

Tuning Lanthanide Reactivity Towards Small Molecules with Electron-Rich Siloxide Ligands**

Julie Andresz, Jacques Pécaut, Pierre-Alain Bayle, and Marinella Mazzanti*

Abstract: The synthesis, structure, and reactivity of stable homoleptic heterometallic LnL_4K_2 complexes of divalent lanthanide ions with electron-rich tris(*tert*-butoxy)siloxide ligands are reported. The $[\text{Ln}(\text{OSi}(\text{OtBu})_3)_4\text{K}_2]$ complexes ($\text{Ln} = \text{Eu}, \text{Yb}$) are stable at room temperature, but they promote the reduction of azobenzene to yield the KPhNNPh radical anion as well as the reductive cleavage of CS_2 to yield CS_3^{2-} as the major product. The Eu^{III} complex of the radical anion PhNNPh is structurally characterized. Moreover, $[\text{Yb}(\text{OSi}(\text{OtBu})_3)_4\text{K}_2]$ can reduce CO_2 at room temperature. Release of the reduction products in D_2O shows the quantitative formation of both oxalate and carbonate in a 1:2.2 ratio. The bulky siloxide ligands enforce the labile binding of the reduction products providing the opportunity to establish a closed synthetic cycle for the Yb^{II} -mediated CO_2 reduction. These studies show that the presence of four electron-rich siloxide ligands renders their Eu^{II} and Yb^{II} complexes highly reactive.

Metal complexes capable of reducing small molecules, such as CO_2 and CS_2 , in a controlled manner and under ambient conditions are a very attractive current target.^[1] The majority of research into metal-mediated transformations of small molecules has focused on d-block transition metals, and is comparatively much less developed for f-block elements.^[2] Notably, the use of f-block elements in the activation and reduction of CO_2 and CS_2 is limited to a few interesting and unprecedented examples.^[2a,b,3] In particular, there are only three reported examples of CO_2 reduction and one example of CS_2 reduction mediated by complexes of lanthanides.^[4] The reduction of diazobenzene, an interesting model substrate for N_2 reduction, was also reported for Sm^{II} complexes,^[2c] but has never been observed for the less-reducing Eu^{II} complexes.

The optimization of the ion size in a given ligand environment provides a versatile tool for tuning the reactivity which is unique to lanthanide ions.^[5] However, out of the 14 lanthanide ions that display similar coordination properties but a range of different ionic radii, the metal-centered reduction of heteroallenes has only been reported for the Sm^{II} ion. This is probably a result of the fact that the highly reducing lanthanide ions, such as Nd^{II} , Tm^{II} , and Dy^{II} ,^[2b,5] are difficult to handle and have different reactivities compared to Sm^{II} . The Eu^{II} and Yb^{II} ions provide easier access to complexes of differently sized ions because of the higher stability of Eu^{II} and Yb^{II} precursors. However, the reductive chemistry of Eu^{II} and Yb^{II} has been limited by the $\text{Ln}^{3+}/\text{Ln}^{2+}$ redox potential of Eu and Yb ions (−0.35 V and −1.15 V versus NHE respectively, NHE = normal hydrogen electrode) that is significantly lower than the $\text{Sm}^{\text{III}}/\text{Sm}^{\text{II}}$ redox potential (−1.55 V versus NHE).

Electron-rich ligands were found to impart unusual reducing properties to the Ce^{3+} ion,^[6] but the use of electron-rich ligands to impart greater reducing ability to Ln^{II} ions with poor reducing ability has not been investigated. In the search for suitable ligands that could confer higher reducing ability to the Eu^{II} and Yb^{II} ions, we have identified tris(*tert*-butoxy)siloxides as attractive bulky, electron-rich ligands that can adopt mono- or bidentate forms and which can support unusual reactivity at reduced metal centers.^[3c,7] Siloxides have rarely been used as ancillary ligands in lanthanide chemistry^[8] with only two structurally characterized examples of dinuclear divalent lanthanide complexes.^[8d,9]

Herein, we show that electron-rich tris(*tert*-butoxy)siloxide ligands (L) can impart stability and unusual reactivity to homoleptic heterodimetallic^[8b,10] LnK_2 “ate” complexes of Yb^{II} and Eu^{II} ions. We report the syntheses and structures of mononuclear $[\text{Ln}^{\text{II}}(\text{OSi}(\text{OtBu})_3)_4\text{K}_2]$ complexes for Sm, Eu, and Yb ions and the first example of heteroallene activation by a Yb^{II} complex. The $[\text{Yb}(\text{OSi}(\text{OtBu})_3)_4\text{K}_2]$ complex is found to promote the reduction of PhNNPh , CS_2 , and CO_2 . Moreover, the bulky siloxide ligands enforce the labile binding of the reduction products providing the opportunity to establish a closed synthetic cycle for the reduction of CO_2 .

The reaction of the trivalent lanthanide salts LnX_3 ($\text{Ln} = \text{Eu}$ or Yb , $\text{X} = \text{OTf}$; $\text{Ln} = \text{Sm}$, $\text{X} = \text{I}$) with $\text{KOSi}(\text{OtBu})_3$ (L; 4 equivalents) affords the “ate” $[\text{Ln}(\text{OSi}(\text{OtBu})_3)_4\text{K}]$ ($\text{Ln}^{\text{III}}\text{L}_4\text{K}$) complexes (Scheme S1, Supporting Information). The structure of complex $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ was determined by single-crystal X-ray diffraction analysis and is shown in Figure 1a. In this structure, the Yb^{III} ion is tetracoordinated by four siloxide ligands bound to the Yb ion in a κ^1 fashion. Three siloxide ligands bridge the Yb and K ions, binding the K ion in a κ^2 mode. The Ln–O bond lengths are in the range of the

[*] J. Andresz, Dr. J. Pécaut, P.-A. Bayle
Laboratoire de Reconnaissance Ionique et
Chimie de Coordination SCIB
UMR-E3 CEA-UJF, INAC, CEA-Grenoble
17 rue des Martyrs, 38054 Grenoble Cedex 09 (France)
Dr. M. Mazzanti
EPFL, ISIC
Batiment CH J2 490
1015 Lausanne (Switzerland)
E-mail: marinella.mazzanti@epfl.ch

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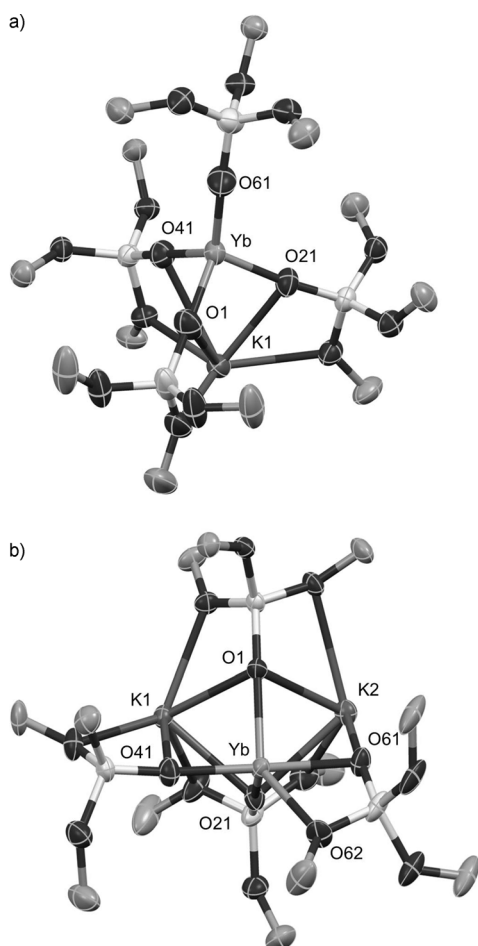


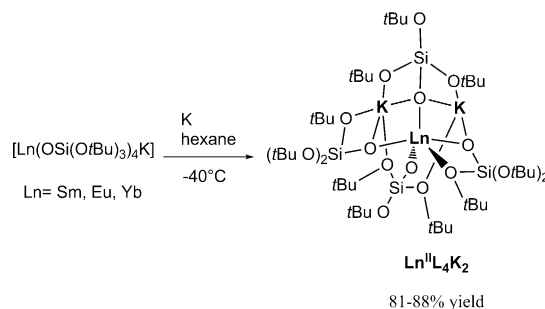
Figure 1. Molecular structures of $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ (a) and $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ (b). Thermal ellipsoids are set at 50% probability. Hydrogens atoms, methyl groups, and disorder are omitted for clarity. Selected bond lengths [Å] in $\text{Yb}^{\text{III}}\text{L}_4\text{K}$: Yb–O1 2.060(2), Yb–O21 2.075(2), Yb–O41 2.070(2), Yb–O61 2.041(2); and in $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$: Yb–O1 2.271(5), Yb–O21 2.272(5), Yb–O41 2.251(6), Yb–O61 2.422(5), Yb–O62 2.571(6).

values reported for mononuclear Yb^{III} phenoxide and siloxide complexes.^[8c,d]

The ^1H NMR spectra of $\text{Ln}^{\text{III}}\text{L}_4\text{K}$ at 25 °C in deuterated toluene and THF show, in both solvents, one single resonance signal for the 108 protons of the complexes, in agreement with the presence of solution species with tetrahedral symmetry. The addition of [18]crown-6 (18C6; 1 equivalent) to a solution of $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ in $[\text{D}_8]\text{THF}$ results in a shift of the ^1H NMR signal of the siloxide from $\delta = 5.48$ to 1.94 ppm. These results suggest the presence in THF of a heterobimetallic structure where the potassium cation adopts a fluxional coordination. The ^1H NMR spectrum of $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ shows a significantly broader resonance signal in toluene compared to THF suggesting the presence of fluxional coordination in toluene.

When the temperature is decreased to –30 °C, the ^1H NMR spectrum of the $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ complex shows the appearance of two different broad resonance signals with an integration ratio of 3:1, in agreement with the solid-state structure and the presence of a heterobimetallic LnK structure in toluene solution (Supporting Information). Variable-temperature ^1H NMR experiments carried out in toluene for

the $\text{Eu}^{\text{III}}\text{L}_4\text{K}$ complex show that the resonance signal of the siloxide broadens and shifts slightly. The ^1H NMR spectrum of the $\text{Sm}^{\text{III}}\text{L}_4\text{K}$ complex in toluene is not significantly affected by the temperature, in agreement with an increased potassium fluxionality. Reduction of $\text{Ln}^{\text{III}}\text{L}_4\text{K}$ in hexane at –40 °C with potassium (1 equivalent) affords the divalent complexes $[\text{Ln}(\text{OSi}(\text{O}t\text{Bu})_3)_4(\text{THF})_x\text{K}_2]$ ($\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$; $\text{Ln} = \text{Eu}$, $x = 1$; $\text{Ln} = \text{Yb}$ or Sm , $x = 0$), which were isolated as pure compounds and in high yield after recrystallization (Scheme 1). The compound $\text{Sm}^{\text{II}}\text{L}_4\text{K}_2$ decomposes at 25 °C



Scheme 1. Synthesis of Ln^{II} tris(*tert*-butoxy)siloxide complexes $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$.

in toluene solution but complexes $\text{Eu}^{\text{II}}\text{L}_4\text{K}_2$ and $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ are stable for weeks in toluene at 25 °C and can be prepared at ambient temperature. Interestingly, only $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ has a low solubility in THF which can be increased by the addition of 18C6 (2 equivalents).

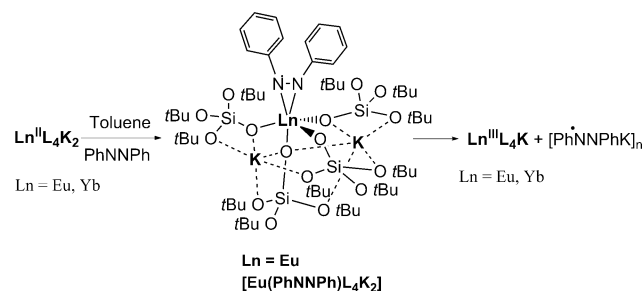
Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$ in toluene at –40 °C for $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$, in hexane at –40 °C for $\text{Sm}^{\text{II}}\text{L}_4\text{K}_2$, and in a hexane/THF 100:1 mixture at –40 °C for $\text{Eu}^{\text{II}}\text{L}_4\text{K}_2$. The structure of $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ (Figure 1 b) shows that the Yb^{II} center is pentacoordinated with five siloxide oxygen atoms in the coordination sphere in a highly distorted geometry. The siloxide ligands bridge the Yb center to two potassium cations, affording a neutral heterobimetallic structure. The solid-state structure of $\text{Sm}^{\text{II}}\text{L}_4\text{K}_2$ is isostructural to the Yb^{II} complex, whereas in the $\text{Eu}^{\text{II}}\text{L}_4\text{K}_2$ complex an additional THF molecule binds one potassium cation (Supporting Information). The $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$ complexes (Table S2) are consistent with the values previously reported for lanthanide phenoxide and siloxide compounds.^[8c,d,9]

The ^1H NMR spectrum of $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$ in deuterated toluene shows only one resonance signal for the 108 protons of the siloxide ligands. Variable-temperature ^1H NMR studies show that the spectrum of $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ in toluene is only slightly affected by the temperature. Addition of crown ether to the $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ complex in deuterated toluene reduces dramatically the solubility of the divalent Yb complex in toluene, suggesting that in the absence of crown ether the potassium remains bound to the siloxide, as found in the solid-state structure. Thus the presence of one unique signal for all the siloxide ligands in toluene solution can be interpreted in term of a fluxional coordination of the potassium cation.

In view of the higher stability of the Eu^{II} and Yb^{II} complexes compared to the Sm^{II} complex, we investigated if

the electron-rich environment provided by the four siloxide ligands could promote the reduction of small molecules. Notably, cyclic voltammetry studies in THF solution (with or without the presence of 18C6) show a large shift of the oxidation potential for the $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$ complexes (Eu: $E_{\text{ox}} = -1.26$ V; Yb: $E_{\text{ox}} = -2.19$ V) compared to LnI_2 (Eu: $E_{\text{ox}} = -0.14$ V; Yb: $E_{\text{ox}} = -0.68$ V), clearly showing the enhancement in reducing ability provided by the siloxide ligand.^[11]

The reaction of $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$ ($\text{Ln} = \text{Eu}, \text{Yb}$) with azobenzene (1 equivalent) in toluene at room temperature affords the trivalent lanthanide complexes $\text{Ln}^{\text{III}}\text{L}_4\text{K}$ ($\text{Ln} = \text{Eu}, \text{Yb}$) and the reduced potassium radical anion of azobenzene KPhNNPh (Scheme 2).



Scheme 2. Reaction of Ln^{II} siloxide complexes ($\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$; $\text{Ln} = \text{Eu}, \text{Yb}$) with diazobenzene (PhNNPh).

The solid-state EPR spectrum of the isolated KPhNNPh radical in suspension in a mixture of toluene/hexane (20/1 v/v) at 19 °C shows an intense signal at approximately $g = 2$, characteristic of an organic radical (see Supporting Information). The solution-state EPR spectrum measured in DME/THF (DME = 1,2-dimethoxyethane) shows a hyperfine structure consistent with the spectrum previously reported for the KPhNNPh radical anion generated in DME solution (see Supporting Information).^[12] The structure of KPhNNPh was determined by X-ray diffraction studies and shows a 2D polymeric structure (Figure 2). The nitrogen atoms of the azobenzene radical are found on two positions with occupation coefficients of 0.66(2) and 0.34(2), respectively. The structural data shows that the N–N bond length between the principal position of the nitrogen atoms N1 (1.331(17) Å) is

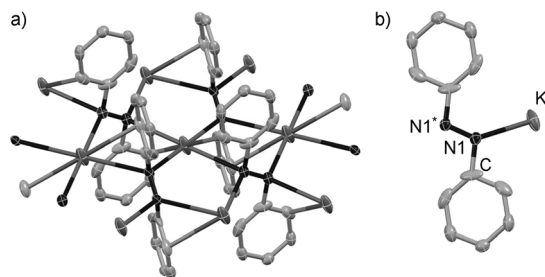


Figure 2. Molecular structure of the 2D polymer (a) and detailed unit (b) of KPhNNPh (thermal ellipsoids set at 50% probability). Disorder and hydrogen atoms were omitted for clarity. Selected bond lengths [Å]: N1–N1* 1.331(17), N1–C 1.432(12), N1–K 2.921(7) (* = $-x, -y+1, -z+1$).

elongated compared to free azobenzene (1.25 Å),^[13] in agreement with the presence of a monoanionic reduced ligand. The value of the N–N bond length in KPhNNPh is in the range of those found^[14] in carbocyclic complexes of Tm^{III} or Sm^{III} containing a monoanionic reduced diazobenzene (1.32–1.39 Å).

Some crystals of the intermediate $[\text{Eu}(\eta^2\text{-PhNNPh})(\text{OSi}(\text{O}t\text{Bu})_3)_4\text{K}_2]$, $[\text{Eu}(\text{PhNNPh})\text{L}_4\text{K}_2]$, were isolated by carrying out the reaction at -40 °C in hexane. In the structure of $[\text{Eu}(\text{PhNNPh})\text{L}_4\text{K}_2]$ (Figure 3) the europium ion is hex-

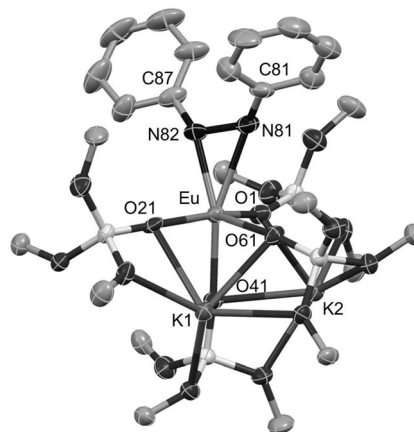


Figure 3. Molecular structure of $[\text{Eu}(\text{PhNNPh})\text{L}_4\text{K}_2]$ (thermal ellipsoids set at 50% probability). Hydrogen atoms, methyl groups, and solvent molecule were omitted for clarity. Selected bond lengths [Å]: Eu–O1 2.276(5), Eu–O21 2.244(4), Eu–O41 2.357(4), Eu–O61 2.237(4), Eu–N81 2.599(5), Eu–N82 2.328(5), N81–N82 1.450(8), N81–C81 1.429(8), N82–C87 1.377(8).

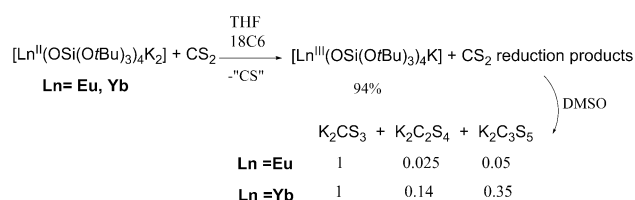
acoordinated in a highly distorted trigonal-prismatic fashion. The N81–N82 bond length (1.450(8) Å) is longer than in the free radical KPhNNPh (1.331(17) Å) and is similar to the N–N simple bond length in hydrazine (1.45 Å).^[13] The Eu–N82 distance is significantly shorter than Eu–N81, suggesting the presence of a radical localized on N82. The azobenzene radical-anion complex, $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{N}_2\text{Ph}_2)(\text{THF})]$, has been previously obtained from the single-electron reduction of azobenzene by the Sm^{II} $[(\text{Cp})_2\text{Sm}(\text{THF})_2]$ complex.^[14b] The analogous Yb^{II} complex leads to the two-electron-reduction product only.^[14b] In all cases, the reduced diazobenzene ligand forms a stable complex and the release of the reduced diazobenzene ligand is not detected.

The structure of $[\text{Eu}(\text{PhNNPh})\text{L}_4\text{K}_2]$ (Figure 3) shows that in spite of the presence of four bulky siloxide ligands, the lanthanide center is still accessible for binding coordinating substrates. Moreover, the presence of four electron-rich siloxide ligands renders their Eu^{II} and Yb^{II} complexes highly reactive. Notably, this reactivity provides the first example of the reduction of azobenzene by a Eu^{II} complex.

This unprecedented reactivity prompted us to investigate the reaction of these complexes with heteroallenes. NMR spectroscopic studies show that the stoichiometric addition of $^{13}\text{CS}_2$ to a THF/18C6 solution of the divalent $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$ ($\text{Ln} = \text{Eu}, \text{Yb}$) complexes affords the trivalent $\text{Ln}^{\text{III}}\text{L}_4\text{K}$ ($\text{Ln} = \text{Eu}, \text{Yb}$) species in 94 % yield (determined

by NMR spectroscopy using naphthalene as an internal standard). The ^{13}C NMR spectrum in deuterated THF of the soluble fraction of the reaction mixture after reaction of the $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$ complex with $^{13}\text{CS}_2$ in THF/18C6 shows the presence of the $\text{Ln}^{\text{III}}\text{L}_4\text{K}$ complex and a signal at $\delta = 266.97$ ppm which is assigned to the $^{13}\text{CS}_3^{2-}$ anion.^[15] The fraction of the reaction mixture which was insoluble in THF was dissolved in $[\text{D}_6]\text{DMSO}$. The ^{13}C NMR spectrum of this fraction showed the presence of $^{13}\text{CS}_3^{2-}$ as a major species. The compounds $\text{C}_2\text{S}_4^{2-}$ (with a resonance signal at $\delta = 264$ ppm) and $\text{C}_3\text{S}_5^{2-}$ (with resonance signals at $\delta = 203$ and 145 ppm)^[16] are also present as minor products. Diffusion of toluene into a DMSO solution of $^{13}\text{CS}_3\text{K}_2$ afforded single crystals suitable for X-ray diffraction of the 3D polymer $[(\text{K}_2\text{CS}_3)_5(\text{DMSO})_{12}]_n$ (Figure S3). Thus, the $\text{Ln}^{\text{III}}\text{L}_4\text{K}$ complexes promote both the reductive coupling of CS_2 to form $\text{C}_2\text{S}_4^{2-}$ and the reductive disproportionation of CS_2 to form CS_3^{2-} and CS. The low stability of CS often prevents its characterization but in this case CS is partly trapped in the $\text{C}_3\text{S}_5^{2-}$ by-product.

The relative ratio of the products obtained from the reduction of CS_2 by $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ in THF/18C6 is $\text{CS}_3^{2-}:\text{C}_2\text{S}_4^{2-}:\text{C}_3\text{S}_5^{2-} = 1:0.14:0.35$. The selectivity for the formation of the CS_3^{2-} species is significantly higher when the complex $\text{Eu}^{\text{II}}\text{L}_4\text{K}_2$ is used to reduce CS_2 ($\text{CS}_3^{2-}:\text{C}_2\text{S}_4^{2-}:\text{C}_3\text{S}_5^{2-} = 1:0.025:0.05$) clearly showing that the nature of the lanthanide ion plays a role in the reduction mechanism (Scheme 3). The relative ratio of the products



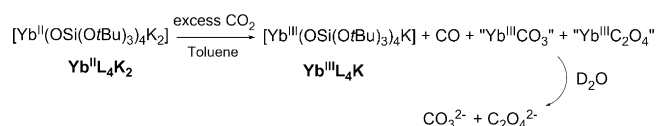
Scheme 3. Reaction of $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$ with CS_2 and ratio of reduction products.

does not change when the reaction is carried out in toluene or in the presence of an excess of CS_2 . The difference in selectivity probably arises from the difference in size (ionic radii of $\text{Yb}^{\text{II}} = 1.02$ Å, $\text{Eu}^{\text{II}} = 1.17$ Å)^[17] of the two metal ions leading to different steric demands in the respective CS_2 -bound reaction intermediates, though the different $\text{Ln}^{3+}/\text{Ln}^{2+}$ redox potentials of the two ions ($\text{Yb} = -1.15$ V, $\text{Eu} = -0.35$ V versus NHE)^[18] might also play a role. These results highlight the advantage of having access to complexes of different Ln^{II} ions in the same ligand environment for tuning selectivity.

Attempts to isolate intermediates with lanthanide-bound reaction products from these reactions were not successful. The steric bulk of the siloxide ligands and the dianionic charge of the thiocarbonate and tetrathiooxalate products are likely to promote the decoordination of the reaction product. However, this selectivity in the reduction of CS_2 by the $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$ complexes suggests that the reaction is indeed occurring by an inner-sphere mechanism. The structure of the intermediate $[\text{Eu}(\text{PhNNPh})\text{L}_4\text{K}_2]$ isolated from the reaction

of Eu^{II} with diazobenzene also supports the fact that sterically less-demanding substrates, such as CS_2 and CO_2 , can coordinate the metal center. Herein, the electron-rich environment provided by the siloxide ligands leads to a reactivity unprecedented for the Eu^{II} and Yb^{II} ions.

The ability of $\text{Ln}^{\text{II}}\text{L}_4\text{K}_2$ ($\text{Ln} = \text{Eu, Yb}$) to reduce CS_2 prompted us to investigate their reactivity with carbon dioxide. The Eu^{II} complex does not react with CO_2 whereas an immediate reaction was observed when a toluene solution of the divalent $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ complex was exposed to excess CO_2 . The ^1H NMR spectra of the reaction mixture after reaction of a toluene solution of $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ with excess $^{13}\text{CO}_2$ show the formation of the trivalent complex $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ (Scheme 4) in



Scheme 4. Reaction of $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ with CO_2 .

approximately 50% yield (evaluated by ^1H NMR spectroscopy using naphthalene as an internal standard). The ^{13}C NMR spectra of these reaction mixtures in toluene or THF show only the presence of the trivalent complex and of free ^{13}CO . This data suggests that mononuclear Yb^{III} complexes containing bound reduction products are also present in solution. Attempts to isolate single crystals of these compounds lead only to the isolation of the $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ complex, suggesting a labile binding of the CO_2 reduction products.

When toluene and excess CO_2 are removed and D_2O is added to release the coordinated reaction products, ^{13}C NMR spectroscopic studies clearly show two resonance signals corresponding to potassium oxalate ($\delta = 173$ ppm) and potassium carbonate ($\delta = 168$ ppm) present in a 1:2.2 ratio. Quantitative ^{13}C NMR spectra measured using ^{13}C -labelled sodium acetate show a total yield (of oxalate and carbonate) of approximately 95%. This confirms that the reaction of the $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ complex with CO_2 leads quantitatively to the reduction of CO_2 to CO, oxalate, and carbonate.

As the reduction of CO_2 by $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ leads to the trivalent $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ complex, we envisaged the possibility to implement this reduction in a closed synthetic cycle.

After $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ undergoes reaction with CO_2 to afford $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ and unidentified substrate-bound Yb^{III} compounds, the addition of KC_8 to the reaction mixture yields $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ with the concomitant formation of side products (some free potassium siloxide is detected). This cycle can be repeated several times and each time $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ is formed in 50% yield. After 5 cycles (see Supporting Information for experimental conditions), the ^1H NMR spectra clearly show a decreased concentration of the active divalent complex and an increased concentration of side products. This experiment suggests that the $\text{Yb}^{\text{III}}\text{L}_4\text{K}$ complex is quantitatively reduced back to the $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$ compound. The synthetic cycle is probably terminated by the formation of carbonate- and oxalate-bound Yb^{III} species that are not further reduced to yield the $\text{Yb}^{\text{II}}\text{L}_4\text{K}_2$

precursor.^[19] Future studies will be directed to investigate the mechanism of CO₂ reduction and to optimize the steric bulk to prevent the coordination of the reaction products to the final complex and to improve selectivity. Such optimization should allow the implementation of a catalytic cycle.

In conclusion, the tris(*tert*-butoxy)siloxide ligand can be used to isolate the heterobimetallic [Ln^{II}(OSi(*tert*Bu)₃)₄K₂] complexes (Ln = Sm, Eu, and Yb). The Eu^{II} complex promotes the reduction of azobenzene and CS₂, affording the first example of azobenzene reduction by Eu^{II} and the first example of trithiocarbonate formation from the reductive splitting of CS₂ promoted by a lanthanide ion. The Yb^{II} complex reduces CO₂ to carbonate and oxalate, to afford the first example of CO₂ reduction by a Yb^{II} center. Thus, these studies show that the electron-rich environment provided by the siloxide ligands leads to a reactivity unprecedented for the Eu^{II} and Yb^{II} ions, and that siloxide “ate” complexes of Eu^{II} and Yb^{II} are very attractive stable precursors for the reduction of heteroallenes. In these systems the bulky siloxide ligands prevent the strong coordination to the final lanthanide complex of the products of the reduction of CS₂ and the azobenzene reaction, setting the basis for the ready exchange of substrates which is a prerequisite for the implementation of catalytic cycles. A suitable tuning of the steric demand should prove very effective for the optimization of selectivity and promote the release of carbonate and oxalate.

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