

Preliminary communication

η^2 -DITHIOMETHYLIRON(II) IONIC COMPLEXES. EVIDENCE FOR A STRONG DEPENDENCE ON THE NATURE OF THE *trans*-PHOSPHORUS LIGANDS BONDED TO IRON

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Summary

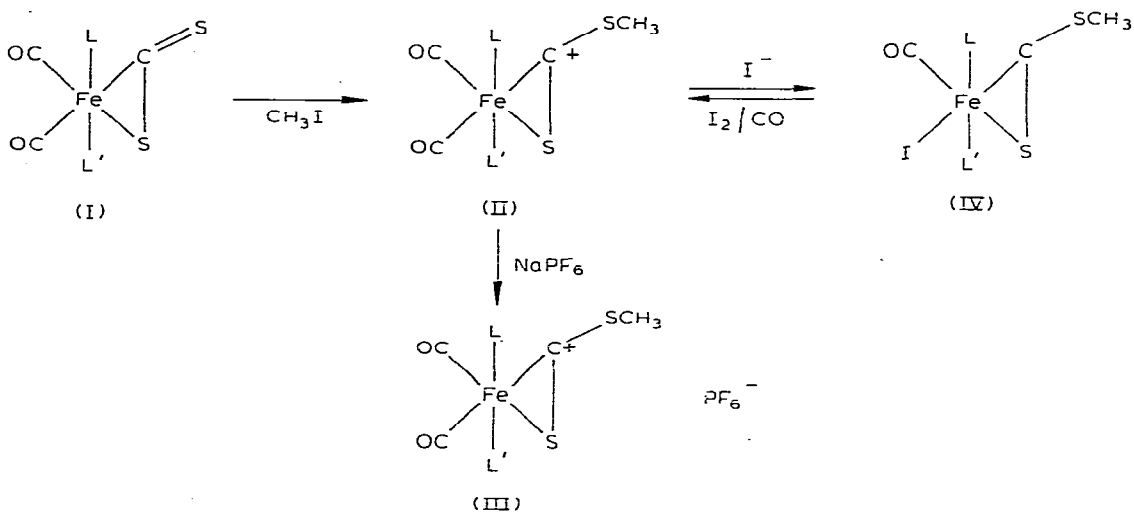
Cationic η^2 -dithiomethyliron(II) complexes have been made by alkylation of the uncoordinated sulfur atom of $\text{Fe}(\text{CO})_2[\eta^2\text{-CS}_2](\text{L})_2$. Surprisingly, only when the phosphorus ligands L are strong donors (PMe_3 , PMe_2Ph) does coordination of iodide take place to give the neutral $\text{Fe}(\eta^2\text{-CS}_2\text{CH}_3)(\text{I})(\text{CO})(\text{L})_2$ derivatives. The ^{13}C NMR spectra of the latter at 215 K indicated the presence of both isomers when L was PMe_2Ph . Reaction with iodine under carbon monoxide regenerated the cationic precursor.

Coordination of carbon disulphide to transition metals enhances the nucleophilicity of CS_2 , which then can react smoothly with electrophiles, as was shown recently in the addition of activated alkynes to $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{L}_2$ complexes [1]. In this case the formed carbeneiron complexes can be isomerised into a heterometallic derivative, but only when strong donor groups (PMe_2Ph , PMe_3) were coordinated to iron [2]. This isomerisation implies that the donor groups on iron destabilize the carbene ligand and favour nucleophilic attack on the iron rather than on a coordinated sulfur atom. To obtain further information about the behaviour of $(\eta^2\text{-CS}_2)\text{Fe}$ complexes we investigated their reaction with alkyl halides.

It has previously been shown that the uncoordinated sulfur atom η^2 -dithiomethyl-osmium or -ruthenium complexes can participate in nucleophilic substitution of alkyl halides. Alkylation of this uncoordinated sulfur atom takes place, and formed η^2 -dithiomethylmetal complexes, which are good precursors for thio-carbonylmetal complexes by alkylthiol elimination promoted either by proton or hydride [3,4].

We report here the synthesis of ionic η^2 -dithiomethyliron(II) complexes (II) by alkylation of η^2 -CS₂Fe derivatives (I) and show that the nature of phosphorus ligands bonded to iron *trans* to the CS₂ ligand strongly influences the behaviour of these complexes.

The η^2 -CS₂Fe complexes I readily reacted with an excess of methyl iodide and gave the cationic derivatives II which result from nucleophilic displacement of iodide by the uncoordinated sulfur atom (Scheme 1). The reaction was com-



SCHEME 1. a: L = L' = P(OMe)₃; b: L = L' = PPh₃; c: L = PPh₃, L' = PMe₂Ph; d: L = L' = PMe₂Ph; e: L = L' = PMe₃.

plete within 2 h at room temperature in dichloromethane, but was faster with the better donor groups (L = PMe₃) (Ie) than with smaller but poorer donor groups (L = P(OMe)₃) (Ia). η^2 -Dithiomethyliron ionic complexes were characterised as their hexafluorophosphate salts, and could be isolated quantitatively with a variety of ligands L IIIa–IIIe even with unsymmetrical phosphorus ligands in the apical positions of IIIc.

III	m.p. (°C)	Rdt. (%)	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{CS}) (\text{cm}^{-1})$ (Nujol)
IIIa	114	97	2060–2000	1187–1152
IIIb	115	94	2045–1975	1145–1120
IIIc	110	85	2040–1980	1140
IIId	150	98	2030–1960	1137–1115
IIIe	95	95	2055–1980	1135

Infrared data show that a decrease of both C≡O and C=S absorption frequencies occurs with an increase in the donor character of the ligands L.

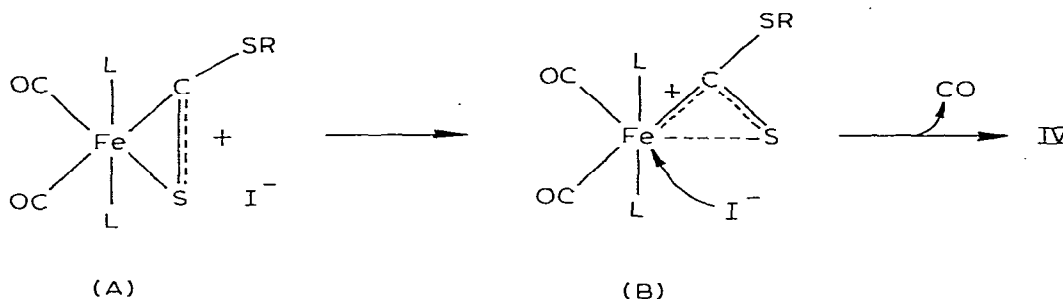
Complexes II give neutral derivatives (IV) by coordination of iodide to iron and loss of one carbonyl, but unexpectedly the reaction takes place only when the strongest donor ligands L are coordinated to iron (L = PMe₂Ph or PMe₃). Thus the compounds IVd and IVe were isolated from dichloromethane solution of IIId and IIe in quantitative yields after 48 h at 25°C or 2 h at reflux.

IV	m.p. (°C)	Rdt. (%)	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{CS})$ (cm^{-1}) (Nujol)
IVd	145	83	1908–1920	1160
IVe	161	80	1902–1915	1155

The ^1H NMR spectra of IIIc and IVd showed the non equivalence of the methyl groups bonded to phosphorus atoms. [$\delta_{\text{P-CH}_3}$ (ppm, CD_3COCD_3): IIIc: 1.81 (t), 2J 9 Hz; 1.91 (t), 2J 9 Hz and IVd: 1.87 (t), 2J 9 Hz; 2.10 (t), 2J 7.5 Hz]. Compounds IV are fluxional as indicated by ^{13}C NMR. No ^{13}CO , $^{13}\text{CS}_2$ or $^{13}\text{CH}_3\text{S}$ signals can be seen at 310 K, but at 215 K both isomers of IVd can be detected [major/minor isomer, $\delta(\text{CS}_2)$ (ppm, CDCl_3): 312.9 (t), $^2J(\text{PC})$ 17.7 Hz; 311.9 (t), $^2J(\text{PC})$ 18.4 Hz; $\delta(\text{CO})$: 219.4 (t), $^2J(\text{PC})$: 30.5 Hz; 220.1 (t), $^2J(\text{PC})$ 32.1 Hz; $\delta(\text{CH}_3\text{S})$: 27.1, 20.8; $\delta(\text{CH}_3\text{P})$: 15.3 (t), $^2J(\text{PC})$ 17.1 Hz; 12.1 (t), $^2J(\text{PC})$ 15.2 Hz].

It is noteworthy that the cations II can be regenerated from complexes IV by iodide abstraction with iodine in dichloromethane, the yield of this reaction being higher under a carbon monoxide atmosphere: compound IIIc was obtained in 15% yield under nitrogen and in 50% yield under carbon monoxide.

The transformation II \rightarrow IV promoted by donor groups L can be understood if we assume that poor donor groups stabilize the electron deficiency on the coordinated C–S bond (Scheme 2, form A) and that, in contrast strong donor



SCHEME 2

ligands L increase the electron density on the coordinated sulfur atom and facilitate its decoordination (Scheme 2, form B), and therefore allow coordination of the anion to iron. Subsequent loss of one carbonyl ligand may lead to the more stable $(\eta^2\text{-CS}_2\text{Me})\text{Fe}$ complex IV.

Roper et al. reported that the salt $[\text{Os}(\eta^2\text{-CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]^+\text{Cl}^-$ was stable towards coordination of chloride whereas the ruthenium analogue easily gave $\text{Ru}(\eta^2\text{-CS}_2\text{Me})(\text{Cl})(\text{CO})(\text{PPh}_3)_2$ [3]. Our results show that not only does coordination of halide depend on the nature of the metal, but also that selection of the ligands makes it possible to facilitate or inhibit the coordination of an anion to the metal of the $\text{M}(\eta^2\text{-CS}_2\text{R})^+$ moiety.

References

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