1,4-Diazabutadienes—Another Example of n/π-Co-ordination Dualism[1]

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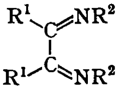
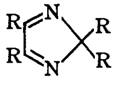
INVESTIGATIONS on dialkylcyanamides as potential π- or n-donating ligands revealed both types of co-ordination depending on the metal chosen. While zerovalent molybdenum or chromium form simple σ-complexes with these ligands,[2] both π- and n-co-ordination is used in dialkylcyanamide-carbonylnickel trimers.[3,4]

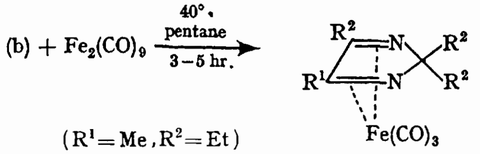
Theoretically, any hetero-multiple-bond system $C{=}\ddot{X}$ containing both π- and n-electrons should be capable of forming either bond type. The stability of the corresponding low-valent metal complexes can be discussed in terms of the ligand's donor and acceptor properties. 1,4-Diazabutadienes of type (a) are excellent n-ligands with zerovalent metals, not least because of their strong π-back-bonding capacity as is demonstrated by their electronic spectra.[5–8]

As n-terms are normally less stable than π-terms, thus giving rise to stronger ligand-to-metal bonds, the probability of π-bonding is small if (i) two or more n-orbitals are in geometrically favourable positions, while (ii) this probability is raised, if two π-donating sites can compete with one n-donor.


(a)

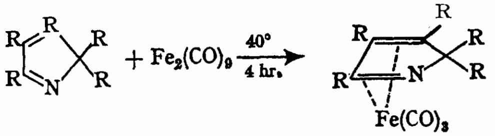

(b)

In open-chain [type (a)] and cyclic [type (b)] diazabutadienes, considerations (i) and (ii) are contrary, favouring π-donation from cyclic diazabutadienes. As expected, cyclic diazabutadienes (b) react under mild conditions in nonpolar solvents with di-iron enneacarbonyl to form orange-red, low-melting, air-sensitive complexes:



The tetra-alkylimidazolenineiron tricarbonyl obtained in 38% yield melts at 66° and starts to sublime at about 55—60°/10^{-2} torr. Its i.r. spectrum shows three carbonyl stretching absorptions at 2049, 1970, and 1940 cm.$^{-1}$, while the strong double-bond absorption of the free ligand at 1577 cm.$^{-1}$ is now hidden under the C–H deformation absorptions. In the mass spectrum, the parent peak appears as well as peaks of fragments originated by successive loss of carbon monoxide. On thermal decomposition the ligand is recovered quantitatively in pure form, this being a valuable method for separating tetra-alkylimidazolenines from their precursors in preparation.

Cyclic and open-chain monoazabutadienes have identical conditions (i)–(ii), thus both types of ligands should be equally able to form π-$Fe(CO)_3$ complexes. Open-chain complexes have recently been described,[8,9] while we report here such a complex from 2,2,3,4,5-pentamethylpyrrolenine:



This complex also shows three carbonyl absorptions at 2045, 1996, and 1940 cm.$^{-1}$. The melting point is 68—70°, but attempted sublimation resulted in decomposition, presumably due to impurities.

It is as yet an open question how far the π-co-ordinated diazabutadiene ring system (b) might deviate from planarity. The three carbonyl absorptions indicate a decrease from C_{3v} to C_{2v} local symmetry for the terminal CO groups. This might be due to partial σ-bond character of the nitrogen–iron bonds, but the same phenomenon is likewise observed with heavily substituted butadienes, *e.g.* in 1,2,3,4-tetraphenylbutadieneiron tricarbonyl.[10] Recently a tetra-azabutadieneiron complex has been prepared,[11] where the ligand might be either π- or n-co-ordinated.

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[1] For previous papers in this series, see refs. 2, 3, 5, and 6.

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