S-F Activation

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The Activation of Sulfur Hexafluoride at Highly Reduced Low-Coordinate Nickel Dinitrogen Complexes**

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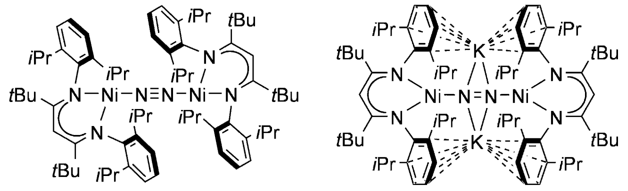
Abstract: *The greenhouse gas sulfur hexafluoride is the common standard example in the literature of a very inert inorganic small molecule that is even stable against O_2 in an electric discharge. However, a reduced β-diketiminate nickel species proved to be capable of converting SF_6 into sulfide and fluoride compounds at ambient standard conditions. The fluoride product complex features an unprecedented $[NiF]^+$ unit, where the Ni atom is only three-coordinate, while the sulfide product exhibits a rare almost linear $[Ni(\mu\text{-}S)Ni]^{2+}$ moiety. The reaction was monitored applying ^1H NMR, IR and EPR spectroscopic techniques resulting in the identification of an intermediate nickel complex that gave insight into the mechanism of the eight-electron reduction of SF_6.*

Sulfur hexafluoride is an extremely inert molecular gas.[1] Accordingly, it is used as a gaseous dielectric medium for high-voltage circuit breakers and as a protecting gas for the casting of magnesium. Also, its long lifetime in the atmosphere is most likely the reason why SF_6 is the most potent greenhouse gas known.[2] Owing to its vast stability towards both nucleophilic and electrophilic attack, reports on its successful chemical activation are scarce and commonly involve harsh conditions, for example elevated pressures and temperatures or strong reducing agents such as elemental alkali metals.[1,3–5]

The conversion of SF_6 in the coordination sphere of transition metals has to date only been described by Ernst and co-workers: Low-valent complexes were reacted with SF_6 to give mixtures of different metal fluorides. The fate of the sulfur remained unclear; in case of late transition metals, the formation of hazardous sulfur fluoride compounds such as S_2F_{10} and SF_4 was discussed.[6]

In previous studies, we have evaluated the behavior of low-coordinate β-diketiminate nickel complexes $[(L^{tBu}Ni^{I})_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)]$ (**I**) and $K_2[(L^{tBu}Ni^{I})_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2^{2-})]$ (**II**; Scheme 1) towards small molecules. In fact, dinitrogen, dihydrogen, and carbon oxides could be activated and/or functionalized.[7] Herein, we show that the same nickel compounds are even capable of converting SF_6 under standard ambient conditions. Compound **I** features a weakly activated N_2 ligand coordinated by two Ni^I centers in an end-on bridging mode. In **II**, the N_2 ligand is further activated by two additional electrons in the system. Previous work has shown that the reaction of **II** with carbon monoxide gives the dinuclear Ni^0 compound $K_2[L^{tBu}Ni^0CO]_2$.[7c] Thus, the N_2 ligand within **II** can be readily displaced, despite its formal diazene character, yielding in the formation of a $[L^{tBu}Ni^0]$ species.



Scheme 1. The dinitrogen nickel complexes $[(L^{tBu}Ni^{I})_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)]$ (**I**) and $K_2[(L^{tBu}Ni^{I})_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2^{2-})]$ (**II**) ($L^{tBu} = [HC(CtBuNC_6H_3(iPr)_2)_2]^-$).

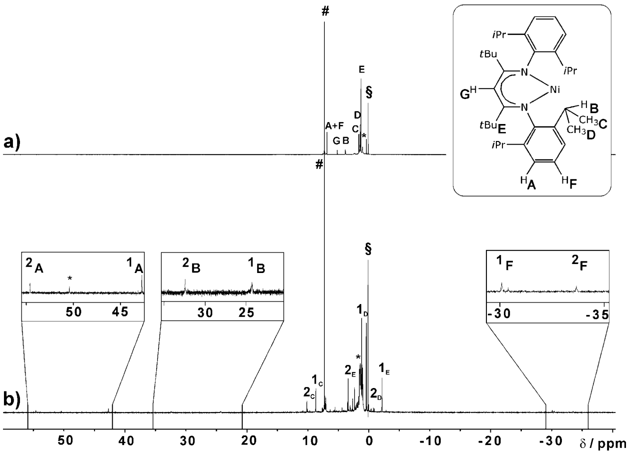


Figure 1. ^1H NMR spectra before and after the reaction of **II** with SF_6. a) diamagnetic starting material $K_2[(L^{tBu}Ni^{I})_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2^{2-})]$ (**II**); b) after one day, the paramagnetic compounds, $[L^{tBu}Ni^{II}F]$ (**1**) and $[(L^{tBu}Ni^{II})_2(\mu\text{-}S)]$ (**2**) are observed in a 2:1 ratio; # $[D_6]$benzene; § TMS; * impurities; yield in **1**: 75 %, **2**: 60 % (in reference to TMS).

As **II** is diamagnetic, we set out to investigate its reaction towards SF_6 with the aid of ^1H NMR spectroscopy (Figure 1). Exposure to SF_6 leads to the complete conversion of **II** within 10 minutes, giving rise to a signal set that is characteristic for the paramagnetic Ni^I complex **I**;[8] concomitantly, potassium

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fluoride is formed.[9] Within one day, the resonances of **I** vanish in favor of two paramagnetically shifted signal sets for two Ni^{II} complexes that we assign to $[L^{tBu}Ni^{II}F]$ (**1**) and $[(L^{tBu}Ni^{II})_2(\mu\text{-}S)]$ (**2**) on the basis of the findings described below. Species **1** and **2** formed in an approximate 2:1 ratio.

No sulfur- or fluorine-containing species other than SF_6 was observed while monitoring the reaction with the aid of ^{19}F NMR and gas-phase IR spectroscopy. Focusing on the band corresponding to the ν_3 vibrational mode of SF_6, time-dependent measurements revealed a rapid decrease of the SF_6 concentration (Figure 2). Owing to diffusion restrictions in the gas cell used, the reaction is decelerated somewhat in comparison to the ^1H NMR experiments. Consistent with the NMR spectroscopic results obtained for **II**, species **I** was found to also react with SF_6, which again yielded **1** and **2** as products.

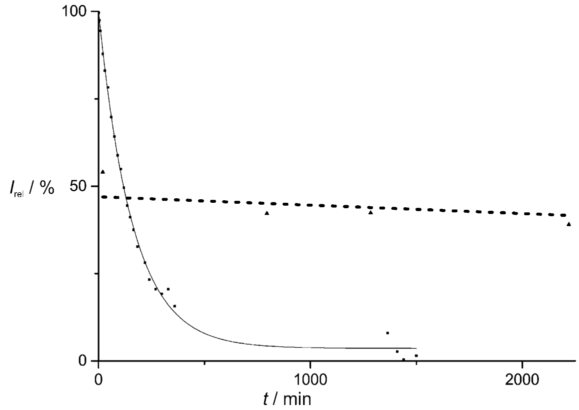


Figure 2. Gas-phase IR spectroscopy: Time dependent change of the intensity of the ν_3 band of SF_6 relative to its initial intensity in course of the reaction of **II** with stoichiometric amounts of SF_6 in benzene (solid line); in a reference experiment, the same set-up with **II** replaced by unreactive $[L^{tBu}Ni^{II}Br]$ was used (dashed line).

Upon exposure of **I** or **II** to more than five equivalents of SF_6, the relative yield in **1** increases at the cost of the yield in **2** and accordingly in metal-bound sulfur. This suggests the concomitant formation of either elemental sulfur or gaseous sulfur fluorides like SF_4 or S_2F_{10}. However, no evidence of the formation of either compound was obtained through elemental analysis, by GC-MS and EI-MS, or applying ^{19}F NMR and EPR spectroscopy.

To confirm the ^1H NMR assignments for **1** and **2**, their independent synthesis was pursued. While the preparation of **1** appears straight forward setting out from the corresponding bromide homologue through halide exchange, it eluded synthesis in attempts using common nucleophilic fluorinating reagents like AgF or Me_3SnF. Ultimately, the metathesis reaction of $[L^{tBu}Ni^{II}Br]$ with $[Me_4N]F$ was successful, when it was carried out in dichlormethane, leading to **1** in up to 61 % yield. Indeed, comparison of the ^1H NMR spectrum of **1** with the spectrum observed after the reaction of **II** with SF_6 revealed identical chemical shifts. During the reaction of a concentrated benzene solution of **I** with an excess of SF_6, **1** precipitated in form of single crystals that were suitable for an X-ray analysis. Its molecular structure is depicted in Figure 3. The nickel atom in **1** is trigonal planar and coordinated by the N atoms and the F atom (sum of bond angles 359.99(9)°). To the best of our knowledge, **1** is the first three-coordinate nickel fluoride complex that has been structurally characterized.

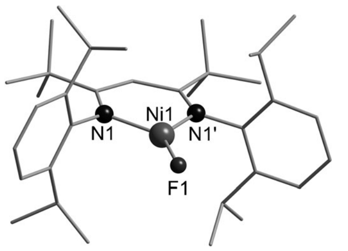


Figure 3. Molecular structure of **1**. H atoms are omitted for clarity.[10]

Attempts to access the sulfide complex **2** in pure form through an independent route have been unsuccessful. This can be rationalized by the lability that should be expected for **2** considering on the one hand the close proximity of the opposite bulky β-diketiminate ligands and on the other hand the high electron density a single chalcogenide atom experiences between two d^8 metal centers (note that $[(L^{tBu}Ni^{II})_2(\mu\text{-}O)]$ is not known yet). However, subsequent to the reaction of **II** with SF_6 in *n*-hexane, single crystals of **2** could be picked from the crude solid reaction product that were suitable for an X-ray analysis, and its molecular structure is illustrated in Figure 4.

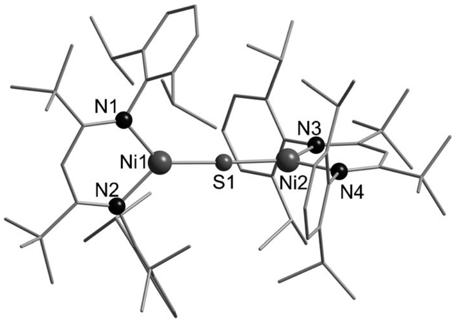
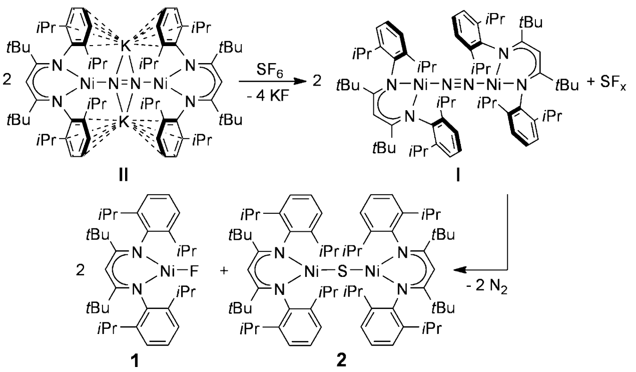


Figure 4. Molecular structure of **2**. H atoms and one molecule of *n*-hexane are omitted for clarity.[10]

In **2**, the two Ni centers are coordinated by the S atom and the N atoms in trigonal planar fashion (sum of bond angles 360.00(9)° and 359.98(10)°, respectively). Most probably because of the strained character of the molecule, the torsion angle of the two opposite C_3N_2Ni planes is close to 90° (N1-N2-N3-N4 86.26(10)°). Species **2** exhibits a rare, almost-linear $[Ni^{II}(\mu\text{-}S)Ni^{II}]^{2+}$ unit.[11] The Ni–S distances in **2** are comparable to those of previously reported tetrahedral Ni^{II} complexes with a linear central arrangement.[11g,h]

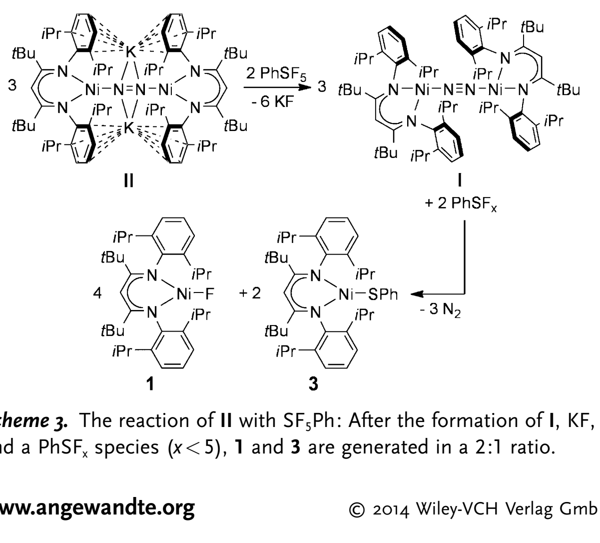
Altogether, the findings indicate a reaction sequence as depicted in Scheme 2. Two equivalents of **II** react quickly with SF_6 to yield four equivalents of potassium fluoride, two equivalents of **I**, and an unknown SF_x compound ($x < 6$), which is not coordinatively bound to a nickel center.



Scheme 2. Reaction of **II** with SF$_6$: Initially, **I**, KF, and a SF$_x$ ($x < 6$) species are formed. Subsequently, **I** reacts with SF$_x$ to give the final products **1** and **2** in a 2:1 ratio.

Subsequently, **I** reacts further with SF$_x$ and unconsumed SF$_6$, respectively, to give **1** and **2** in a 2:1 ratio. As SF$_x$ is more reactive than SF$_6$, a parallel reaction with unconsumed SF$_6$ is noncompetitive if its concentration is low. Attempts to identify the SF$_x$ species were unsuccessful. The formation of sulfur-based radicals or fluorine radicals is unlikely as these should be reduced by **I** instantaneously. Indeed, no radicals were detected by EPR measurements. Also, the formation of soluble diamagnetic compounds such as SF$_4$ or S$_2$F$_{10}$ can be ruled out as they were not detected in gas-phase IR spectroscopic experiments and/or ^{19}F NMR experiments that we conducted at temperatures between −80 °C and 50 °C. A realistic option is the intermediate formation of [SF$_5$]$^-$ salts, which have been found as products of the reduction of SF$_6$ using organic reducing agents: Their insolubility in benzene would explain their elusiveness in ^{19}F NMR spectroscopic investigations, and on the other hand they readily decompose after isolation in vacuo to give SF$_4$ and KF, so that only the latter remains for detection.[4b]

To further support our results concerning the reaction of **II** with SF$_6$, SF$_5$Ph was employed as an easy-to-handle SF$_6$ derivative. Indeed, the reaction of **II** with SF$_5$Ph proceeded analogously: Initially **I** and KF were formed, and ultimately **1** as well as the complex $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Ni}^{\mathrm{II}}\mathrm{SPh}]$ (**3**) were detected as products in a 2:1 ratio (Scheme 3). The reaction rate is higher, indicating that potential intermediate [PhSF$_x$] species ($x < 5$) are more reactive than [SF$_x$] suggested as an intermediate in Scheme 2.



Scheme 3. The reaction of **II** with SF$_5$Ph: After the formation of **I**, KF, and a PhSF$_x$ species ($x < 5$), **1** and **3** are generated in a 2:1 ratio.

Unequivocal identification of **3** again required the development of an independent synthesis. Compound **3** was isolated after the salt metathesis reaction of $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Ni}^{\mathrm{II}}\mathrm{Br}]$ with KSPh in 81 % yield. Single crystals suitable for an X-ray analysis could be obtained by cooling a saturated *n*-hexane solution of **3** to −30 °C. The structure of **3** is displayed in Figure 5. In **3** the coordination sphere of the three-coordinate Ni$^{\mathrm{II}}$ center can best be described as T-shaped planar (sum of bond angles 359.84(7)°). The Ni−S distance is comparable to values reported for other Ni$^{\mathrm{II}}$ arylthiolate complexes.[12]

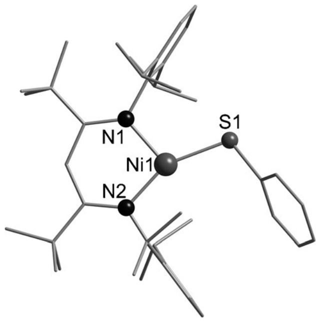


Figure 5. Molecular structure of **3**. H atoms are omitted for clarity.[10]

Sulfur hexafluoride is renowned for its rather inert behavior under extreme conditions. Research focusing on its activation is valuable in two respects: a) to determine the actual limits of its stability, and b) to find ways for its conversion, first as SF$_6$ is the most efficient greenhouse gas, and second as in the long term this may open up non-toxic paths for SF$_5$ functionalization. Still, reports on successful SF$_6$ activation at transition-metal centers are scarce.[6,13] Herein we showed that SF$_6$ (as well as SF$_5$Ph) can be converted within the coordination sphere of a reduced nickel atom bound by β-diketiminato ligands. Additionally, we have successfully identified the resulting fluoride and sulfide products, which are very interesting complexes in their own rights: **1** is the first structurally characterized three-coordinate nickel fluoride complex, while **2** is a rare example of a transition-metal complex exhibiting an almost linear [Ni(μ-S)Ni]$^{2+}$ arrangement. Currently, studies concerning the reactivity of **1** towards silanes and other fluorine accepting compounds are under way. Once a convenient, SF$_6$-free synthesis of **2** has also been developed, its chemical behavior towards small molecules like dioxygen or dihydrogen will be studied.

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[8] As the corresponding signals are very broad, assignment to **I** was also confirmed by the comparison of its EPR spectrum with a spectrum recorded for the reaction mixture. Additionally, **I** was isolated from the reaction mixture and identified IR spectroscopically.

[9] After work-up, a pale solid was isolated that was identified as KF: A ^{19}F NMR spectrum in basic D$_2$O revealed only one resonance for free fluoride. Addition of purchased KF to the sample led to an augmentation of the observed signal. No sulfur could be detected in an elemental analysis.

[10] See the Supporting Information for details on the crystal structure.

[11] Linear [M(μ-S)M]$^{n+}$ arrangements have been observed for only a few Fe, V, Mo, Co, Ni, Cu, U, and Pb compounds: a) M. M. Rodriguez, B. D. Stubbert, C. C. Scarborough, W. W. Brennessel, E. Bill, P. L. Holland, *Angew. Chem.* **2012**, *124*, 8372–8375; *Angew. Chem. Int. Ed.* **2012**, *51*, 8247–8250; b) J. Schiemann, P. Hübener, W. Weiss, *Angew. Chem.* **1983**, *95*, 1021; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 980–981; c) S. Lincoln, S. L. Soong, S. A. Koch, M. Sato, J. E. Enemark, *Inorg. Chem.* **1985**, *24*, 1355–1359; d) T. Yoshida, T. Adachi, K. Matsumura, K. Baba, *Angew. Chem.* **1993**, *105*, 1730–1732; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1621–1623; e) J. E. McDonough, A. Mendiratta, J. J. Curley, G. C. Fortman, S. Fantasia, C. C. Cummins, E. V. Rybak-Akimova, S. P. Nolan, C. D. Hoff, *Inorg. Chem.* **2008**, *47*, 2133–2141; f) S. C. Davies, D. L. Hughes, R. L. Richards, J. R. Sanders, *J. Chem. Soc. Dalton Trans.* **2000**, 719–725; g) C. Mealli, S. Midollini, L. Sacconi, *Inorg. Chem.* **1978**, *17*, 632–637; h) J. Cho, K. M. Van Heuvelen, G. P. A. Yap, T. C. Brunold, C. G. Riordan, *Inorg. Chem.* **2008**, *47*, 3931–3933; i) S. Delgado, P. J. S. Miguel, J. L. Priego, R. Jiménez-Aparicio, C. J. Gómez-García, F. Zamora, *Inorg. Chem.* **2008**, *47*, 9128–9130; j) L. R. Avens, D. M. Barnhart, C. J. Burns, S. D. McKee, W. H. Smith, *Inorg. Chem.* **1994**, *33*, 4245–4254; k) O. P. Lam, F. W. Heinemann, K. Meyer, *Chem. Sci.* **2011**, *2*, 1538–1547; l) L. C. Yu, H. M. Peng, *Russ. J. Coord. Chem.* **2012**, *38*, 392–395.

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