presence of NCMe leads to elimination of NH_2Me and CO to give the corresponding acetonitril containing cation $[(PPh_3)_2Pt(CNMe)(NCMe)]^{2+}$ [4]. It was postulated that the formation of this species involved an intermediate with a molecule of carbon monoxide bonded to the metal, but such an intermediate could not be isolated. We describe here a new type of reaction of isocyanide derivatives with KOH to give a stable carbonyl compound containing a new chelating ligand.

The reaction of $[Fe(dppe)(CNR)_4](ClO_4)_2$ (Ia: R = Ph, Ib: R = *p*-tol) [5] with an excess of KOH in CH_2Cl_2 affords the neutral complexes [Fe(dppe)(CO)(CNR)(RN=C–NR–C=NR) (IIa and IIb respectively) [6 *]. In addition to the bands at 2090 and 1950 cm^{-1} assignable to terminally bonded isocyanide and carbonyl

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* A reference number marked with an asterisk indicates a note in the list of references.

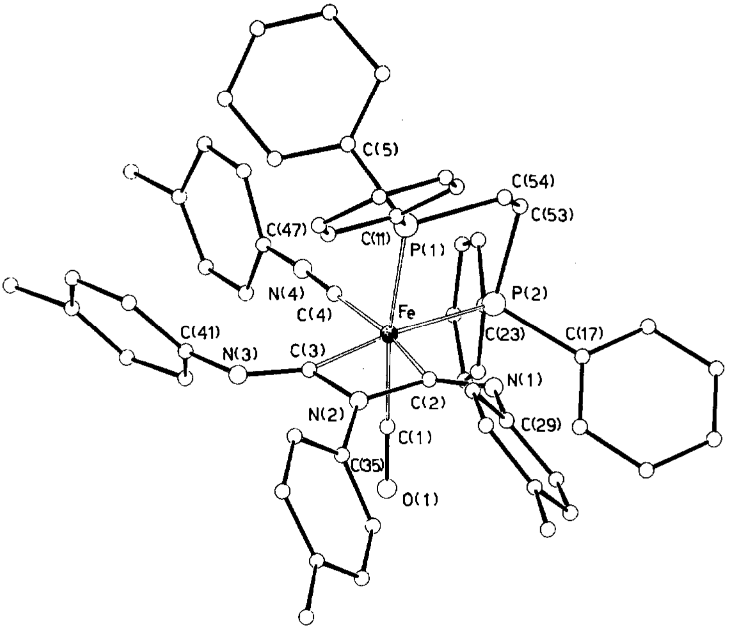

Fig. 1. View of the structure of complex IIb with the atomic numbering scheme. Important bond distances (Å) and angles (°): Fe–P(1) 2.252(3), Fe–P(2) 2.241(4), Fe–C(1) 1.756(11), Fe–C(2) 1.996(8), Fe–C(3) 2.002(12), Fe–C(4) 1.829(9), C(4)–N(4) 1.167(12), C(3)–N(3) 1.278(16), C(3)–N(2) 1.381(11), C(2)–N(2) 1.394(15), C(2)–N(1) 1.252(12), C(1)–O(1) 1.148(14); N(3)–C(3)–Fe 143.6(9), N(3)–C(3)–N(2) 121.1(10), N(2)–C(3)–Fe 95.2(7), C(3)–N(2)–C(2) 103.3(8), N(2)–C(2)–Fe 95.0(6), N(2)–C(2)–N(1) 130.5(9), N(1)–C(2)–Fe 134.4(8), Fe–C(1)–O(1) 177(1).

groups, respectively, compounds IIa and IIb show absorptions at 1630 and 1560 cm^{-1} in the region for C=N stretching frequencies. In order to elucidate unequivocally the structures of these compounds, a single crystal X-ray study of the diethyl ether solvate IIb was undertaken.

Crystal data: $C_{58}H_{52}FeN_4OP_2 \cdot C_4H_{10}O$, $M = 1012.99$, triclinic, space group $P\bar{1}$, a 14.815(7), b 15.428(8), c 12.797(7) Å, α 107.92(3), β 98.27(2), γ 94.42(3)°, V 2731(2) Å^3, $Z = 2$, D_c 1.232 g cm^{-3}, $F(000)$ 1068, μ(Mo-K_α) 3.77 cm^{-1}. The intensities of 8376 independent reflections were measured on a Siemens AED diffractometer (with θ in the range 3–24°); niobium-filtered Mo-K_α radiation and the $\theta/2\theta$ scan technique were used. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 4269 observed reflections (with $I \geqslant 2\sigma(I)$). The diethyl ether molecule of crystallization was found to be disordered and distributed between two positions of equal occupancy factors. Final R and R_w values were 0.092 and 0.098 *.

The structure of IIb is represented in Fig. 1 together with selected bond distances and angles. The iron atom is in a distorted octahedral arrangement, being coordinated by a carbon atom, C(1), from a terminal carbonyl group, a carbon atom, C(4),

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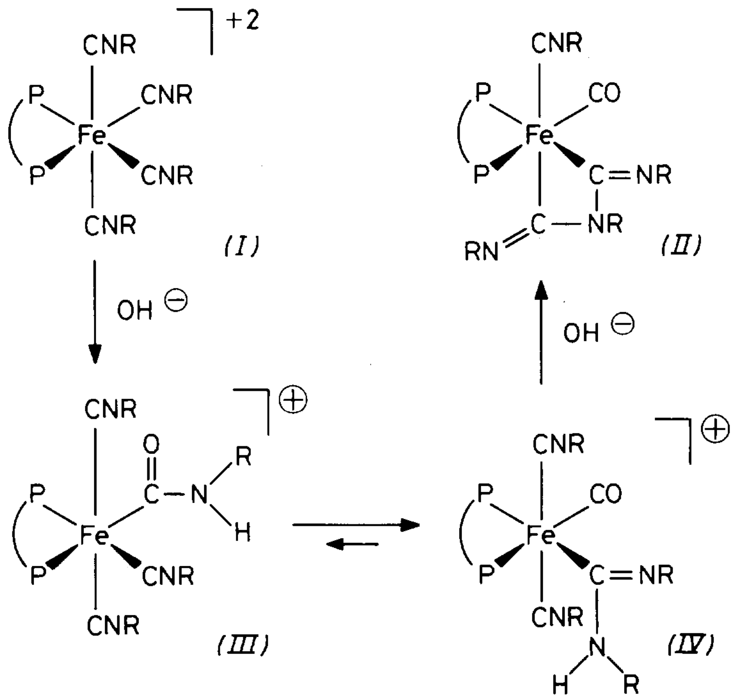
* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield road, Cambridge CB2 1EW, Great Britain.

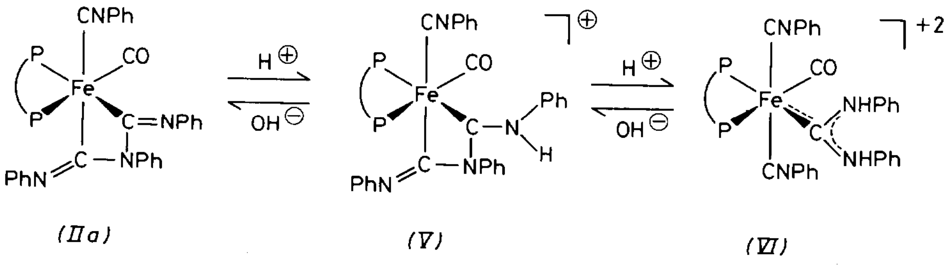


SCHEME 1.

from an isocyanide ligand, two phosphorus atoms from a chelating dppe ligand and two carbon atoms, C(2) and C(3), from a substituted chelating bis(iminomethyl)-amine ligand.

The N(3)C(3)N(2)C(2)N(1) moiety of this last ligand is roughly planar, the deviations from the mean plane through N(3), C(3), N(2), C(2) and N(1) being 0.05(1), −0.03(1), −0.03(1), −0.04(1) and 0.05(1) Å respectively. It is noteworthy the relative positions of the *p*-tolyl substituents of the nitrogen atoms in the ligand, as the N(3)–C(41) bond is *anti* to the C(3)–N(2) bond, whereas the N(1)–C(29) bond is *syn* to the C(2)–N(2) bond, probably owing to steric hindrance by the bulky diphosphine ligand.

A possible mechanism of formation of the complexes II is shown in Scheme 1. Initial attack on the isocyanide by KOH affords the carbamoyl derivative III,



SCHEME 2.

which, as previously reported [7], is in equilibrium with the more stable amidinium compound IV. Finally a new attack by KOH gives the neutral compound II.

Complex IIa can be protonated with 1% perchloric acid to give $\{\overline{\mathrm{Fe(dppe)(CO)(CNPh)[PhN{=}C{-}NPh{-}C}}\mathrm{(NHPh)}\}[\mathrm{ClO_4}]$ (V) (see Scheme 2), which undergoes a second protonation on treatment with 70% perchloric acid to give *trans*-$\{\mathrm{Fe(dppe)(CO)(CNPh)_2[C(NHPh)_2]}\}[\mathrm{ClO_4}]_2$ (VI) [6]. The protonation reaction is reversible, thus treatment of VI with KOH in CH_2Cl_2 gives V in a first step, and compound II is also obtained if the reaction time is prolonged. The pattern of ν(CN) and ν(CO) bands for V is similar to that for II, whereas for compound VI there are two absorptions in the ν(CN) region (2178w and 2148vs cm^{-1}); these are probably due to the A′ and A″ modes (C_s symmetry) in a *trans* arrangement of the isocyanide ligands, indicating that the chelating ring has been opened.

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6 IIa: IR (Cl_2CH_2): ν(CN) 2090s cm^{-1}, ν(CO): 1950s cm^{-1}, not enough soluble for NMR study. IIb: IR (Cl_2CH_2) ν(CN) 2090s cm^{-1}, ν(CO) 1950s cm^{-1}; $^{31}P\{^1H\}$ NMR δ 79.8(d), 74.5(d) ppm, J(PP) 20 Hz. V: IR (Cl_2CH_2): ν(CN) 2125s cm^{-1}, ν(CO) 1982s cm^{-1}; Λ_M 122 Ω^{-1} cm^2 mol^{-1} in acetone 5×10^{-4} M; $^{31}P\{^1H\}$ NMR: δ 71.8(d), 75.4(d) ppm, J(PP) 19 Hz, VI: IR (Cl_2CH_2): ν(CN) 2178w, 2148vs cm^{-1}, ν(CO) 2048s cm^{-1}; Λ_M 220 Ω^{-1} cm^2 mol^{-1} in acetone 5×10^{-4} M; $^{31}P\{^1H\}$ NMR: δ 68.1(d), 71.7(d) ppm, J(PP) 18 Hz. Positive phosphorus chemical shifts are downfield relative to external H_3PO_4.
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