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TOWARD AN UNDERSTANDING OF THE OXYGEN SCAVENGING PROPERTIES OF LITHIUM ZINCATES

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The reaction of ZnMe_2 with 2-pyridylamine $[\text{HN}(2\text{-C}_5\text{H}_4\text{N})\text{Ph}$ **1**], Li^tBu and thereafter with dry air has concomitantly yielded $\{[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{ZnOMeLi}\cdot\text{thf}\}_2^1$ (**2**) and $[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{Zn}[(\mu_3\text{-O})^t\text{Bu}]_2(\text{Li}\cdot\text{thf})_2$ (**3**). The structure of **2** implies the insertion of oxygen into a $[(\text{R}_2\text{N})_2\text{ZnMe}]^-$ ion. To probe this mechanism, we have prepared, characterized, and derivatized $[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{ZnRLi}$ ($\text{R} = {}^n\text{Bu}$, $n = 2$, $\text{L} = \text{thf}$, **4a**; $\text{R} = {}^t\text{Bu}$, $n = 1$, $\text{L} = \text{thf}$, **4b**) (Figure 1). The sequential reaction of $[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{Zn}$ with ${}^n\text{BuLi}$, thf and O_2 gives $\{[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{ZnO}^n\text{BuLi}\cdot n\text{L}\}_2$ ($n = 1$, $\text{L} = \text{thf}$, **5**), the structures of **4a** and **5** strongly suggesting that oxygenation proceeds by insertion into the $\text{Zn}-\text{C}$ bond of an $\{[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{Zn}^n\text{Bu}\}^-$ ion. The treatment of $[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{Zn}$ with ${}^t\text{BuLi}$, thf, and O_2 affords only the previously reported **3**—this being in part rationalized in terms of the steric requirements of O^tBu . Moreover, the structure of **3** is closely related to that of **5**. Formally, this can be described in terms of the rearrangement of $\text{M}-\text{O}$ ($\text{M} = \text{Li}, \text{Zn}$) interactions in response to the presence or absence of a $[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{Zn}$ moiety.

Structural characterization of $\{[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{Zn}^n\text{BuLi}\cdot\text{dme}\}$ (**6**), $\{[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{ZnO}^n\text{BuLi}\cdot 0.5\text{dme}\}_2$ (**7**), and $[\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}]_2\text{Zn}[(\mu_3\text{-O})^t\text{Bu}]_2(\text{Li}_2\cdot\text{dme})$ (**8**), further support this postulated oxygen insertion.

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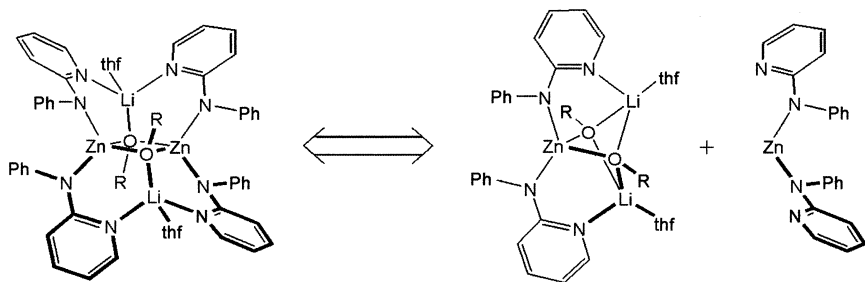


FIGURE 1 The relationship between **4a**-type dimer (left) and a trigonal **3**-type complex with uncoordinated zinc $[\text{Ph}(\text{C}_5\text{H}_4\text{N})\text{N}]_2 \text{Zn}$ (right).

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- [1] R. P. Davies, D. J. Linton, P. Schooler, R. Snaith, and A. E. H. Wheatley, *Chem. Eur. J.*, **7**, 3696 (2001).