The reactivity of aza–diferra–thia tetrahedranes $Fe_2(CO)_6(\mu\text{-SNR})$: reductive cleavage of the S–N bond and CO substitution

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Abstract

The reductive cleavage of the sulfur–nitrogen bond in the tetrahedrane $Fe_2(CO)_6(\mu\text{-SN–CH}_3)$ (3) by means of [LiBEt₃H] was investigated. The dianionic intermediates thus formed were protonated to give a mixture of two isomers of $Fe_2(CO)_6(\mu\text{-NHCH}_3)(\mu\text{-SH})$ (6a/6b) which, in turn, were methylated to $Fe_2(CO)_6(\mu\text{-NHCH}_3)(\mu\text{-SCH}_3)$ (8). Either one or two CO ligands in 3 could be substituted by *tert*-butyl isocyanide.

1. Introduction

Tetrahedranes of the type $Fe_2(CO)_6(\mu\text{-SNR})$ were first prepared by Otsuka et al. [1] and Vrieze and coworkers [2]. The parent complex containing the unsubstituted sulfimide $Fe_2(CO)_6(\mu\text{-SNH})$ (1) was later obtained from $Fe_2(CO)_6(\mu\text{-SN–SiMe}_3)$ (2) by hydrolytic cleavage of the N–SiMe₃ bond [3]. Deprotonation of 1 and subsequent reaction with an electrophile is a versatile method to prepare $Fe_2(CO)_6(\mu\text{-SNR})$ tetrahedranes, and numerous examples are now available [3–7]. However, little is known about the reactivity of aza–diferra–thia tetrahedranes. We have therefore investigated the reductive cleavage of the S–N bond in $Fe_2(CO)_6(\mu\text{-SN–CH}_3)$ (3); the comparable cleavage of the S–S and Se–Se bond is well known in the chemistry of $Fe_2(CO)_6(\mu\text{-S}_2)$ [8] and $Fe_2(CO)_6(\mu\text{-Se}_2)$ [9]. Substituted derivatives of $Fe_2(CO)_6(\mu\text{-SN–CH}_3)$ (3) containing either one or two *tert*-butyl isocyanides instead of carbonyl ligands have also been prepared.

2. Results and discussion

2.1. Reductive cleavage of the S–N bond

The N-methylsulfimide complex $Fe_2(CO)_6(\mu\text{-SN–CH}_3)$ (3) reacts with two equivalents of Li[BEt₃H] in THF at −78 °C to form a red solution of the dianion 4 (Scheme 1). The ¹¹B NMR spectra indicate the presence of two different types of coordinated BEt₃ molecules ($\delta^{11}B = -1$ and 7). If the solution of 4 is allowed to warm to room temperature, a different anion formulated as 5 ($\delta^{11}B = 1$) is formed by loss of one of the coordinated BEt₃ molecules.

Protonation with CF₃COOH at −78 °C converts 4 into $Fe_2(CO)_6(\mu\text{-NHCH}_3)(\mu\text{-SH})$ (6), which might exist in four possible isomeric forms (Scheme 1). Only two of these isomers are present in the solution in a ratio of 4:3 (by ¹H NMR). Owing to the reactivity of the SH groups, separation by column chromatography proved to be impossible. The structural assignment of the two isomers was achieved by ¹H/¹H NOE difference spectroscopy [10]. The NOE difference spectra were recorded at 300 and 500 MHz (2 s of saturation with a decoupling power of 40 db). The 300 MHz spectra are dominated by effects of magnetisation transfer, indicating that interconversion between both isomers takes place readily on the extended NMR timescale.

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Scheme 1.
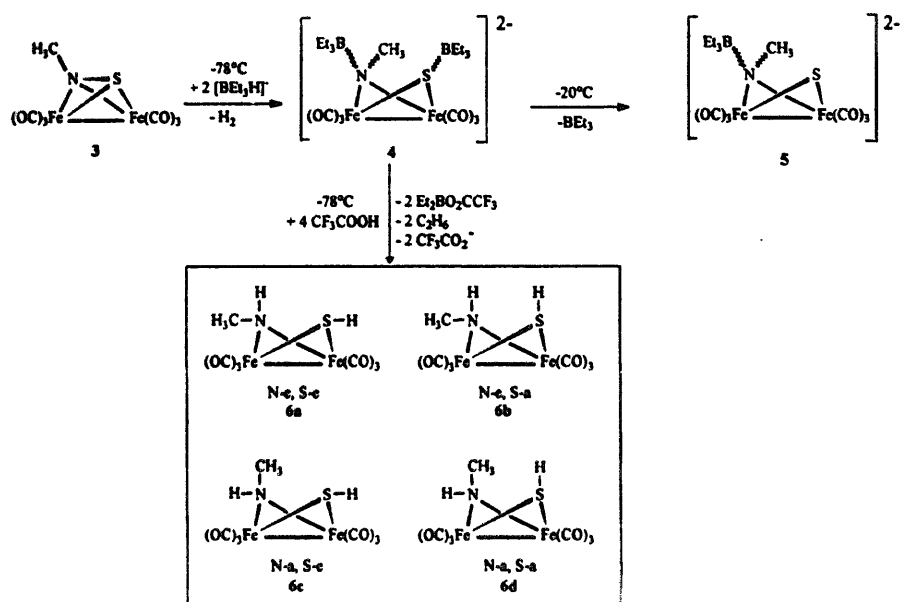
most likely by inversion at the sulfur atom. Since the coupling constant $^3J(^1HNC^1H) = 7.0$ (**6a**) and 5.9 Hz (**6b**) is observed, an SH/NH exchange can be excluded. In the case of the 500 MHz $^1H/^1H$ NOE difference spectra, effects of magnetisation transfer are still detected but are less dominant. Appreciable NOE's of the $^1H(NH)$ and $^1H(SH)$ resonances were observed by saturation of the $^1H(SH)$ or $^1H(NH)$ transitions respectively. Saturation of the $^1H(NMe)$ transitions did not cause any significant NOE of the $^1H(SH)$ resonances, which suggests that the NMe group occupies an equatorial position in both isomers, ruling out the structures **6c** and **6d**. The greater NOE of the $^1H(NH)$ resonances is observed by saturation of the $^1H(SH)$ transitions at $\delta = -3.59$. This signal belongs to the minor isomer for which, therefore, structure **6b** is suggested with the smaller distance between the hydrogen atoms linked to nitrogen and sulfur. The smaller NOE of the $^1H(NH)$ resonance in the analogous experiment (saturation of the $^1H(SH)$ transition at $\delta = -1.27$) then indicates that the major isomer is **6a**. The NMR signals of **6a** and **6b** were further assigned using $^1H/^1H$, $^{13}C/^1H$ and $^{15}N/^1H$ correlation spectroscopy.

The butterfly complexes **6** could not be obtained by hydrogenation of $Fe_2(CO)_6(\mu\text{-SN-CH}_3)$ (**3**) up to 100 bar H_2 and up to 50 °C, even in the presence of catalysts such as palladium on activated carbon or $(Ph_3P)_3RhCl$.

DeKock et al. [11] have explained the opening of the S–S bond in $Fe_2(CO)_6(\mu\text{-S}_2)$ by the S–S antibonding nature of the LUMO. It can be assumed that $Fe_2(CO)_6(\mu\text{-SN-CH}_3)$ (**3**) also possesses an empty molecular orbital of low energy and sulfur–nitrogen antibonding character. According to a cyclic voltammet-

ric study [0.001 M solution measured between +0.3 and −1.7 V in acetonitrile in the presence of tetraethylammonium perchlorate (0.1 M), platinum working electrode (diameter 1 mm), platinum counter electrode, measured with reference to a saturated calomel electrode], the electrochemical reduction is irreversible at a peak potential of −1.41 V.

The complexes $Fe_2(CO)_6(\mu\text{-SNH})$ (**1**) and $Fe_2(CO)_6(\mu\text{-SN-SiMe}_3)$ (**2**) both react with $Li[BEt_3H]$ to form the anion $[Fe_2(CO)_6(\mu\text{-SN-BEt}_3)]^-$ (**7**) by elimination of H_2 or $HSiMe_3$ respectively (Scheme 2).

The SH groups of the isomers of **6** can be methylated either by deprotonation using *n*-butyllithium and subsequent reaction with trimethyloxonium tetrafluoroborate or directly with diazomethane (Scheme 3). The product, $Fe_2(CO)_6(\mu\text{-NHCH}_3)(\mu\text{-SCH}_3)$ (**8**), is obtained as an isomeric mixture of two compounds in the ratio 10:1, separable by column chromatography on silica. The major component can be assigned to the N-e,S-e isomer on the basis of $^1H/^1H$ NOE difference spectra, and agreement with steric arguments.
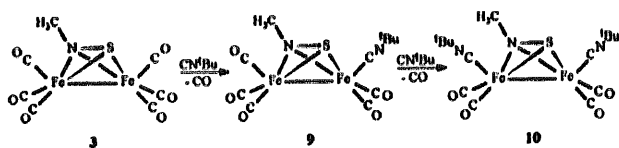

Scheme 2.

Scheme 3.
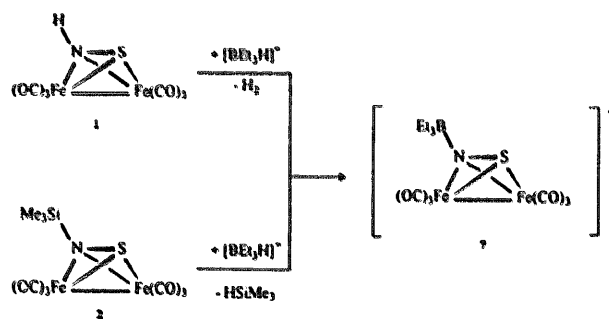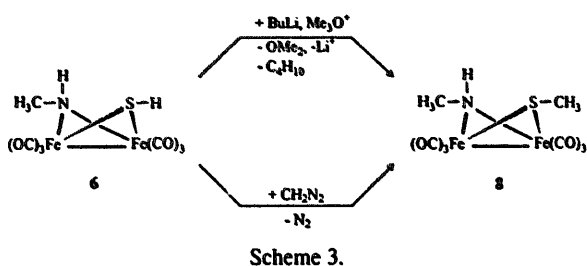
Attempts to deprotonate **8** by either diazabi-cyclo[5.4.0]undec-7-ene, *n*-butyllithium or Li[BEt$_3$H] were unsuccessful, and direct methylation using diazomethane could not be achieved either.

The SH protons of **6a** (δ(^{1}H) = -1.27) and **6b** (δ(^{1}H) = -3.59) are observed at remarkably low frequencies, similar to those of Fe$_2$(CO)$_6$(μ-SH)$_2$ [8] at δ(^{1}H) = $-2.21/0.22$ (a,e isomer), -0.4 (e,e isomer) and -2.43 (a,a isomer). The chemical shifts of the SCH$_3$ protons of **8** (δ(^{1}H) = 1.46, major isomer and 1.39, minor isomer) appear at lower frequencies than those of Fe$_2$(CO)$_6$(μ-SCH$_3$)$_2$ (δ(^{1}H) = 1.62/2.13 (a,e isomer) and 2.07 (e,e isomer)) [8]. Unfortunately, comparison of proton chemical shifts cannot be used to safely identify the isomers of Fe$_2$(CO)$_6$(μ-NHCH$_3$)(μ-SH) (**6**) or Fe$_2$(CO)$_6$(μ-NHCH$_3$)(μ-SCH$_3$) (**8**) involved. The ^{15}N NMR spectra of **6a**, **6b** and **8** (major isomer) show iron satellites; however, the ^{1}J(^{57}Fe,^{15}N) coupling constants of 6.2 to 6.6 Hz are nearly identical to those of Fe$_2$(CO)$_6$(μ-SNH) (**1**) (6.1 Hz) [4] and Fe$_2$(CO)$_6$(μ-SN–SiMe$_3$) (**2**) (5.6 Hz) [7]. The ^{1}J(^{15}N,^{1}H) coupling constant in **6** (70.0 Hz) is significantly smaller than in **1** (89.5 Hz) [4], probably due to the difference in electronegativity of the substituents at the nitrogen atom (CH$_3$ in **6** and S in **1**) and the resulting difference of the s orbital contributions in the N–H bonds.

2.2. Substitution of CO ligands

The tetrahedrane complexes **1** and **3** react with *tert*-butyl isocyanide under thermal conditions. In the case of **3** both mono- and disubstitution take place to give a mixture of **9** and **10**, irrespective of the stoichiometry of the starting materials. Compounds **9** and **10** can be separated by column chromatography. In the case of **1** only monosubstitution to **11** is observed (Scheme 4).

As a result of the substitution at the iron centers, the fast exchange of the CO ligands appears to be blocked.

Scheme 4.

This can be deduced from the ^{13}C NMR spectra of **9** and **11**, which show only one resonance for the undisturbed Fe(CO)$_3$ fragment at room temperature in addition to one signal for each of the carbonyls at the Fe(CO)$_2$ unit. At low temperature (233 K), the ^{13}C(CO) singlet of **3** is split into three signals (δ(^{13}C) = 205.1, 212.0 and 212.2). The low frequency resonance (205.1 ppm) in **3** is tentatively assigned to the carbonyl ligand which lies 'transoid' in the plane containing the iron–iron vector and the midpoint of the S–N bond. There is no low frequency resonance in the ^{13}C NMR spectra of **9**, **10** and **11**, indicating that the CO ligand 'transoid' to the iron–iron bond is replaced by *tert*-butyl isocyanide. All X-ray crystal structure determinations carried out so far for Fe$_2$(CO)$_6$(μ-SNR) tetrahedranes have indicated that the two Fe(CO)$_3$ fragments are arranged in the eclipsed conformation in the solid state [5–7].

No substitution reactions were observed to take place when either **1** or **3** were treated with triphenylphosphane.

2.3. Miscellaneous reactions

We were unable to insert small molecules such as carbene (from diazomethane), nitrene (from ClN(SiMe$_3$)$_2$), carbon monoxide (CO) or transition metal fragments like Pd(PPh$_3$)$_2$ and Ru(CO)$_3$ into the sulfur–nitrogen bond of **1** and **3**. This is in contrast to the reactivity of Fe$_2$(CO)$_6$(μ-S$_2$) [12]. Furthermore, no reaction of **1** and **3** with olefins (stilbene, cyclopentadiene) or acetylenes (phenylacetylene, acetylene dimethylcarboxylate) could be observed, although the addition of alkenes and alkynes to Fe$_2$(CO)$_6$(μ-S$_2$) [13] and Fe$_2$(CO)$_6$(μ-Se$_2$) [14] is well documented. The reaction of Fe$_2$(CO)$_6$(μ-SNH) (**1**) with Co$_2$(CO)$_8$ will be described separately [15].

3. Experimental

All starting materials were obtained from commercial sources. The synthesis of the starting tetrahedrane complexes Fe$_2$(CO)$_6$(μ-SNH) (**1**) [3], Fe$_2$(CO)$_6$(μ-SN–SiMe$_3$) (**2**) [3,4,6] and Fe$_2$(CO)$_6$(μ-SN–CH$_3$) (**3**) [3,5] has been described earlier. The reactions were carried out under argon using standard Schlenk techniques.

3.1. Reductive cleavage of the S–N bond in Fe$_2$(CO)$_6$(μ-SN–CH$_3$) (3)

205 mg (0.6 mmol) **3** [5] were dissolved in 50 ml of THF, and 1.2 ml of a 1.0 molar solution (1.2 mmol) of Li[BEt$_3$H] were added at -78 °C. The color of the solution changed from orange to red. The anion **4** which was formed initially lost BEt$_3$ above -20 °C to give the anion **5**.

4. ^{11}B NMR (THF): δ −1 and 7. IR (THF): ν(CO) 2033m, 1988vs, 1938vs cm^{-1}.

5. ^{11}B NMR (THF): δ 1. IR (THF): ν(CO) 2028m, 1981vs, 1938vs cm^{-1}.

3.2. Protonation of 4 by trifluoroacetic acid

0.18 ml (2.4 mmol) of CF$_3$COOH was added at −78 °C to a THF solution containing 0.6 mmol of **4**. The color of the solution changed immediately from red to orange. After the solution had reached room temperature, the solvent was removed in vacuo and the residue extracted twice with 40 ml of hexane. Evaporation of the solvent led to an isomeric mixture of **6a** and **6b** in the ratio 4:3 (yield 99%). IR (CsI): ν(NH) 3294w, ν(SH) 2358m and 2326m. IR (hexane): ν(CO) 2073m, 2036vs, 1990vs cm^{-1}. Decomposition of the orange crystals started at room temperature.

6a. ^{1}H NMR (C$_6$D$_6$): δ(SH) −1.27s, δ(NH) 0.14(broad), δ(NCH$_3$) 2.01d, $^3J(^1$H,^{1}H) 7.0 Hz. ^{13}C NMR (C$_6$D$_6$): δ(NCH$_3$) 50.7, δ(CO) 209.9. ^{15}N NMR (C$_6$D$_6$): δ −370.1, $^1J(^{15}$N,^{1}H) 70.0, $^1J(^{57}$Fe,^{15}N) 6.4 Hz.

6b. ^{1}H NMR (C$_6$D$_6$): δ(SH) −3.59s, δ(NH) −0.32(broad), δ(NCH$_3$) 2.14d, $^3J(^1$H,^{1}H) 5.9 Hz. ^{13}C NMR (C$_6$D$_6$): δ(NCH$_3$) 50.6, δ(CO) 209.4. ^{15}N NMR (C$_6$D$_6$): δ −362.0, $^1J(^{15}$N,^{1}H) 70.0, $^1J(^{57}$Fe,^{15}N) 6.2 Hz.

3.3. Synthesis of PPh$_4$[Fe$_2$(CO)$_6$(μ-SN=BEt$_3$)]

A solution of 196 mg (0.6 mmol) Fe$_2$(CO)$_6$(SNH) (**1**) [3] in 30 ml THF was treated with 0.6 ml of a 1.0 molar solution of Li[BEt$_3$H] at −78 °C, and 500 mg (1.2 mmol) of PPh$_4$Br was then added. The solution was allowed to warm to room temperature, stirred for 3 h and then filtered. Addition of 100 ml hexane and cooling to −20 °C led to crystallization of the PPh$_4^+$ salt of the anion **7** (orange crystals, decomp. 35 °C, yield 27%). ^{1}H NMR (C$_6$D$_6$): δ(BCH$_2$) 0.02q, δ(CH$_3$) 0.63t, δ(C$_6$H$_5$) 7.46m, 7.61m. ^{11}B NMR (C$_6$D$_6$): δ 1.2. ^{13}C NMR (C$_6$D$_6$): δ(CH$_3$) 11.3, δ(BCH$_2$) 21.7br, δ(ipso-C$_6$H$_5$) 117.6d [89.7], δ(m-C$_6$H$_5$) 131.1d [11.0], δ(o-C$_6$H$_5$) 134.6d [7.3], δ(p-C$_6$H$_5$) 136.2, δ(CO) 213.5br. ^{31}P NMR (C$_6$D$_6$): δ 24.5. IR (THF): ν(CO) 2046m, 1999vs, 1959s, 1950s cm^{-1}.

3.4. Methylation of Fe$_2$(CO)$_6$(μ-NHCH$_3$)(μ-SH) (6)

(i) 206 mg (0.6 mmol) **6** was dissolved in 30 ml THF, and the stoichiometric amount of BuLi (0.375 ml of a 1.6 molar solution) was added at −78 °C. The solution was stirred for 5 min, then the equivalent amount of trimethyloxonium tetrafluoroborate (89 mg, 0.6 mmol) was added. The solution was allowed to warm to room temperature, the solvent removed in vacuo and the

residue extracted three times with hexane (30 ml each). The solution was brought to dryness in vacuo and the product, Fe$_2$(CO)$_6$(μ-NHCH$_3$)(μ-SCH$_3$) (**8**), isolated as an isomeric mixture (10:1) in an overall yield of 69%.

(ii) A THF solution of 206 mg (0.6 mmol) of **6** was reacted with an excess of diazomethane (etheral solution) at room temperature. The solution was stirred for 1 h, then the solvent was removed in vacuo, the residue extracted twice with hexane (40 ml each) and the product (mixture of isomers) isolated from the solution (yield 55%).

The orange crystals decomposed at 128 °C. EI-MS: m/e 357 (30%, M$^+$), 189 (100%, M$^+$−6CO), 173 (70%, Fe$_2$SNCH$_3^+$). IR (CsI): ν(NH) 3278w. IR (hexane): ν(CO) 2068m, 2031vs, 1985vs cm^{-1}. Chromatography on silica gave two fractions:

Zone 1 (major isomer). ^{1}H NMR (C$_6$D$_6$): δ(NH) −0.10(broad), δ(SCH$_3$) 1.46s, δ(NCH$_3$) 1.99d, $^3J(^1$H,^{1}H) 6.6 Hz. ^{13}C NMR (C$_6$D$_6$): δ(SCH$_3$) 18.5, δ(NCH$_3$) 50.1, δ(CO) 210.4. ^{15}N NMR (C$_6$D$_6$): δ −369.6, $^1J(^{57}$Fe,^{15}N) 6.6 Hz.

Zone 2 (minor isomer). ^{1}H NMR (C$_6$D$_6$): δ(NH) 0.66(broad), δ(SCH$_3$) 1.39s, δ(NCH$_3$) 2.20d, $^3J(^1$H,^{1}H) 6.7 Hz. ^{13}C NMR (C$_6$D$_6$): δ(SCH$_3$) 21.2, δ(NCH$_3$) 50.0, δ(CO) 208.9.

3.5. Substitution of carbonyl ligands in Fe$_2$(CO)$_6$(μ-SN=CH$_3$) (3)

A solution containing 239 mg (0.7 mmol) Fe$_2$(CO)$_6$(SN=CH$_3$) (**3**) and 170 μl (1.5 mmol) ^{t}BuNC in 40 ml THF was stirred for two days at room temperature. The solvent was removed in vacuo, the residue extracted three times with pentane (30 ml each) and chromatographed on silica (25 × 2 cm) using pentane for elution.

Zone 1. Fe$_2$(CO)$_5$(CN^{t}Bu)(μ-SN=CH$_3$) (**9**), orange oil, yield 27%. ^{1}H NMR (C$_6$D$_6$): δ(C(CH$_3$)$_3$) 0.83, δ(NCH$_3$) 2.78. ^{13}C NMR (C$_6$D$_6$): δ(C(CH$_3$)$_3$) 30.0, δ(NCH$_3$) 51.7, δ(C(CH$_3$)$_3$) 57.7, δ(Fe(CO)$_3$) 211.4, δ(Fe(CO)$_2$) 213.7 and 214.1. ^{13}C NMR (CDCl$_3$): δ(CN) 155.8 (broad). ^{14}N NMR (C$_6$D$_6$): δ(CN) −189.8. IR (hexane): ν(CN) 2142w; ν(CO) 2041m, 1999s, 1973m, 1965w cm^{-1}. EI-MS: m/e 396 (5%, M$^+$), 256 (40%, M$^+$−5CO), 200 (100%, Fe$_2$(CNH)(SNCH$_3$)$^+$).

Zone 2. Fe$_2$(CO)$_4$(CN^{t}Bu)$_2$(μ-SN=CH$_3$) (**10**), orange oil, yield 50%. ^{1}H NMR (C$_6$D$_6$): δ(C(CH$_3$)$_3$) 0.95, δ(NCH$_3$) 3.12. ^{13}C NMR (C$_6$D$_6$): δ(C(CH$_3$)$_3$) 30.6, δ(NCH$_3$) 51.7, δ(C(CH$_3$)$_3$) 57.2, δ(CN) 159.9(broad), δ(Fe(CO)$_2$) 215.7 and 216.2. ^{14}N NMR (C$_6$D$_6$): δ(CN) −192.2. IR (hexane): ν(CN) 2121m; ν(CO) 2027m, 1995s, 1968m cm^{-1}. EI-MS: m/e 451 (15%, M$^+$), 339 (60%, M$^+$−4CO), 283 (85%, Fe$_2$(CNH)(CN^{t}Bu)(SNCH$_3$)$^+$), 227 (100%, Fe$_2$(CNH)$_2$(SNCH$_3$)$^+$), 200 (55%, Fe$_2$(CNH)(SNCH$_3$)$^+$).

3.6. Substitution of a carbonyl ligand in $Fe_2(CO)_6(\mu\text{-}SNH)$ (1)

A solution containing 196 mg (0.6 mmol) 1 and 80 μl (0.7 mmol) ^tBuNC in 30 ml THF was stirred for two days at room temperature. The THF was removed in vacuo, the residue extracted three times with hexane (50 ml each) and the solvent evaporated. The product, $Fe_2(CO)_5(CN^tBu)(\mu\text{-}SNH)$ (11), is an orange–brown oil, yield 33%. ^1H NMR (C_6D_6): $\delta(C(CH_3)_3)$ 0.86, $\delta(NH)$ 2.66br. ^{13}C NMR (C_6D_6): $\delta(C(CH_3)_3)$ 30.1, $\delta(C(CH_3)_3)$ 57.8, $\delta(CN)$ 156.2, $\delta(Fe(CO)_3)$ 211.6, $\delta(Fe(CO)_2)$ 213.8 and 213.9. ^{14}N NMR (C_6D_6): $\delta(CN)$ -190.6, $\delta(Fe_2SN)$ -379. IR (hexane): $\nu(CN)$ 2144m; $\nu(CO)$ 2045m, 2002vs, 1977s, 1965m, 1953m cm^{-1}. EI-MS: m/e 382 (8%, M^+), 242 (35%, $M^+ - 5CO$), 186 (100%, $Fe_2(CNH)(SNH)^+$), 159 (25%, Fe_2SNH^+).

References

[1] S. Otsuka, T. Yoshida and A. Nakamura, Inorg. Chem., 7 (1968) 1833.

[2] R. Meij, J. van der Helm, D.J. Stufkens and K. Vrieze, J. Chem. Soc., Chem. Commun., (1978) 506; R. Meij, D.J. Stufkens, K. Vrieze, A.M.F. Brouwers, J.D. Schagen, J.J. Zwinselman, A.R. Overbeek and C.H. Stam, J. Organomet. Chem., 170 (1979) 337.

[3] M. Herberhold and W. Bühlmeyer, Angew. Chem., 96 (1984) 64; Angew. Chem., Int. Ed. Engl., 23 (1984) 80.

[4] B. Wrackmeyer, E. Kupce, B. Distler, K. Dirnberger and M. Herberhold, Z. Naturforsch., 46b (1991) 1679.

[5] M. Herberhold, U. Bertholdt and W. Milius, Z. Naturforsch., 50b (1995) 1252.

[6] M. Herberhold, U. Bertholdt, W. Milius, A. Glöckle and B. Wrackmeyer, J. Chem. Soc., Chem. Commun., (1996) 1219.

[7] M. Herberhold, U. Bertholdt, B. Wrackmeyer and W. Milius, Z. Naturforsch., 51b (1996) 1283.

[8] D. Seyferth, R.S. Henderson and L.-C. Song, Organometallics, 1 (1982) 125; D. Seyferth, G.B. Womack, R.S. Henderson, M. Cowie and B.W. Hames, Organometallics, 5 (1986) 1568.

[9] D. Seyferth and R.S. Henderson, J. Organomet. Chem., 204 (1981) 333.

[10] J.K.M. Sanders and J.D. Mersh, Progr. NMR Spectrosc., 15 (1982) 353.

[11] R.L. DeKock, E.J. Baerends and R. Hengelmolen, Organometallics, 3 (1984) 289.

[12] M. Cowie, R.L. DeKock, T.R. Wagenmaker, D. Seyferth, R.S. Henderson and M.K. Gallagher, Organometallics, 8 (1989) 119; P. Mathur and V.D. Reddy, J. Organomet. Chem., 387 (1990) 193.

[13] A. Kramer and I.-P. Lorenz, J. Organomet. Chem., 388 (1990) 187; A. Kramer, R. Lingnau, I.-P. Lorenz and H.A. Mayer, Chem. Ber., 123 (1990) 1821; J. Messelhäuser, I.-P. Lorenz, K. Haug and W. Hiller, Z. Naturforsch., 40b (1985) 1064.

[14] P. Mathur, M.M. Hossain, K. Das and U.C. Sinha, J. Chem. Soc., Chem. Commun., (1993) 46; P. Mathur and M.M. Hossain, Organometallics, 12 (1993) 2398; P. Mathur, A.K. Dash, M.M. Hossain and C.V.V. Satyanarayana, J. Organomet. Chem., 493 (1995) 257.

[15] M. Herberhold, U. Bertholdt and B. Wrackmeyer, submitted to Z. Naturforsch.