

Activation of H₂ and CO by Sulfur-Rich Nickel Model Complexes for [NiFe] Hydrogenases and CO Dehydrogenases^[‡]

Dieter Sellmann,^{[a][†]} Raju Prakash,^{*[a]} and Frank W. Heinemann^[a]

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Reactions of the trinuclear complexes [Ni(RS₃)]₃ [^HS₃²⁻ = bis(2-mercaptophenyl)sulfide(2-) (**1a**) or ^{si}S₃²⁻ = bis(2-mercapto-3-trimethylsilylphenyl)sulfide(2-) (**1b**)] with nucleophiles L (L = NHPnPr₃, NHPCy₃, NHSPPh₂, PnPr₃) afforded the corresponding mononuclear complexes [Ni(L)(^RS₃)] [R = si = SiMe₃; L = NHPnPr₃ (**2b**); L = NHPCy₃ (**3a,b**); L = NHSPPh₂ (**4a,b**); L = PnPr₃ (**5a**)]. X-ray structural determinations showed that **2b**, **3a**, **3b**, **4a**, and **5a** exhibit tetrahedrally distorted planar [Ni(L)(^RS₃)] fragments. Complex **2b** dimerizes through intermolecular N–H···N hydrogen bonding. In contrast to **2b**, complexes **3a** and **4a** exhibit intramolecular hydrogen bonds between thiol groups and NH protons. Complexes **2–4** possess weakly acidic NH protons and undergo D⁺/NH exchange reactions with D₂O or CD₃OD. Complexes **2–4** and [Ni(SiBu)(^RS₃)][–] (**9a,b**) also catalyze D₂/H⁺ exchange in [D₈]THF/H₂O under an elevated pressure of D₂ (18 bar), as confirmed by ¹H NMR spectroscopy. It is proposed that D₂

heterolysis is achieved through attack of the Lewis-acidic nickel centers and the Brønsted-basic sulfur atoms at an η²-D₂ ligand. Complexes **9a** and **9b** are the first sulfur-only nickel complexes that enable the modeling of the [NiFe] hydrogenase catalyzed D₂/H⁺ exchange reaction. Evidence for labile five-coordinate [Ni(CO)(L)(^RS₃)] has been found in the reaction between [Ni(L)(^RS₃)] complexes and CO. The CO adducts of complexes with nitrogenous ligands L such as N₃, NHPR₃ (R = nPr₃, Cy₃), or NHSPPh₂ showed rapid consecutive reactions. The reaction between Et₄N[Ni(N₃)(^{si}S₃)] (**8b**) and CO gave Et₄N[Ni(NCO)(^{si}S₃)] (**10b**), whereas reactions between **2–4** and CO afforded only **1a** or **1b**. Mechanisms are suggested which have the formation of reactive five-coordinated [Ni(CO)(L)(^RS₃)] intermediates in common.

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Introduction

Modeling active sites in metalloenzymes is the motivation for the synthesis of low-molecular-weight complexes that exhibit the structural and reactivity features of the enzyme centers.^[1] A key feature of the active sites of hydrogenases and CO dehydrogenases are nickel atoms in sulfur-dominated coordination spheres.^[1–5] X-ray structural determinations of several [NiFe] hydrogenases^[2,3] and two CO dehydrogenases^[4,5] have established that the active sites contain four-coordinate nickel atoms in tetrahedrally distorted planar coordination spheres of sulfur atoms^[2–5] (Figure 1). These centers are generally accepted to be the location of the reactions catalyzed by hydrogenases [Equation (1a), (1b)] and CO dehydrogenases [Equation (2)].

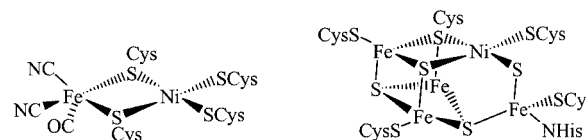
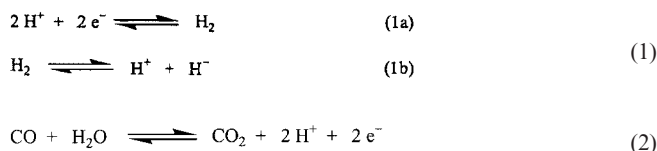


Figure 1. Schematic structures of the active centers in fully reduced [NiFe] hydrogenase from *D. vulgaris* Miyazaki^[2] (left) and the CO dehydrogenase from *C. hydrogenoformans*^[4,5] (right)

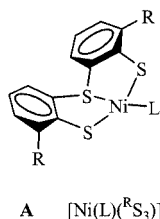
Catalysis of the reactions in Equations (1) and (2) makes hydrogenases and CO dehydrogenases essential for energy metabolism in nature. Low-molecular-weight nickel complexes with sulfur-dominated coordination spheres and reactivity towards H₂, CO, or CO₂ thus have considerable significance for gaining closer insights into the mechanisms of the reactions according to Equations (1) and (2), and for the development of competitive catalysts. Such complexes,

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[a] Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany
Fax: (internat.) + 49-(0)9131/85-27367
E-mail: prakash@anorganik.chemie.uni-erlangen.de

[†] Deceased.

however, are extremely rare. $[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ is one of the very few examples of complexes of type **A**, in which $^{\text{R}}\text{S}_3$ denotes the tridentate sulfur ligands HS_3^- [bis(2-mercaptophenyl)sulfide(2-)] or SiS_3^- [bis(2-mercapto-3-trimethylsilylphenyl)sulfide(2-)] and L neutral or anionic ligands, such as PR_3 , HNPr_3 , Cl^- , N_3^- , or SiBu^- .^[6–9]



Recent findings that the neutral phosphorane imine complex $[\text{Ni}(\text{NHPnPr}_3)(^{\text{H}}\text{S}_3)]$ catalyzes the heterolytic activation of H_2 [Equation (1b)]^[6] and the anionic complex $[\text{Ni}(\text{N}_3)(^{\text{H}}\text{S}_3)]^-$ reacts with CO to give $[\text{Ni}(\text{NCO})(^{\text{H}}\text{S}_3)]^-$ ^[7] prompted us to explore this type of complex in greater detail. This paper focuses on the synthesis and characterization of $[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ and its analogous $[\text{Ni}(\text{L})(^{\text{Si}}\text{S}_3)]$ complexes, and their reactivity towards H_2 . In addition, we extend our investigation towards the reactivity of $[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ complexes with CO in an effort to identify the possible five-coordinate intermediate species by means of spectroscopic techniques.

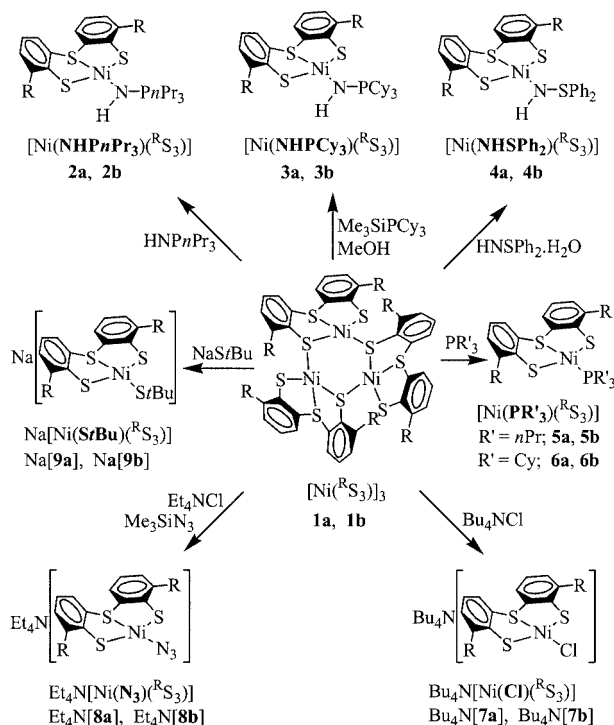
Results and Discussion

Synthesis and Characterization of $[\text{Ni}(\text{L})(^{\text{H}}\text{S}_3)]$ and $[\text{Ni}(\text{L})(^{\text{Si}}\text{S}_3)]$ Complexes

$[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ complexes containing different ligands L are a prerequisite for probing the influence of L upon the potential activation of H_2 and CO. Scheme 1 summarizes the synthesis of such $[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ complexes. The letters **a** and **b** always designate the unsubstituted ($\text{R} = \text{H}$) and substituted ($\text{R} = \text{SiMe}_3 = \text{si}$) complexes, respectively. For the sake of completeness, Scheme 1 also includes complexes **2a**, **5b**, **6a/6b**, $\text{Bu}_4\text{N}[\text{7a/7b}]$, and $\text{Et}_4\text{N}[\text{8b}]$, which have been reported previously.^[8,9] In most cases, the new complexes were obtained by cleavage of the trinuclear starting complexes $[\text{Ni}(^{\text{R}}\text{S}_3)]_3$ (**1a,b**) with nucleophiles L.

Treatment of **1b** with NHPnPr_3 in THF gave purple $[\text{Ni}(\text{NHPnPr}_3)(^{\text{Si}}\text{S}_3)]$ (**2b**) in analogy to the known synthesis of **2a**. The bulkier phosphorane imine HNPCy_3 had to be generated in situ through methanolysis of $\text{Me}_3\text{SiNPCy}_3$ and treated with **1a** and **1b** to afford $[\text{Ni}(\text{HNPCy}_3)(^{\text{R}}\text{S}_3)]$ (**3a,b**). These reactions could be monitored visually by the color change of the THF suspension (**1a**) or THF solution (**1b**) from red-brown to purple-red. Complex **1b** reacted much faster than complex **1a**.

Diphenylsulfimine, HNPh_2 , can potentially coordinate through either its nitrogen or sulfur atom. Reactions of **1a** and **1b** in THF with equimolar amounts of diphenylsulfimine hydrate, $\text{HNPh}_2 \cdot \text{H}_2\text{O}$, afforded the first examples of sulfimine sulfur-only nickel complexes as red-brown



Scheme 1. Synthesis of $[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ complexes ($\text{R} = \text{H} \rightarrow \text{a}$; $\text{R} = \text{SiMe}_3 \rightarrow \text{b}$)

$[\text{Ni}(\text{HNPh}_2)(^{\text{H}}\text{S}_3)]$ (**4a**) and dark-red $[\text{Ni}(\text{HNPh}_2)(^{\text{Si}}\text{S}_3)]$ (**4b**). The X-ray structure determination of **4a** proved that HNPh_2 coordinates to the nickel atom through its N atom like the phosphorane imines.^[8c]

Red-yellow crystals of $[\text{Ni}(\text{PnPr}_3)(^{\text{H}}\text{S}_3)]$ (**5a**) formed instantaneously when a black-brown THF suspension of **1a** was treated with an equivalent amount of PnPr_3 . The analogous synthesis of **5b** could be carried out in homogeneous phase in THF. The chloro complexes $\text{Bu}_4\text{N}[\text{Ni}(\text{Cl})(^{\text{H}}\text{S}_3)]$ ($\text{Bu}_4\text{N}[\text{7a}]$) and $\text{Bu}_4\text{N}[\text{Ni}(\text{Cl})(^{\text{Si}}\text{S}_3)]$ ($\text{Bu}_4\text{N}[\text{7b}]$) were obtained from **1a** and **1b** with Bu_4NCl . The anions **7a** and **7b** were required as precursors for the synthesis of the azido complexes $\text{Et}_4\text{N}[\text{Ni}(\text{N}_3)(^{\text{H}}\text{S}_3)]$ ($\text{Et}_4\text{N}[\text{8a}]$) and $\text{Et}_4\text{N}[\text{Ni}(\text{N}_3)(^{\text{Si}}\text{S}_3)]$ ($\text{Et}_4\text{N}[\text{8b}]$), which formed from the reaction of **1a** and **1b**, respectively, with Et_4NCl and subsequent reaction with Me_3SiN_3 . The sodium derivatives $\text{Na}[\text{Ni}(\text{StBu})(^{\text{H}}\text{S}_3)]$ ($\text{Na}[\text{9a}]$) and $\text{Na}[\text{Ni}(\text{StBu})(^{\text{Si}}\text{S}_3)]$ ($\text{Na}[\text{9b}]$) were obtained from **1a** and **1b** with NaStBu , similar to the formation of similar Bu_4N derivatives reported in the literature.^[8,9]

All new complexes were isolated in analytically pure form, are soluble in THF, CH_2Cl_2 , acetone, DMF, or DMSO, and were characterized by IR and NMR spectroscopy, and mass spectrometry. The molecular structures of **2b**, **3a**, **3b**, **4a**, and **5a** were determined by X-ray crystallography.

The IR (KBr) spectra of the complexes exhibit absorption patterns typical for complexes with $[\text{Ni}(^{\text{H}}\text{S}_3)]$ or $[\text{Ni}(^{\text{Si}}\text{S}_3)]$ fragments. The HNPr_3 and HNPh_2 ligands of **2–4** give rise to sharp $\nu(\text{NH})$ bands in the region

3365–3200 cm⁻¹ and $\nu(\text{NP})$ or $\nu(\text{NS})$ bands in the region 995–915 cm⁻¹. The $\nu(\text{NH})$, $\nu(\text{NP})$, and $\nu(\text{NS})$ bands correspond to those of HNPR_3 [10] and HNSPh_2 [11] complexes reported previously. In comparison to the $\nu(\text{NH})$ band of free HNPr_3 (3368 cm⁻¹), the $\nu(\text{NH})$ band in **2b** (3298 cm⁻¹) is significantly red-shifted. Similarly, the $\nu(\text{NH})$ band of **4a** (3202 cm⁻¹) and **4b** (3210 cm⁻¹) appears at lower wavenumbers than that of free HNSPh_2 (3306 cm⁻¹). [11b] The solid-state IR spectra of **3a** and **4a** also contain weak bands at 2560 cm⁻¹ (**3a**) and 2559 cm⁻¹ (**4a**), indicating the existence of N–H···S(thiolate) bridges. Such hydrogen-bond bridges were confirmed by the X-ray structure determinations.

As judged by their well-resolved NMR spectra, the complexes are diamagnetic. The ¹H NMR spectra of all complexes show a characteristic splitting pattern for the aromatic protons, consisting of either four or three multiplets depending on the fragment $[\text{Ni}(\text{H}_3\text{S}_3)]$ or $[\text{Ni}(\text{S}_3)]$. In **4a** and **4b**, some of these aromatic multiplets are superimposed by SPh_2 signals. The SiMe_3 protons in the $[\text{Ni}(\text{L})(\text{S}_3)]$ complexes give rise to a sharp singlet in the region between $\delta = 0.5$ and 0.3 ppm. The ¹H and ¹³C NMR spectra are consistent with the *C_s* symmetry of all complexes in solution. The NH singlet signals of **2a/b**, **3a/b**, and **4a/b** appear in the high-field region between $\delta = 0.9$ and –1.9 ppm, and their chemical shifts are solvent-dependent. They are always shifted to higher fields when compared with the NH singlets of free HNPr_3 ($\delta = 0.51$ ppm) or HNSPh_2 ($\delta = 1.12$ ppm), possibly indicating a decrease of NH acidity of the HNPR_3 and HNSPh_2 ligands. It should be noted that the NH protons exhibit slightly lower shifts in the $[\text{Ni}(\text{L})(\text{S}_3)]$ complexes **2b**, **3b**, and **4b** than in the corresponding $[\text{Ni}(\text{L})(\text{H}_3\text{S}_3)]$ complexes **2a**, **3a**, and **4a**. This might indicate a slightly higher NH acidity of the $[\text{Ni}(\text{L})(\text{S}_3)]$ complexes, caused by the electron-withdrawing effect of the SiMe_3 groups.

The NH shifts of the HNPR_3 and HNSPh_2 complexes allowed us to determine whether the N–P and N–S bonds in HNPR_3 and HNSPh_2 exhibit single- or double-bond character. Protons at sp²-hybridized N atoms in $\text{HN}=\text{X}$ compounds (X = NH, NO, CH₂, CR₂) such as diazene, nitroxyl, methyleneimines, or ketimines usually exhibit strong low-field shifts ($\delta = 10$ –20 ppm), both in the free and coordinated state. [12] The high-field NH shifts of the HNPR_3 and HNSPh_2 complexes **2**–**4** ($\delta = 0.9$ to –1.9 ppm) thus rather resemble the NH shifts in hydrazine and ammonia complexes and indicate N–P and N–S single bonds with sp³-hybridized N atoms. These considerations suggest the ylidic structures **I** and **II** for the HNPR_3 and HNSPh_2 ligands.



In agreement with these structures, the ¹H and ¹³C NMR spectra of the HNPR_3 and HNSPh_2 complexes **2**–**4** do not show any splitting of the signals when the temperature was

lowered to –80 °C, indicating a free rotation of the PR_3 and SPh_2 fragments around the N–P or N–S bonds, as well as of the NH groups around the Ni–N bonds.

X-ray Crystal Structure Determinations

The molecular structures of $[\text{Ni}(\text{NHPnPr}_3)(\text{S}_3)]$ (**2b**), $[\text{Ni}(\text{NHPCy}_3)(\text{H}_3\text{S}_3)]$ (**3a**), $[\text{Ni}(\text{NHPCy}_3)(\text{S}_3)]$ (**3b**), $[\text{Ni}(\text{HNSPh}_2)(\text{H}_3\text{S}_3)]$ (**4a**), and $[\text{Ni}(\text{PnPr}_3)(\text{H}_3\text{S}_3)]$ (**5a**) were determined by X-ray structure analysis. Figure 2 depicts the molecular structures and Table 1 lists selected distances and angles.

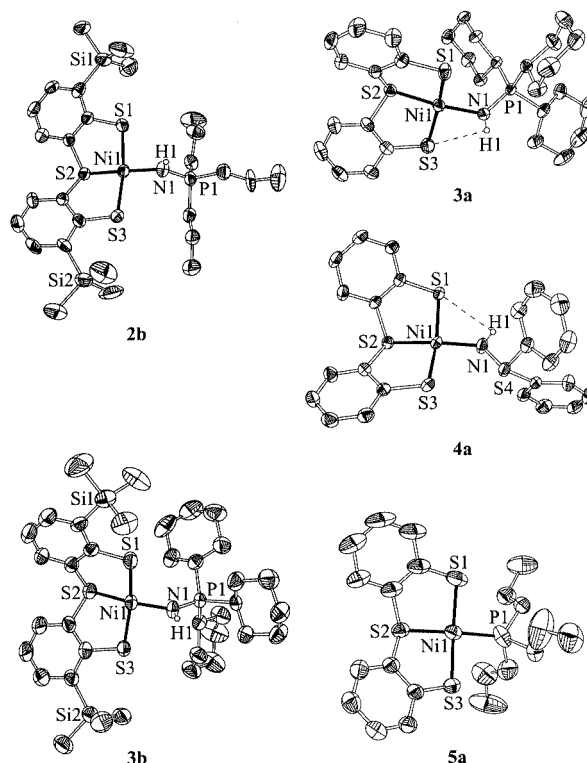


Figure 2. Thermal ellipsoid plots of $[\text{Ni}(\text{NHPnPr}_3)(\text{S}_3)]$ (**2b**), $[\text{Ni}(\text{NHPCy}_3)(\text{H}_3\text{S}_3)]$ (**3a**), $[\text{Ni}(\text{NHPCy}_3)(\text{S}_3)]$ (**3b**), $[\text{Ni}(\text{HNSPh}_2)(\text{H}_3\text{S}_3)]$ (**4a**), $[\text{Ni}(\text{PnPr}_3)(\text{H}_3\text{S}_3)]$ (**5a**) (50% probability ellipsoids; H atoms, except for N-bound ones, omitted)

The unit cells of all complexes contain discrete molecules whose four-coordinate nickel atoms exhibit a tetrahedrally distorted planar coordination, as evidenced by the non-linear S1–Ni1–S3 and S2–Ni1–L angles. This tetrahedral distortion can be traced back to the sp³ hybridization of the central thioether sulfur atom in the R_3S_3 ligands. It leads to a butterfly shape of the nickel–sulfur fragments, the characteristic topology of which also causes a very short Ni–S(thioether) distance of 208–213 pm, which is distinctly shorter than the Ni–S(thiolate) distances (216–220 pm). [7–9]

The Ni–N distances of **2b** [190.6(7) pm], **3a** [193.1(3) pm], **3b** [192.3(4) pm], and **4a** [189.5(2) pm] are similar to that of $[\text{Ni}(\text{NHPnPr}_3)(\text{H}_3\text{S}_3)]$ (**2a**) reported previously, [8c] and indicate the presence of Ni–N single bonds. They are all considerably shorter than the Ni–N distances observed in

Table 1. Selected bond lengths [pm] and angles [°] for [Ni(NHPnPr₃)(^{si}S₃)] (**2b**), [Ni(NHPCy₃)(^HS₃)] (**3a**), [Ni(NHPCy₃)(^{si}S₃)] (**3b**), [Ni(NHSPH₂)(^HS₃)] (**4a**), [Ni(PnPr₃)(^HS₃)] (**5a**)

Compound	2b	3a	3b	4a	5a
Ni1–S1	216.8(3)	218.7(1)	217.0(2)	221.6(1)	216.3(1)
Ni1–S2	208.9(3)	210.7(1)	211.0(2)	211.7(1)	214.1(1)
Ni1–S3	219.9(3)	217.8(1)	217.0(2)	217.7(1)	217.4(1)
Ni1–N1	190.6(7)	193.1(3)	192.3(4)	189.5(2)	219.0(2) ^[a]
N1–P1	160.5(7)	160.9(3)	159.8(5)	159.5(2) ^[b]	
N1–H1	86	73(4)	86	80(3)	
S1–Ni1–S2	89.3(1)	89.41(3)	89.97(7)	87.46(3)	90.25(5)
S1–Ni1–S3	166.4(2)	162.02(4)	159.50(8)	160.27(3)	164.10(5)
S1–Ni1–N1	91.1(2)	96.60(9)	91.2(2)	91.55(8)	93.05(5) ^[a]
S2–Ni1–S3	87.2(1)	88.90(4)	89.83(7)	90.71(3)	88.74(4)
S2–Ni1–N1	172.1(2)	165.83(9)	168.5(2)	165.62(8)	170.77(4) ^[a]
S3–Ni1–N1	94.2(2)	89.23(8)	93.1(2)	94.95(8)	90.42(5) ^[a]
Ni1–N1–P1	128.3(4)	128.4(2)	127.3(3)	125.4(2) ^[b]	
Ni1–N1–H1	116	114(4)	116	122(2)	

^[a] N1=P1. ^[b] P1=S4.

other diamagnetic four-coordinate Ni^{II} complexes (201–203 pm).^[10a,13] The Ni–P distances of [Ni(PnPr₃)(^HS₃)] (**5a**) [219.0(2) pm] and previously reported [Ni(PR₃)(^RS₃)] complexes (R = Me, Ph or Cy) lie in the same range of 219–221 pm.^[8,9] The N–P distances (160 pm) of **2b**, **3a**, and **3b** are identical within the limit of the 3σ criterion. Hydrogen bonds are observed for **2b**, **3a**, and **4a**. Figure 3 illustrates that N–H···N bridges lead to the formation of dimers of [Ni(NHPnPr₃)(^{si}S₃)] (**2b**) which possesses crystallographically imposed inversion symmetry. The hydrogen bonds are concluded from the distances H1···N1a (246 pm) and N1···N1a [322(2) pm], which are shorter than the sum of the corresponding van der Waals radii (N = 155 pm; H = 120 pm).^[14] With respect to the hydrogen bonds, complex **2b** contrasts with the analogous complex [Ni(NHPnPr₃)(^HS₃)] (**2a**) which contains the parent ligand ^HS₃[−]. Complex **2a** also dimerizes in the solid state, however through N–H···S(thiolate) bridges rather than N–H···N bridges.^[8c]

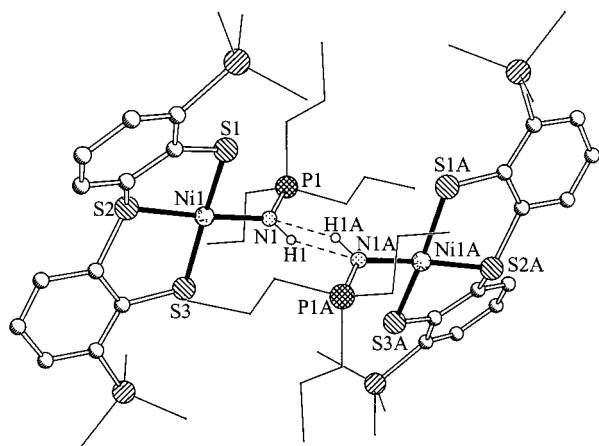
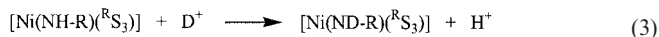


Figure 3. View of the N–H···N hydrogen bond dimers of [Ni(NHPnPr₃)(^{si}S₃)] (**2b**) (H atoms, except for N-bound ones, omitted)

Intramolecular N–H···S(thiolate) bridges are found in [Ni(NHPCy₃)(^HS₃)] (**3a**) and [Ni(NHSPH₂)(^HS₃)] (**4a**). This can be deduced from the distances H1···S3 in **3a** [269(5) pm] and H1···S1 in **4a** [283(3) pm] as well as the distances N1···S3 in **3a** [289.1(3) pm] and N1···S1 in **4a** [295.5(2) pm], which are shorter than the sum of van der Waals radii (N = 155 pm; H = 120 pm; S = 180 pm).^[14] No hydrogen bonds are found in [Ni(NHPCy₃)(^{si}S₃)] (**3b**).

Reactions with Molecular Hydrogen

The heterolytic cleavage of H₂ into H⁺ and H[−] according to Equation (1b) and formation of HD from H₂ and D₂O, respectively, is one of the key reactions catalyzed by hydrogenases. Such a heterolytic H₂ cleavage and H₂/D⁺ or D₂/H⁺ exchange reaction could be proved to be catalyzed by the phosphorane imine and sulfimine complexes. The NH–R' ligands (R' = PnPr₃, PCy₃, SPh₂) in these complexes are excellent probes for unambiguously establishing the H₂ or D₂ heterolysis because they have weakly acidic NH protons that exchange for D⁺. Such an NH/D⁺ exchange was similarly observed for the complexes **2a/b**, **3a/b**, and **4a/b** according to Equation (3).



A concentrated CD₂Cl₂/CH₂Cl₂ solution of the respective complex was treated with D₂O or CD₃OD, and the NH/D⁺ exchange was monitored by ¹H/²D NMR spectroscopy. In the course of 5–20 min, the NH signals of the starting complexes (between δ = 0.80 and −1.96 ppm) disappeared, while the ND signals of the resulting deuterated product complexes could be observed at the same region in the ²D NMR spectrum. After completion of the reactions, the solvents were removed in vacuo; ν(ND) bands in the region of 2480–2420 cm^{−1} of the IR (KBr) spectra of the residues further corroborated the formation of the deuterated complexes.

The D₂/NH exchange was probed with complexes **2b**, **3a/b**, and **4a/b** and the formation of HD was monitored by ¹H NMR spectroscopy. In high-pressure NMR tubes, concentrated CD₂Cl₂ or [D₈]THF solutions of **2b**, **3a/b**, and **4a/b** were pressurized with D₂ (18 bar). ¹H NMR spectra recorded at regular time intervals showed the appearance of the 1:1:1 triplets of HD (*J*_{H,D} = 42.5 Hz) formed according to Equation (4). The HD triplets in the region of δ = 4.2–4.8 ppm reached maximum intensity after 80 h in the case of **2b** and 120 h in the case of **4a**.



The reactions in Equations (3) and (4) thus prove that the [Ni(NHR')(^RS₃)] complexes **2b**, **3a**, **3b**, **4a**, and **4b** catalyze the heterolytic cleavage of D₂ and the exchange of molecular hydrogen with protons that ultimately result from protic solvents such as H₂O or CH₃OH. In a further experiment

we therefore tried to combine these reactions. Initially, we chose the complex **3b** because it proved to have the highest stability towards methanolysis leading to [Ni(^{si}S₃)]₃ and free NHPCy₃. In a high-pressure NMR tube, a concentrated CD₂Cl₂ solution of **3b** and MeOH (50 μL) was pressurized with D₂ (18 bar) and the reaction was monitored by ¹H NMR spectroscopy. Unfortunately, due to the large signals of the MeOH protons the HD signal could not be identified. However, repeating this experiment by changing the solvent to [D₈]THF and the proton source to H₂O yielded a favorable result. A ¹H NMR spectrum of **3b** recorded after 4 d showed the appearance of the 1:1:1 triplets (*J*_{H,D} = 42.5 Hz) of HD in the region of δ = 4.2–4.8 ppm. Interestingly, the intensity of the triplet increases with an increase in reaction time and nearly triples in size after 15 d. The complexes **2a**, **2b**, **3a**, **4a**, and **4b** also exhibit the same behavior.

These positive results prompted us to extend our investigations to complexes Bu₄N[**9a**] and Bu₄N[**9b**] as, like in the active sites of [NiFe] hydrogenases, they exhibit all-sulfur nickel coordination. These complexes were investigated first in the form of their sodium salts Na[**9a**] and Na[**9b**]. In a high-pressure NMR tube, a concentrated solution of Na[**9a**] or Na[**9b**] in a [D₈]THF/H₂O (50 μL) mixture was pressurized with D₂ (18 bar) and the reaction was monitored by ¹H NMR spectroscopy at various time intervals. Figure 4 depicts the ¹H NMR spectra of the HD region of Na[**9a**] in [D₈]THF/H₂O with D₂ pressure at various time intervals. The ¹H NMR spectrum of Na[**9a**] recorded after 1 d does not show any new peaks (Figure 4a), while after 5 d it shows a small 1:1:1 triplet of HD (*J*_{H,D} = 42.5 Hz) in the region between δ = 4.8 and 4.2 ppm (Figure 4b). The concomitant formation of HDO could not be identified due to the large H₂O signal. However, the intensity of the HD triplet increases with increasing reaction time (Figure 4b–d). The reaction was prolonged for 15 d and the intensity of the HD triplet was enhanced to three times that of the initial one, suggesting that the reaction is catalytic. Compound Na[**9b**] undergoes an identical reaction but is more active, giving rise to HD formation in a shorter reaction time (initial HD triplet showed up after 4 d). It is worth mentioning that the complexes remain intact even after 15 d of reaction time. Identical experiments performed without either the complexes Na[**9b**] and Na[**9b**] or H₂O did not show any HD signals. These results unambiguously prove that the reaction is catalytic and the heterolytic cleavage of D₂ must take place at the nickel center via a five-coordinated D₂ intermediate species.

These results suggest that the D₂ heterolysis is achieved through the concerted action of the Lewis-acidic nickel center and the Brønsted-basic thiol atoms upon η²-D₂ ligands. The resulting acidic thiol deuteron exchanges with the H₂O proton to give HDO. The thiol proton and nickel deuteride ion combine to give HD. Release of HD in the consecutive step leaves [Ni(L)(^RS₃)] intact, which can then add another molecule of D₂ to complete the reaction cycle (Scheme 2). It is worthwhile to note that Na[**9a**] and Na[**9b**] are the first completely characterized sulfur-only nickel

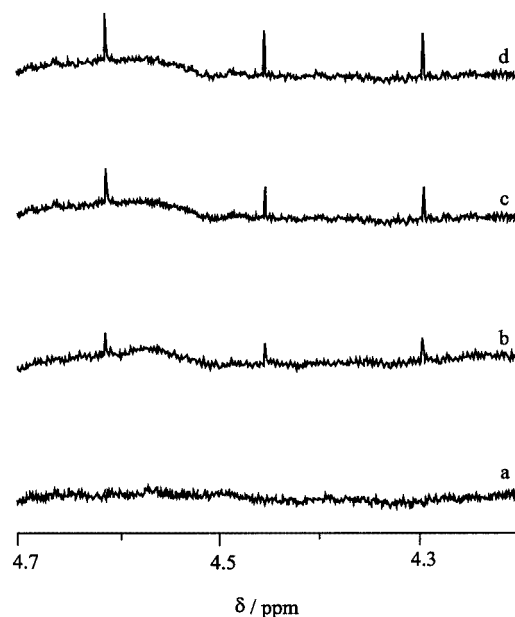
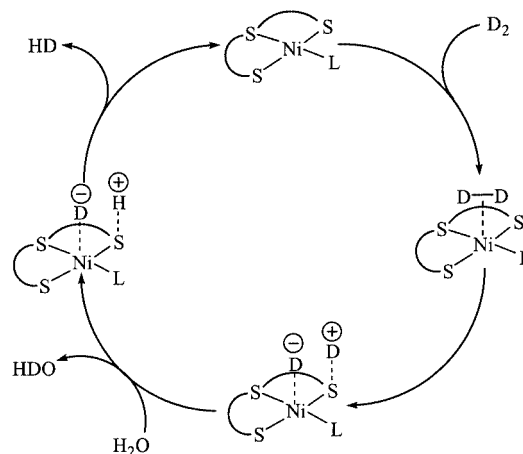


Figure 4. ¹H NMR spectra of the HD region of Na[Ni(S*t*Bu)(^HS₃)] Na[**9a**] in [D₈]THF/H₂O under D₂ (18 bar), recorded after: (a) 1, (b) 5, (c) 10, and (d) 15 d

complexes that model the [NiFe] hydrogenase catalyzed D₂/H⁺ exchange reaction.



Scheme 2. Mechanism of [Ni(L)(^RS₃)]-catalyzed D₂/H₂O exchange reaction

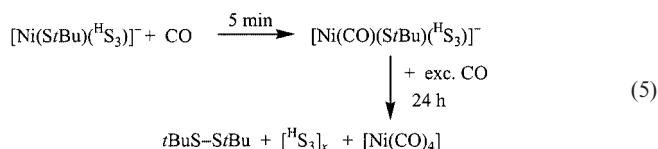
Reactions with CO

Coordination of CO to tetrahedrally distorted planar [NiS₄] sites is postulated as the primary key step in CO dehydrogenase reactions^[15] and is possibly responsible for the inhibition of [NiFe] hydrogenases by CO.^[16] Complexes exhibiting [Ni(CO)(S₄)] cores, however, have never been identified or isolated. Recently, the five-coordinate carbonyl–Ni^I–chalcogenate complexes [Ni(DAPA)(EPh)₂(CO)][−] {DAPA = 2,6-bis[1-(phenylimino)ethyl]pyridine; E = S or Se} and the first five-coordinate carbonyl–Ni^{II}–thiolate complex [Ni(PS3*)(CO)][−] [PS3* =

tris(3-phenyl-2-thiophenyl)phosphane] were reported.^[17] For this reason, the reaction of the nickel complexes $[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ (**2–9**) with CO was investigated. They all possess at least $[\text{NiS}_3]$ cores, and it has been pointed out previously^[8,9] that the characteristic tetrahedral distortion of $[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ complexes could be crucial for their capability to add a fifth ligand.

The distances and angles in the $[\text{Ni}(^{\text{R}}\text{S}_3)]$ cores of all the complexes investigated are almost identical, although the reactivity of the individual $[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ complexes towards CO proved to be extremely different, clearly showing the decisive influence of the coligands L. The influence of the R substituents of the $^{\text{R}}\text{S}_3$ ligands is evidenced by the fact that the $[\text{Ni}(\text{L})(^{\text{Si}}\text{S}_3)]$ complexes always reacted faster than their $[\text{Ni}(\text{L})(^{\text{H}}\text{S}_3)]$ counterparts.

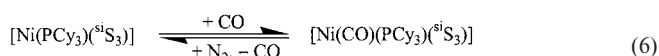
Because the $\text{S}t\text{Bu}^-$ complex $[\text{Ni}(\text{S}t\text{Bu})(^{\text{H}}\text{S}_3)]^-$ (**9a**) has an all-sulfur coordination sphere, it was investigated first in form of its sodium salt $\text{Na}[\text{9a}]$. Bubbling CO gas through a THF solution of $\text{Na}[\text{9a}]$ for 3–5 min gave rise to a $\nu(\text{CO})$ band in the IR spectrum at 2131 cm^{-1} . When this solution was stored under CO for 24 h, a second $\nu(\text{CO})$ band appeared at 2040 cm^{-1} . These bands were assigned to $[\text{Ni}(\text{CO})(\text{S}t\text{Bu})(^{\text{H}}\text{S}_3)]^-$ (2131 cm^{-1}) and $[\text{Ni}(\text{CO})_4]$ (2040 cm^{-1}) which form according to Equation (5).



The reduction of Ni^{II} to Ni^0 is possibly initiated by the reductive elimination of the (labile) $\text{S}t\text{Bu}^-$ ligand. This is suggested by the observation that the substitutionally inert phosphane complex $[\text{Ni}(\text{PCy}_3)(^{\text{Si}}\text{S}_3)]$ does not yield $[\text{Ni}(\text{CO})_4]$ when treated with CO (vide infra).

The $\nu(\text{CO})$ assignment was corroborated by the following experiments. Purging the solutions with N_2 for 10 min led to complete disappearance of the $\nu(\text{CO})$ bands. This indicated that the first step yielding $[\text{Ni}(\text{CO})(\text{S}t\text{Bu})(^{\text{H}}\text{S}_3)]^-$ is reversible. Carrying out the experiment [according to Equation (5)] with ^{13}CO gave rise to $\nu(\text{CO})$ bands at 2085 cm^{-1} ($[\text{Ni}(^{13}\text{CO})(\text{S}t\text{Bu})(^{\text{H}}\text{S}_3)]^-$) and 1995 cm^{-1} ($[\text{Ni}(^{13}\text{CO})_4]$). The isotopic shifts of 45 cm^{-1} agree with theoretical expectations. Formation of the five-coordinate intermediate $[\text{Ni}(\text{CO})(\text{S}t\text{Bu})(^{\text{H}}\text{S}_3)]^-$ was further corroborated by monitoring the reaction by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum shows that treatment of a $[\text{D}_8]\text{THF}$ solution of $\text{Na}[\text{9a}]$ with ^{13}CO (5 bar) in a medium-pressure NMR tube gave rise to ^{13}C NMR signals at $\delta = 198.5$, 192.1 , and 184.7 ppm , which could be assigned to $[\text{Ni}(^{13}\text{CO})(\text{S}t\text{Bu})(^{\text{H}}\text{S}_3)]^-$, $[\text{Ni}(^{13}\text{CO})_4]$, and free ^{13}CO , respectively. This assignment was checked by recording the ^{13}C NMR spectra of ^{13}CO and $[\text{Ni}(\text{CO})_4]$ in $[\text{D}_8]\text{THF}$. In summary, these results suggest that nickel thiolate complexes with a tetrahedrally distorted planar $[\text{NiS}_4]$ core can reversibly coordinate CO, but afford $[\text{Ni}(\text{CO})_4]$ when treated with an excess of CO for longer periods of time.

In the next step, the influence of the phosphane coligands upon CO coordination was probed with $[\text{Ni}(\text{PCy}_3)(^{\text{Si}}\text{S}_3)]$ (**6b**). When CO was bubbled through a THF solution of **6b** according to Equation (6), a $\nu(\text{CO})$ band appeared at 2135 cm^{-1} in the IR spectrum. Purging the solution with a stream of N_2 led to disappearance of the $\nu(\text{CO})$ band and **6b** was regained. This result suggests that $[\text{Ni}(\text{PR}_3)(^{\text{R}}\text{S}_3)]$ complexes can also reversibly add CO. In addition, the $\nu(\text{CO})$ frequency of $[\text{Ni}(\text{CO})(\text{PCy}_3)(^{\text{Si}}\text{S}_3)]$ at 2135 cm^{-1} is similar to that of $[\text{Ni}(\text{CO})(\text{S}t\text{Bu})(^{\text{H}}\text{S}_3)]^-$ (2131 cm^{-1}), indicating that the electron density at the nickel atom is a little lower in the neutral phosphane than in the anionic $\text{S}t\text{Bu}^-$ complex. However, the relatively high wavenumbers indicate a weak binding of the CO ligands, rationalizing their reversible coordination.

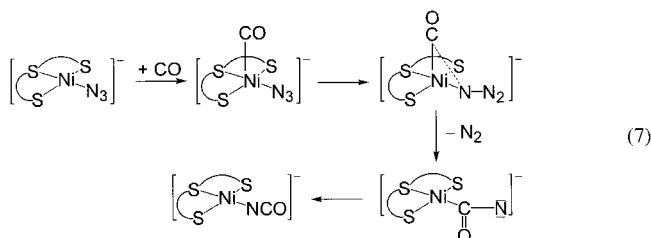


The coligands $\text{S}t\text{Bu}^-$ or PCy_3 in the $[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ complexes $[\text{Ni}(\text{S}t\text{Bu})(^{\text{H}}\text{S}_3)]^-$ (**9a**) and $[\text{Ni}(\text{PCy}_3)(^{\text{Si}}\text{S}_3)]$ (**6b**) do not react with CO, either in the free or complexed state, whereas the nitrogen-containing ligands NHPR_3 , NHSPH_2 , and N_3^- show a distinctly different behavior. In the free state they, too, do not react with CO, however, when functioning as ligands in the $[\text{Ni}(\text{L})(^{\text{R}}\text{S}_3)]$ complexes **2–4** and **8b**, they undergo rapid reactions with equimolar amounts of CO. This demonstrates that the reactions are mediated by the $[\text{Ni}(^{\text{R}}\text{S}_3)]$ fragments, and indicates that both CO and nitrogenous ligands can be activated.

From the mechanistic point of view, the reaction between $\text{Et}_4\text{N}[\text{Ni}(\text{N}_3)(^{\text{Si}}\text{S}_3)]$ (**8b**) and CO can be rationalized best. In THF solution, complex **8b** is thermally stable and resistant to UV photolysis (150 W Hg lamp) over extended periods of time (3 d). When treated with equimolar amounts of CO gas in the dark, however, it rapidly transforms into the NCO complex $\text{Et}_4\text{N}[\text{Ni}(\text{NCO})(^{\text{Si}}\text{S}_3)]$ (**10b**) and N_2 , and complex **10b** could be isolated in nearly quantitative yield (92%). Monitoring the reaction by IR spectroscopy demonstrated that the $\nu(\text{N}_3)$ band of **8b** at 2037 cm^{-1} continuously decreases in intensity while the $\nu(\text{NCO})$ band of **10b** at 2227 cm^{-1} increases.

The analogous reaction of the $^{\text{H}}\text{S}_3$ complex $\text{Bu}_4\text{N}[\text{Ni}(\text{N}_3)(^{\text{H}}\text{S}_3)]$ (**Bu**₄**N**[**8a**]) with CO afforded $\text{Bu}_4\text{N}[\text{Ni}(\text{NCO})(^{\text{H}}\text{S}_3)]$ ^[7] and enabled us to detect a short-lived $[\text{Ni}(\text{CO})(\text{N}_3)(^{\text{H}}\text{S}_3)]^-$ intermediate, with a $\nu(\text{CO})$ band at 2129 cm^{-1} by IR spectroscopy. Such an intermediate could not be found in the reaction between $\text{Et}_4\text{N}[\text{8b}]$ and CO, probably owing to the greater reactivity of **8b** and its intermediates. However, the close analogy between $\text{Bu}_4\text{N}[\text{8a}]$ and $\text{Et}_4\text{N}[\text{8b}]$ suggests identical mechanisms for their reaction with CO [Equation (7)].

Coordination of CO to the $[\text{Ni}(\text{N}_3)(^{\text{R}}\text{S}_3)]^-$ anion leads to activation of CO and N_3^- , release of N_2 and formation of the NCO complex. Related mechanisms have previously



been suggested for four-coordinate azido(phosphane) complexes of Pd^{II}, Pt^{II}, Rh^I and Ir^I.^[18] The phosphorane imine complexes **2a/2b**, **3a/3b**, and the sulfinimine complexes **4a/4b** also react quickly with CO under standard conditions (1 bar, 20 °C). However, the mechanisms of the reactions are less obvious. When a stream of CO was bubbled through CH₂Cl₂ solutions of **2a/2b**, **3a/3b**, or **4a/4b**, the parent complexes [Ni(^RS₃)₃] (**1a** or **1b**) formed and could be isolated in high yields. When the CH₂Cl₂ solutions were each treated with 1 equiv. of CO gas, the reactions proceeded more slowly, and monitoring of the reactions by IR and NMR spectroscopy, and mass spectrometry, yielded hints as to the nature of the intermediates. Experiments with the respective [Ni(L)(^HS₃)] and [Ni(L)(^{si}S₃)] complexes complemented each other. For example, after addition of 1 equiv. of CO, the IR spectrum of the CH₂Cl₂ solution of the phosphorane imine complex [Ni(NHPnPr₃)(^HS₃)] (**2a**) shows a weak band at 2146 cm⁻¹. This band disappeared in the course of 25 h, and a new band at 2227 cm⁻¹ developed simultaneously; its intensity increased over 45 h and then decreased again, while [Ni(^HS₃)₃] (**1a**) started precipitating from the solution (Figure 5). The weak band at 2040 cm⁻¹ corresponds to the side product [Ni(CO)₄] that forms and disappears during the reaction. The same IR spectroscopic behavior was found for CH₂Cl₂ solutions of [Ni(NHPnPr₃)(^{si}S₃)] (**2b**).

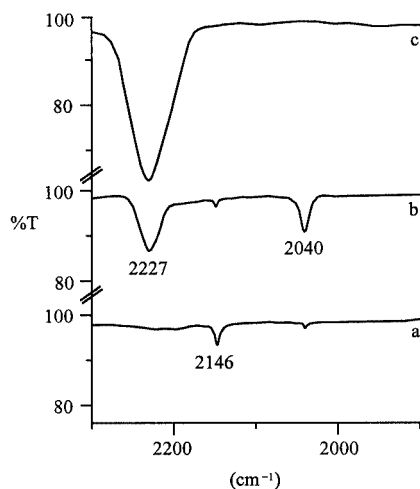
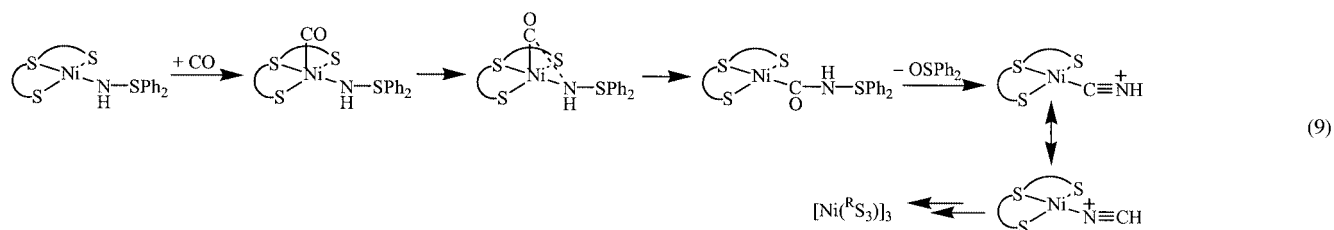
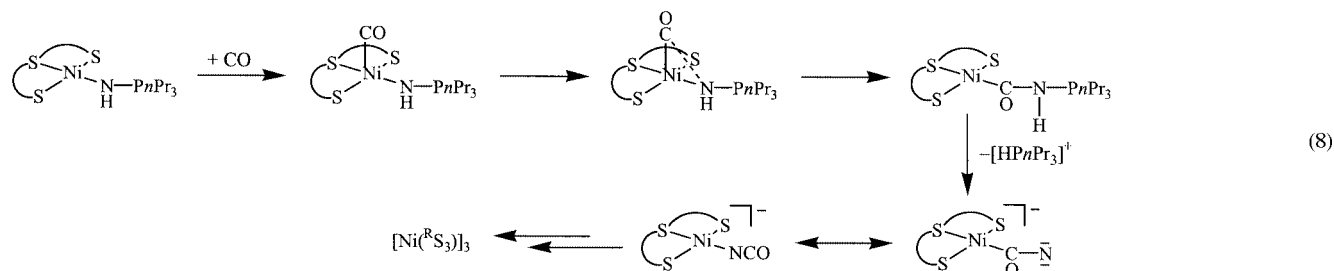


Figure 5. IR spectroscopic monitoring of the reaction between equimolar amounts of [Ni(NHPnPr₃)(^HS₃)] (**2a**) and CO in CH₂Cl₂ solution; the spectra were recorded after (a) 3, (b) 20, and (c) 48 h

The ¹H NMR spectrum of **2a** in CD₂Cl₂ shows the NH signal at δ = -1.82 ppm. After injecting an equimolar amount of CO, this NH signal gradually broadens and disappears and a new doublet appears at δ = 4.85 ppm (*J*_{P,H} = 550 Hz). Similarly, in the ³¹P NMR spectrum of **2a**, the signal at δ = 50.8 ppm disappears gradually in the presence of CO and a new peak appears at δ = 55.1 ppm. This new peak, in turn, vanishes over the course of 30 h to give a new low-intensity doublet at δ = 34.2 ppm (*J*_{P,H} = 527 Hz). All ¹H and ³¹P NMR signals disappear when [Ni(^HS₃)₃] (**1a**) precipitates from the solution. These findings can be interpreted as follows: the initial step is the coordination of CO to give a five-coordinate [Ni(CO)(NHPnPr₃)(^HS₃)] intermediate showing a ν(CO) band at 2146 cm⁻¹ (³¹P NMR: δ = 55.1 ppm). As above, the high frequency of this band indicates that the CO is only weakly bound. Subsequently, the intramolecular nucleophilic addition of the N atom of NHPnPr₃ to CO is followed by the removal of PnPr₃ to give an unstable acylimide species. Then, the deprotonation of the N–H bond by the free PnPr₃ gives [HPnPr₃]⁺ (doublet in the ¹H and ³¹P NMR spectra) and the acyl azide complexes. A similar reactivity has already been reported in coordinated phosphanylamine complexes of Ni^{II} and free PMe₃ to give [HPMe₃]⁺.^[10a] These acyl azides can rearrange to give [HPnPr₃][Ni(NCO)(^HS₃)] [ν(NCO) = 2227 cm⁻¹] according to Equation (8). Unlike Et₄N[Ni(NCO)(^{si}S₃)] (**10b**), [HPnPr₃][Ni(NCO)(^HS₃)] is unstable and undergoes further reactions to give **1a** as the final product. Monitoring the reactions of the ^{si}S₃ complex **2b** by ¹H and ³¹P NMR spectroscopy only showed the replacement of the signals of **2b** by those of **1b**, but did not allow us to draw further conclusions. All attempts to isolate the intermediate species were unsuccessful, even at -78 °C.

After addition of 1 equiv. of CO, the IR spectrum of the CH₂Cl₂ solution of the sulfinimine complex [Ni(NHSPnPr₃)(^HS₃)] (**4a**) shows a weak band at 2148 cm⁻¹. This band disappeared over the course of 1 h, and simultaneously a new band appeared at 2185 cm⁻¹, whose intensity increased over 5 h and then decreased again, while [Ni(^HS₃)₃] (**1a**) started precipitating from the solution. The same IR spectroscopic behavior was found for CH₂Cl₂ solutions of [Ni(NHSPnPr₃)(^{si}S₃)] (**4b**). The SiMe₃ substituents of **4b** were also used as a spectroscopic probe. The ¹H NMR spectra of the reactions in CD₂Cl₂ show that the SiMe₃ singlet of **4b** at δ = 0.36 ppm broadens slightly and is replaced by the two singlets of [Ni(^{si}S₃)₃] (**1b**) at δ = 0.55 and 0.08 ppm.

These findings are interpreted in the following way. The primary step is again the coordination of CO to give a five-coordinate [Ni(CO)(NHSPnPr₃)(^RS₃)] intermediate showing a ν(CO) band at 2148 cm⁻¹. Subsequent reaction between CO and the HNSPnPr₃ ligands leads to deoxygenation of CO resulting in OSPh₂ and coordinated HC=N or HN=C ligands, which give rise to the band at 2185 cm⁻¹. Transition metal complexes with HCN or HNC ligands show ν(CN) bands in the region of 2200–2100 cm⁻¹.^[19] Subsequent decoordination of the HCN ligands results in the formation of [Ni(^RS₃)₃] [Equation (9)].



The mass spectra of the reaction solutions recorded when the band at 2185 cm^{-1} had attained maximum intensity support this interpretation. These spectra exhibit peaks at $m/z = 202$ assignable to OSPh_2 and at 335 (**4a**) or 479 (**4b**), which are compatible with the formation of $[\text{Ni}(\text{HCN})(\text{RS}_3)]$ complexes.

Table 2 summarizes the $\nu(\text{CO})$ frequencies of the CO adducts initially formed and demonstrates that complexes with $^{\text{H}}\text{S}_3$ and $^{\text{Si}}\text{S}_3$ ligands show identical $\nu(\text{CO})$ frequencies. Therefore, the sometimes remarkably different reaction rates of $^{\text{H}}\text{S}_3$ and $^{\text{Si}}\text{S}_3$ complexes might be caused by differences in solubility rather than by changes in the electronic properties. Anionic complexes give rise to lower $\nu(\text{CO})$ frequencies than neutral complexes. This trend of $\nu(\text{CO})$ frequencies is well known from classical carbonylmetal complexes, and it strongly suggests that structurally similar five-coordinate $[\text{Ni}(\text{CO})(\text{L})(\text{RS}_3)]$ species form in all cases. These five-coordinate species can reversibly dissociate CO or undergo rapid consecutive reactions if L is a nitrogenous species having lone-pairs at the N donor such as azide or the ylidic HNPR_3 and HNSPh_2 ligands. The subsequent reactions lead to conversion of CO and the nitrogenous ligand. The final products, which could be isolated, depend on the nitrogenous ligands. If they release inert species such as N_2 in the case of azide, the resulting NCO^- complexes $[\text{Ni}(\text{NCO})(\text{RS}_3)]^-$ can be isolated in good yields. In the case of the phosphorane imine or sulfinimine complexes, an analogous cleavage of N–P or N–S bonds yields species that are still highly reactive and go on reacting until the stable trinuclear $[\text{Ni}(\text{RS}_3)_3]$ complexes form.

It should be noted that the $\nu(\text{CO})$ frequencies of all five-coordinate intermediates (Table 2) are relatively high and, in some cases, even slightly higher than that of free CO in the gas phase (2143 cm^{-1}). Additional measurements corroborated that these bands do not result from dissolved CO.

The CO adducts of the phosphorane imine and sulfinimine complexes thus belong to the class of “non-classical” carbonylmetal complexes which can exhibit $\nu(\text{CO})$ frequencies

Table 2. $\nu(\text{CO})$ frequencies of the primary five-coordinate species $[\text{Ni}(\text{CO})(\text{L})(\text{RS}_3)]$ resulting from $[\text{Ni}(\text{L})(\text{RS}_3)]$ and CO (1 bar) at 20°C

Complex	$\nu(\text{CO})\text{ [cm}^{-1}\text{]}$	Reaction type
$\text{Bu}_4\text{N}[\text{Ni}(\text{N}_3)(^{\text{H}}\text{S}_3)]$ ($\text{Bu}_4\text{N}[\textbf{8a}]$) ^[a]	2129 ^[b]	irr.
$\text{Et}_4\text{N}[\text{Ni}(\text{N}_3)(^{\text{Si}}\text{S}_3)]$ ($\text{Et}_4\text{N}[\textbf{8b}]$)	—	—
$\text{Na}[\text{Ni}(\text{StBu})(^{\text{H}}\text{S}_3)]$ ($\text{Na}[\textbf{9a}]$)	2131 ^[b]	rev.
$\text{Ni}(\text{PCy}_3)(^{\text{Si}}\text{S}_3)$ (6b)	2135 ^[b]	rev.
$\text{Ni}(\text{NHPr}_3)(^{\text{H}}\text{S}_3)$ (2a)	2146 ^[c]	irr.
$\text{Ni}(\text{NHPr}_3)(^{\text{Si}}\text{S}_3)$ (2b)	2146 ^[c]	irr.
$\text{Ni}(\text{NHPCy}_3)(^{\text{H}}\text{S}_3)$ (3a)	2146 ^[c]	irr.
$\text{Ni}(\text{NHPCy}_3)(^{\text{Si}}\text{S}_3)$ (3b)	2146 ^[c]	irr.
$\text{Ni}(\text{NHSPH}_2)(^{\text{H}}\text{S}_3)$ (4a)	2148 ^[c]	irr.
$\text{Ni}(\text{NHSPH}_2)(^{\text{Si}}\text{S}_3)$ (4b)	2148 ^[c]	irr.

[a] Ref.^[7] [b] In THF. [c] In CH_2Cl_2 .

of up to 2280 cm^{-1} .^[20] The high $\nu(\text{CO})$ frequencies of these complexes are rationalized by a subtle interplay of σ -donor, π -acceptor and semipolar contributions in the M–CO bonds.^[21] In accordance with this rationalization, the results obtained here show that binding CO to $[\text{Ni}(\text{L})(\text{RS}_3)]$ complexes not only enhances the polarity of the CO bond but also increases the susceptibility of CO towards attack by nucleophiles. This may be a reason why coordination of CO to the $[\text{NiS}_4]$ core of CO dehydrogenase centers can enable the CO/ CO_2 conversion according to Equation (2) (vide infra).

Conclusion

In the quest for sulfur–nickel complexes that enable us to model the reactivity features and key intermediates of $[\text{NiFe}]$ hydrogenases and CO dehydrogenases, $[\text{Ni}(\text{L})(\text{RS}_3)]$ complexes were synthesized, completely characterized, and investigated with regard to their reactivity towards H_2 and CO. All $[\text{Ni}(\text{L})(\text{RS}_3)]$ complexes exhibit sulfur-dominated and tetrahedrally distorted square-planar coordination

spheres. Complexes **4a** and **4b** are rare examples of sulfimine complexes and are the first sulfimine complexes with only sulfur as ancillary coligands. Introduction of the ³²S₃ ligand enabled us to overcome the solubility problems frequently encountered with nickel complexes of the ³²S₃ parent ligand.

It has been demonstrated that the phosphorane imine and sulfimine complexes **2–4** possess weakly acidic NH protons and catalyze D₂/NH exchange reactions through heterolysis of D₂. The D₂/H⁺ exchange reaction between D₂ and protons from H₂O is also catalyzed by complexes **2–4** and **9**. These reactions unambiguously prove that the D₂/H⁺ exchange is catalytic in nature. The D₂ heterolysis most likely proceeds through attack of the Lewis-acidic nickel and Brønsted-basic sulfur atoms at η²-D₂ ligands. It is worthwhile to note that **9a** and **9b** are the first completely characterized sulfur-only nickel complexes that enable us to model the [NiFe] hydrogenase catalyzed D₂ heterolysis and D₂/H⁺ exchange reactions.

Coordination of CO to four-coordinate nickel centers in sulfur coordination spheres is assumed to be the decisive step in the activation of CO catalyzed by CO dehydrogenases. Evidence for labile five-coordinate [Ni(CO)(L)(^RS₃)] has been found in the reactions of CO with [Ni(L)(^RS₃)] complexes containing neutral and anionic ligands L. The CO adducts of complexes with nitrogenous ligands L such as N₃[−], NHPR₃, or NHSPH₂ showed rapid consecutive reactions demonstrating the activation of CO and ligands L. In extrapolation of these findings it can be hypothesized that simultaneous coordination of CO and H₂O to [Ni(^RS₃)] fragments possibly enables the biological CO dehydrogenase reaction.

Experimental Section

General Methods: Unless noted otherwise, all reactions and manipulations were carried out under nitrogen at room temperature using standard Schlenk techniques. Reaction solutions were stirred continuously. Solvents were freshly 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 CaF₂ cuvettes, solvent bands were compensated for): 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 (downfield shifts are positive) relative to tetramethylsilane (¹H, ¹³C{¹H} NMR) or 85% H₃PO₄ (³¹P{¹H} NMR). MS: Jeol MSTATION 700 spectrometer. Elemental analysis: Carlo Erba EA 1106 or 1108 analyzer. Me₃SiCl, HNSPH₂·H₂O, Et₄NCl, and Bu₄NCl were purchased from either Aldrich or Fluka. HNPnPr₃, Me₃SiNPCy₃,^[22] [Ni(¹H₃)]₃ (**1a**), [Ni(NHPnPr₃)(¹H₃)] (**2a**), [Ni(PCy₃)(¹H₃)] (**6a**), Bu₄N[Ni(Cl)(¹H₃)] (Bu₄N[**7a**]), and Bu₄N[Ni(N₃)(¹H₃)] (Bu₄N[**8b**]) were prepared as described in the literature.^[8] The syntheses of [Ni(³²S₃)]₃ (**1b**), Et₄N[Ni(N₃)(³²S₃)] (Et₄N[**8b**]), [Ni(PnPr₃)(³²S₃)] (**5b**), [Ni(PCy₃)(³²S₃)] (**6b**), and Bu₄N[Ni(Cl)(³²S₃)] (Bu₄N[**7b**]) were described in our previous paper.^[9]

[Ni(NHPnPr₃)(³²S₃)] (**2b**): HNPnPr₃ (0.52 mL, 2.35 mmol) was added to a solution of [Ni(³²S₃)]₃ (**1b**; 800 mg, 0.59 mmol) in THF

(10 mL), and the color changed from black-brown to purple-red in the course of about 6 h. The solution was filtered after 15 h, the purple-red filtrate was reduced in volume to 3 mL and layered with CH₃CN (20 mL). Pink crystals precipitated at −25 °C which were separated after 10 d, washed with cold CH₃CN and dried in vacuo. Yield: 765 mg (69%). C₂₇H₄₆NNiPS₃Si₂ (626.71): calcd. C 51.75, H 7.40, N 2.23, S 15.35; found C 51.88, H 7.53, N 2.10, S 15.21. IR (KBr): $\tilde{\nu}$ = 3298 [ν(NH)], 995 [ν(NP)] cm^{−1}. ¹H NMR (269.7 MHz, [D₈]THF): δ = 7.57 (d, *J*_{H,H} = 7.9 Hz, 2 H, C₆H₃), 7.19 (d, *J*_{H,H} = 6.8 Hz, 2 H, C₆H₃), 6.84 (t, *J*_{H,H} = 7.6 Hz, 2 H, C₆H₃), 2.04 (m, 6 H, PCH₂), 1.73 (m, 6 H, PCH₂CH₂), 1.08 (t, *J*_{H,H} = 6.9 Hz, 9 H, PCH₂CH₂CH₃), 0.38 (s, 18 H, SiMe₃), −1.06 (s, 1 H, NH) ppm. ¹³C NMR (67.8 MHz, [D₈]THF): δ = 159.9, 139.6, 134.8, 134.3, 129.0, 121.3 (C₆H₃), 29.7 (d, ¹*J*_{P,C} = 62.9 Hz), 15.7 (d, *J*_{P,C} = 3.3 Hz), 15.5 (d, *J*_{P,C} = 16.1 Hz, PnPr₃), −0.7 (SiMe₃) ppm. ³¹P NMR (161.8 MHz, [D₈]THF): δ = 50.3 (PnPr₃) ppm. MS (FD, THF): *m/z* = 626 [Ni(NHPnPr₃)(³²S₃)]⁺.

[Ni(NHPCy₃)(³²S₃)] (**3a**): A solution of Me₃SiNPCy₃ (825 mg, 2.24 mmol) in THF (5 mL) and MeOH (1 mL) was added to a black-brown suspension of [Ni(¹H₃)]₃ (**1a**; 525 mg, 0.57 mmol) in THF (15 mL). A purple-red solution formed which was concentrated to dryness after 15 h. The purple-red residue was redissolved in THF (10 mL), and traces of undissolved materials were removed by filtration. The filtrate was reduced in volume to 3 mL, layered with CH₃CN (30 mL) and stored at −25 °C. Pink microcrystals precipitated which were separated after 3 days, washed with cold CH₃CN and Et₂O, and dried in vacuo. Yield: 815 mg (79%). C₃₀H₄₂NNiPS₃ (602.54): calcd. C 59.80, H 7.03, N 2.32, S 15.96; found C 59.82, H 7.19, N 2.35, S 15.58. IR (KBr): $\tilde{\nu}$ = 3364 [ν(NH)], 978 [ν(NP)] cm^{−1}. ¹H NMR (269.7 MHz, [D₈]THF): δ = 7.58 (d, *J*_{H,H} = 7.6 Hz, 2 H, C₆H₄), 7.20 (d, *J*_{H,H} = 7.9 Hz, 2 H, C₆H₄), 6.97 (t, *J*_{H,H} = 7.1 Hz, 2 H, C₆H₄), 6.83 (t, *J*_{H,H} = 7.1 Hz, 2 H, C₆H₄), 2.23–1.32 (m, 33 H, PCy₃), −1.88 (s, 1 H, NH) ppm. ¹³C NMR (67.8 MHz, [D₈]THF): δ = 154.2, 134.2, 129.6, 128.5, 128.0, 121.9 (C₆H₄), 35.3 (d, ¹*J*_{P,C} = 55.3 Hz), 27.8, 27.5 (d, ³*J*_{P,C} = 15 Hz), 26.9 (PCy₃) ppm. ³¹P NMR (161.8 MHz, [D₈]THF): δ = 59.2 (PCy₃) ppm. MS (FD, THF): *m/z* = 602 [Ni(NHPCy₃)(³²S₃)]⁺.

[Ni(NHPCy₃)(³²S₃)] (**3b**): A solution of Me₃SiNPCy₃ (272 mg, 0.74 mmol) in THF (5 mL) and MeOH (1 mL) was added to a solution of [Ni(³²S₃)]₃ (**1b**; 300 mg, 0.22 mmol) in THF (15 mL), and the color changed from black-brown to purple-red in the course of about 3 h. After 15 h, the solution was concentrated to dryness to give a purple-red residue, which was redissolved in THF (10 mL). Undissolved material was removed by filtration. The filtrate was reduced in volume to 3 mL, layered with CH₃CN (30 mL) and stored at −25 °C. Pink microcrystals precipitated which were separated after 4 d, washed with cold CH₃CN and Et₂O, and dried in vacuo. Yield: 412 mg (83%). C₃₆H₅₈NNiPS₃Si₂ (746.90): calcd. C 57.89, H 7.83, N 1.87, S 12.88; found C 57.47, H 7.44, N 1.80, S 12.63. IR (KBr): $\tilde{\nu}$ = 3364 [ν(NH)], 985 [ν(NP)] cm^{−1}. ¹H NMR (269.7 MHz, [D₈]THF): δ = 7.56 (d, *J*_{H,H} = 7.9 Hz, 2 H, C₆H₃), 7.18 (d, *J*_{H,H} = 7.1 Hz, 2 H, C₆H₃), 6.82 (t, *J*_{H,H} = 7.5 Hz, 2 H, C₆H₃), 2.35–1.30 (m, 33 H, PCy₃), 0.38 (s, 18 H, SiMe₃), −1.62 (s, 1 H, NH) ppm. ¹³C NMR (67.8 MHz, CDCl₃): δ = 158.0, 139.5, 134.2, 133.2, 127.9, 126.8 (C₆H₃), 34.3 (d, ¹*J*_{P,C} = 49.5 Hz), 27.0 (d, ²*J*_{P,C} = 6.8 Hz), 26.7 (d, ³*J*_{P,C} = 2.7 Hz), 25.9 (PCy₃), −0.5 (SiMe₃) ppm. ³¹P NMR (161.8 MHz, [D₈]THF): δ = 54.5 (PCy₃) ppm. MS (FD, THF): *m/z* = 746 [Ni(NHPCy₃)(³²S₃)]⁺.

[Ni(NHSPH₂)(³²S₃)] (**4a**): HNSPH₂·H₂O (425 mg, 1.93 mmol) was added to a black-brown suspension of **1a** (500 mg, 0.54 mmol) in THF (10 mL). The resulting suspension was stirred for 12 h, in the course of which it became red-brown. The solution was filtered,

the filtrate reduced in volume to about 3 mL and layered with Et₂O (20 mL). Dark red crystals precipitated at -25°C , which were separated after 7 d, washed with Et₂O and dried in vacuo. Yield: 680 mg (82%). C₂₄H₁₉NNiS₄ (508.38): calcd. C 56.70, H 3.77, N 2.75, S 25.23; found C 56.82, H 3.91, N 2.71, S 25.07. IR (KBr): $\tilde{\nu} = 3202$ [v(NH)], 924 [v(NS)] cm⁻¹. ¹H NMR (269.7 MHz, [D₈]THF): $\delta = 7.75\text{--}7.40$ (m, 12 H, C₆H₄, SPh₂), 7.21 (d, $J_{\text{H,H}} = 7.5$ Hz, 2 H, C₆H₄), 7.00 (t, $J_{\text{H,H}} = 6.5$ Hz, 2 H, C₆H₄), 6.85 (t, $J_{\text{H,H}} = 6.4$ Hz, 2 H, C₆H₄), 0.89 (s, 1 H, NH) ppm. ¹³C NMR (67.8 MHz, [D₈]THF): $\delta = 153.0, 134.6, 132.4, 131.8, 130.4, 130.0, 128.9, 128.4, 127.8, 122.4$ (C₆H₄, SPh₂) ppm. MS (FD, THF): $m/z = 508$ [Ni(NHSPPh₂)(³Si₃)⁺].

[Ni(NHSPPh₂)(³Si₃)] (4b): A solution of HNPh₂·H₂O (128 mg, 0.58 mmol) in THF (5 mL) was added to a solution of **1b** (250 mg, 0.18 mmol) in THF (10 mL) and the color changed from black-brown to brown-red in the course of about 6 h. The solution was filtered after 12 h, reduced in volume to 3 mL and layered with pentane (20 mL). Dark-red microcrystals precipitated at -25°C which were separated after 7 d, washed with pentane and dried in vacuo. Yield: 282 mg (78%). C₃₀H₃₅NNiS₄Si₂ (652.75): calcd. C 55.20, H 5.40, N 2.15, S 19.65; found C 55.91, H 5.90, N 2.28, S 19.02. IR (KBr): $\tilde{\nu} = 3210$ [v(NH)], 916 [v(NS)] cm⁻¹. ¹H NMR (269.7 MHz, [D₈]THF): $\delta = 7.75\text{--}7.40$ (m, 12 H, C₆H₃, SPh₂), 7.19 (d, $J_{\text{H,H}} = 6.1$ Hz, 2 H, C₆H₃), 6.84 (t, $J_{\text{H,H}} = 6.8$ Hz, 2 H, C₆H₃), 0.83 (s, 1 H, NH), 0.36 (s, 18 H, SiMe₃) ppm. ¹³C NMR (67.8 MHz, [D₈]THF): $\delta = 159.2, 139.8, 134.9, 134.8, 132.3, 131.8, 130.4, 129.3, 128.4, 121.6$ (C₆H₃, SPh₂), -0.4 (SiMe₃) ppm. MS (FD, THF): $m/z = 653$ [Ni(NHSPPh₂)(³Si₃)⁺].

[Ni(PnPr₃)(³Si₃)] (5a): PnPr₃ (0.3 mL, 1.49 mmol) was added to a black-brown suspension of **1a** (445 mg, 0.48 mmol) in THF (10 mL). In the course of about 10 min, a red-yellow solution formed which was filtered after 1 h. The filtrate was reduced in volume to 2 mL, layered with hexane (20 mL) and stored at -25°C . Dark red crystals precipitated which were separated after 2 d, washed with hexane and dried in vacuo. Yield: 645 mg (95%). C₂₁H₂₉NiPS₃ (467.33): calcd. C 53.97, H 6.26, S 20.58; found C 54.06, H 6.38, S 20.37. ¹H NMR (269.7 MHz, CDCl₃): $\delta = 7.66$ (dd, $J_{\text{H,H}} = 1.2, 8.1$ Hz, 2 H, C₆H₄), 7.39 (d, $J_{\text{H,H}} = 1.3, 7.9$ Hz, 2 H, C₆H₄), 7.09 (dt, $J_{\text{H,H}} = 1.3, 7.9$ Hz, 2 H, C₆H₄), 6.98 (dt, $J_{\text{H,H}} = 1.4, 7.3$ Hz, 2 H, C₆H₄), 1.72 (m, 6 H, PCH₂), 1.65 (m, 6 H, PCH₂CH₂), 1.04 (t, $J_{\text{H,H}} = 6.6$ Hz, 9 H, PCH₂CH₂CH₃) ppm. ¹³C NMR (100.4 MHz, CDCl₃): $\delta = 152.1$ (d, $^1J_{\text{P,C}} = 12.5$ Hz), 132.4, 129.8, 128.5, 127.4, 122.5 (C₆H₄), 25.4 (d, $^1J_{\text{P,C}} = 26.4$ Hz), 17.8 (d, $J_{\text{P,C}} = 1.7$ Hz), 16.0 (d, $J_{\text{P,C}} = 14.0$ Hz) (PnPr₃) ppm. ³¹P NMR (161.8 MHz, CDCl₃): $\delta = 13.5$ (PnPr₃) ppm. MS (FD, THF): $m/z = 467$ [Ni(PnPr₃)(³Si₃)⁺].

D⁺/NH Exchange Reactions of 2a/2b, 3a/3b, and 4a/4b with D₂O or CD₃OD: In an NMR tube, D₂O or CD₃OD (50 μL) was added to a saturated solution of the respective complex (ca. 50 mg) in CD₂Cl₂ or CH₂Cl₂. The reactions were monitored by recording the ¹H/²D NMR spectra and measuring the intensity of the NH or ND signals. After completion of the reactions (5–20 min), the solvents were removed in vacuo and the resulting residue was identified by IR (KBr) spectroscopy. The deuterated complexes each exhibited a v(ND) band in the region 2480–2420 cm⁻¹.

D₂/NH Exchange Reactions of 2b, 3a/3b, and 4a/4b with D₂ and Identification of HD: In a high-pressure NMR tube (524-PV-1, Wilmad, USA), a concentrated solution of the respective complex (ca. 50 mg) in CD₂Cl₂ or [D₈]THF was pressurized with D₂ (18 bar). The reactions were monitored by recording ¹H NMR spectra. The formation of HD gave rise to a 1:1:1 triplet ($J_{\text{H,D}} = 42.5$ Hz) in the region of $\delta = 4\text{--}5$ ppm after 80–120 h.

D₂/H₂O Exchange Reaction of 2a/2b, 3a/3b, 4a/4b, and Na[9a]/Na[9b]: In a high-pressure NMR tube, a concentrated solution of the respective complex (ca. 50 mg) in [D₈]THF, after addition of H₂O (50 μL), was pressurized with D₂ (18 bar). The reactions were monitored by recording ¹H NMR spectra at regular time intervals for 15 d. The formation of HD gave rise to a 1:1:1 triplet ($J_{\text{H,D}} = 42.5$ Hz) in the region of $\delta = 4\text{--}5$ ppm.

Et₄N[Ni(NCO)(³Si₃)] (10b) from Et₄N[Ni(N₃)(³Si₃)] (8b) and CO: CO gas (16.5 mL, 0.74 mmol) was injected into a Schlenk tube in the dark containing a solution of **8b** (450 mg, 0.72 mmol) in THF (10 mL) and fitted with a septum. The color of the solution changed from purple to dark-red in the course of ca 15 h. The solution was filtered after 24 h, reduced in volume to ca. 2 mL and layered with pentane (20 mL). Dark-red microcrystals precipitated at -25°C which were separated after 4 d, washed with pentane and dried in vacuo. Yield: 412 mg (92%). C₂₇H₄₄N₂NiO₃Si₂ (623.73): calcd. C 51.99, H 7.11, N 4.49, S 15.42; found C 52.41, H 7.43, N 4.27, S 15.38. IR (KBr): $\tilde{\nu} = 2227$ [v(NCO)] cm⁻¹. ¹H NMR (269.7 MHz, [D₈]acetone): $\delta = 7.63$ (d, $J_{\text{H,H}} = 7.9$ Hz, 2 H, C₆H₃), 7.20 (d, $J_{\text{H,H}} = 7.1$ Hz, 2 H, C₆H₃), 6.89 (t, $J_{\text{H,H}} = 7.9$ Hz, 2 H, C₆H₃), 3.42 (m, 8 H, NCH₂), 1.29 (t, $J_{\text{H,H}} = 7.3$ Hz, 12 H, NCH₂CH₃), 0.35 (s, 18 H, SiMe₃) ppm. ¹³C NMR (67.8 MHz, [D₈]acetone): $\delta = 160.4, 139.7, 135.0, 133.9$ (C₆H₃), 132.0 (NCO), 129.1, 121.4 (C₆H₃), 53.1, 7.7 (Et₄N), -0.5 (SiMe₃) ppm.

[Ni(³Si₃)]₃ (1a) from [Ni(NHR)(³Si₃)] [R = PnPr₃ (2a), PCy₃ (3a), SPh₂ (4a)] and CO. General Procedure: An equimolar amount of CO was injected into a Schlenk tube containing a CH₂Cl₂ solution (ca. 10 mL) of the respective complex and fitted with a septum. In the course of several hours, depending on the complex, the color of the CH₂Cl₂ solution changed from purple or yellow-red to dark-red. Subsequently, dark-brown microcrystals of **1a** precipitated, which were separated, washed with MeOH and/or pentane and dried in vacuo.

[Ni(³Si₃)]₃ (1a) from 2a and CO: From 215 mg (0.445 mmol) of **2a** and 10.0 mL (0.446 mmol) of CO. The reaction was complete after 50 h. Yield: 93 mg (67%). C₃₆H₂₄Ni₃S₉ (921.25): calcd. C 46.94, H 2.63, S 31.33; found C 46.81, H 2.56, S 30.83. MS (FD, DMF): $m/z = 921$ [Ni(³Si₃)₃]⁺, 614 [Ni(³Si₃)₂]⁺.

[Ni(³Si₃)]₃ (1a) from 3a and CO: From 210 mg (0.348 mmol) of **3a** and 7.85 mL (0.350 mmol) of CO gas. Reaction time 78 h. Yield: 79 mg (74%).

[Ni(³Si₃)]₃ (1a) from 4a and CO: From 200 mg (0.393 mmol) of **4a** and 8.9 mL (0.397 mmol) of CO gas. Reaction time 5 h. Yield: 94 mg (78%).

[Ni(³Si₃)]₃ (1b) from [Ni(NHR)(³Si₃)] [R = PnPr₃ (2b), PCy₃ (2b), SPh₂ (4b)] and CO. General Procedure: An equimolar amount of CO was injected into a Schlenk tube containing a CH₂Cl₂ solution (ca. 10 mL) of the respective complex and fitted with a septum. In the course of several hours, depending on the complex, the color of the CH₂Cl₂ solution changed from purple or yellow-red to red-brown. The solution was filtered, reduced in volume to ca. 2 mL and layered with MeOH (20 mL). Dark-red crystals of **1b** precipitated at -25°C , which were separated after 3–7 d, washed with MeOH and dried in vacuo.

[Ni(³Si₃)]₃ (1b) from 2b and CO: From 185 mg (0.295 mmol) of **2b** and 6.7 mL (0.299 mmol) of CO gas. Reaction time 40 h. Yield: 81 mg (61%).

[Ni(³Si₃)]₃ (1b) from 3b and CO: From 224 mg (0.300 mmol) of **3b** and 6.8 mL (0.304 mmol) of CO gas. Reaction time 65 h. Yield: 87 mg (64%).

Table 3. Selected crystallographic data for [Ni(NHPnPr₃)(^{si}S₃)] (**2b**), [Ni(NHPCy₃)(^HS₃)] (**3a**), [Ni(NHPCy₃)(^{si}S₃)] (**3b**), [Ni(NHSPH₂)(^HS₃)] (**4a**), and [Ni(PnPr₃)(^HS₃)] (**5a**)

	2b	3a	3b	4a	5a
Empirical formula	C ₂₇ H ₄₆ NNiPS ₃ Si ₂	C ₃₀ H ₄₂ NNiPS ₃	C ₃₆ H ₅₈ NNiPS ₃ Si ₂	C ₂₄ H ₁₉ NNiS ₄	C ₂₁ H ₂₉ NiPS ₃
<i>M_r</i> (g mol ^{−1})	626.69	602.51	746.87	508.35	467.30
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>
<i>a</i> [pm]	1154.8(2)	1084.2(1)	1107.4(1)	1295.2(1)	1231.9(1)
<i>b</i> [pm]	1659.7(2)	1452.1(1)	1532.1(2)	1536.0(2)	1640.8(1)
<i>c</i> [pm]	1913.2(3)	1937.8(1)	2383.9(2)	1126.8(1)	2295.4(2)
α [°]	73.43(1)	90	90	90	90
β [°]	84.60(1)	105.40(1)	90	101.08(1)	90
γ [°]	76.20(1)	90	90	90	90
<i>V</i> [nm ³]	3.4118(9)	2.9413(4)	4.0446(7)	2.1999(4)	4.6397(6)
<i>Z</i>	4	4	4	4	8
$\rho_{\text{calcd.}}$ [g cm ^{−3}]	1.220	1.361	1.227	1.535	1.338
μ [mm ^{−1}]	0.886	0.947	0.758	1.274	1.179
Crystal size [mm]	0.30 × 0.18 × 0.06	0.60 × 0.55 × 0.42	0.70 × 0.50 × 0.10	0.60 × 0.55 × 0.42	0.70 × 0.62 × 0.44
2 θ range [°]	3.6–50.0	3.5–56.0	3.4–52.0	4.1–58.0	3.5–54.0
<i>T</i> _{min} / <i>T</i> _{max}	—	0.321/0.360	0.385/0.441	0.189/0.250	0.168/0.222
Measd. refl.	12546	8815	8876	7153	6197
Indep. refl.	10615	7086	7956	5846	5067
Obsd. refl.	4824	4806	5464	4241	3487
Ref. parameters	649	451	403	347	266
Max/min resid. density	462/−446	397/−328	342/−452	390/−311	482/−756
[e [−] nm ^{−3}]					
<i>R</i> 1; ^[a] <i>wR</i> 2 ^[b] [%]	7.63; 17.80	4.88; 11.32	6.48; 16.30	3.88; 8.49	4.87; 12.15
Abs. struct. parameter	—	—	0.03(2)	—	—

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

[Ni(^{si}S₃)]₃ (**1b**) from **4b** and CO: From 112 mg (0.172 mmol) of **4b** and 3.9 mL (0.174 mmol) of CO gas. Reaction time 3 h. Yield: 62 mg (80%).

Monitoring the Reactions of 2a/2b, 3a/3b, and 4a/4b with CO by ¹H and ³¹P NMR Spectroscopy: An equimolar amount of CO was injected into an NMR tube containing the solution of the respective complex (ca. 50 mg) in CD₂Cl₂ (ca. 0.6 mL) and fitted with a septum. ¹H and ³¹P NMR spectra were recorded at regular time intervals.

X-ray Structure Determination of [Ni(NHPnPr₃)(^{si}S₃)] (2b**), [Ni(NHPCy₃)(^HS₃)] (**3a**), [Ni(NHPCy₃)(^{si}S₃)] (**3b**), [Ni(NHSPH₂)(^HS₃)] (**4a**), and [Ni(PnPr₃)(^HS₃)] (**5a**):** In the course of 10 d, red-brown blocks of **2b** crystallized at −25 °C from a saturated THF solution of **2b** layered with CH₃CN. In an NMR tube at −25 °C, in the course of 3 d dark-red blocks of **3a** crystallized from a CDCl₃ solution of **3a** layered with Et₂O. Red-violet plates of **3b** crystallized from a hot CH₃CN solution (65 °C) of **3b**, which was slowly cooled to −30 °C. Red-brown crystals of **4a** were grown in the course of 7 d from a saturated CH₂Cl₂ solution of **4a** that was layered with hexane at −30 °C. Red-brown blocks of **5a** crystallized from a concentrated THF solution of **5a**, which was layered with hexane at −30 °C. Suitable single crystals were either embedded in protective perfluoro polyether oil or sealed in glass capillaries under N₂. Data were collected at 210 K (**2b** and **5a**), 220 K (**3a** and **4a**), or 295 K (**3b**) with a Siemens P4 diffractometer using Mo-*K*_α radiation (λ = 71.073 pm), a graphite monochromator, and the ω -scan technique. With the exception of **2b**, semiempirical absorption corrections using ψ -scans were performed. All structures were solved by direct methods, and full-matrix least-squares refinement was carried out on *F*² using SHELXTL NT 5.1.^[23] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of **3a** and **4a** were located in a difference Fourier map and were either

refined with a fixed common isotropic displacement parameter (**3a**) or were refined isotropically (**4a**). In all other compounds, the H atoms were geometrically positioned with isotropic displacement parameters being 1.5-times *U*(eq) of the corresponding C or N atom. One of the *n*-propyl groups of **5a** is disordered. Two alternative sites were refined giving site-occupancy factors of 0.711(8) (site A) and 0.289(8) (site B). The unit cell of **2b** contains two symmetrically independent molecules. Selected crystallographic data are summarized in Table 3.^[24]

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- [24] CCDC-213454 (**2b**), -213455 (**3a**), -213456 (**3b**), -213457 (**4a**) and -213458 (**5a**) 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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