

Preliminary communication

Using metal–metal bond forming reactions as a synthetic strategy towards building polymers containing Fe–Fe and Fe–Sn–Fe bonds

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Abstract

Linked cyclopentadienyl ligands coupled with metal–metal bond forming reactions provides a synthetic route towards the construction of polymers contain the repeat units (Fe–Fe–link) and (Fe–Sn–Fe–link).

Keywords: Cyclopentadienyl; Polymers; Spectroscopy; Iron; Tin

1. Introduction

The synthesis of polymers in which the polymer backbone contains a metal atom is an area of current interest due to their potentially useful chemical and physical properties [1]. Synthetic routes to systems with single or isolated metal atoms in the repeat unit have been well established [2,3]. A strategy which will allow the construction of polymers containing M–M and M–M'–M moieties is now reported. The underlying strategy is to couple linked cyclopentadienyl ligands with conventional metal–metal bond forming reactions, Scheme 1.

Step (a) may be an oxidation, i.e. iodination to produce the diiodide $\text{IM}(\text{L}_n)\text{CpXCpM}(\text{L}_n)\text{I}$ or a reduction to give the metallodianion $\text{M}(\text{L}_n)\text{CpXCpM}(\text{L}_n)^{2-}$, whilst step (b) is a salt elimination (see Scheme 2).

This strategy was tested by reducing **1a** with sodium amalgam in tetrahydrofuran to give the dianion **2a** which was then reacted with $(\eta\text{-C}_5\text{HMe}_4)\text{Fe}(\text{CO})_2\text{I}$, **3** to give the tetra-iron dimer **4a** as the principal product

(57%). Its structure was determined crystallographically [4] and is illustrated in Fig. 1. The complex adopts a *trans* arrangement about both its metal–metal bonds and the $\text{CH}(\text{NMe}_2)\text{CH}(\text{NMe}_2)$ link between the rings. Four methyl substituents were used on the cyclopentadienyl ring of **3** to permit complete characterisation of all the expected reaction products from this reaction by ν MC–O IR.

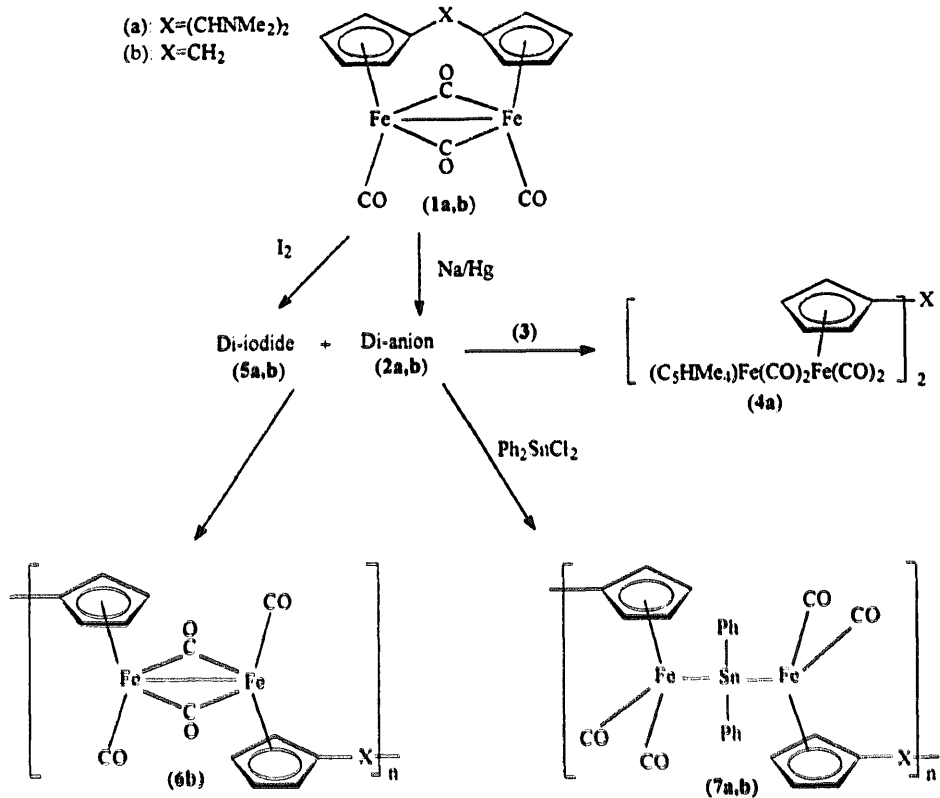
As the presence of NMe_2 groups in **1a** complicate its scission with I_2 , attention was directed to **1b**, [5], one of the products of the reaction of $\text{C}_5\text{H}_5\text{CH}_2\text{C}_5\text{H}_5$ with $\text{Fe}_2(\text{CO})_9$. Complex **1b** was also characterised crystallographically [4], Fig. 2. The structure of **1b** is relatively strain free and the complex contains an almost perfect (non-crystallographic) mirror plane. **1b** can be reduced to its dianion **2b** and cleaved with I_2 to its diiodide **5b**. These two react to give a relatively high molecular weight polymer which is shown by IR spectroscopy to contain the $\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ moiety in 47% yield.

Both dianions **2a** and **2b**, react with Ph_2SnCl_2 and give **7a** and **7b** respectively. The ν MC–O IR frequencies are given in Table 1. The polymers are soluble in dichloromethane but unlike related monomers and dimers [6] are insoluble in hexane and diethyl ether. The polymers were difficult to purify (current methods rely on precipitation from dichloromethane solution using diethyl ether) and the C, H and N analytical data are

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Scheme 1.



Scheme 2.

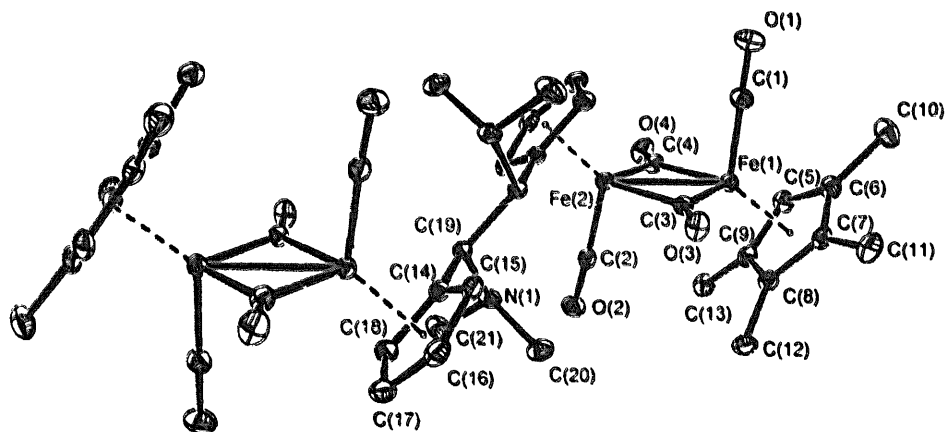


Fig. 1. The molecular structure of (4a), hydrogens omitted.

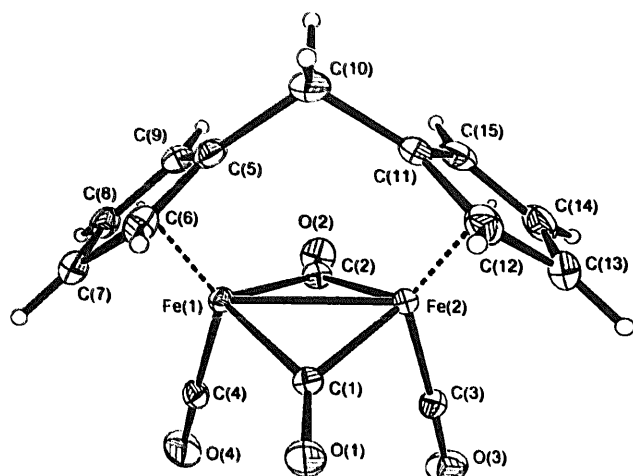


Fig. 2. The molecular structure of (1b).

always lower than expected. The presence of 1 and Cl impurities in 6 and 7 was confirmed by X-ray fluorescence measurements on an SCM. The claim that 6 and 7 are polymers is based on the following.

- (1) Their ν MC–O IR frequencies are close to but different from model compounds.
- (2) 6 and 7 unlike related monomers and dimers, do not move on TLC plates.
- (3) Measured molecular weights (osmometry) are 8000 for 6b and 8500 for 7a.

While the molecular weights obtained are more indicative of high oligomers rather than polymers, removal of impurities will increase these values considerably.

Since the metal–metal bond formation is the polymer generating step and as this takes place in the reaction of $C_3H_5-CH_2-C_3H_5$ with $Fe_2(CO)_9$ (used to synthesise 1b) it was decided to look for polymers in the crude reaction product. A red powder precipitated when toluene solutions of the crude product were treated with hexane. This red powder had similar properties to 6 and 7 but its ν MC–O IR frequencies (CH_2Cl_2 solution) were lower than those of 6b: 1990, 1947 and 1768 cm^{-1} , and its solubility in CH_3CN was insufficient to give an IR spectrum.

Attempts to both purify 6 and 7 and to extend this reaction to polymers with only metal atoms in the backbone are in progress.

Table 1
IR spectral data in CH_2Cl_2 solution (ν MC–O, cm^{-1})

Complex	IR data
1(a)	1993, 1953 1770
1(b)	1994, 1955 1776
4(a)	1983, 1941 1757
6(b)	1993, 1952 1769
7(a)	1991, 1970, 1933, 1926
7(b)	1996, 1974.5, 1941.1, 1927

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References and notes

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- [4] All non polymeric compounds gave satisfactory analytical data. *Crystallography*. The structures were solved by direct methods, SHELXS-86 [7], and refined by full matrix least squares using SHELXL-93 [8]. SHELX operations were rendered paperless using ORTEP which was also used to obtain the drawings [9]. Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. All calculations were performed on a Silicon Graphics R4000 computer. 1b: $C_{15}H_{10}Fe_2O_4$, monoclinic, $P2_1/c$, $a = 7.8203(9)$, $b = 12.497(2)$, $c = 14.011(2)$ Å, $\beta = 92.27(2)^\circ$, $U = 1368.2(3)$ Å³, $Z = 4$, $D_c = 1.776$, $R(\text{int}) = 0.02$, 2372 reflections with $2131 > 2\sigma$, R_1 (all data) 2.91%, wR_2 (all data) 9.84%. 4a: $C_{42}H_{48}Fe_4N_2O_8$, monoclinic, $P2_1/c$, $a = 9.431(2)$, $b = 13.436(2)$, $c = 16.237(2)$ Å, $\beta = 106.58(2)^\circ$, $U = 1972.0(6)$ Å³, $Z = 2$, $D_c = 1.570$, $R(\text{int}) = 0.02$, 6836 reflections with $3571 > 2\sigma$, R_1 (all data) 10.88%, wR_2 (all data) 14.53%.
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