Synthesis and Characterization of Aza-Trimetalla Tetrahedranes

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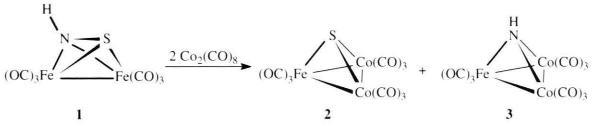
Cluster, NMR Spectra

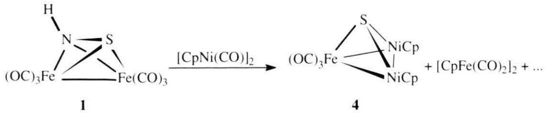
The sulfimide complex $Fe_2(CO)_6(\mu\text{-SNH})$ (**1**) reacts with $Co_2(CO)_8$ to form a 1:1 mixture of the known clusters $FeCo_2(CO)_9(\mu_3\text{-S})$ (**2**) and $FeCo_2(CO)_9(\mu_3\text{-NH})$ (**3**). The aza-tetrahedrane **3** may be used as a precursor for the synthesis of the new aza-trimetalla tetrahedranes $Fe_2Co(CO)_9(\mu\text{-H})(\mu_3\text{-NH})$ (**5**), $CpMoFeCo(CO)_8(\mu_3\text{-NH})$ (**6**), $CpNiFeCo(CO)_6(\mu_3\text{-NH})$ (**7**) and $(CpNi)_2Fe(CO)_3(\mu_3\text{-NH})$ (**8**) which were obtained from exchange reactions of **3** with $Na_2[Fe(CO)_4]$, $Na[CpMo(CO)_3]$ and $[CpNi(CO)]_2$. However, the reactions of **3** with $Na_2[Fe(CO)_4]$ and $Fe_3(CO)_{12}$ gave $Fe_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-NH})$ (**9**) only as a minor product in addition to large amounts of $Fe_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-S})$ (**10**). The ^1H NMR spectra of **3** and **5** - **9** show a broadened triplet for the NH proton between $\delta(^1H)$ 8.21 and 9.53. Chemical shifts $\delta(^{14}N)$ were determined most efficiently by heteronuclear $^1H\{^{14}N\}$ double resonance experiments. The $\delta(^{14}N)$ values for aza-trimetalla tetrahedranes (-180 to -202) indicate delocalized bonding between the μ_3-bridging nitrogen atom and the metal triangle.

Introduction

Aza-trimetalla [1, 2] as well as trimetalla-thia tetrahedranes [3, 4] are known since the mid-sixties. There are numerous methods of preparation which, however, often lead only to certain trimetalla tetrahedrane species, and are not generally applicable. In contrast, trimetalla-thia tetrahedranes may be obtained systematically by metal exchange reactions [5]. In continuing our investigations of the reactivity of $Fe_2(CO)_6(\mu\text{-SNH})$ (**1**) [6], we report on a new route to $FeCo_2(CO)_9(\mu_3\text{-NH})$ (**3**) and the syntheses of similar aza-trimetalla tetrahedranes.



Scheme 1



Scheme 2

Results and Discussion

Synthesis

The cluster $Fe_2(CO)_6(\mu\text{-SNH})$ (**1**) reacts with two equivalents of $Co_2(CO)_8$ within 24 h in boiling toluene to form a mixture of the trimetalla tetrahedranes $FeCo_2(CO)_9(\mu_3\text{-S})$ (**2**) [3] and $FeCo_2(CO)_9(\mu_3\text{-NH})$ (**3**) [1] (Scheme 1). Formally the reaction may be explained by the cleavage of **1** into the fragments $Fe(CO)_3(S)$ and $Fe(CO)_3(NH)$, respectively, and subsequent trapping with $Co_2(CO)_8$. The separation of the two clusters was achieved by column chromatography but, unfortunately, several runs with small amounts of the mixture are necessary because the elution rates are very similar. Compound **2** may be obtained in better yield by other methods [3]. In the case of the aza-trimetalla tetrahedrane **3**, this new route afforded the highest yield (48%) compared with literature procedures [1].

The analogous reaction of **1** with other dimetallic precursors such as $[CpNi(CO)]_2$, $[Cp^*Cr(CO)_2]_2$ and $[CpMo(CO)_3]_2$ failed to give aza-trimetalla tetrahedranes. From the reaction of $Fe_2(CO)_6(\mu\text{-SNH})$ (**1**) with $[CpNi(CO)]_2$, only $(CpNi)_2Fe(CO)_3(\mu_3\text{-S})$ (**4**) [7] (see Experimental) and $[CpFe(CO)_2]_2$ could be isolated (Scheme 2), wheras no reaction took place between **1** (decomposition) and the group 6 dimetallic clusters (recovered unchanged).

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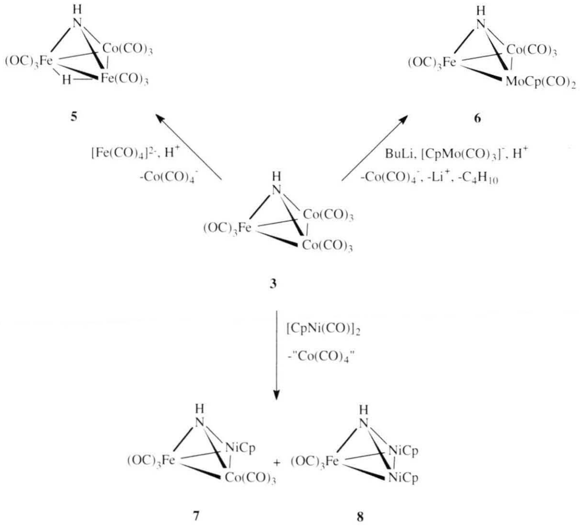
Since the systematic preparation of tetrahedral aza-trimetalla clusters starting from $Fe_2(CO)_6(\mu$-SNH) (**1**) was unsuccessful, we tried to obtain complexes of this type starting with $FeCo_2(CO)_9(\mu_3$-NH) (**3**) via metal fragment substitution. This method had proven to be effective in the syntheses of trimetalla-thia tetrahedranes [5].

The reaction of **3** with two equivalents of tetracarbonylferrate in boiling THF gave, after acidic hydrolysis, $Fe_2Co(CO)_9(\mu$-H$)(\mu_3$-NH) (**5**) (Scheme 3). While the first exchange of a $Co(CO)_3$ fragment to give **5** takes place readily, the formation of $Fe_3(CO)_9(\mu$-H$)_2(\mu_3$-NH) (**9**) could not be observerd.

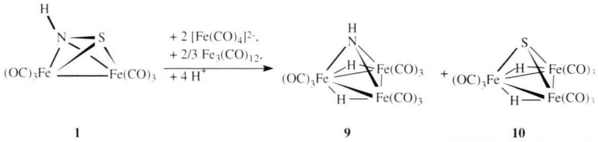


Scheme 3

Similarly, only one of the $Co(CO)_3$ fragments of **3** could be replaced in the reaction with $[CpMo(CO)_3]^-$ to form $CpMoFeCo(CO)_8(\mu_3$-NH) (**6**) (Scheme 3). The yield of **6** was markedly increased if the starting tetrahedrane $FeCo_2(CO)_9(\mu_3$-NH) (**3**) was deprotonated prior to the reaction. Again, there was no evidence for exchange of the second $Co(CO)_3$ unit of **3**.

Using the dimeric nickel complex $[CpNi(CO)]_2$, which is powerful in exchanging $Co(CO)_3$ groups in $FeCo_2(CO)_9(\mu_3$-S) (**2**) [5], two $Co(CO)_3$ fragments of **3** were replaced stepwise leading to $CpNiFeCo(CO)_6(\mu_3$-NH) (**7**) and $(CpNi)_2Fe(CO)_3(\mu_3$-NH) (**8**), respectively (Scheme 3).

The aza-trimetalla tetrahedranes **6** and **7** are chiral; no attempts were made to separate the enantiomers. The aza-triferra tetrahedrane $Fe_3(CO)_9(\mu$-H$)_2(\mu_3$-NH) (**9**) was identified in the presence of a large exess (1:20) of $Fe_3(CO)_9(\mu$-H$)_2(\mu$-S) (**10**) [3b] as a minor product of the reaction of $Fe_2(CO)_6(\mu$-SNH) (**1**) with $Na_2[Fe(CO)_4]/Fe_3(CO)_{12}$ (Scheme 4). This reaction was originally planned to induce oxidative addition of the tetracarbonylferrate to the S-N bond of **1**. Attempts to separate **9** and **10** by column chromatography on silica failed because of decomposition. The molar ratio of **9** and **10**(1:20), as well as the exclusive formation of **4** during the reaction of $Fe_2(CO)_6(\mu$-SNH) (**1**) with $[CpNi(CO)]_2$ suggest that nitrogen-metal intermediates are less stable then the sulfur-metal fragments. This, in turn, may be the reason for the less effective formation of aza-trimetalla tetrahedranes as compared to their sulfur analogues.



Scheme 4

NMR spectroscopic results

The ^1H, ^{13}C, ^{14}N and ^{59}Co NMR data are listed in Table I. The ^1H(NH) resonances are broadened 1:1:1 triplets except for $Fe_2Co(CO)_9(\mu$-H$)(\mu_3$-NH) (**5**) where the triplet is well resolved (Fig. 1). This indicates reduced quadrupolar relaxation rates of the ^{14}N nuclei in these clusters. Generally the triplets cover a range of about 150 Hz. Therefore and because of the inherent low solubility of the aza-trimetalla tetrahedranes, the recording of ^1H NMR spectra requires prolonged accumulation times. The ^1H NMR signals of the hydridic and the NH protons in **5** reveal a small unresolved coupling, detected by the slight decrease of the line width of the hydridic ^1H resonance in a homonuclear decoupling experiment at -20°C. Satellites due to $^1J(^{57}Fe,^1H)$ could not be resolved at the bottom of the $^1H(\mu$-H) resonance signal.

Table II contains literature data of both $\delta(^1H)$ and $^1J(^{14}N,^1H)$ of μ_3-NH groups. The δ(NH) values cover a range of at least 6.5 ppm. The changes in the chemical shift of the μ_3-NH proton are apparently

Table I. ^{1}H, ^{13}C, ^{14}N and ^{59}Co NMR data δ[J] of the aza-trimetalla tetrahedranes **3** and **5** to **9**.

Aza-trimetalla tetrahedrane	^{1}H NMR	^{13}C NMR	^{14}N NMR[a]	^{59}Co NMR[b]
$Co_2Fe(CO)_9(\mu_3\text{-}NH)$ (**3**)	9.28 [58.1][c]	202.4 (br.)	-180	-2068(8200)
$CoFe_2(CO)_9(\mu\text{-}H)(\mu_3\text{-}NH)$ (**5**)	8.78 [57.6] (NH); -20.11 (M_3H)	206.7	-202	-2322(6600)
$CpMoCoFe(CO)_8(\mu_3\text{-}NH)$ (**6**)	8.87 [50]	94.1 (Cp); 200.9; 209.8; 230.3; 232.7 (CO)	-194	-2454(4300)
$CpNiCoFe(CO)_6(\mu_3\text{-}NH)$ (**7**)	9.53 [52]	88.8 (Cp); 211.7 (CO)	-184	-2062(5000)
$(CpNi)_2Fe(CO)_3(\mu_3\text{-}NH)$ (**8**)	9.28 [50]	87.1 (Cp); 212.8 (CO)	-194	-
$Fe_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}NH)$ (**9**)	8.21 [51] (NH); -23.33 (Fe_3H_2)	206.4	not measured	-

[a]: $\delta(^{14}N)$ from $^1H\{^{14}N\}$ experiments ± 1ppm; [b]: Widths at half height ($h_{1/2}$) in Hz are given in parentheses; [c]: $^1J[^{14}N^1H]$ ±1.5 Hz are given in square brackets.

Table II. ^{1}H NMR data of aza-trimetalla tetrahedranes.

Aza-trimetalla tetrahedrane	δ(NH)	$^1J\ [^{14}N^1H]$ [Hz]
$Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ [2a]	9.4	57
$FeCo_2(CO)_9(\mu_3\text{-}NH)$ [2b]	10.6[a]	
$FeRu_2(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ [2b]	6.5	54
$FeRu_2(CO)_8[P(OMe)_3](\mu_3\text{-}CO)(\mu_3\text{-}NH)$ [2b]	6.7	43
$Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ [2b]	5.7	54
$Ru_3H_2(CO)_9(\mu_3\text{-}NH)$ [2e]	6.36	55.2
$Os_3H_2(CO)_9(\mu_3\text{-}NH)$ [2d]	4.06	
$Os_3H_4(CO)_8(\mu_3\text{-}NH)$ [2d]	4.42	
$W_3(O^iPr)_6(\mu_2\text{-}O^iPr)_3(\mu_3\text{-}O^iPr)(\mu_3\text{-}NH)$ [2g]	9.87	

[a]: Our value: 9.28ppm.

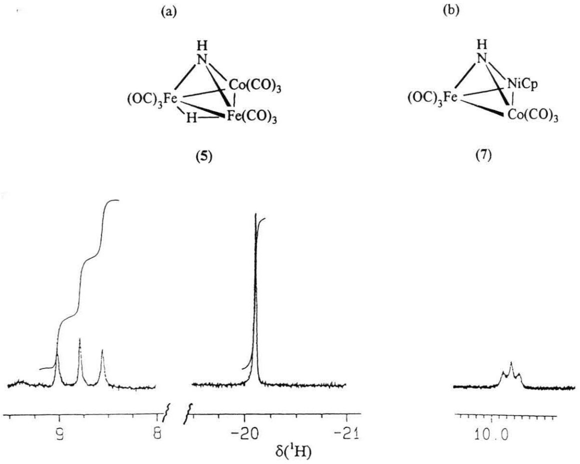


Fig. 1. 250.13 MHz ^{1}H NMR spectra of the aza-trimetalla tetrahedranes **5** (a) and **7** (b).

dominated by the composition of the metal triangle. Usually the μ_3-NH resonances are shifted to lower frequencies if heavy metals form the triangle. The only exception so far is the $W_3(\mu_3\text{-}NH)$ cluster which, however, possesses a completely different ligand sphere. The δ(NH) values of the tetrahedranes **5** to **9** are found in the area typical of $Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ [2a] and $Co_2Fe(CO)_9(\mu_3\text{-}NH)$ [2b]. The single molybdenum atom in the framework of **6** obviously has a negligible influence.

The magnitude of $^1J(^{14}N,^1H)$ of the tetrahedranes **5** to **9** as well as the data cited in Table II fall in the range which has also been found for ammonium ions [8].

The $\delta(^{14}N)$ data could be obtained most efficiently by selective heteronuclear double resonance $^1H\{^{14}N\}$ experiments; ^{1}H-detected (inverse) 2D $^1H/^{15}N$ nuclear shift correlations (Fig. 2) require a lot of spectrometer time, and a single experiment may not be reliable if the $\delta(^{15}N)$ value is unknown. Suprisingly, the δ(N) values of aza-trimetalla tetra-

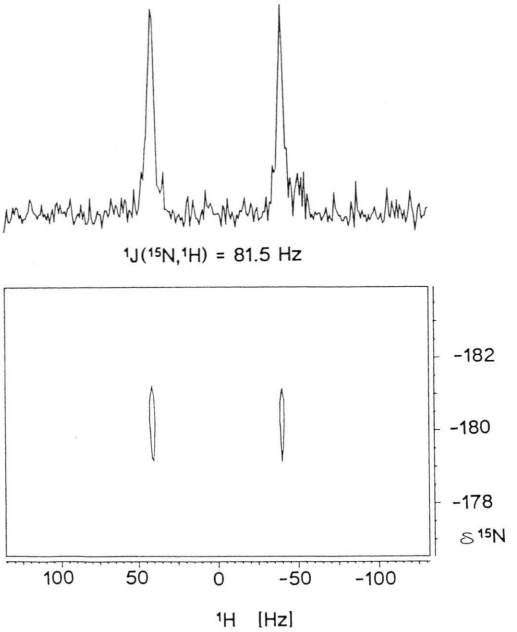


Fig. 2. 500.13 MHz ^1H-detected (inverse) 2D $^1H/^{15}N$ (HMQC) [11]) shift correlation of $FeCo_2(CO)_9(\mu_3\text{-}NH)$ (**3**) (saturated in C_6D_6, 24 hours spectrometer time).

hedranes were found between δ = -180 and -202, shifted to higher frequencies when compared with $Fe_2(CO)_6(\mu\text{-}SNH)$ (**1**) [6b]. This nitrogen nuclear deshielding indicates strong delocalization of the bonding between NH and the metal triangle. According to extended Hückel MO calculations, the frontier orbitals of $M_3(CO)_9$ fragments always consist of contributions from more than one metal [9]. The bonding orbitals of the σ and π type in M_3NH tetrahedranes are shown qualitatively in Fig. 3, illustrating this delocalization. The $^{13}C(CH)$ nucleus in $Co_3(CO)_9(\mu_3\text{-}CH)$, isoelectronic with **3**, is also deshielded ($\delta^{13}C$ = 263 [10]), most likely for the same reason.

Experimental

All starting materials were obtained from commercial sources. The synthesis of the starting tetrahedrane complex, $Fe_2(CO)_6(\mu\text{-}SNH)$ (**1**) [6a], has been described earlier. The reactions were carried out under argon using standard Schlenk techniques. Bruker AM 500 and Bruker ARX 250 spectrometers were used to record the NMR spectra. Chemical shifts δ^1H, $\delta^{13}C$ and $\delta^{14}N$ are given with respect to Me_4Si [$\delta^1H(C_6D_5H)$ = 7.15, $\delta^{13}C(C_6D_6)$ = 128.0] and external neat $MeNO_2$.

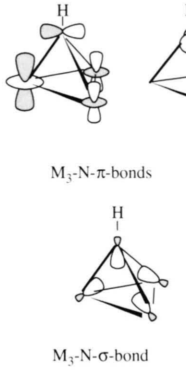


Fig. 3. Qualitative description of N-M_3 σ and π bonding in aza-trimetalla tetrahedranes.

$Co_2Fe(CO)_9(\mu_3\text{-}NH)$ (3)

A solution of 392 mg (1.2 mmol) of $Fe_2(CO)_6(\mu\text{-}SNH)$ (**1**) and 821 mg (2.4 mmol) of $Co_2(CO)_8$ in 150 ml of toluene was heated for 2 d at 100°C. A small amount of metal was deposited from the brown to black solution as a metallic mirror. Silica was added to the reaction mixture; the solvent was then removed *in vacuo* and the material thereby adsorbed on silica. Separation of the products was achieved in several portions by column chromatography (2 x 40 cm, silica/pentane) each time with about a fifth part of the mixture.

Zone 1: $Co_2Fe(CO)_9(\mu_3\text{-}S)$ (**2**) [3], yield 48%.

Zone 2: $Co_2Fe(CO)_9(\mu_3\text{-}NH)$ (**3**) [1]: brown to black crystals, yield 48%. – IR (CsI): ν(NH) 3357w, IR (hexane): ν(CO) 2101vw, 2059s, 2045m, 2036m, 1981vw, 1973vw. EI-MS: 441 (30%, M^+), 189 (100%, M^+-9CO), 130 (65%, $CoFeNH^+$).

$(CpNi)_2Fe(CO)_3(\mu_3\text{-}S)$ (4)

A solution of 392 mg (1.2 mmol) of $Fe_2(CO)_6(\mu\text{-}SNH)$ (**1**) and 725 mg (2.4 mmol) of $[CpNi(CO)]_2$ in 150 ml of toluene was heated for 2 d at 100°C. The solution turned black, and the deposition of a metal mirror was observed. The solvent was removed *in vacuo,* and silica was added to transform the oily residue into a solid material. Separation of the products was achieved by column chromatography (2 x 40 cm, silica/pentane) in small portions.

Zone 1: $Cp_2Ni_2Fe(CO)_3(\mu_3\text{-}S)$ (**4**) [7], brown to black crystals, yield 18%. – IR (hexane): ν(CO) 2028s, 1962m, 1954m. EI-MS: 418 (10%, M^+), 334 (28%, M^+- 3CO), 269 (25%, $CpNi_2FeS^+$), 186 (100%, Cp_2Fe^+). ^1H NMR (C_6D_6): δ = 4.91; ^{13}C NMR (C_6D_6): δ = 87.7(Cp), 212.9(CO).

Zone 2: $[CpFe(CO)_2]_2$: red crystals, yield 30%.

CoFe$_2$(CO)$_9$(μ-H)(μ_3-NH) (**5**)

A solution of 176 mg (0.4 mmol) of Co$_2$Fe(CO)$_9$(μ_3-NH) (**3**) and 171 mg (0.8 mmol) of Na$_2$[Fe(CO)$_4$] in 40 ml of THF was heated for 4 d at 65°C (partial metal separation). The solvent was removed *in vacuo*, and the residue treated with about 50 ml of degassed water and 50 ml of hexane. The solvent mixture was acidified to pH = 1 by HCl and the product transferred to the hexane layer by shaking. Compound **5** was isolated after separation of the layers, drying (Na$_2$SO$_4$) and removing the solvent.
CoFe$_2$H(CO)$_9$(μ_3-NH) (**5**), brown to black crystals, yield 37%. – IR(CsI): ν(NH) 3397w, IR (hexane): ν(CO) 2101vw, 2062m, 2055s, 2047m, 2036w, 2025m, 1980w. EI-MS: 339 (1%, M$^+$), 187 (15%, M$^+$-9CO), 130 (20%, FeCoNH$^+$).

CpMoCoFe(CO)$_8$(μ_3-NH) (**6**)

A solution containing 132 mg (0.3 mmol) of Co$_2$Fe(CO)$_9$(μ_3-NH) (**3**), 0.19 ml of a 1.6 molar solution of BuLi in hexane and 160 mg (0.6 mmol) of Na[CpMo(CO)$_3$] in 100 ml of toluene was heated for 3 d at 90°C (partial metal separation). 42 μl (0.9 mmol) of CF$_3$COOH were added, the solvent removed *in vacuo*, and the product purified by column chromatography (2 x 40 cm, silica/ pentane).
CpMoCoFe(CO)$_8$(μ_3-NH) (**6**), brown to black crystals, yield 34%. – IR(CsI): ν(NH) 3355w, IR (hexane): ν(CO) 2071m, 2025s, 2009s, 1971m, 1963w, 1854w. EI-MS: 517 (20%, M$^+$), 291 (100%, M$^+$-8CO), 235 (30%, CpMoCoNH$^+$).

(CpNi)$_2$Fe(CO)$_3$(μ_3-NH) (**7**) *and CpNiCoFe(CO)$_6$(μ_3-NH)* (**8**)

A solution of 220 mg (0.5 mmol) of Co$_2$Fe(CO)$_9$(μ_3-NH) (**3**) and 302 mg (1.0 mmol) of [CpNi(CO)]$_2$ in 100 ml of toluene was heated for 3 d at 90°C (partial metal separation). Silica was added to the reaction mixture, the solvent then removed *in vacuo* and the product mixture thereby adsorbed on silica. Separation of the products was achieved by column chromatography (2 x 40 cm, silica/pentane).
Zone 1: Cp$_2$Ni$_2$Fe(CO)$_3$(μ_3-NH) (**7**), brown to black crystals, yield 15%. – IR(CsI): ν(NH) 3383w, IR (hexane): ν(CO) 2073m, 2029s, 2018m, 2010m, 1969w, 1965m. EI-MS: 401 (25%, M$^+$), 317 (100%, M$^+$-3CO), 251 (20%, CpNi$_2$FeN$^+$), 186 (30%,Ni$_2$FeN$^+$),
Zone 2: CpNiCoFe(CO)$_6$(μ_3-NH) (**8**), brown to black crystals, yield 48%. IR(CsI): ν(NH) 3376w, IR (hexane): ν(CO) 2031s, 1970s. EI-MS: 421 (15%, M$^+$), 253 (100%, M$^+$-6CO), 187 (15%, CoNiFeN$^+$).

Mixture of Fe$_3$(CO)$_9$(μ-H)$_2$(μ_3-NH) (**9**) *and Fe$_3$(CO)$_9$(μ-H)$_2$(μ_3-S)* (**10**)

A solution of 147 mg (0.45 mmol) of Fe$_2$(CO)$_6$(SNH) (**1**), 193 mg (0.9 mmol) of Na$_2$[Fe(CO)$_4$] and 151 mg (0.3 mmol) of Fe$_3$(CO)$_{12}$ in 40 ml of THF was heated for 2 d at 65°C (partial metal separation). 0.14 ml (1.8 mmol) of CF$_3$COOH were added and the solvent was removed *in vacuo*. The residue was extracted with hexane (3 x 30 ml). Chromatographic workup failed because of decomposition of the products on silica.

Acknowledgements

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