Characterisation and Structure of HFe$_3$(CO)$_{10}$CNMe$_2$: a Reformulation of the Hydride reported previously as HFe$_3$(CO)$_{11}$NMe$_2$

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Summary The compound reported previously as HFe$_3$(CO)$_{11}$NMe$_2$ is now shown by high-resolution mass spectrometry to be HFe$_3$(CO)$_{10}$CNMe$_2$, a novel hydride of iron; its probable structure is inferred from Mössbauer and other spectroscopic evidence.

RHEE, RYANG, and TSUTSUMI recently described a red-black crystalline hydride which they formulated from microanalysis as HFe$_3$(CO)$_{11}$NMe$_2$.[1] The n.m.r. spectrum had absorptions at τ 6·0 (singlet, 6H) and 27·8 (singlet, 1H) and the i.r. spectrum showed bands in the terminal carbonyl region (2080—1978 cm^{-1}) and also an iron–hydrogen bond ($\delta_{\text{Fe-H}}$ 770 cm^{-1}). We now report the results of mass spectrometric and Mössbauer spectroscopic studies on this compound which lead to its reformulation.

The highest peak in the mass spectrum corresponds to HFe$_3$(CO)$_{10}$CNMe$_2^+$ (calc. *m/e* 504·8118, found 504·8118 for ^{56}Fe isotope) and not HFe$_3$(CO)$_{11}$NMe$_2^+$ (calculated *m/e* 521). Since oxygen loss from the latter, prior to ionization, is unlikely, HFe$_3$(CO)$_{10}$CNMe$_2^+$ is considered to be the parent ion. Fragmentation occurred by stepwise loss of carbonyl groups, without competitive loss of hydrogen, to give the series of ions HFe$_3$(CO)$_n$CNMe$_2^+$ (n = 0—9), the lightest of which, HFe$_3$CNMe$_2^+$, was confirmed by accurate mass-measurement (calc. *m/e* 224·8626, found 224·8621); this fragment did lose hydrogen as evidenced by the relatively high intensity of the peak at *m/e* 224. Such behaviour is typical of species in which the hydrogen occupies a bridging position.[2] Hydrogen was also lost from fragments at *m/e* 113 and 169 (probably HFe$_2^+$ and HFe$_3^+$, respectively) and from HFe$_3$C$^+$ (calc. *m/e* 180·8126, found 180·8122) and HFe$_2$(CO)CNMe$_2^+$ (calc. *m/e* 196·9226, found 196·9205). If it is assumed that no rearrangements are involved in the production of the last two fragments, their presence has significant structural implications: the former would indicate that the CNMe$_2$ carbon atom is attached directly to the iron framework in the original molecule, and the latter that the hydrogen and CNMe$_2$ group are associated with the same pair of iron atoms.

Mössbauer parameters (±0·01 mm s^{-1}) *at* 77K

Compound*		Chemical isomer shift δ/(mm s^{-1})	Quadrupole splitting Δ/(mm s^{-1})	Width at half-height Γ/(mm s^{-1})
Fe$_3$(CO)$_{12}$	a	+0·05	0·13	0·28, 0·28
	b	+0·11	1·13	0·30, 0·30
HFe$_3$(CO)$_{10}$CNMe$_2$	a	+0·04	0·16	0·22, 0·24
	b	−0·04	0·94	0·24, 0·24

* (a) refers to the unique iron and (b) to the two equivalent iron atoms in Figure 2. Chemical isomer shifts relative to iron.

In Figure 1 the known Mössbauer spectrum of Fe$_3$(CO)$_{12}$[3,4] is compared with that of HFe$_3$(CO)$_{10}$CNMe$_2$. The similarity of the spectra suggests a close relationship between the structure of the two compounds. If the spectra are computed on this basis (Table) the central peak, which arises from the unique iron atom of Fe$_3$(CO)$_{12}$, remains almost unaltered in the hydride spectrum. Having previously demonstrated the sensitivity of the electric field gradient at this particular iron atom to substitution,[3,5] we are confident that the Fe(CO)$_4$ moiety is retained in HFe$_3$(CO)$_{10}$CNMe$_2$. By contrast, the outer doublet, although still extremely sharp, is shifted appreciably to negative velocity implying that the two equivalent iron atoms of Fe$_3$(CO)$_{12}$ have both experienced an increase in *s* electron density at their nuclei and remain equivalent.

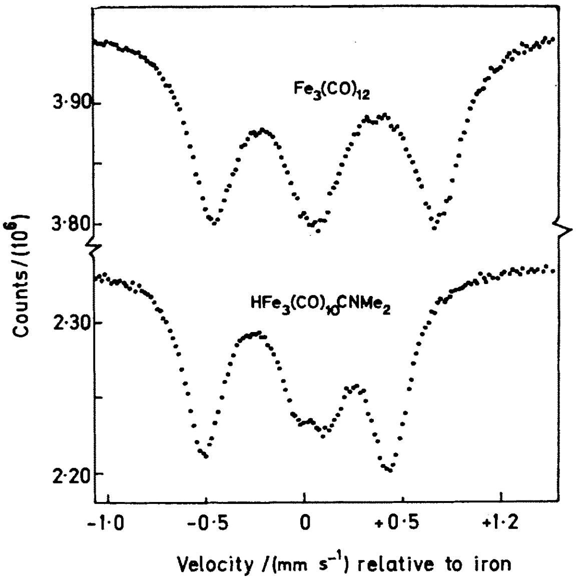

FIGURE 1. *Mössbauer spectra of* Fe$_3$(CO)$_{12}$ *and* HFe$_3$(CO)$_{10}$CNMe$_2$.

The structure which we consider best fits the available evidence and which also satisfies the inert-gas formulation is shown in Figure 2. The two bridging carbonyl groups of

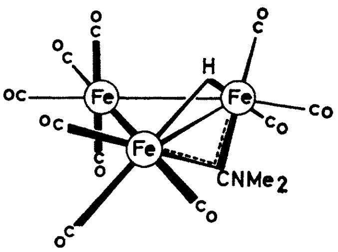

FIGURE 2. *Structure of* $HFe_3(CO)_{10}CNMe_2$

$Fe_3(CO)_{12}$ have been replaced by hydrogen and a $CNMe_2$ group. Both of these features are also consistent with the n.m.r. data mentioned earlier, the high-field resonance being in a region characteristic of bridging rather than terminal metal-bonded hydrogen,[6] and the τ value for the methyl protons being comparable with the low values observed by Fischer *et al.* for some chromium carbonyl derivatives containing a similar methylaminocarbene grouping.[7] In other *N*-dimethyl compounds the values are much higher.

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[1] I. Rhee, M. Ryang, and S. Tsutsumi, *Chem. Comm.*, 1968, 455.

[2] B. F. G. Johnson, J. Lewis, and P. W. Robinson, *J. Chem. Soc.* (*A*), 1970, 1684.

[3] See R. Greatrex and N. N. Greenwood, *Discuss. Faraday Soc.*, 1969, **47**, 126 and references therein for a discussion of this spectrum.

[4] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1969, **91**, 1351.

[5] W. S. McDonald, J. R. Moss, G. Raper, B. L. Shaw, R. Greatrex, and N. N. Greenwood, *Chem. Comm.*, 1969, 1295.

[6] N. N. Greenwood, J. W. Akitt, W. Errington, T. C. Gibb, and B. P. Straughan, "Spectroscopic Properties of Inorganic and Organometallic Compounds, Vol. 2," Specialist Periodical Report, The Chemical Society, London, 1969, ch. 1.

[7] E. Moser and E. O. Fischer, *J. Organometallic Chem.*, 1968, **15**, 147; 1969, **16**, 275.