Synthesis and Fluxional Character of Derivatives of the Type $[HFe_3(CO)_{10}(\mu_2\text{-}CNR_2)]$ and $[HFe_3(CO)_9(\mu_3\text{-}CH{=}NR)]$

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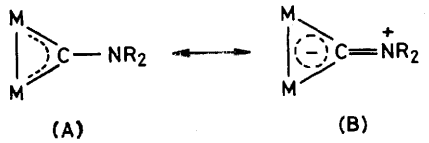
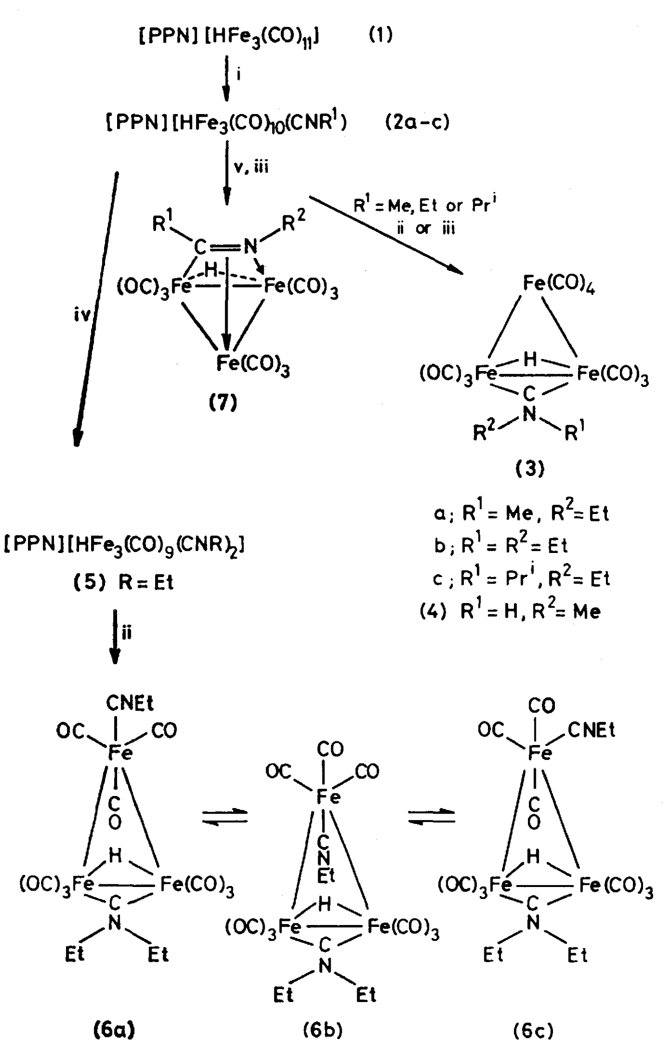
Summary Isonitrile substitution at room temperature of $[PPN][HFe_3(CO)_{11}]$ $[PPN = (Ph_3P)_2N^+]$ to yield the substituted anion $[PPN][HFe_3(CO)_{10}(CNR)]$, followed by protonation or alkylation, gives complexes of the type $[HFe_3(CO)_{10}(\mu_2\text{-}CNR^1R^2)]$ (R^1 = alkyl, R^2 = Et, H) which 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-CNR$_2$ 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-CNR$_2$ ligand, together with the first example of restricted C–N bond rotation in such a complex.



(A) (B)

Reaction of equimolar amounts of [PPN][HFe$_3$(CO)$_{11}$] (**1**)[3] [PPN = (Ph$_3$P)$_2$N$^+$] and R^{1}NC (R^1 = Me, Et, or Pr^i) (Scheme 1) followed by alkylation and purification yields the complexes [HFe$_3$(CO)$_{10}$(CNR^{1}R^2)] (**3a**—**c**), isolated as air-stable, red-purple solids [i.r. (**3c**) (hexane) 2082m, 2035s, 2023s, 2004m, 1994m, 1989sh, 1974m, and 1958w cm^{-1}]. The intermediacy of the substituted [PPN][HFe$_3$(CO)$_{10}$(CNR^1)] species (**2a**—**c**) thus seems likely, although we have not as yet attempted their isolation.



SCHEME 1. Reagents and conditions: i, R^{1}NC, CH$_2$Cl$_2$, 25 °C, R^1 = Me, Et, or Pr^i; ii, Et$_3$OBF$_4$, CH$_2$Cl$_2$, 25 °C; iii, HSO$_3$CF$_3$, Et$_2$O, 25 °C; iv, excess of EtNC, 25 °C, CH$_2$Cl$_2$; v, 40 °C, tetrahydrofuran.

The variable-temperature ^{1}H n.m.r. spectra of (**3c**) best exemplify the phenomenon of C–N rotation (Figure). At −60 °C, the diastereotopic nature of the CH(C*H*$_3$)$_2$ resonance is clear (although superimposed on the CH$_2$C*H*$_3$ resonance), while the C*H*$_2$CH$_3$ resonance exhibits an AB pattern. On warming, changes typical of an exchanging system are observed; the high-temperature limiting spectrum exhibits a single CH(C*H*$_3$)$_2$ doublet and a simple quartet for the C*H*$_2$CH$_3$ resonance. From the coalescence temperature of the CH(C*H*$_3$)$_2$ resonance, an activation energy of 54 kJ mol^{-1} may be calculated. Throughout, the M–H resonance at δ −18 remains sharp.

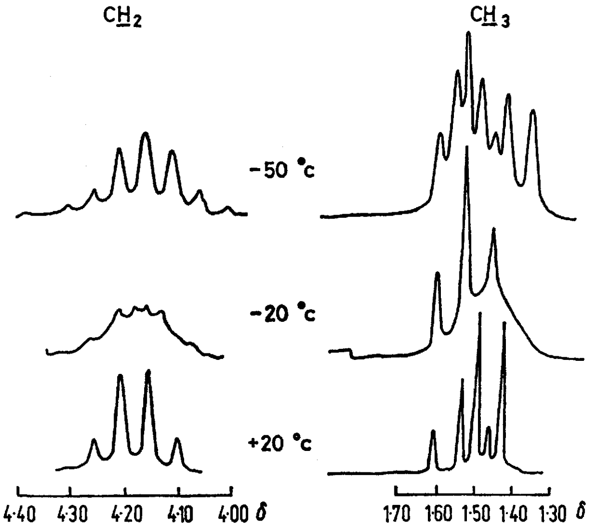
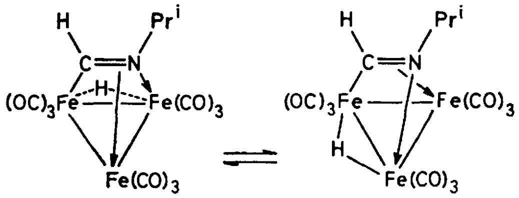


FIGURE. ^{1}H N.m.r. spectra of (**3c**) in CD$_2$Cl$_2$.

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 ^{13}C 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 [Fe$_3$(CO)$_{11}$(CNMe)]. It is known that protonation of (**1**) at −80 °C yields the analogous [HFe$_3$(CO)$_{10}$(COH)] which decomposes above −30 °C to give [Fe$_3$(CO)$_{12}$].[4] More prolonged reaction of CNEt with (**1**), followed by alkylation and purification, yields the monosubstituted [HFe$_3$(CO)$_9$(CNEt$_2$)(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**) (R^1 = H, R^2 = Pr^i). 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 = Me, R^2 = H has been isolated from reaction of acetonitrile with $[HFe_3(CO)_{11}]^-$,[5] while $[H_2Os_3(CO)_9(CNPh)]$ is known to undergo isonitrile insertion to yield a complex of similar structure. Complex (**7**) is also fluxional. Thus, the ^1H n.m.r. spectrum at −50 °C exhibits the two doublets expected for the $CH(CH_3)_2$ 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.



Scheme 2

We are currently exploring the generality of the synthetic method, and are examining the reactivity of the μ_2-CNR_2 and μ_3-CH=NR ligands.

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