JOM 23568

Further applications of the NCO^- insertion into a C–SR bond: synthesis of the bis(μ-acylisocyanide) complex $[Fe_2(CO)_2(Cp)_2\{\mu\text{-}CNC(O)SMe\}_2]$ *

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(Received December 14, 1992)

Abstract

The complex $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CS)(\mu\text{-}CSMe)]SO_3CF_3$ (**1**) reacts with N^nBu_4NCO to give $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CS)\{\mu\text{-}CNC(O)SMe\}]$ (**2**). This reaction has been carried out separately for both the *cis* and *trans* isomers of **1**. Complex *cis*-**2** undergoes *S*-methylation with $MeOSO_2CF_3$ affording the novel thiocarbyne derivative $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CSMe)\{\mu\text{-}CNC(O)SMe\}]SO_3CF_3$ (**3**), into which in turn an additional NCO^- anion inserts to yield the bis(μ-acylisocyanide) complex $[Fe_2(CO)_2(Cp)_2\{\mu\text{-}CNC(O)SMe\}_2]$ (**4**). All the reactions described are stereospecific and the derivatives **2–4** do not exhibit *cis–trans* isomerization.

1. Introduction

In view of the high reactivity of acyl isocyanides [1,2] much effort has been directed toward stabilizing a variety of CNC(O)R (R = Ph, NMe_2, OEt or SMe) molecules by coordination at metal centres in both mononuclear [3–8] and dinuclear complexes [9–11]. Notwithstanding the suggested similarity between acylisocyanide and CO as ligands, both of which exhibit weak σ donor and excellent π acceptor ability [12,13], only a few examples of complexes containing more than one CNC(O)R have been reported. The complexes $[TPPFe(CNCOPh)_2]$(TPP = tetraphenylporphyrinate) [14] and $[CpCo\{NC(O)OR\}_2]$ (R = Ph or adamantyl) [15] have been conveniently prepared by direct synthesis from the corresponding isocyanides CNC(O)R, whereas Fehlhammer *et al.* obtained the dinuclear $[Fe_2(CO)_2(Cp)_2\{\mu\text{-}CNC(O)OCy\}_2$ (Cy = cyclohexyl) as a by-product of the reaction of $Cl_2CNC(O)OCy$ and $Na[CpFe(CO)_2]$ [10]. This is the only example of a bis(μ-acylisocyanide) derivative. Here we report the stepwise synthesis of an additional example, namely, $[Fe_2(CO)_2(Cp)_2\{\mu\text{-}CNC(O)SMe\}_2]$ (**4**), which has been obtained by extending our recently discovered insertion of the cyanate anion into the C–S bond of the bridging thiocarbyne [11].

2. Result and discussion

Like the complex $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]^+$ [11], the *cis*-isomer (terminal CO groups on the same side of the molecule) of $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CS)(\mu\text{-}CSMe)]^+$ (**1**) [16] reacts with N^nBu_4NCO to form stereospecifically within 10 hours the neutral air stable *cis*-$[Fe_2(CO)_2(Cp)_2(\mu\text{-}CS)\{\mu\text{-}CNC(O)SMe\}]$ (**2**) (Scheme 1). The *trans*-**1** isomer, which we have been able to obtain from the *trans*-$[Fe_2(CO)_2(Cp)_2(\mu\text{-}CS)_2]$ by using stoichiometric amounts of $MeSO_3CF_3$ in refluxing CH_2Cl_2, also reacts with NCO^- to yield the *trans*-**2** complex. Type **2** derivatives have been characterized by their NMR and IR spectroscopic data (see Experimental section). The presence of the two bridging ligands CS and CNC(O)SMe {for *trans*-**2** complex: IR spectrum in KBr pellet 1139, ν(CS), 1634 ν(C=N), 1673 νCO(acyl) cm^{-1}; ^{13}C NMR spectrum in CD_2Cl_2 solution δ = 376.8 (*C*S), 271.8 (*C*=N) and 172.9 (*C*O, acyl) ppm}, together with the ν(CO) at 1977 cm^{-1} in CH_2Cl_2 strongly support the proposed structure. Unlike the complex $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CO)\{\mu\text{-}CNC(O)SMe\}]$ [11], which has been shown to exist in CH_2Cl_2 solution in both the *cis* and *trans* forms, type **2** com-

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* Dedicated to Professor Gian Paolo Chiusoli in recognition of his important contributions to organometallic chemistry and its applications in organic synthesis.

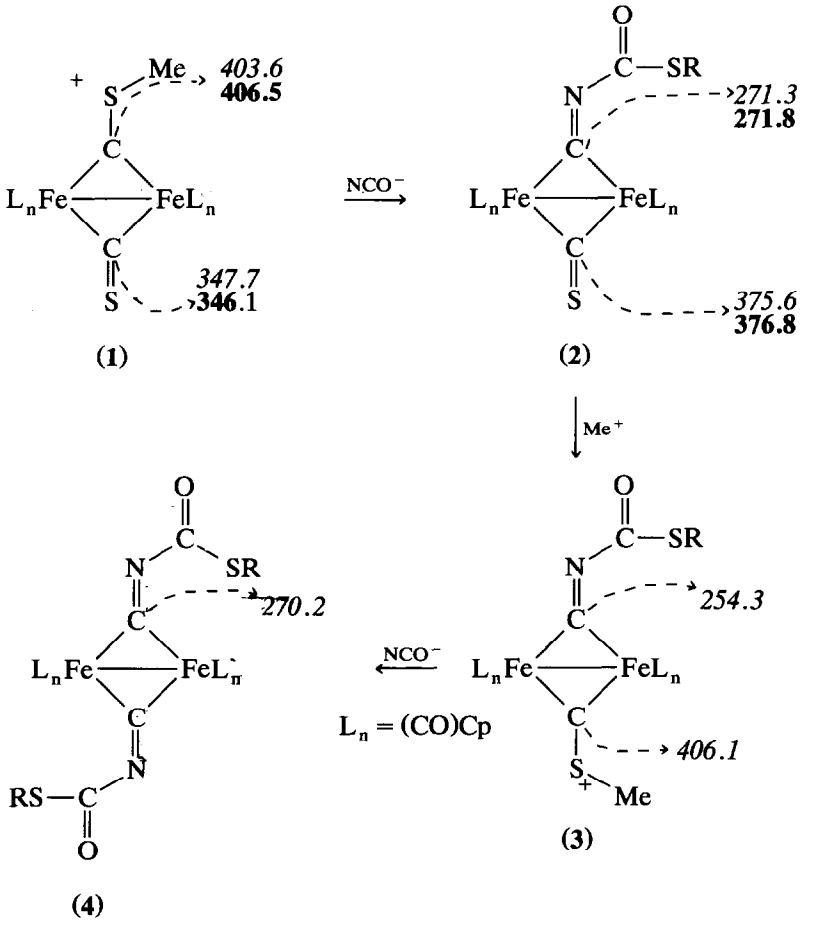
0022-328X/93/$6.00

plexes do not *cis–trans* isomerize on standing for 24 h in the same solvent at room temperature. Furthermore, the absence of any absorption in the range of 2100–2020 cm^{-1}, where the terminally coordinated CNR ligands are expected to absorb, indicates the exclusive preference of the carbothioalkoxyisocyanide ligand for the bridging site.

By analogy with $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CS)(\mu\text{-}CNMe)]$ [17], the reaction of the *cis*-**2** with $MeSO_3CF_3$ is at the thione sulfur atom, the most nucleophilic site, readily affording the bridging thiocarbyne complex $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CSMe)(\mu\text{-}CNC(O)SMe)]SO_3CF_3$ (*cis*-**3**). No evidence of *N*-methylation was observed even when a large excess of $MeSO_3CF_3$ was used, nor in experiments run for several days at room temperature, nor in refluxing CH_2Cl_2 for 4 h, although the related $[Fe_2(CO)(Cp)_2(\mu\text{-}CSMe)(CNMe)_2]^+$ complex undergoes a second *N*-alkylation [17].

The following observations are in agreement with the structure proposed for the bright red, cationic derivative *cis*-**3**: (i) the shift toward higher wavenumbers of the *cis*-CO stretching pattern (2042s, 2015w cm^{-1} in CH_2Cl_2) compared to the absorptions in the precursor *cis*-**2**; (ii) the disappearance of ν(C=S) to be replaced by ν(C–SMe) at 1027 cm^{-1}; (iii) the comparable values of the ^{13}C resonance of the bridged thiocarbyne C atom (δ = 406.1 ppm) with that of *cis*-**1** (δ = 403.6 ppm). *Cis*-**3** shows two distinct signals for Cp in the NMR spectra [^1H δ = 5.46, 5.37 ppm in CD_2NO_3; ^{13}C δ = 92.6, 93.1 ppm in CD_2Cl_2] as well as for CO groups [^{13}C δ = 207.1, 207.3]. The non-equivalence of the terminally bonded ligands is attributable to hindered rotation around the C–SMe bond, or to a slow rate of inversion at the sulfur atom on the NMR time scale. A similar behaviour has also been found in the related cationic *cis* and *trans* complexes $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CSMe)(\mu\text{-}CS)]^+$.

The thiocarbyne complex *cis*-**3** is susceptible to a second NCO^- insertion, thus confirming the peculiarity of the cyanate anion in promoting the fission of the C–S bond through nucleophilic addition at an electrophilic C atom [11,18]. The reaction, which goes to completion within 3 h, occurs stereospecifically, affording (70% yield) the bis(μ-acylisocyanide) complex



Scheme 1. $^{13}C\{^1H\}$ NMR data for the bridging C atoms (*cis* isomer data in italics and *trans* isomer data in bold).

$[Fe_2(CO)_2(Cp)_2\{\mu\text{-CNC(O)SMe}\}_2]$ (*cis*-**4**), together with traces of the *cis*-**2** (7% yield). These complexes have been separated by column chromatography.

The nature of the bright-orange *cis*-**4** complex, with the two bridging acylisocyanides, has been proved by spectroscopic analysis (see Experimental section), that also indicates the presence of only one isomer in solution. In contrast $[Fe_2(Cp)_2(CO)_2(CNMe)_2]$ has been demonstrated to exist in solution as a mixture of two principal isomers [19], and this difference is attributed to the electron withdrawing nature of the CNC(O)SMe ligands.

It is noteworthy that the compound **4** gives access to new carbene derivatives through *N*-alkylation and subsequent nucleophilic addition at the μ-C [11]. Studies of this reaction are in progress.

3. Experimental details

All the reactions were carried out under nitrogen. Infrared spectra were recorded on a Perkin Elmer 983-G spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Gemini 200 spectrometer with $SiMe_4$ as internal standard. Elemental analyses were determined by Pascher Microanalytical Laboratorium (Remagen Germany). The complex $[Fe_2(CO)_2(Cp)_2(\mu\text{-CS})_2]$ in both its *cis* and *trans* forms was synthesized as previously reported [16].

3.1. Synthesis of $[Fe_2(CO)_2(Cp)_2(\mu\text{-CS})(\mu\text{-CSMe})]SO_3CF_3$ (cis- and trans-1)

The *cis*-**1** was prepared by a slightly modified literature method [16]. The addition of $MeSO_3CF_3$ (350 μL, 3.14 mmol) to a stirred solution of *cis*-$[Fe_2(CO)_2(Cp)_2(\mu\text{-CS})_2]$ (0.8 g, 2.07 mmol) in CH_2Cl_2 (15 mL) caused a change from dark to bright green. After 1 h the reaction mixture was layered with Et_2O at −20°C. The crystals obtained were washed several times with ether (5 × 5 mL) and dried under vacuum. Yield 1.06 g (93%). M.p. 170–175°C. IR (in KBr): ν(CO) 2047 (s); 2019 (m); ν(CS) 1163 (s); ν(C–SMe) 1031 (s) cm^{-1}. ^1H NMR (in CD_3NO_2): δ 5.54, 5.45 (s, 10 H, Cp); 3.61 (s, 3H, CS*Me*) ppm. $^{13}C\{^1H\}$ NMR (in CD_3NO_2): δ 403.6 (*C*SMe); 347.7 (μ-CS); 203.1 (CO, br); 91.2, 90.5 (Cp); 33.1 (CS*Me*) ppm.

The *trans*-**1** complex was obtained by treating the *trans*-$[Fe_2(CO)_2(Cp)_2(\mu\text{-CS})_2]$ (0.8 g, 2.07 mmol) with a stoichiometric amount of $MeSO_3CF_3$ (235 μL, 2.07 mmol) in refluxing CH_2Cl_2 (15 mL). After 1 h the resulting green solution was worked up using the procedure described for the *cis* form. Yield 1.00 g of green crystalline solid (88%). Samples of *trans*-**1** contain variable amounts (less than 10%) of the *cis* isomer from the NMR analyses. IR (in KBr): ν(CO) 2005 (s); ν(CS) 1175 (s); ν(C–SMe) 1030 (s) cm^{-1}. ^1H NMR (in CD_3NO_2): δ 5.47, 5.34 (s, 10 H, Cp); 3.70 (s, 3H, CS*Me*) ppm. $^{13}C\{^1H\}$ NMR (in CD_3NO_2): δ 406.5 (*C*SMe): 346.1 (μ-CS); 202.1, 201.9 (CO); 93.2, 91.9 (Cp); 32.3 (CS*Me*) ppm.

3.2. Synthesis of $[Fe_2(CO)_2(Cp)_2(\mu\text{-CS})\{\mu\text{-CNC(O)SMe}\}]$ (cis- and trans-2)

To a stirred solution of $[Fe_2(CO)_2(Cp)_2(\mu\text{-CS})(\mu\text{-CSMe})]SO_3CF_3$ (**1**) (200 mg, 0.36 mmol) in CH_2Cl_2 (15 ml) was added dropwise a slight excess of N^nBu_4NCO (120 mg, 0.42 mmol) dissolved in 15 mL of the same solvent. After 10 h the IR absorptions of the cationic precursor had disappeared and the mixture changed from green to deep grey. The solution was taken to dryness under vacuum and the residue chromatographed on an alumina column (10 × 3 cm) with CH_2Cl_2–petroleum ether (1:1 = v:v). The grey (*cis*) or violet (*trans*) isomer fractions, depending on the stereochemistry of the precursor were then collected, evaporated to dryness and the residue crystallized from CH_2Cl_2–hexane.

cis-**2**; deep grey crystals. Yield 55.8 mg (35%) M.p. 114–116°C (dec). IR (in KBr): ν(CO) 1995(s), 1961 (w); ν(CO)acyl) 1664 (m); ν(CN) 1629 (s); ν (CS) 1141 (s); ν(C–SMe) 1058 (s) cm^{-1}. ^1H NMR (in $CDCl_3$): δ 4.90 (s, 10 H, Cp); 2.42 (s, 3H, Me) ppm. $^{13}C\{^1H\}$ NMR (in CD_2Cl_2): δ 375.6 (CS); 271.3 (μ-CN); 210.8 (CO); 173.7 (acyl-CO); 91.9 (Cp); 13.9 (SMe) ppm. MS (*m/e*, %): 443 (M^+, 20); 415 ($M^+ - CO$, 30); 387 ($M^+ - 2CO$, 50); 268 ($Fe_2Cp_2CN^+$, 80); 121 ($CpFe^+$, 100). Anal. Found: C, 43.5; H, 3.0. $C_{16}H_{13}Fe_2NO_3S_2$ calc.: C, 43.4; H, 2.96%.

trans-**2**; deep violet crystals. Yield 57.4 mg (36%). M.p. 118–120°C (dec). IR (in KBr): ν(CO) 1972(s); ν(CN) 1634(s); ν(CO acyl 1673(m); ν(CS) 1139(s); ν(C–SMe) 1053(s) cm^{-1}. ^1H NMR (in $CDCl_3$): δ 4.81 (s, 10 H, Cp); 2.45 (s, 3H, Me) ppm. $^{13}C\{^1H\}$ NMR (in CD_2Cl_2): δ 376.8 (CS); 271.8 (μ-CN); 211.7 (CO); 172.9 (CO) acyl; 94.5 (Cp); 14.1 (SMe) ppm.

3.3. Synthesis of $[Fe_2(CO)_2(Cp)_2(\mu\text{-CSMe})\{\mu\text{-CNC(O)SMe}\}]SO_3CF_3$ (cis-3)

The addition of $MeSO_3CF_3$ (50 μL, 0.44 mmol) to a stirred solution of *cis*-**2** (146 mg, 0.33 mmol) in CH_2Cl_2 (20 mL) caused a sharp change of the solution from grey to bright red. After 2h the resulting solution was layered with ether and cooled at −20°C to give red crystals of *cis*-**3**. Yield 196.4 mg (98%). M.p. 125–130°. IR (in KBr): ν(CO) 2038 (s); 2010 (sh); ν(CO)acyl 1702 (m); ν(CN) 1652 (s); ν(C–SMe) 1031 (s) cm^{-1}. ^1H NMR (in $CDCl_3$): δ 5.46, 5.37 (s, 10 H, Cp); 3.56 (s, 3H, CS*Me*); 2.47 [s, 3H, C(O)S*Me*] ppm. $^{13}C\{^1H\}$ NMR (in CD_2Cl_2): δ 406.1 (*C*SMe); 254.3 (μ-CN); 207.3,

207.1 (CO); 175.5 (acyl-CO); 93.1, 92.6 (Cp); 38.9 (CS*Me*); 14.5 [C(O)S*Me*] ppm. Anal. Found: C, 35.5; H, 2.7 $C_{18}H_{16}F_3Fe_2NO_6S_3$ calc.: C, 35.6; H, 2.66%.

3.4. Synthesis of $[Fe_2(CO)_2(Cp)_2\{\mu\text{-}CNC(O)SMe\}_2]$ (cis-4)

Compound **3** (200 mg, 0.33 mmol) was dissolved in 10 mL of CH_2Cl_2 and treated dropwise with the stoichiometric amount of N^nBu_4NCO in the same solvent (15 mL). After stirring for 3 h the resulting bright orange solution was reduced to a small volume under vacuum and chromatographed on alumina with CH_2Cl_2–petroleum ether (2:1 = v:v). The first grey band gave 10 mg (7% yield) of *cis*-**2**. The second orange band was collected and evaporated to dryness at reduced pressure. Orange crystals of *cis*-**4** were obtained from petroleum ether layered on CH_2Cl_2 at −20°C to yield 116 mg of compound (70%). M.p. 219–221°C. IR (in KBr): ν(CO) 1997 (m), 1966 (w); ν(CN) 1610 (vs); ν(CO)acyl 1654 (m); ν(CSMe) 1060 (s) cm^{-1}. ^1H NMR (in $CDCl_3$): δ 4.33 (s, 10H, Cp); 2.42 (s, 3H, SMe) ppm. $^{13}C\{^1H\}$ NMR (in CD_2Cl_2): δ 89.2 (Cp); 210.7 (CO); 270.2 (CN); 173.7 (CO) acyl); 14.0 (SMe) ppm. MS (*m/e*): 500 (M^+); 444 ($M^+ - 2CO$); 268 ($Fe_2Cp_2CN^+$). Anal. Found: C, 43.3; H, 3.2. $C_{18}H_{16}Fe_2N_2O_4S_2$ calc.: C, 43.2; H, 3.22%.

Acknowledgements

We thank the C.N.R. and Ministero della Università e Ricerca Scientifica (M.U.R.S.T.) for financial support.

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