Synthesis and Fluxional Character of Derivatives of the Type
$[\text{HFe}_8(\text{CO})_{16}(\mu_2-\text{CNR}_2)]$ and $[\text{HFe}_8(\text{CO})_6(\mu_2-\text{CH}=\text{NR})]$}

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Summary Isonitrile substitution at room temperature of
$[\text{PPN}][\text{HFe}_8(\text{CO})_{11}]$ [PPN = (Ph$_3$P)$_2$N$^+$] to yield the
substituted anion $[\text{PPN}][\text{HFe}_8(\text{CO})_{16} (\text{CNR})]$, followed by
protonation or alkylation, gives complexes of the type
$[\text{HFe}_8(\text{CO})_{16}(\mu_2-\text{CNR})]$ ($R^1 = \text{alkyl, } R^3 = \text{Et, H}$) 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,

and several reports have appeared describing the
preparation by diverse methods of derivatives containing a 
\( \mu_2 \)-CNR 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 \( \mu_2 \)-CNR ligand,
together with the first example of restricted C-N bond
rotation in such a complex.

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

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

The results thus indicate that the carbonyl 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 dis-
cussed elsewhere.

Protonation of (2a) yields the expected complex (4) which
decomposes in the solid state over a period of hours to yield
[Fe\(_2\)(CO)\(_{11}\)(CNMe)]. It is known that protonation of (1) at
\(-80 ^\circ\text{C}\) yields the analogous [HFe\(_3\)(CO)\(_{11}\)(COH)] which
decomposes above \(-30 ^\circ\text{C}\) to give [Fe\(_2\)(CO)\(_{11}\)]. More
prolonged reaction of CNEt with (1), followed by alkylation
and purification, yields the monosubstituted [HFe\(_3\)(CO)\(_{11}\)(CNEt)]
(6), presumably via the intermediary of the
substituted anion (5). The complexity of the i.r. spectrum of (6)
(hexane, 2058m, 2016s, 2008s, 2000m, 1935m, 1900m, 1882m, 1970s, 1975s,
1900m, 1960m, 1950w, and 1938w \( \text{cm}^{-1}\)) 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 ^\circ\text{C}
for several hours, protonation yields not (4), but the
\( \mu_2 \)-formimidoyl derivative (7) (R\(^1\) = H, R\(^2\) = Pr\(^1\)). This
complex is clearly derived from insertion of co-ordinated
isonitrile into the M–H–M bond of (2c). An isostructural

**Scheme 1.** Reagents and conditions: i, R\(_2\)NC, CH\(_2\)Cl\(_2\), 25 ^\circ\text{C},
R\(^1\) = Me, Et, or Pr\(^1\); ii, Et\(_2\)OBF\(_4\), CH\(_2\)Cl\(_2\),
25 ^\circ\text{C}; iii, HSO\(_3\)CF\(_3\), Et\(_2\)O, 25 ^\circ\text{C}; iv, excess of EtNC,
25 ^\circ\text{C}, CH\(_2\)Cl\(_2\); v, 40 ^\circ\text{C}, tetrahydrofuran.
compound with $R^1 = \text{Me}$, $R^2 = \text{H}$ has been isolated from reaction of acetonitrile with $[\text{HFe}_6\text{(CO)}_{11}]^{-}$, while $[\text{H}_2\text{Os}_6\{\text{CO}\}_8\text{(CNPh)}]$ is known to undergo isonitrile insertion to yield a complex of similar structure. Complex (7) is also fluxional. Thus, the $^1\text{H}$ n.m.r. spectrum at $-50\,^\circ\text{C}$ 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 $0\,^\circ\text{C}$. 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 $\mu_2\text{-CNR}_3$ and $\mu_3\text{-CH}=$NR ligands.

![Scheme 2](image)

\begin{align*}
\text{Scheme 2}
\end{align*}

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