

# Unusual nickel-mediated C–S cleavage of alkyl and aryl sulfoxides†

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The first examples of transition metal mediated C–S cleavage of sulfoxides containing  $sp^2$ - and  $sp^3$ -hybridized carbon bonds attached to the sulfur atom and the first example of a structurally characterized complex featuring an oxygen-bound sulfinyl ligand are presented.

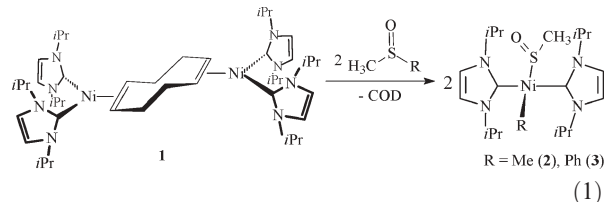
Transition metal mediated carbon–element bond cleavage and bond formation reactions are important processes in chemistry because they provide the key steps in the building of complex molecules from simple precursors. Insertion of transition metal complexes into C–E bonds in solution can lead to the development of new selective and efficient processes for the utilization of organic molecules, and this type of reaction therefore plays a dominant role in transition metal mediated stoichiometric and catalytic transformations. In this contribution, we report the isolation and structural characterization of reaction products of an unusual nickel-catalyzed C–S cleavage reaction of bonds between  $sp^2$ - and  $sp^3$ -hybridized carbon atoms and the sulfur atom of sulfoxides.

The widespread use of sulfoxides in synthesis<sup>1,2</sup> makes carbon–sulfur insertion reactions particularly desirable for higher oxidation state sulfur. In previous work, it has been found that the C–S bonds of sulfoxides and sulfones are cleaved during nickel-catalyzed reactions with Grignard-reagents, and that sulfur containing functional groups are readily replaced by carbon-containing substituents.<sup>3</sup> The groups of Wenkert and Kagan, for example, reported cross coupling reactions of aryl methyl sulfones and aryl methyl sulfoxides with MeMgBr in the presence of 10 mol%  $[\text{NiCl}_2(\text{PPh}_3)_2]$  to afford toluene derivatives.<sup>4</sup> Although no reaction intermediates have been observed or isolated, a nickel(0) catalyst is a likely active species and a conceivable reaction pathway for this transformation includes the activation of the C–S bond by a nickel(0) intermediate.

We recently reported the synthesis and characterization of the NHC (N-heterocyclic carbene) stabilized nickel complex  $[\text{Ni}_2(\text{iPr}_2\text{Im})_4(\text{COD})]$  **1** ( $\text{iPr}_2\text{Im}$  = 1,3-di(isopropyl)imidazole-2-ylidene), which is a source of the reactive  $[\text{Ni}(\text{iPr}_2\text{Im})_2]$  complex fragment in stoichiometric as well as catalytic transformations.<sup>5</sup> Complex **1** is an excellent catalyst for the insertion of diphenylacetylene into the 2,2'-C–C bond of biphenylene under activation of the carbon–carbon bond and is very efficient in C–F activation reactions of fluorinated arenes.<sup>5</sup> Since conclusive evidence of  $sp^2$ - and  $sp^3$ -carbon–sulfur bond cleavage of sulfoxides is currently not available, we became interested in the activation of sulfoxides and the reactions of sulfinyl containing ligands in the

coordination sphere of transition metals. The reactivity of the metal–sulfur linkage in metallasulfoxides is virtually unexplored.<sup>6</sup> We note, however, the special case of an insertion of an  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)]$  complex fragment into the C(sp)–S bond of an alkynyl sulfoxide reported recently.<sup>7</sup> Another example might be a likely intermediate of C(sp)–S bond fission in the palladium catalyzed sulfinylzincation using alkynyl sulfoxides reported by Maezaki and Tanaka and co-workers.<sup>8</sup>

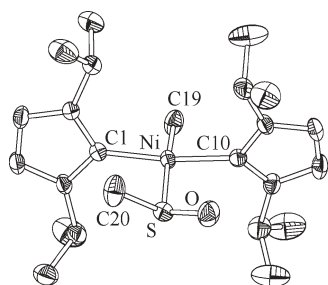
Rather surprisingly, the reactions of dinuclear **1** with two equivalents of dimethyl sulfoxide (dmsO) or phenyl methyl sulfoxide (pmsO) in toluene smoothly lead to products of  $sp^3$ -C–S(O) bond cleavage of dmsO and  $sp^2$ -C–S(O) bond cleavage of pmsO. The activation products  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{Me})(\text{SOMe})]$  **2** and  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{Ph})(\text{SOMe})]$  **3** (eqn (1)) were isolated as yellow solids in good yields and were characterized by elemental analyses, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and IR spectroscopy as well as X-ray crystallography.‡



While elemental analyses of **2** and **3** are in accord with the addition of dmsO and pmsO to the  $[\text{Ni}(\text{iPr}_2\text{Im})_2]$  complex fragment, the first evidence for C–S activation, rather than adduct formation, came from the EI/MS data obtained for **2**. In this spectrum, the signals with the highest masses were assigned to  $\text{M}^+ - \text{SOMe}$ , i.e. the loss of a methyl sulfinyl moiety was observed under the conditions of mass spectroscopy. The <sup>1</sup>H-NMR spectra of **1** and **2** reveal signal patterns typically obtained for pseudo  $C_s$  type structures in solution, which is in accordance with a *trans* alignment of the carbene ligands in solution and thus excludes potential complexes of the type  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-}(S,O)\text{-OS}\{\text{R}\}\text{Me})]$ , assuming a relatively high rotation barrier of the  $\eta^2$  coordinated sulfoxide ligand. Furthermore, coordination of the dimethyl sulfoxide *via* its O or S atom to afford complexes of the type  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{OSMe}_2)]$  or  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{OSMe}_2)]$  was excluded due to the occurrence of two sets of signals for the sulfoxide methyl groups in the <sup>1</sup>H-NMR spectrum of **2**. The proton resonance of the methyl group attached to the nickel atom in  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{Me})(\text{SOMe})]$  **2** was detected significantly upfield shifted as a singlet at  $-0.52$  ppm, whereas the methyl sulfinyl ligand gives rise to a resonance at 2.35 ppm. For  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{Ph})(\text{SOMe})]$  **3**, the protons of the methyl group attached to the sulfur atom were detected at 2.16 ppm and those of the phenyl ligand, as a multiplet at 6.73 ppm and a doublet at 7.11 ppm. In the IR spectra of **2** and **3**, strong absorption bands at

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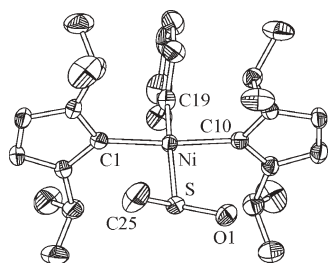


**Fig. 1** ORTEP diagram of the molecular structure of  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{Me})(\text{SOMe})]$  (**2**) in the solid state (ellipsoids set at the 40% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Ni–C(1) 1.891(2), Ni–C(10) 1.886(2), Ni–C(19) 2.000(3), Ni–S 2.201(1), S–C(20) 1.800(4), S–O 1.536(2); C(1)–Ni–C(10) 172.54(10), C(19)–Ni–S 170.26(10), C(1)–Ni–C(19) 88.62(11), C(10)–Ni–C(19) 86.55(11), C(1)–Ni–S 93.14(8), C(10)–Ni–S 92.58(8), Ni–S–C(20) 108.58(12), Ni–S–O 116.56(9).

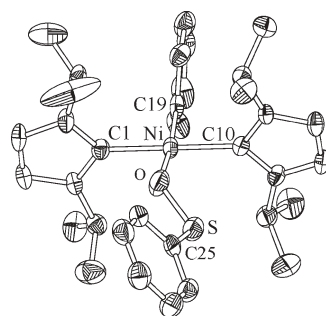
937  $\text{cm}^{-1}$  (**2**) and 945  $\text{cm}^{-1}$  (**3**), respectively, were tentatively assigned to the S=O stretch of the sulfinyl moiety present in the molecule, although this part of the IR spectrum is significantly overlaid by vibrations of the NHC ligand. To prove our findings unequivocally, crystals of **2** and **3** suitable for X-ray diffraction have been grown from saturated toluene or toluene–thf solutions (Fig. 1 and 2). $\ddagger$

The molecular structures of **2** and **3** clearly reveal in both cases a methyl sulfinyl ligand attached *via* the sulfur atom to the nickel atom and thus support the occurrence of C–S activation of dmsO and pmso. The nickel–carbon distances are unexceptional<sup>9</sup> and the Ni–S bond lengths of 2.201(1) Å and 2.214(1) Å are in the range typically observed for other metallasulfoxides.<sup>6</sup> The S=O distances of 1.536(2) Å and 1.531(2) Å are slightly elongated compared to the S=O distances reported for dmsO (1.494 Å) and are on the upper limit of the range observed for transition metal complexes with S-bonded sulfoxide ligands (1.398–1.524 Å).<sup>10b</sup> The sulfur lone pairs of **2** and **3** do not seem to be involved in bonding, as the angles Ni–S–O of 116.56(9) $^\circ$  (**2**) and 116.89(9) $^\circ$  (**3**) and Ni–S–C of 108.58(12) $^\circ$  (**2**) and 109.59(14) $^\circ$  (**3**) reveal.

Dimethyl sulfoxide is a widely applied solvent in transition metal chemistry. Furthermore, there exists a rich chemistry of sulfoxide stabilized late transition metal halides and dmsO

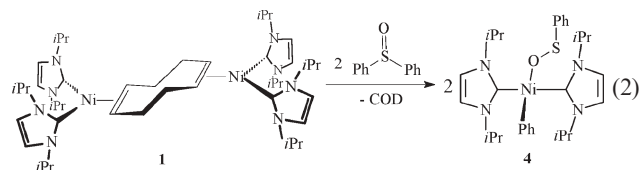


**Fig. 2** ORTEP diagram of the molecular structure of  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{Ph})(\text{SOMe})]$  (**3**) in the solid state (ellipsoids set at the 40% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Ni–C(1) 1.904(3), Ni–C(10) 1.887(3), Ni–C(19) 1.930(3), Ni–S 2.214(1), S–C(25) 1.795(4), S–O(1) 1.531(2); C(1)–Ni–C(10) 174.53(10), C(19)–Ni–S 166.93(9), C(1)–Ni–C(19) 90.78(11), C(10)–Ni–C(19) 87.12(11), C(1)–Ni–S 92.39(8), C(10)–Ni–S 90.78(8), C(25)–S–O(1) 103.23(18), Ni–S–C(25) 109.59(14), Ni–S–O(1) 116.89(9).



**Fig. 3** ORTEP diagram of the molecular structure of  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{Ph})(\text{OSPh})]$  (**4**) in the solid state (ellipsoids set at the 40% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Ni–C(1) 1.903(5), Ni–C(10) 1.917(4), Ni–C(19) 1.898(5), Ni–O 1.936(4), O–S 1.593(4), S–C(25) 1.731(5); C(10)–Ni–C(1) 180.0(2), C(19)–Ni–O 172.60(17), C(10)–Ni–O 94.32(15), C(1)–Ni–O 85.70(16), C(10)–Ni–C(19) 89.29(16), C(1)–Ni–C(19) 90.69(17), Ni–O–S 119.3(2), O–S–C(25) 102.9(2).

complexes in particular, which are widely used as precursors in inorganic synthesis.<sup>10</sup> Despite the existence of numerous metal sulfoxide and metal sulfone complexes, evidence of general carbon–sulfur bond cleavage in sulfoxides has not been given before. To further substantiate our findings, diphenyl sulfoxide (dpsO) was reacted with **1**. Interestingly, the reaction of dpsO with **1** also leads to C–S activation of the sulfoxide, but affords  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{Ph})(\text{OSPh})]$  **4**, a product in which the phenyl sulfinyl ligand is bound *via* the oxygen atom to the nickel atom (eqn (2)). The evidence for this coordination mode, however, is mainly based on the infrared spectrum and on the solid state X-ray crystal structure of complex **4** (Fig. 3). In the IR spectrum of this complex, no strong vibration is detectable in the range expected for the S=O stretch of the sulfinyl ligand. We attribute this coordination mode either to deactivation of the S-donor atom by the phenyl substituent or to increased steric congestion of the phenyl sulfinyl moiety.



S/O linkage isomerism is well known in di(organyl) sulfoxide chemistry. Complex **4**, however, is the first example of a structurally characterized complex featuring an O-bound sulfinyl ligand. The S–O bonding distance of 1.593(4) Å in **4** is only slightly elongated compared to the S–O bond lengths in **2** (1.536(2) Å) and **3** (1.531(2) Å), but is significantly larger than the S–O bond length in dpsO (1.492(1) Å)<sup>10b</sup> and is in the range typically observed for S–O single bonds in tosylates. The Ni–O distance of 1.936(4) Å observed in **4** is significantly shorter compared to the average Ni–O distance of 2.11(3) Å observed for oxygen-bound di(organyl) sulfoxide ligands in nickel(II) complexes,<sup>10b</sup> but is in the upper range expected for four-coordinate nickel alkoxides. Ni–O distances in these compounds are typically observed in a range of 1.85–1.90 Å, but examples with Ni–O bond lengths over 1.90 Å are reported in the literature.<sup>11</sup> Preliminary DFT calculations

performed on **4** reveal a significant degree of nickel–oxygen  $\pi$  antibonding character in the highest occupied orbitals of this compound and thus explain the rather long nickel–oxygen bond distance. First experiments show that the sulfinyl moiety can be transferred to organic substrates in stoichiometric reactions. The reaction of **3** with methyl iodide, for example, affords dmsO and  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{Ph})(\text{I})]$ .

To conclude, we presented here the first examples of transition metal mediated C–S cleavage reactions of sulfoxides containing  $\text{sp}^2$ - and  $\text{sp}^3$ -hybridized carbon bonds attached to the sulfur atom. Complex **4** represents the first structurally characterized example of a complex featuring an oxygen-bound sulfinyl ligand and thus demonstrates the ambivalence of O versus S binding of sulfoxide ligands. These findings should be of interest for bioinorganic chemists, since nickel sulfinyl moieties  $[\text{Ni}-\text{S}(=\text{O})\text{R}]$  are of possible significance to the deactivation of nickel-containing enzymes. Furthermore, these results might have an impact on the use of sulfoxides in metal mediated transformations, *i.e.* the activation of sulfinyl-containing ligands in connection with transition metal catalyzed sulfinyl transfer reactions or a possible racemization/enantiomerization of sulfoxide ligands in the coordination sphere of transition metals. Further work on the chemical behaviour of such compounds is in progress.

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## Notes and references

† CCDC 626501 to CCDC 626503 contain the supplementary crystallographic data for the structures of compounds **2–4**. These structures were solved by direct methods (SHELXS-97) and refined by full matrix least squares methods on  $F^2$  (SHELXL-97).<sup>12</sup> For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618632g

Crystal data for **2**, CCDC 626501:  $\text{C}_{27}\text{H}_{46}\text{N}_4\text{NiOS}$ ,  $M = 533.45$ , monoclinic,  $a = 8.9991(6)$  Å,  $b = 12.2314(5)$  Å,  $c = 27.8178(18)$  Å,  $\beta = 93.695(8)^\circ$ ,  $V = 3055.6(3)$  Å<sup>3</sup>,  $T = 203(2)$  K, space group  $P2_1/n$ ,  $Z = 4$ , radiation Mo-K $\alpha$  ( $\lambda = 0.71073$  Å),  $F(000) = 1152$ ,  $\mu = 0.727$  mm<sup>-1</sup>, reflections collected: 11 807, independent reflections: 5239 ( $R_{\text{int}} = 0.0433$ ), observed reflections [ $I > 2\sigma(I)$ ]: 3852,  $R1$  ( $I > 2\sigma(I)$ ) = 0.0400,  $wR2$  ( $I > 2\sigma(I)$ ) = 0.0945, goodness-of-fit on  $F^2$ : 0.989.

Crystal data for **3**, CCDC 626502:  $\text{C}_{30.5}\text{H}_{47.5}\text{N}_4\text{NiO}_{1.5}\text{S}$ ,  $M = 585.00$ , monoclinic,  $a = 39.4440(18)$  Å,  $b = 10.1660(14)$  Å,  $c = 17.216(3)$  Å,  $\beta = 100.999(18)^\circ$ ,  $V = 6776(1)$  Å<sup>3</sup>,  $T = 203(2)$  K, space group  $C2/c$ ,  $Z = 8$ , radiation Mo-K $\alpha$  ( $\lambda = 0.71073$  Å),  $F(000) = 2516$ ,  $\mu = 0.662$  mm<sup>-1</sup>, reflections collected: 24 628, independent reflections: 6319 ( $R_{\text{int}} = 0.0541$ ), observed reflections [ $I > 2\sigma(I)$ ]: 5261,  $R1$  ( $I > 2\sigma(I)$ ) = 0.0486,  $wR2$  ( $I > 2\sigma(I)$ ) = 0.1420, goodness-of-fit on  $F^2$ : 1.071.

Crystal data for **4**, CCDC 626503:  $\text{C}_{30}\text{H}_{42}\text{N}_4\text{NiOS}$ ,  $M = 565.45$ , orthorhombic,  $a = 10.861(2)$  Å,  $b = 19.288(4)$  Å,  $c = 28.695(6)$  Å,  $V = 6011(2)$  Å<sup>3</sup>,  $T = 203(2)$  K, space group  $Pbca$ ,  $Z = 8$ , radiation Mo-K $\alpha$  ( $\lambda = 0.71073$  Å),  $F(000) = 2416$ ,  $\mu = 0.743$  mm<sup>-1</sup>, reflections collected: 27 925, independent reflections: 4295 ( $R_{\text{int}} = 0.0718$ ), observed reflections [ $I > 2\sigma(I)$ ]: 3813,  $R1$  ( $I > 2\sigma(I)$ ) = 0.0645,  $wR2$  ( $I > 2\sigma(I)$ ) = 0.1696, goodness-of-fit on  $F^2$ : 1.255.

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