# Evidence of π,π-Co-ordination of 1,4-Diazabuta-1,3-dienes (dab) after Photolysis of [Fe(CO)$_3$(dab)] in Argon and Carbon Monoxide Matrices at 10 K

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It is shown that 1,4-diazabuta-1,3-diene (dab) ligands containing substituents on the nitrogen atoms which are not too bulky can undergo a changeover from σ,σ-*N,N'* to π,π-co-ordination in [Fe(CO)$_3$(dab)] if this complex is irradiated in an Ar or CO matrix at 10 K into its lowest energy absorption band.

The co-ordinating properties of 1,4-diazabuta-1,3-dienes (dab; $R^1N{=}CR^2{-}CR^3{=}NR^1$) are well established. These properties and the chemistry of metal–dab complexes have been reviewed recently by Vrieze and Van Koten.[1] So far π,π-co-ordination, commonly observed for butadienes in low-valence metal complexes, has only tentatively been proposed for cyclic dab ligands,[2] but it has not been found for normal open-chain dab ligands. Here we report the first evidence for π,π-co-ordination *via* both C=N bonds of simple dab ligands in [Fe(CO)$_3$(dab)] after photolysis in an Ar or CO matrix at 10 K. The preparation, structural, and bonding properties of some of these complexes have been described,[3,4] while their

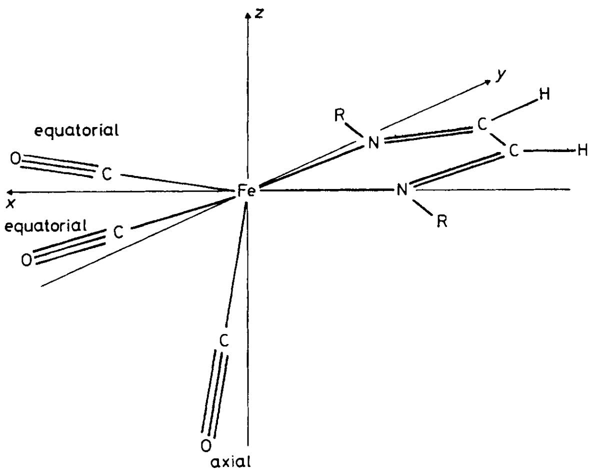

**Figure 1.** Molecular structure of [Fe(CO)$_3$(dab)].

thermal and photochemical reactions in solution have been studied by Trogler *et al.*[5,6] The structure shown in Figure 1 demonstrates the σ,σ-*N*,*N'*-co-ordination of the dab ligand.

These complexes all possess allowed electronic transitions at about 500 nm, which have been shown by M.O. calculations and resonance Raman (r.R.) spectroscopy[4] to be accompanied by only minor changes in the conformation of the complex. In contrast with this, the complexes all show high quantum yields (Φ *ca.* 0.2) for photosubstitution of a carbonyl ligand by nucleophiles upon irradiation into this absorption band.[6,7] Because of these small conformational changes in the excited state, the photochemistry of these and the corresponding tetra-azadiene complexes has been explained by Trogler *et al.*[6] as involving a fast conversion of electronic into vibrational energy. As a result of the excess of vibrational energy the metal–carbon bond will then be broken. However, this dissociative mechanism cannot explain why all [Fe(CO)$_3$(dab)] complexes are photochemically stable in solution *in the absence* of a substituting ligand. In order to elucidate the mechanism of this photochemistry the complex [Fe(CO)$_3$-(chxdab)] (chxdab = $C_6H_{11}N{=}CHCH{=}NC_6H_{11}$) was photolysed in an Ar matrix at 10 K. Figure 2 shows the i.r. spectral changes of this complex in the CO stretching region after different times of irradiation (λ 514.5 nm) in an Ar matrix at 10 K. The spectra were measured on a Nicolet 7199 B FT-IR interferometer with a liquid nitrogen-cooled HgCdTe-detector.

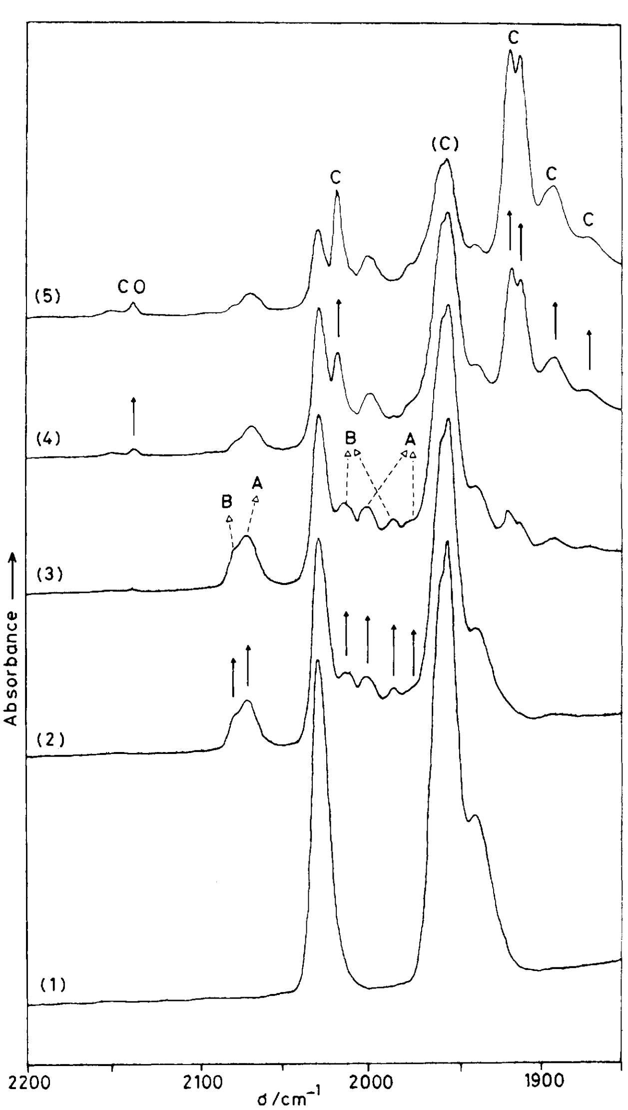

**Figure 2.** I.r. spectral changes of the carbonyl stretching modes of [Fe(CO)$_3$(chxdab)] in an Ar matrix at 10 K after irradiation at λ = 514.5 nm (*p* = 100 mW). Irradiation times: (1), 0 min; (2), 15 min; (3), 50 min; (4), 2 h; (5), 6 h.

The parent compound (spectrum 1) shows the three vibrations of the Fe(CO)$_3$ moiety, which has $C_s$ symmetry in the complex.[4] After 15 min of irradiation new bands appear at 2077, 2069, 2012, 2001, 1984, and 1972 cm$^{-1}$ (spectrum 2). No free carbon monoxide is then detected. This photoproduct will therefore contain the same Fe(CO)$_3$ moiety as the parent compound, although its carbonyl vibrations are clearly shifted to higher frequency. The six new bands can be assigned to two different isomers (A) and (B). This assignment is supported by the observation that the bands assigned to isomer (B) disappear more rapidly upon further irradiation than those of isomer (A) (see spectra 4 and 5). Also, in N$_2$ and CO matrices only the three bands of isomer (A) are observed. Upon annealing at 30 K these bands are replaced by those of isomer (B) owing to isomerization. These isomers most probably differ in the orientation of the Fe(CO)$_3$ group with respect to the dab ligand. The shift to higher frequency indicates a decrease of the iron-to-carbonyl π-back-bonding, which implies an increase of π-back-bonding from iron to the dab ligand. The latter effect can take place as a result of a change-over from σ,σ-*N*,*N'* chelation to π,π-co-ordination of the dab-ligand. In fact, the CO frequencies of both isomers (A) and (B) agree well with those of [Fe(CO)$_3$($\eta^4$-butadiene)].[8] This assignment is supported further by the changes in the i.r. spectra of the complex in a CO matrix between 1300 and 1500 cm$^{-1}$ (Figure 3). In this region the parent compound has $\nu_S$(CN) at 1480 cm$^{-1}$ and ν(CC) at 1343 cm$^{-1}$, while the band at 1453 cm$^{-1}$ arises from a CH bending mode (spectrum i, Figure 3). Upon irradiation, the bands due to $\nu_S$(CN) and ν(CC) disappear and two new bands appear at 1365 and 1349 cm$^{-1}$ (spectrum ii). These bands are attributed to $\nu_S$(CN) and ν(CC) of the π,π-co-ordinated dab. This assignment agrees with our expectation of a large shift of $\nu_S$(CN) to lower frequency and a small shift of ν(CC) to higher frequency on going from σ,σ- to π,π-co-ordination, since the lowest π* level of dab is antibonding between C and N and bonding between the C-atoms of the di-imine group. After prolonged irradiation this photoproduct decomposes and a second photoproduct is formed with release of carbon monoxide. The CO

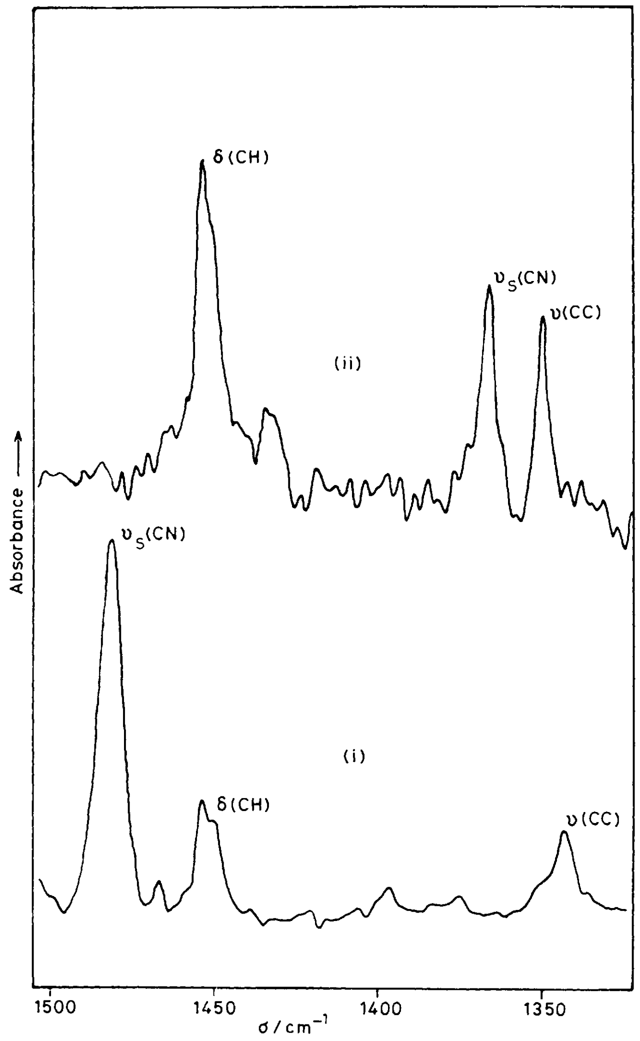

**Figure 3.** I.r. spectra (1300—1500 cm$^{-1}$) of (i) [Fe(CO)$_3$(chxdab)] and (ii) of its first photoproduct in a CO matrix at 10 K. Spectrum (ii) was obtained by subtraction of (i) from a spectrum taken after 15 min of irradiation at $\lambda$ = 514.5 nm ($p$ = 40 mW).

frequencies of this second product (Figure 2, bands C) are only slightly shifted to higher frequency with respect to those of [Fe(CO)$_2$L($\sigma$,$\sigma$-*N*,*N*′-dab)] complexes (L = *N*- or *P*-donor ligand) and are therefore assigned to the [Fe(CO)$_2$($\sigma$,$\sigma$-*N*,*N*′-dab)] fragment.

Complexes with more bulky dab ligands such as Bu$^t$N=CHCH=NBu$^t$ and Pr$^i_2$CHN=CHCH=NCHPr$^i_2$ show only weak bands due to the $\pi$,$\pi$-co-ordinated complex. Apparently, $\pi$,$\pi$-co-ordination is only favourable for dab ligands with small substituents at the co-ordinating nitrogen atoms. This is also evident from our observation that for the *N*,*N*′-bis-(2,6-diisopropylphenyl)-dab complex only the second photoproduct is observed, but for the corresponding bis-(*p*-tolyl)-dab complex the first one is observed also. $\pi$,$\pi$-Co-ordination is very unlikely for iminomethyl pyridine ligands ($C_5H_4N$–CH=NR) and indeed no such photoproduct is observed for complexes of these ligands. From the fact that these latter complexes are not photolysed at all in matrices, it can be concluded that $\pi$,$\pi$-co-ordination is a necessary primary step for the formation of the second photoproduct. The implications which these results have for the mechanism of the photochemistry of these complexes in solution will be discussed elsewhere.[7]

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