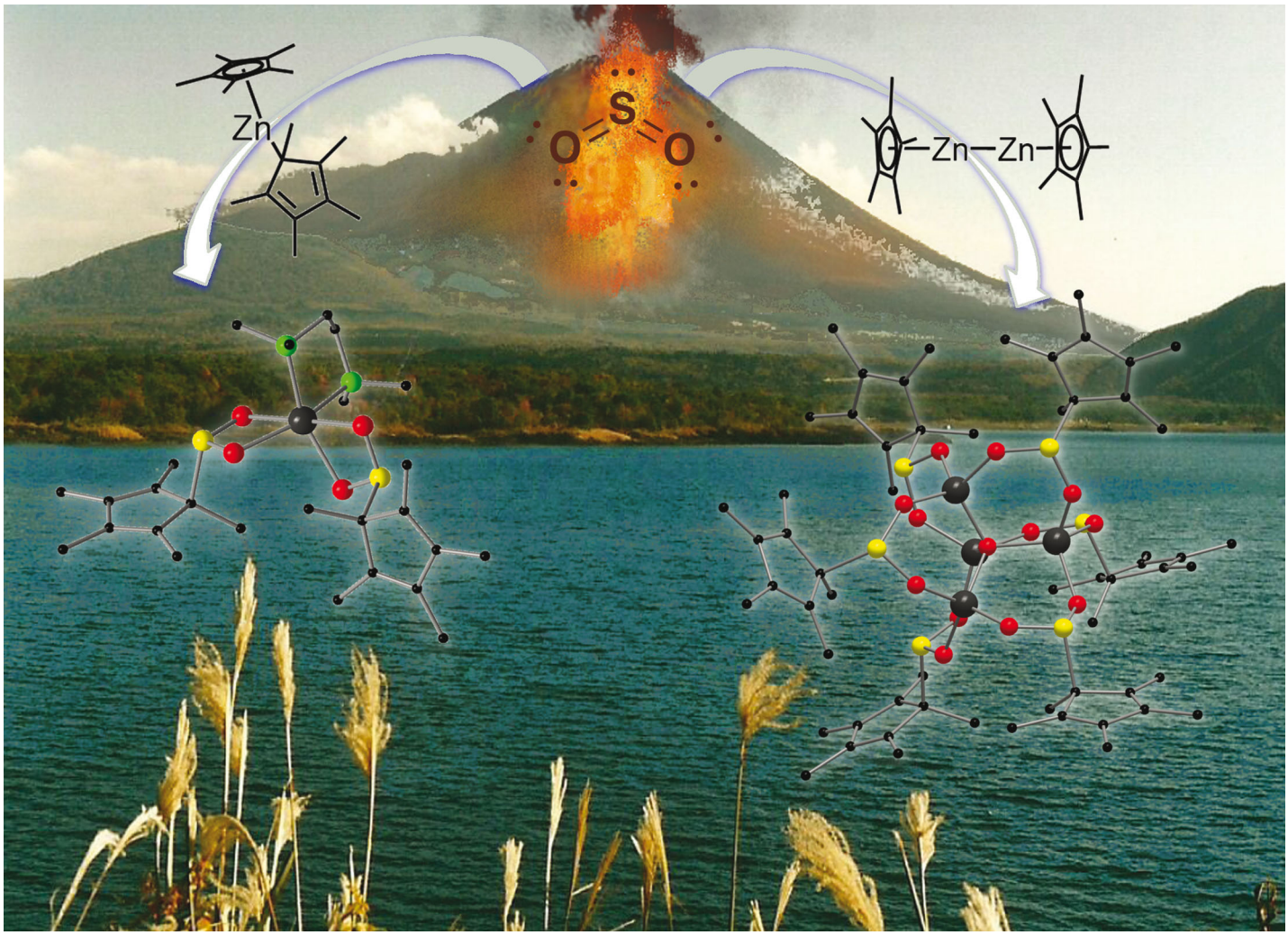

Showcasing research from the laboratory of Dr Peter Roesky, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany.

Activation of SO_2 by $[Zn(Cp^*)_2]$ and $[(Cp^*)Zn^I–Zn^I(Cp^*)]$

The cover shows reactions of SO_2, which comes out of volcanoes, with $[Zn(Cp^*)_2]$ and $[(Cp^*)Zn^I–Zn^I(Cp^*)]$. The sulfinate complex, $[Zn(O_2SCp^*)_2(tmeda)]$ (left), and the sulfinate/oxo cluster $[Zn_4(O_2SCp^*)_6O]$ (right), are formed.

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Activation of SO_2 by $[Zn(Cp^*)_2]$ and $[(Cp^*)Zn^I–Zn^I(Cp^*)]$†

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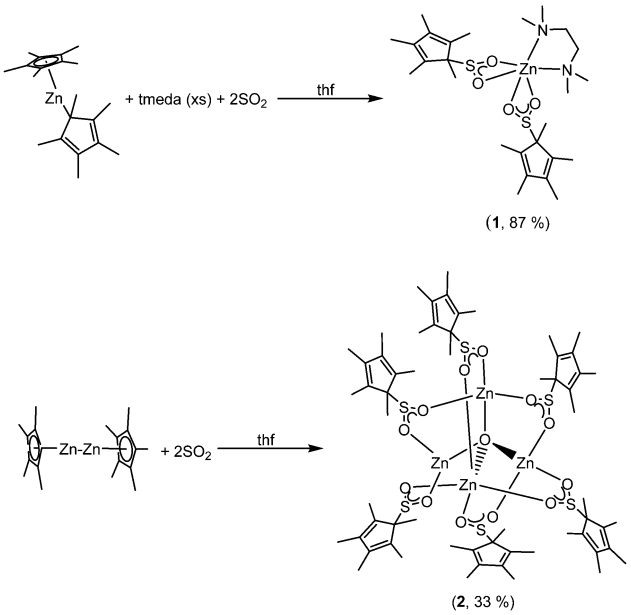
Interesting reactivity was observed in reactions of SO_2 with $[Zn(Cp^*)_2]$ and $[(Cp^*)Zn^I–Zn^I(Cp^*)]$. These reactions proceeded with insertion of SO_2 into the Zn–C bonds. Spectacularly, the lability of the C–S bond in the O_2SCp^* ligands led to the thermal decomposition of $[Zn(O_2SCp^*)_2(tmeda)]$ to afford $[Zn_2(\mu\text{-}SO_3)(\mu\text{-}S_2O_4)(tmeda)_2]$.

The reduction of SO_2 to elemental sulfur (the Claus process) or sodium dithionite are important industrial reactions, but the primary use of SO_2 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_2 by molecular species spanning much of the periodic table. Reactions of low-valence complexes with SO_2 can form dithionite complexes[1] but insertion of SO_2 into M–O[2] or M–C bonds,[1b,c,3] affording sulfite and sulfinate complexes, respectively, is also known, along with other reactions.[4] However, despite these recent advances, reactions of SO_2 with zinc complexes remain poorly studied, with the few reports thus far only detailing insertion reactions.[3,5] Herein, we report the reactions between SO_2 and the zinc complexes, $[Zn(Cp^*)_2]$ and $[(Cp^*)Zn^I–Zn^I(Cp^*)]$ ($Cp^* = C_5Me_5^-$).

When two equivalents of SO_2 were condensed onto a stirring solution of $[Zn(Cp^*)_2]$ 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_2 insertion product, $[Zn(O_2SCp^*)_2(tmeda)]$ (**1**), was obtained in good yield (Scheme 1).



Scheme 1 Syntheses of $[Zn(O_2SCp^*)_2(tmeda)]$ (**1**) and $[Zn_4(O_2SCp^*)_6O]$ (**2**).

Complex **1** crystallised from thf in the monoclinic space group, *P*2/*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.* $[Zn\{O_2C(CH{=}CH)CH_3\}_2(tmeda)]$[6] and $[Zn(O_2CCH_3)_2(tmeda)]$.[7] 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.[3,5]

When $[(Cp^*)Zn^I–Zn^I(Cp^*)]$ was treated with SO_2, complete oxidation of Zn^I to Zn^{II} was observed, and the zinc oxo-cluster, $[Zn_4(O_2SCp^*)_6O]$ (**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

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† 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

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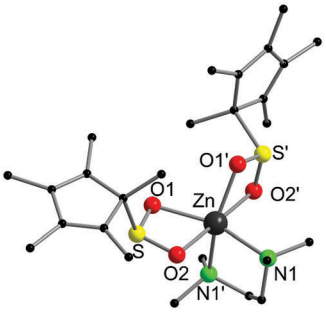

Fig. 1 Molecular structure of $[Zn(O_2SCp^*)_2(tmeda)]$ (**1**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Zn(1)–O(1) = 2.1139(12), Zn(1)–O(2) = 2.2340(12), Zn(1)–N(1) = 2.1665(14). Half of the molecule is generated by symmetry.

from insertion of SO_2 into the Zn–Cp* bonds, analogously to **1**, and possibly reduction of SO_2 or an *in situ* formed derivative by the Zn–Zn bond to abstract an oxygen atom, but other pathways cannot be ruled out.[8] We do not think that water is a likely source of the oxide ion since we used high purity SO_2 and complex **2** was isolated multiple times from different batches of $[(Cp^*)Zn^I–Zn^I(Cp^*)]$.[9] Furthermore, we did not ever observe the formation of Zn metal, which would accompany disproportionation, and thus we believe that the Zn–Zn unit is oxidised by SO_2 or an *in situ* formed derivative, *e.g.* the O_2SCp^* 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 SO_2 by a low-valent metal complex. The reductive cleavage of SO_2 into SO and O^{2-} is generally unfavourable due to the instability of SO, and this highlights the impressive reducing ability of Zn^I in the current case, when even trivalent uranium[2b] or divalent lanthanide[1b,c] systems, which feature highly reducing and oxophilic metal centres, have proven incapable of abstracting an oxygen atom from SO_2. It is worth noting that it has been reported that CO_2 does not react with $[(Cp^*)Zn^I–Zn^I(Cp^*)]$.[10] We repeated this reaction and found the same result.

Complex **2**·1.5(C_5H_{12}) crystallised from pentane in the triclinic space group, $P\bar{1}$. The complex has a pentanuclear $[Zn_4O]$ 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 O_2SCp^* ligands, with six such ligands in total. Such a $[Zn_4O]$ core is a common feature in zinc-oxo complexes, and it is also a very popular node in MOF chemistry.[11] 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 O_2SCp^* ligands, giving six such ligands in the complex (Fig. 2).

Complex **2** is the sulfinate analogue of $[Zn_4(O_2CCp^*)_6O]$.[11c] In contrast to complex **1**, the Zn–O(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 Zn–O bond lengths. The Zn–O(oxide) bond lengths also fall in the same range as the Zn–O(sulfinate) bond lengths. Unsurprisingly,

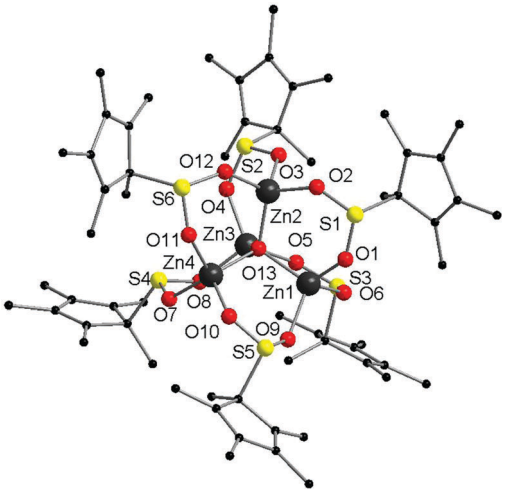

Fig. 2 Molecular structure of $[Zn_4(O_2SCp^*)_6O]$·1.5(C_5H_{12}) (**2**·1.5(C_5H_{12})). Hydrogen atoms and lattice solvent have been omitted for clarity. One of the O_2SCp^* moieties (corresponding to S(6)) is disordered over two positions, so only one of the conformations is shown. Selected bond lengths (Å): Zn(1)–O(1) = 1.939(5), Zn(1)–O(6) = 1.943(5), Zn(1)–O(9) = 1.969(5), Zn(1)–O(13) = 1.958(6).

the Zn–O bond lengths in **2** are very similar to those in $[Zn_4(O_2CCp^*)_6O]$.

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

^{1}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 O_2SCp^* ligands only give rise to two broad signals, in contrast to the three sharp singlets in a 2 : 2 : 1 ratio observed for O_2CCp^* [11c] or S_2CCp^* [12] ligands bound to Zn cations. The broadness of the signals for the O_2SCp^* ligands is indicative of rapid exchange of the Cp* ring carbon atoms and the sulfur atom of the SO_2 moiety. This hinted that the instability of the complexes was due to the lability of the C–S bond in the O_2SCp^* ligands. The ^{1}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}H NMR spectroscopy showed that one of the decomposition products was $(C_5Me_5)_2$. The origin of this species is the coupling of two $Cp^{*\bullet}$ radicals, which form from the loss of one electron per Cp* anion (eqn (1)). Evans has demonstrated that $[Ln(Cp^*)_3]$ complexes are highly reducing despite having the lanthanide ions in their highest accessible oxidation state, and the area has been termed sterically-induced reduction.[13] Similar Cp*-based reductions have recently been observed in Zn chemistry,[14] but base-induced reduction from a functionalised Cp* ligand is, to the best of our knowledge, unprecedented.

$$2(C_5Me_5)^- \rightarrow (C_5Me_5)_2 + 2e^- \quad (1)$$

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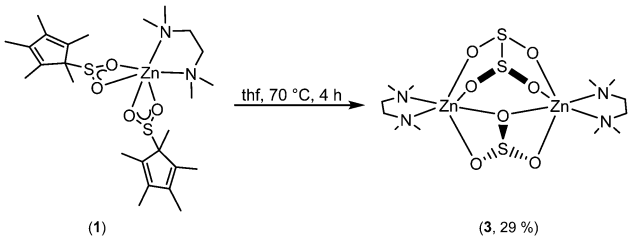

Scheme 2 Formation of $[Zn_2(\mu\text{-}SO_3)(\mu\text{-}S_2O_4)(tmeda)_2]$ (**3**) from the thermal decomposition of $[Zn(O_2SCp^*)_2(tmeda)]$ (**1**).

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 $[Zn_2(\mu\text{-}SO_3)(\mu\text{-}S_2O_4)(tmeda)_2]$ (**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, $[Zn(S_2O_4)(NC_5H_5)]$.[15] 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 $[Zn(\mu\text{-}SO_3)(phen)]_2$[16] (phen = 1,10-phenanthroline) and $[Zn(\mu\text{-}SO_3)(bipy)]_2$[17] (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 (SO_3^{2-}) can be rationalised by a combination of deoxygenation of an SO_2 moiety to yield a Zn oxo species, and subsequent insertion of another molecule of SO_2 into the Zn–O bond to form the sulfite ligand. Recently, we showed that SO_2 can insert into a metal oxide bridge (M–O–M) to give the corresponding

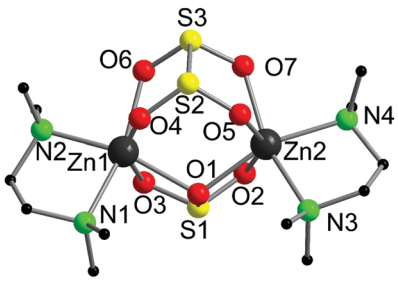

Fig. 3 Molecular structure of $[Zn_2(\mu\text{-}SO_3)(\mu\text{-}S_2O_4)(tmeda)_2]$·thf (**3**·thf). Hydrogen atoms and lattice solvent have been omitted for clarity. Selected bond lengths (Å): Zn(1)–O(1) = 2.142(2), Zn(1)–O(3) = 2.162(2), Zn(1)–O(4) = 2.100(2), Zn(1)–O(6) = 2.143(2), Zn(1)–N(1) = 2.203(3), 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).

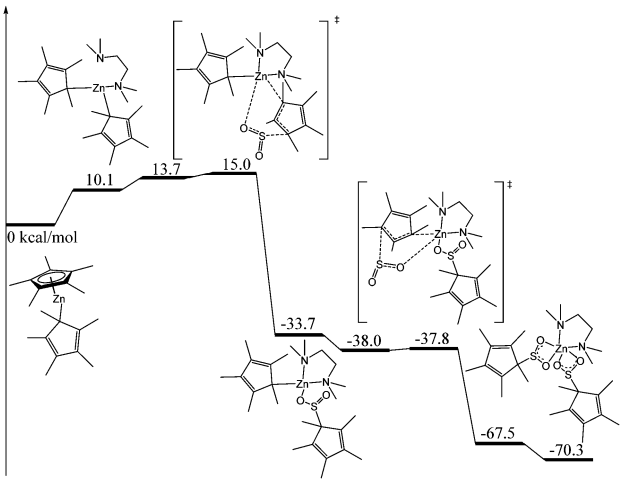

Fig. 4 Computed enthalpy profile (kcal mol^{-1}) for the reaction of SO_2 with $[Zn(Cp^*)_2]$ at room temperature.

sulfite complex, ($M\text{–}SO_3\text{–}M$).[2a] The dithionite ligand ($S_2O_4^{2-}$) presumably arises from homolytic cleavage of the C–S bond in O_2SCp^*, formally giving the two radical species, $SO_2^{\bullet-}$ and $Cp^{*\bullet}$. Both of these species can couple to form $S_2O_4^{2-}$ and $(C_5Me_5)_2$, 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 SO_2 into $[Zn(Cp^*)_2]$ 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 η^5-Cp* ligand, which then becomes sigma-bonded through one carbon atom. This shift was found to be endothermic by 10.1 kcal mol^{-1} but it is crucial for the subsequent reactivity with SO_2. Indeed, from this complex, the approach of SO_2 leads to the partial decoordination of a Cp* ligand, which is then able to nucleophilically attack the incoming SO_2 molecule. Starting from the tmeda-coordinated complex, the barrier for such an attack is very low (4.9 kcal mol^{-1} or 15.0 kcal mol^{-1} with respect to the tmeda-free decamethylzinconcene). This reaction yields an intermediate that appears to be quite stable (−33.7 kcal mol^{-1} with respect to the entrance channel). In this intermediate, the inserted 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 SO_2 molecule leads to a similar process as described before. Indeed, the second Cp* ligand gets decoordinated and nucleophilically attacks the coordinated SO_2. The barrier for this second insertion is negligible (a few tenths of a kcal mol^{-1}), in line with a facile process. As for the first insertion, this second one is strongly exothermic by 29.7 kcal mol^{-1}, yielding the formation of complex **1**. The Cp* ligand, often considered an innocent ligand, reacts like an alkyl group. Such reactivity appears to be enhanced by the sigma-coordination of the Cp* ligand in the complex (favoured by the coordination of tmeda), and this has been observed before in zinc Cp* chemistry.[11c,12,14b]

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In summary, the reactions of the zinc complexes, $[Zn(Cp^*)_2]$ and $[(Cp^*)Zn^I–Zn^I(Cp^*)]$, with SO_2 yielded the sulfinate complex, $[Zn(O_2SCp^*)_2(tmeda)]$ (**1**), and the sulfinate/oxo cluster, $[Zn_4(O_2SCp^*)_6O]$ (**2**), respectively. In both cases, nucleophilic attack of the Cp* ligand on the incoming SO_2 molecule was observed, and in the reaction with $[(Cp^*)Zn^I–Zn^I(Cp^*)]$, complete oxidation of the $Zn^I–Zn^I$ bond was observed. DFT calculations clearly show the decoordination of the Cp* ligand, followed by nucleophilic attack on the SO_2 molecule, and finally, coordination of the newly formed O_2SCp^{*-} 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, $[Zn_2(\mu\text{-}SO_3)(\mu\text{-}S_2O_4)(tmeda)_2]$ (**3**), in modest yield. This multi-step activation of SO_2 is noteworthy since activation of SO_2 by molecular systems tends to stop after insertion or coupling.

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