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REACTION OF Fe₃(CO)₁₂ WITH CHLOROFORMIMINIUM CHLORIDES

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Summary

Chloroformiminium chlorides react with $Fe_3(CO)_{12}$ to give mononuclear secondary dialkylimmoniocarbenes, $R_2NCHFe(CO)_4$, and trinuclear tertiary dialkylimmoniocarbene hydrides, $HFe_3(CO)_{10}CNR_2$.

Chloroformiminium chloride $[R_2NCHCl]Cl$ (I) is known as a convenient source of secondary carbene—metal complexes $[MCH(NMe_2)L_n]$. Its reactions with d^8 metal complexes (Ru^0, Ir^I, Pt^{II}) , have been studied, and d^6 adducts were obtained by three-fragment oxidative addition, a term coined by Lappert et al. [1-3].

Reactions of I involving salt elimination from transition-metallate dianions $(Cr^{-II}, Mo^{-II}, W^{-II}, Fe^{-II})$ have been studied, and also those involving salt elimination from transition-metallate monoanion precursors $(Mo^0, W^0, Mn^{-I}, Re^{-I}, Co^{-1})$ with concomitant oxidative addition [2,3]. The complex Na₂[Fe(CO)₄] reacts with I or dimethyl(methylene)ammonium iodide [4] to give a mononuclear aminocarbene complex Fe{CH(NMe₂)}(CO)₄. In contrast, iron carbonyls Fe(CO)₅ and Fe₃(CO)₁₂ react with diethylaminoacetylene to give a dinuclear dialkyl-aminocarbene by reductive cleavage of the carbon–carbon triple bond [5].

It seemed likely that reductive cleavage of the C—Cl bond of I would also occur if $Fe_3(CO)_{12}$ were used as a starting material instead of the dianion, and so $Fe_3(CO)_{12}$ was treated with I in THF solution. Under these conditions two complexes were obtained: a trinuclear iminocarbene hydride II and a mononuclear carbene III:

$$\begin{bmatrix} R \\ R \\ R \end{bmatrix} Cl^{-} + Fe_{3}(CO)_{12} \rightarrow HFe_{3}(CO)_{10}CN \\ R \\ (I) \\ (II) \\ (III) \\ (III)$$

$$(a, R = CH_3; b, R = C_2H_5)$$

Complex II is also formed from dimethylformamide and benzoyl chloride [6].

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

In its ¹H NMR spectrum (CDCl₃) 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 δ 4.4 and 1.5 ppm, respectively. In its IR spectrum (CCl₄) six bands are observed in the 2075–1970 cm⁻¹ region.

The yellow complex Fe(CO)₄CHNR₂ (III) is very unstable in air, but can be stored in a sealed tube in vacuo. Its ¹H NMR spectrum (CDCl₃) shows one hydrogen resonance; for IIIa this is at δ 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 δ 3.50 and 3.62 ppm. The ethyl groups of IIIb exhibit two distinct quartets at δ 3.6 and 4.1 ppm and two sets of triplets at 1.3 and 1.5 ppm. In the infrared spectrum (in CCl₄) four bands are observed, at 2045, 1980, 1950 and 1930 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°C) displayed by compounds IIa and IIb, correspond to the fragment HFe₃(CO)₃CNR₂⁺ and those exhibited (90 eV, 30°C) by compounds IIIa and IIIb (both 100%) to the fragment FeCHNR₂⁺. Loss of hydrogen from the fragments HFe₃CNR₂⁺ 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 FeCHNR₂⁺ also loose 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

TABLE 1

The salts $[R_2N^+=CHCl]Cl^-$ (I) (R = Me, Et) were prepared by addition of oxalyl chloride to dialkylformamide in carbon tetrachloride solution [8].

Complex	M.p. (°C)	Analysis found (caled.) (%)			
		С	Н	N	
HFe ₃ (CO) ₁₀ CN(CH ₃) ₂	170	30.94	1.38	2.80	
		(30.90)	(1.39)	(2.72)	
HFe ₃ (CO) ₁₀ CN(C ₂ H ₅) ₂	90	33.94	2.15	2.70	
		(33.77)	(2.08)	(2.63)	
Fe(CO) ₄ CHN(CH ₃) ₂	57	36.87	2.90	6.98	
		(37.33)	(3.13)	(6.23)	
$Fe(CO)_4CHN(C_2H_5)_2$	34	42.60	4.31	5.48	
		(42.72)	(4.38)	(5.53)	

MELTING POINTS AND ANALYTICAL DATA OF THE COMPLEXES II AND III

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°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°C/0.01 mmHg (yield: a, 12%, b, 14%).

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

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