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On the Mechanism of Formation of Dehydroguanidino-ironcarbonyl Complexes from Carbodiimides

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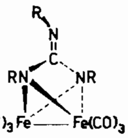
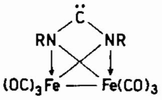
Symmetrical carbodimides, RN=C=NR, (R = ^{i}Pr and C_6H_{11}) are known to react with pentacarbonyliron, in refluxing heptane, to produce dehydroguanidinodiiron complexes (I) [1].



I

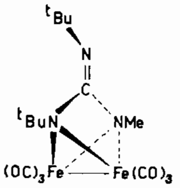


II

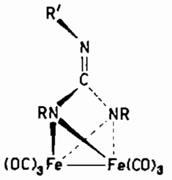
The formulation, which was originally suggested on spectroscopic grounds, was confirmed by a crystal structure determination of the cyclohexyl derivative, which showed that the coordinated nitrogen atoms were perpendicular to the axis of the Fe–Fe bond. In the cyclohexyl reaction, the isonitrile complex, $(C_6H_{11}NC)Fe(CO)_4$, was also isolated. The mechanism proposed for this interesting condensation–elimination reaction required, first, the formation of a dinuclear carbene complex (II). The carbene then combined with a further molecule of carbodiimide, with cleavage of a carbon–nitrogen double bond and elimination of isonitrile, to give (I). The isonitrile was trapped, in the reaction medium, as a tetracarbonyliron complex.

It occurred to us that the proposed mechanism could be easily tested by means of the corresponding reactions with unsymmetrical carbodiimides; if the postulate of a dinuclear carbene complex is correct, then no dehydroguanidino complex, in which both coordinated nitrogens bear the same substituent, should be obtained.

Methyl-t-butylcarbodiimide, MeN=C=N^{t}Bu, in its reaction with pentacarbonyliron, in refluxing heptane over 80 h, yielded two dehydroguanidino complexes, $[(^{t}BuN)_2(MeN)C]Fe_2(CO)_6$ (III) and $[(MeN)_2(^{t}BuN)C]Fe_2(CO)_6$ (IVa), and the two possible isonitrile compounds $^{t}BuNCFe(CO)_4$ and $MeNCFe(CO)_4$ (characterised by IR [2]), after column chromatography on alumina. The dehydroguanidinodiiron complexes were obtained as orange solids and characterised analytically and mass spectrometrically.



III



IVa (R = Me; R′ = ^{t}Bu)
IVb (R = Me; R′ = C_6H_{11})

Their formulation was established definitively by ^{1}H NMR spectroscopy in $CDCl_3$. Thus, the di-t-butyl derivative (III) showed two singlets for the t-butyl protons (δ 1.22 and 1.28 ppm, 18H) and another for the methyl protons (δ 2.93 ppm, 3H) at lower field. The dimethyl compound (IVa) gave only two signals; the resonance at δ 2.73 (6H) corresponded to the two equivalent methyl groups on the coordinated nitrogens, and the other, at δ 1.28 (9H), to the t-butyl protons on the uncoordinated nitrogen. The structural arrangement formally allows for more complex ^{1}H NMR spectra; thus, in the dimethyl compound, the environment of the methyl groups on the coordinated nitrogens is made strictly non-equivalent by the disposition of the t-butyl group on the imine nitrogen with respect to the Fe_2C plane. The failure to observe this additional complexity is probably an indication of a rapid flipping of the t-butyl substituent from one side to the other. Similarly, in the case of the previously reported dehydrotri-isopropylguanidino complex, only two sets of isopropyl signals were observed in the room temperature ^{1}H spectrum [1].

Dehydroguanidino complexes were also obtained from the reactions of MeN=C=N^{t}Bu with $Fe_2(CO)_9$ in refluxing hexane; overall the reaction times were shorter and the conditions milder (factors which should serve to reduce the possibility of intramolecular rearrangement of the dehydroguanidino-complexes), but yields of products were lower. In a corresponding reaction of $C_6H_{11}N{=}C{=}NMe$ with $Fe_2(CO)_9$, the formation of two dehydroguanidino compounds, together with $C_6H_{11}NCFe(CO)_4$, was inferred by infrared monitoring of the several chromatographic bands, but only one complex was isolable. It is formulated as (IVb) on the basis of its ^{1}H NMR spectrum which shows a singlet at δ 2.8, indicating the equivalence of the two methyl groups, and a complex band at δ 2.2–1.0 and a smaller broad resonance at δ 3.7, for the ring protons on the cyclohexyl group.

In the reactions with unsymmetrical carbodiimides, the observation of complexes with equivalent methyl groups is clearly incompatible with the proposed carbene mechanism. Our failure to observe the other symmetrical species, with equivalent t-butyl and cyclohexyl groups respectively, is interesting, and

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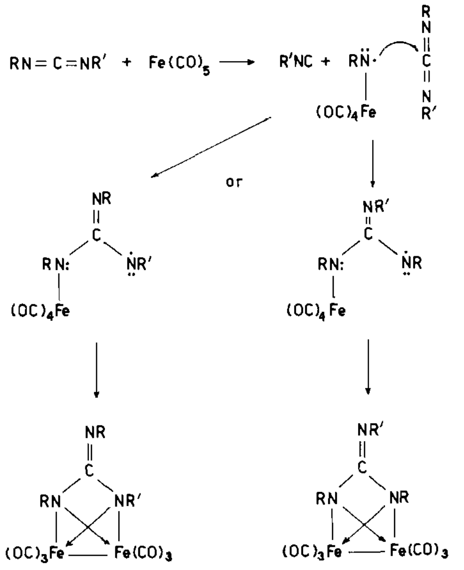

Scheme.

probably indicates a significant steric preference in the reaction. The steric influence of the t-butyl group is important in inhibiting other facile reactions of carbodiimides; for example di-t-butylcarbodiimide does not undergo a 1,2-addition reaction with methanol [3], and does not self-polymerise [4].

In view of the low yields of products obtained (around 5–10%) and the complexity of reaction (most of the iron carbonyl appears to be converted into red, gummy, air-sensitive materials, soluble only in polar solvents, and which possibly contain mixtures of metal carbonyl anions), we are cautious in offering our own mechanistic interpretation. However, we suggest that the initial formation of a mononuclear metal nitrene species, rather than a dinuclear carbene, might more satisfactorily explain the product distributions. The elimination of isonitrile would then occur in the first stage of the reaction, and the formation of the dehydroguanidine would then result from the attack of a further molecule of carbodiimide on the metal nitrene. The mechanism is represented in the Scheme. There is theoretically no restraint on combinations of the alkyl groups, and for an unsymmmetrical carbodiimide, four different products are possible.

As support for this reaction scheme, we note that several nitrene complexes of transition metals in low oxidation states have been reported (*e.g.* ^{t}BuN(π-CpNi)$_3$ [5] and (MeN)$_2$Fe$_3$(CO)$_9$ [6]). Additionally, the property of organic azides and isocyanates, which together with carbodiimides form part of the heterocumulene family, to act as precursors of nitrene species in organometallic chemistry, is well established [7]. Specifically, a similar mechanism has previously been suggested to rationalise the reactions of isocyanates and azides with iron carbonyls. Thus the formation of the urylene complex, [(MeN)$_2$CO]-Fe$_2$(CO)$_6$, from methylisocyanate, and of (PhN)$_2$-Fe$_2$(CO)$_6$ from azidobenzene, have been discussed in terms of the initial catalytic formation of an iron-nitrene complex [6]. Interestingly, the compound, (PhN)$_2$Fe$_2$(CO)$_6$, was found to decompose spontaneously in solution to give the urylene species [(PhN)$_2$CO]Fe$_2$(CO)$_6$, presumably by CO capture. However, in the reactions with carbodiimides, we were unable to detect urylene products, and this particular reaction pathway is clearly unimportant here.

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