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Dehydrogenative desulfurization of thiourea derivatives to give carbodiimides, using hydrosilane and an iron complex†

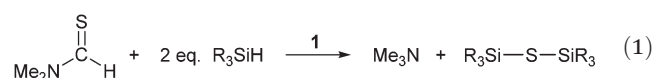Kazumasa Hayasaka,[a] Kozo Fukumoto[b] and Hiroshi Nakazawa*[a]

Dehydrogenative desulfurization of thiourea derivatives (RNHC(S)NHR′) has been achieved, to give carbodiimides (RN=C=NR′), in the reaction with hydrosilane and (η^5-C_5H_5)Fe(CO)$_2$Me. The obtained carbodiimide reacted with (η^5-C_5H_5)Fe(CO)(SiR$_3$) formed in the reaction to give an N-silylated η^2-amidino iron complex, which was isolated and then characterized by X-ray analysis.
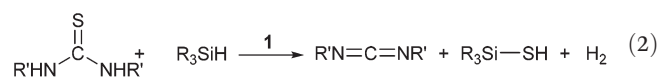
Introduction

Carbodiimides (RN=C=NR′) are commonly used as dehydrating agents in organic syntheses and as organic building blocks for many chemicals, because they have nucleophilic moieties at the nitrogen atoms and an electrophilic center at the carbon atom.[1] Recently, carbodiimides have elegantly been utilized as facile starting materials to prepare guanidine derivatives (guanylation reaction)[2] and as one component in multicomponent reactions (MCRs).[3] Carbodiimides have been synthesized by several methods including the dehydrogenative deoxidization of ureas,[4] the dehydrogenative desulfurization of thioureas,[5] and the thermolysis–decarboxylation of isocyanates.[6] Carbodiimides have been synthesized on an industrial scale using ureas or thioureas and phosgene (COCl$_2$). Phosgene is known to be a poisonous gas. The following reagents have also been reported for the conversion of thioureas to carbodiimides: N,N-dimethyl-4-aminopyridine (DMAP),[5e,l] triphenylphosphine dibromide (Ph$_3$PBr$_2$),[5h] arylsulfonyl chlorides (RSO$_2$Cl),[4g,5k] and metal oxides (HgO,[5b,m,6e] PbO[5d]). DMAP, HgO, and PbO are also toxic. These reagents should therefore be replaced by other non-toxic chemicals. It is generally accepted that iron is one of the best candidates as a precious metal surrogate because of its price, abundance, and environmental compatibility.[7]

We recently reported that N,N-dimethylthioformamide (Me$_2$NC(S)H) could be converted into an amine (NMe$_3$) and a disilathiane (R$_3$SiSSiR$_3$) in a reaction with hydrosilane (R$_3$SiH), with the help of CpFe(CO)$_2$Me (Cp = η^5-C_5H_5) (**1**; eqn (1)).[8] The key steps for achieving C=S bond cleavage are shown in Scheme 1. The C=S bond in thioamide coordinates in an η^1-fashion to a 16e iron complex bearing a silyl group, and the complex is converted into an η^2-complex. Then, the silyl migration from the iron center to the sulfur atom via Si hypervalent structure occurs. Thus, an Fe–C–S three-membered-ring complex is formed. This migration is followed by C–S bond cleavage in the coordination sphere. The bond cleavage gives a carbene complex. In this reaction sequence the silyl migration triggers the cleavage of a C=S bond. Recently, we reported that this type of reaction, *i.e.*, a silyl-migration-induced reaction (SiMI reaction),[8,9] has been involved in C–CN,[9f] N–CN,[9e] O–CN,[9b] and C=O[9d] bond cleavage.

$$\underset{Me_2N}{\overset{S}{\underset{\|}{C}}}\!\!-\!\!H \;+\; 2\text{ eq. }R_3SiH \;\xrightarrow{\;1\;}\; Me_3N \;+\; R_3Si\!-\!S\!-\!SiR_3 \qquad (1)$$

In this paper, we report the first example of the conversion of a thiourea derivative (RNHC(S)NHR′) to a carbodiimide (RN=C=NR′) in a reaction with hydrosilane, with the help of **1**. This reaction involves desulfurization of the C=S moiety and two hydrogen abstractions from the nitrogens (eqn (2)).
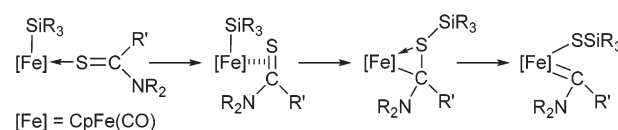
$$\underset{R'HN}{\overset{S}{\underset{\|}{C}}}\!\!-\!\!NHR' \;+\; R_3SiH \;\xrightarrow{\;1\;}\; R'N\!=\!C\!=\!NR' \;+\; R_3Si\!-\!SH \;+\; H_2 \qquad (2)$$

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Scheme 1 Reaction sequences of C=S bond cleavage.

Results and discussion

A solution of equimolar amounts of N,N'-diisopropylthiourea (^{i}PrNHC(S)NH^{i}Pr), (EtO)$_3$SiH, and iron complex **1** in THF was heated at 60 °C for 24 h (Table 1, entry 1). The ^{1}H NMR and GC-MS spectra of the product revealed the formation of N,N'-diisopropylcarbodiimide (^{i}PrN=C=N^{i}Pr), showing that the dehydrogenative desulfurization of ^{i}PrNHC(S)NH^{i}Pr was achieved in this system. Complex **1** was essential for the dehydrogenative desulfurization of thiourea, because the carbodiimide was not formed without **1** (entry 2). The conversion was also observed under photo-irradiation instead of thermal conditions, although the efficiency was insufficient (entry 3). Transition-metal complexes other than **1** were active for the conversion, but the efficiencies were lower than that of **1** (entries 4–11). The effect of the amount of **1** on the conversion yield of the carbodiimide was examined and it was found that 2 equiv. of **1** with respect to the thiourea and (EtO)$_3$SiH gave better formation of the carbodiimide (76%, entry 12). Details of the results on the effect of the type of hydrosilane and the molar ratio of **1**:^{i}PrNHC(S)NH^{i}Pr:(EtO)$_3$SiH on the reactivity are shown in the ESI.†

To check the scope and limitation of the dehydrogenative desulfurization of thiourea, several thiourea derivatives were examined; the results are summarized in Table 2. PhNHC(S)NH$_2$, ^{i}PrNHC(S)NH^{i}Pr, C$_6$H$_{11}$NHC(S)NHC$_6$H$_{11}$, PhNHC(S)NHPh, (o-CH$_3$C$_6$H$_4$)NHC(S)NH(o-CH$_3$C$_6$H$_4$), and (p-CH$_3$C$_6$H$_4$)NHC(S)NH(p-CH$_3$C$_6$H$_4$) were converted into the corresponding carbodiimides in good to excellent yields (Table 2, entries 1–7). With a urea, C$_6$H$_{11}$NHC(O)NHC$_6$H$_{11}$ corresponding to C$_6$H$_{11}$NHC(S)NHC$_6$H$_{11}$ showing an excellent conversion, only a trace amount of carbodiimide was formed (entry 8).

Scheme 2 shows the proposed reaction sequences for the reaction of **1** with R$_3$SiH and R'NHC(S)NHR″. A 16e species, CpFe(CO)(SiR$_3$) (**B**), is formed from **1** via CO insertion into the Fe–Me bond (**A**), oxidative addition of an Si–H bond in R$_3$SiH,

Table 1 Dehydrogenative desulfurization of N,N'-diisopropylthiourea with hydrosilane and a transition-metal methyl complex

$$\text{complex} + {}^{i}\text{PrNHC(S)NH}^{i}\text{Pr} + \text{(EtO)}_3\text{SiH} \xrightarrow[\text{in THF, 24 h}]{60\ °C} {}^{i}\text{PrN=C=N}^{i}\text{Pr}$$

Entry	Complex	Yield^{a}/%
1	CpFe(CO)$_2$Me (**1**)	59
2	—	0
3^{b}	CpFe(CO)$_2$Me	Trace
4	(C$_5$Me$_5$)Fe(CO)$_2$Me	27
5	Fe(CO)$_5$	54
6	CpMo(CO)$_3$Me	13
7	(C$_5$Me$_5$)Mo(CO)$_3$Me	18
8	Mo(CO)$_6$	24
9	CpW(CO)$_3$Me	Trace
10	(C$_5$Me$_5$)W(CO)$_3$Me	Trace
11	W(CO)$_6$	Trace
12	CpFe(CO)$_2$Me^{c}	76

^{a} Yield obtained by GC-MS. ^{b} Photo-irradiation at 5 °C. ^{c} Molar ratio of **1**:thiourea:(EtO)$_3$SiH was 2 : 1 : 1.

Table 2 Dehydrogenative desulfurization of thiourea derivatives under heating

$$\text{RNHC(S)NHR} \xrightarrow[\text{60 °C, in THF, 24 h}]{\text{2 eq. CpFe(CO)}_2\text{Me (1), (EtO)}_3\text{SiH}} \text{RN=C=NR}$$

| Entry	Thiourea	Yield^{a}/%
1	PhNHC(S)NH$_2$	>95
2	^{i}PrNHC(S)NH^{i}Pr	76^{b}
3	C$_6$H$_{11}$NHC(S)NHC$_6$H$_{11}$	>95
4	PhNHC(S)NHPh	>95
5	(o-CH$_3$C$_6$H$_4$)NHC(S)NH(o-CH$_3$C$_6$H$_4$)	>95
6	(p-CH$_3$C$_6$H$_4$)NHC(S)NH(p-CH$_3$C$_6$H$_4$)	63
7	EtNHC(S)NH(CH$_2$)$_3$NMe$_2$	46^{b}
8	C$_6$H$_{11}$NHC(O)NHC$_6$H$_{11}$	Trace

^{a} The value is based on the concentration of thiourea and isolated yield. ^{b} GC-MS yield.

and reductive elimination of CH$_3$CHO. R'NHC(S)NHR″ interacts with **B** to form an η^1-R'NHC(S)NHR″ complex through the sulfur atom, which then isomerizes to an η^2-R'NHC(S)NHR″ complex (**C**). Then, silyl migration from iron to the sulfur atom via an Si hypervalent structure occurs to form an Fe–C–S three-membered-ring complex (**D**). Dissociation of the sulfur in **D** and the subsequent oxidative addition of the C–S bond toward iron give a carbene complex (**E**). These reaction sequences from **1** to **E** are similar to those proposed for the desulfurization of N,N-dimethylthioformamide by hydrosilane with the help of **1**, in which an iron carbene complex corresponding to **E** was isolated and structurally characterized.[8] The relatively strong C=S bond in the thiourea is cleaved; the cleavage is induced by silyl migration. If intramolecular addition of one of the N–H bonds to the Fe=C double bond in **E** takes place, **F** is formed. A similar addition has been proposed in the reaction of **1** with R$_3$SiH and RNHC(S)R to give an imine (RN=CHR).[10] Reductive elimination of R$_3$SiS–H from **F** gives **G**. Then, β-hydrogen elimination of the other N–H bond results in the formation of **H**. Finally, dissociation of carbodiimide R'N=C=NR″ from **H** forms the 16e hydride complex (**I**). It is likely that **I** reacts with R$_3$SiH present in the reaction system to give CpFe(CO)(H)$_2$(SiR$_3$), which then undergoes reductive elimination of H$_2$ to give **B**. The reaction of CpFe(CO)X (X = alkyl, aryl, amino, alkoxy, hydride) with R$_3$SiH to give CpFe(CO)(SiR$_3$) has been postulated as the final step of the above-mentioned SiMI reactions. However, the reaction of thiourea with R$_3$SiH with the help of **1** shown in this paper proceeds stoichiometrically but not catalytically. Why not? The reaction of CpFe(CO)(py)(SiR$_3$) [py = pyridine] (R = Et (**2**), Ph (**4**)) with N,N'-diisopropylcarbodiimide gives the clue.

Complexes **2** and **4** reacted with ^{i}PrN=C=N^{i}Pr to give N-silylated η^2-amidino complexes **3** and **5**, respectively (Scheme 3). NMR monitoring of the reaction mixture revealed that these reactions took place cleanly at room temperature in benzene for **2**, and at 60 °C in THF for **4**. As **5** was isolated as single crystals, X-ray analysis was conducted. The molecular structure is depicted in Fig. 1. Complex **5** adopts a three-legged piano-stool geometry. The bond distance of Fe–C2 (1.917 Å) is shorter than that of a typical Fe=C double bond in a Fischer-
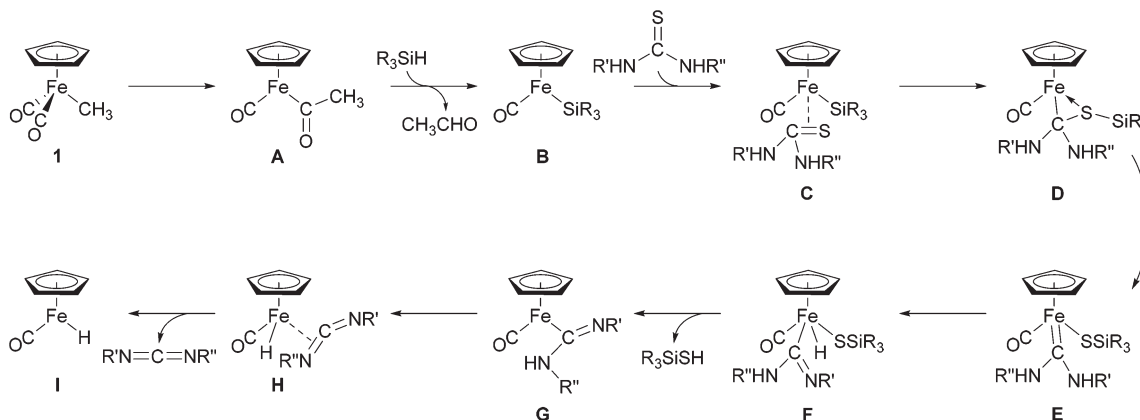
Scheme 2 Proposed reaction sequences.
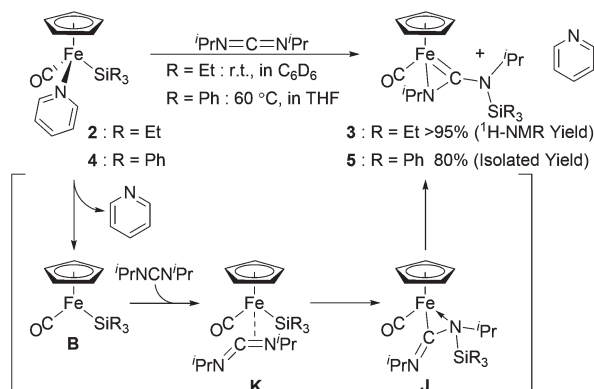
Scheme 3 Synthesis of N-silylated η²-amidino Fe complexes.
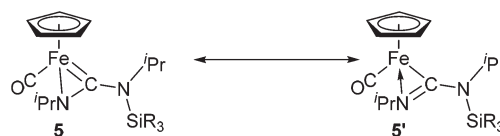
Scheme 4 Two possible canonical forms of **5**.

typical C–N single bond (1.47 Å) to that of a typical C=N double bond (1.27 Å).[12] The C2–N1 bond length (1.259 Å) is slightly shorter than a typical C=N double bond, indicating that the bond has a double bond character. This is attributable to some contribution of the canonical form **5′** (Scheme 4). The sum of the angles around C2, N1, and N2 is approximately 360°, which is consistent with sp² hybridization of C2, N1, and N2. These results indicate that the nitrogen lone pair is delocalized in the carbene carbon plane. The pathway from **2** to **3** and from **4** to **5** can be considered as follows (Scheme 3): (i) dissociation of py in **2/4** gives **B**, (ii) carbodiimide coordination forms **K**, (iii) silyl migration from iron to nitrogen yields **J**, (iv) isomerization from **J** to **3/5** readily takes place.

The conversion of **2/4** to **3/5** in good yields indicates that 16e silyl iron species **B** readily reacts with carbodiimide. Once carbodiimide is formed according to the reaction sequences in Scheme 1, **B** is expected to react with carbodiimide. The reaction of **1**, $^{i}PrHNC(S)NH^{i}Pr$, and Ph_3SiH in a 1 : 1 : 1 molar ratio was conducted and the formation of **5** was observed, although the yield was less than 10%. Therefore, the reaction of **B** with carbodiimide may be one of the reasons for making this reaction system non-catalytic.
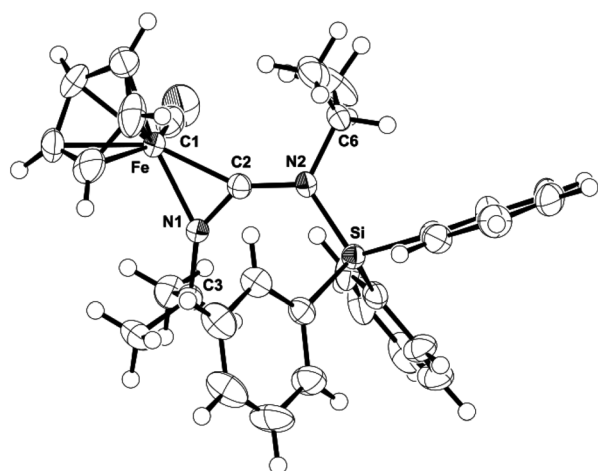

Fig. 1 ORTEP drawing of **5**. Selected bond lengths (Å) and angles (°): Fe–C1 1.724(5), Fe–C2 1.917(4), Fe–N1 1.937(3), C2–N1 1.259(4), C2–N2 1.366(4), N1–C3 1.464(5), N2–C6 1.495(5), N2–Si 1.761(3); Fe–C2–N1 71.8(2), Fe–C2–N2 152.6(3), N1–C2–N2 135.6(3), Fe–N1–C2 70.1(2), Fe–N1–C3 141.3(2), C2–N1–C3 143.4(3), C2–N2–C6 116.7(3), C2–N2–Si 122.8(3), C6–N2–Si 120.5(2).

type carbene (e.g., Dillen et al. reported 1.974 Å in an iron complex).[11] The bond length between the carbene C2 and the nitrogen atom N2 (C2–N2 = 1.366 Å) ranges from that of a

Conclusions

This paper reports the first example of the conversion of thioureas to carbodiimides using a readily available and environmentally friendly iron complex. The findings are important both fundamentally and industrially. It should also be noted that, for thioformamides ($R_2NC(S)H$), the iron complex **1** and hydrosilane can exhibit strong C=S bond cleavage

(desulfurization) and hydrogenation at the thiocarbonyl carbon, whereas for the structurally related thioureas (RNHC-(S)NHR), **1** and hydrosilane exhibit C=S bond cleavage and dehydrogenation. The creation of a catalytic cycle for the conversion of thioureas to carbodiimides is now under investigation.

Experimental section

General method

All reactions were carried out under a nitrogen atmosphere by using Schlenk tube or sealed glass tube techniques. CH_2Cl_2 and $CHCl_3$ were distilled from calcium hydride (CaH_2), pentane, hexane, benzene, toluene, THF, and ether were distilled from sodium and benzophenone prior to use and stored under nitrogen. Methyl complexes $CpM(CO)_nMe$, $(C_5Me_5)M$-$(CO)_nMe$ (M = Fe, $n = 2$;[13] M = Mo,[14] W,[13a] $n = 3$) and $CpFe(CO)$-$(py)(SiR_3)$ (R = Et,[15] Ph[9f]) were synthesized according to the reported methods. The other chemicals were commercially available. [1]H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were recorded on a JEOL JNM-AL 400 spectrometer. The residual peaks of the solvent were used as an internal standard for ^{1}H and ^{13}C{^{1}H} NMR spectra. Peak positions of the ^{29}Si NMR spectra were referenced to external tetramethylsilane ($\delta = 0$ ppm). GC-MS were recorded on SHIMADZU Gas Chromatograph-Mass Spectrometry QP-2010 Plus.

Dehydrogenative desulfurization of thiourea using hydrosilane and 1

THF (3.0 mL), $CpFe(CO)_2Me$ (**1**) (57.5 mg, 3.0 mmol), thiourea (1.5 mmol), and $(EtO)_3SiH$ (25.9 μL, 1.5 mmol) were charged in a Schlenk tube, and the solution was heated at 60 °C for 24 h. After the volatile materials were removed under vacuum, the residue was washed with hexane (5 mL, 3 times) at −60 °C and dried under reduced pressure. The residue was solved in ether (25 mL). The solution was passed through a glass filter and the solvent (ether) of the eluate was removed under vacuum to give carbodiimide as a white powder.

When $^iPrNHC(S)NH^iPr$ and $EtNHC(S)NH(CH_2)_3NMe_2$ were used, THF (3.0 mL), $CpFe(CO)_2Me$ (**1**) (57.5 mg, 3.0 mmol), thiourea (1.5 mmol), and $(EtO)_3SiH$ (25.9 μL, 1.5 mmol) were charged in a Schlenk tube, and the solution was heated at 60 °C for 24 h. 1,3,5-Trimethylbenzene (214 μL, 1.50 mmol) was added to the solution as an internal standard and the GC-MS spectrum was measured. The amount of the carbodiimides produced was evaluated by relative intensity of signals of the product and the internal standard.

The carbodiimides produced were identified by the comparison of the NMR spectra of the authentic compounds prepared according to the literature method for PhN=C=NH being in equilibrium with PhNH−C≡N[16] and PhN=C=NPh.[17] The other carbodiimides produced were identified by the comparison of the NMR spectra of the commercial compounds.

Synthesis of *N*-silylated η²-amidinocomplex CpFe(CO)(ⁱPrNCN-(SiEt₃)ⁱPr-κ²N,C) (3)

$CpFe(CO)(py)(SiEt_3)$ (**2**) (1.9 g, 5.5 mmol) was treated with $^iPrN=C=N^iPr$ (852 μL, 5.5 mmol) in benzene (4.6 mL) at r.t. for 12 h. Removal of volatile materials under reduced pressure led to the formation of $CpFe(CO)(^iPrNCN(SiEt_3)^iPr-\kappa^2N,C)$ (**3**) as a dark-red oil (2.0 g, 91%). ^{1}H-NMR (δ, in C_6D_6): 0.75 (d, $J = 5.2$ Hz, 3H, NCH*Me*₂), 0.82–1.19 (m, 18H, NCH*Me*₂, SiCH₂C*H*₃), 1.26 (t, $J = 7.5$ Hz, 6H, SiCH₂C*H*₃), 3.40 (septet, $J = 6.7$ Hz, 1H, NC*H*Me₂), 3.66 (septet, $J = 6.1$ Hz, 1H, NC*H*Me₂), 4.47 (s, 5H, Cp). ^{13}C{^{1}H} NMR (δ, in C_6D_6): 5.29 (s, Si*C*H₂CH₃), 7.38 (s, SiCH₂*C*H₃), 22.11 (s, NCH*Me*₂), 23.13 (s, NCH*Me*₂), 23.78 (s, NCH*Me*₂), 46.54 (s, N*C*HMe₂), 50.94 (s, N*C*HMe₂), 80.97 (s, Cp), 169.72 (s, Fe=C), 226.16 (s, CO). ^{29}Si{^{1}H} NMR (δ, in C_6D_6): 16.82 (s). IR (cm⁻¹, KBr): ν(CO): 1894, ν(C=N): 1623.

Synthesis of *N*-silylated η²-amidino complex CpFe(CO)(ⁱPrNCN-(SiPh₃)ⁱPr-κ²N,C) (5)

$CpFe(CO)(py)(SiPh_3)$ (**4**) (2.7 g, 5.5 mmol) was treated with $^iPrN=C=N^iPr$ (852 μL, 5.5 mmol) in THF (4.6 mL) at 60 °C for 12 h. Removal of volatile materials under reduced pressure led to the formation of $CpFe(CO)(^iPrNCN(SiPh_3)^iPr-\kappa^2N,C)$ (**5**) as an orange powder (2.4 g, 80%). ^{1}H NMR (δ, in C_6D_6): −0.05 (d, $J = 4.9$ Hz, 3H, NCH*Me*₂), 0.49 (d, $J = 4.9$ Hz, 3H, NCH*Me*₂), 1.61 (d, $J = 5.8$ Hz, 3H, NCH*Me*₂), 1.75 (d, $J = 5.8$ Hz, 3H, NCH*Me*₂), 2.79 (septet, $J = 6.7$ Hz, 1H, NC*H*Me₂), 4.32 (septet, $J = 5.5$ Hz, 1H, NC*H*Me₂), 4.54 (s, 5H, Cp), 7.20–7.59 (m, 15H, SiPh₃). ^{13}C{^{1}H} NMR (δ, in C_6D_6): 21.63 (s, NCH*Me*₂), 22.69 (s, NCH*Me*₂), 23.57 (s, NCH*Me*₂), 24.70 (s, NCH*Me*₂), 45.87 (s, N*C*HMe₂), 53.58 (s, N*C*HMe₂), 80.32 (s, Cp), 128.30 (s, SiPh₃), 130.57 (s, SiPh₃), 133.56 (s, SiPh₃), 136.24 (s, SiPh₃), 164.24 (s, Fe=C), 220.76 (s, CO). ^{29}Si{^{1}H} NMR (δ, in C_6D_6): −12.71 (s). IR (cm⁻¹, KBr): ν(CO): 1888, ν(C=N): 1678. MS(FAB) Calcd for $C_{31}H_{34}FeN_2OSi$ [M]⁺: 534.1790, Found: 534.1782.

X-ray crystal structure determination of 5

Orange crystals of **5** suitable for an X-ray diffraction study were obtained through crystallization from toluene/pentane. The single crystal was mounted on a glass capillary. Data for **5** were collected at 200(2) K on a Rigaku/MSC Mercury CCD area-detector diffractometer equipped with monochromated MoKα radiation. Calculations for **5** were performed with the teXane crystallographic software package of Molecular Structure Corporation. Crystal Data: $C_{31}H_{34}FeN_2OSi$, $M = 534.54$, $0.22 \times 0.08 \times 0.08$ mm³, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.637(2)$ Å, $b = 11.752(3)$ Å, $c = 12.788(3)$ Å, $\alpha = 75.248(10)°$, $\beta = 85.249(12)°$, $\gamma = 87.497(12)°$, $V = 1395.3(5)$ Å³, $Z = 2$, μ(MoKα) = 0.609 mm⁻¹, $D_{calc} = 1.272$ g cm⁻³, 13 883 reflections collected, 6266 ($R_{int} = 0.489$), $R_1 = 0.1060$ [$I > 2\sigma(I)$], $R_w = 0.1612$ (all reflections), and goodness of fit = 1.185.

Acknowledgements

Notes and references

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