

Synthesis and Fluxional Character of Derivatives of the Type [HFe₃(CO)₁₀(μ₂-CNR₂)] and [HFe₃(CO)₉(μ₃-CH=NR)]

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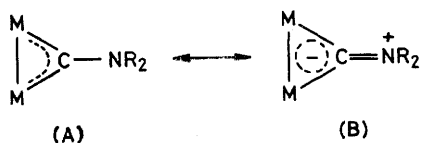
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Summary Isonitrile substitution at room temperature of [PPN][HFe₃(CO)₁₁] [PPN = (Ph₃P)₂N⁺] to yield the substituted anion [PPN][HFe₃(CO)₁₀(CNR)], followed by protonation or alkylation, gives complexes of the type [HFe₃(CO)₁₀(μ₂-CNR¹R²)] (R¹ = alkyl, R² = Et, H) which exhibit restricted rotation about the C-N bond; at higher

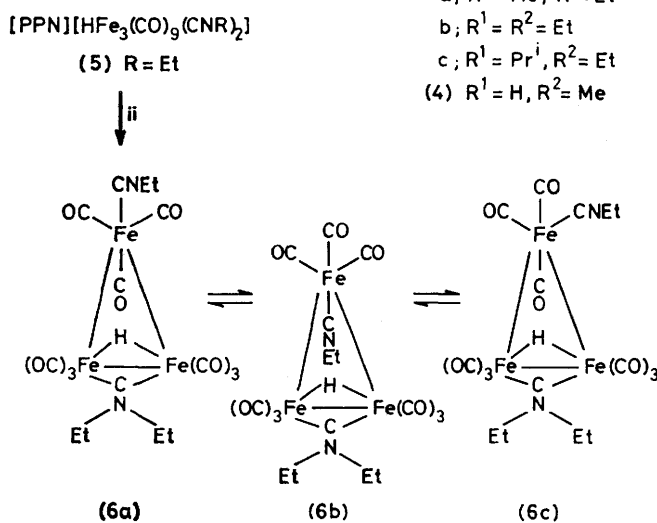
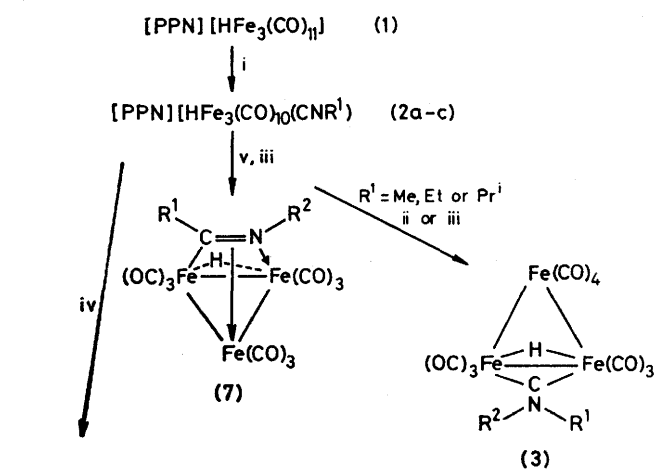
temperatures, products resulting from isonitrile insertion into the M-H bond may be observed.

THERE is currently some interest in the chemistry of cluster complexes containing bridging carbene or carbyne ligands,¹ and several reports have appeared describing the

preparation by diverse methods of derivatives containing a μ_2 -CNR₂ ligand.² X-Ray crystallographic and n.m.r. spectral data have been interpreted primarily in terms of the iminium structure (B). We report here a potential method for synthesis of complexes containing the μ_2 -CNR₂ ligand, together with the first example of restricted C-N bond rotation in such a complex.



Reaction of equimolar amounts of [PPN][HFe₃(CO)₁₁] (**1**)³ [PPN = (Ph₃P)₂N⁺] and R¹NC (R¹ = Me, Et, or Prⁱ) (Scheme 1) followed by alkylation and purification yields the complexes [HFe₃(CO)₁₀(CNR¹R²)] (**3a-c**), isolated as air-stable, red-purple solids [i.r. (**3c**) (hexane) 2082m, 2035s, 2023s, 2004m, 1994m, 1989sh, 1974m, and 1958w



SCHEME 1. Reagents and conditions: i, R¹NC, CH₂Cl₂, 25 °C, R¹ = Me, Et, or Prⁱ; ii, Et₃OBF₄, CH₂Cl₂, 25 °C; iii, HSO₃CF₃, Et₂O, 25 °C; iv, excess of EtNC, 25 °C, CH₂Cl₂; v, 40 °C, tetrahydrofuran.

cm⁻¹). The intermediacy of the substituted [PPN][HFe₃(CO)₁₀(CNR¹)] species (**2a-c**) thus seems likely, although we have not as yet attempted their isolation.

The variable-temperature ¹H n.m.r. spectra of (**3c**) best exemplify the phenomenon of C-N rotation (Figure). At -60 °C, the diastereotopic nature of the CH(CH₃)₂ resonance is clear (although superimposed on the CH₂CH₃ resonance), while the CH₂CH₃ resonance exhibits an AB pattern. On warming, changes typical of an exchanging system are observed; the high-temperature limiting spectrum exhibits a single CH(CH₃)₂ doublet and a simple quartet for the CH₂CH₃ resonance. From the coalescence temperature of the CH(CH₃)₂ resonance, an activation energy of 54 kJ mol⁻¹ may be calculated. Throughout, the M-H resonance at δ -18 remains sharp.

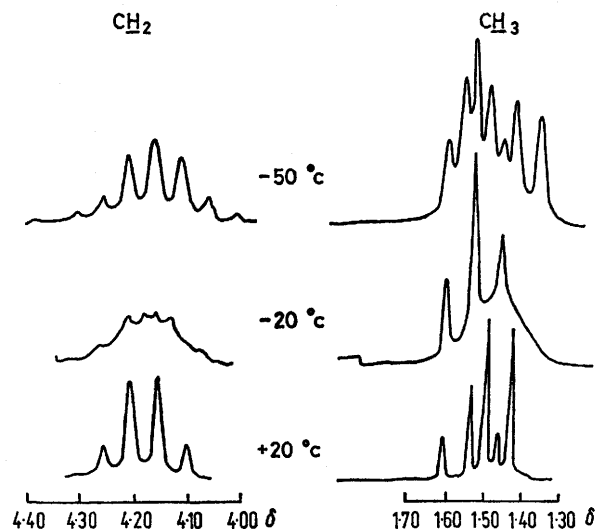


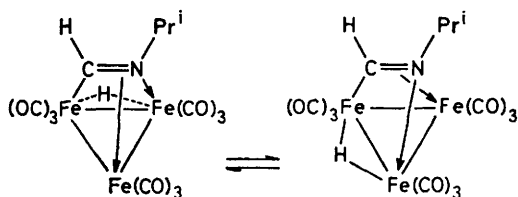
FIGURE. ¹H N.m.r. spectra of (**3c**) in CD₂Cl₂.

The results thus indicate that the carbyne structure (A) makes a significant contribution to the resonance hybrid. An independent fluxional process involving the carbonyl ligands is apparent from the ¹³C spectra, and will be discussed elsewhere.

Protonation of (**2a**) yields the expected complex (**4**) which decomposes in the solid state over a period of hours to yield [Fe₃(CO)₁₁(CNMe)]. It is known that protonation of (**1**) at -80 °C yields the analogous [HFe₃(CO)₁₀(COH)] which decomposes above -30 °C to give [Fe₃(CO)₁₂].⁴ More prolonged reaction of CNET with (**1**), followed by alkylation and purification, yields the monosubstituted [HFe₃(CO)₉(CNET₂)(CNET)] (**6**), presumably *via* the intermediacy of the disubstituted anion (**5**). The complexity of the i.r. spectrum of (**6**) (hexane, 2058m, 2016s, 2008s, 2000m, 1993m, 1900m, 1982m, 1976s, 1972sh, 1966sh, 1960m, 1950w, and 1938w cm⁻¹) indicates a mixture of isomers, and n.m.r. studies show clearly that the complex exists as the three interconverting isomers (**6a-c**).

If a solution of (**2c**) in tetrahydrofuran is heated at 40 °C for several hours, protonation yields not (**4**), but the μ_3 -formimidoyl derivative (**7**) (R¹ = H, R² = Prⁱ). This complex is clearly derived from insertion of co-ordinated isonitrile into the M-H-M bond of (**2c**). An isostructural

compound with $R^1 = \text{Me}$, $R^2 = \text{H}$ has been isolated from reaction of acetonitrile with $[\text{HFe}_3(\text{CO})_{11}]^-$,⁵ while $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{CNPh})]$ is known to undergo isonitrile insertion to yield a complex of similar structure. Complex (7) is also



SCHEME 2

fluxional. Thus, the ^1H n.m.r. spectrum at -50°C exhibits the two doublets expected for the $\text{CH}(\text{CH}_3)_2$ group on the basis of a static structure. On warming, broadening and coalescence yield eventually a single sharp doublet at 0°C . This is most likely associated with the process presented in Scheme 2.

We are currently exploring the generality of the synthetic method, and are examining the reactivity of the $\mu_2\text{-CNR}_2$ and $\mu_3\text{-CH=NR}$ ligands.

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