Highly Soluble Sulfur-Rich [Ni(L)($^{si}S_3$)] Complexes Containing the New Ligand Bis(2-mercapto-3-trimethylsilylphenyl) Sulfide(2−) ($^{si}S_3{}^{2-}$)[‡]

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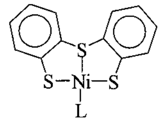
Dedicated to Professor Joachim Strähle on the occasion of his 65th birthday

Keywords: Nickel / S ligands / Silicon / Hydrazine / Nicotinamide

The new organosulfur ligands $^{si}S_3$-H_2 [$^{si}S_3{}^{2-}$ = bis(2-mercapto-3-trimethylsilylphenyl) sulfide(2–)] and $^{ca}S_3$-H_2 [$^{ca}S_3{}^{2-}$ = bis(2-mercapto-3-carboxyphenyl) sulfide(2–)] were synthesized from $^{H}S_3$-H_2 [$^{H}S_3{}^{2-}$ = bis(2-mercaptophenyl) sulfide(2–)], *n*-butyllithium, and Me_3SiCl or CO_2/H^+. Reaction of $^{si}S_3$-H_2 with $Ni(ac)_2{\cdot}4H_2O$ gave the air-stable and well-soluble trinuclear complex [Ni($^{si}S_3$)]$_3$ (**1**) whose structure was determined by X-ray crystallography. Reactions of complex **1** with nucleophiles L [L = PR_3 (R = *n*Pr, Ph, Cy), N_2H_4, S*t*Bu$^-$, and Cl^-] yielded the corresponding neutral or anionic complexes, which were isolated as [Ni(PR_3)($^{si}S_3$)] [R = *n*Pr (**2**), Ph (**3**), Cy (**4**)], Bu_4N[Ni(Cl)($^{si}S_3$)] (**5**), Bu_4N[Ni(S*t*Bu)($^{si}S_3$)] (**6**), and [Ni(N_2H_4)($^{si}S_3$)] (**8**). The azido complex Et_4N[Ni(N_3)($^{si}S_3$)] (**7**) was prepared from Me_3SiN_3 and the precursor chloro complex Et_4N[Ni(Cl)($^{si}S_3$)]. Reaction of **1** with NH_3 yielded labile [Ni(NH_3)($^{si}S_3$)] (**9**), which was characterized in solution by ^1H and ^{13}C NMR spectroscopy. Analogously, **1** reacts with nicotinamide (NA) or diethylnicotinamide ($NAEt_2$) to give, from equilibrium reactions, the corresponding mononuclear [Ni(L)($^{si}S_3$)] complexes with L = NA, $NAEt_2$. X-ray structure determinations showed that **1**, **3**, **4**, **5**, and **7** all exhibit tetrahedrally distorted planar [Ni(L)($^{si}S_3$)] fragments. Complex **7** is the first structurally characterized azidonickel complex with a coligand having exclusively sulfur donors.

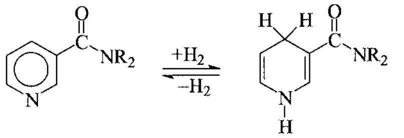
Introduction

The discovery of nickel cysteinate units in the active centers of [NiFe] hydrogenases[1−3] and CO dehydrogenases[4] accounts for much of the current interest in nickel thiolate complexes. Numerous efforts have been made in order to find low molecular weight complexes that model the nickel cysteinate site and the reactivity of these enzymes.[5−10] In this context, we have recently found that [Ni(L)($^{H}S_3$)] complexes containing the [Ni($^{H}S_3$)] complex fragment[11−13] $^{H}S_3{}^{2-}$ = bis(2-mercaptophenyl) sulfide(2−) and L = NHP*n*Pr_3 or $N(SiMe_3)_2{}^-$ as coligands exhibit reactions relevant to [NiFe] hydrogenases and CO dehydrogenases, e.g., catalysis of H_2/D_2O exchange[14] and deoxygenation of CO, CO_2, and SO_2.[15]



[Ni(L)($^{H}S_3$)]

The unique reactivity of these complexes could be traced back to the formation of [Ni(L′)(L)($^{H}S_3$)] intermediates (L′ = H_2, CO, CO_2, SO_2) exhibiting five-coordinate nickel centers. The heterolysis of H_2 catalyzed by [Ni(NHP*n*Pr_3)($^{H}S_3$)][14] prompted us to investigate the activation of H_2 by other [Ni(L)($^{H}S_3$)] complexes, and a particularly intriguing goal was to use H_2 for intramolecularly hydrogenating ligands which can exist in the hydro and dehydro form such as the nicotinamide/dihydronicotinamide couple (NA/NAH_2) [Equation (1)].



(1)

The prerequisite for corresponding experiments were [Ni(NA)($^{H}S_3$)] complexes. Although NA complexes are known

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[‡] Transition Metal Complexes with Sulfur Ligands, 154. Part 153: D. Sellmann, F. Geipel, F. Lauderbach, F. W. Heinemann, *Angew. Chem.* **2002**, *114*, 654−656; Angew. Chem. Int. Ed. 2002, 41, 632−634.

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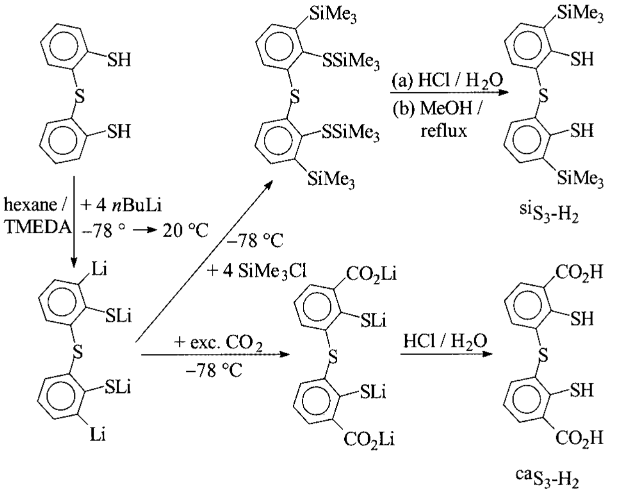
to exist,[16] they could not be obtained with $[Ni(^{H}S_3)]$ fragments. A major obstacle was the fact that $[Ni(L)(^{H}S_3)]$ complexes frequently are only very sparingly soluble in common organic solvents. A prime example is the trinuclear parent complex $[Ni(^{H}S_3)]_3$ which is practically insoluble in all solvents. Due to this we have now tried to obtain better soluble derivatives by introducing $SiMe_3$ or CO_2H substituents into the $^{H}S_3$-H_2 ligand. This paper reports on the synthesis of two new ligands, and a series of nickel complexes with the $SiMe_3$ derivative $^{si}S_3^{2-}$ = bis(2-mercapto-3-trimethylsilylphenyl) sulfide(2−).

Results and Discussion

Synthesis of $SiMe_3$ and CO_2H Derivatives of $^{H}S_3$-H_2

The new ligands $^{si}S_3$-H_2 and $^{ca}S_3$-H_2, where "si" and "ca" denote $SiMe_3$ and CO_2H substituents in the *ortho* position to the SH functions, were obtained in one-pot reactions according to Scheme 1.



Scheme 1. Synthesis of $^{si}S_3$-H_2 and $^{ca}S_3$-H_2

The synthesis route made use of previous results obtained by other authors and us showing that aromatic sulfur compounds such as $S(C_6H_5)$ can be lithiated with excess butyllithium.[17,11]

Treatment of $^{H}S_3$-H_2 with 4 equiv. of *n*BuLi in a hexane/TMEDA mixture (TMEDA = *N*,*N'*-tetramethylethylenediamine) yielded a white to yellow precipitate. This precipitate was not characterized in detail, and its structure, indicated in Scheme 1, was concluded only from subsequent reactions. Treatment of the heterogeneous mixture with 4 equiv. of $SiMe_3Cl$, acidification with hydrochloric acid, and extraction with Et_2O yielded a product in which the thiol functions of $^{si}S_3$-H_2 were still partially silylated by the $SiMe_3$ groups. These $SiMe_3$ groups were removed in boiling MeOH (yielding Me_3SiOMe_3) and the resultant $^{si}S_3$-H_2 was obtained as a brown viscous oil. It was identified by elemental analysis and spectroscopic methods, and could be used for synthesis of complexes without further purification.

In an analogous reaction, treatment of the heterogeneous mixture obtained from $^{H}S_3$-H_2 and butyllithium with gaseous CO_2 and subsequent acidification yielded $^{ca}S_3$-H_2. Upon recrystallization from acetone, it was obtained in green-yellow needles.

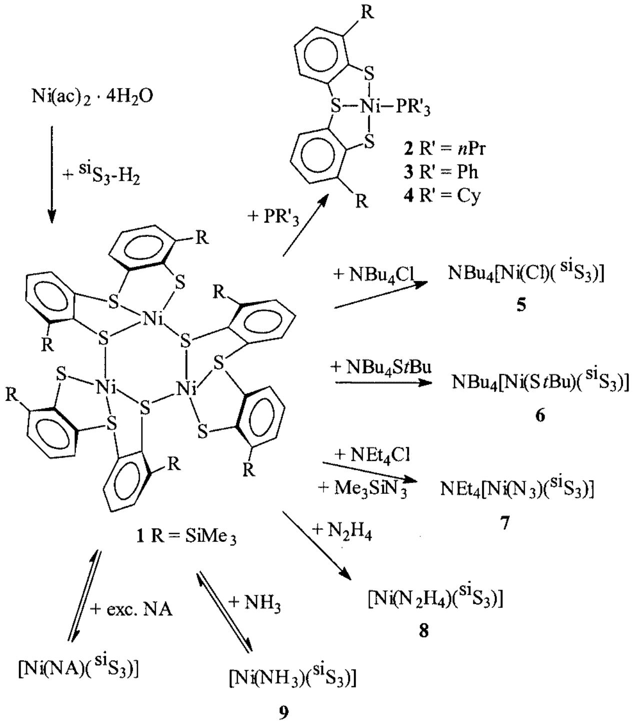
The ^{1}H NMR spectrum of $^{si}S_3$-H_2 exhibits three multiplets for the six aromatic protons, a broad singlet for the two thiols and a sharp singlet for the $SiMe_3$ protons. The ^{1}H NMR spectrum of $^{ca}S_3$-H_2 shows a similar pattern for the aromatic protons and broad peaks at δ = 7.28 and 11.85 ppm for the SH and CO_2H protons. It is worth noting that the SH proton shift is influenced by the benzene ring substituents and appears $\delta \approx 4.5$ ppm at lower field in $^{ca}S_3$-H_2 than in $^{si}S_3$-H_2. The number and shift of the ^{13}C resonances in the $^{13}C\{^{1}H\}$ NMR spectra of $^{si}S_3$-H_2 and $^{ca}S_3$-H_2 established that both of the ligands possess C_2 symmetry in solution.

Synthesis, Reaction, and Characterization of Complexes with $[Ni(^{si}S_3)]$ Fragments

The starting complex $[Ni(^{si}S_3)]_3$ (**1**) was formed in a straightforward reaction from $Ni(ac)_2 \cdot 4H_2O$ and $^{si}S_3$-H_2 in THF/MeOH mixtures. A dark brown solution resulted from which **1** was obtained analytically pure and in high yield (87%). Complex **1** is stable towards air and moisture for extended periods of time and soluble in many common organic solvents, e.g., THF, CH_2Cl_2, acetone, Et_2O, toluene, hexane, MeCN, DMF, DMSO. In MeOH or pentane, **1** is sparingly soluble. Complex **1** fulfilled one of the expectations connected with the synthesis of $^{si}S_3$-H_2, showing good solubility in organic solvents in which the parent complex $[Ni(^{H}S_3)]_3$ proved insoluble. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1** were compatible with the trinuclear structure indicated in Scheme 2. This structure was confirmed by a single-crystal X-ray structure determination.

Subsequent experiments were aimed at cleaving trinuclear $[Ni(^{si}S_3)]_3$ and probing the coordination of σ and σ-π ligands to the $[Ni(^{si}S_3)]$ fragment. Scheme 2 summarizes the reactions of **1** yielding mononuclear $[Ni(L)(^{si}S_3)]$ complexes. Treatment of **1** with phosphanes gave $[Ni(PR_3)(^{si}S_3)]$ with R = *n*-Pr (**2**), Ph (**3**), and Cy (**4**). The reactions could be monitored by the practically instantaneous color change of the THF solution from red-brown to yellow-red or orange, and they took place much faster than the analogous reactions of the parent $[Ni(^{H}S_3)]_3$ complex with the phosphanes. The phosphane derivatives **2**, **3**, and **4** proved inert with regard to substitution of the phosphane ligands.

Substitution-labile $[Ni(L)(^{si}S_3)]$ complexes were obtained with L = Cl^- and $S\mathit{t}Bu^-$. Treatment of **1** with an equimolar amount of Bu_4NCl yielded dark purple needles of $Bu_4N[Ni(Cl)(^{si}S_3)]$ (**5**). With $Bu_4NS\mathit{t}Bu$, brown microcrystals of $Bu_4N[Ni(S\mathit{t}Bu)(^{si}S_3)]$ (**6**) were obtained. The chloro derivative $[Ni(Cl)(^{si}S_3)]^-$ enabled the synthesis of the azido complex, which was not accessible directly from **1**. For this purpose **1** was first treated with Et_4NCl to give $Et_4N[Ni(Cl)(^{si}S_3)]$ in situ. Subsequent addition of Me_3SiN_3 yielded $Et_4N[Ni(N_3)(^{si}S_3)]$ (**7**) which was isolated as violet needles. Complexes **5** and **7** demonstrated that typical σ-



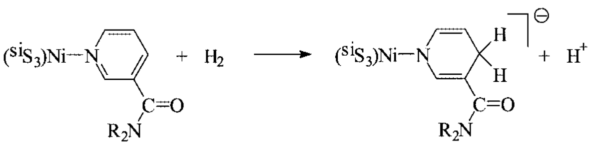
Scheme 2. Synthesis and reactions of $[Ni(^{si}S_3)]_3$ complexes

donor ligands can form stable adducts with $[Ni(^{si}S_3)]$ fragments. With hydrazine, **1** could directly be cleaved to give dark-red $[Ni(N_2H_4)(^{si}S_3)]$ (**8**). The analogous reaction with NH_3 yielded a very labile species that could be generated and characterized only in situ in an NMR tube. All attempts to isolate $[Ni(NH_3)(^{si}S_3)]$ in the solid state remained unsuccessful.

Hydride or CO derivatives of $[Ni(^{si}S_3)]$ could not be obtained. At high pressures of CO (100 bar), minor amounts of **1** were converted into $Ni(CO)_4$ in the course of 10 d. The resulting $Ni(CO)_4$ could be isolated by fractional condensation and was identified by its ν(CO) IR band at 2040 cm^{-1}.[10e]

All of the complexes **1−9** proved to be very soluble in THF, CH_2Cl_2, acetone, toluene, MeCN, DMF, and DMSO. As judged by their NMR spectra, they are diamagnetic. The ^1H NMR spectra of all mononuclear complexes **2−9** show a typical splitting pattern for the aromatic protons, consisting of three multiplets, and an $SiMe_3$ singlet. The intense $SiMe_3$ singlet is also well suited for probing the purity of the complexes. In addition, the $SiMe_3$ singlet in the ^1H NMR spectrum indicates C_s symmetry of the $[Ni(^{si}S_3)]$ fragments in **2−9**. This is corroborated by ^{13}C and ^{31}P NMR spectra as well as by the X-ray structure determination of **3**, **4**, **5**, and **7**. The azido complex **7** shows a characteristic $\nu(N_3)$ band at 2037 cm^{-1}in the IR spectrum, in the solid state as well as in CH_2Cl_2 solution. It is noted that **7** is the first structurally characterized azidonickel complex with a coligand exclusively having sulfur donors.

The formation and characterization of the complexes **7**, **8**, and also **9** proved the capability of the $[Ni(^{si}S_3)]$ fragment to bind σ-donor amine ligands, though the ammonia derivative **9** showed that the resulting mononuclear complexes may be labile. Nevertheless, much effort was spent on the synthesis of $[Ni(^{si}S_3)]$ complexes with nicotinamide (NA) or nicotinamide derivatives (NAR_2) as coligands. The aim of these efforts was to form species that could be hydrogenated by molecular hydrogen according to Equation (2).



(2)

In this reaction we wanted to make use of the heterolytic cleavage of H_2 observed to be catalyzed by $[Ni(NHPnPr_3)(^{H}S_3)]$ in order to achieve the chemical "storage" of H_2 characteristic for the NAD/NADH couple. Taking the pK_a values of different nicotinamide derivatives into account,[18] we have focused on the coordination of either NA or diethylnicotinamide ($NAEt_2$), and treated **1** or the substitution-labile complexes **5** and **6** with varying amounts of NA or $NAEt_2$, ranging from 1:1 ratios to a large excess of NA or $NAEt_2$. In these experiments, mixtures of **1**, the nicotinamide $[Ni(L)(^{si}S_3)]$ complexes and uncoordinated nicotinamide derivatives were obtained that could not be separated. The color change of the THF reaction solutions from dark-brown to red indicated that a reaction took place. Using the $SiMe_3$ signals as a spectroscopic probe enabled us to monitor the reaction course by ^1H NMR spectroscopy. Figure 1 illustrates the reaction between **1** and NA. Figure 1 (a) shows the two $SiMe_3$ singlets of the starting complex **1** at $\delta = 0.57$ and 0.09 ppm. Addition of 1 equiv. of NA gives rise to a new $SiMe_3$ singlet at $\delta = 0.33$ ppm indicating the formation of $[Ni(NA)(^{si}S_3)]$, while the intensity of the two signals of **1** decreases. The intensity of the signal at $\delta = 0.33$ ppm increases when more NA is added. Figure 1 (c) demonstrates that at a 1:10 ratio of **1**/NA, which equals an approximately threefold excess of NA, complex **1** has been converted almost entirely into the derivative $[Ni(NA)(^{si}S_3)]$. Analogous spectra were observed for the reaction between **1** and $NAEt_2$. However, attempts to

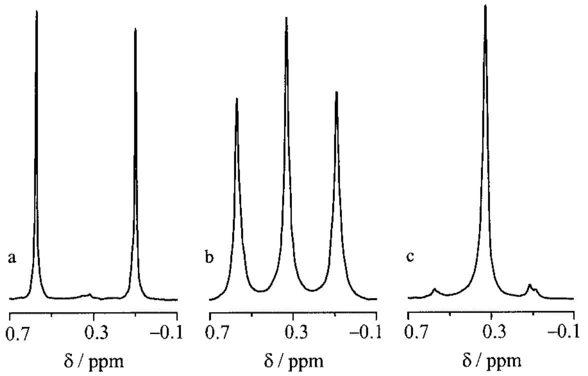


Figure 1. $SiMe_3$ region of ^1H NMR spectra of $[Ni(^{si}S_3)]_3$ in $[D_8]$THF (a) before and (b) after addition of 1 equiv. and (c) after addition of 10 equiv. of nicotinamide

crystallize the $[Ni(NA)(^{si}S_3)]$ or $[Ni(NAEt_2)(^{si}S_3)]$ complexes from such solutions or to remove the excess of NA or $NAEt_2$ by extraction were unsuccessful. In the latter case, the starting complex **1** was regenerated. This clearly demonstrates that the reaction between **1** and NA or $NAEt_2$ is an equilibrium reaction [Equation (3)].

$$[Ni(^{si}S_3)]_3 + 3\ NA \rightleftharpoons 3\ [Ni(NA)(^{si}S_3)] \qquad (3)$$

In this regard, the reactions between **1** and NA or $NAEt_2$ compare with the reversible formation of $[Ni(NH_3)(^{si}S_3)]$ from **1** and NH_3. Because it proved impossible to isolate $[Ni(NA)(^{si}S_3)]$ or $[Ni(NAEt_2)(^{si}S_3)]$ in a pure state, mixtures of the complexes and the respective free NA or $NAEt_2$ were treated with molecular hydrogen in an autoclave at pressures ranging from 10 to 100 bar. However, in no case could the formation of dihydronicotinamide derivatives be observed. The most plausible explanation is that $[Ni(NA)(^{si}S_3)]$ and $[Ni(NAEt_2)(^{si}S_3)]$ complexes, unlike the phosphorane imine complex $[Ni(NHP\mathit{n}Pr_3)(^{H}S_3)]$, do not catalytically heterolyze H_2 or if they do, do not enable the necessary subsequent hydride transfer from the nickel atom to the NA ligand.

X-ray Structure Determinations

Crystal structures of $[Ni(^{si}S_3)]_3{\cdot}0.5CD_2Cl_2$ (**1**$\cdot0.5CD_2Cl_2$), $[Ni(^{si}S_3)]_3{\cdot}2THF{\cdot}3MeOH$ (**1**$\cdot$2THF$\cdot$3MeOH), $[Ni(PPh_3)(^{si}S_3)]$ (**3**), $[Ni(PCy_3)(^{si}S_3)]{\cdot}2CDCl_3$ (**4**$\cdot2CDCl_3$), $Bu_4N[Ni(Cl)(^{si}S_3)]{\cdot}0.625THF{\cdot}0.375Et_2O$ (**5**$\cdot0.625THF\cdot0.375Et_2O$), $Et_4N[Ni(N_3)(^{si}S_3)]{\cdot}THF$ (**7**$\cdot$THF) were determined by X-ray structure analysis. Figures 2 and 3 depict ORTEP diagrams of the structures, Tables 1 and 2 list selected distances and angles.

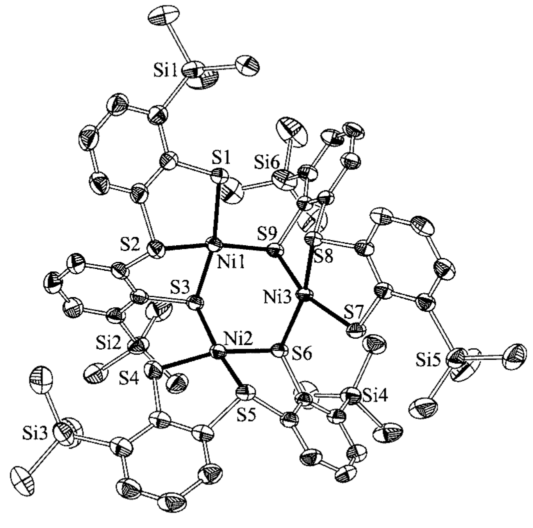


Figure 2. ORTEP diagram of $[Ni(^{si}S_3)]_3{\cdot}0.5CD_2Cl_2$ (**1**$\cdot0.5CD_2Cl_2$) (50% probability ellipsoids; hydrogen atoms and solvent molecule omitted)

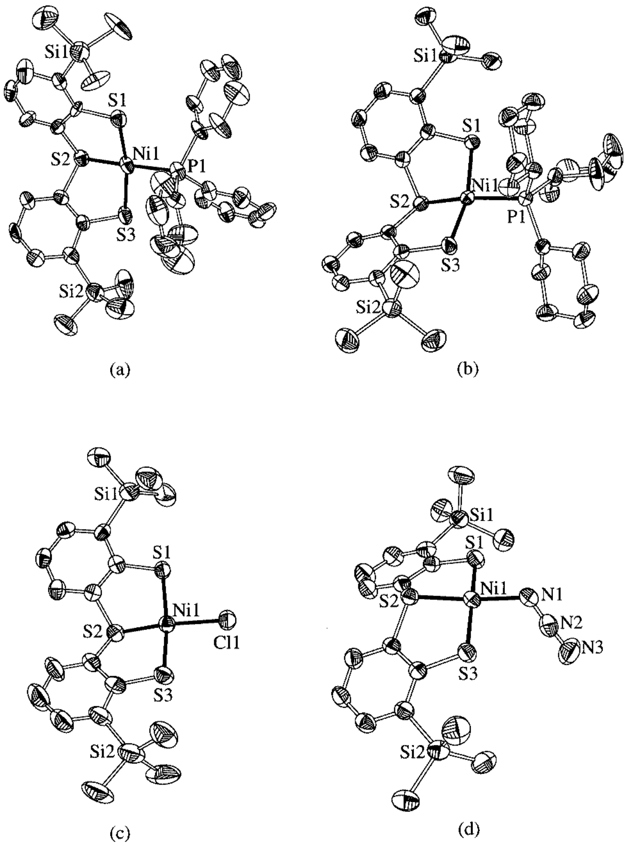


Figure 3. ORTEP diagrams of (a) $[Ni(PPh_3)(^{si}S_3)]$ (**3**), (b) $[Ni(PCy_3)(^{si}S_3)]{\cdot}2CDCl_3$ (**4**$\cdot2CDCl_3$), (c) $Bu_4N[Ni(Cl)(^{si}S_3)]{\cdot}0.625THF{\cdot}0.375Et_2O$ (**5**$\cdot0.625THF\cdot0.375Et_2O$), and (d) $Et_4N[Ni(N_3)(^{si}S_3)]{\cdot}THF$ (**7**$\cdot$THF) (50% probability ellipsoids; hydrogen atoms, solvent molecules, and cations omitted)

Table 1. Selected distances [pm] and angles [°] for $[Ni(^{si}S_3)]_3{\cdot}0.5CD_2Cl_2$ (**1**$\cdot0.5CD_2Cl_2$) (three independent $[Ni(^{si}S_3)]$ units; the columns refer to: a: Ni1, S1, S2, S3; b: Ni2, S4, S5, S6; c: Ni3, S7, S8, S9)

Compound	$[Ni(^{si}S_3)]_3$ (**1**)		
	a	b	c
Ni1−S1	215.6(1)	214.9(1)	214.8(1)
Ni1−S2	214.4(1)	214.4(1)	214.3(1)
Ni1−S3	219.4(1)	220.2(1)	222.2(1)
Ni1−S9	219.8(1)	220.6(1)	221.7(1)
Ni1···Ni2	334.6(2)	321.3(6)	327.5(6)
S3···S9	305.8(1)	312.1(4)	318.7(3)
S1−Ni1−S2	91.12(4)	89.74(4)	90.89(3)
S1−Ni1−S3	159.82(4)	162.99(4)	158.06(4)
S1−Ni1−S9	95.84(3)	93.42(4)	95.25(3)
S2−Ni1−S3	88.77(3)	89.61(3)	87.46(3)
S2−Ni1−S9	167.50(4)	169.90(4)	165.23(4)
S3−Ni1−S9	88.25(3)	90.15(3)	91.75(3)
Ni1−S3−Ni2	99.00(4)	93.29(3)	95.61(3)

The unit cells of all compounds contain discrete molecules or ions. The unit cells of **3** and **5** each contain two crystallographically independent molecules, exhibiting essentially identical bond lengths and angles, of which only one molecule is shown in Figure 2. All compounds exhibit four-coordinate nickel centers in a strongly tetrahedrally distorted planar coordination. The tetrahedral distortion

Table 2. Selected distances [pm] and angles [°] for $[Ni(PPh_3)(^{si}S_3)]$ (**3**), $[Ni(PCy_3)(^{si}S_3)]\cdot 2CDCl_3$ (**4**$\cdot 2CDCl_3$), $Bu_4N[Ni(Cl)(^{si}S_3)]\cdot 0.625THF\cdot 0.375Et_2O$ (**5**$\cdot 0.625THF\cdot 0.375Et_2O$), and $Et_4N[Ni(N_3)(^{si}S_3)]\cdot THF$ (**7**$\cdot$THF)

Compound	**3** (Ni−PPh_3)	**4** (Ni−PCy_3)	**5** (Ni−Cl)	**7** (Ni−N_3)
Ni1−S1	216.5(3)	217.3(1)	218.3(3)	216.9(2)
Ni1−S2	213.0(4)	213.5(1)	208.7(2)	211.1(2)
Ni1−S3	219.7(4)	215.3(2)	217.3(3)	218.2(2)
Ni1−L	221.3(4)	221.7(2)	220.3(2)	191.3(4)
N1−N2				118.5(6)
N2−N3				115.8(6)
S1−Ni1−S2	90.1(2)	88.14(4)	88.1(1)	89.78(5)
S1−Ni1−S3	164.2(2)	160.00(6)	162.3(1)	167.31(6)
S1−Ni1−L	90.3(2)	93.35(4)	93.0(1)	91.4(2)
S2−Ni1−S3	86.0(2)	90.00(5)	90.3(1)	89.15(5)
S2−Ni1−L	176.9(2)	165.05(5)	165.3(1)	173.4(2)
S3−Ni1−L	94.5(2)	93.54(4)	93.1(1)	91.1(2)
Ni1−N1−N2				121.2(3)
N1−N2−N3				175.6(6)

can be traced back to the sp^3-hybridized thioether S donors of the $^{si}S_3$ ligand, leading to a butterfly-like shape of the resulting $[Ni(^{si}S_3)]$ fragments. The characteristic topology of the $^{si}S_3$ ligand also causes the Ni−S(thioether) distances to always be shorter than the Ni−S(thiolate) distances. In this respect, $[Ni(^{si}S_3)]$ complexes are analogous to $[Ni(^{H}S_3)]$ complexes that contain the $^{H}S_3$ parent ligand and have been described previously.[11−13]

Trimerization of $[Ni(^{si}S_3)]$ fragments by thiolate bridges leads to **1**. Complex **1** contains a cyclohexane-like six-membered $[NiS]_3$ ring with a chair conformation, and the structure of **1** parallels that of the parent complex $[Ni(^{H}S_3)]_3$.[12] All bridging Ni−S(thiolate) distances in the six-membered $[NiS]_3$ ring, ranging from 219.4(1) to 222.2(1) pm, are distinctly longer than the terminal Ni−S(thiolate) distances [214.3(1) to 215.6(1) pm]. This elongation of bridging Ni−S distances rationalizes the ready dissociation of **1** in solution when treated with suitable monodentate ligands.

In the complexes **3**, **4**, **5**, and **7**, the fourth coordination site of the $[Ni(^{si}S_3)]$ fragments is occupied by PPh_3, PCy_3, Cl^-, or N_3^-. The distances and angles in **3**, **4**, **5**, and **7** lie in the range observed for analogous $[Ni(L)(^{H}S_3)]$ complexes, and thus far, show no anomalies.[10−15] For example, the Ni−S(thioether) distance is always shorter than the Ni−S(thiolate) distances and the $[Ni(^{si}S_3)]$ fragments exhibit their typical butterfly shape. The N−N distances [118.5(6) and 115.8(6) pm] and Ni−N1−N2 angle [121.2(3)°] in **7** are characteristic for azide complexes in which the azide ligand binds end-on as a σ-donor to the metal atom.[19,20]

Conclusion

This work describes the synthesis of the new ligands $^{si}S_3$-H_2 and $^{ca}S_3$-H_2 and a series of $[Ni(L)(^{si}S_3)]$ complexes. The major aim of the investigations was to find complexes with $[Ni(^{si}S_3)]$ fragments that are well soluble in common solvents and more reactive than the $[Ni(^{H}S_3)]$ parent complexes. These objectives have been reached and, unlike the $[Ni(^{H}S_3)]$ parent fragment, the $[Ni(^{si}S_3)]$ complex fragment has been proved to bind even nicotinamide or diethylnicotinamide, though only in equilibrium reactions. Attempts to hydrogenate the nicotinamide complexes in solution to give dihydronicotinamide derivatives, however, remains unsuccessful.

Experimental Section

General Methods: Unless stated otherwise, all reactions and manipulations were carried out under nitrogen at room temperature using standard Schlenk techniques. All solvents were dried and distilled before use. As far as possible, reactions were monitored by IR or NMR spectroscopy. Physical measurements were carried out with the following instruments: IR (KBr discs or CaF_2 cuvettes, solvent bands were compensated), Perkin−Elmer 983, 1620 FT-IR and 16PC FT-IR; NMR: Jeol JMM-GX 270, Jeol JMM-EX 270, and Lambda LA 400 with the residual protio-solvent signal used as an internal reference. Chemical shifts are quoted in the δ scale (down field shifts are positive) relative to tetramethylsilane (^{1}H, $^{13}C\{^{1}H\}$ NMR) or 85% H_3PO_4 ($^{31}P\{^{1}H\}$ NMR). Mass spectra: Jeol MSTATION 700 spectrometer. Elemental analyses: Carlo Erba EA 1106 or 1108 analyzer. Me_3SiCl, Me_3SiN_3, HS*t*Bu, Bu_4NCl, Et_4NCl, N_2H_4 (1 M solution in THF), nicotinamide, *N*,*N*-diethylnicotinamide were purchased from either Aldrich or Fluka. $^{H}S_3$-H_2 was prepared as described in the literature.[11]

$^{si}S_3$-H_2: With continuous vigorous stirring under argon, *n*BuLi in hexane (2.5 M, 45 mL, 112.51 mmol) was slowly added to a suspension of $^{H}S_3$-H_2 (6.49 g, 25.92 mmol) in hexane (200 mL) at −78 °C. After addition of TMEDA (31 mL, 206.01 mmol), the temperature was raised gradually to 25 °C. Stirring was continued for another 72 h, in the course of which the color of the suspension turned from white to yellow. This suspension was cooled to −78 °C, $SiMe_3Cl$ (15 mL, 118.03 mmol) was added slowly, and stirring was continued for 1 h at −78 °C and 24 h at 25 °C, in the course of which the color of the suspension changed back to white. H_2O (50 mL) was added, and all volatile components were removed in vacuo. A red-brown highly viscous residue remained which was dissolved in Et_2O (500 mL). The resulting Et_2O solution was washed by extraction with hydrochloric acid (5%, 3 × 200 mL) and a saturated $NaCl/H_2O$ solution (2 × 100 mL), and dried with solid Na_2SO_4. Removal of all volatile components in vacuo yielded a yellow-red viscous residue, which was dissolved in MeOH (150 mL) and heated to reflux for 12 h. Removal of volatile components in vacuo gave a red-brown viscous oil of $^{si}S_3$-H_2, which could be used for the synthesis of complexes without further purification. Yield: 9.55 g (93%). $C_{18}H_{26}S_3Si_2$ (394.78): calcd. C 54.76, H 6.65, S 24.39; found C 55.01, H 6.58, S 24.28. MS (FD, THF): *m*/*z* = 394 [M^+]. ^{1}H NMR (269.7 MHz, C_6D_6): δ = 7.23 (d, 2 H, C_6H_3), 7.10 (d, 2 H, C_6H_3), 6.78 (t, 2 H, C_6H_3), 4.61 (br, 2 H, SH), 0.35 (s, 18 H, $SiMe_3$) ppm. $^{13}C\{^{1}H\}$ NMR (67.8 MHz, C_6D_6): δ = 141.3, 140.9, 134.6, 134.4, 133.0, 126.3 (C_6H_3), −0.2 ($SiMe_3$) ppm.

$^{ca}S_3$-H_2: To a suspension of $^{H}S_3$-H_2 (7.05 g, 28.17 mmol) in hexane (150 mL), *n*BuLi in hexanes (2.5 M, 45 mL, 112.51 mmol) was added slowly at −78 °C. Under vigorous stirring, TMEDA (31 mL, 206.01 mmol) was added and the temperature gradually raised to 25 °C. The mixture was stirred for another 72 h, in the course of which the color of the suspension turned from white to yellow. This suspension was cooled down again to −78 °C, CO_2 was bubbled through for 30 min under vigorous stirring and the mixture was gradually warmed to 0 °C in the course of 1 h. All volatile components were removed in vacuo. The resulting mixture was treated with cold water (50 mL) and concentrated hydrochloric acid (70 mL). The resulting mixture was extracted with a mixture of Et_2O (100 mL) and THF (30 mL). The extract was dried with Na_2SO_4 and the solvents were evaporated to give a dry pale yellow residue. This was recrystallized from acetone (60 mL) at −20 °C. Green yellow needles precipitated, which were separated after 2 d, washed with cold acetone (10 mL, 0 °C) and dried in vacuo. Yield: 4.83 g (51%). $C_{14}H_{10}O_4S_3$ (338.43): calcd. C 49.69, H 2.98, S 28.42; found C 49.99, H 3.36, S 27.78. MS (FD, THF): *m*/*z* = 338 [M$^+$]. IR (KBr): $\tilde{\nu}$ = 2980 [ν(OH)], 2484 [ν(SH)], 1652 [ν(COOH)] cm^{-1}. ^{1}H NMR (399.7 MHz, [D$_8$]THF): δ = 11.85 (br, 2 H, COOH), 8.06 (d, 2 H, C_6H_3), 7.30 (d, 2 H, C_6H_3), 7.28 (s, 2 H, SH), 7.08 (t, 2 H, C_6H_3) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, [D$_8$]THF): δ = 167.7 (COOH), 141.5, 135.3, 133.2, 131.2, 126.6, 123.6 (C_6H_3) ppm.

[Ni(^{si}S$_3$)]$_3$ (1): ^{si}S$_3$-H$_2$ (3.00 g, 7.60 mmol) in THF (40 mL) was added dropwise to a solution of Ni(ac)$_2$·4H$_2$O (1.90 g, 7.65 mmol) in MeOH (25 mL). A dark brown solution formed which was stirred for 24 h and then concentrated to dryness. The resulting dark brown residue was redissolved in hexane (20 mL), traces of insoluble particles were removed by filtration after 30 min, and the filtrate was layered with MeOH (50 mL). A dark brown powder precipitated, which was separated, washed with MeOH (30 mL) and pentane (25 mL), and dried in vacuo. Yield: 3.02 g (87%). $C_{54}H_{72}Ni_3S_9Si_6$ (1354.36): calcd. C 47.89, H 5.36, S 21.31; found C 47.58, H 5.53, S 20.98. MS (FD, THF): *m*/*z* = 1354 [M$^+$], 902 [Ni(^{si}S$_3$)]$_2{}^+$. ^{1}H NMR (399.7 MHz, [D$_8$]THF): δ = 7.82 (d, 1 H, C_6H_3), 7.68 (d, 1 H, C_6H_3), 7.40 (d, 1 H, C_6H_3), 7.28 (t, 1 H, C_6H_3), 7.24 (d, 1 H, C_6H_3), 6.96 (t, 1 H, C_6H_3), 0.55 (s, 9 H, SiMe$_3$), 0.08 (s, 9 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, [D$_8$]THF): δ = 158.8, 146.7, 145.1, 139.3, 138.5, 135.4, 134.8, 132.2, 130.9, 127.8, 127.6, 122.1 (C_6H_3), 0.6, −0.6 (SiMe$_3$) ppm.

[Ni(P*n*Pr$_3$)(^{si}S$_3$)] (2): P*n*Pr$_3$ (0.16 mL, 0.99 mmol) was added to a solution of **1** (400 mg, 0.30 mmol) in THF (15 mL). The solution instantaneously changed its color from dark brown to dark yellow, was filtered after 1 h, reduced in volume to 2 mL, and layered with pentane (20 mL). Orange microcrystals precipitated which were separated after 5 d, washed with pentane (10 mL), and dried in vacuo. Yield: 435 mg (80%). $C_{27}H_{45}NiPS_3Si_2$ (611.694): calcd. C 53.02, H 7.42, S 15.73; found C 53.28, H 7.24, S 15.47. MS (FD, THF): *m*/*z* = 611 [M$^+$]. ^{1}H NMR (269.7 MHz, CDCl$_3$): δ = 7.64 (d, 2 H, C_6H_3), 7.24 (d, 2 H, C_6H_3), 6.94 (t, 2 H, C_6H_3), 1.74 (m, 6 H, PCH$_2$), 1.06 (m, 6 H, PCH$_2$CH$_2$), 0.37 (s, 18 H, SiMe$_3$), 0.05 (t, 9 H, PCH$_2$CH$_2$CH$_3$) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$): δ = 159.0 (d, $^3J_{P,C}$ = 13.2 Hz), 141.1, 135.1, 133.6, 129.1, 122.3 (C_6H_3), 26.7 (d, $^1J_{P,C}$ = 26.40 Hz), 18.7, 16.7 (d, $^3J_{P,C}$ = 14.1 Hz) (PCH$_2$CH$_2$CH$_3$), 0.0 (SiMe$_3$) ppm. ^{31}P{^{1}H} NMR (161.8 MHz, CDCl$_3$): δ = 14.6 [P*n*(C$_3$H$_7$)$_3$] ppm.

[Ni(PPh$_3$)(^{si}S$_3$)] (3): Whilst stirring, a solution of PPh$_3$ (200 mg, 0.76 mmol) and **1** (280 mg, 0.21 mmol) in THF (10 mL) was heated to reflux for 5 min, in the course of which the color changed from dark brown to red. The red solution was stirred for another 30 min at room temperature, then combined with MeOH (30 mL), filtered, and reduced in volume to ca. 5 mL. Red microcrystals precipitated which were separated after 3 d, washed with MeOH (10 mL), and dried in vacuo. Yield: 268 mg (76%). $C_{36}H_{39}NiPS_3Si_2$ (713.72): calcd. C 60.58, H 5.51, S 13.48; found C 60.48, H 5.80, S 13.51. MS (FD, THF): *m*/*z* = 712 [M$^+$]. ^{1}H NMR (269.7 MHz, [D$_6$]acetone): δ = 7.94 (d, 2 H, C_6H_3), 7.83−7.52 (m, 15 H, C_6H_5), 7.28 (d, 2 H, C_6H_3), 7.04 (t, 2 H, C_6H_3), 0.12 (s, 18 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (67.8 MHz, [D$_6$]acetone): δ = 159.5 (d, $^3J_{PC}$ = 14 Hz), 143.0, 135.4, 135.3 (d, J_{PC} = 10.8 Hz), 133.3, 131.7, 130.4 (d, $^1J_{PC}$ = 47.4 Hz) 129.6, 129.1 (d, J_{PC} = 10.2 Hz), 122.7 [C_6H_3, P(C$_6$H$_5$)$_3$], −0.8 (SiMe$_3$) ppm. ^{31}P{^{1}H} NMR (161.8 MHz, [D$_6$]acetone): δ = 29.4 [P(C$_6$H$_5$)$_3$] ppm.

[Ni(PCy$_3$)(^{si}S$_3$)] (4): A solution of PCy$_3$ (200 mg, 0.71 mmol) in THF (2 mL) was added dropwise to a solution of **1** (300 mg, 0.22 mmol) in THF (10 mL). Over the course of ca. 5 min, the color of the solution changed from dark brown to dark yellow. The solution was stirred for 3 h, filtered, reduced in volume to ca. 2 mL, and layered with MeOH (20 mL). Yellow-red microcrystals precipitated, which were separated after 3 d, washed with MeOH (10 mL), and dried in vacuo. Yield: 452 mg (93%). $C_{36}H_{57}NiPS_3Si_2$ (731.889): calcd. C 59.08, H 7.85, S 13.14; found C 59.32, H 7.96, S 12.69. MS (FD, THF): *m*/*z* = 731 [M$^+$]. ^{1}H NMR (399.7 MHz, CDCl$_3$): δ = 7.74 (d, 2 H, C_6H_3), 7.28 (d, 2 H, C_6H_3), 6.98 (t, 2 H, C_6H_3), 2.10−1.28 (m, 33 H, PCy$_3$), 0.37 (s, 18 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$): δ = 159.0 (d, $^3J_{PC}$ = 10 Hz), 141.2, 135.0, 133.1 (d, $^4J_{PC}$ = 1.6 Hz), 128.7, 122.0 (C_6H_3), 34.5 (d, $^1J_{PC}$ = 20.1 Hz), 30.7, 28.5 (d, $^3J_{PC}$ = 11 Hz), 27.1 [P(C$_6$H$_{11}$)$_3$], 0.0 (SiMe$_3$) ppm. ^{31}P{^{1}H} NMR (161.8 MHz, CDCl$_3$): δ = 31.9 [P(C$_6$H$_{11}$)$_3$] ppm.

Bu$_4$N[Ni(Cl)(^{si}S$_3$)] (5): Bu$_4$NCl (210 mg, 0.76 mmol) was added to a dark brown solution of **1** (312 mg, 0.23 mmol) in THF (10 mL). The solution was stirred for 12 h, over the course of which its color changed to violet. The solution was filtered, reduced in volume to 2 mL, and layered with Et$_2$O (20 mL). Pink crystals precipitated which were separated after 7 d, washed with Et$_2$O (15 mL), and dried in vacuo. Yield: 410 mg (81%). $C_{34}H_{60}ClNNiS_3Si_2$ (729.377): calcd. C 55.99, H 8.29, N 1.92, S 13.19; found C 56.01, H 8.32, N 2.07, S 12.72. ^{1}H NMR (269.7 MHz, [D$_8$]THF): δ = 7.60 (d, 2 H, C_6H_3), 7.18 (d, 2 H, C_6H_3), 6.79 (t, 2 H, C_6H_3), 3.57 (m, 8 H, NCH$_2$), 1.76 (m, 8 H, NCH$_2$CH$_2$), 1.39 [m, 8 H, N(CH$_2$)$_2$CH$_2$], 0.87 [m, 12 H, N(CH$_2$)$_3$CH$_3$], 0.36 (s, 18 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (67.8 MHz, [D$_8$]THF): δ = 161.6, 139.6, 134.7, 134.6, 128.9, 120.7 (C_6H_3), 59.7, 35.1, 20.7, 14.2 [N(CH$_2$)$_3$CH$_3$], −0.2 (SiMe$_3$) ppm.

Bu$_4$N[Ni(S*t*Bu)(^{si}S$_3$)] (6): Whilst stirring, NaS*t*Bu (1 mL of 1 M MeOH solution, 1.00 mmol) was added to a solution of **1** (300 mg, 0.22 mmol) in THF (10 mL). After 1 h, Bu$_4$NOH (0.68 mL, 1 M MeOH solution, 0.68 mmol) was added and the stirring continued for another 2 h. A dark brown solution resulted, which was filtered, concentrated in volume to 2 mL, and layered with pentane (15 mL). Dark brown microcrystals precipitated which were separated after 5 d, washed with pentane (5 mL) and dried in vacuo. Yield: 340 mg (65%). $C_{38}H_{69}NNiS_4Si_2$ (783.106): calcd. C 58.28, H 8.88, N 1.79, S 16.37; found C 58.43, H 8.97, N 1.91, S 15.89. ^{1}H NMR (269.7 MHz, CDCl$_3$): δ = 7.52 (d, 2 H, C_6H_3), 7.14 (d, 2 H, C_6H_3), 6.78 (t, 2 H, C_6H_3), 3.32 (m, 8 H, NCH$_2$), 1.59 (m, 8 H, NCH$_2$CH$_2$), 1.53 (s, 9 H, S*t*Bu), 1.31 [m, 8 H, N(CH$_2$)$_2$CH$_2$], 0.88 [m, 12 H, N(CH$_2$)$_3$CH$_3$], 0.34 (s, 18 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (67.8 MHz, CDCl$_3$): δ = 161.6, 139.5, 133.7, 133.0, 127.9, 119.7 (C_6H_3), 58.9 (NCH$_2$), 40.4, 36.8 (S*t*Bu), 24.2, 19.7 13.9 [N(CH$_2$)$_3$CH$_3$], −0.5 (SiMe$_3$) ppm.

Et$_4$N[Ni(N$_3$)(^{si}S$_3$)] (7): A solution of Et$_4$NCl (95 mg, 0.57 mmol) and **1** (250 mg, 0.19 mmol) in THF (10 mL) was stirred for 3 h, over the course of which the color changed from dark brown to purple. Me$_3$SiN$_3$ (0.1 mL, 0.76 mmol) was added, whereupon the color became slightly lighter. After 1 h, all volatile materials were removed in vacuo, the residue was redissolved in THF (10 mL). The THF solution was filtered, reduced in volume to 2 mL and layered with pentane (15 mL). Violet needles precipitated, which were separated after 4 d, washed with pentane (10 mL), and dried in vacuo. Yield: 285 mg (82%). $C_{26}H_{44}N_4NiS_3Si_2$ (623.729): calcd. C 50.07, H 7.11, N 8.98, S 15.42; found C 50.61, H 7.40, N 8.70, S 15.19 − IR (KBr): $\tilde{\nu}$ = 2037 [$\nu(N_3)$] cm^{-1}. ^1H NMR (269.7 MHz, $CDCl_3$): δ = 7.48 (d, 2 H, C_6H_3), 7.26 (d, 2 H, C_6H_3), 6.90 (t, 2 H, C_6H_3), 3.40 (m, 8 H, NCH_2), 1.20 (t, 12 H, NCH_2CH_3), 0.37 (s, 18 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (67.8 MHz, $CDCl_3$): δ = 157.9, 140.0, 134.5, 132.9, 127.8, 120.9 (C_6H_3), 52.6, 7.8 [$N(CH_2CH_3)_4$], −0.9 ($SiMe_3$) ppm.

[Ni(N_2H_4)($^{si}S_3$)] (8): Addition of N_2H_4 (2 mL of 1 M THF solution, 2.00 mmol) to a solution of **1** (250 mg, 0.19 mmol) in THF (10 mL) led to a rapid color change from dark brown to orange. The solution was stirred for 2 h and stored at −30 °C for 12 h. At this temperature, the excess free hydrazine that crystallized from the solution could be removed by filtration at −30 °C. The filtrate was reduced in volume to 2 mL and layered with pentane (20 mL). Dark red crystals precipitated which were separated, washed with pentane (10 mL) and dried in vacuo. Yield: 242 mg (90%). $C_{18}H_{28}N_2NiS_3Si_2$ (489.499): calcd. C 44.71, H 5.84, N 5.79, S 19.90; found C 45.01, H 5.88, N 5.51, S 19.43. IR (KBr): $\tilde{\nu}$ = 3350 [ν(NH)] cm^{-1}. ^1H NMR (269.7 MHz, [D_8]THF): δ = 7.62 (d, 2 H, C_6H_3), 7.25 (d, 2 H, C_6H_3), 6.90 (t, 2 H, C_6H_3), 4.83 (b, 2 H, NH_2NH_2), 3.32 (b, 2 H, NH_2), 0.39 (s, 18 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (67.8 MHz, [D_8]THF): δ = 157.6, 140.9, 135.5, 134.5, 129.9, 122.4 (C_6H_3), −0.4 ($SiMe_3$) ppm.

[Ni(NH_3)($^{si}S_3$)] (9): This compound was synthesized in an NMR tube and characterized only by ^1H and ^{13}C NMR spectra: NH_3 gas (2.5 mL, 0.15 mmol) was injected into the dark brown solution of **1** (25 mg, 0.02 mmol) in [D_8]THF contained in an NMR tube. The color of the solution immediately changed to red. The ^1H and ^{13}C NMR spectra of the solutions indicated the complete conversion of **1** into **9**. ^1H NMR (269.7 MHz, [D_8]THF): δ = 7.63 (d, 2 H, C_6H_3), 7.23 (d, 2 H, C_6H_3), 6.89 (t, 2 H, C_6H_3), 2.27 (b, 3 H, NH_3), 0.37 (s, 18 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (67.8 MHz, [D_8]THF): δ = 158.4, 140.6, 135.3, 134.5, 129.6, 122.0 (C_6H_3), −0.5 ($SiMe_3$) ppm.

[Ni(L)($^{si}S_3$)] Complexes (L = NA or $NAEt_2$): In a typical experiment, NA (0.5 g, 4.09 mmol) or $NAEt_2$ (1.0 mL, 5.95 mmol) was added to a dark brown solution of **1** (500 mg, 0.37 mmol) in THF (10 mL). The solution was stirred for 48 h, over the course of which its color changed to yellow red. The solution was filtered, reduced in volume to 2 mL, and layered with Et_2O (20 mL). Yellow red powders precipitated which were separated after 5 d, washed with Et_2O (15 mL), and dried in vacuo. Elemental analyses and IR and NMR spectra indicated that these powders were mixtures of [Ni(L)($^{si}S_3$)] and **1,** which could not be separated.

^1H NMR Spectroscopic Monitoring of the Reactions between 1 and NA or $NAEt_2$: To a dark brown solution of **1** (25 mg, 0.02 mmol) in [D_8]THF, NA, or $NAEt_2$ (1−10 equiv.) was added stepwise, and the ^1H NMR spectra were recorded after every addition. The $SiMe_3$ signals were used as a spectroscopic probe to monitor the formation of the corresponding [Ni(L)($^{si}S_3$)] complex.

X-ray Structure Determination of [Ni($^{si}S_3$)]$_3$·0.5CD_2Cl_2 (1·0.5CD_2Cl_2), [Ni($^{si}S_3$)]$_3$·2THF·3MeOH (1·2THF·3MeOH), [Ni(PPh_3)($^{si}S_3$)] (3), [Ni(PCy_3)($^{si}S_3$)]·2$CDCl_3$ (4·2$CDCl_3$), Bu_4N[Ni(Cl)($^{si}S_3$)]·0.625THF·0.375Et_2O (5·0.625THF·0.375Et_2O), Et_4N[Ni(N_3)($^{si}S_3$)]·THF (7·THF): In an NMR tube at −30 °C, black blocks of [Ni($^{si}S_3$)]$_3$·0.5CD_2Cl_2 (**1**·0.5CD_2Cl_2) crystallized in the course of 10 d from a CD_2Cl_2 solution of **1** which had been layered with MeOH. From THF/MeOH mixtures, **1** crystallized as **1**·2THF·3MeOH. The crystallographic data of this solvate have been deposited. Red cubes of **3** and orange-prisms of **4**·2$CDCl_3$

Table 3. Selected crystallographic data for [Ni($^{si}S_3$)]$_3$·0.5CD_2Cl_2 (**1**·0.5CD_2Cl_2), [Ni(PPh_3)($^{si}S_3$)] (**3**), [Ni(PCy_3)($^{si}S_3$)]·2$CDCl_3$ (**4**·2$CDCl_3$), Bu_4N[Ni(Cl)($^{si}S_3$)]·0.625THF·0.375Et_2O (**5**·0.625THF·0.375Et_2O), and Et_4N[Ni(N_3)($^{si}S_3$)]·THF (**7**·THF)

	1·0.5CD_2Cl_2	**3**	**4**·2$CDCl_3$	**5**·0.625THF·0.375Et_2O	**7**·THF
Empirical formula	$C_{54.50}H_{72}ClDNi_3S_9Si_6$	$C_{36}H_{39}NiPS_3Si_2$	$C_{38}H_{57}Cl_6D_2NiPS_3Si_2$	$C_{38}H_{68.75}ClNNiOS_3Si_2$	$C_{30}H_{52}N_4NiOS_3Si_2$
Formula mass [g/mol]	1397.79	713.71	972.61	802.21	695.83
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	*C*2/*c*	*Cc*	*P*2$_1$2$_1$2$_1$	*P*2$_1$/*c*	*Pbca*
a [pm]	3232.3(3)	2664.0(8)	1236.2(1)	1343.8(2)	1951.2(2)
b [pm]	2452.3(3)	1883.1(6)	1720.6(2)	3057.9(4)	1572.2(2)
c [pm]	1996.6(2)	1518.2(5)	2266.2(2)	2237.9(3)	2404.8(4)
α [°]	90	90	90	90	90
β [°]	118.88(1)	105.10(3)	90	95.16(1)	90
γ [°]	90	90	90	90	90
V [nm^3]	13.858(3)	7.353(4)	4.8202(8)	9.159(2)	7.377(2)
Z	8	8	4	8	8
$d_{calcd.}$[g/cm^3]	1.340	1.289	1.337	1.164	1.253
μ [mm^{-1}]	1.253	0.831	0.974	0.698	0.789
Crystal size [mm]	0.80×0.70×0.35	0.55×0.30×0.10	0.64×0.60×0.42	0.90×0.80×0.20	0.96×0.48×0.36
2θ range[°]	3.6−54.0	3.5−54.0	3.6−56.0	3.6−50.0	3.7−54.0
T_{min}/T_{max}	0.358/0.419	0.984/1.000	0.224/0.269	0.278/0.341	0.261/0.340
Measd. refl.	16730	16914	12783	19091	9574
Indep. refl.	15146	8679	11611	16114	8046
Obsd. refl.	10965	2691	8889	6482	4403
Ref. parameters	882	787	467	881	380
*R*1$^{[a]}$; *wR*2[%]	4.39; 10.57	5.09; 8.63	5.52; 13.88	8.64; 21.32	6.60; 16.67
Abs. struct. parameters		0.01(2)	0.00(2)		

[a] [$I > 2\sigma(I)$].

were grown at −20 °C over the course of 3−5 d from a concentrated THF solution which was layered with MeOH. Red-violet plates of **5**·0.625THF·0.375Et_2O formed over the course of 7 d when a saturated THF solution of **5** was layered with Et_2O at −30 °C. Red-black crystals of **7**·THF were obtained from a dilute THF/acetone mixture of **7** which was layered with pentane and stored for 8 d at −30 °C. Suitable single crystals were embedded in protective perfluoro polyether or were sealed in glass capillaries under N_2. Data were collected at 200 K (**1**·0.5CD_2Cl_2, **5**·0.625THF·0.375Et_2O, **7**·THF), 220 K (**4**·2$CDCl_3$) or 293 K (**3**) with a Siemens P4 diffractometer or a Nicolet R 3m/V diffractometer (**3**) using Mo-K_α radiation (λ = 71.073 pm), a graphite monochromator, and the ω-scan technique. For all compounds a semiempirical absorption correction using ψ-scans has been performed. The structures were solved by direct methods, full-matrix least-squares refinement was carried out on F^2 (SHELXTL NT 5.1).[21] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of **1**·0.5CD_2Cl_2 were located from a difference Fourier map, while in all other compounds the H atoms were geometrically positioned with isotropic displacement parameters being 1.5 times *U*(eq) of the preceding carbon atom. One *n*-butyl group in the cation of **5**·0.625THF·0.375Et_2O was found to be disordered. Two alternative sites could be refined with occupancy factors of 57(2) and 43(2)%, respectively. One THF and one Et_2O molecule of the included solvent share a single site. These disordered molecules have been refined using several restraints. Selected crystallographic data are summarized in Table 3.[22]

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[1] [1a] J. R. Lancaster, *FEBS Lett.* **1980**, *115*, 285−288. [1b] E. G. Graf, R. K. Thauer, *FEBS Lett.* **1981**, *136*, 165−169. [1c] R. Cammack, V. M. Fernandez, K. Schneider, in: *Bioinorganic Chemistry of Nickel* (Ed.: J. R. Lancaster, Jr.), VCH, Weinheim, **1988**, p. 167−190. [1d] M. W. W. Adams, *Biochem. Biophys. Acta* **1990**, *1020*, 115−145. [1e] A. F. Kolodziej, *Progr. Inorg. Chem.* **1994**, *41*, 493−598. [1f] S. P. Albracht, *Biochem. Biophys. Acta* **1994**, *1188*, 167−204. [1g] M. Y. Darensbourg, E. J. Lyon, J. J. Smee, *Coord. Chem. Rev.* **2000**, *206−207*, 553−561.

[2] [2a] A. Volbeda, M. H. Charon, C. Piras, E. C. Hatchikian, M. Frey, J. C. Fontecilla-Camps, *Nature (London)* **1995**, *373*, 580−587. [2b] R. Cammack, *Nature (London)* **1995**, *373*, 556−557. [2c] A. Volbeda, E. Garcin, C. Piras, A. L. de Lacey, V. M. Fernandes, E. C. Hatchikian, *J. Am. Chem. Soc.* **1996**, *118*, 12989−12996. [2d] Y. Higuchi, N. Yasuoka, *Structure (London)* **1997**, *5*, 1671−1680.

[3] [3a] E. Garcin, X. Vernede, E. C. Hatchikian, A. Volbeda, M. Frey, J. C. Fontecilla-Camps, *Structure (London)* **1999**, *7*, 557−566. [3b] Y. Higuchi, H. Ogata, K. Miki, N. Yasuoka, T. Yagi, *Structure (London)* **1999**, *7*, 549−556.

[4] [4a] A. S. W. Ragsdale, J. E. Clark, G. Ljungdahl, L. L. Lundie, H. L. Drake, *J. Biol. Chem.* **1983**, *258*, 2364−2369. [4b] R. B. Diekert, M. Ritter, *FEBS Lett.* **1983**, *151*, 41−44. [4c] C. Y. Ralston, H. Wang, S. W. Ragsdale, M. Kumar, N. J. Spangler, P. W. Ludden, W. Gu, R. M. Jones, D. S. Patil, S. P. Cramer, *J. Am. Chem. Soc.* **2000**, *122*, 10553−10560. [4d] A. L. De Lacey, C. Stadler, C. Cavazza, E. C. Hatchikian, V. M. Fernandez, *J. Am. Chem. Soc.* **2000**, *122*, 11232−11233. [4e] H. Dobbek, V. Svetlitchnyi, L. Gremer, R. Huber, O. Meyer, *Science* **2001**, *293*, 1281−1285.

[5] [5a] H. J. Krüger, R. H. Holm, *Inorg. Chem.* **1989**, *28*, 1148−1155. [5b] M. Kumar, G. J. Colpas, R. O. Day, M. J. Maroney, *J. Am. Chem. Soc.* **1989**, *111*, 8323−8325. [5c] M. Frey, *Struct. Bond* **1998**, 97−126. [5d] H. Wang, C. Y. Raltson, D. S. Patil, R. M. Jones, W. M. Verhagen, M. Adams, P. C. Riordan, C. A. Marganian, P. Mascharak, J. Kovacs, C. C. Miller, T. J. Collins, S. Brooker, P. D. Croucher, K. Wang, E. I. Steifel, S. P. Cramer, *J. Am. Chem. Soc.* **2000**, *122*, 10544−10552.

[6] [6a] S. Fox, Y. Wang, A. Silver, M. Millar, *J. Am. Chem. Soc.* **1990**, *112*, 3218−3220. [6b] H. J. Krüger, G. Peng, R. H. Holm, *Inorg. Chem.* **1991**, *30*, 734−742. [6c] P. Stavropoulos, M. C. Muetterties, M. Carriè, R. H. Holm, *J. Am. Chem. Soc.* **1991**, *113*, 8485−8492. [6d] N. Baidya, M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **1991**, *30*, 929−937. [6e] E. J. Lyon, I. P. Georgakaki, J. H. Reibenspies, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2001**, *123*, 3268−3278.

[7] [7a] J. D. Franolic, W. Y. Wang, M. Millar, *J. Am. Chem. Soc.* **1992**, *114*, 6587−6588. [7b] G. J. Colpas, R. O. Day, M. J. Maroney, *Inorg. Chem.* **1992**, *31*, 5053−5055. [7c] M. A. Halcrow, G. Christou, *Chem. Rev.* **1994**, *94*, 2421−2481. [7d] M. T. B. Rauchfuss, S. M. Contakes, S. C. N. Hsu, M. A. Reynolds, S. R. Wikson, *J. Am. Chem. Soc.* **2001**, *123*, 6933−6934.

[8] [8a] S. A. Mirza, R. O. Day, M. J. Maroney, *Inorg. Chem.* **1996**, *35*, 1992−1995. [8b] G. Musie, P. J. Farmer, T. Tuntulani, J. H. Reibenspies, M. Y. Darensbourg, *Inorg. Chem.* **1996**, *35*, 2176−2183. [8c] F. Osterloh, W. Saak, D. Haase, S. Pohl, *Chem. Commun.* **1996**, 777−778. [8d] C-H. Lai, J. H. Reibenspies, M. Y. Darensbourg, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2390−2392. [8e] Th. L. James, L. Cai, M. C. Muetterties, R. H. Holm, *Inorg. Chem.* **1996**, *35*, 4148−4161.

[9] [9a] F. Osterloh, W. Saak, D. Haase, S. Pohl, *Chem. Commun.* **1997**, 979−980. [9b] G. Henkel, M. Kockerling, A. Müller, *Bioinorg. Chem.* **1997**, 456−467. [9c] J. C. A. Grapperhaus, M. Y. Darensbourg, *Acc. Chem. Res.* **1998**, *31*, 451−459. [9d] E. Bouwman, R. K. Henderson, A. L. Spek, J. Reedijk, *Eur. J. Inorg. Chem.* **1999**, *4*, 217−219.

[10] [10a] D. Sellmann, S. Fünfgelder, G. Pöhlmann, F. Knoch, M. Moll, *Inorg. Chem.* **1990**, *29*, 4772−4778. [10b] D. Sellmann, S. Fünfgelder, F. Knoch, M. Moll, *Z. Naturforsch., Teil B* **1991**, *46*, 1601−1608. [10c] D. Sellmann, H. Schillinger, F. Knoch, M. Moll, *Z. Naturforsch., Teil B* **1992**, *47*, 748−753. [10d] D. Sellmann, W. Prechtel, F. Knoch, M. Moll, *Inorg. Chem.* **1993**, *32*, 538−546. [10e] D. Sellmann, D. Häußinger, F. Knoch, M. Moll, *J. Am. Chem. Soc.* **1996**, *118*, 5368−5374. [10f] D. Sellmann, C. Allmann, F. W. Heinemann, F. Knoch, J. Sutter, *J. Organomet. Chem.* **1997**, *541*, 291−305.

[11] D. Sellmann, D. Häußinger, F. W. Heinemann, *Eur. J. Inorg. Chem.* **1999**, 1715−1725.

[12] D. Sellmann, F. Geipel, F. W. Heinemann, *Eur. J. Inorg. Chem.* **2000**, 271−279.

[13] D. Sellmann, F. Geipel, F. W. Heinemann, *Eur. J. Inorg. Chem.* **2000**, 59−63.

[14] D. Sellmann, F. Geipel, M. Moll, *Angew. Chem. Int. Ed.* **2000**, *39*, 561−563.

[15] D. Sellmann, F. Geipel, F. W. Heinemann, *Chem. Eur. J.* **2000**, *6*, 4279−658.

[16] [16a] A. Kobayashi, R. Takatori, I. Kikuchi, H. Konno, K. Sakamoto, O. Ishitani, *Organimetallics* **2001**, 3361−3363. [16b] S. Fukuzumi, K. Ohkubo, M. Fujitsuka, O. Ito, M. C. Teichmann, E. Maisonhaute, C. Amatore, *Inorg. Chem.* **2001**, *40*, 1213−1219. [16c] C. Kim, I. Novozhilova, M. Scott, G. Kimberly, A. Bagley, P. Coppens, *Inorg. Chem.* **2000**, *39*, 5791−5795. [16d] S. V. Zelenak, *Main Group Met. Chem.* **1999**, *22*, 179−184. [16e] M. Rivas, *New. J. Chem.* **1998**, *22*, 1315−1318. [16f] J. R. Burke, P. A. Fery, *J. Org. Chem.* **1996**, *61*, 530−533. [16g] B. Schiott, Ya-Jun Zheng, T. C. Bruice, *J. Am. Chem. Soc.* **1998**, *120*, 7192−7200. [16h] R. N. Mukerjee, M. S. Venkateshan, *J. Inorg. Nucl. Chem.* **1976**, *38*, 917−919.

[17] [17a] G. D. Figuly, C. K. Loop, J. C. Martin, *J. Am. Chem. Soc.* **1989**, *111*, 654−658. [17b] E. Block, V. Eswarakrishnan, M.

Gernon, G. Ofori-Okai, C. Saha, K. Tang, J. Zubieta, *J. Am. Chem. Soc.* **1989**, *111*, 658−665. [17c] K. Smith, C. M. Lindsay, G. J. Pritchard, *J. Am. Chem. Soc.* **1989**, *111*, 665−669.

[18] [18a] C. D. Johnson, I. Roberts, P. G. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1981**, 409−413. [18b] *Handbook of Chemistry and Physics* (Ed.: R. C. Weast), 68th ed., CRC, Florida, **1988**, pp. D159−D163.

[19] [19a] J-P. Costes, F. Dahan, J. M. Dominguez-Vera, J-P. Laurent, J. Ruiz, J. Sotiropoulos, *Inorg. Chem.* **1994**, *33*, 3809−3813. [19b] A. Becalska, R. J. Batchelor, F. W. B. Einstein, R. H. Hill, B. J. Palmer, *Inorg. Chem.* **1992**, *31*, 3118−3123.

[20] Z. Dori, R. F. Zialo, *Chem. Rev.* **1973**, *73*, 247−254.

[21] *SHELXTL NT 5.1*, Bruker Axs, Inc., Madison, WI, U.S.A. **1998**.

[22] CCDC-170684 (**1**·0.5CD_2Cl_2), -170685 (**1**·2THF·3MeOH), -170686 (**3**), -170687 (**4**·2$CDCl_3$), -170688 (**5**·0.625THF·0.375Et_2O), and -170689 (**7**·THF) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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