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Activation of  $\text{SO}_2$  by  $[\text{Zn}(\text{Cp}^*)_2]$  and  $[(\text{Cp}^*)\text{Zn}'-\text{Zn}'(\text{Cp}^*)]$

The cover shows reactions of  $\text{SO}_2$ , which comes out of volcanoes, with  $[\text{Zn}(\text{Cp}^*)_2]$  and  $[(\text{Cp}^*)\text{Zn}'-\text{Zn}'(\text{Cp}^*)]$ . The sulfinate complex,  $[\text{Zn}(\text{O}_2\text{SCp}^*)_2(\text{tmeda})]$  (left), and the sulfinate/oxo cluster  $[\text{Zn}_4(\text{O}_2\text{SCp}^*)_6\text{O}]$  (right), are formed.

As featured in:



See Peter W. Roesky et al., *Chem. Commun.*, 2016, 52, 13090.



Cite this: *Chem. Commun.*, 2016, 52, 13090

Received 8th July 2016,  
Accepted 16th September 2016

DOI: 10.1039/c6cc05638e

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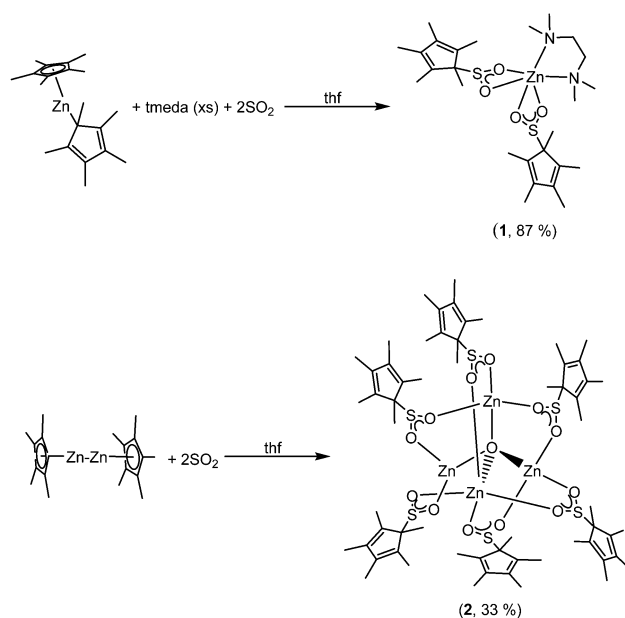
## Activation of SO<sub>2</sub> by [Zn(Cp\*)<sub>2</sub>] and [(Cp\*)Zn<sup>I</sup>–Zn<sup>I</sup>(Cp\*)]†

Rory P. Kelly,<sup>a</sup> Neda Kazeminejad,<sup>a</sup> Carlos A. Lamsfus,<sup>b</sup> Laurent Maron<sup>b</sup> and Peter W. Roesky<sup>\*a</sup>

Interesting reactivity was observed in reactions of SO<sub>2</sub> with [Zn(Cp\*)<sub>2</sub>] and [(Cp\*)Zn<sup>I</sup>–Zn<sup>I</sup>(Cp\*)]. These reactions proceeded with insertion of SO<sub>2</sub> into the Zn–C bonds. Spectacularly, the lability of the C–S bond in the O<sub>2</sub>SCp\* ligands led to the thermal decomposition of [Zn(O<sub>2</sub>SCp\*)<sub>2</sub>(tmeda)] to afford [Zn<sub>2</sub>(μ–SO<sub>3</sub>)(μ–S<sub>2</sub>O<sub>4</sub>)(tmeda)<sub>2</sub>].

The reduction of SO<sub>2</sub> to elemental sulfur (the Claus process) or sodium dithionite are important industrial reactions, but the primary use of SO<sub>2</sub> is in the manufacture of sulfuric acid *via* the contact process. Befitting its industrial importance, there has been renewed academic interest in the activation of SO<sub>2</sub> by molecular species spanning much of the periodic table. Reactions of low-valence complexes with SO<sub>2</sub> can form dithionite complexes<sup>1</sup> but insertion of SO<sub>2</sub> into M–O<sup>2</sup> or M–C bonds,<sup>1b,c,3</sup> affording sulfite and sulfinate complexes, respectively, is also known, along with other reactions.<sup>4</sup> However, despite these recent advances, reactions of SO<sub>2</sub> with zinc complexes remain poorly studied, with the few reports thus far only detailing insertion reactions.<sup>3,5</sup> Herein, we report the reactions between SO<sub>2</sub> and the zinc complexes, [Zn(Cp\*)<sub>2</sub>] and [(Cp\*)Zn<sup>I</sup>–Zn<sup>I</sup>(Cp\*)] (Cp\* = C<sub>5</sub>Me<sub>5</sub><sup>–</sup>).

When two equivalents of SO<sub>2</sub> were condensed onto a stirring solution of [Zn(Cp\*)<sub>2</sub>] in thf, a white solid precipitated immediately. The white solid that formed did not dissolve to any appreciable extent, even with heating. However, when the same reaction was performed in the presence of tmeda (tmeda = *N,N'*-tetramethylethylenediamine), a clear solution was obtained. From this solution, the SO<sub>2</sub> insertion product, [Zn(O<sub>2</sub>SCp\*)<sub>2</sub>(tmeda)] (**1**), was obtained in good yield (Scheme 1).



Scheme 1 Syntheses of [Zn(O<sub>2</sub>SCp\*)<sub>2</sub>(tmeda)] (**1**) and [Zn<sub>4</sub>(O<sub>2</sub>SCp\*)<sub>6</sub>O] (**2**).

Complex **1** crystallised from thf in the monoclinic space group, *P2<sub>1</sub>/c*. The molecular structure and selected bond lengths are listed in Fig. 1. The six-coordinate zinc atom features a distorted octahedral coordination geometry environment, reminiscent of related carboxylate complexes, *e.g.* [Zn{O<sub>2</sub>C(CH=CH)CH<sub>3</sub>}<sub>2</sub>(tmeda)]<sup>6</sup> and [Zn(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(tmeda)].<sup>7</sup> The Zn–O bond lengths (2.1139(12) and 2.2340(12) Å) are unequal in length, but this is also observed in the aforementioned carboxylate complexes, and it is presumably a result of the hexacoordination of the zinc atom in complex **1**. It is a rare example of a Zn sulfinate complex, although other examples have been reported.<sup>3,5</sup>

When [(Cp\*)Zn<sup>I</sup>–Zn<sup>I</sup>(Cp\*)] was treated with SO<sub>2</sub>, complete oxidation of Zn<sup>I</sup> to Zn<sup>II</sup> was observed, and the zinc oxo-cluster, [Zn<sub>4</sub>(O<sub>2</sub>SCp\*)<sub>6</sub>O] (**2**), was obtained in moderate yield (Scheme 1). This reaction was performed multiple times and **2** is the only product that has been isolated to date. Complex **2** evidently arose

<sup>a</sup> Institute of Inorganic Chemistry Karlsruhe Institute of Technology (KIT), Engesserstraße 15, 76131 Karlsruhe, Germany. E-mail: roesky@kit.edu; Fax: +49 721 6084 4854

<sup>b</sup> LPCNO, CNRS & INSA, Université Paul Sabatier, 135 Avenue de Rangueil, Toulouse 31077, France

† Electronic supplementary information (ESI) available: Full experimental procedures and data, computational data and crystallographic data. CCDC 1490513–1490514. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc05638e





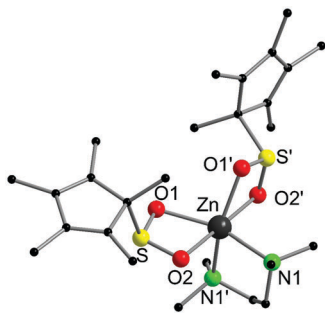


Fig. 1 Molecular structure of  $[\text{Zn}(\text{O}_2\text{SCp}^*)_2(\text{tmeda})]$  (**1**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å):  $\text{Zn}(1)-\text{O}(1) = 2.1139(12)$ ,  $\text{Zn}(1)-\text{O}(2) = 2.2340(12)$ ,  $\text{Zn}(1)-\text{N}(1) = 2.1665(14)$ . Half of the molecule is generated by symmetry.

from insertion of  $\text{SO}_2$  into the  $\text{Zn}-\text{Cp}^*$  bonds, analogously to **1**, and possibly reduction of  $\text{SO}_2$  or an *in situ* formed derivative by the  $\text{Zn}-\text{Zn}$  bond to abstract an oxygen atom, but other pathways cannot be ruled out.<sup>8</sup> We do not think that water is a likely source of the oxide ion since we used high purity  $\text{SO}_2$  and complex **2** was isolated multiple times from different batches of  $[(\text{Cp}^*)\text{Zn}^{\text{I}}-\text{Zn}^{\text{I}}(\text{Cp}^*)]$ .<sup>9</sup> Furthermore, we did not ever observe the formation of Zn metal, which would accompany disproportionation, and thus we believe that the  $\text{Zn}-\text{Zn}$  unit is oxidised by  $\text{SO}_2$  or an *in situ* formed derivative, e.g. the  $\text{O}_2\text{SCp}^*$  ligands. It is difficult to rule out other sources, e.g. thf cleavage, and attempts to do so have so far been inconclusive. Nonetheless, our case quite possibly represents a rare case of deoxygenation of  $\text{SO}_2$  by a low-valent metal complex. The reductive cleavage of  $\text{SO}_2$  into  $\text{SO}$  and  $\text{O}^{2-}$  is generally unfavourable due to the instability of  $\text{SO}$ , and this highlights the impressive reducing ability of  $\text{Zn}^{\text{I}}$  in the current case, when even trivalent uranium<sup>2b</sup> or divalent lanthanide<sup>1b,c</sup> systems, which feature highly reducing and oxophilic metal centres, have proven incapable of abstracting an oxygen atom from  $\text{SO}_2$ . It is worth noting that it has been reported that  $\text{CO}_2$  does not react with  $[(\text{Cp}^*)\text{Zn}^{\text{I}}-\text{Zn}^{\text{I}}(\text{Cp}^*)]$ .<sup>10</sup> We repeated this reaction and found the same result.

Complex **2**· $1.5(\text{C}_5\text{H}_{12})$  crystallised from pentane in the triclinic space group,  $P\bar{1}$ . The complex has a pentanuclear  $[\text{Zn}_4\text{O}]$  core featuring four zinc atoms coordinated tetrahedrally around a central oxide ion. Each Zn atom is further ligated by one oxygen atom of three separate  $\text{O}_2\text{SCp}^*$  ligands, with six such ligands in total. Such a  $[\text{Zn}_4\text{O}]$  core is a common feature in zinc-oxo complexes, and it is also a very popular node in MOF chemistry.<sup>11</sup> The zinc atoms are all four coordinate, in contrast to the six-coordinate zinc atom in complex **1**. The distorted tetrahedral coordination sphere of each zinc atom is completed by coordination to one oxygen atom of three separate bridging  $\text{O}_2\text{SCp}^*$  ligands, giving six such ligands in the complex (Fig. 2).

Complex **2** is the sulfinate analogue of  $[\text{Zn}_4(\text{O}_2\text{CCp}^*)_6\text{O}]$ .<sup>11c</sup> In contrast to complex **1**, the  $\text{Zn}-\text{O}(\text{sulfinate})$  bond lengths are shorter (1.90(2)–1.99(2) Å), and this is presumably a function of the lower coordination number in complex **2**. The lower coordination in complex **2** also accounts for the shorter  $\text{Zn}-\text{O}$  bond lengths. The  $\text{Zn}-\text{O}(\text{oxide})$  bond lengths also fall in the same range as the  $\text{Zn}-\text{O}(\text{sulfinate})$  bond lengths. Unsurprisingly,

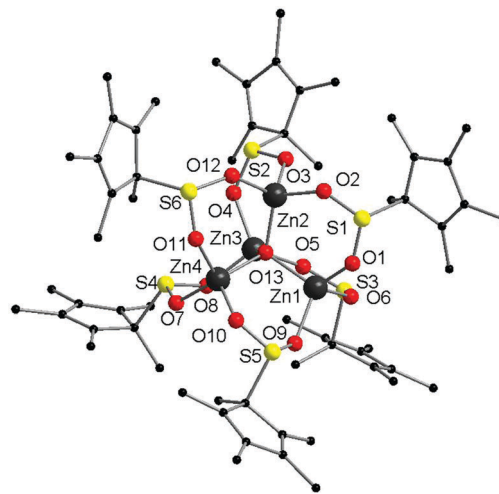


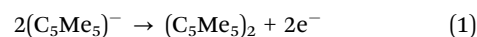
Fig. 2 Molecular structure of  $[\text{Zn}_4(\text{O}_2\text{SCp}^*)_6\text{O}] \cdot 1.5(\text{C}_5\text{H}_{12})$  (**2**· $1.5(\text{C}_5\text{H}_{12})$ ). Hydrogen atoms and lattice solvent have been omitted for clarity. One of the  $\text{O}_2\text{SCp}^*$  moieties (corresponding to S(6)) is disordered over two positions, so only one of the conformations is shown. Selected bond lengths (Å):  $\text{Zn}(1)-\text{O}(1) = 1.939(5)$ ,  $\text{Zn}(1)-\text{O}(6) = 1.943(5)$ ,  $\text{Zn}(1)-\text{O}(9) = 1.969(5)$ ,  $\text{Zn}(1)-\text{O}(13) = 1.958(6)$ .

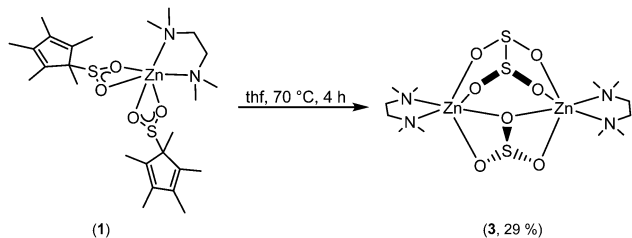
the  $\text{Zn}-\text{O}$  bond lengths in **2** are very similar to those in  $[\text{Zn}_4(\text{O}_2\text{CCp}^*)_6\text{O}]$ .

Both **1** and **2** were characterised by NMR (*vide infra*) and IR spectroscopy, and satisfactory microanalyses were obtained for both complexes.

$^1\text{H}$  NMR studies of **1** and **2** revealed that the complexes are thermally unstable and that they slowly decompose in solution to form multiple products. An interesting feature of **1** is that the  $\text{O}_2\text{SCp}^*$  ligands only give rise to two broad signals, in contrast to the three sharp singlets in a 2:2:1 ratio observed for  $\text{O}_2\text{CCp}^*$ <sup>11c</sup> or  $\text{S}_2\text{CCp}^*$ <sup>12</sup> ligands bound to Zn cations. The broadness of the signals for the  $\text{O}_2\text{SCp}^*$  ligands is indicative of rapid exchange of the  $\text{Cp}^*$  ring carbon atoms and the sulfur atom of the  $\text{SO}_2$  moiety. This hinted that the instability of the complexes was due to the lability of the  $\text{C}-\text{S}$  bond in the  $\text{O}_2\text{SCp}^*$  ligands. The  $^1\text{H}$  NMR spectrum of complex **2** is much more complex than that of **1**, and no obvious assignment has yet proved possible, even after obtaining spectra at low temperatures. It seems likely that there is dissociation of the complex into multiple species upon dissolution.

Much to our surprise, monitoring the decomposition of **1** by  $^1\text{H}$  NMR spectroscopy showed that one of the decomposition products was  $(\text{C}_5\text{Me}_5)_2$ . The origin of this species is the coupling of two  $\text{Cp}^*$  radicals, which form from the loss of one electron per  $\text{Cp}^*$  anion (eqn (1)). Evans has demonstrated that  $[\text{Ln}(\text{Cp}^*)_3]$  complexes are highly reducing despite having the lanthanide ions in their highest accessible oxidation state, and the area has been termed sterically-induced reduction.<sup>13</sup> Similar  $\text{Cp}^*$ -based reductions have recently been observed in Zn chemistry,<sup>14</sup> but base-induced reduction from a functionalised  $\text{Cp}^*$  ligand is, to the best of our knowledge, unprecedented.





Scheme 2 Formation of  $[\text{Zn}_2(\mu\text{-SO}_3)(\mu\text{-S}_2\text{O}_4)(\text{tmeda})_2]$  (**3**) from the thermal decomposition of  $[\text{Zn}(\text{O}_2\text{SCp}^*)_2(\text{tmeda})]$  (**1**).

In an effort to study these intriguing decomposition reactions, complex **1** was generated *in situ* and then heated at 70 °C for several hours. Although the decomposition reaction is complex, we isolated single crystals of  $[\text{Zn}_2(\mu\text{-SO}_3)(\mu\text{-S}_2\text{O}_4)(\text{tmeda})_2]$  (**3**) in modest yield (Scheme 2). Importantly, the reaction is repeatable. Complex **3** is highly insoluble, thus preventing its characterisation by NMR spectroscopy, but it was characterised by X-ray crystallography, IR spectroscopy and microanalysis.

Complex **3**·thf crystallised from thf in the monoclinic space group,  $P2_1/c$ . The molecular structure is shown in Fig. 3, along with selected bond lengths. The dinuclear complex features two six-coordinate zinc atoms that are each bound to one tmeda ligand, one bridging dithionite ligand and one bridging sulfite ligand. The binding of the sulfite and dithionite ligands to the two zinc atoms is slightly asymmetric. Surprisingly, to the best of our knowledge the only other Zn complex containing dithionite ligands is the simple Zn salt,  $[\text{Zn}(\text{S}_2\text{O}_4)(\text{NC}_5\text{H}_5)]$ .<sup>15</sup> On the other hand, there are multiple examples of Zn sulfite complexes, but they remain a fairly limited class, and most examples feature polymeric arrays. However, related bimetallic complexes such as  $[\text{Zn}(\mu\text{-SO}_3)(\text{phen})_2]$ <sup>16</sup> (phen = 1,10-phenanthroline) and  $[\text{Zn}(\mu\text{-SO}_3)(\text{bipy})_2]$ <sup>17</sup> (bipy = 2,2'-bipyridine) are known.

Whilst it is difficult to state exactly what occurs during this decomposition reaction, the presence of the sulfite ligand ( $\text{SO}_3^{2-}$ ) can be rationalised by a combination of deoxygenation of an  $\text{SO}_2$  moiety to yield a Zn oxo species, and subsequent insertion of another molecule of  $\text{SO}_2$  into the Zn–O bond to form the sulfite ligand. Recently, we showed that  $\text{SO}_2$  can insert into a metal oxide bridge (M–O–M) to give the corresponding

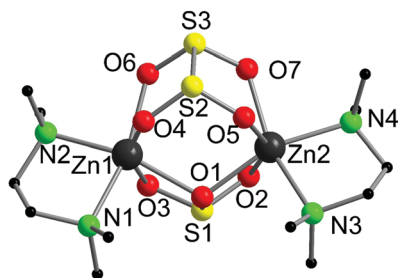


Fig. 3 Molecular structure of  $[\text{Zn}_2(\mu\text{-SO}_3)(\mu\text{-S}_2\text{O}_4)(\text{tmeda})_2]\cdot\text{thf}$  (**3**·thf). Hydrogen atoms and lattice solvent have been omitted for clarity. Selected bond lengths (Å): Zn(1)–O(1) = 2.142(2), Zn(1)–O(3) = 2.162(2), Zn(1)–O(4) = 2.100(2), Zn(1)–O(6) = 2.143(2), Zn(1)–N(1) = 2.203(3), Zn(2)–O(1) = 2.096(2), Zn(2)–O(2) = 2.347(3), Zn(2)–O(5) = 2.103(2), Zn(1)–O(7) = 2.099(2), Zn(2)–N(3) = 2.189(3).

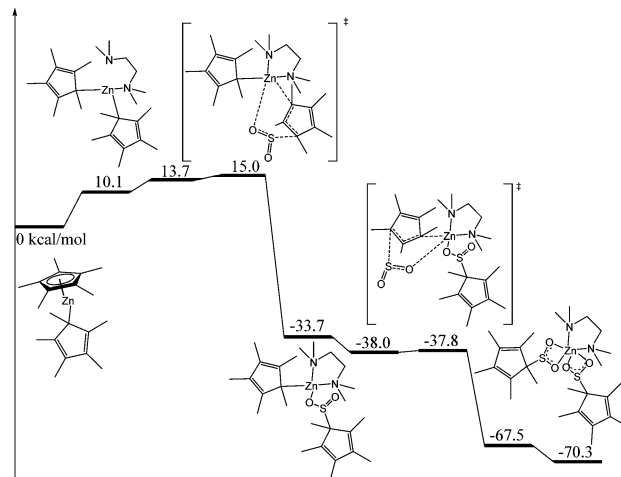


Fig. 4 Computed enthalpy profile ( $\text{kcal mol}^{-1}$ ) for the reaction of  $\text{SO}_2$  with  $[\text{Zn}(\text{Cp}^*)_2]$  at room temperature.

sulfite complex, (M– $\text{SO}_3$ –M).<sup>2a</sup> The dithionite ligand ( $\text{S}_2\text{O}_4^{2-}$ ) presumably arises from homolytic cleavage of the C–S bond in  $\text{O}_2\text{SCp}^*$ , formally giving the two radical species,  $\text{SO}_2^{\bullet-}$  and  $\text{Cp}^{\bullet}$ . Both of these species can couple to form  $\text{S}_2\text{O}_4^{2-}$  and  $(\text{C}_5\text{Me}_5)_2$ , respectively, the latter of which was detected in solution. Subtle changes in reaction conditions presumably affect the outcome of these reactions but it is a spectacular demonstration of the reactivity of these complexes. The decomposition of **1** to afford **3** was deemed to be too complicated to model computationally but we modelled the insertion of  $\text{SO}_2$  into  $[\text{Zn}(\text{Cp}^*)_2]$  to yield **1** (Fig. 4).

The reaction begins with the coordination of a tmeda molecule to the zinc atom, inducing a haptotropic shift of the originally  $\eta^5\text{-Cp}^*$  ligand, which then becomes sigma-bonded through one carbon atom. This shift was found to be endothermic by  $10.1 \text{ kcal mol}^{-1}$  but it is crucial for the subsequent reactivity with  $\text{SO}_2$ . Indeed, from this complex, the approach of  $\text{SO}_2$  leads to the partial decoordination of a  $\text{Cp}^*$  ligand, which is then able to nucleophilically attack the incoming  $\text{SO}_2$  molecule. Starting from the tmeda-coordinated complex, the barrier for such an attack is very low ( $4.9 \text{ kcal mol}^{-1}$  or  $15.0 \text{ kcal mol}^{-1}$  with respect to the tmeda-free decamethylzincocene). This reaction yields an intermediate that appears to be quite stable ( $-33.7 \text{ kcal mol}^{-1}$  with respect to the entrance channel). In this intermediate, the inserted  $\text{SO}_2$  molecule only interacts with the Zn centre through one oxygen atom in order to maintain the four-fold coordination around the metal. The approach of a second  $\text{SO}_2$  molecule leads to a similar process as described before. Indeed, the second  $\text{Cp}^*$  ligand gets decoordinated and nucleophilically attacks the coordinated  $\text{SO}_2$ . The barrier for this second insertion is negligible (a few tenths of a  $\text{kcal mol}^{-1}$ ), in line with a facile process. As for the first insertion, this second one is strongly exothermic by  $29.7 \text{ kcal mol}^{-1}$ , yielding the formation of complex **1**. The  $\text{Cp}^*$  ligand, often considered an innocent ligand, reacts like an alkyl group. Such reactivity appears to be enhanced by the sigma-coordination of the  $\text{Cp}^*$  ligand in the complex (favoured by the coordination of tmeda), and this has been observed before in zinc  $\text{Cp}^*$  chemistry.<sup>11c,12,14b</sup>



In summary, the reactions of the zinc complexes,  $[\text{Zn}(\text{Cp}^*)_2]$  and  $[(\text{Cp}^*)\text{Zn}^{\text{I}}-\text{Zn}^{\text{I}}(\text{Cp}^*)]$ , with  $\text{SO}_2$  yielded the sulfinate complex,  $[\text{Zn}(\text{O}_2\text{SCp}^*)_2(\text{tmeda})]$  (**1**), and the sulfinate/oxo cluster,  $[\text{Zn}_4(\text{O}_2\text{SCp}^*)_6\text{O}]$  (**2**), respectively. In both cases, nucleophilic attack of the  $\text{Cp}^*$  ligand on the incoming  $\text{SO}_2$  molecule was observed, and in the reaction with  $[(\text{Cp}^*)\text{Zn}^{\text{I}}-\text{Zn}^{\text{I}}(\text{Cp}^*)]$ , complete oxidation of the  $\text{Zn}^{\text{I}}-\text{Zn}^{\text{I}}$  bond was observed. DFT calculations clearly show the decoordination of the  $\text{Cp}^*$  ligand, followed by nucleophilic attack on the  $\text{SO}_2$  molecule, and finally, coordination of the newly formed  $\text{O}_2\text{SCp}^*$  sulfinate anion. Somewhat surprisingly, these complexes are thermally unstable due to the lability of the C–S bond of the sulfinate ligands. In the case of complex **1**, thermally-induced decomposition allowed us to isolate the mixed dithionite/sulfite complex,  $[\text{Zn}_2(\mu\text{-SO}_3)(\mu\text{-S}_2\text{O}_4)(\text{tmeda})_2]$  (**3**), in modest yield. This multi-step activation of  $\text{SO}_2$  is noteworthy since activation of  $\text{SO}_2$  by molecular systems tends to stop after insertion or coupling.

This work was supported by the DFG-funded transregional collaborative research center SFB/TRR 88 “3MET”. LM would like to thank the Alexander-von-Humboldt Foundation, Chinese Academy of Science and ANR for financial support. CalMip is also gratefully acknowledged for a generous grant of computing time.

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