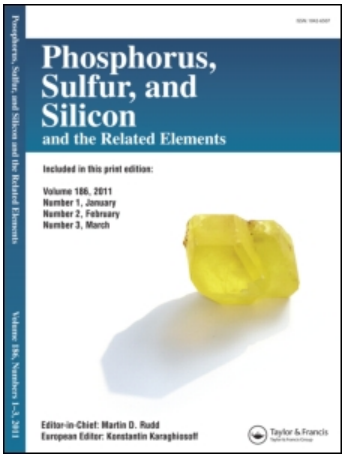

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TOWARD AN UNDERSTANDING OF THE OXYGEN SCAVENGING PROPERTIES OF LITHIUM ZINCATES

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The reaction of $ZnMe_2$ with 2-pyridylamine [HN(2-C_5H_4N)Ph **1**], Li^{t}Bu and thereafter with dry air has concomitantly yielded $\{[Ph(2\text{-}C_5H_4N)N]_2ZnOMeLi\cdot thf\}_2$[1] (**2**) and $[Ph(2\text{-}C_5H_4N)N]_2Zn[(\mu_3\text{-}O)\,{}^tBu]_2(Li\cdot thf)_2$ (**3**). The structure of **2** implies the insertion of oxygen into a $[(R_2N)_2ZnMe]^-$ ion. To probe this mechanism, we have prepared, characterized, and derivatized $[Ph(2\text{-}C_5H_4N)N]_2ZnRLi$ (R = ^{n}Bu, n = 2, L = thf, **4a**; R = ^{t}Bu, n = 1, L = thf, **4b**) (Figure 1). The sequential reaction of $[Ph(2\text{-}C_5H_4N)N]_2Zn$ with ^{n}BuLi, thf and O_2 gives $\{[Ph(2\text{-}C_5H_4N)N]_2ZnO^nBuLi\cdot nL\}_2$ (n = 1, L = thf, **5**), the structures of **4a** and **5** strongly suggesting that oxygenation proceeds by insertion into the Zn—C bond of an $\{[Ph(2\text{-}C_5H_4N)N]_2Zn^nBu\}^-$ ion. The treatment of $[Ph(2\text{-}C_5H_4N)N]_2Zn$ with ^{t}BuLi, thf, and O_2 affords only the previously reported **3**—this being in part rationalized in terms of the steric requirements of O^{t}Bu. Moreover, the structure of **3** is closely related to that of **5**. Formally, this can be described in terms of the rearrangement of M—O (M = Li, Zn) interactions in response to the presence or absence of a $[Ph(2\text{-}C_5H_4N)N]_2Zn$ moiety.

Structural characterization of $\{[Ph(2\text{-}C_5H_4N)N]_2Zn^nBuLi\cdot dme\}$(**6**), $\{[Ph(2\text{-}C_5H_4N)N]_2ZnO^nBuLi\cdot 0.5dme\}_2$ (**7**), and $[Ph(2\text{-}C_5H_4N)N]_2Zn[(\mu_3\text{-}O)^tBu]_2(Li_2\cdot dme)$ (**8**), further support this postulated oxygen insertion.

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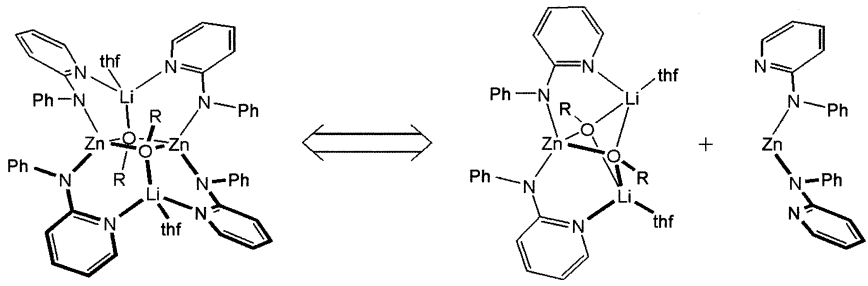

FIGURE 1 The relationship between **4a**-type dimer (left) and a trigonal **3**-type complex with uncoordinated zinc $[Ph(C_5H_4N)N]_2$ Zn (right).

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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).