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New Aspects of the Reaction between tBu–N=CH–CH=N–tBu and $Fe_2(CO)_9$, solving the Controversy about the Coordination Mode of the DAB Ligand in $Fe(CO)_3$ (tBu–N=CH–CH=N–tBu) (DAB = 1,4-diazabutadiene)

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$Fe_2(CO)_9$ and tBu–N=CH–CH=N–tBu react to form $Fe(CO)_3$(tBu–N=CH–CH=N–tBu), tBu–N–CH=CH–N–(tBu)–CO and $Fe(CO)_5$ in equimolar amounts. The $Fe(CO)_3$(tBu–N=CH–CH=N–tBu) complex contains the DAB (1,4-diazabutadiene) ligand in the σ,σ-coordination mode, which is in contradiction with the earlier assumption that the DAB ligand is σ,π-coordinated.

tBu–N–CH=CH–N–(tBu)CO can be prepared by reacting DAB with CO in a pressure vessel, using $Fe_2(CO)_9$ as a catalyst. Only three catalytic cycles could be obtained using CO pressures ranging from 2.5 to 60 atm. A possible reaction mechanism is discussed.

Introduction

In the last few years many metal carbonyl DAB complexes have been prepared, containing the DAB ligand (1,4-diazabutadiene) in the σ,σ-coordination mode (*i.e.* coordination via the two lone pairs on nitrogen [1–10]), but only a few examples have been reported in which DAB uses its π-electrons for coordination. This coordination mode is very important for the activation and conversion of the C=N double bond [11, 12] and has been observed in $Fe_2(CO)_6$(DAB) [13], $Ru_2(CO)_6$(DAB) [12], $Os_2(CO)_6$(DAB) [14], $Os_3(CO)_9$(DAB) [14] and $MnCo(CO)_6$(DAB) [15]. In these complexes the DAB ligand is a six electron donor, bridging two metal atoms. The only example of a four electron σ,π-coordination mode was claimed by tom Dieck *et al.* in $Fe(CO)_3$(DAB) complexes [16]. This coordination mode only occurred when the group attached to the imine nitrogen atoms of the diimine skeleton contained a quaternary carbon atom. In all other cases σ,σ-coordination was observed, which was reported earlier by Otsuka [7] (Fig. 1).

Some controversy existed in the literature about the actual coordination mode of the DAB ligands in $Fe(CO)_3$(DAB). In cases where tom Dieck *et al.* claimed σ,π-coordination [16], Frühauf *et al.* did not observe the spectroscopic data on which the assumption of σ,π-coordination was based [13]. Since we considered mononuclear species with σ,π-coordinated DAB ligands as possible intermediates in the reaction mechanism for the formation of $Mo_2(CO)_6$(IAE) (IAE = bis(alkyliminoalkylamino)-ethane-N,N′) [11], we reinvestigated the reaction between tBu–N=CH–CH=N–tBu and $Fe_2(CO)_9$ in order to find out whether or not σ,π-coordination occurs in $Fe(CO)_3$(DAB). The ligand tBu–N=CH–CH=N–tBu was chosen as a representative of ligands for which σ,π-coordination was suggested.

Results

$Fe_2(CO)_9$ and tBu–N=CH–CH=N–tBu react in hexane forming an intense purple solution, containing three products. After separation, $Fe(CO)_3$(tBu–N=CH–CH=N–tBu), tBu–N–CH=CH–N–(tBu)–CO (di-tert.butyl-imidazolone) and $Fe(CO)_5$ were isolated in equimolar amounts indicating that $Fe_2(CO)_9$ and tBu–N=CH–CH=N–tBu react according to eqn. 1

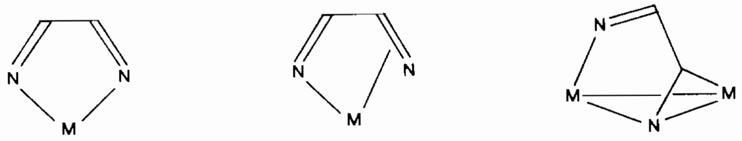

Fig. 1. The three coordination modes under discussion.

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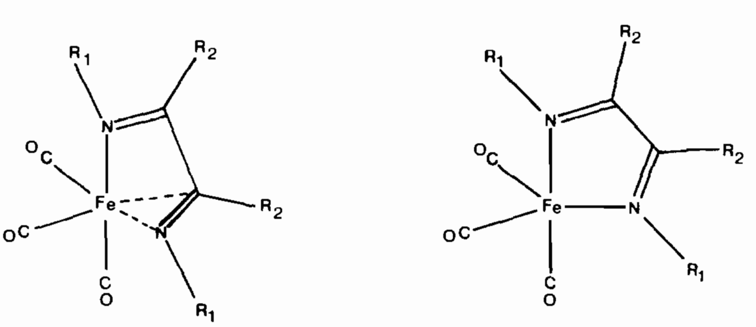

Fig. 2. The two proposed isomeric forms of $Fe(CO)_3(DAB)$.

TABLE I. NMR Data of $Fe(CO)_3$ (tBu–N=CH–CH=N–tBu) and $\overline{\text{tBu–N–CH=CH–N–(tBu)–CO}}$ (δ ppm relative to TMS).

^1H NMR							
$Fe(CO)_3(DAB)$ (lit. value)[a] [16]	1.44(tBu)	1.65(tBu)	6.35(im)	8.01(im)			
$Fe(CO)_3(DAB)$ (observed)[a]		1.64(tBu)		8.01(im)			
imidazolone[a]	1.44(tBu)		6.35(im)				
Fe(CO)(DAB)[b]	1.67(tBu)	7.64(im)					
imidazolone[b]	1.57(tBu)	6.23(im)					
13C NMR							
$Fe(CO)_3(DAB)$ (lit. value) [19]	28.2(tBu);	33.7(tBu);	54.6(tBu);	64.0(tBu);	106.5(im);	142.9(im)	216.3(CO)
$Fe(CO)_3(DAB)$ (observed)		33.8(tBu)		63.8(tBu)		142.8(im)	216.3(CO)
imidazolone	27.9(tBu)		54.3(tBu)		106.3(olefin C)	151.9(C=O)	

[a] Solvent C_6D_6. [b] Solvent $CDCl_3$.

$$Fe_2(CO)_9 + 2DAB \rightarrow Fe(CO)_3(DAB) + \overline{\text{R–N–CH=CH–N–(R)–CO}} + Fe(CO)_5 \qquad (1)$$

Imidazolone ($\overline{\text{R–N–CH=CH–N–(R)–CO}}$) has been found before as a side product of the reaction between $Fe_2(CO)_9$ and DAB [13]. Our results show that exactly 50% of the DAB present in the reaction mixture reacts with one of the carbonyls of $Fe_2(CO)_9$, to form the five-membered ring imidazolone, which is a cyclic urea. Since ureas and cyclic ureas have extensive pharmaceutical and industrial applications [17, 18], we tried to convert the imidazolone formation into a catalytic process, in which we succeeded only partially.

When the reaction between $Fe_2(CO)_9$ and tBu–N=CH–CH=N–tBu was carried out under carbon monoxide in a pressure vessel at 60 °C, di-tert.butyl-imidazolone was obtained in a 3 to 1 molar ratio with respect to the catalyst $Fe_2(CO)_9$, using forty times excess of tBu–N=CH–CH=N–tBu and a CO pressure of 2.5 atm. Varying the CO pressure between 2.5 atm and 60 atm and altering the ratio DAB to $Fe_2(CO)_9$ from 25 to 1 up to 100 to 1, did not influence the yield of di-tert.butyl-imidazolone (relative to $Fe_2(CO)_9$). The imidazolone formation was also temperature independent between 20 °C and 60 °C.

NMR Data

The two proposed isomeric forms of $Fe(CO)_3(DAB)$, which are shown in Fig. 2, can easily be distinguished by NMR spectroscopy. The two imine protons are expected to give a singlet in the ^1H NMR spectra near 8 ppm [1, 3, 4]. In the ^{13}C NMR spectra one signal is observed for the imine carbon atoms near 140 ppm [19], which is 20 ppm upfield as compared with the free ligands [4].

The ^1H NMR chemical shifts reported earlier [16] for $Fe(CO)_3$-(tBu–N=CH–CH=N-tBu) are 8.01 and 6.35 ppm for the imine protons and 1.65 and 1.44 ppm for the tert.butyl groups. The upfield shift of one of the two imine protons was explained by π-coordination of one of the C=N moieties, while the asymmetry in the coordinated ligand seemed confirmed by the appearance of two signals for the tert. butyl groups. However, the two inequivalent imine protons did not give an AX-pattern as has been observed in $M_2(CO)_6(DAB)$ complexes (M = Fe, Ru,

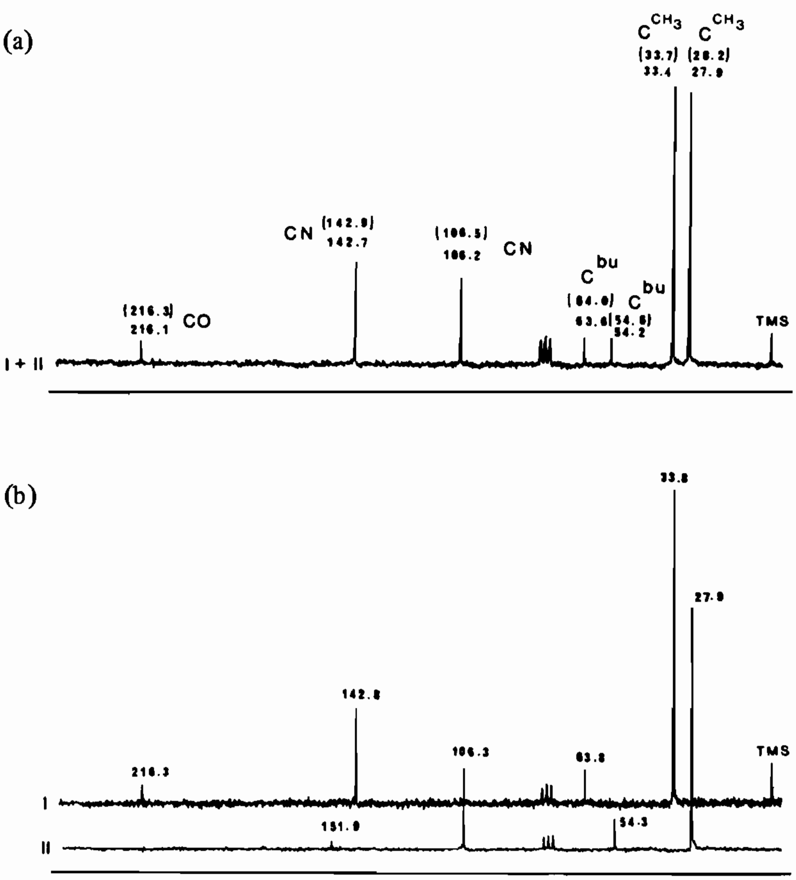

Fig. 3. a. ^{13}C NMR spectrum of the crude reaction product of $Fe_2(CO)_9$ and tBu–N=CH–CH=N–tBu, which is in perfect agreement with the literature assignment [19]. b. ^{13}C NMR spectra of pure $Fe(CO)_3$(tBu–N=CH–CH=N–tBu) and pure tBu-imidazolone after separation.

Os; Mn, Re–Co) [12–15], for which σ,π-coordination has been established. As an even more convincing evidence for the σ,π-coordination mode in $Fe(CO)_3$-(tBu–N=CH–CH=N-tBu) the ^{13}C-NMR data have been published by Liebfritz and tom Dieck: *i.e.* 142.9 and 106.5 ppm for the imine carbon atoms 64.0 and 54.6 ppm for the quaternary carbon atoms of the tert.butyl groups and 33.7 and 28.2 ppm for the methyl carbon atoms of the tert.butyl groups [19] (Table I).

The ^1H NMR spectrum of $Fe(CO)_3$(tBu–N=CH–CH=N–tBu) which we have prepared, contained exclusively one singlet at 8.01 ppm for the imine protons and one singlet at 1.65 ppm for the tert. butyl groups. These data clearly demonstrate that the ligand is in the σ,σ-coordination mode. It is important to note that we observed the chemical shifts of di-tert.butyl-imidazolone at 6.35 ppm (olefinic protons) and 1.44 ppm (tBu). A combination of the chemical shifts of $Fe(CO)_3$(tBu–N=CH–CH=N–tBu) and di-tert.butyl-imidazolone gives the values reported earlier in the literature for the σ,π-coordinated DAB ligand in $Fe(CO)_3$(tBu–N=CH–CH=N–tBu) [16]. Obviously the complexes for which σ,π-coordination was claimed by tom Dieck *et al.* in fact were mixtures of $Fe(CO)_3$(DAB) and imidazolone, in a one to one molar ratio.

This conclusion is furthermore confirmed by ^{13}C NMR data. In Fig. 3b the ^{13}C NMR spectra are shown of $Fe(CO)_3$(tBu–N=CH–CH=N–tBu) containing only the signals at 142.8, 63.8 and 33.8 ppm for the coordinated DAB ligand and of tBu-imidazolone containing the signals at 151.9 (C=O), 106.3 (olefin C), 54.3 (tBu) and 27.9 ppm (tBu). The spectrum shown in 3a, which has been interpreted as resulting from σ,π-coordination [19] and which has been published as additional evidence for this coordination mode [19], is the sum of the spectra shown in Fig. 3b.

The ^1H NMR and ^{13}C NMR data show that the σ,π-coordination mode does not exist in $Fe(CO)_3$-(DAB) complexes.

Mass Spectrometry

The composition of $Fe(CO)_3$(tBu–N=CH–CH=N–tBu) is confirmed by mass spectrometry. The observed fragmentation is given in Table II.

TABLE II. Observed Fragmentation of $Fe(CO)_3(tBu\text{–}N{=}CH\text{–}CH{=}N\text{–}tBu)$.

Fragment	m/e
$[Fe(CO)_3(tBu\text{–}N{=}CH\text{–}CH{=}N\text{–}tBu]^+$	308
$[Fe(CO)_2(tBu\text{–}N{=}CH\text{–}CH{=}N\text{–}tBu]^+$	280
$[Fe(CO)(tBu\text{–}N{=}CH\text{–}CH{=}N\text{–}tBu]^+$	252
$[Fe(tBu\text{–}N{=}CH\text{–}CH{=}N\text{–}tBu]^+$	224
$[Fe(tBu\text{–}N{=}CH\text{–}CH{=}N\text{–}C(CH_3)_2]^+$	209
$[tBu\text{–}N{=}CH\text{–}CH{=}N\text{–}tBu]^+$	168
$[(tBu\text{–}N{=}CH\text{–}CH{=}N\text{–}C(CH_3)_2]^+$	153
Fe^+	56

Discussion

In the discussion of the formation of $Mo_2(CO)_6$-(IAE) (IAE = bis(alkyliminoalkylamino)ethane) we considered σ,π-coordinated DAB ligands as possible intermediates. For the only precedent known in the literature of a four electron σ,π-coordination mode we have shown now that it does not exist. However, we have evidence that σ,π-coordination really appears to be an important feature in the activation of the C=N bond with respect to the C–C bond formation. In the syntheses of $Ru_2(CO)_n(IAE)$ (n = 4 or 5) we isolated $Ru_2(CO)_6(DAB)$ as an intermediate which contains DAB in a six electron σ,π-coordination mode [12].

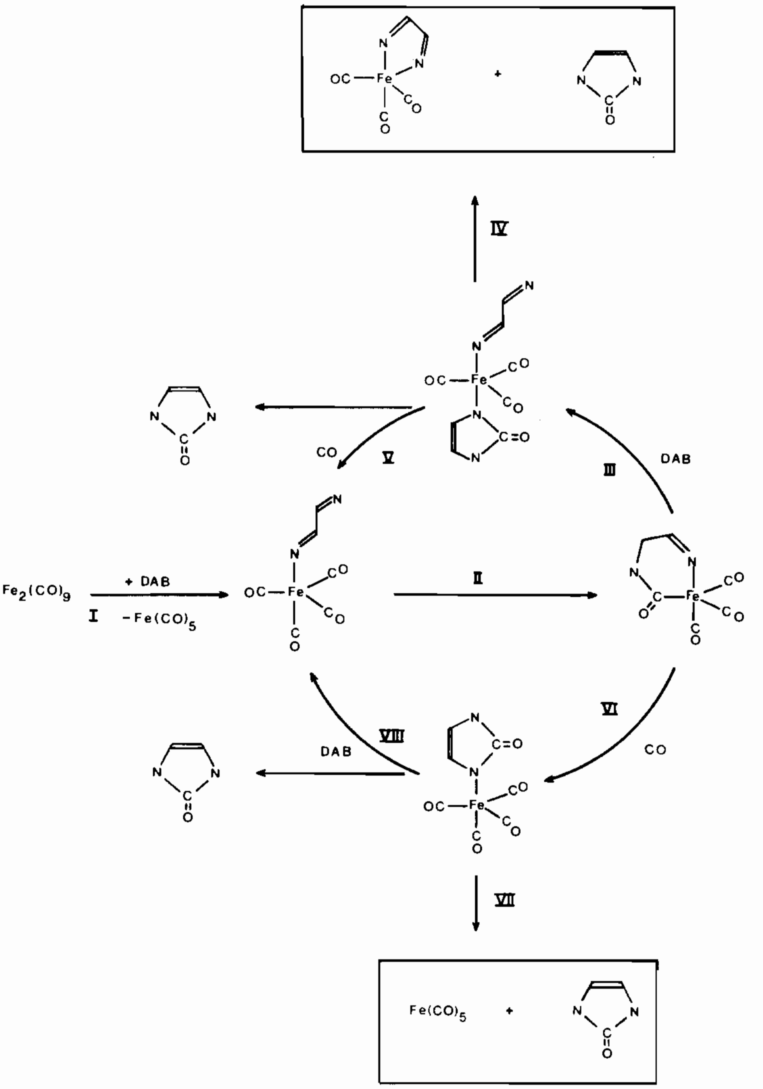

Fig. 4. Proposed reaction scheme for the formation of imidazolone.

A striking feature of the reaction between $Fe_2(CO)_9$ and tBu–N=CH–CH=N–tBu is that di-tert. butyl-imidazolone is formed in equimolar amounts with $Fe(CO)_3$(tBu–N=CH–CH=N–tBu). This gives important information about a possible reaction mechanism. Since the reaction is not a simple substitution of CO, which is obvious from the molar ratio of the reaction products (see eqn. 1), the first step in the reaction sequence must be addition of DAB to $Fe_2(CO)_9$. Consequently, the metal carbonyl dimer will break, forming $Fe(CO)_5$ and $Fe(CO)_4$(DAB). In the latter complex, for which we propose a structure analogous to $Fe(CO)_4$(pyridine) and $Fe(CO)_4$(pyrazine) [20], the DAB ligand is coordinated as a monodentate. This coordination mode has been observed before in $Cr(CO)_5$(DAB) [1], R_3PPtCl_2(DAB), and *trans*-$Cl_2Pd(DAB)_2$ [21]. For the next step in the reaction mechanism we assume *cis–trans* isomerization of the DAB ligand, followed by nucleophilic attack of the free C=N fragment on one of the carbonyls in the equatorial plane. A six membered ring is formed containing a ketone. Nucleophilic attack of a C=N fragment on a carbonyl has earlier been observed by de Roode in $M(\pi\text{-}C_5H_5)$(HC-(N-phenyl)N(CO)phyenyl)$(CO)_2$ [22] (M = Cr, Mo, W).

When the reaction is carried out under nitrogen, ring closure will occur involving attack of a DAB ligand forming $Fe(CO)_3$(DAB)(imidazolone). Because of the very poor coordination properties of imidazolone, it can easily be displaced by the uncoordinated C=N fragment of the monodentate DAB ligand, forming $Fe(CO)_3$(DAB) and imidazolone. This mechanism is shown in Fig. 4, reaction steps I, II, III and IV.

When the reaction is carried out under CO pressure, the situation is much more complicated as is shown in Fig. 4. There are several competing reactions, III and VI, IV and V, VII and VIII, of which IV and VII terminate the cyclic process. Reaction route IV has already been discussed above and depends on the DAB present in the reaction mixture, while reaction VII involves CO in the displacement reaction, which must be present to make the reaction catalytic. It was obvious from the colour of the reaction mixture directly after the reaction under CO, that at low pressures termination reaction IV was important, forming the highly coloured $Fe(CO)_3$(DAB). At high CO pressure the resulting reaction mixture was almost colourless, which means that reaction VII must have been the terminating step.

Although the proposed mechanism is speculative, it can rationalize the formation of $Fe(CO)_5$, $Fe(CO)_3$(DAB) and imidazolone in 1:1:1 molar ratio under stoichiometric conditions, as well as the catalytic formation of imidazolone under CO pressure. Furthermore, the model explains why the reaction is rapidly terminated under low as well as under high CO pressures.

Experimental

The ^1H NMR spectra have been recorded using a Varian T60 spetrometer, the ^{13}C NMR spectra have been obtained with a Varian CFT 20 equipment, the IR spectra with a Perkin-Elmer 283 infrared spectrophotometer and the mass spectra using a Varian Mat 711.

Hexane was distilled from P_2O_5 before use.

tBu–N=CH–CH=N–tBu

Glyoxal (100 mmol; 30% solution in water) and 200 mmol of tBu–NH_2 were stirred for ½ h in 200 ml of water. The crude reaction product precipitates as a white solid and was filtered of. The white solid materials was dissolved in 100 ml of hexane and the water was separated from the hexane layer. The solution was dried on $MgSO_4$ and the pure product was obtained by crystallization at –70 °C, yielding 60% of white crystals.

$Fe(CO)_3$(tBu–N=CH–CH=N–tBu) and tBu–N–CH=CH–N–(tBu)CO

$Fe(CO)_3$(tBu–N=CH–CH=N–tBu) and tBu–N–CH=CH–N–(tBu)CO have been prepared as described earlier [7, 13], using silicagel 60 that was dried and deoxygenated at 180 °C at 10^{-3} mm Hg for at least 3 h.

Catalytic Formation of tBu–N–CH=CH–N–(tBu)CO

The reactions were carried out in an autoclave of 25 ml using 30 ml of hexane. After the reaction the $Fe(CO)_3$(tBu–N=CH–CH=N–tBu), which was formed also, was destroyed by stirring the solution in the air after which the solution was filtered over filter earth. The hexane was removed under vacuum without any warming and the yield of imidazolone was determined by integrating the NMR spectrum of the product mixture, which always consisted of tBu-imidazolone and tBu–N=CH–CH=N–tBu. Determination of the molar ratio of these two products by HPLC gave the same result.

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