Transition Metal Complexes with Sulfur Ligands, Part 146[+]

Activation and Desoxygenation of CO, CO_2, and SO_2 with Sulfur-Rich Azide and Amide $[Ni(L)('S_3')]$ Complexes ($'S_3'^{2-}$ = Bis(2-mercaptophenyl)sulfide (2 −))

Dieter Sellmann,* Franz Geipel, and Frank W. Heinemann[a]

Abstract: The azide and amide complexes $(NBu_4)[Ni(N_3)('S_3')]$ (**2**) and $(NBu_4)[Ni\{N(SiMe_3)_2\}('S_3')]$ (**4**) were found to react with CO, CO_2, and SO_2 under very mild conditions at temperatures down to −50 °C. Depending on the N oxidation state of the nitrogen ligands, addition or partial to complete desoxygenation of the oxides takes place. The reaction between **2** and CO gives $(NBu_4)[Ni(NCO)('S_3')]$ (**3**). The reactions between **4** and CO, CO_2, and SO_2 afford selectively the cyano, isocyanato, and sulfinylimido complexes $(NBu_4)[Ni(X)('S_3')]$ with $X = CN^-$ (**5**), NCO^- (**3**), and NSO^- (**6**). The silyl groups act as oxygen acceptors. Mechanisms are suggested which have in common the formation of reactive five-coordinate $(NBu_4)[Ni(L)(L')('S_3')]$ intermediates. In these reactions, highly activated L and L′ react with each other. The complexes were characterized by standard methods, and $(NBu_4)[Ni(CN)('S_3')]$ (**5**) was also analyzed by X-ray crystallography.

Keywords: activation · N ligands · nickel · S ligands

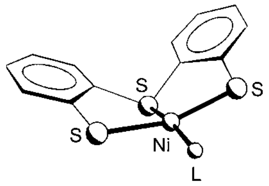
Introduction

The transition metal catalyzed activation and chemical conversion of small molecules such as CO_2, CO, SO_2, or H_2 are of considerable interest with regard to metal oxidoreductases,[1] waste gas purification catalysts,[2] sequestration of CO_2,[3] production of hydrogen,[4] and the use of CO_2/CO as unlimited carbon sources for organic syntheses.[5]

Our interest in this area mainly results from the search for complexes that model the active sites *and* reactivity of metal sulfur enzymes. With respect to CO_2, CO, and H_2, CO dehydrogenases and hydrogenases are of prime interest, and the discovery of nickel sulfur sites as active centers in these enzymes accounts for much of the current interest in nickel thiolate/thioether chemistry.[6, 7]

In this context, we have investigated the coordination chemistry of $[Ni^{II}(L)('S_3')]$ complexes and their Pd and Pt homologues.[8]

The $[Ni(L)('S_3')]$ complexes, $L = PR_3$, SR^-, CN^-, Cl^-, N_3^-, NSO^-, NCS^-, and $HNPnPr_3$ are diamagnetic and exhibit a characteristic distorted coordination geometry, which is neither planar nor tetrahedral.[8, 9] They form from the parent complex $[Ni('S_3')]_3$ and the respective L, or by exchange reactions of $[Ni(Cl)('S_3')]^-$ and $[Ni(StBu)('S_3')]^-$ with L. Five-coordinate Ni species are probable intermediates in these reactions.



$[Ni(L)('S_3')]$

It was recently proved that the phosphorane imine complex $[Ni(NHPnPr_3)('S_3')]$ catalyzes the heterolysis of molecular hydrogen and the H_2/D^+ exchange reaction,[10] which is a key reaction of hydrogenases.[11] In this case, the η^2-H_2 complex $[Ni(H_2)(NHPnPr_3)('S_3')]$ has been suggested to be the reactive five-coordinate intermediate. $[Ni(NHPnPr_3)('S_3')]$ is the first nickel complex modeling the nickel cysteinate site and reactivity of [NiFe] hydrogenases.[10]

Here we want to report reactions of the azide and amide complexes $[Ni(N_3)('S_3')]^-$ and $[Ni\{N(SiMe_3)_2\}('S_3')]^-$ with CO_2, CO, and SO_2 that result in addition or desoxygenation of CO_2, CO, and SO_2.

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Results

The azide complex $(NBu_4)[Ni(N_3)('S_3')]$ (**2**) had previously been obtained by treatment of the trinuclear parent complex $[Ni('S_3')]_3$ (**1**) with NBu_4N_3 in THF (Scheme 1).

When we investigated the reactivity of **2**, we also tried to photolyze the azido ligand of **2** by UV irradiation. However, **2** proved totally inert towards UV photolysis, even over periods of more than 24 h.

In the next experiment, we wanted to substitute the azido ligand of **2** with CO, either thermally or by photoassisted reactions, and so we replaced the protective atmosphere of dinitrogen by carbon monoxide. To our considerable surprise, the seemingly inert **2** started to react, even without the use of heat or irradiation. The color of the solution of **2** in THF slowly changed from purple to red, and within the course of 17 h, complex **2** transformed into the isocyanato derivative $(NBu_4)[Ni(NCO)('S_3')]$ (**3**). The reaction was monitored by UV/Vis spectroscopy. The spectra exhibited two isosbestic points at 460 and 520 nm, which indicated the complete conversion of **2** into **3**; this reaction did not yield any other complex as a by-product (Figure 1a).

The IR spectroscopic monitoring afforded hints on the pathway of the reaction (Figure 1b). In the region of 2300–1900 $\mathrm{cm^{-1}}$, the IR spectrum of **2** in THF under N_2 shows only the $\nu(N_3)$ band at 2037 $\mathrm{cm^{-1}}$. After replacement of N_2 by an atmosphere of CO, a small band at 2129 $\mathrm{cm^{-1}}$ appeared. In the course of the reaction, this band disappeared again, while the $\nu(N_3)$ band of **2** decreased in size, and the $\nu(NCO)$ band of the resulting **3** simultaneously increased in size. The small band at 2129 $\mathrm{cm^{-1}}$ could be indicative of an intermediary nickel carbonyl complex. Because we were never able to detect the formation of a CO complex such as $[Ni(CO)('S_3')]$, we assign the intermediary band at 2129 $\mathrm{cm^{-1}}$ to the five-coordinate CO adduct $[Ni(CO)(N_3)('S_3')]^-$, which is labile and transforms under loss of N_2 into the final product $[Ni(NCO)('S_3')]^-$.

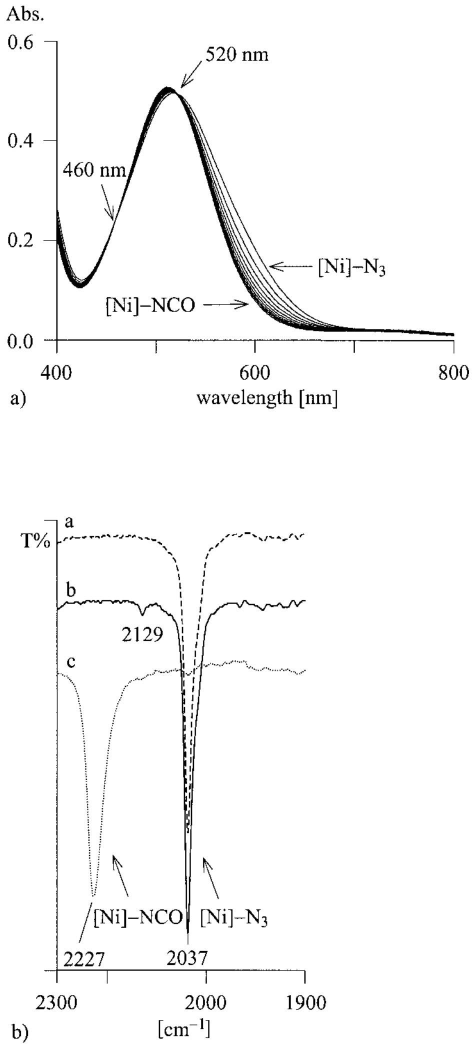
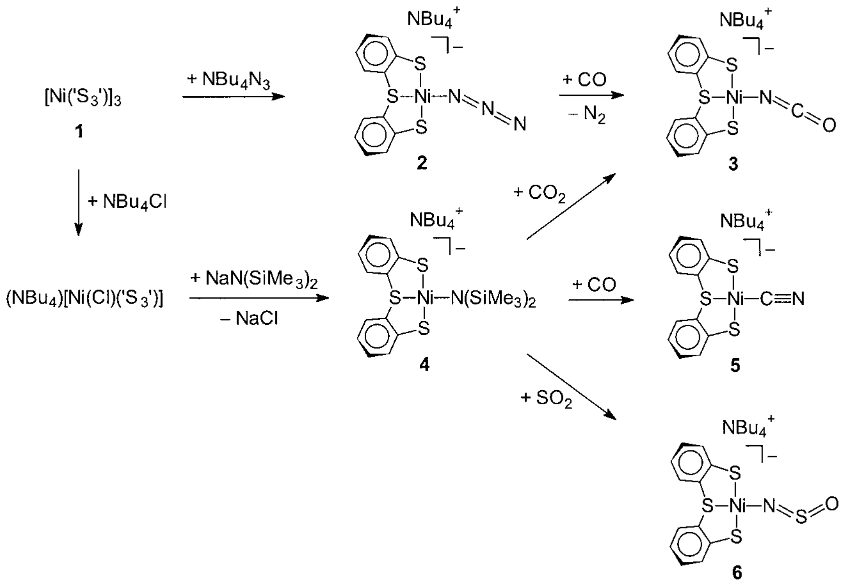


Figure 1. Monitoring the reaction between $(NBu_4)[Ni(N_3)('S_3')]$ (**2**) and CO in THF by a) UV/Vis and b) IR spectroscopy (line a: $(NBu_4)[Ni(N_3)('S_3')]$ (**2**) in THF; line b: in the presence of CO; line c: complete formation of $(NBu_4)[Ni(NCO)('S_3')]$ (**3**).



Scheme 1. Synthesis and reactions of azido and amido $[Ni(L)('S_3')]$ complexes.

An analogous experiment with isotopically labeled ^{13}C further corroborated the assignment of the 2129 $\mathrm{cm^{-1}}$ band. With ^{13}CO, the same reaction took place, but no band at 2129 $\mathrm{cm^{-1}}$ could be observed. The $\nu(CO)$ band of the intermediary $[Ni(^{13}CO)(N_3)('S_3')]^-$ is expected in the region 2080–2085 $\mathrm{cm^{-1}}$[12] and thus it is obscured by the baseline of $\nu(N_3)$ band at 2037 $\mathrm{cm^{-1}}$. The $\nu(NCO)$ band of the $[Ni(N^{13}CO)('S_3')]^-$ appeared at 2168 $\mathrm{cm^{-1}}$ with an isotopic shift of 59 $\mathrm{cm^{-1}}$ to the corresponding $\nu(NCO)$ band of $[Ni(N^{12}CO)('S_3')]^-$ at 2227 $\mathrm{cm^{-1}}$.

The remarkable reaction of **2** with CO prompted us to search for other $[Ni(L)('S_3')]$ complexes, which are able to react with CO. A promising complex in this regard was the silylamido species $[Ni\{N(SiMe_3)_2\}('S_3')]^-$. Attempts to obtain it from the trinuclear parent complex **1** and $LiN(SiMe_3)_2$ remained unsuccessful. However, the reaction of $(NBu_4)[Ni(Cl)('S_3')]$, which contains a labile chloro ligand, with $NaN(SiMe_3)_2$ in THF yielded $(NBu_4)[Ni\{N(SiMe_3)_2\}('S_3')]$ (**4**). The formation of NaCl probably provides the driving force of the reaction. Complex **4** is extremely sensitive towards air and moisture. It is also thermally labile and decomposes at temperatures above −30 °C. For these reasons, **4** could not be isolated in the solid state, but was synthesized at −50 °C and handled in solution at temperatures between −50 and −78 °C. The formation of **4** was indicated by the characteristic dark blue color of **4** and could unambiguously be proved by ^1H NMR spectroscopy. When the violet suspension of $(NBu_4)[Ni(Cl)('S_3')]$ in THF was combined with one molar equivalent of solid $NaN(SiMe_3)_2$ at −78 °C and warmed to −50 °C, a dark blue to black blue solution resulted, from which NaCl precipitated. Monitoring this reaction in $[D_8]$THF by ^1H NMR spectroscopy showed that the signal pattern of $(NBu_4)[Ni(Cl)('S_3')]$ in the aromatic region was completely replaced by the signal pattern of **4** (Figure 2).

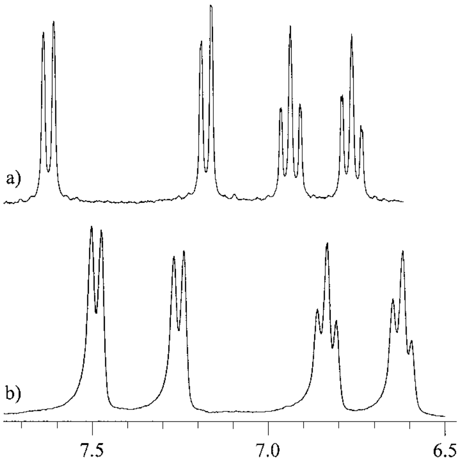


Figure 2. Aromatic region of the ^1H NMR spectra of a) $(NBu_4)[Ni(Cl)('S_3')]$ and b) after addition of $NaN(SiMe_3)_2$ and complete formation of $(NBu_4)[Ni\{N(SiMe_3)_2\}('S_3')]$ (**4**) (in $[D_8]$THF at −50 °C).

As discussed previously,[8b] this pattern of four multiplets in the aromatic region is typical for $[Ni('S_3')]$ fragments and is characteristically shifted by the respective coligands L. In addition to the aromatic signals, the ^1H NMR spectrum of **4** in $[D_8]$THF exhibits the NBu_4^+ signals and the $N(SiMe_3)_2$ singlet of correct intensity at $\delta = 0.3$. The reactivity of **4** was probed with solutions of **4** in THF; solutions of **4** were freshly prepared in situ. Color changes and IR spectra served for monitoring the reactions.

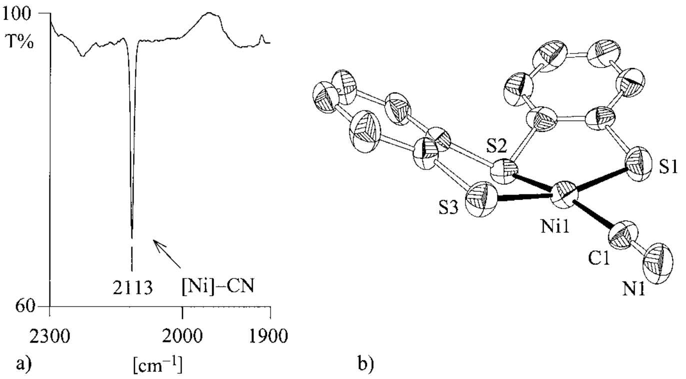


Figure 3. a) IR solution spectrum of the reaction between $[Ni\{N(SiMe_3)_2\}('S_3')]^-$ and CO, which yields $[Ni(CN)('S_3')]^-$ and b) ORTEP plot of the anion of $(NBu_4)[Ni(CN)('S_3')]$ (**5**) (50% probability ellipsoids; hydrogen atoms omitted). Selected bond lengths [pm] and angles [°]: Ni1–S1 217.2(2), Ni1–S2 214.0(2), Ni1–S3 217.0(2), Ni1–C1 188.7(8); S1-Ni1-S3 163.4(1), S2-Ni1-C1 168.8(2), S1-Ni1-S2 90.2(1), S2-Ni1-S3 90.2(1), S1-Ni1-C1 91.1(2), S3-Ni1-C1 91.7(2), Ni1-C1-N1 176.2(8).

When CO was introduced for one minute into the solution of **4** in THF at −78 °C, the color turned from dark blue to yellow brown. The IR spectrum of the solution, recorded at room temperature, exhibited a ν(CN) band at 2113 cm^{-1} (Figure 3a). Storing the reaction mixture at −30 °C for one week afforded dark brown to black brown crystals in yields higher than 70%. The X-ray structure analysis of a single crystal revealed the formation of $(NBu_4)[Ni(CN)('S_3')]$ (**5**). Elemental analyses and routine spectroscopy (IR, ^1H, and ^{13}C NMR) proved the identity of single crystals and bulk material. The anion of **5** exhibits practically identical molecular parameters to the anion of $(NMe_4)[Ni(CN)('S_3')]$, which had previously been obtained from $[Ni('S_3')]_2$ and NMe_4CN.[8a] Figure 3b depicts the molecular structure of **5** and lists important bond lengths and angles.

The desoxygenation of CO by **4** to give cyano ligands under very mild conditions also prompted us to probe the desoxygenation of CO_2. When CO_2 was introduced into solutions of **4** in THF at −78 °C, a color change from dark blue to red occurred within the course of five minutes. The IR spectrum of the reaction mixture, recorded again at room temperature, exhibited the $\nu(CO_2)$ band at 2334 and, in addition, a band at 2227 cm^{-1}, which was assigned to a ν(NCO) band (Figure 4).

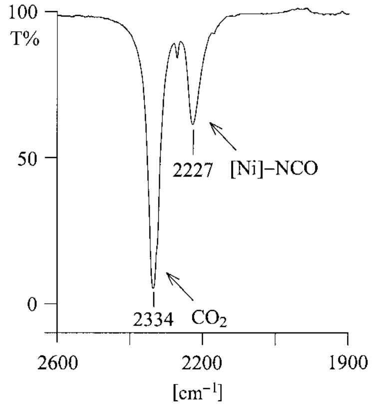


Figure 4. IR solution spectrum of the reaction between $(NBu_4)[Ni\{N(SiMe_3)_2\}('S_3')]$ (**4**) and CO_2, which yields $(NBu_4)[Ni(NCO)('S_3')]$ (**3**).

Work up of the reaction mixture gave $(NBu_4)[Ni(NCO)('S_3')]$ (**3**) in yields of 87%. It was identified by standard methods and proved to be identical to the complex obtained from $(NBu_4)[Ni(N_3)('S_3')]$ (**2**) and CO.

A reaction also took place between SO_2 and **4** in THF at −78 °C. Addition of a drop of liquid SO_2 or the introduction of SO_2 gas into the solution caused an instantaneous color change from dark blue to orange. Work up yielded the NSO complex $(NBu_4)[Ni(NSO)('S_3')]$ (**6**). Complex **6** was also characterized by standard methods and, in addition, by comparison with an authentic sample obtained previously from $(NBu_4)[Ni(S\mathit{t}Bu)('S_3')]$ and Me_3SiNSO.[8b]

Discussion

This paper describes reactions of CO, CO_2, and SO_2 with azido and amido complexes of the $[Ni('S_3')]$ fragment. Under very mild conditions, they yield cyano, isocyanato, and sulfinylimido $[Ni(X)('S_3')]^-$ complexes. The mechanistic details of these reactions remain unknown, but plausible suggestions can be made.

The thermal or photochemical conversion reactions of azido complexes with CO and vice versa of carbonyl complexes with azide ions to give NCO derivatives are known.[13] Examples are the thermal reactions between $[Pd(N_3)_2(PPh_3)_2]$ and CO that yield $[Pd(NCO)_2(PPh_3)_2]$[14] or the reaction between $Cr(CO)_6$ and N_3^- to give $[Cr(NCO)(CO)_5]^-$.[15] The thermal reactions are suggested to proceed via a five-coordinate $[Pd(CO)(N_3)_2(PPh_3)_2]$ species, and the latter reaction probably occurs by a nucleophilic addition of N_3^- to a metal-bound CO. In photochemical reactions involving metal azido complexes, frequently metal nitrene intermediates are invoked, which subsequently can react with CO to give [M−NCO] groups.[16]

The inertness of $(NBu_4)[Ni(N_3)('S_3')]$ (**2**) towards UV irradiation excludes the occurrence of a free "nitrene" intermediate such as $[Ni(N)('S_3')]^-$ that could give $[Ni(NCO)('S_3')]^-$ upon reaction with CO. The formation of $(NBu_4)[Ni(NCO)('S_3')]$ (**3**) is more plausibly explained by an associative mechanism, which was originally suggested by W. Beck et al. for square-planar d^8 complexes of Pd^{II}, Pt^{II}, Rh^{I}, and Ir^{I}.[13a] In accordance with this mechanism, we propose in Scheme 2 that $[Ni(N_3)('S_3')]^-$ first adds CO to give the labile five-coordinate species **A**. The subsequent intramolecular nucleophilic addition of N_3^- to the *cis*-CO group via the species **B** gives the acylazide species **C**, which releases N_2 to give the acylnitrene **D**. Species **D** rearranges to the stable NCO complex **E**.

This mechanism is equivalent to an intramolecular N ligand substitution by CO converting a labile five-coordinate species into stable four-coordinate Ni^{II} species. The small intermediary band at 2129 cm^{-1} (see above) supports the existence of species **A**.

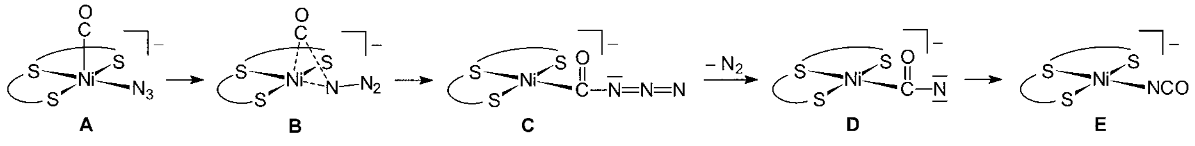
An analogous mechanism in Scheme 3 can be proposed for the reaction between $(NBu_4)[Ni\{N(SiMe_3)_2\}('S_3')]$ (**4**) and CO. In the $N(SiMe_3)_2^-$ ligand, however, the N atom is in a lower oxidation state than the N atoms of the azide ion, and the Me_3Si groups are suited as oxygen acceptors.

According to Scheme 3, the primary step is again the formation of a CO adduct **F**, in which the coligands CO and $N(SiMe_3)_2^-$ are labilized. The $N(SiMe_3)_2^-$ ligand adds nucleophilically to the *cis*-CO group; this leads, via **G**, to the insertion product **H**. Desoxygenation of **H** by the removal of $O(SiMe_3)_2$ finally gives the cyano complex $[Ni(CN)('S_3')]^-$. Thus, the $N(SiMe_3)_2^-/CO$ reaction gives CN^-,[17] while the N_3^-/CO reaction, which involves two electrons less, yields NCO^-.

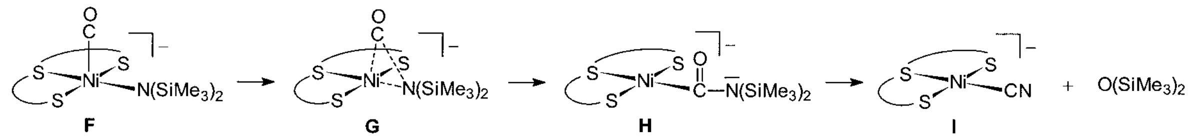
Addition and insertion reactions of CO_2 and SO_2 to or into metal ligand bonds have been described on many occasions.[18] Desoxygenation reactions under mild conditions, however, are rare. For example, complexes such as $[Ln\{N(SiMe_3)_2\}_3]$ reversibly react with CO_2 without the formation of either $O(SiMe_3)_2$ or NCO groups.[19] Furthermore, CO_2 and SO_2 also react directly with alkaline salts of $N(SiMe_3)_2^-$, for example, $NaN(SiMe_3)_2$. These reactions unselectively lead to a large number of products and give, for example, carbodiimide, silylated carbodiimides, cyanate, and carbonate, or in the case of SO_2, compounds such as Na_2SO_3, $S(NSiMe_3)_2$, and $N(SiMe_3)_3$, but no Na[NSO].[20] In this regard, the reactions of CO_2 and SO_2 with $[Ni\{N(SiMe_3)_2\}('S_3')]^-$, which occur at temperatures as low as −50 °C and selectively yield single products, are remarkable and indicate a considerable CO_2 and SO_2 activation.

It is therefore tempting to suggest mechanisms for these reactions that are analogous to those for the CO reactions, which include labile five-coordinate adducts, insertion, and rearrangement reactions. These mechanisms, of course, are only tentative and do not exclude alternative possibilities.

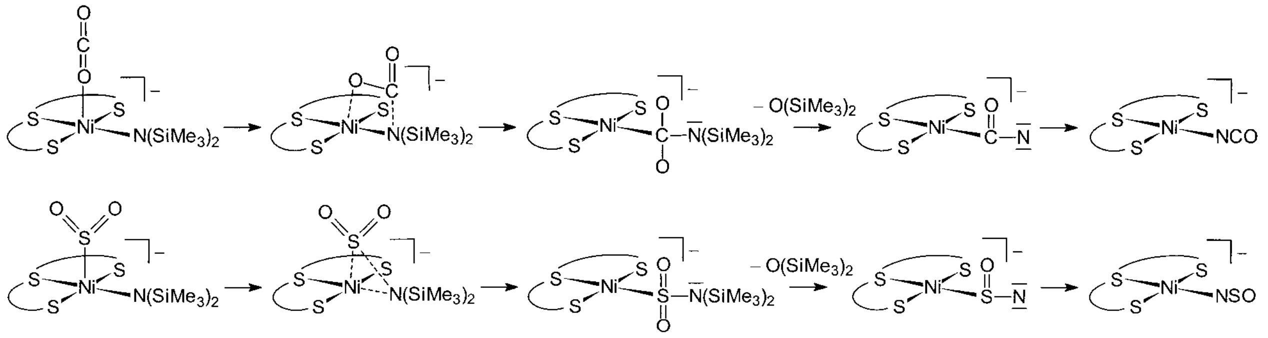
Scheme 4 suggests an end-on coordination for CO_2. Insertion into the Ni−N bond gives a species with two CO single bonds and strongly negative O atoms; this favors the formation of $O(SiMe_3)_2$. Rearrangement of the Ni−CON species gives $[Ni(NCO)('S_3')]^-$. The sulfur lone pair might favor the SO_2 binding by the sulfur atom.[21] The subsequent



Scheme 2. Proposed mechanism for the reaction between $(NBu_4)[Ni(N_3)('S_3')]$ (**2**) and CO.



Scheme 3. Proposed mechanism for the reaction between $(NBu_4)[Ni\{N(SiMe_3)_2\}('S_3')]$ (**4**) and CO.



Scheme 4. Proposed mechanisms for the reactions between $(NBu_4)[Ni\{N(SiMe_3)_2\}('S_3')]$ (**4**) and CO_2, or SO_2.

steps are analogous to the CO_2 steps. It is noteworthy that $(NBu_4)[Ni(NSO)('S_3')]$ (**6**) is the first metal NSO complex directly obtained from SO_2.[22]

Conclusion

This paper has shown that CO, CO_2, and SO_2 react under very mild conditions with sulfur-rich Ni^{II} complexes, which contain the $'S_3'^{2-}$ ligand and N_3^- or $N(SiMe_3)_2^-$ coligands; these reactions yield $[Ni(X)('S_3')]^-$ complexes with $X = CN^-$, NCO^-, and NSO^-. The reactions of $[Ni\{N(SiMe_3)_2\}('S_3')]^-$ with CO, CO_2, and SO_2 lead to complete or partial desoxygenation of the oxides. Mechanisms have been suggested for these reactions, which have in common the formation of reactive five-coordinate $[Ni^{II}(L)(L')('S_3')]^-$ intermediates. In these intermediates, L as well as L′ are activated such that they can react with each other in the coordination sphere of the $[Ni('S_3')]$ fragments.

Experimental Section

General methods: Unless noted otherwise, all reactions and spectroscopic measurements were carried out at room temperature under nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible, reactions were monitored by IR, UV/Vis, and NMR spectroscopy. Spectra were recorded on the following instruments: IR (KBr discs or CaF_2 cuvettes with compensation of the solvent bands): Perkin Elmer 983, 1620 FTIR; NMR: JEOL-JNM-GX 270, EX 270 with the protio-solvent signal used as an internal reference. Chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane (^1H, $^{13}C\{^1H\}$ NMR); UV/Vis: Shimadzu UV3101 PC spectrometer (The cuvette was connected by means of a glass tube with a flask containing the CO gas.); elemental analyses: Carlo Erba EA 1106 or 1108 analyzer. $NaN(SiMe_3)_2$ was purchased from Aldrich. The gases CO, CO_2, and SO_2 were used as received in commercial steel pressure cylinders. $[Ni('S_3')]_3$ (**1**), $(NBu_4)[Ni(N_3)('S_3')]$ (**2**), and $(NBu_4)[Ni(Cl)('S_3')]$ were prepared by literature methods.[8b]

Syntheses and reactions

$(NBu_4)[Ni(NCO)('S_3')]$ (3) from $(NBu_4)[Ni(N_3)('S_3')]$ (2) and CO: Without stirring, a purple solution of **2** (330 mg, 0.56 mmol) in THF (50 mL) was kept under an atmosphere of CO for 17 h, during which time a dark red solution of **3** formed. It was concentrated in volume to approximately 10 mL and layered with iPr_2O (10 mL). Dark red crystals precipitated, which were separated after five days, washed with iPr_2O, and dried in vacuo. Yield: 307 mg (93 %). ^1H NMR (269.7 MHz, $[D_6]$acetone): $\delta = 7.65$ (d, 2H; C_6H_4), 7.21 (d, 2H; C_6H_4), 7.03 (m, 2H; C_6H_4), 6.89 (m, 2H; C_6H_4), 3.47 (m, 8H; NCH_2), 1.81 (m, 8H; NCH_2CH_2), 1.43 (m, 8H; $N(CH_2)_2CH_2$), 0.90 (t, 12H; $N(CH_2)_3CH_3$); $^{13}C\{^1H\}$ NMR (67.7 MHz, $[D_6]$acetone): $\delta = 130.4$ (NCO) (This signal could be observed only when complex **3** had been prepared from **2** and isotopically labeled ^{13}CO.), 154.5, 134.0, 129.5, 128.9, 128.1, 122.1 (C_6H_4), 59.3, 24.5, 20.4, 13.9 ($NC_{16}H_{36}$); IR (KBr): $\tilde{\nu} = 2227\ cm^{-1}$ (NCO); elemental analysis calcd for $C_{29}H_{44}N_2NiOS_3$ (591.55) (%): C 58.88, H 7.50, N 4.74, S 16.26; found: C 58.53, H 7.77, N 4.74, S 16.21.

^1H NMR spectroscopic characterization of $(NBu_4)[Ni\{N(SiMe_3)_2\}('S_3')]$ (4): At $-78\,°C$, solid $NaN(SiMe_3)_2$ (24.0 mg, 0.12 mmol) was added to a violet suspension of $(NBu_4)[Ni(Cl)('S_3')]$ (58.5 mg, 0.10 mmol) in $[D_8]$THF (2 mL). ^1H NMR spectra were recorded of the resulting dark blue solution. ^1H NMR (269.6 MHz, $[D_8]$THF, $-50\,°C$): $\delta = 7.47$ (d, 2H; C_6H_4), 7.26 (d, 2H; C_6H_4), 6.83 (m, 2H; C_6H_4), 6.62 (m, 2H; C_6H_4), 3.10 (m, 8H; NCH_2), 1.56 (m, 8H; NCH_2CH_2), 1.35 (m, 8H; $N(CH_2)_2CH_2$), 0.94 (t, 12H; $N(CH_2)_3CH_3$), 0.30 (s, 18H; $SiCH_3$).

$(NBu_4)[Ni(L)('S_3')]$ with $L = NCO^-$ (3), CN^- (5), and NSO^- (6) from $(NBu_4)[Ni\{N(SiMe_3)_2\}('S_3')]$ (4) and CO_2, CO, or SO_2: Whilst stirring at $-78\,°C$, an equimolar amount of $NaN(SiMe_3)_2$ was added to violet suspensions of $(NBu_4)[Ni(Cl)('S_3')]$ in THF (30 mL). In order to achieve the complete formation of **4**, the reaction mixtures were warmed to a maximum of $-50\,°C$ for 15 min. Dark blue solutions resulted, which were recooled to $-78\,°C$ and subsequently treated with CO_2, CO, or SO_2. The color of the solutions changed after corresponding times. The complete formation of **3**, **5**, or **6** was monitored by IR spectroscopy. After warming to room temperature, precipitated NaCl and traces of other undissolved materials were removed by centrifugation. Removal of all volatile components in vacuo gave residues, which were digested with Et_2O (ca. 10 mL), separated, washed with Et_2O, and dried in vacuo.

$(NBu_4)[Ni(NCO)('S_3')]$ (3): Starting from $(NBu_4)[Ni(Cl)('S_3')]$ (252 mg, 0.43 mmol) and $NaN(SiMe_3)_2$ (83 mg, 0.43 mmol); 5 min CO_2 gas; dark red powder. Yield: 221 mg (87 %). This material was spectroscopically identified and had identical NMR and IR spectra to compound **3** obtained from $(NBu_4)[Ni(N_3)('S_3')]$ (**2**) and CO (see above).

$(NBu_4)[Ni(CN)('S_3')]$ (5): Starting from $(NBu_4)[Ni(Cl)('S_3')]$ (417 mg, 0.71 mmol) and $NaN(SiMe_3)_2$ (137 mg, 0.71 mmol); 1 min CO; brown single crystals were grown from the mother liquor stored at $-30\,°C$ for one week. Yield: 300 mg (73 %). ^1H NMR (269.7 MHz, $[D_6]$acetone): $\delta = 7.78$ (d, 2H; C_6H_4), 7.26 (d, 2H; C_6H_4), 7.04 (m, 2H; C_6H_4), 6.92 (m, 2H; C_6H_4), 3.46 (m, 8H; NCH_2), 1.80 (m, 8H; NCH_2CH_2), 1.41 (m, 8H; $N(CH_2)_2CH_2$), 0.93 (t, 12H; $N(CH_2)_3CH_3$); $^{13}C\{^1H\}$ NMR (67.8 MHz, $[D_6]$acetone): $\delta = 156.3$, 133.3, 130.0, 128.7, 128.3, 124.9, 122.1 (C_6H_4, CN), 59.4, 24.4, 20.2, 13.9 ($NC_{16}H_{36}$); IR (KBr): $\tilde{\nu} = 2110\ cm^{-1}$ (CN); elemental analysis calcd for $C_{29}H_{44}N_2NiS_3$ (575.55) (%): C 60.52, H 7.71, N 4.87, S 16.71; found: C 60.25, H 8.35, N 4.52, S 16.64.

$(NBu_4)[Ni(NSO)('S_3')]$ (6): Starting from $(NBu_4)[Ni(Cl)('S_3')]$ (306 mg, 0.52 mmol) and $NaN(SiMe_3)_2$ (100 mg, 0.52 mmol); a drop of condensed SO_2; orange powder. Yield: 248 mg (78 %). ^1H NMR (269.6 MHz, $[D_8]$THF): $\delta = 7.59$ (d, 2H; C_6H_4), 7.19 (d, 2H; C_6H_4), 6.95 (m, 2H; C_6H_4), 6.81 (m, 2H; C_6H_4), 3.41 (m, 8H; NCH_2), 1.65 (m, 8H; NCH_2CH_2), 1.35 (m, 8H; $N(CH_2)_2CH_2$), 0.85 (t, 12H; $N(CH_2)_3CH_3$); $^{13}C\{^1H\}$ NMR (67.8 MHz, $[D_8]$THF): $\delta = 155.8$, 134.1, 129.9, 128.4, 128.2, 121.5 (C_6H_4), 59.6, 25.0, 20.7, 14.2 ($NC_{16}H_{36}$); IR (KBr): $\tilde{\nu} = 1230\ cm^{-1}$ $_{asym}$(NSO), 1030 cm^{-1} $_{sym}$(NSO); elemental analysis calcd for $C_{28}H_{44}N_2NiOS_4$ (611.60) (%): C 54.99, H 7.25, N 4.58, S 20.97; found: C 54.75, H 7.22, N 4.21, S 20.28.

Crystal structure analysis of $(NBu_4)[Ni(CN)('S_3')]$ (5): A suitable single crystal ($0.55 \times 0.40 \times 0.30\ mm^3$) obtained directly from the reaction solution was sealed in a glass capillary under N_2. Orthorhombic, $Pna2_1$ (no. 33), $Z = 4$, $a = 1622.8(4)$, $b = 1307.8(2)$, $c = 1441.0(2)$, $V = 3058(1)$ Å^3, $\rho_{calcd} = 1.250$ g cm^{-3}, and $\mu = 0.859$ mm^{-1}. Data were collected at 200 K on a Siemens P4 diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), a graphite monochromator, and ω-scan technique (8° min^{-1}, $4° < 2\Theta < 54°$). There were 4558 measured reflections and 4037 unique reflections of which 2804 were observed ($F_o \geq 4\sigma(F)$).

The structure was solved by direct methods (SHELXTL 5.03).[23] Full-matrix least-squares refinement was carried out on F^2 (SHELXTL 5.03), final R values $R1 = 0.0532$, $wR2 = 0.1416$ for 320 refined parameters. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically positioned with isotropic displacement parameters being 1.5 times U(eq) of the preceding carbon atom.[24]

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[24] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144029 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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