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Mendeleev Commun., 1991, **1(3)**, 99–101

Mendeleev
Communications

Communal Products of Nucleophilic Attack at Iron Carbene and Photolysis of Iron Alkyl Complexes. Crystal Structures of $CpFe\{CHS(CH_2)_2S\}(CO)L$ (L = CO and PPh_3) and $[CpFe\{CHS(CH_2)_2S\}(CO)]_2$

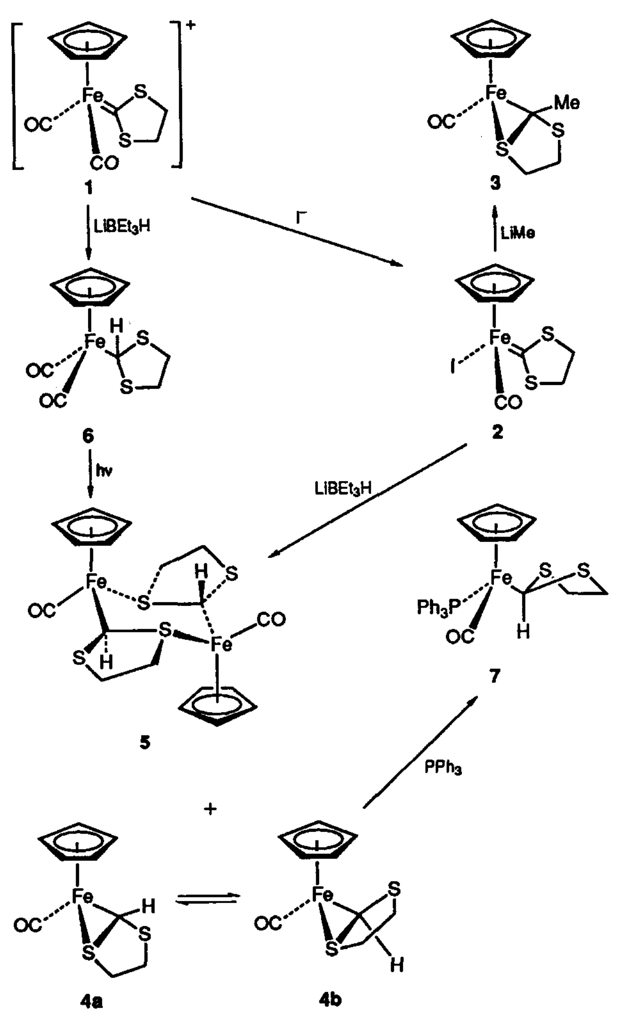
Harry Adams, Neil A. Bailey, Jeremy J. Laskowski, Christopher Ridgway and Mark J. Winter

Department of Chemistry, The University, Sheffield S3 7HF, UK

Treatment of the carbene $CpFeI(CO)\{{=}CHS(CH_2)_2S\}$ with $LiBEt_3H$ or photolysis of the alkyl $CpFe\{CHS(CH_2)_2S\}(CO)_2$ results in a mixture of $CpFe\{\eta^2\text{-}CHS(CH_2)_2S\}(CO)$, containing a labile Fe—S bond, and a dimeric species, the tricyclic diferradithiacyclohexane $[CpFe\{CHS(CH_2)_2S\}(CO)]_2$.

Neutral and cationic Fischer type carbene complexes are susceptible to nucleophilic attack. We previously reported a number of reactions in which nucleophilic attack (Nu^-) at the carbene in various complexes $CpMI(CO)_2({=}CRX)$ (M = Mo, W; ${=}CRX$ = heteroatom stabilized carbene) results in iodide loss and coordination of X at the metal in forming complexes $CpM\{\eta^2\text{-}C(Nu)X\}(CO)_2$.[1,2,3] We report here results arising in related dithiacarbene iron systems, and relate these and other observations to carbonyl substitution reactions.

Treatment of the known carbene $[CpFe(CO)_2\{{=}CS(CH_2)_2S\}]^+$ **1**[4] with I^- at ambient temperature results in iodide for carbonyl exchange and formation of the new neutral iodoiron carbene complex $CpFeI(CO)\{{=}CS(CH_2)_2S\}$ **2** isolated in 61% yield. The carbene atom of **2** is subject to nucleophilic attack in common with other carbenes.[2,3,5] The consequence of nucleophilic attack by anionic nucleophiles is an intermediate anion which loses iodide while one sulphur coordinates to the iron. The consequences are complexes



Scheme 1

containing Fe—CR—S units. Thus reaction with LiMe affords complex **3**. This exists as just a single isomer. On the other hand reaction with the hydride source LiBEt$_3$H results in complex **4** whose NMR spectra show the presence of two isomers, probably with structures **4a** and **4b**. The presence of two isomers of **4** was unexpected since related molecules of the type CpMo{η^2-CH(CH$_2$)$_3$O}(CO)$_2$ and CpMo{η^2-CH(CH$_2$)$_3$NMe}(CO)$_2$ exist as only one isomer.[2,3] An unoptimized small amount of dimer [CpFe{CHS(CH$_2$)$_2$S} (CO)]$_2$ **5** is also produced in this reaction. This is a very unusual tricyclic molecule whose crystal structure† is displayed in Fig. 1. There are two essentially identical independent molecules. Both molecules are centrosymmetric dimers, situated across crystallographic inversion centres at [0, 0, 0] and [0.5, 0.5, 0.5]. Each iron atom is bonded to a conventional (η-C$_5$H$_5$), to a linear CO, and to the α-carbon atom of a 2,5-dithiacyclopentyl ring. The coordination is completed by the formation of a Fe—S bond to a centrosymmetrically related fragment, resulting in a strong dimer and a Fe—C—S—Fe—C—S ring which adopts a chair configuration. Molecules containing the diferradithiacyclohexane Fe—C—S—Fe—C—S ring appear to be unknown.

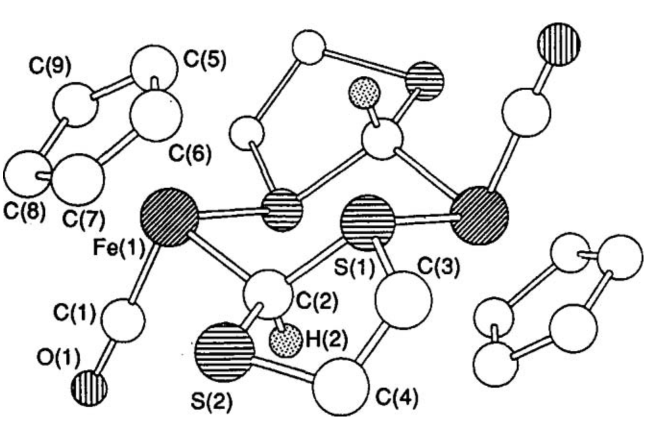


Fig. 1 Molecular structure of [CpFe{CHS(CH$_2$)$_2$S}(CO)]$_2$ **5**

The reaction between the cationic carbene complex [CpFe(CO)$_2${=CS(CH$_2$)$_2$S}]$^+$ **1** and LiBEt$_3$H results in nucleophilic hydride attack at the carbene atom to form the neutral complex CpFe{CHS(CH$_2$)$_2$S}(CO)$_2$ **6**, in effect a substituted 1,3-dithiacyclopentane. The X-ray crystal structure of this complex‡ is illustrated in Fig. 2. It consists of a conventional CpFe(CO)$_2$ unit bound to a 2,5-diathiacyclopentyl ligand. The ring itself is hinged about the S···S vector by 44° in a direction away from the cyclopentadienyl ring: the hydrogen atom on C(8) is directed towards the cyclopentadienyl ring and is at a distance of 2.57 Å from the iron.

Complex **4** reacts with PPh$_3$ by cleavage of the Fe—S bond, rather than CO substitution, to form the phosphine complex **7**

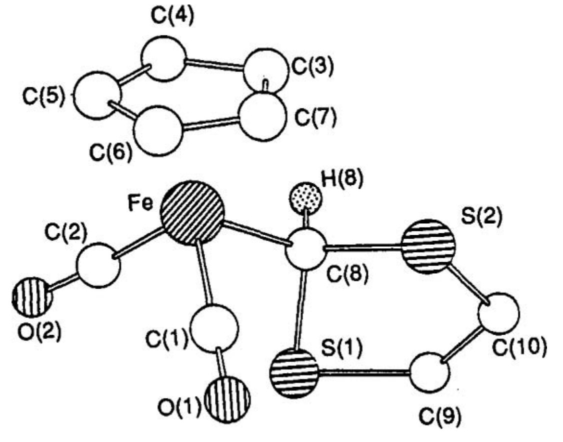


Fig. 2 Molecular structure of CpFe{CHS(CH$_2$)$_2$S}(CO)$_2$ **6**

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† *Crystal data* for **5**: [CpFe{CHS(CH$_2$)$_2$S}(CO)]$_2$, triclinic, $a = 7.302(2)$, $b = 7.977(3)$, $c = 17.466(6)$ Å, $\alpha = 85.88(3)$, $\beta = 87.96(3)$, $\gamma = 79.39(3)$°, $U = 997.2(6)$ Å^3, $D_c = 1.693$ g cm^{-3}, $Z = 2$, space group $P\bar{1}$ (C_i^1, No. 2); Mo-Kα radiation ($\lambda = 0.71069$ Å), μ(Mo-Kα) = 18.68 cm^{-1}, $F(000) = 519.93$. Data ($3.5 < 2\theta < 50°$) collected on a Nicolet R3 diffractometer by the ω-scan method. Structure solved by conventional Patterson and Fourier techniques and refined by blocked cascade least squares methods to a final $R = 0.0504$ ($R_w = 0.0463$, 171 parameters) with allowance for the thermal anisotropy of all ordered non-hydrogen atoms (the carbon atoms of the disordered Cp rings were permitted a common isotropic thermal parameter for each ring site) using the 2662 independent reflections for which $|F|/\sigma(|F|) > 3.0$. Weighting scheme $w^{-1} = [\sigma^2(F) + 0.00032(F)^2]$. Atomic coordinates, bond lengths and angles and thermal parameters for **5**, **6** and **7** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1991, Issue 1.

‡ *Crystal data* for **6**: [CpFe{η^1-CHS(CH$_2$)$_2$S}(CO)$_2$, monoclinic, $a = 11.69(5)$, $b = 8.935(26)$, $c = 12.02(4)$ Å, $\beta = 112.41(28)$°, $U = 1161(7)$ Å^3, $D_c = 1.615$ g cm^{-3}, $Z = 4$, space group $P2_1/c$ (C_{2h}^5, No. 14); Mo-Kα radiation ($\lambda = 0.71069$ Å), μ(Mo-Kα) = 16.19 cm^{-1}, $F(000) = 575.92$. Data ($3.5 < 2\theta < 50°$) collected on a Nicolet R3 diffractometer by the ω-scan method. Structure solved by conventional Patterson and Fourier techniques and refined by blocked cascade least squares methods to a final $R = 0.0873$ (136 parameters) with allowance for the thermal anisotropy of all non-hydrogen atoms (except those of the cyclopentadienyl ring of lower occupancy) for the 2387 independent reflections for which $|F|/\sigma(|F|) > 3.0$. The Cp ring was found to be rotationally disordered and occupancies were refined to 0.73/0.27. Unit weights were used throughout.

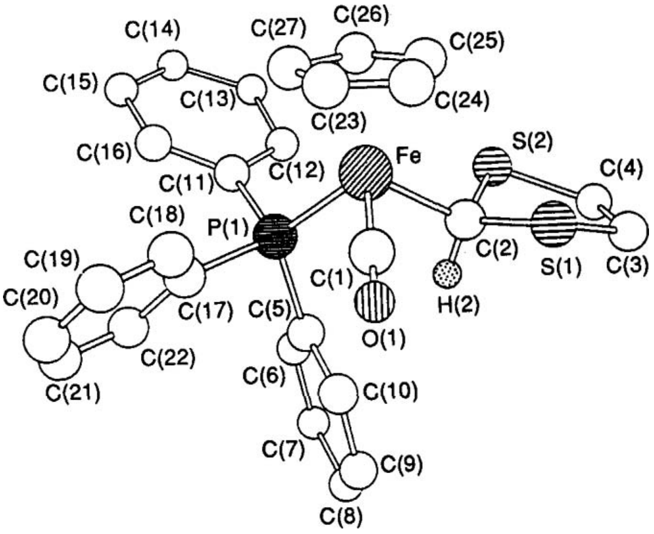

Fig. 3 Molecular structure of CpFe{η^1-CHS(CH_2)$_2$S}(CO)(PPh_3) **7**

whose molecular structure[§] is displayed in Fig. 3. The structure is unusual. The molecule is a conventional CpFe(CO)(PPh_3) unit bound to a 2,5-dithiacyclopentyl ring (Fe—C 2.08 Å), which has an envelope conformation, with a fold about the S···S line of 36°. This ligand is attached to the iron such that the hydrogen on C(2) is directed *away* from the cyclopentadienyl ring, in contrast to the conformation found in the (η-C_5H_5)Fe$(CO)_2$ analogue. This could have given rise to short contacts between the more upwardly directed sulphur atoms and the cyclopentadienyl ring, although in fact the shortest such contact is S(2)···C(25) 3.24 Å.

Photolysis of complex **6** results in carbonyl loss to form complex **4** and traces of complex **5**. A related reaction is observed on photolysis of CpFe{CHS(CH_2)$_3$S}$(CO)_2$ [available by treatment of CpFeI$(CO)_2$ with LiCHS(CH_2)$_3$S[6]]. In this case photolysis results in a mixture of CpFe{η^2 – CHS(CH_2)$_2$S}(CO) and the dimeric species [CpFe{CHS(CH_2)$_3$S}(CO)]$_2$ in unoptimized yields of 4 and 9% respectively.

Photochemical substitution reactions of metal carbonyl complexes M$(CO)_n$ frequently proceed better in a coordinating solvent, typically tetrahydrofuran (thf). The rôle of the coordinating solvent is to stabilize an unsaturated intermediate as M$(CO)_{n-1}$ (thf) prior to eventual replacement by the incoming ligand. The sequence **6**$\rightarrow$**4**$\rightarrow$**7** is related in the sense that stabilization of the coordinatively unsaturated intermediate is achieved, but in this case by an intramolecular donor atom (sulphur) rather than a solvent atom. Formation of the dimeric species also constitutes stabilization of an unsaturated intermediate, but now by an intermolecular rather than an intramolecular source of sulphur.

We are pleased to acknowledge financial assistance from the SERC and The Royal Society. C.R. is grateful to the SERC for a postgraduate studentship.

Received in USSR, 1st May 1991
Received in UK, 11th April 1991; *Com. 1/01700D*

[§] *Crystal data* for **7**: CpFe{η^1-CHS(CH_2)$_2$S}(CO)(PPh_3), orthorhombic, a = 14.928(32), b = 9.756(20), c = 16.839(29) Å, U = 2452(8) Å^3, D_m = 1.40, D_c = 1.399 g cm^{-3}, Z = 4, space group $Pna2_1$ (C_{2v}^9, No. 33); Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 8.59 cm^{-1}, F(000) = 1071.86. Data (6.5 < 2θ < 50°) collected on a Stoe Stadi-2 diffractometer by the ω-scan method. Structure solved by conventional Patterson and Fourier techniques and refined by blocked cascade least squares methods to a final R = 0.0544 with allowance for the thermal anisotropy of all non-hydrogen atoms (except two isotropic carbon atoms) using the 972 independent reflections for which $I/\sigma(I) > 3.0$. Unit weights were used throughout.

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