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## COMMUNICATION

## The Synthesis and Structure of $[\text{Zn}(\text{TEMPO})_2]_2$ and $[\text{Zn}(\mu\text{-H})(\mu^2\text{-}\eta^1\text{-}\eta^1\text{-TEMPO})]_6$

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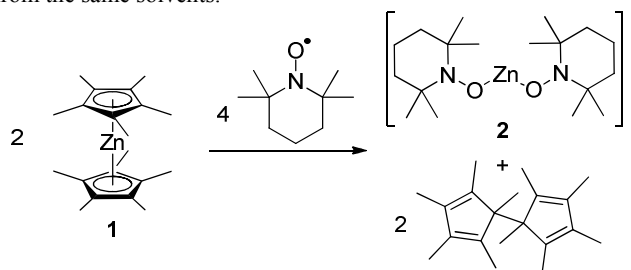
**The commercially available radical TEMPO (2,2,6,6-Tetramethylpiperidin-1-yloxy) reacts with  $[\text{ZnCp}^*_2]$  (**1**) to yield the homoleptic compound  $[\text{Zn}(\text{TEMPO})_2]_2$  (**2**) through coupling of two  $\text{Cp}^*$  radicals. Compound **1** reacts with  $\text{H}_2$  to afford the hydride complex  $[\text{Zn}(\mu\text{-H})(\mu^2\text{-}\eta^1\text{-}\eta^1\text{-TEMPO})]_6$  (**3**) featuring a planar  $\text{Zn}_6\text{H}_6$  ring in the solid state. Preliminary data suggest the formation of **3** proceeds via a radical mechanism.**

The chemistry of metallocenes, despite their discovery many years ago,<sup>1,2</sup> continues to attract great attention,<sup>3</sup> finding countless applications in catalytic polymerization,<sup>4</sup> asymmetric catalysis<sup>5</sup> or C–H bond activation.<sup>6</sup> In the case of decamethylzincocene,  $\text{ZnCp}^*_2$  (**1**,  $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) reactivity studies have shown it to be an effective precursor for a variety of  $\text{Cp}^*\text{Zn}$  compounds<sup>7</sup> and  $\text{Cp}^*$  transfer agent.<sup>8</sup> Carmona and coworkers have reported the isolation of the first compound bearing the dimetallic  $[\text{Zn}_2\text{Cp}^*_2]$  from **1**.<sup>9</sup> The  $\text{Zn}(\text{I})$  species  $[\text{Zn}_2\text{Cp}^*_2]$  is believed to proceed *via* combination of two  $[\text{ZnCp}^*]^\bullet$  radicals. Subsequent studies by Power<sup>10</sup> and Fischer<sup>7b</sup> illustrated reductive elimination from dimeric species as a pathway to related  $\text{Zn}(\text{I})$  species. We previously reported the  $\text{H}_2$  activation by zincocenes and formation of  $[\text{Zn}_2\text{Cp}^*_2]$  from **1** under  $\text{H}_2$  atmosphere.<sup>11</sup> Attempt to intercept radical intermediates, prompted the study of reactions with various trapping reagents.<sup>11b</sup> During the course of these studies (**1**) was found to react with the radical 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO). Herein we report the formation of  $[\text{Zn}(\text{TEMPO})_2]_2$  (**2**) and the subsequent reaction of **2** with  $\text{H}_2$  to yield  $[\text{Zn}(\mu\text{-H})(\mu^2\text{-}\eta^1\text{-}\eta^1\text{-TEMPO})]_6$  (**3**).

The addition of a solution of  $[\text{ZnCp}^*_2]$  (**1**) in  $\text{C}_6\text{D}_6$  to a solution of TEMPO (two equivalents) in  $\text{C}_6\text{D}_6$  leads to a color change from red to pale yellow. NMR spectroscopy of the reaction mixture showed  $\text{C}_{10}\text{Me}_{10}$  and a new compound **2**, although much of **2** crystallized from solution (Scheme 1). An analogous reaction was reported for the conversion of  $[\text{Sm}(\text{Cp}^*)_3]$  with TEMPO to form the  $[\text{Sm}(\text{TEMPO})_3]_2$ .<sup>12</sup>

Isolated **2** is sparingly soluble in  $\text{C}_6\text{D}_6$  and leads to broad resonances of low analytical value. However, the use of  $[\text{D}_6]$ pyridine leads to definitive NMR data, which show one set of TEMPO resonances. Heteronuclear 2D NMR experiments were required to assign an extremely broad  $^{13}\text{C}$  NMR signal at 34 ppm to the methyl

groups of the TEMPO moiety. A dimeric or oligomeric structure of **2** is believed to be the reason for the observation of broad resonances and solvent dependent chemical shifts in the NMR spectra. Whereas a dimer was established by X-ray methods, the exact nuclearity or the presence of an equilibrium was not determined in  $\text{C}_6\text{D}_6$  or  $\text{D}_5$ -pyridine solution. The present TEMPO induced radical coupling of two  $\text{Cp}^*$ -ligands and generation of **2** was found to proceed in a variety of polar ( $\text{Et}_2\text{O}$ ) and non-polar (pentane) solvents. The preparation of **2** was optimized and high yields of **2** were isolated using toluene or benzene as a reaction medium and by crystallization from the same solvents.

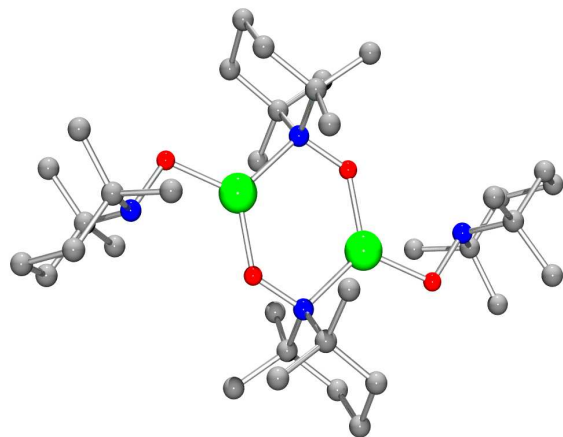


**Scheme 1.** Reaction of **1** and TEMPO to yield  $[\text{Zn}(\text{TEMPO})_2]_2$  (**2**).

Crystals of **2** were subjected to X-ray structure determination and the formula  $[\text{Zn}(\text{TEMPO})_2]_2$  was unequivocally established (Figure 1). The structure of **2** is dimeric with a planar  $\text{Zn}_2\text{N}_2\text{O}_2$  ring, one terminal and one bridging ( $\mu^2\text{-}\eta^1\text{-}\eta^1\text{-}$ )ON- $\text{C}_5\text{H}_6\text{Me}_4$  ligand. The Zn–O bond lengths are 1.857(2) and 1.870(2) Å and the Zn–N distances are 2.054(2) Å. In the bridging and terminal TEMPO ligands, the N–O bond lengths are similar (bridging: O–N: 1.441(2) Å; terminal O–N: 1.463(2) Å) and in agreement with a reduced, anionic TEMPO ligand. While the  $\mu^2\text{-}\eta^1\text{-}\eta^1\text{-}$ bridging mode has no precedent in zinc chemistry, the observed parameters are comparable to known Zn-TEMPO compounds. Power has reported the monomeric species  $[\text{ArZnTEMPO}]$  (Ar =  $\text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_2\text{-2,4,6-}i\text{Pr}_3)_2$ ) with Zn–O = 1.845(2) Å, Zn–N = 2.204(2) Å and N–O = 1.504(2) Å.<sup>10a</sup> This species also exhibits a quasi-side-on TEMPO coordination, with primary binding through oxygen and a relatively close approach of the Zn...N interaction. O'Hara reported heterobimetallic  $[(\text{TMEDA})\text{Na}(\mu\text{-TMP})(\mu\text{-TEMPO})\text{Zn}(t\text{Bu})]$ , where the oxygen atom of TEMPO bridges Na and Zn with Zn–O = 1.968(1) Å and N–O = 1.448(2) Å.<sup>13</sup> Carmona and coworkers described a  $\mu^2\text{-O}$

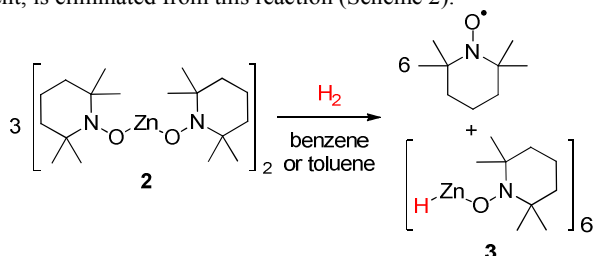
bridging mode for the TEMPO ligand in the related compound  $[\text{ZnEt}(\text{TEMPO})_2]$  (Zn–O: 1.922(1) Å, N–O: 1.439(2) Å.<sup>9a</sup>

The facile and high yield route to **2** is surprising in the light of the work of Carmona and coworkers<sup>9a</sup> who reported the formation of only “small, albeit isolable amounts of the binuclear compound  $[\text{ZnEt}(\text{TEMPO})_2]$ ” resulted from the reaction of **1** with TEMPO and  $\text{ZnEt}_2$  (ratio: 1/0.6/1).<sup>9a</sup> In addition, they reported no reaction of TEMPO with either  $[\text{ZnCp}^*_2]$  or  $\text{ZnEt}_2$ .



**Figure 1.** Pov-ray depiction of **2**. Hydrogen atoms omitted for clarity. C: grey, N: blue, O: red, Zn: green.

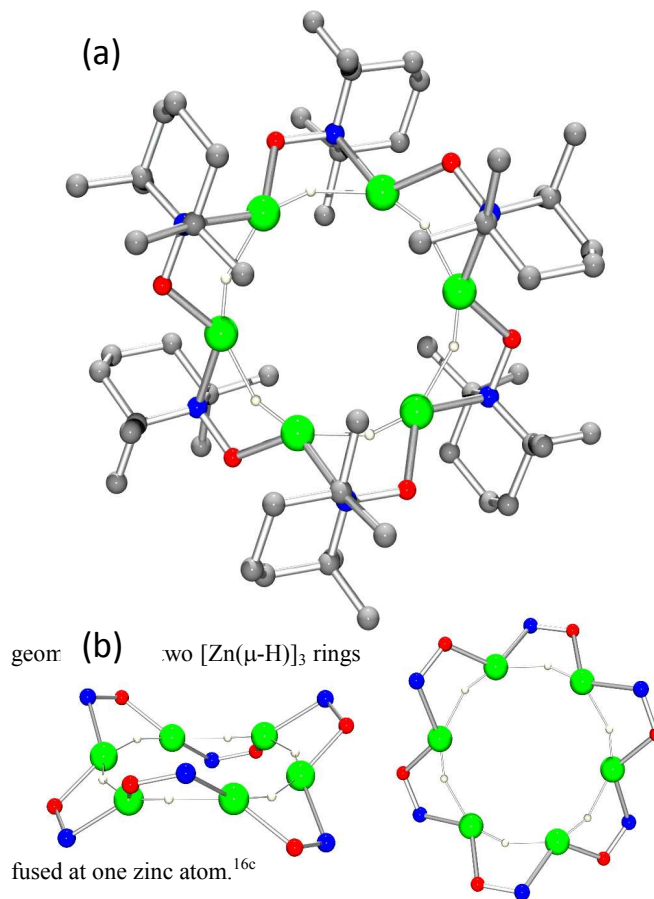
Our earlier finding that **1** reacts with  $\text{H}_2$  to yield the Zn(I) compound  $\text{Zn}_2\text{Cp}^*_2$ ,<sup>11a</sup> and Power's observation of  $\text{H}_2$  elimination upon reaction of  $[\text{ArZnH}]_2$  with TEMPO<sup>10a</sup> prompted us to test the reactivity of **2** with  $\text{H}_2$ . To this end, a suspension of **2** in  $\text{C}_6\text{D}_6$  was exposed to  $\text{H}_2$  (4 bar) and monitored by  $^1\text{H}$  NMR spectroscopy revealing the slow conversion of **2** to a new species after 10 min. Whereas the aliphatic region showed only multiple broad and overlapping resonances, a new broad singlet was observed at 3.63 ppm. The chemical shift of this resonance as well as the absence of  $^1J_{\text{CH}}$  coupling indicated the formation of a zinc hydride complex. After 2 days, the consumption of **2** was complete and the new product **3** precipitated from solution. A single crystal X-ray diffraction study of **3** established the formula  $[\text{Zn}(\mu\text{-H})(\mu^2\text{-}\eta^1\text{-}\eta^1\text{-TEMPO})_6(\text{C}_6\text{H}_6)]$  (Figure 2).<sup>14</sup> The formation of **3** from the reaction of **2** with  $\text{H}_2$  did not lead to the formation of the TEMPO-derived alcohol (TEMPOH),<sup>15</sup> as a by-product as evidenced from the absence of the corresponding  $^1\text{H}$  NMR resonances. Instead, the pale red color leads us to conclude that free TEMPO, which is NMR silent, is eliminated from this reaction (Scheme 2).



**Scheme 2.** Reaction of **2** with  $\text{H}_2$  to form the hydride complex **3**

The structure of **3** in the solid state features bridging  $\mu^2\text{-}\eta^1\text{-}\eta^1\text{-ON-C}_5\text{H}_6\text{Me}_4$  ligands decorating the periphery of an almost planar  $\text{Zn}_6\text{H}_6$  ring with the TEMPO ligands positioned on alternating sides of the  $\text{Zn}_6\text{H}_6$  plane. The hydride atom was located in the different map and refined with a fixed thermal parameter to be 1.26 Å from

Zn and 1.58 Å from the adjacent Zn atom. Earlier reports of zinc hydrides with bridging or terminal hydride ligands report bond lengths of ca. Zn–H<sub>bridging</sub> 1.7–1.8 Å<sup>16</sup> and Zn–H<sub>terminal</sub> 1.4–1.5 Å<sup>11a, 16d, 17</sup>, respectively. The Zn–H–Zn angle of 163.3° is large and likely dictated by the cyclic arrangement of the hexamer. The intermetallic distance is 2.809 Å and precludes any Zn $\cdots$ Zn interaction. The Zn–H stretching frequency was not unambiguously identified in the IR spectrum, which is dominated by intense absorption bands due to the TEMPO ligand.<sup>15, 18</sup> It is interesting and noteworthy that Coles *et al.* reported the pentanuclear zinc hydride  $[\text{Zn}_5\text{R}_4\text{H}_6]$  (R = C(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>hpp); hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine) which is not planar but of a spiro



**Figure 2.** Pov-ray depictions of (a) **3** and (b) heteroatom cores of **3**. Solvent and non-hydridic hydrogen atoms omitted for clarity. C: grey, N: blue, O: red, Zn: green.

The reaction of **2** with  $\text{H}_2$  is a rare example of a zinc alkoxide activating dihydrogen. This is thought to proceed via a radical mechanism. In situ studies indicated a negative effect of NHC addition in the conversion of **2** to **3** and a reaction rate depended on the nature of the NHC. It is interesting that the formation of **3** is conceptually the reverse of the previously reported  $\text{H}_2$  elimination upon reaction of  $[\text{ArZnH}]_2$  with TEMPO.<sup>10a</sup>

## Conclusions

In summary, dexamethylzincocene (**1**) reacts with the radical TEMPO to eliminate  $\text{C}_{10}\text{Me}_{10}$  and form the homoleptic species  $[\text{Zn}(\text{TEMPO})_2]_2$  (**2**) in which the TEMPO ligands bridge the Zn centers via the oxygen and nitrogen atoms. Subsequent reaction of **2** with  $\text{H}_2$  yields the hydride complex

[Zn( $\mu$ -H)( $\mu^2$ - $\eta^1$ : $\eta^1$ -TEMPO)]<sub>6</sub> (**3**), which features a planar Zn<sub>6</sub>H<sub>6</sub> ring. Whereas the TEMPO induced elimination of H<sub>2</sub> from a zinc hydride was reported previously,<sup>10a</sup> our findings report the H<sub>2</sub> induced elimination of TEMPO to form a zinc hydride. These results have important implications regarding the redox chemistry of zinc and the activation of small molecules by organozinc compounds.

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### Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, NMR spectra of **2** and **3**, FTIR of **2**. See DOI: 10.1039/c000000x/CCDC:1000444-1000445.

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