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# Synthesis and reactivity of a nickel(II) thioperoxide complex: demonstration of sulfide-mediated N<sub>2</sub>O reduction†

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The thiohyponitrite ([SNNO]<sup>2-</sup>) complex, [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(κ<sup>2</sup>-SNNO)] (L<sup>tBu</sup> = ((2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NC(<sup>t</sup>Bu)<sub>2</sub>CH), extrudes N<sub>2</sub> under mild heating to yield [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(η<sup>2</sup>-SO)] (**1**), along with minor products [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(η<sup>2</sup>-OSSO)] (**2**) and [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(η<sup>2</sup>-S<sub>2</sub>)] (**3**). Subsequent reaction of **1** with carbon monoxide (CO) results in the formation of [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(η<sup>2</sup>-SCO)] (**4**), [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(S,O:κ<sup>2</sup>-SCO<sub>2</sub>)] (**5**), [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(κ<sup>2</sup>-CO<sub>3</sub>)] (**6**), carbonyl sulfide (COS) (**7**), and [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(S<sub>2</sub>CO)] (**8**). To rationalize the formation of these products we propose that **1** first reacts with CO to form [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(S)] (**I**) and CO<sub>2</sub>, via O-atom abstraction. Subsequently, complex **I** reacts with CO or CO<sub>2</sub> to form **4** and **5**, respectively. Similarly, the formation of complex **6** and COS can be rationalized by the reaction of **1** with CO<sub>2</sub> to form a putative Ni(II) monothiothiocarbonate, [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(κ<sup>2</sup>-SOCO<sub>2</sub>)] (**11**). The Ni(II) monothiothiocarbonate subsequently transfers a S-atom to CO to form COS and [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(κ<sup>2</sup>-CO<sub>3</sub>)] (**6**). Finally, the formation of **8** can be rationalized by the reaction of COS with **I**. Critically, the observation of complexes **4** and **5** in the reaction mixture reveals the stepwise conversion of [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(κ<sup>2</sup>-SNNO)] to **1** and then **I**, which represents the formal reduction of N<sub>2</sub>O by CO.

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## Introduction

Nitrous oxide (N<sub>2</sub>O) features a long atmospheric lifetime and large global warming potential (*ca.* 300 times larger than CO<sub>2</sub>), making it an important greenhouse gas.<sup>1–4</sup> Anthropogenic sources of N<sub>2</sub>O include agriculture, fossil fuel combustion, adipic acid synthesis, and nitric acid production.<sup>1,5</sup> The latter two sources use on-site N<sub>2</sub>O mitigation to remove N<sub>2</sub>O from the effluent stream, either by decomposition to the elements<sup>6</sup> or reduction to N<sub>2</sub> and H<sub>2</sub>O, but neither of these methods is completely effective and some N<sub>2</sub>O is still released into the atmosphere.<sup>7</sup>

Given the above considerations, the development of new catalysts for N<sub>2</sub>O reduction could help reduce its impact on global temperatures.<sup>1,8</sup> Not surprisingly, a large number of heterogeneous systems have been developed to catalyze this reaction.<sup>9</sup> Of most relevance to the current study are the catalyst systems used for automotive applications, which consist of nanoparticulate Pt and Rh on a ceramic support. This process uses partially oxidized fuel (*i.e.*, CO) to reduce N<sub>2</sub>O, forming N<sub>2</sub>

and CO<sub>2</sub>.<sup>9</sup> Sita and co-workers developed a homogeneous version of this transformation, mediated by the Mo(II) complex, Cp\*Mo(NCN)(CO)<sub>2</sub> (NCN = <sup>i</sup>PrNC(Me)N<sup>i</sup>Pr).<sup>10</sup> In this process, N<sub>2</sub>O oxidizes Cp\*Mo(NCN)(CO)<sub>2</sub> to form a Mo(IV) oxo, Cp\*Mo(NCN)(O), which then reacts with CO to form CO<sub>2</sub> and regenerate Cp\*Mo(NCN)(CO)<sub>2</sub>. However, an N–N bond cleavage reaction, which results in irreversible formation of Cp\*Mo(NCN)(NCO)(NO), was found to be competitive with oxo formation. Similarly, Limberg and co-workers reported the stoichiometric oxidation of a Ni(0) CO complex, [K]<sub>2</sub>[L<sup>tBu</sup>Ni<sup>0</sup>(CO)]<sub>2</sub>, with N<sub>2</sub>O to form a carbonate complex, [K]<sub>6</sub>[L<sup>tBu</sup>Ni<sup>II</sup>(CO<sub>3</sub>)]<sub>6</sub>, and N<sub>2</sub>.<sup>11</sup> Subsequent release of carbonate from the metal center was not discussed. The homogeneous hydrogenation of N<sub>2</sub>O has also been explored.<sup>12,13</sup> For example, in 2015 Piers and co-workers reported an Ir(III) pincer carbene complex that could hydrogenate N<sub>2</sub>O;<sup>14</sup> however, this system was not reported to be catalytic. More recently, Milstein and co-workers reported that the Ru pincer complex, [(PNP)RuH(CO)(OH)] (PNP = 2,6-[CH<sub>2</sub>P<sup>i</sup>Pr<sub>2</sub>]<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N)), was an effective catalyst for the hydrogenation of N<sub>2</sub>O, achieving a turnover number of *ca.* 400.<sup>15</sup>

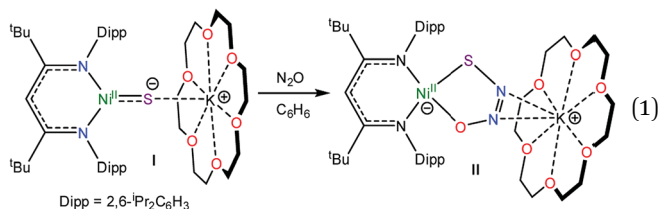
Recently, we reported the activation of N<sub>2</sub>O by the “masked” terminal nickel sulfide complex, [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(S)] (**I**) (L<sup>tBu</sup> = ((2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NC(<sup>t</sup>Bu)<sub>2</sub>CH), which yielded an unprecedented thiohyponitrite complex, [K(18-crown-6)][L<sup>tBu</sup>Ni<sup>II</sup>(κ<sup>2</sup>-SNNO)] (**II**) (eqn (1)).<sup>16</sup> Given the challenge of activating N<sub>2</sub>O,<sup>17</sup> and the novelty of the [SNNO]<sup>2-</sup> ligand in **II**, we endeavored to

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explore its reactivity in greater detail. Herein, we describe the first reactivity study of the  $[\text{SNNO}]^{2-}$  ligand in an effort to uncover new routes to  $\text{N}_2\text{O}$  reduction.



## Results and discussion

### Synthesis of an $[\eta^2\text{-SO}]^{2-}$ complex

Gentle heating of a toluene- $d_8$  solution of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-SNNO})]$  (**II**) at 45 °C results in the complete disappearance of **II** over the course of 6 d. A  $^1\text{H}$  NMR spectrum of this reaction mixture reveals the presence of a new  $\gamma\text{-CH}$  resonance at 5.43 ppm (Fig. S2 and 3 $^\dagger$ ), which we have assigned to the thioperoxide complex,  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$  (**1**). A preliminary kinetic analysis suggests that the formation of **1** is first-order with respect to complex **II**, indicating that this transformation is unimolecular (Fig. S25 $^\dagger$ ). Also present in these spectra are two minor  $\gamma\text{-CH}$  resonances. The first, observed at 5.53 ppm, has been tentatively assigned to the disulfur dioxide complex,  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-OSSO})]$  (**2**), and the second resonance at 5.47 ppm, has been assigned to the disulfide complex,  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-S}_2)]$  (**3**). Work-up of the reaction mixture affords  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$  (**1**) as an orange crystalline solid in 82% yield (eqn (2)). The solid state molecular structure of **1** is shown in Fig. 1. Complex **1** features a rare example of an  $\eta^2$ -thioperoxide ( $[\eta^2\text{-SO}]^{2-}$ ) ligand, which is formed *via*  $\text{N}_2$  extrusion from the thiohyponitrite fragment. The  $[\eta^2\text{-SO}]^{2-}$  ligand in **1** is disordered over two positions in a 97 : 3 ratio, which are related by a  $\text{C}_2$  rotation about the Ni–K axis. It possesses an S–O bond length of 1.656(3) Å, consistent with an S–O single bond.<sup>18</sup> For comparison, the S=O distance in free S=O is substantially shorter (1.48108(8) Å), due to its higher bond order.<sup>19</sup> The Ni–S (2.127(1) Å) and Ni–O (1.954(3) Å) distances in **1** are both consistent with single bonds and are comparable with those found in the starting material (**II**), while the Ni–N bond lengths (1.881(4) and 1.900(4) Å) are similar to those observed in other square planar  $\text{L}^{\text{R}}\text{Ni}^{\text{II}}$  complexes.<sup>16,20</sup>

The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **1** are consistent with its formulation as a  $\text{C}_s$  symmetric, diamagnetic, square planar  $\text{Ni}^{\text{II}}$  complex. The  $^1\text{H}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  features two *tert*-butyl resonances at 1.32 and 1.37 ppm and a single  $\gamma\text{-CH}$  resonance at 5.54 ppm. The IR spectrum (KBr pellet) of **1** reveals a strong  $\nu_{\text{SO}}$  mode at 902  $\text{cm}^{-1}$ , which is consistent with values reported for other  $[\eta^2\text{-SO}]^{2-}$  ligands (883, 873  $\text{cm}^{-1}$ ).<sup>21,22</sup> Only a handful of structurally-characterized thioperoxide complexes are known,<sup>23–26</sup> including  $[(\text{triphos})\text{Rh}(\mu\text{-}\eta^2, \eta^1\text{-SO})_2\text{Rh}(\text{triphos})][\text{BPh}_4]_2$  (triphos =  $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ ),  $[\{\text{RhCl}(\mu\text{-}\eta^2, \eta^1\text{-SO})(\text{PPh}_3)_2\}_2]$ , and  $\text{Fe}_3(\mu_3\text{-SO})(\text{S})(\text{CO})_9$ .<sup>21,27,28</sup> The iron example is notable because it can be prepared by O-atom transfer to

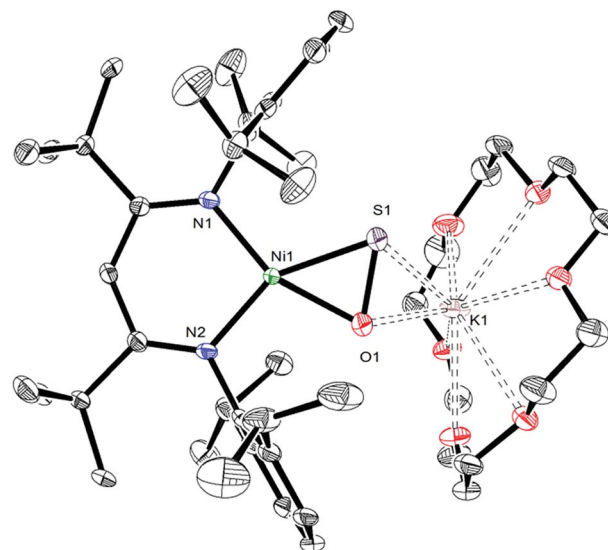


Fig. 1 ORTEP drawing of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]\cdot\text{C}_7\text{H}_8$  ( $1\cdot\text{C}_7\text{H}_8$ ) shown with 50% thermal ellipsoids. Hydrogen atoms, a  $\text{C}_7\text{H}_8$  solvate molecule, and one orientation of the disordered  $[\eta^2\text{-SO}]^{2-}$  ligand have been omitted for clarity. Selected metrical parameters: S1–O1 1.656(3) Å, Ni1–S1 2.127(1) Å, Ni1–O1 1.954(3) Å, Ni1–N1 1.881(4) Å, Ni1–N2 1.900(4) Å, S1–K1 3.162(2) Å, O1–K1 2.881(3) Å, N1–Ni1–N2 99.2(2)°, N1–Ni1–S1 110.0(1)°, N2–Ni1–O1 103.2(1)°, S1–Ni1–O1 47.65(9)°.

$\text{Fe}_3(\text{S})_2(\text{CO})_9$ ,<sup>29</sup> a manner of preparation that is similar to that of **1**. Interestingly, Mankad and co-workers suggest that a transient SO complex is formed upon reaction of  $[(\text{IPr}^*)\text{Cu}]_2(\mu\text{-S})$  with  $\text{N}_2\text{O}$ ,<sup>30</sup> a transformation that parallels our conversion of **I** to **II** and then **1**.

As mentioned above, we also observe formation of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-OSSO})]$  (**2**), as a minor side product, during the conversion of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-SNNO})]$  to **1**. Despite its presence in trace amounts, we have been able to obtain a few single crystals of **2** as orange plates from the reaction mixture. The solid state molecular structure of **2** is shown in Fig. 2. It features the first example of a co-planar  $[\text{OSSO}]^{2-}$  ligand (OSSO dihedral angle = 2°). The  $[\eta^2\text{-OSSO}]^{2-}$  ligand in **2** is bound to the Ni center in an  $\eta^2$  fashion, *via* both sulfur atoms, while the O atoms are bound to the  $[\text{K}(18\text{-crown-6})]^+$  cation in a  $\kappa^2$  fashion. Its S–S distance is 2.093(3) Å, while the S–O distances are 1.485(5) and 1.496(7) Å. For comparison, the S–S (2.0245(6) Å) and S–O (1.458(2) Å) distances in free  $\text{S}_2\text{O}_2$  are shorter than those observed for **2**,<sup>31–33</sup> consistent with the reduced S–S and S–O bond orders anticipated for the  $[\text{OSSO}]^{2-}$  fragment in the former.<sup>31,34,35</sup> Notably, complex **2** is only the third OSSO complex to be reported and only second to be structurally characterized.<sup>29,36–38</sup>

To account for the presence of **2** in the reaction mixture, we hypothesize that complex **1** undergoes a formal disproportionation, forming **2** and an equivalent of unobserved  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^0]$ . However, because of the low yield (typically less than 3% relative to complex **1**, as assessed by  $^1\text{H}$  NMR spectroscopy), this transformation must be very inefficient. The low yield has also impeded our ability to fully characterize this complex.



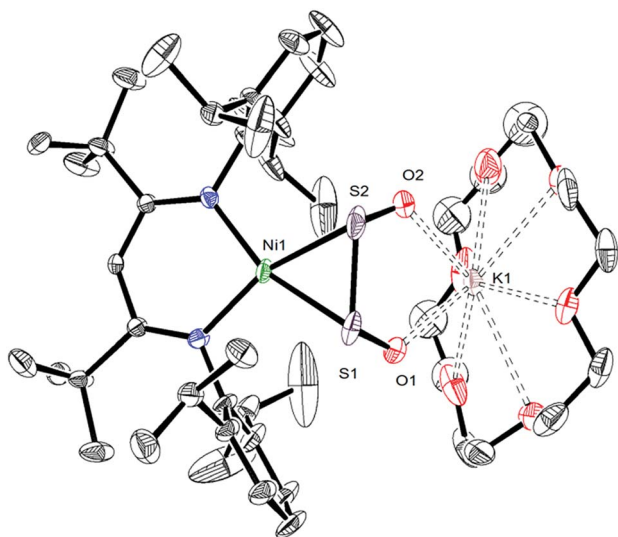


Fig. 2 ORTEP drawing of  $[K(18\text{-crown-}6)][L^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-OSSO})]\cdot 2\text{C}_6\text{H}_{14}$  ( $2\cdot 2\text{C}_6\text{H}_{14}$ ) shown with 50% thermal ellipsoids. Hydrogen atoms and  $\text{C}_6\text{H}_{14}$  solvate molecules have been omitted for clarity. Selected metrical parameters: S1–S2 2.093(3) Å, S1–O1 1.485(5) Å, S2–O2 1.496(7) Å, Ni1–S1 2.181(2) Å, Ni1–S2 2.173(2) Å, Ni1–N1 1.920(4) Å, Ni1–N2 1.925(4) Å, O1–K1 2.747(4) Å, O2–K1 2.777(6) Å, N1–Ni1–N2 97.3(2)°, N1–Ni1–S1 102.1(1)°, N2–Ni1–S2 102.9(1)°, O1–S1–S2 107.4(2)°, O2–S2–S1 107.4(2)°.

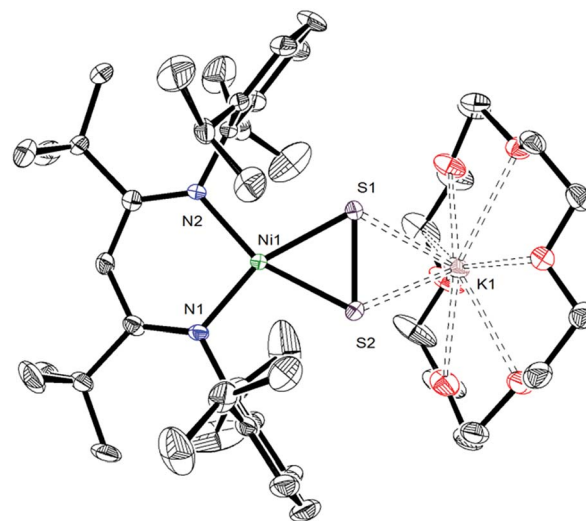


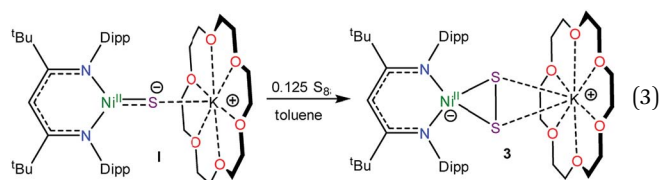
Fig. 3 ORTEP drawing of  $[K(18\text{-crown-}6)][L^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-S}_2)]\cdot 2\text{C}_7\text{H}_8$  ( $3\cdot 2\text{C}_7\text{H}_8$ ) shown with 50% thermal ellipsoids. Hydrogen atoms and  $\text{C}_7\text{H}_8$  solvate molecules have been omitted for clarity. Selected metrical parameters: S1–S2 2.050(2) Å, Ni1–S1 2.202(2) Å, Ni1–S2 2.199(2) Å, Ni1–N1 1.900(4) Å, Ni1–N2 1.906(4) Å, S1–K1 3.248(2) Å, S2–K1 3.249(2) Å, N1–Ni1–N2 98.0(2)°, N1–Ni1–S2 103.1(1)°, N2–Ni1–S1 103.4(1)°.

### Synthesis of an $[\eta^2\text{-S}_2]^{2-}$ complex

To further support the formation of the disulfide ( $[\eta^2\text{-S}_2]^{2-}$ ) complex,  $[K(18\text{-crown-}6)][L^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-S}_2)]$  (**3**), during the synthesis of **1**, we endeavored to independently synthesize **3**. We, and others, have previously shown that terminal metal sulfides can react with  $\text{S}_8$  to form metal disulfides.<sup>39–41</sup> Thus, we explored the reaction of  $[K(18\text{-crown-}6)][L^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$  (**I**) with elemental sulfur. Addition of 0.125 equiv. of  $\text{S}_8$  to a toluene solution of  $[K(18\text{-crown-}6)][L^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$  results in a rapid color change from brown to orange. Work-up of the reaction mixture affords  $[K(18\text{-crown-}6)][L^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-S}_2)]$  (**3**), as an orange crystalline solid in 81% yield (eqn (3)). The solid state molecular structure of **3** is shown in Fig. 3. The disulfide ( $\text{S}_2^{2-}$ ) ligand in **3** has a S–S distance of 2.050(2) Å, consistent with a single bond.<sup>18</sup> This distance is comparable to those reported for other  $\text{Ni}^{\text{II}}(\eta^2\text{-S}_2)$  complexes.<sup>42–49</sup> The Ni–S distances (2.202(2) and 2.199(2) Å) in **3** are consistent with single bonds, and are much longer than the Ni–S bond length in the starting material (**I**, 2.064(2) Å). Finally, the Ni–N bonds in **3** are similar to those found in other square planar  $\text{Ni}^{\text{II}}$   $\beta$ -diketiminato complexes.<sup>16,49,50</sup>

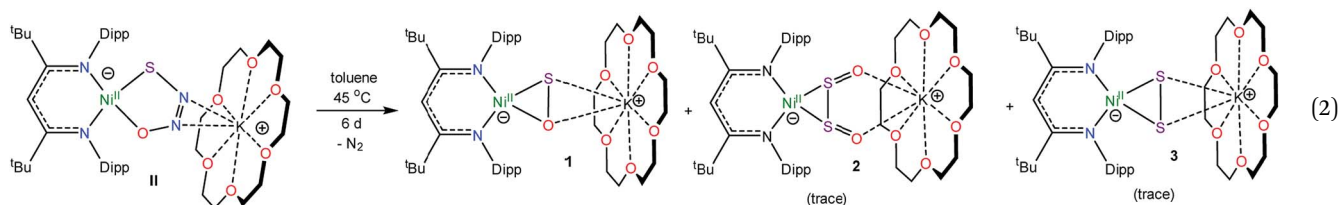
The  $^1\text{H}$  NMR spectrum of **3** in toluene- $d_8$  (Fig. S7†) is consistent with a  $C_{2v}$  symmetric, diamagnetic, square planar

$\text{Ni}^{\text{II}}$  complex and features one *tert*-butyl resonance at 1.30 ppm and a single  $\gamma\text{-CH}$  resonance at 5.46 ppm. Importantly, this latter resonance is also present in the *in situ*  $^1\text{H}$  NMR spectrum of the thermolysis of **II** (Fig. S3†), confirming the formation of **3** during that reaction, *via* an as-yet-unknown mechanism.



### Reactivity of the $[\eta^2\text{-SO}]^{2-}$ ligand

While the reactivity of the SO ligand has not been well established, it is known to react with phosphines. For example, Schmid and co-workers reported that  $[(\text{diphos})_2\text{Ir}(\eta^2\text{-OSSO})][\text{Cl}]$  reacted with  $\text{PPh}_3$  to form  $\text{Ph}_3\text{PO}$ ,  $\text{Ph}_3\text{PS}$ , and  $[(\text{diphos})_2\text{IrCl}]$ .<sup>36</sup> Similarly, Rauchfuss and co-workers demonstrated that  $\text{Cp}_2\text{-Nb}(\text{S}_2\text{O})\text{Cl}$  reacted with  $\text{Ph}_3\text{P}$  to form  $\text{Cp}_2\text{Nb}(\text{O})\text{Cl}$  and two equiv. of  $\text{Ph}_3\text{PS}$ .<sup>29</sup> Both transformations were presumed to proceed through an unobserved SO intermediate. More recently, Mizobe *et al.* reported that  $\text{PPh}_3$  could abstract an O-atom from the





thioperoxide ligand in  $[(\text{Cp}'\text{RuCl})_2(\text{SbCl}_2)(\mu\text{-Cl})(\mu_3\text{-}\kappa^2\text{-SO})]$  ( $\text{Cp}' = \text{C}_5\text{Me}_4\text{Et}$ ).<sup>25</sup> In contrast, the reactivity of the SO ligand with CO has not been studied. Accordingly, we explored the reactivity of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$  (**1**) with this substrate. Thus, exposure of a  $\text{C}_6\text{D}_6$  solution of complex **1** to an atmosphere of  $^{13}\text{C}$  results in complete consumption of **1** after 6 h. A  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (Fig. S11†) of the reaction mixture reveals the formation of several  $^{13}\text{C}$ -enriched products, indicating the incorporation of  $^{13}\text{C}$ . Specifically, this spectrum features resonances at 214.7, 177.3, 165.3, and 152.9 ppm, which are assignable to  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SCO})]$  (**4**),<sup>51</sup>  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S},\text{O}:\kappa^2\text{-SCO}_2)]$  (**5**),  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]$  (**6**), and SCO (**7**),<sup>52</sup> respectively (Scheme 1). This spectrum also features a minor  $^{13}\text{C}$ -enriched resonance at 206.9 ppm, which we have tentatively assigned to  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S}_2\text{CO})]$  (**8**), on the basis of the similarity of its dithiocarbonate ( $[\text{S}_2\text{CO}]^{2-}$ ) chemical shift with those reported for other dithiocarbonate complexes.<sup>52–54</sup>

A  $^1\text{H}$  NMR spectrum of the reaction mixture further supports these assignments. Specifically, an examination of the  $\gamma\text{-CH}$  region of this spectrum reveals overlapping resonances at 5.48 ppm (Fig. S10†), which are assignable to  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SCO})]$  (**4**)<sup>51</sup> and  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S},\text{O}:\kappa^2\text{-SCO}_2)]$  (**5**), and a resonance at 5.42 ppm, assignable to  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]$  (**6**). This spectrum also contains a minor resonance at 5.57 ppm that has been tentatively assigned to  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S}_2\text{CO})]$  (**8**). Interestingly, at short reaction times, we observe the presence of a paramagnetic intermediate in the reaction mixture (Fig. S9†). We have identified this intermediate as the  $\text{Ni}^{\text{II}}$  sulfide,  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$  (**1**), on the basis of the similarity of its  $^1\text{H}$  NMR resonances with those of the previously characterized material.<sup>16</sup> For example, this intermediate features diagnostic resonances at  $-130.25$ ,  $-0.63$ , and  $5.87$  ppm, which are assignable to the  $\gamma$ -proton of the  $\text{L}^{\text{tBu}}$  ligand, its  $^t\text{Bu}$  substituents, and one environment of its diastereotopic  $^i\text{Pr}$  methyl groups, respectively. For comparison, these resonances appear at  $-115.21$ ,  $-0.88$ , and  $6.56$  ppm, respectively, for authentic **1**.<sup>16</sup> This intermediate is quickly formed upon addition of  $^{13}\text{C}$ , but its signals immediately begin to decay, and they are completely absent after 6 h (Fig. S9†).

We also characterized the products of the reaction of **1** and CO by IR spectroscopy. An IR spectrum of the reaction residue, dissolved in hexanes, reveals the presence of  $\nu_{\text{CO}}$  modes at 2021, 1666, and  $1620\text{ cm}^{-1}$  (Fig. S24†), which are assignable to the  $\nu_{\text{CO}}$

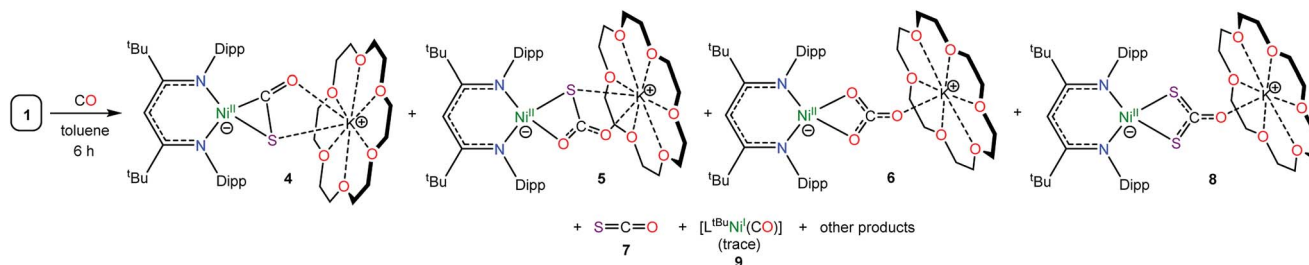
modes of  $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{CO})]$  (**9**),<sup>55</sup>  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SCO})]$  (**4**),<sup>51</sup> and  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]$  (**6**), respectively. Curiously, though, we do not observe any signals in the  $^1\text{H}$  NMR spectrum of the reaction mixture that could be assigned to paramagnetic **9**, suggesting that it is only a minor product of the reaction.

The  $^{13}\text{C}$  NMR spectrum of the *in situ* reaction mixture also features a minor  $^{13}\text{C}$ -enriched resonance at 178.5, as well as a major resonance at 191.4 ppm (Fig. S11†). While these two resonances remain unassigned, we know that neither of the peaks is assignable to  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-CO}_2)]$  (**10**), as we have performed the independent synthesis of this complex for spectroscopic comparison (see below). We also do not observe a resonance that could be assignable to free  $\text{CO}_2$ .

Finally, we observe no reaction between  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$  (**1**) and  $\text{PPh}_3$  in  $\text{C}_6\text{D}_6$ , according to  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopies. The lack of reactivity of the  $[\text{SO}]^{2-}$  ligand in **1** with  $\text{PPh}_3$  is somewhat surprising on the basis of thermodynamic considerations,<sup>56</sup> and could reflect steric shielding of the  $[\text{SO}]^{2-}$  ligand by the bulky Dipp substituents.

### Synthesis of an $[\text{S},\text{O}:\kappa^2\text{-SCO}_2]^{2-}$ complex

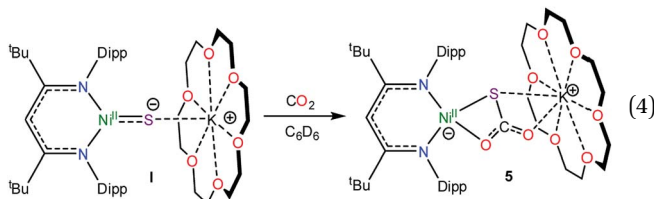
To further support the formation of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S},\text{O}:\kappa^2\text{-SCO}_2)]$  (**5**) upon reaction of **1** with CO, we pursued its synthesis *via* an independent route. Thus, exposure of a  $\text{C}_6\text{D}_6$  solution of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$  (**1**) to excess carbon dioxide ( $\text{CO}_2$ ) results in a rapid color change from deep brown to gold. The  $^1\text{H}$  NMR spectrum of the reaction mixture taken 15 min after addition of  $\text{CO}_2$  reveals full consumption of the starting material and formation of a new diamagnetic product whose spectroscopic signatures are consistent with a square planar  $\text{Ni}^{\text{II}}$  complex.<sup>51</sup> Work-up of the reaction mixture provides **5** as a pale brown crystalline solid in 57% yield (eqn (4)). The solid state molecular structure of **5** is shown in Fig. 4. The thio-carbonate ( $[\text{S},\text{O}:\kappa^2\text{-SCO}_2]^{2-}$ ) ligand in **5** features a  $\mu:\kappa^2$  binding mode and is disordered over two positions, which are related by a  $C_2$  rotation about the Ni–K vector, in a 87 : 13 ratio. The S–C (1.756(4) Å) and O–C (1.279(5) and 1.238(4) Å) bond lengths in **5** are consistent with those observed for previously reported  $[\text{SCO}_2]^{2-}$  complexes,<sup>57,58</sup> while the Ni–S and Ni–O distances are 2.234(1) Å and 1.922(3) Å, respectively. Moreover, the K–S and K–O distances are 3.531(1) Å and 2.715(3) Å, respectively, which are comparable to other K–S and K–O dative interactions.<sup>59,60</sup> Finally, the Ni–N distances in **5** are comparable to those found in the starting material.<sup>16</sup> To the best of our



Scheme 1



knowledge, complex **5** is the first structurally characterized transition metal complex containing the  $[\text{S},\text{O}:\kappa^2\text{-SCO}_2]^{2-}$  ligand. Other structurally characterized thiocarbonate complexes include  $\{[(\text{ArO})_3\text{N}]\text{U}\}_2(\mu\text{-}\eta^1,(\text{O}):\kappa^2(\text{O},\text{S})\text{SCO}_2)$ , prepared by reaction of  $\{[(\text{ArO})_3\text{N}]\text{U}\}_2(\mu\text{-S})$  with  $\text{CO}_2$ , and  $[\text{Cp}^*\text{Sm}(\mu\text{-}\eta^1:\kappa^2\text{-SCO}_2)\text{SmCp}^*]_2$ , prepared *via* reaction of  $[(\text{Cp}^*\text{Sm})_2(\mu\text{-O})]$  with  $\text{COS}$ .<sup>57,58</sup>



The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **5** in benzene- $d_6$  features a resonance at 177.3 ppm, which we have assigned to the  $[\text{S},\text{O}:\kappa^2\text{-SCO}_2]^{2-}$  moiety (Fig. S13<sup>†</sup>). This chemical shift is identical to the resonance assigned to this complex in the *in situ*  $^{13}\text{C}$  NMR spectrum of the reaction of **1** with  $\text{CO}$  (Fig. S11<sup>†</sup>). Moreover, the  $^1\text{H}$  NMR spectrum of **5** in  $\text{C}_6\text{D}_6$  features a  $\gamma\text{-CH}$  resonance at 5.48 ppm. This resonance is also present in the *in situ*  $^1\text{H}$  NMR spectrum of the reaction mixture of **1** and  $^{13}\text{CO}$  (Fig. S10<sup>†</sup>), further confirming its formation in that transformation. Overall, these data conclusively demonstrate that complex **5** is formed during reduction of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$  (**1**) with  $\text{CO}$ .

### Synthesis of an $[\kappa^2\text{-CO}_3]^{2-}$ complex

To further support the formation of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}(\kappa^2\text{-CO}_3)]$  (**6**) upon reaction of **1** with  $\text{CO}$ , we pursued its synthesis

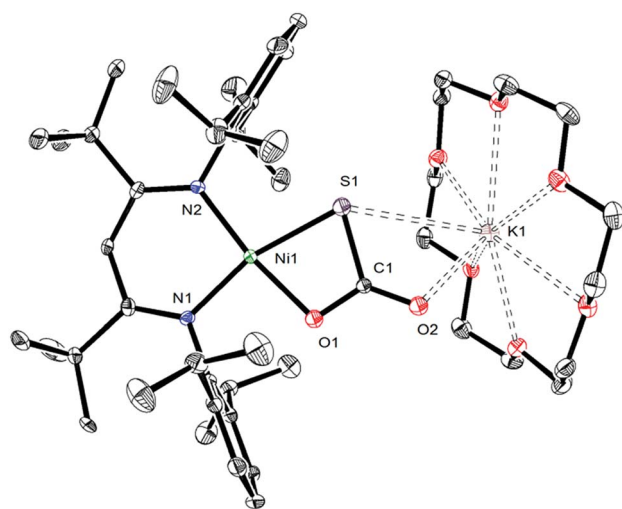
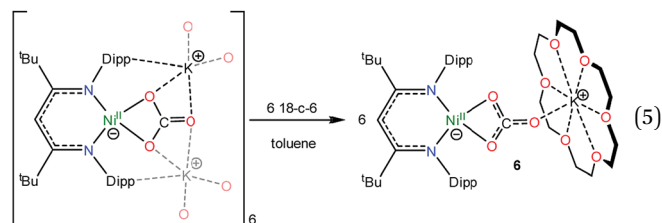


Fig. 4 ORTEP drawing of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S},\text{O}:\kappa^2\text{-SCO}_2)]\cdot 1.5\text{C}_7\text{H}_8$  ( $5\cdot 1.5\text{C}_7\text{H}_8$ ) shown with 50% thermal ellipsoids. Hydrogen atoms,  $\text{C}_7\text{H}_8$  solvate molecules, and one orientation of the disordered  $[\text{S},\text{O}:\kappa^2\text{-SCO}_2]^{2-}$  ligand have been omitted for clarity. Selected metrical parameters: S1–C1 1.756(4) Å, O1–C1 1.279(5) Å, O2–C1 1.238(4) Å, Ni1–S1 2.234(1) Å, Ni1–O1 1.922(3) Å, Ni1–N1 1.904(3) Å, Ni1–N2 1.899(3) Å, S1–K1 3.531(1) Å, O2–K1 2.715(3) Å, S1–C1–O1 108.0(3)°, S1–C1–O2 126.2(3)°, O1–C1–O2 125.9(4)°, N1–Ni1–N2 96.7(1)°, N1–Ni1–O1 91.5(1)°, N2–Ni1–S1 99.22(9)°.

*via* an independent route. The hexameric nickel carbonate complex,  $[\text{K}]_6[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]_6$ ,<sup>11</sup> first reported by Limberg and coworkers in 2012, was found to serve as a convenient starting material for the synthesis of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]$  (**6**). Addition of 6 equiv. of 18-crown-6 to a suspension of  $[\text{K}]_6[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]_6$  results in the formation of complex **6** in 52% yield (eqn (5)). Its solid state molecular structure is shown in Fig. 5. The carbonate ( $\text{CO}_3^{2-}$ ) ligand in **6** features a  $\mu:\kappa^2,\eta^1$  binding mode, identical to that observed for the trithiocarbonate ( $\text{CS}_3^{2-}$ ) ligand in  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}(\kappa^2\text{-CS}_3)]$ .<sup>50</sup> The O1–C1 (1.306(7) Å), O2–C1 (1.309(7) Å), and O3–C1 (1.242(7) Å) bond lengths in **6** are consistent with those reported for  $[\text{K}]_6[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]_6$ ,<sup>11</sup> while the Ni–O1 and Ni–O2 distances are 1.882(4) and 1.901(4) Å, respectively, which are similar to those reported for the starting material.



The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **6** in  $\text{C}_6\text{D}_6$  features a resonance at 165.3 ppm, which is assignable to the  $[\text{CO}_3]^{2-}$  moiety (Fig. S15<sup>†</sup>). This chemical shift matches the resonance assigned to this complex in the *in situ*  $^{13}\text{C}$  NMR spectrum of the reaction mixture of **1** and  $^{13}\text{CO}$  (Fig. S11<sup>†</sup>). In addition, the  $^1\text{H}$  NMR spectrum of **6** in  $\text{C}_6\text{D}_6$  features a  $\gamma\text{-CH}$  resonance at 5.42 ppm,

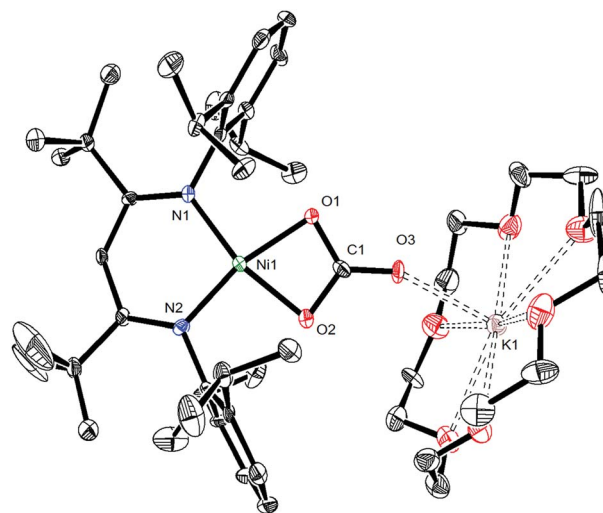


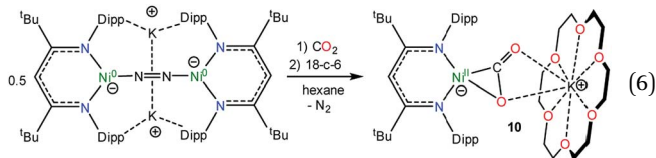
Fig. 5 ORTEP drawing of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]\cdot 0.5\text{C}_5\text{H}_{12}$  ( $6\cdot 0.5\text{C}_5\text{H}_{12}$ ) shown with 50% thermal ellipsoids. Hydrogen atoms, a  $\text{C}_5\text{H}_{12}$  solvate molecule, and a second independent molecule of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]$  have been omitted for clarity. Selected metrical parameters: C1–O1 1.306(7) Å, C1–O2 1.309(7) Å, C1–O3 1.242(7) Å, Ni1–O1 1.882(4) Å, Ni1–O2 1.901(4) Å, Ni1–N1 1.883(5) Å, Ni1–N2 1.879(5) Å, O3–K1 2.510(4) Å, O1–C1–O2 110.8(5)°, O1–C1–O3 125.0(6)°, N1–Ni1–N2 97.9(2)°, N1–Ni1–O1 96.6(2)°, N2–Ni1–O2 96.5(2)°.



which is present in the *in situ*  $^1\text{H}$  NMR spectrum of the reaction mixture of **1** and  $^{13}\text{CO}$  (Fig. S10†). The IR spectrum (hexanes solution) of **6** features a strong  $\nu_{\text{CO}}$  mode at  $1620\text{ cm}^{-1}$ , which is also present in a solution IR spectrum of the reaction mixture formed upon addition of CO to **1** (Fig. S24†). Overall, these data conclusively demonstrate that complex **6** is formed during reduction of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$  (**1**) with CO.

### Synthesis of an $[\eta^2\text{-CO}_2]^{2-}$ complex

In an effort to assign the resonance at 191.4 ppm in the *in situ*  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the reaction of **1** and  $^{13}\text{CO}$ , we endeavored to independently synthesize the carbon dioxide complex,  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-CO}_2)]$  (**10**). We rationalized that **10** was a plausible reaction product, given the formation of  $\text{CO}_2$  during the reaction (see below). Several previously reported  $\text{Ni}(\text{CO}_2)$  complexes have been synthesized by reaction of  $\text{CO}_2$  with a  $\text{Ni}^0$  precursor.<sup>61–64</sup> In a similar vein, the  $\text{Ni}(0)\text{-N}_2$  complex,  $[\text{K}]_2[\text{L}^{\text{tBu}}\text{Ni}^0(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)\text{Ni}^0\text{L}^{\text{tBu}}]$ , previously reported by Limberg and co-workers in 2009,<sup>65</sup> was found to serve as an effective  $\text{Ni}^0$  source for the synthesis of **10**. Thus, exposure of  $[\text{K}]_2[\text{L}^{\text{tBu}}\text{Ni}^0(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)\text{Ni}^0\text{L}^{\text{tBu}}]$  to two equiv. of  $\text{CO}_2$ , followed by addition of 18-crown-6, resulted in the formation of **10** (eqn (6)), which was isolated as pale orange plates in 41% yield after work-up. Its formulation was confirmed by X-ray crystallography and its solid state molecular structure is shown in Fig. 6.



Complex **10** features a square planar  $\text{Ni}^{\text{II}}$  center ligated by the  $\beta$ -diketiminato ligand and a  $[\text{CO}_2]^{2-}$  ligand. The  $[\text{CO}_2]^{2-}$  ligand in **10** features a  $\mu\text{:}\eta^2\text{:}\kappa^2$  binding mode, similar to that observed for the  $[\text{COS}]^{2-}$  ligand in complex **4**. The  $[\text{CO}_2]^{2-}$  ligand in **10** is disordered over two positions, in a 76 : 24 ratio, which are related by a  $C_2$  rotation axis about the Ni–K vector. The Ni1–O1 (1.897(6) Å) and Ni1–C1 (1.890(6) Å) distances are consistent with those previously reported for the  $\text{Ni}(\eta^2\text{-CO}_2)$  fragment.<sup>61,62,64,66,67</sup> Additionally, the Ni–N bonds in **10** are consistent with those found in other square planar  $\text{Ni}^{\text{II}}$   $\beta$ -diketiminato complexes.<sup>16,49,50</sup>

The  $^1\text{H}$  NMR spectrum of **10** in  $\text{C}_6\text{D}_6$  is consistent with that expected for a  $C_s$  symmetric, square planar  $\text{Ni}^{\text{II}}$  complex. It features two *tert*-butyl resonances at 1.42 and 1.34 ppm, and a single  $\gamma$ -CH resonance at 5.42 ppm. Its  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum in  $\text{C}_6\text{D}_6$  features a resonance at 167.2 ppm, which we have assigned to the  $[\eta^2\text{-CO}_2]^{2-}$  ligand. This chemical shift is consistent with those reported for previously isolated  $\text{Ni}(\eta^2\text{-CO}_2)$  complexes.<sup>62–64</sup> Most importantly, however, these resonances are not observed in the *in situ*  $^{13}\text{C}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra of the reaction between **1** and  $^{13}\text{CO}$  (Fig. S10 and 11†). Thus, we can definitively conclude that complex **10** is not being formed in that reaction. Finally, complex **10** features a  $\nu_{\text{CO}}$  mode at  $1664\text{ cm}^{-1}$  in its IR spectrum (KBr pellet), which is

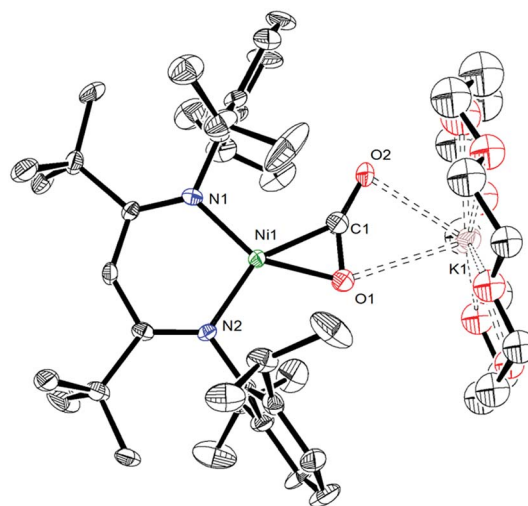


Fig. 6 ORTEP drawing of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-CO}_2)]\cdot 2\text{C}_6\text{H}_6$  (**10**· $2\text{C}_6\text{H}_6$ ) shown with 50% thermal ellipsoids. Hydrogen atoms,  $\text{C}_6\text{H}_6$  solvate molecules, and second orientations of the  $\text{CO}_2$  and 18-crown-6 fragments have been omitted for clarity. Selected metrical parameters: C1–O1 1.231(9) Å, C1–O2 1.221(1) Å, Ni1–C1 1.890(6) Å, Ni1–O1 1.897(6) Å, Ni1–N1 1.901(6) Å, Ni1–N2 1.896(5) Å, O1–K1 2.980(6) Å, O2–K1 2.71(1) Å, O1–C1–O2 144.0(8)°, N1–Ni1–N2 99.2(2)°, N1–Ni1–C1 112.2(3)°, N2–Ni1–O1 110.7(3)°.

similar to those reported for other nickel  $\text{CO}_2$  complexes.<sup>62–64</sup> This vibration is also not present in the *in situ* IR spectrum (recorded in hexanes) of the reaction residue formed upon reaction of **1** with CO (Fig. S24†).

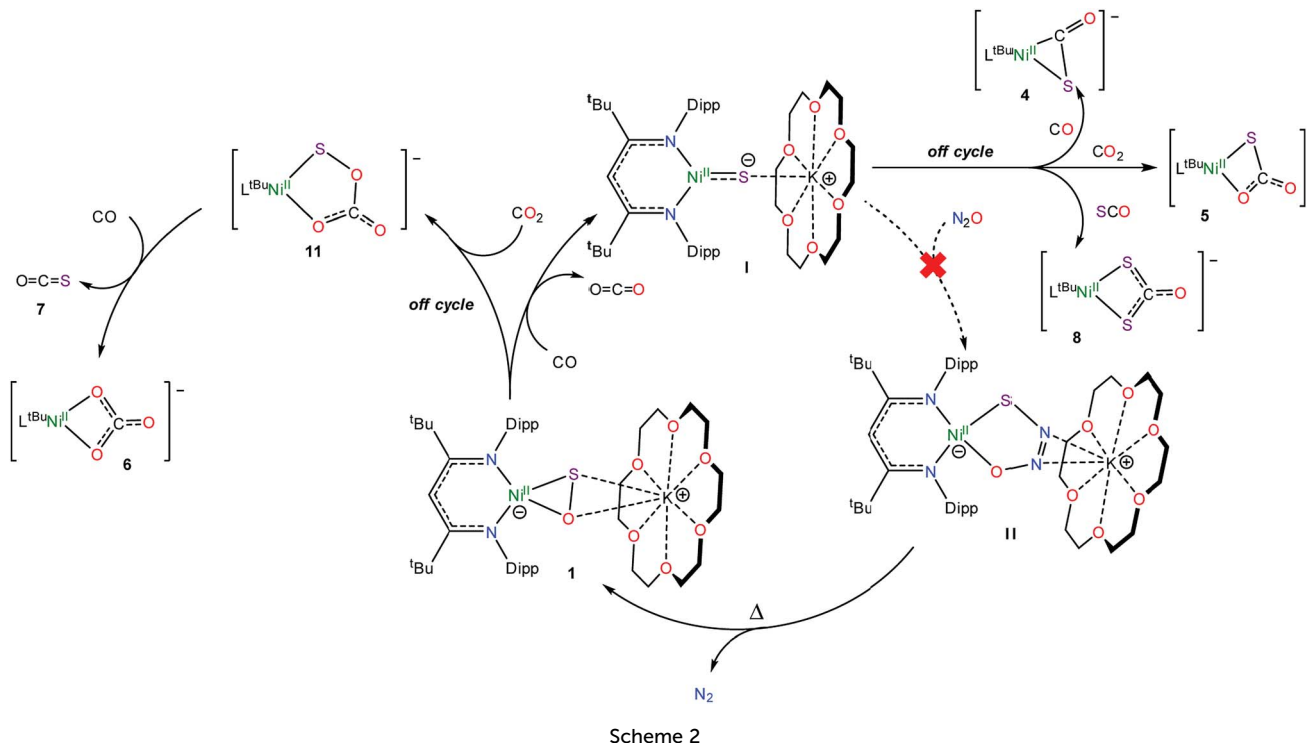
### Mechanistic considerations

To rationalize the formation of complexes **4** and **5**, we propose that CO initially reacts with **1** to form  $\text{CO}_2$  and  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$  (**I**) (Scheme 2). Complex **I** then reacts with either CO or  $\text{CO}_2$  to yield  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SCO})]$  (**4**) or  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S},\text{O}:\kappa^2\text{-SCO}_2)]$  (**5**), respectively. Significantly, their presence, along with the observation of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$  (**I**) in the reaction mixture, demonstrates the formal reduction of  $\text{N}_2\text{O}$  by CO, as originally envisioned. That said, the reaction rates of **I** with CO and  $\text{CO}_2$  are qualitatively similar to the reaction rate of **I** with  $\text{N}_2\text{O}$ . As a consequence, **I** is unlikely to be an effective catalyst for  $\text{N}_2\text{O}$  reduction because off-cycle reactions with CO and  $\text{CO}_2$  would be competitive with the desired  $\text{N}_2\text{O}$  capture reaction (Scheme 2).

To rationalize the formation of complex **6** and COS, we propose that reaction of the newly formed  $\text{CO}_2$  with unreacted **1** results in the formation of a transient, unobserved nickel monothiothiocarbonate complex,  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-SOCO}_2)]$  (**11**). Complex **11** then transfers a sulfur atom to CO to form  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]$  (**6**) and COS (**7**) (Scheme 2), both of which were confirmed to be present in the *in situ* reaction mixture. This hypothesis also nicely explains the presence of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-S}_2\text{CO})]$  (**8**), which could be formed *via* the reaction of **7** with **I** (Scheme 2). While a monothiothiocarbonate complex has not been previously reported, the reaction of metal peroxides ( $\text{O}_2^{2-}$ ) with  $\text{CO}_2$  is

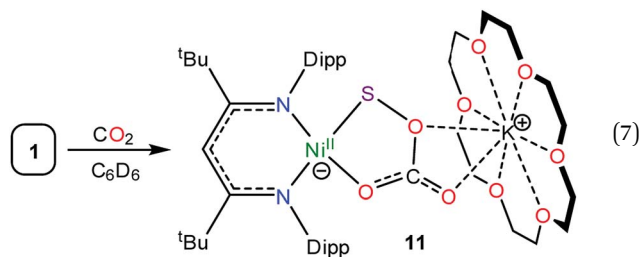






known to yield peroxocarbonate ( $[\text{OOCO}_2]^{2-}$ ) complexes.<sup>68–71</sup> Similarly, metal disulfides ( $\text{S}_2^{2-}$ ) are known to react with  $\text{CS}_2$  to form perthiocarbonates ( $[\text{SSCS}_2]^{2-}$ ).<sup>72,73</sup> Moreover, peroxocarbonates are known to be very effective O-atom donors.<sup>69,74–77</sup>

Consistent with this hypothesis, reaction of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$  (**1**) with  $\text{CO}_2$  in  $\text{C}_6\text{D}_6$  results in the rapid formation of a new diamagnetic  $\text{Ni}^{\text{II}}$  complex, as evidenced by the appearance of diagnostic resonances at 4.49 ppm ( $\gamma\text{-CH}$ ) and 1.20 ppm ( $t\text{Bu}$ ) in the *in situ*  $^1\text{H}$  NMR spectrum of the reaction mixture (Fig. S18†). We have assigned these resonances to the monothiothiocarbonate complex  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-SOCO}_2)]$  (**11**) (eqn (7)). Complex **11** is the only product observed in the reaction mixture. These results provide further support for the overall reaction mechanism proposed in Scheme 2 and suggest that  $(\text{SOCO}_2)^{2-}$  could function as a very effective a S-atom transfer reagent.<sup>78</sup>



## Conclusions

Gentle thermolysis of the thiohyponitrite complex,  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-SNNO})]$ , results in extrusion of  $\text{N}_2$  and formation of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$ , a rare example of

a structurally characterized SO complex, along with trace amounts of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-OSSO})]$  and  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-S}_2)]$ .  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$  reacts rapidly with CO, forming the “masked” terminal  $\text{Ni}(\text{II})$  sulfide intermediate,  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$ , along with  $\text{CO}_2$ , *via* O-atom abstraction. This  $\text{Ni}(\text{II})$  sulfide intermediate then reacts with CO or  $\text{CO}_2$  to form  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SCO})]$  and  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S},\text{O}:\kappa^2\text{-SCO}_2)]$ , respectively.  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$  can also react with the newly formed  $\text{CO}_2$  to form a putative monothiothiocarbonate complex,  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-SOCO}_2)]$ , which can then transfer an S atom to CO, forming COS and  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]$ .

Significantly, the observation of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$  in the reaction mixture, along with the formation of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SCO})]$  and  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S},\text{O}:\kappa^2\text{-SCO}_2)]$ , confirms that the SO ligand is susceptible to O-atom abstraction by CO, which had not been previously demonstrated. More importantly, these reaction products reveal the stepwise conversion of  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-SNNO})]$  to  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]$  and then  $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$ , which represents a formal reduction of  $\text{N}_2\text{O}$  by CO, forming  $\text{N}_2$  and  $\text{CO}_2$ . Significantly, this transformation parallels the chemistry mediated by nano-particulate Pt/Rh in catalytic converters. In contrast to the metal-centered redox of the catalytic converter example, however, the redox chemistry in our system occurs at the sulfide ligand, while the nickel center remains in the 2+ oxidation state at every step. The use of ligand-centered redox is an intriguing strategy for  $\text{N}_2\text{O}$  reduction and we suggest that the study of model systems, such as the one presented in this manuscript, could inspire the design of a new generation of homogeneous and heterogeneous  $\text{N}_2\text{O}$  reduction catalysts.



## Conflicts of interest

The authors declare no competing financial interests.

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