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Synthesis and reactivity of a nickel(II) thioperoxide complex: demonstration of sulfide-mediated N₂O reduction†

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The thiohyponitrite ([SNNO]²⁻) complex, [K(18-crown-6)][L^{tBu}Ni^{II}(κ²-SNNO)] (L^{tBu} = ((2,6-ⁱPr₂C₆H₃)NC(^tBu)₂CH), extrudes N₂ under mild heating to yield [K(18-crown-6)][L^{tBu}Ni^{II}(η²-SO)] (**1**), along with minor products [K(18-crown-6)][L^{tBu}Ni^{II}(η²-OSSO)] (**2**) and [K(18-crown-6)][L^{tBu}Ni^{II}(η²-S₂)] (**3**). Subsequent reaction of **1** with carbon monoxide (CO) results in the formation of [K(18-crown-6)][L^{tBu}Ni^{II}(η²-SCO)] (**4**), [K(18-crown-6)][L^{tBu}Ni^{II}(S,O:κ²-SCO₂)] (**5**), [K(18-crown-6)][L^{tBu}Ni^{II}(κ²-CO₃)] (**6**), carbonyl sulfide (COS) (**7**), and [K(18-crown-6)][L^{tBu}Ni^{II}(S₂CO)] (**8**). To rationalize the formation of these products we propose that **1** first reacts with CO to form [K(18-crown-6)][L^{tBu}Ni^{II}(S)] (**I**) and CO₂, via O-atom abstraction. Subsequently, complex **I** reacts with CO or CO₂ to form **4** and **5**, respectively. Similarly, the formation of complex **6** and COS can be rationalized by the reaction of **1** with CO₂ to form a putative Ni(II) monothio-percarbonate, [K(18-crown-6)][L^{tBu}Ni^{II}(κ²-SOCO₂)] (**11**). The Ni(II) monothio-percarbonate subsequently transfers a S-atom to CO to form COS and [K(18-crown-6)][L^{tBu}Ni^{II}(κ²-CO₃)] (**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^{tBu}Ni^{II}(κ²-SNNO)] to **1** and then **I**, which represents the formal reduction of N₂O by CO.

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Introduction

Nitrous oxide (N₂O) features a long atmospheric lifetime and large global warming potential (*ca.* 300 times larger than CO₂), making it an important greenhouse gas.^{1–4} Anthropogenic sources of N₂O include agriculture, fossil fuel combustion, adipic acid synthesis, and nitric acid production.^{1,5} The latter two sources use on-site N₂O mitigation to remove N₂O from the effluent stream, either by decomposition to the elements⁶ or reduction to N₂ and H₂O, but neither of these methods is completely effective and some N₂O is still released into the atmosphere.⁷

Given the above considerations, the development of new catalysts for N₂O reduction could help reduce its impact on global temperatures.^{1,8} Not surprisingly, a large number of heterogeneous systems have been developed to catalyze this reaction.⁹ 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 N₂O, forming N₂

and CO₂.⁹ Sita and co-workers developed a homogeneous version of this transformation, mediated by the Mo(II) complex, Cp*Mo(NCN)(CO)₂ (NCN = ⁱPrNC(Me)NⁱPr).¹⁰ In this process, N₂O oxidizes Cp*Mo(NCN)(CO)₂ to form a Mo(IV) oxo, Cp*Mo(NCN)(O), which then reacts with CO to form CO₂ and regenerate Cp*Mo(NCN)(CO)₂. 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]₂[L^{tBu}Ni⁰(CO)]₂, with N₂O to form a carbonate complex, [K]₆[L^{tBu}Ni^{II}(CO₃)]₆, and N₂.¹¹ Subsequent release of carbonate from the metal center was not discussed. The homogeneous hydrogenation of N₂O has also been explored.^{12,13} For example, in 2015 Piers and co-workers reported an Ir(III) pincer carbene complex that could hydrogenate N₂O;¹⁴ 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-[CH₂PⁱPr₂]₂(C₅H₃N)), was an effective catalyst for the hydrogenation of N₂O, achieving a turnover number of *ca.* 400.¹⁵

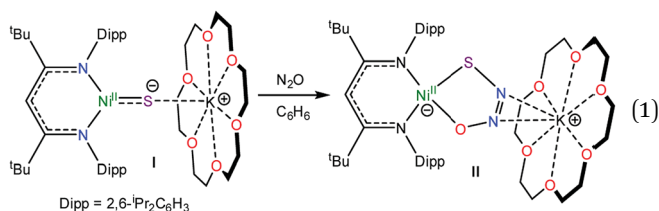
Recently, we reported the activation of N₂O by the “masked” terminal nickel sulfide complex, [K(18-crown-6)][L^{tBu}Ni^{II}(S)] (**I**) (L^{tBu} = ((2,6-ⁱPr₂C₆H₃)NC(^tBu)₂CH), which yielded an unprecedented thiohyponitrite complex, [K(18-crown-6)][L^{tBu}Ni^{II}(κ²-SNNO)] (**II**) (eqn (1)).¹⁶ Given the challenge of activating N₂O,¹⁷ and the novelty of the [SNNO]²⁻ 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 N_2O 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 ^1H NMR spectrum of this reaction mixture reveals the presence of a new $\gamma\text{-CH}$ resonance at 5.43 ppm (Fig. S2 and 3 †), 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 †). 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 η^2 -thioperoxide ($[\eta^2\text{-SO}]^{2-}$) ligand, which is formed *via* 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 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.¹⁸ For comparison, the S=O distance in free S=O is substantially shorter (1.48108(8) Å), due to its higher bond order.¹⁹ 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.^{16,20}

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** are consistent with its formulation as a C_s symmetric, diamagnetic, square planar Ni^{II} complex. The ^1H NMR spectrum of **1** in C_6D_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 ν_{SO} mode at 902 cm^{-1} , which is consistent with values reported for other $[\eta^2\text{-SO}]^{2-}$ ligands (883, 873 cm^{-1}).^{21,22} Only a handful of structurally-characterized thioperoxide complexes are known,^{23–26} 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 $\text{Fe}_3(\mu_3\text{-SO})(\text{S})(\text{CO})_9$.^{21,27,28} The iron example is notable because it can be prepared by O-atom transfer to

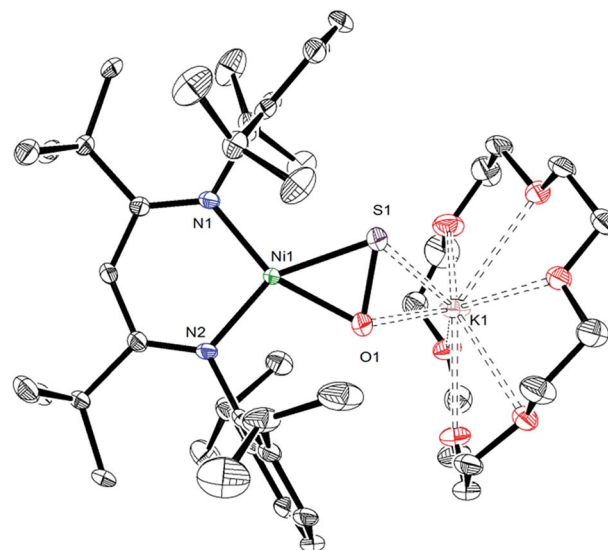


Fig. 1 ORTEP drawing of $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SO})]\cdot\text{C}_7\text{H}_8$ ($1\cdot\text{C}_7\text{H}_8$) shown with 50% thermal ellipsoids. Hydrogen atoms, a C_7H_8 solvate molecule, and one orientation of the disordered $[\eta^2\text{-SO}]^{2-}$ 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)°.

$\text{Fe}_3(\text{S})_2(\text{CO})_9$,²⁹ 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 N_2O ,³⁰ 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 η^2 fashion, *via* both sulfur atoms, while the O atoms are bound to the $[\text{K}(18\text{-crown-6})]^+$ cation in a κ^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 S_2O_2 are shorter than those observed for **2**,^{31–33} consistent with the reduced S–S and S–O bond orders anticipated for the $[\text{OSSO}]^{2-}$ fragment in the former.^{31,34,35} Notably, complex **2** is only the third OSSO complex to be reported and only second to be structurally characterized.^{29,36–38}

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 ^1H NMR spectroscopy), this transformation must be very inefficient. The low yield has also impeded our ability to fully characterize this complex.



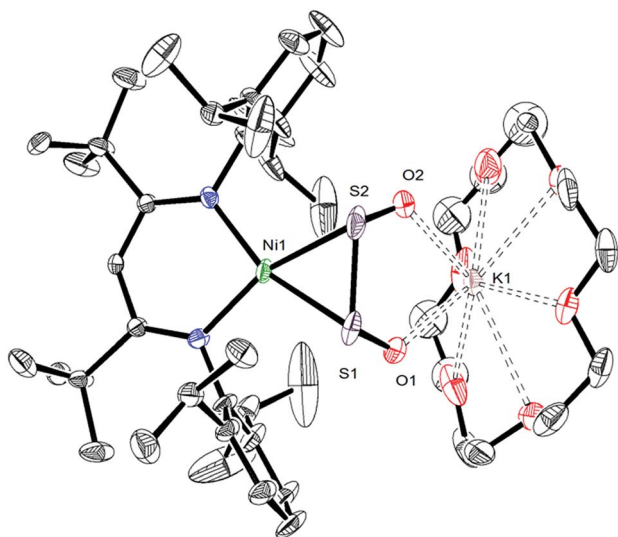


Fig. 2 ORTEP drawing of $[K(18\text{-crown-6})][L^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-OSSO})]\cdot 2\text{C}_6\text{H}_{14}$ ($2\cdot 2\text{C}_6\text{H}_{14}$) shown with 50% thermal ellipsoids. Hydrogen atoms and C_6H_{14} solvate molecules have been omitted for clarity. Selected metrical 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)°.

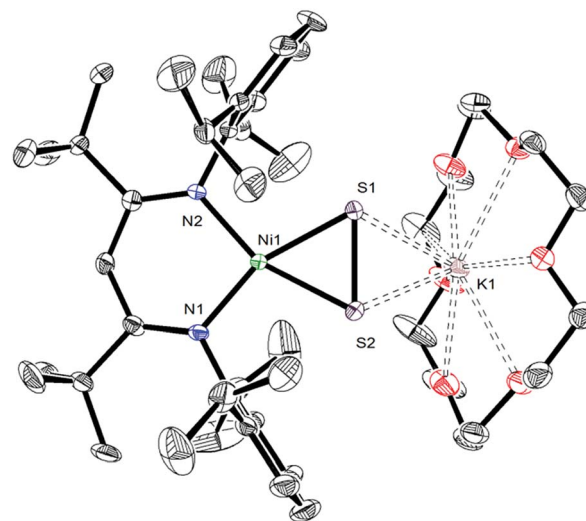


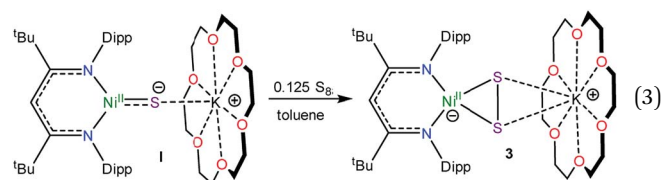
Fig. 3 ORTEP drawing of $[K(18\text{-crown-6})][L^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-S}_2)]\cdot 2\text{C}_7\text{H}_8$ ($3\cdot 2\text{C}_7\text{H}_8$) shown with 50% thermal ellipsoids. Hydrogen atoms and C_7H_8 solvate molecules have been omitted for clarity. Selected metrical parameters: 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 S_8 to form metal disulfides.^{39–41} 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 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 (S_2^{2-}) ligand in **3** has a S–S distance of 2.050(2) Å, consistent with a single bond.¹⁸ This distance is comparable to those reported for other $\text{Ni}^{\text{II}}(\eta^2\text{-S}_2)$ complexes.^{42–49} 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 Ni^{II} β -diketiminato complexes.^{16,49,50}

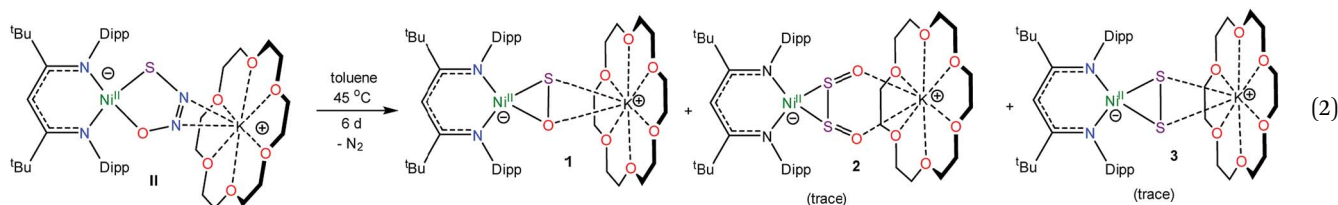
The ^1H NMR spectrum of **3** in toluene- d_8 (Fig. S7†) is consistent with a C_{2v} symmetric, diamagnetic, square planar

Ni^{II} complex and features one *tert*-butyl resonance at 1.30 ppm and a single γ -CH resonance at 5.46 ppm. Importantly, this latter resonance is also present in the *in situ* ^1H 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 PPh_3 to form Ph_3PO , Ph_3PS , and $[(\text{diphos})_2\text{IrCl}]$.³⁶ Similarly, Rauchfuss and co-workers demonstrated that $\text{Cp}_2\text{-Nb}(\text{S}_2\text{O})\text{Cl}$ reacted with Ph_3P to form $\text{Cp}_2\text{Nb}(\text{O})\text{Cl}$ and two equiv. of Ph_3PS .²⁹ Both transformations were presumed to proceed through an unobserved SO intermediate. More recently, Mizobe *et al.* reported that PPh_3 could abstract an O-atom from the



thioperoxide ligand in $[(\text{Cp}'\text{RuCl})_2(\text{SbCl}_2)(\mu\text{-Cl})(\mu_3\text{-}\kappa^2\text{-SO})]$ ($\text{Cp}' = \text{C}_5\text{Me}_4\text{Et}$).²⁵ 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 C_6D_6 solution of complex **1** to an atmosphere of ^{13}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}C -enriched products, indicating the incorporation of ^{13}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**),⁵¹ $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S},\text{O}:\kappa^2\text{-SCO}_2)]$ (**5**), $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]$ (**6**), and SCO (**7**),⁵² respectively (Scheme 1). This spectrum also features a minor ^{13}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.^{52–54}

A ^1H 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**)⁵¹ 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 Ni^{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 ^1H NMR resonances with those of the previously characterized material.¹⁶ For example, this intermediate features diagnostic resonances at -130.25 , -0.63 , and 5.87 ppm, which are assignable to the γ -proton of the L^{tBu} ligand, its ^tBu substituents, and one environment of its diastereotopic ^iPr methyl groups, respectively. For comparison, these resonances appear at -115.21 , -0.88 , and 6.56 ppm, respectively, for authentic **1**.¹⁶ This intermediate is quickly formed upon addition of ^{13}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 ν_{CO} modes at 2021, 1666, and 1620 cm^{-1} (Fig. S24†), which are assignable to the ν_{CO}

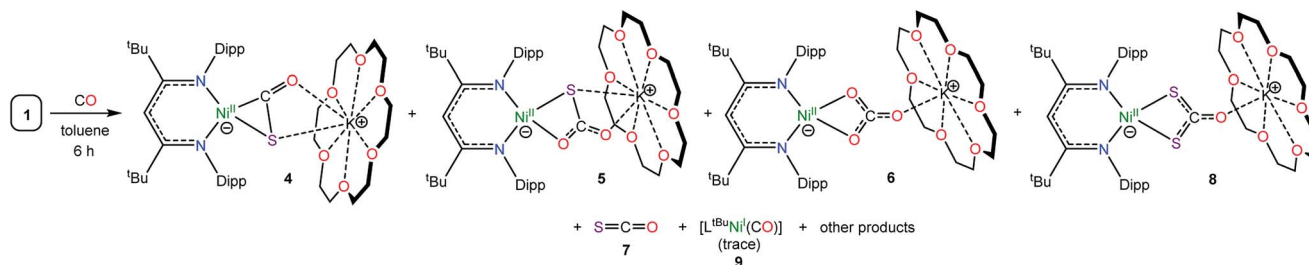
modes of $[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{CO})]$ (**9**),⁵⁵ $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-SCO})]$ (**4**),⁵¹ and $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]$ (**6**), respectively. Curiously, though, we do not observe any signals in the ^1H 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}C NMR spectrum of the *in situ* reaction mixture also features a minor ^{13}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 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 PPh_3 in C_6D_6 , according to ^1H and ^{31}P NMR spectroscopies. The lack of reactivity of the $[\text{SO}]^{2-}$ ligand in **1** with PPh_3 is somewhat surprising on the basis of thermodynamic considerations,⁵⁶ 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

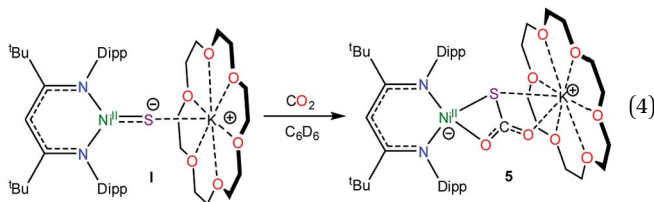
To further support the formation of $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S},\text{O}:\kappa^2\text{-SCO}_2)]$ (**5**) upon reaction of **1** with CO, we pursued its synthesis *via* an independent route. Thus, exposure of a C_6D_6 solution of $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S})]$ (**1**) to excess carbon dioxide (CO_2) results in a rapid color change from deep brown to gold. The ^1H NMR spectrum of the reaction mixture taken 15 min after addition of 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 Ni^{II} complex.⁵¹ 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,^{57,58} 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.^{59,60} Finally, the Ni–N distances in **5** are comparable to those found in the starting material.¹⁶ 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 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 COS .^{57,58}



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[†]). This chemical shift is identical to the resonance assigned to this complex in the *in situ* ^{13}C NMR spectrum of the reaction of **1** with CO (Fig. S11[†]). Moreover, the ^1H NMR spectrum of **5** in C_6D_6 features a $\gamma\text{-CH}$ resonance at 5.48 ppm. This resonance is also present in the *in situ* ^1H NMR spectrum of the reaction mixture of **1** and ^{13}CO (Fig. S10[†]), 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 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 CO , we pursued its synthesis

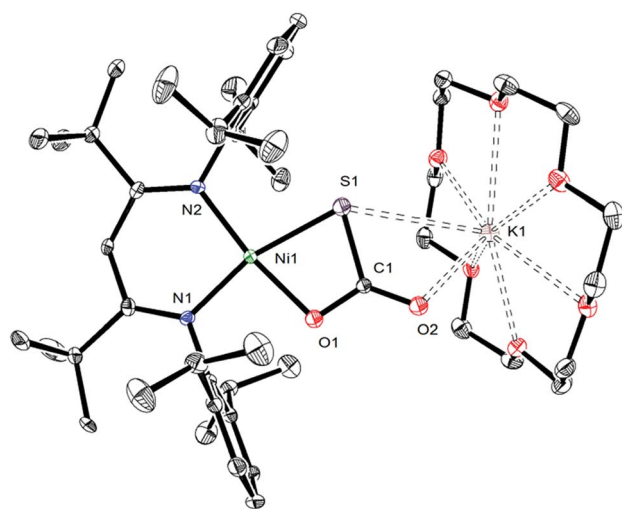
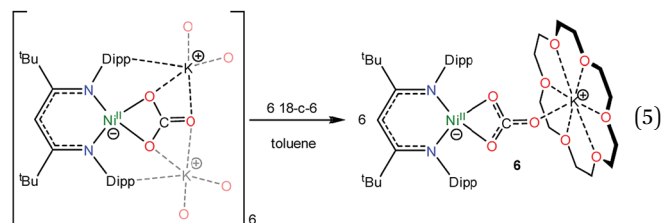


Fig. 4 ORTEP drawing of $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\text{S},\text{O}:\kappa^2\text{-SCO}_2)]\cdot 1.5\text{C}_7\text{H}_8$ ($5\cdot 1.5\text{C}_7\text{H}_8$) shown with 50% thermal ellipsoids. Hydrogen atoms, C_7H_8 solvate molecules, and one orientation 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, $[\text{K}]_6[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]_6$,¹¹ 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 (CO_3^{2-}) ligand in **6** features a $\mu:\kappa^2,\eta^1$ binding mode, identical to that observed for the trithiocarbonate (CS_3^{2-}) ligand in $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}(\kappa^2\text{-CS}_3)]$.⁵⁰ 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 $[\text{K}]_6[\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]_6$,¹¹ 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 C_6D_6 features a resonance at 165.3 ppm, which is assignable to the $[\text{CO}_3]^{2-}$ moiety (Fig. S15[†]). This chemical shift matches the resonance assigned to this complex in the *in situ* ^{13}C NMR spectrum of the reaction mixture of **1** and ^{13}CO (Fig. S11[†]). In addition, the ^1H NMR spectrum of **6** in C_6D_6 features a $\gamma\text{-CH}$ resonance at 5.42 ppm,

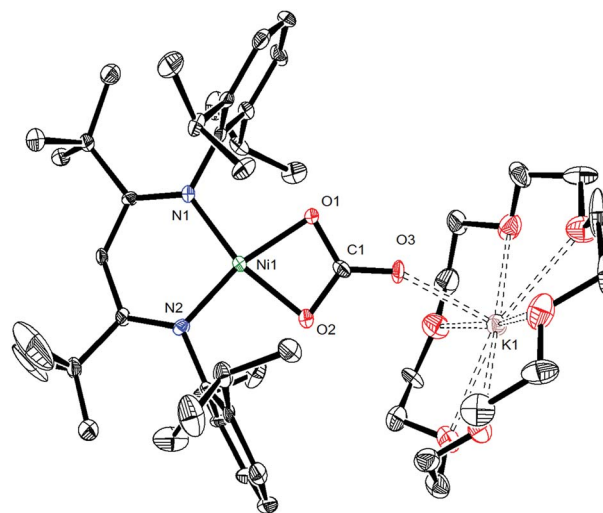


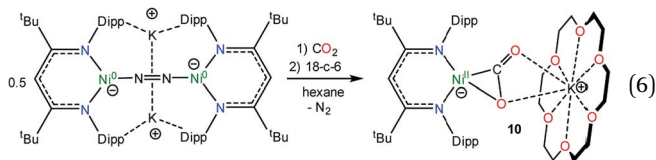
Fig. 5 ORTEP drawing of $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-CO}_3)]\cdot 0.5\text{C}_5\text{H}_{12}$ ($6\cdot 0.5\text{C}_5\text{H}_{12}$) shown with 50% thermal ellipsoids. Hydrogen atoms, a C_5H_{12} solvate molecule, and a second independent molecule 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* ^1H NMR spectrum of the reaction mixture of **1** and ^{13}CO (Fig. S10†). The IR spectrum (hexanes solution) of **6** features a strong ν_{CO} mode at 1620 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}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 CO_2 during the reaction (see below). Several previously reported $\text{Ni}(\text{CO}_2)$ complexes have been synthesized by reaction of CO_2 with a Ni^0 precursor.^{61–64} 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 2009,⁶⁵ was found to serve as an effective 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 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 Ni^{II} center ligated by the β -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.^{61,62,64,66,67} Additionally, the Ni–N bonds in **10** are consistent with those found in other square planar Ni^{II} β -diketiminato complexes.^{16,49,50}

The ^1H NMR spectrum of **10** in C_6D_6 is consistent with that expected for a C_s symmetric, square planar Ni^{II} complex. It features two *tert*-butyl resonances at 1.42 and 1.34 ppm, and a single γ -CH resonance at 5.42 ppm. Its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in C_6D_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.^{62–64} Most importantly, however, these resonances are not observed in the *in situ* $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra of the reaction between **1** and ^{13}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 ν_{CO} mode at 1664 cm^{-1} in its IR spectrum (KBr pellet), which is

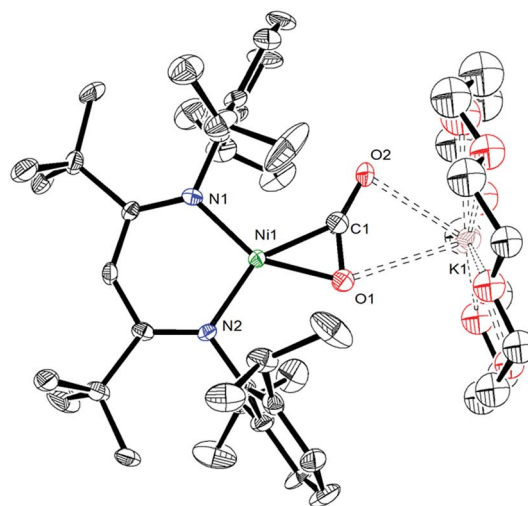


Fig. 6 ORTEP drawing of $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\eta^2\text{-CO}_2)]\cdot 2\text{C}_6\text{H}_6$ (**10**· $2\text{C}_6\text{H}_6$) shown with 50% thermal ellipsoids. Hydrogen atoms, C_6H_6 solvate molecules, and second orientations of the CO_2 and 18-crown-6 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)°.

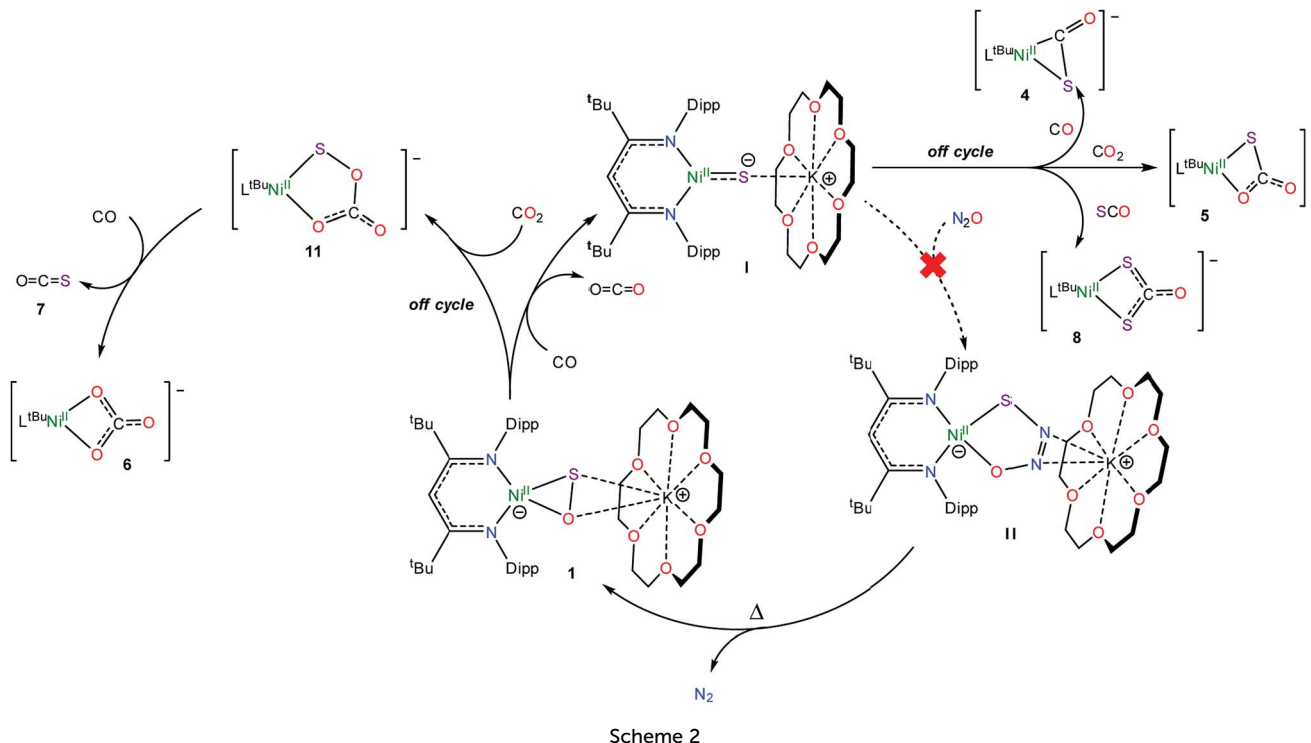
similar to those reported for other nickel CO_2 complexes.^{62–64} This vibration is also not present in the *in situ* IR spectrum (recorded in hexanes) of the reaction residue formed upon reaction of **1** with CO (Fig. S24†).

Mechanistic considerations

To rationalize the formation of complexes **4** and **5**, we propose that CO initially reacts with **1** to form 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 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 N_2O by CO, as originally envisioned. That said, the reaction rates of **I** with CO and CO_2 are qualitatively similar to the reaction rate of **I** with N_2O . As a consequence, **I** is unlikely to be an effective catalyst for N_2O reduction because off-cycle reactions with CO and CO_2 would be competitive with the desired N_2O capture reaction (Scheme 2).

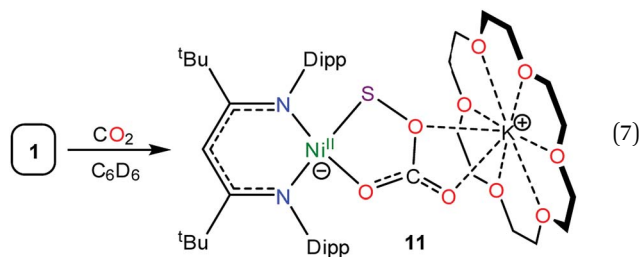
To rationalize the formation of complex **6** and COS, we propose that reaction of the newly formed CO_2 with unreacted **1** results in the formation of a transient, unobserved nickel monothiothiocarbonate complex, $[\text{K}(18\text{-crown-6})][\text{L}^{\text{tBu}}\text{Ni}^{\text{II}}(\kappa^2\text{-SOCO}_2)]$ (**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 (O_2^{2-}) with CO_2 is





known to yield peroxocarbonate ($[\text{OOCO}_2]^{2-}$) complexes.^{68–71} Similarly, metal disulfides (S_2^{2-}) are known to react with CS_2 to form perthiocarbonates ($[\text{SSCS}_2]^{2-}$).^{72,73} Moreover, peroxocarbonates are known to be very effective O-atom donors.^{69,74–77}

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 CO_2 in C_6D_6 results in the rapid formation of a new diamagnetic Ni^{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* ^1H 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.⁷⁸



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 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 CO_2 , *via* O-atom abstraction. This $\text{Ni}(\text{II})$ sulfide intermediate then reacts with CO or 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 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 N_2O by CO, forming N_2 and 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 N_2O 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 N_2O reduction catalysts.



Conflicts of interest

The authors declare no competing financial interests.

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