



It was found to be analogous to the ruthenium complex obtained from the reaction of  $\text{Ru}_3(\text{CO})_{12}$  with (dimethylaminomethyl)trimethyltin [7].

In its  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) II (a and b) exhibits a characteristic hydride resonance at  $-18.2$  ppm, indicating that the hydrogen is bonded directly to the iron atom. The two methyl groups of IIb give rise to a quartet and a triplet at  $\delta$  4.4 and 1.5 ppm, respectively. In its IR spectrum ( $\text{CCl}_4$ ) six bands are observed in the  $2075-1970\text{ cm}^{-1}$  region.

The yellow complex  $\text{Fe}(\text{CO})_4\text{CHNR}_2$  (III) is very unstable in air, but can be stored in a sealed tube in vacuo. Its  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) shows one hydrogen resonance; for IIIa this is at  $\delta$  10.9 ppm and for IIIb at 11.4 ppm. Such values are characteristic of a hydrogen atom bonded to a carbene. The two methyl groups of IIIa give rise to two singlets at  $\delta$  3.50 and 3.62 ppm. The ethyl groups of IIIb exhibit two distinct quartets at  $\delta$  3.6 and 4.1 ppm and two sets of triplets at 1.3 and 1.5 ppm. In the infrared spectrum (in  $\text{CCl}_4$ ) four bands are observed, at 2045, 1980, 1950 and  $1930\text{ cm}^{-1}$ .

The highest mass-spectral peaks of all compounds correspond to the molecular ions ( $m/e$  IIa: found 504.8070, calcd. 504.8114; IIb: found 532.8432, calcd. 532.8425; IIIa: found 224.9762, calcd. 224.9721; IIIb: found 253.0015, calcd. 253.0033). Fragmentation undoubtedly occurs by stepwise loss of carbonyl groups. The strongest peaks (90 eV,  $60^\circ\text{C}$ ) displayed by compounds IIa and IIb, correspond to the fragment  $\text{HFe}_3(\text{CO})_3\text{CNR}_2^+$  and those exhibited (90 eV,  $30^\circ\text{C}$ ) by compounds IIIa and IIIb (both 100%) to the fragment  $\text{FeCHNR}_2^+$ . Loss of hydrogen from the fragments  $\text{HFe}_3\text{CNR}_2^+$  is evidenced by the relatively high intensities of the respective peaks (IIa, found 223.8546, 25%, calcd. 223.8548; IIb, found 251.8731, 30%, calcd. 251.8857) in comparison with those of the parent ions. The ions  $\text{FeCHNR}_2^+$  also lose hydrogen, but the intensities of the relevant peaks are comparatively low (IIIa, found 111.9834, 5.3%, calcd. 111.9847; IIIb, found 140.0157, 1.7%, calcd. 140.0159).

## Experimental

The salts  $[\text{R}_2\text{N}^+=\text{CHCl}]\text{Cl}^-$  (I) ( $\text{R} = \text{Me}, \text{Et}$ ) were prepared by addition of oxalyl chloride to dialkylformamide in carbon tetrachloride solution [8].

TABLE I  
MELTING POINTS AND ANALYTICAL DATA OF THE COMPLEXES II AND III

Complex	M.P. ( $^\circ\text{C}$ )	Analysis found (calcd.) (%)		
		C	H	N
$\text{HFe}_3(\text{CO})_{10}\text{CN}(\text{CH}_3)_2$	170	30.94 (30.90)	1.38 (1.39)	2.80 (2.72)
$\text{HFe}_3(\text{CO})_{10}\text{CN}(\text{C}_2\text{H}_5)_2$	90	33.94 (33.77)	2.15 (2.08)	2.70 (2.63)
$\text{Fe}(\text{CO})_4\text{CHN}(\text{CH}_3)_2$	57	36.87 (37.33)	2.90 (3.13)	6.98 (6.23)
$\text{Fe}(\text{CO})_4\text{CHN}(\text{C}_2\text{H}_5)_2$	34	42.60 (42.72)	4.31 (4.38)	5.48 (5.53)

*Preparation of  $HFe_3(CO)_{10}CNR_2$  and  $Fe(CO)_4CHNR_2$ .*  $Fe_3(CO)_{12}$  (0.01 mol) and chloroformiminium chloride (0.01 mol) in THF (60 ml) solution were heated under nitrogen at  $53^\circ C$  for 1 h. The progress of the reaction was monitored by TLC on silica gel until the green colour of  $Fe_3(CO)_{12}$  disappeared. The solvent was then evaporated in vacuo; the residue was dissolved in ether and the solution was washed with water and then evaporated. In chromatography on a silica gel column, the trinuclear deep-red complex II was eluted with hexane and recrystallized from the same solvent (yield: a, 11%, b, 16%). Subsequent elution with benzene gave the mononuclear yellow complex III, which was sublimed at  $40^\circ C/0.01$  mmHg (yield: a, 12%, b, 14%).

The analysis and the melting points of the complexes are summarized in Table 1.

## References

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